NEW 5.6.1.F, "Wastewater, Pharmaceutical, and Antibiotic Compounds" (separate pdf)
NEW 5.6.4.A, "Arsenic Speciation" (separate pdf)

A6. Field Measurements
- 6.0 General Information and Guidelines (Version 1.1, 7/03)
- 6.1 Temperature (Version 1.2, 4/04)
- 6.2 Dissolved Oxygen (4/98)
- 6.3 Specific Electrical Conductance (4/98)
- 6.4 pH (Version 1.2, 7/03)
- 6.5 Reduction-Oxidation Potential-Electrode Method (4/98)
- 6.6 Alkalinity and Acid Neutralizing Capacity (2nd edition, 9/2001)
- 6.7 Turbidity (4/98)

A7. Biological Indicators (Third Edition, 11/03)
- 7.0. Five-day Biochemical Oxygen Demand (360 KB pdf)
- 7.1. Fecal Indicator Bacteria (8.52 MB pdf)
- 7.2. Fecal Indicator Viruses (324 KB pdf)
- 7.3. Protozoan Pathogens (1.21 MB pdf)

A8. Bottom-Material Samples (10/97)
A9. Safety in Field Activities (10/97)

To inquire about obtaining the *National Field Manual* contact USGS Information Services (1-888-ASK-USGS) or e-mail nfm-owq@usgs.gov

---

Citation Information for the *National Field Manual*

Citation for the complete manual:
U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, available online at http://pubs.water.usgs.gov/twri9A. [Chapter updates and revisions are ongoing and are summarized at http://water.usgs.gov/owq/FieldManual/mastererrata.html]

Citations for individual chapters:

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., 1998, Preparations for water sampling: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A1, accessed *__date__* at http://pubs.water.usgs.gov/twri9A1/

Lane, S.L., Flanagan, Sarah, and Wilde, F.D., March 2003, Selection of equipment for water sampling (v. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A2, accessed *__date__* at http://pubs.water.usgs.gov/twri9A2/

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., March 2003, Cleaning of Equipment for water sampling (v. 1.2): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A3, accessed *__date__* at http://pubs.water.usgs.gov/twri9A3/

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., September 1999, Collection of water

samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed __*date*__ at http://pubs.water.usgs.gov/twri9A4/

Wilde, F.D., Radtke, D.B., Gibs, Jacob, and Iwatsubo, R.T., eds., April 2004, Processing of water samples (version 2.1): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A5, accessed __*date*__ at http://pubs.water.usgs.gov/twri9A5/ (Separate updates for 5.6.1.F, "Wastewater, pharmaceutical, and antibiotic compounds," and 5.6.4.A, "Arsenic speciation," are provided on the Web page.)

Wilde, F.D., Radtke, D.B., eds., chapter sections variously dated, Field measurements: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, accessed __*date*__ at http://pubs.water.usgs.gov/twri9A6/ (Chapter sections are cited by author and date.)

> Example of citation for a section: Rounds, S.A., and Wilde, F.D., eds., September 2001, Alkalinity and acid neutralizing capacity (2d ed.): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6., section 6.6, accessed __*date*__ from http://pubs.water.usgs.gov/twri9A6/

Myers, D.N., and Wilde, F.D., eds., November 2003, Biological indicators (3d ed.): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7, accessed __*date*__ at http://pubs.water.usgs.gov/twri9A7/ (Chapter sections are cited by author and date.)

> Example of citation for a section: Delzer, G.C., and McKenzie, S.W., November 2003, Five-day biochemical oxygen demand (3d ed.): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7. section 7.0, accessed __*date*__ from http://pubs.water.usgs.gov/twri9A7/

Radtke, D.B., October 1997, Bottom-material samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A8, accessed __*date*__ at http://pubs.water.usgs.gov/twri9A8/

Lane, S.L., and Fay, R.G., October 1997, Safety in field activities: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A9, accessed __*date*__ at http://pubs.water.usgs.gov/twri9A9/

Users with visual disabilities can visit this site for conversion tools and information to help make PDF files accessible.

Return to Water Resources Information
Return to Water Quality Information Pages
Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Privacy Statement || Disclaimer || Accessibility
Last Modified: April 15, 2004 imc
URL: http://water.usgs.gov/owq/FieldManual/index.html



Water Resources--Office of Water Quality

This document is also available in pdf format:

Ch1.pdf

- **Comments/errata page**
- **Citation Information**

CHAPTER A1. PREPARATIONS FOR WATER SAMPLING

Cover/Title Page
Back of Title Page
Foreword

Abstract
Introduction
- Purpose and scope
- Requirements and recommendations
- Field manual review and revision
- Acknowledgments

A1. Preparations for Water Sampling
- 1.0 Field-personnel responsibilities
- 1.1 Field-trip preparations
  - 1.1.1 Checklists of equipment, supplies, and activities
  - 1.1.2 Data-quality plans and preparations
- 1.2 Surface water
  - 1.2.1 Selection of sampling sites
    - 1.2.1.A Flowing-water sites
    - 1.2.1.B Still-water sites
  - 1.2.2 Information for National Water Information System (NWIS) files and field folders
    - 1.2.2.A NWIS files
    - 1.2.2.B Field folders

1.3 Ground water
1.3.1 Site reconnaissance and well selection
1.3.2 Information for National Water Information system (NWIS) files; well files; and field folders
1.3.2.A NWIS files
1.3.2.B Well files
1.3.2.C Field folders

Selected references and internal documents

Publications on Techniques of Water -Resources Investigations

Illustrations

1-1 Example of presampling activities checklist
1-2 Checklist for contents of surface-water-sampling field folder
1-3 Example of a well-information checklist for a well file and field folder
1-4 Checklist for contents of ground-water-sampling field folder
1-5 Example of (*A*) site- and well-location maps and (*B*) well-site sketch with well-site information

Tables

1-1 Minimum information required for electronic storage of site and surface-water-quality data the U.S. Geological Survey (USGS) National Water Information System (NWIS)
1-2 Considerations for well selection and well installation
1-3 Example of site-reconnaissance activities
1-4 Minimum information required for electronic storage of site and ground-water quality data the U.S. Geological Survey National Water Information System (NWIS)

⇨ Section A1--Preparation for water sampling
⇧ Return to National Field Manual Complete Contents Page
⇧ Return to Water Quality Information Pages

Submit a question or comment related to this National Field Manual.
Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 12:14:54 Fri 02 Apr 2004
Privacy Statement || Disclaimer || Accessibility
URL: http://water.usgs.gov/owq/FieldManual/chapter1/Ch1_contents.html

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data



Chapter A1. PREPARATIONS FOR WATER SAMPLING

By
Franceska D. Wilde, Dean B. Radtke,
Jacob Gibs, and Rick T. Iwatsubo

USGS

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, *Secretary*

U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, *Acting Director*

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

For additional information write to:

Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192
ISBN = 0-607-90623-5

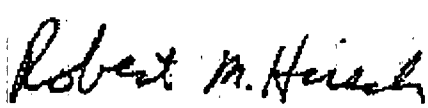
Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286, Federal Center
Denver, CO 80225

Foreword

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.



Robert M. Hirsch
Chief Hydrologist

USGS
science for a changing world

Water Resources--Office of Water Quality

National Field Manual CHAPTER A1. PREPARATIONS FOR WATER SAMPLING

By Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses field-trip preparations, including selection of sample-collection sites for studies of surface-water quality, site reconnaissance and well selection for studies of ground-water quality, and the establishment of electronic files and field files for a sampling site.

Each chapter of the *National Field Manual* will be published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect water-quality data. Chapter A1 addresses preparations for collecting water samples at surface-water and ground-water sites. **Formal training and field apprenticeship are needed in order to correctly implement the protocols and guidelines described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" and consists of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Chapters of the National Field Manual are referred to in the text by the abbreviation "NFM" followed by the chapter number (or chapter and section number). For example, NFM 4 refers to Chapter 4 on "Collection of Water Samples." NFM 4.1 refers to the section on surface-water sampling methods.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and

communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

This chapter of the *National Field Manual* informs field personnel of the major steps needed to prepare for water-quality data-collection activities, select surface-water sampling sites, make reconnaissance visits to ground-water sampling sites and select wells that will meet scientific objectives, and set up electronic and paper files. Study design and data-network design are beyond the scope of this publication. This chapter is not a tutorial on statistical methods of site selection and does not address well installation.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual* the terms "required" and "recommended" have the following USGS-specific meanings:

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are cited in this publication. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes one or several acceptable alternatives to a given procedure or equipment selection on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this publication to the extent that such documents are available. Specific data-quality requirements, study objectives, or other constraints may affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection must be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to incorporate technical advances, correct any errors, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to nfm-owq@usgs.gov). Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>.

ACKNOWLEDGMENTS

The information included in the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include unpublished USGS training and field manuals and technical

memorandums. The authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for this National Field Manual: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, M.T. Koterba, C.E. Lamb, W.W. Lapham, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The authors are indebted to the following colleagues for reviews that improved the technical quality of this report: B.A. Bernard, R.W. Boulger, J.O. Brunett, T.K. Edwards, G.D. Glysson, J.R. Gray, M.A. Hardy, R.L. Rickman, S.K. Sando, R.L. Snyder, and Y.E. Stoker. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from L.S. Rogers, C.T. Mendelsohn, L.E. Menoyo, and A.M. Weaver was instrumental in maintaining the quality of this report.

The editors wish to thank and pay tribute to R.W. Lee and S.W. McKenzie, who were responsible for final technical review, and who contributed to the accuracy, quality, and usability of this report.

Special thanks go to T.L. Miller, whose encouragement and faith in this project has been instrumental to its achievement; and to D.A. Rickert, for providing the support needed to produce a national field manual for water-quality studies.

---

[1]"District" refers to an organizational unit of the USGS, Water Resources Division, in any of the States or Territories of the United States.

⇨ A1--Preparations for water sampling
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

National Field Manual CHAPTER A1. PREPARATIONS FOR WATER SAMPLING

By Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses field-trip preparations, including selection of sample-collection sites for studies of surface-water quality, site reconnaissance and well selection for studies of ground-water quality, and the establishment of electronic files and field files for a sampling site.

Each chapter of the *National Field Manual* will be published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect water-quality data. Chapter A1 addresses preparations for collecting water samples at surface-water and ground-water sites. **Formal training and field apprenticeship are needed in order to correctly implement the protocols and guidelines described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" and consists of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Chapters of the National Field Manual are referred to in the text by the abbreviation "NFM" followed by the chapter number (or chapter and section number). For example, NFM 4 refers to Chapter 4 on "Collection of Water Samples." NFM 4.1 refers to the section on surface-water sampling methods.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and

communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

This chapter of the *National Field Manual* informs field personnel of the major steps needed to prepare for water-quality data-collection activities, select surface-water sampling sites, make reconnaissance visits to ground-water sampling sites and select wells that will meet scientific objectives, and set up electronic and paper files. Study design and data-network design are beyond the scope of this publication. This chapter is not a tutorial on statistical methods of site selection and does not address well installation.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual* the terms "required" and "recommended" have the following USGS-specific meanings:

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and selected District or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are cited in this publication. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes one or several acceptable alternatives to a given procedure or equipment selection on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this publication to the extent that such documents are available. Specific data-quality requirements, study objectives, or other constraints may affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection must be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to incorporate technical advances, correct any errors, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to nfm-owq@usgs.gov). Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>.

ACKNOWLEDGMENTS

The information included in the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include unpublished USGS training and field manuals and technical

memorandums. The authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for this National Field Manual: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, M.T. Koterba, C.E. Lamb, W.W. Lapham, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The authors are indebted to the following colleagues for reviews that improved the technical quality of this report: B.A. Bernard, R.W. Boulger, J.O. Brunett, T.K. Edwards, G.D. Glysson, J.R. Gray, M.A. Hardy, R.L. Rickman, S.K. Sando, R.L. Snyder, and Y.E. Stoker. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from L.S. Rogers, C.T. Mendelsohn, L.E. Menoyo, and A.M. Weaver was instrumental in maintaining the quality of this report.

The editors wish to thank and pay tribute to R.W. Lee and S.W. McKenzie, who were responsible for final technical review, and who contributed to the accuracy, quality, and usability of this report.

Special thanks go to T.L. Miller, whose encouragement and faith in this project has been instrumental to its achievement; and to D.A. Rickert, for providing the support needed to produce a national field manual for water-quality studies.

---

[1]"District" refers to an organizational unit of the USGS, Water Resources Division, in any of the States or Territories of the United States.

⇨ A1--Preparations for water sampling
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

National Field Manual CHAPTER A1. PREPARATIONS FOR WATER SAMPLING

By Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses field-trip preparations, including selection of sample-collection sites for studies of surface-water quality, site reconnaissance and well selection for studies of ground-water quality, and the establishment of electronic files and field files for a sampling site.

Each chapter of the *National Field Manual* will be published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect water-quality data. Chapter A1 addresses preparations for collecting water samples at surface-water and ground-water sites. **Formal training and field apprenticeship are needed in order to correctly implement the protocols and guidelines described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" and consists of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Chapters of the National Field Manual are referred to in the text by the abbreviation "NFM" followed by the chapter number (or chapter and section number). For example, NFM 4 refers to Chapter 4 on "Collection of Water Samples." NFM 4.1 refers to the section on surface-water sampling methods.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and

communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

This chapter of the *National Field Manual* informs field personnel of the major steps needed to prepare for water-quality data-collection activities, select surface-water sampling sites, make reconnaissance visits to ground-water sampling sites and select wells that will meet scientific objectives, and set up electronic and paper files. Study design and data-network design are beyond the scope of this publication. This chapter is not a tutorial on statistical methods of site selection and does not address well installation.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual* the terms "required" and "recommended" have the following USGS-specific meanings:

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are cited in this publication. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes one or several acceptable alternatives to a given procedure or equipment selection on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this publication to the extent that such documents are available. Specific data-quality requirements, study objectives, or other constraints may affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection must be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to incorporate technical advances, correct any errors, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to nfm-owq@usgs.gov). Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>.

ACKNOWLEDGMENTS

The information included in the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include unpublished USGS training and field manuals and technical

memorandums. The authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for this National Field Manual: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, M.T. Koterba, C.E. Lamb, W.W. Lapham, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The authors are indebted to the following colleagues for reviews that improved the technical quality of this report: B.A. Bernard, R.W. Boulger, J.O. Brunett, T.K. Edwards, G.D. Glysson, J.R. Gray, M.A. Hardy, R.L. Rickman, S.K. Sando, R.L. Snyder, and Y.E. Stoker. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from L.S. Rogers, C.T. Mendelsohn, L.E. Menoyo, and A.M. Weaver was instrumental in maintaining the quality of this report.

The editors wish to thank and pay tribute to R.W. Lee and S.W. McKenzie, who were responsible for final technical review, and who contributed to the accuracy, quality, and usability of this report.

Special thanks go to T.L. Miller, whose encouragement and faith in this project has been instrumental to its achievement; and to D.A. Rickert, for providing the support needed to produce a national field manual for water-quality studies.

---

[1]"District" refers to an organizational unit of the USGS, Water Resources Division, in any of the States or Territories of the United States.

⇨A1--Preparations for water sampling
⇧Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

National Field Manual CHAPTER A1. PREPARATIONS FOR WATER SAMPLING

By Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses field-trip preparations, including selection of sample-collection sites for studies of surface-water quality, site reconnaissance and well selection for studies of ground-water quality, and the establishment of electronic files and field files for a sampling site.

Each chapter of the *National Field Manual* will be published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect water-quality data. Chapter A1 addresses preparations for collecting water samples at surface-water and ground-water sites. **Formal training and field apprenticeship are needed in order to correctly implement the protocols and guidelines described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" and consists of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Chapters of the National Field Manual are referred to in the text by the abbreviation "NFM" followed by the chapter number (or chapter and section number). For example, NFM 4 refers to Chapter 4 on "Collection of Water Samples." NFM 4.1 refers to the section on surface-water sampling methods.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and

communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

This chapter of the *National Field Manual* informs field personnel of the major steps needed to prepare for water-quality data-collection activities, select surface-water sampling sites, make reconnaissance visits to ground-water sampling sites and select wells that will meet scientific objectives, and set up electronic and paper files. Study design and data-network design are beyond the scope of this publication. This chapter is not a tutorial on statistical methods of site selection and does not address well installation.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual* the terms "required" and "recommended" have the following USGS-specific meanings:

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and selected District or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are cited in this publication. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes one or several acceptable alternatives to a given procedure or equipment selection on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this publication to the extent that such documents are available. Specific data-quality requirements, study objectives, or other constraints may affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection must be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to incorporate technical advances, correct any errors, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to nfm-owq@usgs.gov). Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>.

ACKNOWLEDGMENTS

The information included in the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include unpublished USGS training and field manuals and technical

memorandums. The authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for this National Field Manual: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, M.T. Koterba, C.E. Lamb, W.W. Lapham, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The authors are indebted to the following colleagues for reviews that improved the technical quality of this report: B.A. Bernard, R.W. Boulger, J.O. Brunett, T.K. Edwards, G.D. Glysson, J.R. Gray, M.A. Hardy, R.L. Rickman, S.K. Sando, R.L. Snyder, and Y.E. Stoker. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from L.S. Rogers, C.T. Mendelsohn, L.E. Menoyo, and A.M. Weaver was instrumental in maintaining the quality of this report.

The editors wish to thank and pay tribute to R.W. Lee and S.W. McKenzie, who were responsible for final technical review, and who contributed to the accuracy, quality, and usability of this report.

Special thanks go to T.L. Miller, whose encouragement and faith in this project has been instrumental to its achievement; and to D.A. Rickert, for providing the support needed to produce a national field manual for water-quality studies.

---

[1]"District" refers to an organizational unit of the USGS, Water Resources Division, in any of the States or Territories of the United States.

⇨ A1--Preparations for water sampling
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section A1.pdf

A1.
PREPARATIONS FOR WATER SAMPLING

By Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

This chapter of the National Field Manual for the Collection of Water-Quality Data provides guidelines for field personnel as they prepare to select and (or) evaluate surface-water and ground-water sampling sites, establish site files, and prepare for sample-collection field trips.

1.0
FIELD-PERSONNEL RESPONSIBILITIES

Before sample collection begins, field personnel must take steps to ensure that the samples collected will be representative of the aqueous system being investigated. A representative water sample is a sample that typifies ("represents") that part of the aqueous system to be studied and is delineated by the objectives and scope of the study. USGS data-collection efforts often take a whole-system approach, meaning that data-collection methods ensure representation of an entire stream reach or aquifer volume. A modified approach is needed for studies in which samples are representative of a specific part or aspect of an aqueous system instead of the entire system; for example, a study of aquatic ecology may establish nearshore boundaries on the system, and an oil-spill study may target only the surface of a water-table aquifer within a designated boundary or circumference.

- **Be alert to sample representativeness.** The data are no better than the confidence that can be placed in how well the sample represents the aqueous system (Feltz and Culbertson, 1972).
- **Plan to collect quality-control samples.** Quality-control checks applied during laboratory analyses of the samples cannot compensate for data that are biased because samples were not representative of the aqueous system or because samples were improperly collected and processed.

Field personnel are also responsible for providing the necessary information to establish USGS National Water Information System (NWIS)[2] site files for each sampling site and for checking to see that the site file is functional, that the information it contains is correct, and that updates are made promptly.

Update files promptly:

- **The Ground-Water Site Inventory (GWSI)** file contains site information.

- **The Quality-of-Water Data (QWDATA)** file contains field and laboratory data.
- **The Automatic Data Processing System (ADAPS)** file contains time-series information.

---

[2]National Water Information System (NWIS) is the hydrologic data base for the U.S. Geological Survey. Updated versions are released periodically.

⇨ Field-Trip Preparations
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section A1.pdf

1.1
FIELD-TRIP PREPARATIONS

All details of a field trip need to be planned well in advance. Adequate time must be scheduled in the workplan to review data requirements and make field-trip preparations—a common mistake is to put off these activities until the last minute.

Before selecting sites or making other preparations:

- Understand the purpose for which the various types of data will be collected and the aqueous system that each sample should represent.
- Review the study workplan, especially types of measurements and samples needed.
- Make field reconnaissance trips before selecting sampling sites, if possible.
  - -- Note conditions that could affect sampling operations (such as the seasonal high or low streamflow, flowing wells, or site-access peculiarities).
  - -- Evaluate potential sources of contamination at the site, based on target analytes[3] to be collected.
- Review site files and field folders. (Note site location, description and access, and review any previously collected physical, chemical, and biological data.)
- Obtain and keep current with training and the laboratory requirements associated with your data-collection activities.

Before selecting equipment:

Understand the physical and chemical limitations of each piece of equipment, in order to meet data-collection objectives and data-quality requirements[4] (refer to NFM 2). Verify and test, if possible, the operational range of the sampling equipment to be used.

Before starting field work:

- Review site files and update and review the field folder for each site from which samples and ancillary data will be collected (see sections 1.2.2 and 1.3.2).
- Review the safety plan and be sure that you have the training needed if you will be working at sites designated as hazardous (see NFM 9)

Plan ahead! Take adequate time to prepare.

1.1.1
CHECKLISTS OF EQUIPMENT, SUPPLIES, AND ACTIVITIES

Each study needs to establish and follow a protocol for data-collection activities. Checklists help ensure that equipment and supplies will be ordered on time, that data-collection activities will be completed appropriately, and that data-quality requirements will be met (fig. 1-1). Most checklists are generic to all projects and sites (for example, vehicle and equipment maintenance checklists), but may need to be customized (for example, items listed, quantities of equipment and supplies, number of batteries, and types of sample bottles and other equipment). The types of information and examples of items listed on the next page are usually included when developing checklists.

Types of information	Examples of items or activities in checklists
Calendar of planned field trips	Prepare calendars/checklists that include sampling dates, members of field team, vehicle(s) to be used.
Presampling activities	Prepare checklists; for example, field-trip preparations checklist (fig. 1-1) and well- information checklist (fig. 1-3).
Postsampling activities	Update field folders and computer files. Log in samples (Analytical Services Request form). Store and dispose of hazardous materials properly. Check that all equipment is clean and properly stored.
Field equipment and supplies	Prepare lists of equipment/supplies for each field site (see NFM 2). Prepare a list of items to be ordered.
Equipment/supplies maintenance and testing	Prepare a checklist of maintenance/testing for field-measurement instruments (see NFM 6). Test sample-collection and processing equipment. Charge or replace batteries.
Vehicle maintenance	Check fluids, battery, tires, lights, cleanliness.
Sample-collection, -processing, -shipping, and -documentation information and supplies	Prepare headers on forms (such as field, chain-of- custody, and Analytical Services Request forms); prepare bottle labels. Prepare lists of chemical constituents, with analytical schedules, methods, laboratory codes; bottle type and volume; sample handling, treatment, and preservation procedures; shipment; quality-control samples.
Field-folder contents	Prepare list of logistical information needed for each site, such as permission to access site, keys, maps.
Safety equipment and information	Keep a copy of NFM 9 for field use and list special considerations for the site, such as personal flotation devices.

FIELD-TRIP PREPARATIONS

PROJECT: _____ SITES: _____ DATE: _____

✓	Preeld activity	Comments
	Order supplies	Ordered 3 cases Ultrex for site #2 Completed on _____ , by _____ .
	Prepare deionized water (in-house system) Check prior laboratory analysis	Last change of cartridges, on _____ Last chemical analysis on _____ , by _____ , Conductivity checks out , by _____
	Check expiration dates on reagents	Need _____ conductivity standard(s) Need pH _____ buffer(s)
	Clean and test equipment	Completed on _____ , by _____ Problems _____
	Collect equipment blanks	Completed on _____ , by _____ Results reviewed by _____ (District water-quality specialist or project chief)
	Clean sample bottles	Completed on _____ , by _____
	Label sample bottles, prepare eld forms	Completed on _____ , by _____
	Obtain permission for site access	Completed on _____ , by _____
	Check eld vehicle for safety equipment and supplies, such as material safety data sheets, ares, and remote communi-cations system (NFM 9)	Completed on _____ , by _____
	Charge/replace batteries	Completed by _____
	Update eld folder	Completed by _____
	Make travel reservations, arrangements	Completed by _____
	Provide supervisor witheld-trip and call-in (check-in) schedule	Provided on _____ to _____
	Other	

Figure 1-1. Example of a presampling activities checklist.

1.1.2 DATA-QUALITY PLANS AND PREPARATIONS

USGS policy that water-quality data be of a defined and documented quality is described in Horowitz and others (1994) and Office of Water Quality Technical Memorandum 93.11 (see "Selected References and Internal Documents"). Every study should have a written document that describes study objectives, data-quality requirements, and a quality-assurance plan. Some of the information needed to ensure data quality is described in District quality-assurance plans. Discipline specialists (District and Regional specialists, discipline offices at USGS headquarters in Reston, Va., and USGS National Research Program scientists) can provide specific instructions and updates relating to quality-assurance procedures and policies for the collection of water-quality, surface-water, and ground-water data.

Field personnel are responsible for determining whether the equipment and methods being used could impair sample quality. For the most part, this determination involves collecting quality-control samples and analyzing the results. Field personnel must plan and prepare for routine checks on data quality.

- **Examine field and laboratory results as soon as possible, preferably before the next sample-collection field trip.** Results indicating potential bias in the data will alert you to the changes needed in equipment, equipment-cleaning procedures, or field methods used.
- **Be prepared to collect additional blanks, replicates, or other field quality-control samples,** based on your judgment of the effects of field conditions on sample collection. Field conditions are unpredictable, and adverse or unexpected conditions could necessitate additional steps to document data quality.

Quality-control samples are collected either in the office laboratory or at the field site, depending on their specific purpose (see NFM 3, "Cleaning of Equipment for Water Sampling," NFM 4, "Collection of Water Samples," and NFM 5, "Processing of Water Samples"). Field personnel must be familiar with the various types of quality-control samples and know how and when to collect them in order to comply with USGS quality-assurance requirements. Collection of blank samples (blanks) is mandatory. Blanks are samples of laboratory-prepared and -analyzed water that are processed through the equipment in the same manner as the environmental sample, but after the equipment has been cleaned and prepared for field use.

In preparation for collection of quality-control samples, solutions of the appropriate type and quality must be obtained for blank and standard reference material samples. Field personnel should use water for blank samples that is certified by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo. Laboratory certification should indicate that the blank water has target-analyte concentrations that are less than the method-detection limits. Blank water for determination of inorganic constituents needs to be the inorganic blank water obtained from the Quality of Water Service Unit in Ocala, Fla.; blanks for analysis of organic compounds require either pesticide blank water or volatile/pesticide blank water, both of which can be obtained from NWQL. Standard/reference materials generally are obtained from the National Institute of Standards and Technology.

- **Collect equipment blanks before beginning the field effort.**
  - Equipment blanks are processed through clean equipment in the controlled setting of an office laboratory.
  - **Process an equipment blank at least once a year for each set of sample-contacting equipment.** This applies to new equipment to be used for the first time, to equipment that will be cleaned with a new cleaning procedure, and to equipment that has not been tested with an equipment blank for 1 year.
  - **Do not collect or process environmental samples until the annual equipment blank data have been reviewed.** The field personnel or the water-quality specialist needs to ensure that the equipment blanks are either free of contamination or have concentrations small enough to be insignificant at the current analytical limits (Horowitz and others, 1994).
- **Collect field blanks at the field site under the same conditions as environmental samples.** Field blanks can provide information on the efficacy of the equipment cleaning procedures used and on ambient atmospheric contamination.

Data quality begins before the first sample is collected—be aware of data-quality requirements and potential sources of contamination.

---

[3]"Target analyte" refers to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured properties such as temperature, specific electrical conductance (conductivity), dissolved-oxygen concentration, pH, Eh, alkalinity, color, or turbidity. The *Concise Chemical and Technical Dictionary*, 4th edition (Bennett, 1986) defines "analyte" as "Substance being determined in an analysis."

[4]As used in this publication, the term "data-quality requirements" refers to that subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the allowable variability to fulfill the scientific objectives of the study.

⇨ Section 1.2 Surface Water
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section A1.pdf

1.1
FIELD-TRIP PREPARATIONS

All details of a field trip need to be planned well in advance. Adequate time must be scheduled in the workplan to review data requirements and make field-trip preparations—a common mistake is to put off these activities until the last minute.

Before selecting sites or making other preparations:

- Understand the purpose for which the various types of data will be collected and the aqueous system that each sample should represent.
- Review the study workplan, especially types of measurements and samples needed.
- Make field reconnaissance trips before selecting sampling sites, if possible.
  - -- Note conditions that could affect sampling operations (such as the seasonal high or low streamflow, flowing wells, or site-access peculiarities).
  - -- Evaluate potential sources of contamination at the site, based on target analytes[3] to be collected.
- Review site files and field folders. (Note site location, description and access, and review any previously collected physical, chemical, and biological data.)
- Obtain and keep current with training and the laboratory requirements associated with your data-collection activities.

Before selecting equipment:

Understand the physical and chemical limitations of each piece of equipment, in order to meet data-collection objectives and data-quality requirements[4] (refer to NFM 2). Verify and test, if possible, the operational range of the sampling equipment to be used.

Before starting field work:

- Review site files and update and review the field folder for each site from which samples and ancillary data will be collected (see sections 1.2.2 and 1.3.2).
- Review the safety plan and be sure that you have the training needed if you will be working at sites designated as hazardous (see NFM 9)

Plan ahead! Take adequate time to prepare.

1.1.1
CHECKLISTS OF EQUIPMENT, SUPPLIES, AND ACTIVITIES

Each study needs to establish and follow a protocol for data-collection activities. Checklists help ensure that equipment and supplies will be ordered on time, that data-collection activities will be completed appropriately, and that data-quality requirements will be met (fig. 1-1). Most checklists are generic to all projects and sites (for example, vehicle and equipment maintenance checklists), but may need to be customized (for example, items listed, quantities of equipment and supplies, number of batteries, and types of sample bottles and other equipment). The types of information and examples of items listed on the next page are usually included when developing checklists.

Types of information	Examples of items or activities in checklists
Calendar of planned field trips	Prepare calendars/checklists that include sampling dates, members of field team, vehicle(s) to be used.
Presampling activities	Prepare checklists; for example, field-trip preparations checklist (fig. 1-1) and well- information checklist (fig. 1-3).
Postsampling activities	Update field folders and computer files. Log in samples (Analytical Services Request form). Store and dispose of hazardous materials properly. Check that all equipment is clean and properly stored.
Field equipment and supplies	Prepare lists of equipment/supplies for each field site (see NFM 2). Prepare a list of items to be ordered.
Equipment/supplies maintenance and testing	Prepare a checklist of maintenance/testing for field-measurement instruments (see NFM 6). Test sample-collection and processing equipment. Charge or replace batteries.
Vehicle maintenance	Check fluids, battery, tires, lights, cleanliness.
Sample-collection, -processing, -shipping, and -documentation information and supplies	Prepare headers on forms (such as field, chain-of- custody, and Analytical Services Request forms); prepare bottle labels. Prepare lists of chemical constituents, with analytical schedules, methods, laboratory codes; bottle type and volume; sample handling, treatment, and preservation procedures; shipment; quality-control samples.
Field-folder contents	Prepare list of logistical information needed for each site, such as permission to access site, keys, maps.
Safety equipment and information	Keep a copy of NFM 9 for field use and list special considerations for the site, such as personal flotation devices.

FIELD-TRIP PREPARATIONS

PROJECT: _____ SITES: _____ DATE: _____

✓	Preeld activity	Comments
	Order supplies	Ordered 3 cases Ultrex for site #2 Completed on _____ , by _____ .
	Prepare deionized water (in-house system) Check prior laboratory analysis	Last change of cartridges, on _____ Last chemical analysis on _____ , by _____ . Conductivity checks out , by _____
	Check expiration dates on reagents	Need _____ conductivity standard(s) Need pH _____ buffer(s)
	Clean and test equipment	Completed on _____ , by _____ Problems _____
	Collect equipment blanks	Completed on _____ , by _____ Results reviewed by _____ (District water-quality specialist or project chief)
	Clean sample bottles	Completed on _____ , by _____
	Label sample bottles, prepare eld forms	Completed on _____ , by _____
	Obtain permission for site access	Completed on _____ , by _____
	Check eld vehicle for safety equipment and supplies, such as material safety data sheets, ares, and remote communi-cations system (NFM 9)	Completed on _____ , by _____
	Charge/replace batteries	Completed by _____
	Update eld folder	Completed by _____
	Make travel reservations, arrangements	Completed by _____
	Provide supervisor with eld-trip and call-in (check-in) schedule	Provided on _____ to _____
	Other	

Figure 1-1. Example of a presampling activities checklist.

1.1.2 DATA-QUALITY PLANS AND PREPARATIONS

USGS policy that water-quality data be of a defined and documented quality is described in Horowitz and others (1994) and Office of Water Quality Technical Memorandum 93.11 (see "Selected References and Internal Documents"). Every study should have a written document that describes study objectives, data-quality requirements, and a quality-assurance plan. Some of the information needed to ensure data quality is described in District quality-assurance plans. Discipline specialists (District and Regional specialists, discipline offices at USGS headquarters in Reston, Va., and USGS National Research Program scientists) can provide specific instructions and updates relating to quality-assurance procedures and policies for the collection of water-quality, surface-water, and ground-water data.

Field personnel are responsible for determining whether the equipment and methods being used could impair sample quality. For the most part, this determination involves collecting quality-control samples and analyzing the results. Field personnel must plan and prepare for routine checks on data quality.

- **Examine field and laboratory results as soon as possible, preferably before the next sample-collection field trip.** Results indicating potential bias in the data will alert you to the changes needed in equipment, equipment-cleaning procedures, or field methods used.
- **Be prepared to collect additional blanks, replicates, or other field quality-control samples,** based on your judgment of the effects of field conditions on sample collection. Field conditions are unpredictable, and adverse or unexpected conditions could necessitate additional steps to document data quality.

Quality-control samples are collected either in the office laboratory or at the field site, depending on their specific purpose (see NFM 3, "Cleaning of Equipment for Water Sampling," NFM 4, "Collection of Water Samples," and NFM 5, "Processing of Water Samples"). Field personnel must be familiar with the various types of quality-control samples and know how and when to collect them in order to comply with USGS quality-assurance requirements. Collection of blank samples (blanks) is mandatory. Blanks are samples of laboratory-prepared and -analyzed water that are processed through the equipment in the same manner as the environmental sample, but after the equipment has been cleaned and prepared for field use.

In preparation for collection of quality-control samples, solutions of the appropriate type and quality must be obtained for blank and standard reference material samples. Field personnel should use water for blank samples that is certified by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo. Laboratory certification should indicate that the blank water has target-analyte concentrations that are less than the method-detection limits. Blank water for determination of inorganic constituents needs to be the inorganic blank water obtained from the Quality of Water Service Unit in Ocala, Fla.; blanks for analysis of organic compounds require either pesticide blank water or volatile/pesticide blank water, both of which can be obtained from NWQL. Standard/reference materials generally are obtained from the National Institute of Standards and Technology.

- **Collect equipment blanks before beginning the field effort.**
  - Equipment blanks are processed through clean equipment in the controlled setting of an office laboratory.
  - **Process an equipment blank at least once a year for each set of sample-contacting equipment.** This applies to new equipment to be used for the first time, to equipment that will be cleaned with a new cleaning procedure, and to equipment that has not been tested with an equipment blank for 1 year.
  - **Do not collect or process environmental samples until the annual equipment blank data have been reviewed.** The field personnel or the water-quality specialist needs to ensure that the equipment blanks are either free of contamination or have concentrations small enough to be insignificant at the current analytical limits (Horowitz and others, 1994).
- **Collect field blanks at the field site under the same conditions as environmental samples.** Field blanks can provide information on the efficacy of the equipment cleaning procedures used and on ambient atmospheric contamination.

Data quality begins before the first sample is collected—be aware of data-quality requirements and potential sources of contamination.

---

[3]"Target analyte" refers to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured properties such as temperature, specific electrical conductance (conductivity), dissolved-oxygen concentration, pH, Eh, alkalinity, color, or turbidity. The *Concise Chemical and Technical Dictionary*, 4th edition (Bennett, 1986) defines "analyte" as "Substance being determined in an analysis."

[4]As used in this publication, the term "data-quality requirements" refers to that subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the allowable variability to fulfill the scientific objectives of the study.

⇨ Section 1.2 Surface Water
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section A1.pdf

1.1
FIELD-TRIP PREPARATIONS

All details of a field trip need to be planned well in advance. Adequate time must be scheduled in the workplan to review data requirements and make field-trip preparations—a common mistake is to put off these activities until the last minute.

Before selecting sites or making other preparations:

- Understand the purpose for which the various types of data will be collected and the aqueous system that each sample should represent.
- Review the study workplan, especially types of measurements and samples needed.
- Make field reconnaissance trips before selecting sampling sites, if possible.
  - -- Note conditions that could affect sampling operations (such as the seasonal high or low streamflow, flowing wells, or site-access peculiarities).
  - -- Evaluate potential sources of contamination at the site, based on target analytes[3] to be collected.
- Review site files and field folders. (Note site location, description and access, and review any previously collected physical, chemical, and biological data.)
- Obtain and keep current with training and the laboratory requirements associated with your data-collection activities.

Before selecting equipment:

Understand the physical and chemical limitations of each piece of equipment, in order to meet data-collection objectives and data-quality requirements[4] (refer to NFM 2). Verify and test, if possible, the operational range of the sampling equipment to be used.

Before starting field work:

- Review site files and update and review the field folder for each site from which samples and ancillary data will be collected (see sections 1.2.2 and 1.3.2).
- Review the safety plan and be sure that you have the training needed if you will be working at sites designated as hazardous (see NFM 9)

Plan ahead! Take adequate time to prepare.

1.1.1
CHECKLISTS OF EQUIPMENT, SUPPLIES, AND ACTIVITIES

Each study needs to establish and follow a protocol for data-collection activities. Checklists help ensure that equipment and supplies will be ordered on time, that data-collection activities will be completed appropriately, and that data-quality requirements will be met (fig. 1-1). Most checklists are generic to all projects and sites (for example, vehicle and equipment maintenance checklists), but may need to be customized (for example, items listed, quantities of equipment and supplies, number of batteries, and types of sample bottles and other equipment). The types of information and examples of items listed on the next page are usually included when developing checklists.

Types of information	Examples of items or activities in checklists
Calendar of planned field trips	Prepare calendars/checklists that include sampling dates, members of field team, vehicle(s) to be used.
Presampling activities	Prepare checklists; for example, field-trip preparations checklist (fig. 1-1) and well- information checklist (fig. 1-3).
Postsampling activities	Update field folders and computer files. Log in samples (Analytical Services Request form). Store and dispose of hazardous materials properly. Check that all equipment is clean and properly stored.
Field equipment and supplies	Prepare lists of equipment/supplies for each field site (see NFM 2). Prepare a list of items to be ordered.
Equipment/supplies maintenance and testing	Prepare a checklist of maintenance/testing for field-measurement instruments (see NFM 6). Test sample-collection and processing equipment. Charge or replace batteries.
Vehicle maintenance	Check fluids, battery, tires, lights, cleanliness.
Sample-collection, -processing, -shipping, and -documentation information and supplies	Prepare headers on forms (such as field, chain-of- custody, and Analytical Services Request forms); prepare bottle labels. Prepare lists of chemical constituents, with analytical schedules, methods, laboratory codes; bottle type and volume; sample handling, treatment, and preservation procedures; shipment; quality-control samples.
Field-folder contents	Prepare list of logistical information needed for each site, such as permission to access site, keys, maps.
Safety equipment and information	Keep a copy of NFM 9 for field use and list special considerations for the site, such as personal flotation devices.

FIELD-TRIP PREPARATIONS

PROJECT: _____ SITES: _____ DATE: _____

✓	Predld activity	Comments
	Order supplies	Ordered 3 cases Ultrex for site #2 Completed on _____ , by _____ .
	Prepare deionized water (in-house system) Check prior laboratory analysis	Last change of cartridges, on _____ Last chemical analysis on _____ , by _____ . Conductivity checks out , by _____
	Check expiration dates on reagents	Need _____ conductivity standard(s) Need pH _____ buffer(s)
	Clean and test equipment	Completed on _____ , by _____ Problems _____
	Collect equipment blanks	Completed on _____ , by _____ Results reviewed by _____ (District water-quality specialist or project chief)
	Clean sample bottles	Completed on _____ , by _____
	Label sample bottles, prepare eld forms	Completed on _____ , by _____
	Obtain permission for site access	Completed on _____ , by _____
	Check eld vehicle for safety equipment and supplies, such as material safety data sheets, ares, and remote communi-cations system (NFM 9)	Completed on _____ , by _____
	Charge/replace batteries	Completed by _____
	Update eld folder	Completed by _____
	Make travel reservations, arrangements	Completed by _____
	Provide supervisor with eld-trip and call-in (check-in) schedule	Provided on _____ to _____
	Other	

Figure 1-1. Example of a presampling activities checklist.

1.1.2 DATA-QUALITY PLANS AND PREPARATIONS

USGS policy that water-quality data be of a defined and documented quality is described in Horowitz and others (1994) and Office of Water Quality Technical Memorandum 93.11 (see "Selected References and Internal Documents"). Every study should have a written document that describes study objectives, data-quality requirements, and a quality-assurance plan. Some of the information needed to ensure data quality is described in District quality-assurance plans. Discipline specialists (District and Regional specialists, discipline offices at USGS headquarters in Reston, Va., and USGS National Research Program scientists) can provide specific instructions and updates relating to quality-assurance procedures and policies for the collection of water-quality, surface-water, and ground-water data.

Field personnel are responsible for determining whether the equipment and methods being used could impair sample quality. For the most part, this determination involves collecting quality-control samples and analyzing the results. Field personnel must plan and prepare for routine checks on data quality.

- **Examine field and laboratory results as soon as possible, preferably before the next sample-collection field trip.** Results indicating potential bias in the data will alert you to the changes needed in equipment, equipment-cleaning procedures, or field methods used.
- **Be prepared to collect additional blanks, replicates, or other field quality-control samples,** based on your judgment of the effects of field conditions on sample collection. Field conditions are unpredictable, and adverse or unexpected conditions could necessitate additional steps to document data quality.

Quality-control samples are collected either in the office laboratory or at the field site, depending on their specific purpose (see NFM 3, "Cleaning of Equipment for Water Sampling," NFM 4, "Collection of Water Samples," and NFM 5, "Processing of Water Samples"). Field personnel must be familiar with the various types of quality-control samples and know how and when to collect them in order to comply with USGS quality-assurance requirements. Collection of blank samples (blanks) is mandatory. Blanks are samples of laboratory-prepared and -analyzed water that are processed through the equipment in the same manner as the environmental sample, but after the equipment has been cleaned and prepared for field use.

In preparation for collection of quality-control samples, solutions of the appropriate type and quality must be obtained for blank and standard reference material samples. Field personnel should use water for blank samples that is certified by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo. Laboratory certification should indicate that the blank water has target-analyte concentrations that are less than the method-detection limits. Blank water for determination of inorganic constituents needs to be the inorganic blank water obtained from the Quality of Water Service Unit in Ocala, Fla.; blanks for analysis of organic compounds require either pesticide blank water or volatile/pesticide blank water, both of which can be obtained from NWQL. Standard/reference materials generally are obtained from the National Institute of Standards and Technology.

- **Collect equipment blanks before beginning the field effort.**
  - Equipment blanks are processed through clean equipment in the controlled setting of an office laboratory.
  - **Process an equipment blank at least once a year for each set of sample-contacting equipment.** This applies to new equipment to be used for the first time, to equipment that will be cleaned with a new cleaning procedure, and to equipment that has not been tested with an equipment blank for 1 year.
  - **Do not collect or process environmental samples until the annual equipment blank data have been reviewed.** The field personnel or the water-quality specialist needs to ensure that the equipment blanks are either free of contamination or have concentrations small enough to be insignificant at the current analytical limits (Horowitz and others, 1994).
- **Collect field blanks at the field site under the same conditions as environmental samples.** Field blanks can provide information on the efficacy of the equipment cleaning procedures used and on ambient atmospheric contamination.

Data quality begins before the first sample is collected—be aware of data-quality requirements and potential sources of contamination.

---

[3]"Target analyte" refers to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured properties such as temperature, specific electrical conductance (conductivity), dissolved-oxygen concentration, pH, Eh, alkalinity, color, or turbidity. The *Concise Chemical and Technical Dictionary*, 4th edition (Bennett, 1986) defines "analyte" as "Substance being determined in an analysis."

[4]As used in this publication, the term "data-quality requirements" refers to that subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the allowable variability to fulfill the scientific objectives of the study.

⇨ Section 1.2 Surface Water
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section 1.2.pdf

1.2 SURFACE WATER

Before sample collection, sampling sites must be selected (section 1.2.1). For each sampling site, NWIS files and a field folder must be established, updated, and reviewed (section 1.2.2).

- The study team is responsible for selecting sampling sites and conditions (such as time of year, flow rate or stage) that will yield samples representative of the aqueous system being studied.
  - -- Each body of flowing and still surface water has a unique set of conditions that needs to be identified and considered in the site-selection process.
  - -- Field personnel must be trained in the correct and current water-quality data-collection procedures and must exercise judgment gained from field experience in order to make appropriate site selections.
- The study team is responsible for establishing and maintaining files for each sampling site.
  - -- Careful and complete documentation of site information and data collected must be input to electronic and paper files.
  - -- The field folder must include all the information necessary for efficient field operations.

1.2.1 SELECTION OF SAMPLING SITES

Once field work has begun, field personnel must select the point(s) or transect(s) at which samples will be collected. In most bodies of flowing or still water, a single sampling site or point is not adequate to describe the sampling area's physical properties and the distribution and abundance of chemical constituents or biological communities. Location, distribution, and number of surface-water sampling sites can affect the quality of resulting data. Generic guidelines for selecting flowing-water and still-water sites are described in this section.

When selecting surface-water sampling sites:

- Safety of field personnel comes first.
- Consider the study objectives, types of data needed, equipment needs, and sampling methods.
- Obtain all available historical information.
- Consider physical characteristics of the area, such as size and shape, land use, tributary and runoff characteristics, geology, point and nonpoint sources of contamination, hydraulic conditions, climate, water depth, and fluvial-sediment transport characteristics.

- Consider chemical and biological characteristics of the area (aquatic and terrestrial).

1.2.1.A
Flowing-Water Sites

Flowing-water sites refer to streams (fast or slow, intermittent, ephemeral, or perennial), canals, ditches, and flumes of all sizes and shapes, or to any other surface feature in which water moves unidirectionally. All or parts of reservoirs and estuaries that flow unidirectionally are considered to be flowing water. **Global-positioning system (GPS) equipment is useful to identify sampling-site location.** Determine latitude and longitude from maps or by land-survey techniques.

Flowing-water sampling sites optimally are located:

- At or near a stream-gaging station, to obtain concurrent surface-water discharge data required for computing constituent-transport loads and to determine discharge/constituent-concentration relations. (Measure discharge at time of sampling if a stream-gaging station is not at or near the sampling site or if discharge cannot be rated or estimated with sufficient accuracy.)
- In straight reaches with uniform flow, with a uniform and stable bottom contour, and where constituents are mixed along the cross section.
- Far enough above and below confluences of streamflow or point sources of contamination to avoid sampling a cross section where flows are poorly mixed or not unidirectional.
- In reaches upstream from bridges or other structures, to avoid contamination from the structure or from a road surface.
- In unidirectional flow that does not include eddies. (If eddies are present within the channel, sample only the unidirectional flow.)
- At or near a transect in a reach where other data are collected (such as data for suspended sediment, bedload, bottom material, or biological material) and (or) for which historical data are available.
- At a cross section where samples can be collected at any stage throughout the period of study, if possible.

After a tentative selection of a sampling site, develop a preliminary profile of field measurements[5] at various locations along the cross section (NFM 4 and NFM 6). The field-measurement profile is used to indicate reach homogeneity (see TECHNICAL NOTE). Final site selection is based on a comparison of these field measurements with the data requirements of the study.

> **TECHNICAL NOTE:** The preferred sampling method and number of verticals to be sampled within the stream cross section that are needed to obtain a sample that is sufficiently representative depends on stream homogeneity as indicated by the field-measurement profile and stream-discharge or other data, as well as by study objectives. Sampling methods are described in NFM 4. Note that the field-measurement profile is a useful guideline, but might not be representative of chemical homogeneity for the analytes of interest. Also, it might be desirable to move to a sampling site upstream or downstream to adjust for seasonal variation or extreme flow conditions.

The guidelines used for selecting sampling sites on ephemeral and intermittent streams are the same as those for perennial streams. Ephemeral and intermittent stream sites need additional planning and examination to account, for example, for conditions related to rapidly changing stage and discharge that

can occur as a result of flash flooding or urban runoff.

CAUTION: Any stream, including an ephemeral or intermittent stream, can rapidly become too deep and swift to wade safely.

1.2.1.B
Still-Water Sites

Still-water sites refer to all sizes and shapes of lakes, reservoirs, ponds, swamps, marshes, riverine backwaters, or any other body of surface water where water generally does not move unidirectionally. All or parts of reservoirs that do not flow unidirectionally could be considered to be still water.

When locating still-water sampling sites:

- Use in situ field measurements to help determine vertical and spatial distribution of sampling locations.
- Avoid areas near structures such as harbors, boat ramps, piers, fuel docks, and moored houseboats (to avoid point sources of contamination), unless these structures are part of the study.
- Select sites with a record of historical data, if possible.

1.2.2
INFORMATION FOR NATIONAL WATER INFORMATION SYSTEM (NWIS) FILES AND FIELD FOLDERS

Field personnel are responsible for establishing and maintaining electronic and paper site files. The information required for establishing electronic records in NWIS and for creating field folders for surface-water sampling sites is summarized below.

1.2.2.A
NWIS Files

USGS policy requires specific information on surface-water sampling sites to be stored in the site file in NWIS (Edwards and others, 1987; Hubbard, 1992; WRD Memorandum 92.59). Results of water analyses are stored in the water-quality file (QWDATA) of NWIS. The Automatic Data Processing System (ADAPS) contains continuous records of water levels and water quality. The minimum information required for establishing electronic files in NWIS for surface water is listed in table 1-1. Individual studies and District offices may have additional data-storage requirements.

If the site location has been identified:

- Establish or check the NWIS site file before the field trip.
- Update the files promptly after the field trip.
- Fill in information that is needed by, or could be useful to, the study in addition to the information shown on table 1-1.

RULE OF THUMB:
Before starting fieldwork—Make sure the NWIS file is established.
After fieldwork—Input updates to NWIS files promptly.

Table 1-1. Minimum information required for electronic storage of site and surface-water-quality data in the U.S. Geological Survey (USGS) National Water Information System (NWIS)

[GWSI, Ground-Water Site Inventory; QWDATA, Quality of Water Data]

Information required for creation of a surface-water site in NWIS[1, 2]		
Data description	Component (C) number for data entry into GWSI	Example (Description of code)
Agency code	C4	USGS
Station Identification Number	C1	11530500
Station Name	C12	Klamath River near Klamath, Cal.
Latitude	C9	413052
Longitude	C10	1235957
District/User	C6	06 (California)
State	C7	06 (California)
County	C8	015 (Del Norte)
Agency Use	C803	A (Active)
Station Type	C802	SW

Information required for storage of sample analyses in the water-quality file of NWIS (QWDATA)[1]		
Data description	Alpha parameter code	Sample data (Description of code)
Agency code	AGNCY	USGS
Station Identification Number	STAID	11530500
Sample Medium	MEDIM	9 (surface water)
Sample Type	STYPE	9 (regular sample)
Hydrologic ("Hydro") Event	EVENT	9 (routine sample)
Hydrologic ("Hydro") Condition	HSTAT	9 (stable stage)
Date (year/month/day)	DATES	19880909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields are available in NWIS that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether a non-USGS agency collected the data.

[2]Modified from Ground-Water Site Schedule Form 9-1904-A, May 1991. Also refer to Mathey (1991) and Garcia and others (1997).

1.2.2.B
Field Folders

Selected information that is needed for reference while at a surface-water site is kept in a field folder. The field folder contains information needed by trained personnel to locate and safely collect and process water samples. The field folder is taken along on each sampling trip. General contents of the field folder are listed on the field-folder checklist (fig. 1-2), but the folder should be customized

according to study needs.

Field-folder checklist: surface-water quality		
	Item	Comments
	Station description: • Location of gaging station (if one is present). • Location of sample-collection sites: high and low streamflows. • Hydrologic and geologic sections. • Name of landowner, tenant, or other responsible party. • Site access instructions (for example, call owner or site operator before arrival at site, obtain key to unlock security gate). • Photographs to document site conditions.	
	Maps to site (State and local)	
	Profiles of cross section of stream channel at sampling location(s). • Stream-bottom geometry. • Physical and chemical measurements.	
	Safety information (NFM 9): • Nearest emergency facilities. • Phone numbers (home) of study chief or supervisor. • Traffic condition and traffic plan showing where to park, placement of flags and cones. • Location of power lines. • Environmental hazards, such as weather and animal	
	Sampling schedule: • Laboratory analyses to be requested and associated codes. • When to collect samples (high or low flow).	
	Bottle types needed for each analytical schedule.	
	Analytical Services Request form(s) and example of a completed form.	
	Sampling instructions: • Cumulative-discharge curves at about 10-, 50-, and 90-percent duration. • Velocity cross sections at about 10-, 50-, and 90-percent duration. • Equipment to use at various flows. • low-duration curve. • Discharge rating curves and (or) tables.	
	Shipping instructions: • Amount of ice to use. • Mailing labels to and from laboratory. • Location of nearest post office or shipping agent.	
	Surface-water field form and an example of completed form.	
	A tabulation sheet for each type of bacteria enumerated at the site (include example with date of sample, streamflow, volumes filtered, dilutions, plate counts).	

	Plots of field-measured data (last 5-10 years of record); if there is a good enough relation to show outliers, include: • Conductivity versus streamflow. • Conductivity versus alkalinity. • Temperature versus time.	
	Statistical summary of historical water data: • Seasonal, maximum-minimum values. • Discharge-related maximum-minimum values.	
	Special equipment needed to address site-specific conditions: • Sampling. • Safety.	

Figure 1-2. Checklist for contents of surface-water sampling field folder.

[5]Field-measurement methods are described in NFM 6. The profile of the cross section usually includes measurements such as specific electrical conductance (conductivity), pH, temperature, dissolved oxygen, and turbidity.

⇨ 1.3 Ground Water
⇧ Return to Section1.1 Field-trip preparation
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section 1.2.pdf

1.2 SURFACE WATER

Before sample collection, sampling sites must be selected (section 1.2.1). For each sampling site, NWIS files and a field folder must be established, updated, and reviewed (section 1.2.2).

- The study team is responsible for selecting sampling sites and conditions (such as time of year, flow rate or stage) that will yield samples representative of the aqueous system being studied.
  - -- Each body of flowing and still surface water has a unique set of conditions that needs to be identified and considered in the site-selection process.
  - -- Field personnel must be trained in the correct and current water-quality data-collection procedures and must exercise judgment gained from field experience in order to make appropriate site selections.
- The study team is responsible for establishing and maintaining files for each sampling site.
  - -- Careful and complete documentation of site information and data collected must be input to electronic and paper files.
  - -- The field folder must include all the information necessary for efficient field operations.

1.2.1 SELECTION OF SAMPLING SITES

Once field work has begun, field personnel must select the point(s) or transect(s) at which samples will be collected. In most bodies of flowing or still water, a single sampling site or point is not adequate to describe the sampling area's physical properties and the distribution and abundance of chemical constituents or biological communities. Location, distribution, and number of surface-water sampling sites can affect the quality of resulting data. Generic guidelines for selecting flowing-water and still-water sites are described in this section.

When selecting surface-water sampling sites:

- Safety of field personnel comes first.
- Consider the study objectives, types of data needed, equipment needs, and sampling methods.
- Obtain all available historical information.
- Consider physical characteristics of the area, such as size and shape, land use, tributary and runoff characteristics, geology, point and nonpoint sources of contamination, hydraulic conditions, climate, water depth, and fluvial-sediment transport characteristics.

- Consider chemical and biological characteristics of the area (aquatic and terrestrial).

1.2.1.A
Flowing-Water Sites

Flowing-water sites refer to streams (fast or slow, intermittent, ephemeral, or perennial), canals, ditches, and flumes of all sizes and shapes, or to any other surface feature in which water moves unidirectionally. All or parts of reservoirs and estuaries that flow unidirectionally are considered to be flowing water. **Global-positioning system (GPS) equipment is useful to identify sampling-site location.** Determine latitude and longitude from maps or by land-survey techniques.

Flowing-water sampling sites optimally are located:

- At or near a stream-gaging station, to obtain concurrent surface-water discharge data required for computing constituent-transport loads and to determine discharge/constituent-concentration relations. (Measure discharge at time of sampling if a stream-gaging station is not at or near the sampling site or if discharge cannot be rated or estimated with sufficient accuracy.)
- In straight reaches with uniform flow, with a uniform and stable bottom contour, and where constituents are mixed along the cross section.
- Far enough above and below confluences of streamflow or point sources of contamination to avoid sampling a cross section where flows are poorly mixed or not unidirectional.
- In reaches upstream from bridges or other structures, to avoid contamination from the structure or from a road surface.
- In unidirectional flow that does not include eddies. (If eddies are present within the channel, sample only the unidirectional flow.)
- At or near a transect in a reach where other data are collected (such as data for suspended sediment, bedload, bottom material, or biological material) and (or) for which historical data are available.
- At a cross section where samples can be collected at any stage throughout the period of study, if possible.

After a tentative selection of a sampling site, develop a preliminary profile of field measurements[5] at various locations along the cross section (NFM 4 and NFM 6). The field-measurement profile is used to indicate reach homogeneity (see TECHNICAL NOTE). Final site selection is based on a comparison of these field measurements with the data requirements of the study.

> **TECHNICAL NOTE:** The preferred sampling method and number of verticals to be sampled within the stream cross section that are needed to obtain a sample that is sufficiently representative depends on stream homogeneity as indicated by the field-measurement profile and stream-discharge or other data, as well as by study objectives. Sampling methods are described in NFM 4. Note that the field-measurement profile is a useful guideline, but might not be representative of chemical homogeneity for the analytes of interest. Also, it might be desirable to move to a sampling site upstream or downstream to adjust for seasonal variation or extreme flow conditions.

The guidelines used for selecting sampling sites on ephemeral and intermittent streams are the same as those for perennial streams. Ephemeral and intermittent stream sites need additional planning and examination to account, for example, for conditions related to rapidly changing stage and discharge that

can occur as a result of flash flooding or urban runoff.

CAUTION: Any stream, including an ephemeral or intermittent stream, can rapidly become too deep and swift to wade safely.

1.2.1.B
Still-Water Sites

Still-water sites refer to all sizes and shapes of lakes, reservoirs, ponds, swamps, marshes, riverine backwaters, or any other body of surface water where water generally does not move unidirectionally. All or parts of reservoirs that do not flow unidirectionally could be considered to be still water.

When locating still-water sampling sites:

- Use in situ field measurements to help determine vertical and spatial distribution of sampling locations.
- Avoid areas near structures such as harbors, boat ramps, piers, fuel docks, and moored houseboats (to avoid point sources of contamination), unless these structures are part of the study.
- Select sites with a record of historical data, if possible.

1.2.2
INFORMATION FOR NATIONAL WATER INFORMATION SYSTEM (NWIS) FILES AND FIELD FOLDERS

Field personnel are responsible for establishing and maintaining electronic and paper site files. The information required for establishing electronic records in NWIS and for creating field folders for surface-water sampling sites is summarized below.

1.2.2.A
NWIS Files

USGS policy requires specific information on surface-water sampling sites to be stored in the site file in NWIS (Edwards and others, 1987; Hubbard, 1992; WRD Memorandum 92.59). Results of water analyses are stored in the water-quality file (QWDATA) of NWIS. The Automatic Data Processing System (ADAPS) contains continuous records of water levels and water quality. The minimum information required for establishing electronic files in NWIS for surface water is listed in table 1-1. Individual studies and District offices may have additional data-storage requirements.

If the site location has been identified:

- Establish or check the NWIS site file before the field trip.
- Update the files promptly after the field trip.
- Fill in information that is needed by, or could be useful to, the study in addition to the information shown on table 1-1.

RULE OF THUMB:
Before starting fieldwork—Make sure the NWIS file is established.
After fieldwork—Input updates to NWIS files promptly.

Table 1-1. Minimum information required for electronic storage of site and surface-water-quality data in the U.S. Geological Survey (USGS) National Water Information System (NWIS)

[GWSI, Ground-Water Site Inventory; QWDATA, Quality of Water Data]

Information required for creation of a surface-water site in NWIS[1, 2]		
Data description	Component (C) number for data entry into GWSI	Example (Description of code)
Agency code	C4	USGS
Station Identification Number	C1	11530500
Station Name	C12	Klamath River near Klamath, Cal.
Latitude	C9	413052
Longitude	C10	1235957
District/User	C6	06 (California)
State	C7	06 (California)
County	C8	015 (Del Norte)
Agency Use	C803	A (Active)
Station Type	C802	SW
Information required for storage of sample analyses in the water-quality file of NWIS (QWDATA)[1]		
Data description	Alpha parameter code	Sample data (Description of code)
Agency code	AGNCY	USGS
Station Identification Number	STAID	11530500
Sample Medium	MEDIM	9 (surface water)
Sample Type	STYPE	9 (regular sample)
Hydrologic ("Hydro") Event	EVENT	9 (routine sample)
Hydrologic ("Hydro") Condition	HSTAT	9 (stable stage)
Date (year/month/day)	DATES	19880909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields are available in NWIS that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether a non-USGS agency collected the data.

[2]Modified from Ground-Water Site Schedule Form 9-1904-A, May 1991. Also refer to Mathey (1991) and Garcia and others (1997).

1.2.2.B
Field Folders

Selected information that is needed for reference while at a surface-water site is kept in a field folder. The field folder contains information needed by trained personnel to locate and safely collect and process water samples. The field folder is taken along on each sampling trip. General contents of the field folder are listed on the field-folder checklist (fig. 1-2), but the folder should be customized

according to study needs.

Field-folder checklist: surface-water quality		
	Item	Comments
	Station description: • Location of gaging station (if one is present). • Location of sample-collection sites: high and low streamflows. • Hydrologic and geologic sections. • Name of landowner, tenant, or other responsible party. • Site access instructions (for example, call owner or site operator before arrival at site, obtain key to unlock security gate). • Photographs to document site conditions.	
	Maps to site (State and local)	
	Profiles of cross section of stream channel at sampling location(s). • Stream-bottom geometry. • Physical and chemical measurements.	
	Safety information (NFM 9): • Nearest emergency facilities. • Phone numbers (home) of study chief or supervisor. • Traffic condition and traffic plan showing where to park, placement of flags and cones. • Location of power lines. • Environmental hazards, such as weather and animal	
	Sampling schedule: • Laboratory analyses to be requested and associated codes. • • When to collect samples (high or low flow).	
	Bottle types needed for each analytical schedule.	
	Analytical Services Request form(s) and example of a completed form.	
	Sampling instructions: • Cumulative-discharge curves at about 10-, 50-, and 90-percent duration. • Velocity cross sections at about 10-, 50-, and 90-percent duration. • Equipment to use at various flows. • low-duration curve. • Discharge rating curves and (or) tables.	
	Shipping instructions: • Amount of ice to use. • Mailing labels to and from laboratory. • Location of nearest post office or shipping agent.	
	Surface-water field form and an example of completed form.	
	A tabulation sheet for each type of bacteria enumerated at the site (include example with date of sample, streamflow, volumes filtered, dilutions, plate counts).	

	Plots of field-measured data (last 5-10 years of record); if there is a good enough relation to show outliers, include: • Conductivity versus streamflow. • Conductivity versus alkalinity. • Temperature versus time.	
	Statistical summary of historical water data: • Seasonal, maximum-minimum values. • Discharge-related maximum-minimum values.	
	Special equipment needed to address site-specific conditions: • Sampling. • Safety.	

Figure 1-2. Checklist for contents of surface-water sampling field folder.

[5]Field-measurement methods are described in NFM 6. The profile of the cross section usually includes measurements such as specific electrical conductance (conductivity), pH, temperature, dissolved oxygen, and turbidity.

⇨ 1.3 Ground Water
⇧ Return to Section1.1 Field-trip preparation
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section 1.3.pdf

1.3
GROUND WATER

Ground water is sampled from various types of existing wells or wells installed specifically for a study.

- **Water-supply wells** are wells that are installed primarily for supply of public, irrigation, domestic, commercial, or industrial water and usually are equipped with a dedicated high-capacity pump. The term "supply well" is used in this publication.
- **Observation wells** are wells or piezometers that are installed (usually without a dedicated pump) for the purpose of collecting hydrologic data. The term generally has been applied to wells installed to observe and determine hydrologic characteristics of an aquifer (Lapham and others, 1997).
- **Monitor wells** are observation wells that are installed specifically for assessment of physical, chemical, and biological characteristics of the aquifer. Low-capacity portable pumps are commonly used for sampling, but monitoring wells can be equipped with a dedicated pump. The term "monitoring well" is used in this publication.

Information is compiled about the well and well site during site-reconnaissance visits, well installation, and subsequent data-collection efforts at the site. This information is used to help select the well(s) needed for study. The ground-water site inventory is compiled in the office and verified in the field. In an office inventory, the study team identifies existing wells or well sites and compiles background information and available records for those wells. The field inventory is completed during reconnaissance trips in which well location is verified, additional information is collected, and the suitability of the site for study objectives is determined. For each well, the inventory of site and well information is entered into the NWIS water-quality (QWDATA) and ground-water site inventory (GWSI) data bases and is added to the file created for the well (well file).

1.3.1
SITE RECONNAISSANCE AND WELL SELECTION

Field personnel critically evaluate existing and installed wells to determine whether they will yield samples that are representative of the environment targeted for study.

As a member of the study team:

- Be prepared to participate in office- and field-related aspects of selecting and installing wells (see Lapham and others, 1997, for details).

- Be familiar with study objectives and requirements for data collection and quality.
- Be familiar with considerations for well selection and well installation (summarized in table 1-2).

Information gathered from a site reconnaissance visit can help determine whether an existing well or a proposed well-installation site meets the criteria established by the study. Site reconnaissance visits also ensure efficient field operations and could be a critical factor in site selection or rejection. These site visits commonly are needed to verify the location and condition of wells, evaluate site characteristics, and make modifications to the site and adjustments to sampling plans to allow sampling to proceed. Before leaving for the site, determine the activities that are to be completed and make the necessary preparations (table 1-3).

Keep in mind the primary concerns for water-quality studies:

- The sample must represent the system intended for study.
- Sample integrity must be maintained.

Site visits also can be used to identify areas of ground-water recharge and discharge, test field equipment, test well-purging and sampling procedures, conduct aquifer tests, make preliminary field measurements, and identify the presence of target analytes.

Review safety plans and procedures before leaving for the field.

Table 1-2. Considerations for well selection and well installation

[Modified from Lapham and others, 1997]

Well location
• Location conforms to the study's network design for areal and depth distribution. • Land-use/land-cover characteristics, if relevant, are consistent with study objectives. • Site is accessible for equipment needed for well installation and sample collection.
Hydrogeologic unit(s)
• Hydrogeologic unit(s) that contribute water to the well can be identified. • Depth and thickness of targeted hydrogeologic unit(s) are known or can be determined. • Yield of water is adequate for sampling (typically, a minimum of 1 gallon per minute).
Well records, description, design, materials, and structure
• Available records (for example, logs of well drilling, completion, and development) have sufficient information to meet the criteria established by the study. • Borehole or casing/screen diameter is adequate for equipment. • Depth to top and bottom of sample-collection (open or screened) interval is known (to determine area contributing water to well). • Length of well screen is proportional to the vertical and areal scale of investigation. • Well has only one screened or open interval, if possible. (Packers can be used to isolate the interval of interest, but packers might not completely isolate zones in unconsolidated or highly fractured aquifers. If packers are used, materials of construction must be compatible with analytes to be studied.) • Top of well screen is several feet below mean annual low-water table to reduce chances of well going dry and to

avoid sampling from unsaturated intervals.
- Filter pack is of a reasonable length (a long interval compared with length of screened or open interval usually results in uncertainty as to location of the source of water to well).
- Well-construction materials do not leach or sorb substances that could alter ambient target-analyte concentrations.
- Well-structure integrity and communication with the aquifer are sound. (Checks include annual depth-to-bottom measurements, borehole caliper and downhole-camera video logs, and aquifer tests.)

Pump type, materials, performance, and location of sampler intake

- Supply wells have water-lubricated turbine pumps rather than oil-lubricated turbine pumps. (Avoid suction-lift, jet, or gas-contact pumps, especially for analytes affected by pressure changes, exposure to oxygen, or that partition to a gas phase.)
- Pump and riser-pipe materials do not affect target-analyte concentrations.
- Effects of pumping rate on measurements and analyses have been or will be evaluated.
- Sampler intake is ahead of water treatments, pressure tanks, or holding tanks.

Table 1-3. Example of site-reconnaissance activities

Before the site visit

Review considerations for well selection and installation (summarized in table 1-2).

Review background information collected.

Obtain permission to gain access to the site and to collect samples from the well.

Update well files: record changes in ownership and land use.

Contact utility companies (gas, water, and electric) before digging or drilling.

Determine whether the pump may or may not be removed from well by field personnel. (Owner's permission is required to remove a pump—you could be liable for damage to pump or well.)

Be sure that you get information needed about the site that could interfere with or interrupt sampling. For example,

- Hours of pump operation and scheduled downtime
- Pumping rate or rates
- Holding tanks or chemical treatments
- Electrical service to the site
- Scheduled maintenance for pumps or related equipment
- Scheduled site maintenance, such as painting, construction, and defoliation
- Seasonal water-level declines that make the well unusable
- Times of denied access; for example, no access while the owner is out of town
- Special site-access needs; for example, clearance with a site owner or site operator, keys to unlock access to the site, animals
- Restrictions on the location

Record conditions that could compromise study objectives, including potential point or nonpoint sources of contamination. For example,

- Nearby wells that could affect well hydraulics
- Condition of well—for example, rusting or punctured casing, poor surface seal
- Land use and land cover or changes in land use and land cover
- Application of salt on nearby roads during winter, or application or use of herbicides and pesticides
- Landfills or other waste-management facilities
- Industrial, commercial, and agricultural complexes and discharges

During the site visit

Measure water level in each well. Record water-level data on the appropriate form(s).

Identify potential difficulties with the type of equipment and sample-collection methodology to be used. (Note that sampling plans will have to be modified accordingly.)

Update field folders.

- Note site conditions that could affect the quality of data collected from that well.
- Note change(s) in land use.

Verify well identification number and make sure that it is clearly and permanently labeled.

- Check that identification corresponds with what is in the field folder and on site and location maps
- Correct any mistakes or uncertainty about well identification and well location.

Verify type of pump, well diameter, and use of holding tanks, pressure tanks, chemical treatments.

- Check whether oil is floating on the water column in a well equipped with an oil- lubricated pump.
- Make sure that the downhole treatment system is turned off before collecting water samples.
- Determine if a portable pump or another intended sampling device is suitable for use.

Establish optimum pumping rate(s) for purging and sample collection and decide where to route excess discharge.

- Adjust pumping rate to ensure adequate purging of the well without entrainment of atmospheric gases due to excessive drawdown.
- Route water away from the well to prevent (1) creating muddy and slippery conditions and (2) damage to or defacement of the property to which you were granted access.

Check that well structure is intact

- Wells used for ground-water studies should be "sounded" annually to check whether depth to bottom corresponds with well construction information or whether the well is filling with loose materials (U.S. Geological Survey, 1980; Lapham and others, 1997). A decrease in depth to bottom could indicate that the well casing is collapsing, or that there is a breach or corrosion of well screen or casing, or that the well is improperly designed to retain aquifer materials.
- Borehole caliper and downhole-camera video logs can identify a damaged or broken well casing. A downhole camera can identify a plugged screen or accumulation of sediment in the well.
- Aquifer tests, such as slug tests, can be used to check the hydraulic connection between the well and the aquifer. Aquifer tests, however, are generally beyond the scope of site reconnaissance.
- The surface seal of a USGS monitoring well should be intact and the well should be capped. Concrete pad should be repaired if cracked or separated from outer casing. A tight-fitting well cap should have a small ventilation hole.

Check well access for sample-collection points.

- Sample-collection points need to be near the wellhead, ahead of where water enters pressure tanks, holding tanks, or treatment systems.
- At wells where an access point close to the well is not available, it might be possible to install a hose bibb or tap at the wellhead. Because it usually is not possible to control the pumping rate of a supply well, the field person may need to set up a hose-and-valve system to control the rate at which water is sampled and to reduce the likelihood of backflow of water stored in plumbing lines.

Check well access for water-level measurements. The construction of some supply wells makes water-level measurements difficult or impossible.

- Although it is often possible to slip a weighted steel or electric well tape below the pump to get a water-level measurement, the pump can be damaged if the weight or tape becomes entangled in the pump. The weight should be connected so that it will snap off of the tape under stress.
- Water levels can be estimated through the air line on some wells.

- Sometimes field personnel are permitted to remove the pump from the well to get a measurement; however, pump removal can be difficult, time consuming, and potentially unsafe, and could damage the pump.
- A note should be made in the well file if there is no access for a depth measurement.

1.3.2 INFORMATION FOR NATIONAL WATER INFORMATION SYSTEM (NWIS) FILES, WELL FILES, AND FIELD FOLDERS

USGS policy requires specific information on ground-water sampling sites to be stored in NWIS (Edwards and others, 1987; Hubbard, 1992; WRD Memorandum 92.59). Paper documents, such as agreements between the well owner and the USGS for use of the well, also are necessary and are stored in well files and field folders.

- Much of the information needed to set up files for existing wells can be obtained from well owners, drillers, records from state or local jurisdictions, and well-construction logs.
- Information that will be needed to set up well files for new wells is recorded by field personnel as the new well is installed (Lapham and others, 1997).

RULE OF THUMB:
Before starting fieldwork—Make sure the NWIS file is established.
After fieldwork—Update NWIS files promptly.

1.3.2.A NWIS Files

Within the NWIS system, well information, ground-water levels, and water-quality data are stored in three data bases: the Ground-Water Site Inventory (GWSI), Quality of Water Data (QWDATA), and the Automatic Data Processing System (ADAPS). All wells for which data are stored must be identified by an electronic record in NWIS.

- GWSI primarily contains (1) descriptive information about the site and well and (2) noncontinuous water-level data. Specific information entered into GWSI is used to create an NWIS site file.
- QWDATA contains results of water-quality analyses, noncontinuous water-level data, and other data related to water-quality analysis.
- ADAPS contains continuous records of water levels and water quality.

The minimum information required for establishing electronic files in GWSI and QWDATA is shown in table 1-4. Individual studies and District offices may have additional data-storage requirements. For example, the GUNIT (geologic unit) code provides important information for ground-water studies.

When creating or updating a GWSI site-file record, fill in information that is needed by, or useful to, the study, in addition to the required information shown in table 1-4.

Table 1-4. Minimum information required for electronic storage of site and ground-water-quality data in the U.S. Geological Survey National Water Information System (NWIS)

[GWSI, Ground-Water Site Inventory; QWDATA, Quality of Water Data]

Information required for creation of a ground-water file in NWIS[1,2] (GWSI)		
Data description	**Component (C) number for data entry into GWSI**	**Example (Description of code)**
Agency code	C4	USGS
Station Identification Number (Latitude/longitude/sequence no.)	C1	394224075340501
Station Name		
Latitude	C12	KE Be 61
Longitude	C9	394224
Station locator sequence number	C10	0753405
District/User	C815	01
State	C6	24 (Maryland)
County	C7	10 (Delaware)
Agency Use	C8	003 (Sussex)
Station Type	C803	A (Active)
Data Reliability	C802	6 (Well)
Site Type	C3	C (Field Checked)
Use of site	C2	W (Well)
	C23	O (Observation)

Information required for storage of sample analyses in the water-quality file of NWIS (QWDATA)[1]		
Data description	**Alpha parameter code**	**Sample data (Description of code)**
Agency code	AGNCY	USGS
Station Identification Number	STAID	394224075340501
Sample Medium	MEDIM	6 (ground water)
Sample Type	STYPE	2 (blank sample)
Hydrologic ("Hydro") Event	EVENT	9 (routine sample)
Hydrologic ("Hydro") Condition	HSTAT	A (not determined)
Date (year/month/day)	DATES	19880909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields from those shown are available in NWIS and QWDATA that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether a non-USGS agency collected the data.

[2]From Ground-Water Site Schedule Form 9-1904-A, May 1991. Also refer to Mathey (1991) and Garcia and others (1997).

1.3.2.B
Well Files

A well file also must be established for each well selected or installed for the study or in a data network. At the outset of the study, it is useful to refer to a checklist of the items and types of information needed for the well file (fig. 1-3).

WELL-INFORMATION CHECKLIST, Page 1 of 2

Project name and identification number: _____
Latitude-longitude: _____ Sequence number: _____
Other site or well ID: _____ Station name: _____

Indicate well type: Public, Domestic, Commercial, Industrial, Irrigation, Observation, Monitoring, Other _____

Item in well file	Date item filed
Criteria for well selection or installation	
Ground-Water Site Inventory (GWSI) data entered into National Water Information System (NWIS)	
Paper copy of GWSI form	
Copies of agreement to complete activity (for example, drilling or sampling) _____	
List agreements _____	
Copies of field forms and logs:	
Well-drilling record	
Driller's log	
Lithologic log	
Cuttings	
Cores	
Aquifer tests: (list types) _____	
Geophysical logs: (list types) _____	
Well-construction record	
Well-development record	
Well-maintenance checks: (list types) _____	
Well-location information:	
Latitude-longitude and method of determination	
Well-location map(s)	
Site-sketch map	
Written description of location	
Well-casing elevation (elevation, and method and date of determination)	
Photographs of well and vicinity (with measuring/sampling points identified)	
Land use/land cover form (Lapham and others, 1997)	

Figure 1-3. Example of a well-information checklist for a well file and field folder.

WELL-INFORMATION CHECKLIST, Page 2 of 2

Item in well file	Date item filed
Water-quality records for each sampling event (for example, purging, field measurements, field forms, sampling history) and copies of laboratory analyses requested	
Water-level measurements - current:	
Water-level measurements - historical:	
Record of well leveling (survey)	
Pumping schedule/history	
Type of pump in well and location of intake	

Description of measuring point for water levels: _____

Description of collection point for samples from

Supply wells _____

Monitoring wells _____

Other information (for example, geologic unit, aquifer name):

Figure 1-3. Example of a well-information checklist for a well file and field folder—*Continued.*

The well file is the repository of the information compiled for the well, and it should contain documentation for site selection, well inventory, well installation, and sample collection.

- Include well-construction information to the extent that it is available (Lapham and others, 1997).
- Include water-quality information, hydrogeologic field forms and logs, and plots of water-quality data and other hydrologic, geologic, geochemical, or geophysical information available for the well or field site.
- Include a log of well-maintenance and well-integrity checks and tests, geophysical logs and surveys, results of aquifer tests, analyses of cores or cuttings of geologic materials, and analyses from previously collected samples from the well or from a nearby well.

1.3.2.C
Field Folders

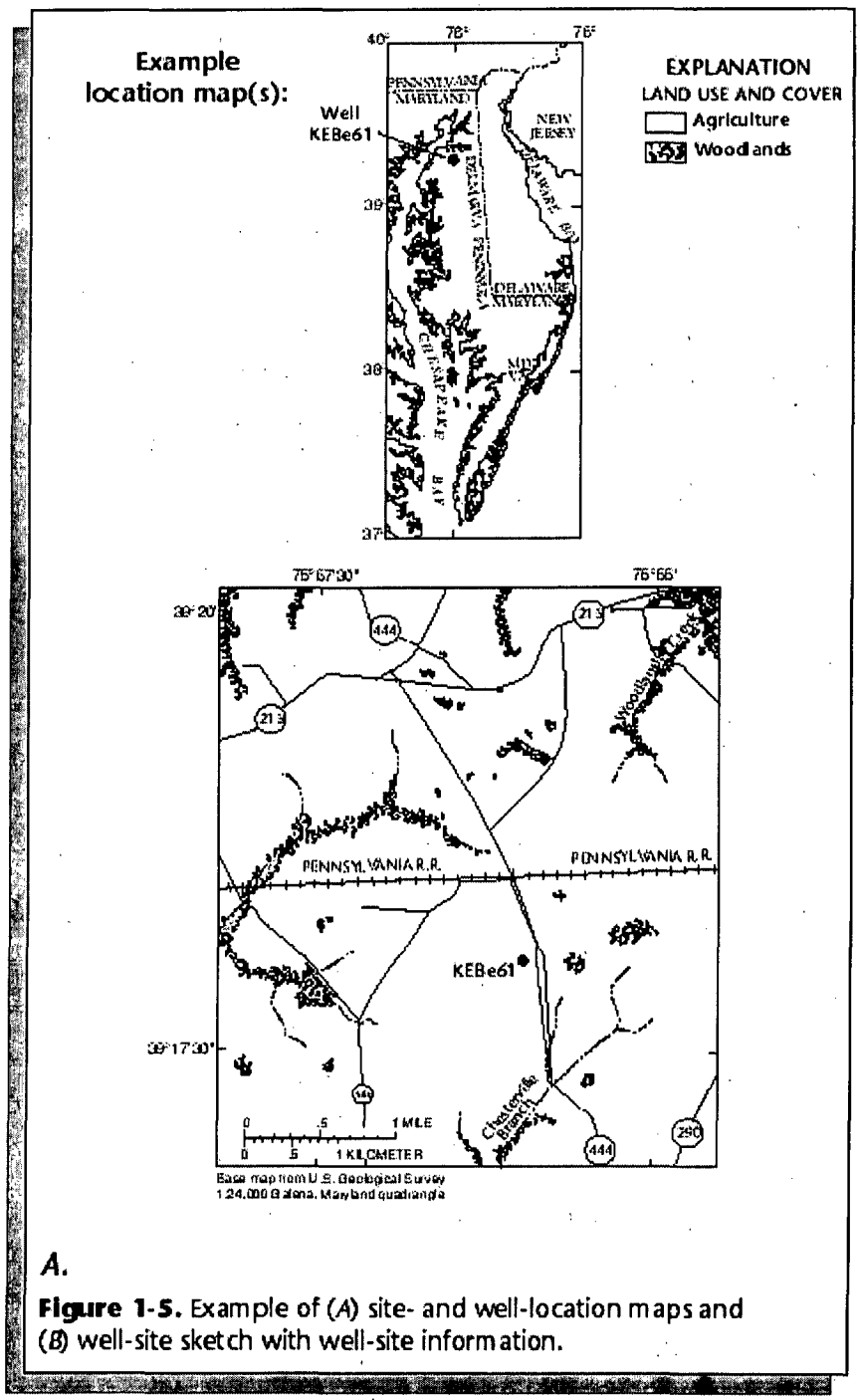
Selected information related to the well file and electronic records is kept in a field folder. The field folder contains information needed by personnel to locate and gain access to the site and to collect and process ground-water samples. The field folder should be taken along on each visit to the well for reference at the field site. The generic contents of a field folder are listed in the field folder checklist

(fig. 1-4). Examples of site-location maps and a site sketch are shown in figure 1-5.

Field-folder checklist: ground-water quality		
	Item	Comments
	Forms (new forms and (or) examples of completed forms): • Permission forms—must be signed by proper authority. • Analytical Services Request form(s). • Ground-water field form and well-inventory form.	
	Equipment and supplies checklists.	
	Field-techniques manuals.	
	Site location and description: • Maps showing location and identification number of well(s). • Name of landowner, tenant, or other responsible party. • Site access instructions (call owner; get keys or tools needed for security gate, well house, well protective casing). • Photographs and land use/land cover form to document site conditions. • Well dimensions and construction.	
	Sampling schedule and instructions: • Laboratory analyses, codes, and bottle types • Preservation requirements. • Quality-control samples. • Location of sampler intake during sample collection. • Pumping rate for purging and sampling.	
	Purging instructions: • Number of well volumes. • Rate of pumping; containment and discharge of purge water. • Location of sampler intake during purging. • Field measurements and stability protocols. • Previous field-measurement and purge-volume records. • Place to discharge excess water.	
	Water-level measurements: • Location of measuring point. • Previous records from well.	
	Safety information: • Nearest emergency facilities; home phone number of supervisor. • Diagram of where to park, placement of flags and cones. • Traffic conditions; location of power lines. • Environmental hazards such as weather and animals.	
	Ancillary information: • Geologic section(s). • Hydrologic section(s).	

	• Borehole geophysical logs.	
	Shipping instructions: • Mailing labels; location of nearest post office or shipping agent. • Ice or holding time requirements.	

Figure 1-4. Checklist for contents of ground-water sampling field folder.



A.

Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch with well-site information.

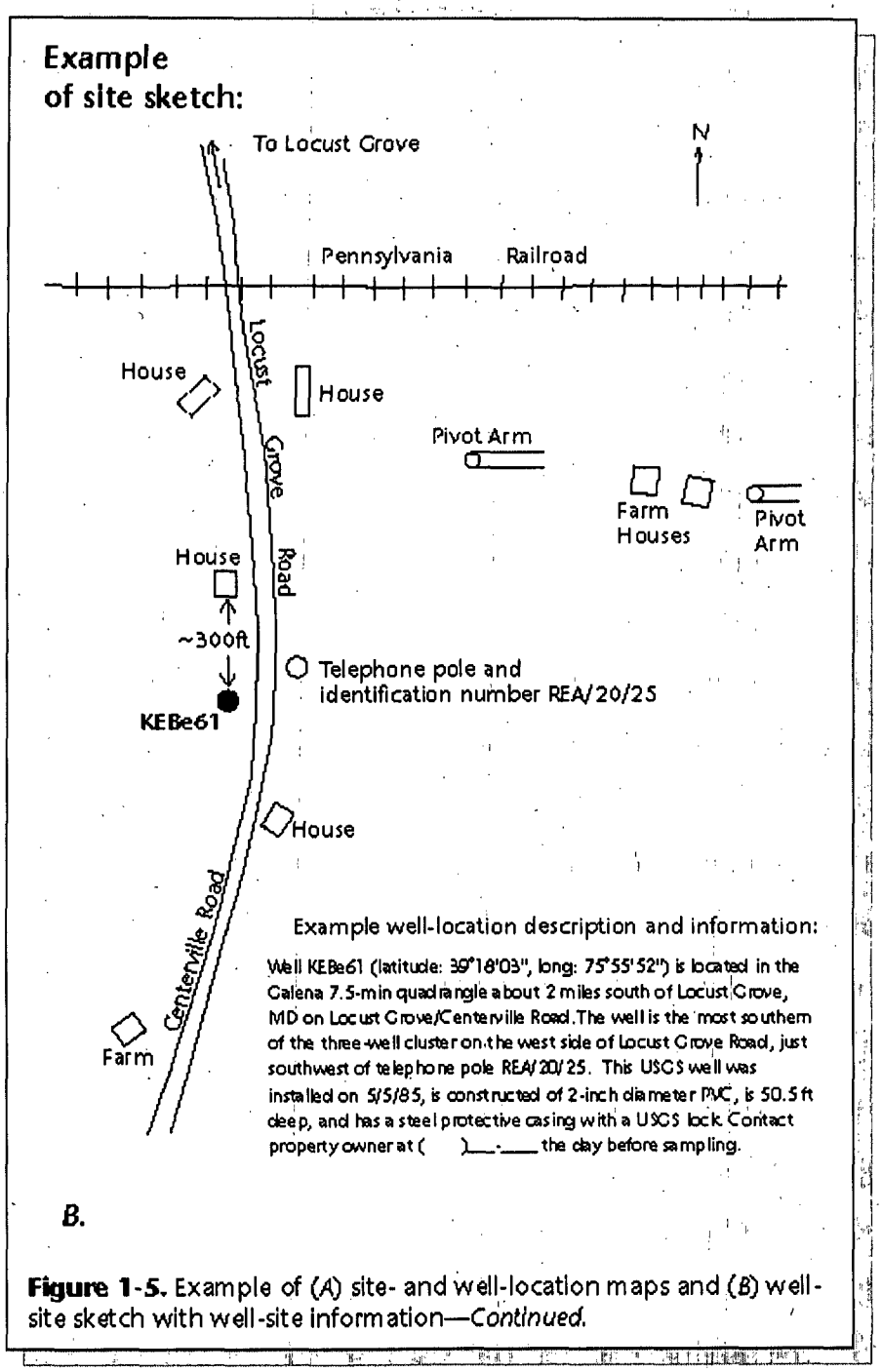


Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch with well-site information—*Continued.*

⇨ Selected references and internal documents
⇧ Return to Section 1.2 Surface water
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section 1.3.pdf

1.3 GROUND WATER

Ground water is sampled from various types of existing wells or wells installed specifically for a study.

- **Water-supply wells** are wells that are installed primarily for supply of public, irrigation, domestic, commercial, or industrial water and usually are equipped with a dedicated high-capacity pump. The term "supply well" is used in this publication.
- **Observation wells** are wells or piezometers that are installed (usually without a dedicated pump) for the purpose of collecting hydrologic data. The term generally has been applied to wells installed to observe and determine hydrologic characteristics of an aquifer (Lapham and others, 1997).
- **Monitor wells** are observation wells that are installed specifically for assessment of physical, chemical, and biological characteristics of the aquifer. Low-capacity portable pumps are commonly used for sampling, but monitoring wells can be equipped with a dedicated pump. The term "monitoring well" is used in this publication.

Information is compiled about the well and well site during site-reconnaissance visits, well installation, and subsequent data-collection efforts at the site. This information is used to help select the well(s) needed for study. The ground-water site inventory is compiled in the office and verified in the field. In an office inventory, the study team identifies existing wells or well sites and compiles background information and available records for those wells. The field inventory is completed during reconnaissance trips in which well location is verified, additional information is collected, and the suitability of the site for study objectives is determined. For each well, the inventory of site and well information is entered into the NWIS water-quality (QWDATA) and ground-water site inventory (GWSI) data bases and is added to the file created for the well (well file).

1.3.1 SITE RECONNAISSANCE AND WELL SELECTION

Field personnel critically evaluate existing and installed wells to determine whether they will yield samples that are representative of the environment targeted for study.

As a member of the study team:

- Be prepared to participate in office- and field-related aspects of selecting and installing wells (see Lapham and others, 1997, for details).

- Be familiar with study objectives and requirements for data collection and quality.
- Be familiar with considerations for well selection and well installation (summarized in table 1-2).

Information gathered from a site reconnaissance visit can help determine whether an existing well or a proposed well-installation site meets the criteria established by the study. Site reconnaissance visits also ensure efficient field operations and could be a critical factor in site selection or rejection. These site visits commonly are needed to verify the location and condition of wells, evaluate site characteristics, and make modifications to the site and adjustments to sampling plans to allow sampling to proceed. Before leaving for the site, determine the activities that are to be completed and make the necessary preparations (table 1-3).

Keep in mind the primary concerns for water-quality studies:

- The sample must represent the system intended for study.
- Sample integrity must be maintained.

Site visits also can be used to identify areas of ground-water recharge and discharge, test field equipment, test well-purging and sampling procedures, conduct aquifer tests, make preliminary field measurements, and identify the presence of target analytes.

Review safety plans and procedures before leaving for the field.

Table 1-2. Considerations for well selection and well installation

[Modified from Lapham and others, 1997]

Well location
• Location conforms to the study's network design for areal and depth distribution. • Land-use/land-cover characteristics, if relevant, are consistent with study objectives. • Site is accessible for equipment needed for well installation and sample collection.
Hydrogeologic unit(s)
• Hydrogeologic unit(s) that contribute water to the well can be identified. • Depth and thickness of targeted hydrogeologic unit(s) are known or can be determined. • Yield of water is adequate for sampling (typically, a minimum of 1 gallon per minute).
Well records, description, design, materials, and structure
• Available records (for example, logs of well drilling, completion, and development) have sufficient information to meet the criteria established by the study. • Borehole or casing/screen diameter is adequate for equipment. • Depth to top and bottom of sample-collection (open or screened) interval is known (to determine area contributing water to well). • Length of well screen is proportional to the vertical and areal scale of investigation. • Well has only one screened or open interval, if possible. (Packers can be used to isolate the interval of interest, but packers might not completely isolate zones in unconsolidated or highly fractured aquifers. If packers are used, materials of construction must be compatible with analytes to be studied.) • Top of well screen is several feet below mean annual low-water table to reduce chances of well going dry and to

avoid sampling from unsaturated intervals.
- Filter pack is of a reasonable length (a long interval compared with length of screened or open interval usually results in uncertainty as to location of the source of water to well).
- Well-construction materials do not leach or sorb substances that could alter ambient target-analyte concentrations.
- Well-structure integrity and communication with the aquifer are sound. (Checks include annual depth-to-bottom measurements, borehole caliper and downhole-camera video logs, and aquifer tests.)

Pump type, materials, performance, and location of sampler intake

- Supply wells have water-lubricated turbine pumps rather than oil-lubricated turbine pumps. (Avoid suction-lift, jet, or gas-contact pumps, especially for analytes affected by pressure changes, exposure to oxygen, or that partition to a gas phase.)
- Pump and riser-pipe materials do not affect target-analyte concentrations.
- Effects of pumping rate on measurements and analyses have been or will be evaluated.
- Sampler intake is ahead of water treatments, pressure tanks, or holding tanks.

Table 1-3. Example of site-reconnaissance activities

Before the site visit
Review considerations for well selection and installation (summarized in table 1-2).
Review background information collected.
Obtain permission to gain access to the site and to collect samples from the well.
Update well files: record changes in ownership and land use.
Contact utility companies (gas, water, and electric) before digging or drilling.
Determine whether the pump may or may not be removed from well by field personnel. (Owner's permission is required to remove a pump—you could be liable for damage to pump or well.)
Be sure that you get information needed about the site that could interfere with or interrupt sampling. For example, • Hours of pump operation and scheduled downtime • Pumping rate or rates • Holding tanks or chemical treatments • Electrical service to the site • Scheduled maintenance for pumps or related equipment • Scheduled site maintenance, such as painting, construction, and defoliation • Seasonal water-level declines that make the well unusable • Times of denied access; for example, no access while the owner is out of town • Special site-access needs; for example, clearance with a site owner or site operator, keys to unlock access to the site, animals • Restrictions on the location
Record conditions that could compromise study objectives, including potential point or nonpoint sources of contamination. For example, • Nearby wells that could affect well hydraulics • Condition of well—for example, rusting or punctured casing, poor surface seal • Land use and land cover or changes in land use and land cover • Application of salt on nearby roads during winter, or application or use of herbicides and pesticides • Landfills or other waste-management facilities • Industrial, commercial, and agricultural complexes and discharges
During the site visit

Measure water level in each well. Record water-level data on the appropriate form(s).

Identify potential difficulties with the type of equipment and sample-collection methodology to be used. (Note that sampling plans will have to be modified accordingly.)

Update field folders.

- Note site conditions that could affect the quality of data collected from that well.
- Note change(s) in land use.

Verify well identification number and make sure that it is clearly and permanently labeled.

- Check that identification corresponds with what is in the field folder and on site and location maps
- Correct any mistakes or uncertainty about well identification and well location.

Verify type of pump, well diameter, and use of holding tanks, pressure tanks, chemical treatments.

- Check whether oil is floating on the water column in a well equipped with an oil- lubricated pump.
- Make sure that the downhole treatment system is turned off before collecting water samples.
- Determine if a portable pump or another intended sampling device is suitable for use.

Establish optimum pumping rate(s) for purging and sample collection and decide where to route excess discharge.

- Adjust pumping rate to ensure adequate purging of the well without entrainment of atmospheric gases due to excessive drawdown.
- Route water away from the well to prevent (1) creating muddy and slippery conditions and (2) damage to or defacement of the property to which you were granted access.

Check that well structure is intact

- Wells used for ground-water studies should be "sounded" annually to check whether depth to bottom corresponds with well construction information or whether the well is filling with loose materials (U.S. Geological Survey, 1980; Lapham and others, 1997). A decrease in depth to bottom could indicate that the well casing is collapsing, or that there is a breach or corrosion of well screen or casing, or that the well is improperly designed to retain aquifer materials.
- Borehole caliper and downhole-camera video logs can identify a damaged or broken well casing. A downhole camera can identify a plugged screen or accumulation of sediment in the well.
- Aquifer tests, such as slug tests, can be used to check the hydraulic connection between the well and the aquifer. Aquifer tests, however, are generally beyond the scope of site reconnaissance.
- The surface seal of a USGS monitoring well should be intact and the well should be capped. Concrete pad should be repaired if cracked or separated from outer casing. A tight-fitting well cap should have a small ventilation hole.

Check well access for sample-collection points.

- Sample-collection points need to be near the wellhead, ahead of where water enters pressure tanks, holding tanks, or treatment systems.
- At wells where an access point close to the well is not available, it might be possible to install a hose bibb or tap at the wellhead. Because it usually is not possible to control the pumping rate of a supply well, the field person may need to set up a hose-and-valve system to control the rate at which water is sampled and to reduce the likelihood of backflow of water stored in plumbing lines.

Check well access for water-level measurements. The construction of some supply wells makes water-level measurements difficult or impossible.

- Although it is often possible to slip a weighted steel or electric well tape below the pump to get a water-level measurement, the pump can be damaged if the weight or tape becomes entangled in the pump. The weight should be connected so that it will snap off of the tape under stress.
- Water levels can be estimated through the air line on some wells.

- Sometimes field personnel are permitted to remove the pump from the well to get a measurement; however, pump removal can be difficult, time consuming, and potentially unsafe; and could damage the pump.
- A note should be made in the well file if there is no access for a depth measurement.

1.3.2 INFORMATION FOR NATIONAL WATER INFORMATION SYSTEM (NWIS) FILES, WELL FILES, AND FIELD FOLDERS

USGS policy requires specific information on ground-water sampling sites to be stored in NWIS (Edwards and others, 1987; Hubbard, 1992; WRD Memorandum 92.59). Paper documents, such as agreements between the well owner and the USGS for use of the well, also are necessary and are stored in well files and field folders.

- Much of the information needed to set up files for existing wells can be obtained from well owners, drillers, records from state or local jurisdictions, and well-construction logs.
- Information that will be needed to set up well files for new wells is recorded by field personnel as the new well is installed (Lapham and others, 1997).

RULE OF THUMB:
Before starting fieldwork—Make sure the NWIS file is established.
After fieldwork—Update NWIS files promptly.

1.3.2.A NWIS Files

Within the NWIS system, well information, ground-water levels, and water-quality data are stored in three data bases: the Ground-Water Site Inventory (GWSI), Quality of Water Data (QWDATA), and the Automatic Data Processing System (ADAPS). All wells for which data are stored must be identified by an electronic record in NWIS.

- GWSI primarily contains (1) descriptive information about the site and well and (2) noncontinuous water-level data. Specific information entered into GWSI is used to create an NWIS site file.
- QWDATA contains results of water-quality analyses, noncontinuous water-level data, and other data related to water-quality analysis.
- ADAPS contains continuous records of water levels and water quality.

The minimum information required for establishing electronic files in GWSI and QWDATA is shown in table 1-4. Individual studies and District offices may have additional data-storage requirements. For example, the GUNIT (geologic unit) code provides important information for ground-water studies.

When creating or updating a GWSI site-file record, fill in information that is needed by, or useful to, the study, in addition to the required information shown in table 1-4.

Table 1-4. Minimum information required for electronic storage of site and ground-water-quality data in the U.S. Geological Survey National Water Information System (NWIS)

[GWSI, Ground-Water Site Inventory; QWDATA, Quality of Water Data]

Information required for creation of a ground-water file in NWIS[1,2] (GWSI)		
Data description	**Component (C) number for data entry into GWSI**	**Example (Description of code)**
Agency code	C4	USGS
Station Identification Number (Latitude/longitude/sequence no.)	C1	394224075340501
Station Name		
Latitude	C12	KE Be 61
Longitude	C9	394224
Station locator sequence number	C10	0753405
District/User	C815	01
State	C6	24 (Maryland)
County	C7	10 (Delaware)
Agency Use	C8	003 (Sussex)
Station Type	C803	A (Active)
Data Reliability	C802	6 (Well)
Site Type	C3	C (Field Checked)
Use of site	C2	W (Well)
	C23	O (Observation)

Information required for storage of sample analyses in the water-quality file of NWIS (QWDATA)[1]		
Data description	**Alpha parameter code**	**Sample data (Description of code)**
Agency code	AGNCY	USGS
Station Identification Number	STAID	394224075340501
Sample Medium	MEDIM	6 (ground water)
Sample Type	STYPE	2 (blank sample)
Hydrologic ("Hydro") Event	EVENT	9 (routine sample)
Hydrologic ("Hydro") Condition	HSTAT	A (not determined)
Date (year/month/day)	DATES	19880909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields from those shown are available in NWIS and QWDATA that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether a non-USGS agency collected the data.

[2]From Ground-Water Site Schedule Form 9-1904-A, May 1991. Also refer to Mathey (1991) and Garcia and others (1997).

1.3.2.B
Well Files

A well file also must be established for each well selected or installed for the study or in a data network. At the outset of the study, it is useful to refer to a checklist of the items and types of information needed for the well file (fig. 1-3).

WELL-INFORMATION CHECKLIST, Page 1 of 2

Project name and identification number: _____
Latitude-longitude: _____ Sequence number: _____
Other site or well ID: _____ Station name: _____

Indicate well type: Public, Domestic, Commercial, Industrial, Irrigation, Observation, Monitoring, Other _____

Item in well file	Date item filed
Criteria for well selection or installation	
Ground-Water Site Inventory (GWSI) data entered into National Water Information System (NWIS)	
Paper copy of GWSI form	
Copies of agreement to complete activity (for example, drilling or sampling)	
List agreements	
Copies of field forms and logs:	
Well-drilling record	
Driller's log	
Lithologic log	
Cuttings	
Cores	
Aquifer tests: (list types)	
Geophysical logs: (list types)	
Well-construction record	
Well-development record	
Well-maintenance checks: (list types)	
Well-location information:	
Latitude-longitude and method of determination	
Well-location map(s)	
Site-sketch map	
Written description of location	
Well-casing elevation (elevation, and method and date of determination)	
Photographs of well and vicinity (with measuring/sampling points identified)	
Land use/land cover form (Lapham and others, 1997)	

Figure 1-3. Example of a well-information checklist for a well file and field folder.

WELL-INFORMATION CHECKLIST, Page 2 of 2

Item in well file	Date item filled
Water-quality records for each sampling event (for example, purging, field measurements, field forms, sampling history) and copies of laboratory analyses requested	
Water-level measurements - current:	
Water-level measurements - historical:	
Record of well leveling (survey)	
Pumping schedule/history	
Type of pump in well and location of intake	

Description of measuring point for water levels: _____

Description of collection point for samples from

Supply wells _____

Monitoring wells _____

Other information (for example, geologic unit, aquifer name):

Figure 1-3. Example of a well-information checklist for a well file and field folder—*Continued.*

The well file is the repository of the information compiled for the well, and it should contain documentation for site selection, well inventory, well installation, and sample collection.

- Include well-construction information to the extent that it is available (Lapham and others, 1997).
- Include water-quality information, hydrogeologic field forms and logs, and plots of water-quality data and other hydrologic, geologic, geochemical, or geophysical information available for the well or field site.
- Include a log of well-maintenance and well-integrity checks and tests, geophysical logs and surveys, results of aquifer tests, analyses of cores or cuttings of geologic materials, and analyses from previously collected samples from the well or from a nearby well.

1.3.2.C
Field Folders

Selected information related to the well file and electronic records is kept in a field folder. The field folder contains information needed by personnel to locate and gain access to the site and to collect and process ground-water samples. The field folder should be taken along on each visit to the well for reference at the field site. The generic contents of a field folder are listed in the field folder checklist

(fig. 1-4). Examples of site-location maps and a site sketch are shown in figure 1-5.

Field-folder checklist: ground-water quality		
	Item	Comments
	Forms (new forms and (or) examples of completed forms): • Permission forms—must be signed by proper authority. • Analytical Services Request form(s). • Ground-water field form and well-inventory form.	
	Equipment and supplies checklists.	
	Field-techniques manuals.	
	Site location and description: • Maps showing location and identification number of well(s). • Name of landowner, tenant, or other responsible party. • Site access instructions (call owner; get keys or tools needed for security gate, well house, well protective casing). • Photographs and land use/land cover form to document site conditions. • Well dimensions and construction.	
	Sampling schedule and instructions: • Laboratory analyses, codes, and bottle types • Preservation requirements. • Quality-control samples. • Location of sampler intake during sample collection. • Pumping rate for purging and sampling.	
	Purging instructions: • Number of well volumes. • Rate of pumping; containment and discharge of purge water. • Location of sampler intake during purging. • Field measurements and stability protocols. • Previous field-measurement and purge-volume records. • Place to discharge excess water.	
	Water-level measurements: • Location of measuring point. • Previous records from well.	
	Safety information: • Nearest emergency facilities; home phone number of supervisor. • Diagram of where to park, placement of flags and cones. • Traffic conditions; location of power lines. • Environmental hazards such as weather and animals.	
	Ancillary information: • Geologic section(s). • Hydrologic section(s).	

	• Borehole geophysical logs.	
	Shipping instructions: • Mailing labels; location of nearest post office or shipping agent. • Ice or holding time requirements.	

Figure 1-4. Checklist for contents of ground-water sampling field folder.

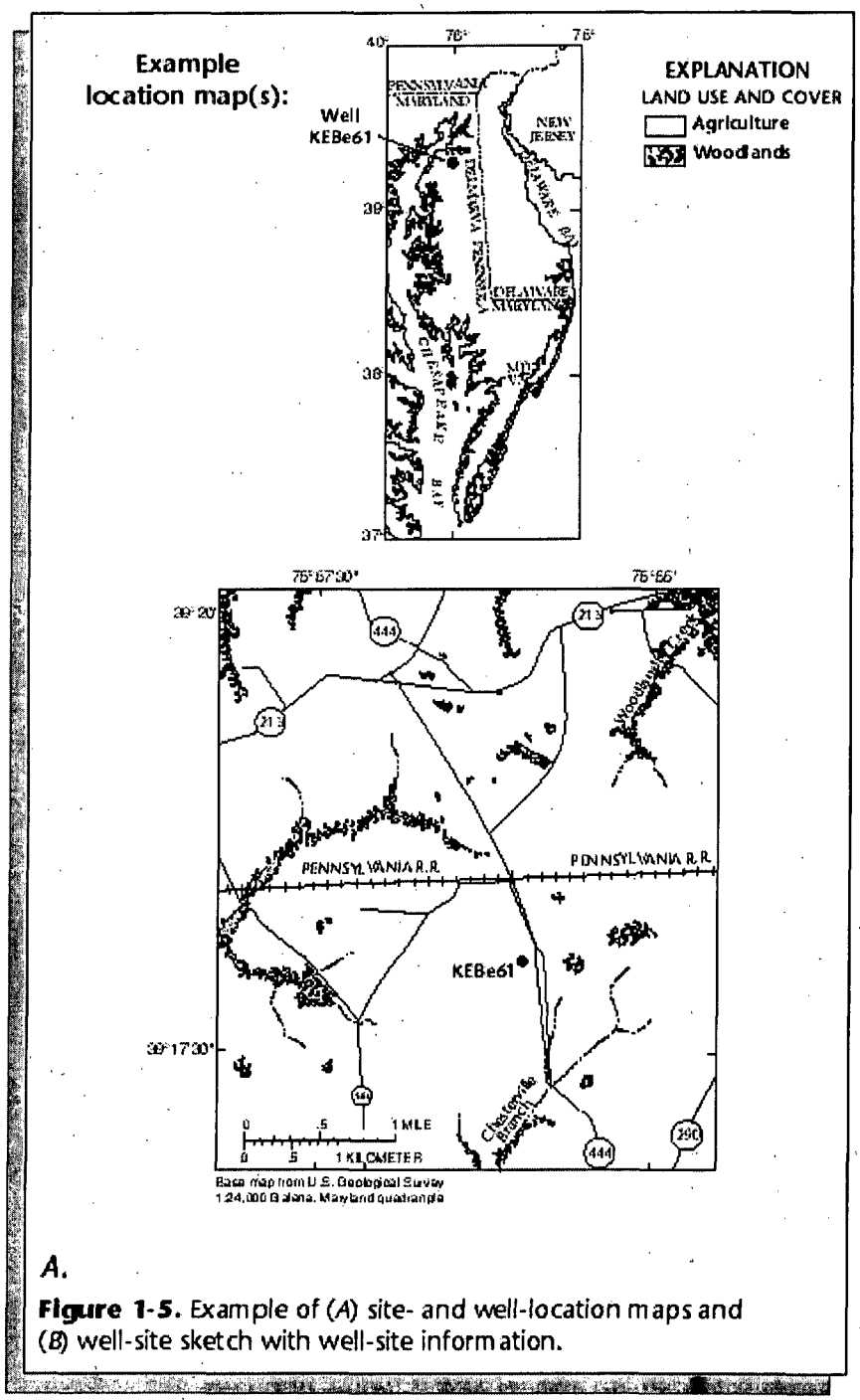


Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch with well-site information.

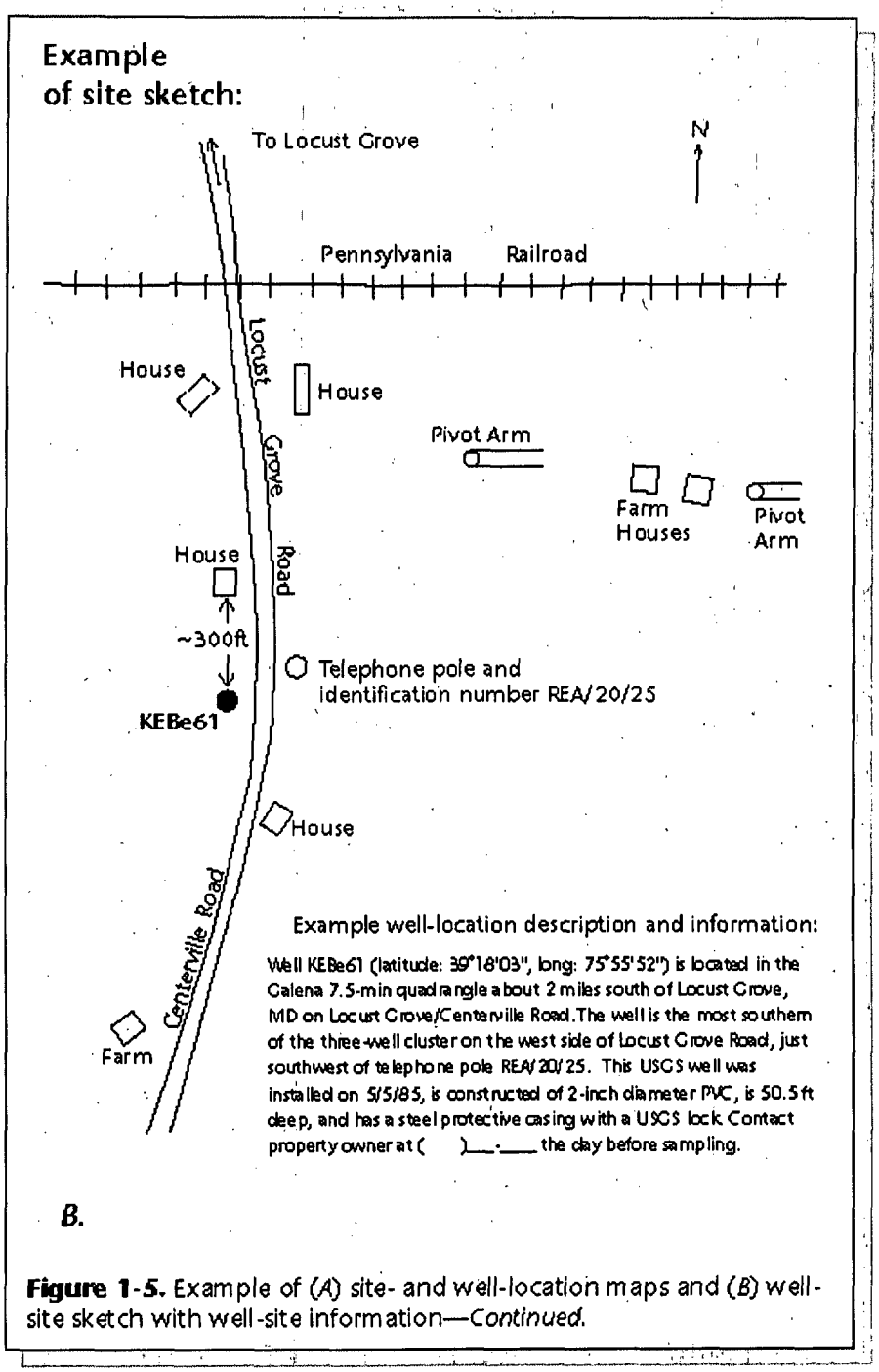


Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch with well-site information—*Continued.*

⇨ Selected references and internal documents
⇧ Return to Section 1.2 Surface water
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section A1.pdf

1.1
FIELD-TRIP PREPARATIONS

All details of a field trip need to be planned well in advance. Adequate time must be scheduled in the workplan to review data requirements and make field-trip preparations—a common mistake is to put off these activities until the last minute.

Before selecting sites or making other preparations:

- Understand the purpose for which the various types of data will be collected and the aqueous system that each sample should represent.
- Review the study workplan, especially types of measurements and samples needed.
- Make field reconnaissance trips before selecting sampling sites, if possible.
  - -- Note conditions that could affect sampling operations (such as the seasonal high or low streamflow, flowing wells, or site-access peculiarities).
  - -- Evaluate potential sources of contamination at the site, based on target analytes[3] to be collected.
- Review site files and field folders. (Note site location, description and access, and review any previously collected physical, chemical, and biological data.)
- Obtain and keep current with training and the laboratory requirements associated with your data-collection activities.

Before selecting equipment:

Understand the physical and chemical limitations of each piece of equipment, in order to meet data-collection objectives and data-quality requirements[4] (refer to NFM 2). Verify and test, if possible, the operational range of the sampling equipment to be used.

Before starting field work:

- Review site files and update and review the field folder for each site from which samples and ancillary data will be collected (see sections 1.2.2 and 1.3.2).
- Review the safety plan and be sure that you have the training needed if you will be working at sites designated as hazardous (see NFM 9)

Plan ahead! Take adequate time to prepare.

1.1.1
CHECKLISTS OF EQUIPMENT, SUPPLIES, AND ACTIVITIES

Each study needs to establish and follow a protocol for data-collection activities. Checklists help ensure that equipment and supplies will be ordered on time, that data-collection activities will be completed appropriately, and that data-quality requirements will be met (fig. 1-1). Most checklists are generic to all projects and sites (for example, vehicle and equipment maintenance checklists), but may need to be customized (for example, items listed, quantities of equipment and supplies, number of batteries, and types of sample bottles and other equipment). The types of information and examples of items listed on the next page are usually included when developing checklists.

Types of information	Examples of items or activities in checklists
Calendar of planned field trips	Prepare calendars/checklists that include sampling dates, members of field team, vehicle(s) to be used.
Presampling activities	Prepare checklists; for example, field-trip preparations checklist (fig. 1-1) and well- information checklist (fig. 1-3).
Postsampling activities	Update field folders and computer files. Log in samples (Analytical Services Request form). Store and dispose of hazardous materials properly. Check that all equipment is clean and properly stored.
Field equipment and supplies	Prepare lists of equipment/supplies for each field site (see NFM 2). Prepare a list of items to be ordered.
Equipment/supplies maintenance and testing	Prepare a checklist of maintenance/testing for field-measurement instruments (see NFM 6). Test sample-collection and processing equipment. Charge or replace batteries.
Vehicle maintenance	Check fluids, battery, tires, lights, cleanliness.
Sample-collection, -processing, -shipping, and -documentation information and supplies	Prepare headers on forms (such as field, chain-of- custody, and Analytical Services Request forms); prepare bottle labels. Prepare lists of chemical constituents, with analytical schedules, methods, laboratory codes; bottle type and volume; sample handling, treatment, and preservation procedures; shipment; quality-control samples.
Field-folder contents	Prepare list of logistical information needed for each site, such as permission to access site, keys, maps.
Safety equipment and information	Keep a copy of NFM 9 for field use and list special considerations for the site, such as personal flotation devices.

FIELD-TRIP PREPARATIONS

PROJECT: _____ SITES: _____ DATE: _____

✓	Preeld activity	Comments
	Order supplies	Ordered 3 cases Ultrex for site #2 Completed on _____ , by _____ .
	Prepare deionized water (in-house system) Check prior laboratory analysis	Last change of cartridges, on _____ Last chemical analysis on _____ , by _____ , Conductivity checks out , by _____
	Check expiration dates on reagents	Need _____ conductivity standard(s) Need pH _____ buffer(s)
	Clean and test equipment	Completed on _____ , by _____ Problems _____
	Collect equipment blanks	Completed on _____ , by _____ Results reviewed by _____ (District water-quality specialist or project chief)
	Clean sample bottles	Completed on _____ , by _____
	Label sample bottles, prepare eld forms	Completed on _____ , by _____
	Obtain permission for site access	Completed on _____ , by _____
	Check eld vehicle for safety equipment and supplies, such as material safety data sheets, arés, and remote communi-cations system (NFM 9)	Completed on _____ , by _____
	Charge/replace batteries	Completed by _____
	Update eld folder	Completed by _____
	Make travel reservations, arrangements	Completed by _____
	Provide supervisor with eld-trip and call-in (check-in) schedule	Provided on _____ to _____
	Other	

Figure 1-1. Example of a presampling activities checklist.

1.1.2 DATA-QUALITY PLANS AND PREPARATIONS

USGS policy that water-quality data be of a defined and documented quality is described in Horowitz and others (1994) and Office of Water Quality Technical Memorandum 93.11 (see "Selected References and Internal Documents"). Every study should have a written document that describes study objectives, data-quality requirements, and a quality-assurance plan. Some of the information needed to ensure data quality is described in District quality-assurance plans. Discipline specialists (District and Regional specialists, discipline offices at USGS headquarters in Reston, Va., and USGS National Research Program scientists) can provide specific instructions and updates relating to quality-assurance procedures and policies for the collection of water-quality, surface-water, and ground-water data.

Field personnel are responsible for determining whether the equipment and methods being used could impair sample quality. For the most part, this determination involves collecting quality-control samples and analyzing the results. Field personnel must plan and prepare for routine checks on data quality.

- **Examine field and laboratory results as soon as possible, preferably before the next sample-collection field trip.** Results indicating potential bias in the data will alert you to the changes needed in equipment, equipment-cleaning procedures, or field methods used.
- **Be prepared to collect additional blanks, replicates, or other field quality-control samples,** based on your judgment of the effects of field conditions on sample collection. Field conditions are unpredictable, and adverse or unexpected conditions could necessitate additional steps to document data quality.

Quality-control samples are collected either in the office laboratory or at the field site, depending on their specific purpose (see NFM 3, "Cleaning of Equipment for Water Sampling," NFM 4, "Collection of Water Samples," and NFM 5, "Processing of Water Samples"). Field personnel must be familiar with the various types of quality-control samples and know how and when to collect them in order to comply with USGS quality-assurance requirements. Collection of blank samples (blanks) is mandatory. Blanks are samples of laboratory-prepared and -analyzed water that are processed through the equipment in the same manner as the environmental sample, but after the equipment has been cleaned and prepared for field use.

In preparation for collection of quality-control samples, solutions of the appropriate type and quality must be obtained for blank and standard reference material samples. Field personnel should use water for blank samples that is certified by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo. Laboratory certification should indicate that the blank water has target-analyte concentrations that are less than the method-detection limits. Blank water for determination of inorganic constituents needs to be the inorganic blank water obtained from the Quality of Water Service Unit in Ocala, Fla.; blanks for analysis of organic compounds require either pesticide blank water or volatile/pesticide blank water, both of which can be obtained from NWQL. Standard/reference materials generally are obtained from the National Institute of Standards and Technology.

- **Collect equipment blanks before beginning the field effort.**
  - Equipment blanks are processed through clean equipment in the controlled setting of an office laboratory.
  - **Process an equipment blank at least once a year for each set of sample-contacting equipment.** This applies to new equipment to be used for the first time, to equipment that will be cleaned with a new cleaning procedure, and to equipment that has not been tested with an equipment blank for 1 year.
  - **Do not collect or process environmental samples until the annual equipment blank data have been reviewed.** The field personnel or the water-quality specialist needs to ensure that the equipment blanks are either free of contamination or have concentrations small enough to be insignificant at the current analytical limits (Horowitz and others, 1994).
- **Collect field blanks at the field site under the same conditions as environmental samples.** Field blanks can provide information on the efficacy of the equipment cleaning procedures used and on ambient atmospheric contamination.

Data quality begins before the first sample is collected—be aware of data-quality requirements and potential sources of contamination.

---

[3]"Target analyte" refers to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured properties such as temperature, specific electrical conductance (conductivity), dissolved-oxygen concentration, pH, Eh, alkalinity, color, or turbidity. The *Concise Chemical and Technical Dictionary*, 4th edition (Bennett, 1986) defines "analyte" as "Substance being determined in an analysis."

[4]As used in this publication, the term "data-quality requirements" refers to that subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the allowable variability to fulfill the scientific objectives of the study.

⇨ Section 1.2 Surface Water
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section 1.3.pdf

1.3 GROUND WATER

Ground water is sampled from various types of existing wells or wells installed specifically for a study.

- **Water-supply wells** are wells that are installed primarily for supply of public, irrigation, domestic, commercial, or industrial water and usually are equipped with a dedicated high-capacity pump. The term "supply well" is used in this publication.
- **Observation wells** are wells or piezometers that are installed (usually without a dedicated pump) for the purpose of collecting hydrologic data. The term generally has been applied to wells installed to observe and determine hydrologic characteristics of an aquifer (Lapham and others, 1997).
- **Monitor wells** are observation wells that are installed specifically for assessment of physical, chemical, and biological characteristics of the aquifer. Low-capacity portable pumps are commonly used for sampling, but monitoring wells can be equipped with a dedicated pump. The term "monitoring well" is used in this publication.

Information is compiled about the well and well site during site-reconnaissance visits, well installation, and subsequent data-collection efforts at the site. This information is used to help select the well(s) needed for study. The ground-water site inventory is compiled in the office and verified in the field. In an office inventory, the study team identifies existing wells or well sites and compiles background information and available records for those wells. The field inventory is completed during reconnaissance trips in which well location is verified, additional information is collected, and the suitability of the site for study objectives is determined. For each well, the inventory of site and well information is entered into the NWIS water-quality (QWDATA) and ground-water site inventory (GWSI) data bases and is added to the file created for the well (well file).

1.3.1 SITE RECONNAISSANCE AND WELL SELECTION

Field personnel critically evaluate existing and installed wells to determine whether they will yield samples that are representative of the environment targeted for study.

As a member of the study team:

- Be prepared to participate in office- and field-related aspects of selecting and installing wells (see Lapham and others, 1997, for details).

- Be familiar with study objectives and requirements for data collection and quality.
- Be familiar with considerations for well selection and well installation (summarized in table 1-2).

Information gathered from a site reconnaissance visit can help determine whether an existing well or a proposed well-installation site meets the criteria established by the study. Site reconnaissance visits also ensure efficient field operations and could be a critical factor in site selection or rejection. These site visits commonly are needed to verify the location and condition of wells, evaluate site characteristics, and make modifications to the site and adjustments to sampling plans to allow sampling to proceed. Before leaving for the site, determine the activities that are to be completed and make the necessary preparations (table 1-3).

Keep in mind the primary concerns for water-quality studies:

- The sample must represent the system intended for study.
- Sample integrity must be maintained.

Site visits also can be used to identify areas of ground-water recharge and discharge, test field equipment, test well-purging and sampling procedures, conduct aquifer tests, make preliminary field measurements, and identify the presence of target analytes.

Review safety plans and procedures before leaving for the field.

Table 1-2. Considerations for well selection and well installation

[Modified from Lapham and others, 1997]

Well location
• Location conforms to the study's network design for areal and depth distribution. • Land-use/land-cover characteristics, if relevant, are consistent with study objectives. • Site is accessible for equipment needed for well installation and sample collection.
Hydrogeologic unit(s)
• Hydrogeologic unit(s) that contribute water to the well can be identified. • Depth and thickness of targeted hydrogeologic unit(s) are known or can be determined. • Yield of water is adequate for sampling (typically, a minimum of 1 gallon per minute).
Well records, description, design, materials, and structure
• Available records (for example, logs of well drilling, completion, and development) have sufficient information to meet the criteria established by the study. • Borehole or casing/screen diameter is adequate for equipment. • Depth to top and bottom of sample-collection (open or screened) interval is known (to determine area contributing water to well). • Length of well screen is proportional to the vertical and areal scale of investigation. • Well has only one screened or open interval, if possible. (Packers can be used to isolate the interval of interest, but packers might not completely isolate zones in unconsolidated or highly fractured aquifers. If packers are used, materials of construction must be compatible with analytes to be studied.) • Top of well screen is several feet below mean annual low-water table to reduce chances of well going dry and to

avoid sampling from unsaturated intervals.
- Filter pack is of a reasonable length (a long interval compared with length of screened or open interval usually results in uncertainty as to location of the source of water to well).
- Well-construction materials do not leach or sorb substances that could alter ambient target-analyte concentrations.
- Well-structure integrity and communication with the aquifer are sound. (Checks include annual depth-to-bottom measurements, borehole caliper and downhole-camera video logs, and aquifer tests.)

Pump type, materials, performance, and location of sampler intake

- Supply wells have water-lubricated turbine pumps rather than oil-lubricated turbine pumps. (Avoid suction-lift, jet, or gas-contact pumps, especially for analytes affected by pressure changes, exposure to oxygen, or that partition to a gas phase.)
- Pump and riser-pipe materials do not affect target-analyte concentrations.
- Effects of pumping rate on measurements and analyses have been or will be evaluated.
- Sampler intake is ahead of water treatments, pressure tanks, or holding tanks.

Table 1-3. Example of site-reconnaissance activities

Before the site visit

Review considerations for well selection and installation (summarized in table 1-2).

Review background information collected.

Obtain permission to gain access to the site and to collect samples from the well.

Update well files: record changes in ownership and land use.

Contact utility companies (gas, water, and electric) before digging or drilling.

Determine whether the pump may or may not be removed from well by field personnel. (Owner's permission is required to remove a pump—you could be liable for damage to pump or well.)

Be sure that you get information needed about the site that could interfere with or interrupt sampling. For example,

- Hours of pump operation and scheduled downtime
- Pumping rate or rates
- Holding tanks or chemical treatments
- Electrical service to the site
- Scheduled maintenance for pumps or related equipment
- Scheduled site maintenance, such as painting, construction, and defoliation
- Seasonal water-level declines that make the well unusable
- Times of denied access; for example, no access while the owner is out of town
- Special site-access needs; for example, clearance with a site owner or site operator, keys to unlock access to the site, animals
- Restrictions on the location

Record conditions that could compromise study objectives, including potential point or nonpoint sources of contamination. For example,

- Nearby wells that could affect well hydraulics
- Condition of well—for example, rusting or punctured casing, poor surface seal
- Land use and land cover or changes in land use and land cover
- Application of salt on nearby roads during winter, or application or use of herbicides and pesticides
- Landfills or other waste-management facilities
- Industrial, commercial, and agricultural complexes and discharges

During the site visit

Measure water level in each well. Record water-level data on the appropriate form(s).

Identify potential difficulties with the type of equipment and sample-collection methodology to be used. (Note that sampling plans will have to be modified accordingly.)

Update field folders.

- Note site conditions that could affect the quality of data collected from that well.
- Note change(s) in land use.

Verify well identification number and make sure that it is clearly and permanently labeled.

- Check that identification corresponds with what is in the field folder and on site and location maps
- Correct any mistakes or uncertainty about well identification and well location.

Verify type of pump, well diameter, and use of holding tanks, pressure tanks, chemical treatments.

- Check whether oil is floating on the water column in a well equipped with an oil- lubricated pump.
- Make sure that the downhole treatment system is turned off before collecting water samples.
- Determine if a portable pump or another intended sampling device is suitable for use.

Establish optimum pumping rate(s) for purging and sample collection and decide where to route excess discharge.

- Adjust pumping rate to ensure adequate purging of the well without entrainment of atmospheric gases due to excessive drawdown.
- Route water away from the well to prevent (1) creating muddy and slippery conditions and (2) damage to or defacement of the property to which you were granted access.

Check that well structure is intact

- Wells used for ground-water studies should be "sounded" annually to check whether depth to bottom corresponds with well construction information or whether the well is filling with loose materials (U.S. Geological Survey, 1980; Lapham and others, 1997). A decrease in depth to bottom could indicate that the well casing is collapsing, or that there is a breach or corrosion of well screen or casing, or that the well is improperly designed to retain aquifer materials.
- Borehole caliper and downhole-camera video logs can identify a damaged or broken well casing. A downhole camera can identify a plugged screen or accumulation of sediment in the well.
- Aquifer tests, such as slug tests, can be used to check the hydraulic connection between the well and the aquifer. Aquifer tests, however, are generally beyond the scope of site reconnaissance.
- The surface seal of a USGS monitoring well should be intact and the well should be capped. Concrete pad should be repaired if cracked or separated from outer casing. A tight-fitting well cap should have a small ventilation hole.

Check well access for sample-collection points.

- Sample-collection points need to be near the wellhead, ahead of where water enters pressure tanks, holding tanks, or treatment systems.
- At wells where an access point close to the well is not available, it might be possible to install a hose bibb or tap at the wellhead. Because it usually is not possible to control the pumping rate of a supply well, the field person may need to set up a hose-and-valve system to control the rate at which water is sampled and to reduce the likelihood of backflow of water stored in plumbing lines.

Check well access for water-level measurements. The construction of some supply wells makes water-level measurements difficult or impossible.

- Although it is often possible to slip a weighted steel or electric well tape below the pump to get a water-level measurement, the pump can be damaged if the weight or tape becomes entangled in the pump. The weight should be connected so that it will snap off of the tape under stress.
- Water levels can be estimated through the air line on some wells.

- Sometimes field personnel are permitted to remove the pump from the well to get a measurement; however, pump removal can be difficult, time consuming, and potentially unsafe, and could damage the pump.
- A note should be made in the well file if there is no access for a depth measurement.

1.3.2 INFORMATION FOR NATIONAL WATER INFORMATION SYSTEM (NWIS) FILES, WELL FILES, AND FIELD FOLDERS

USGS policy requires specific information on ground-water sampling sites to be stored in NWIS (Edwards and others, 1987; Hubbard, 1992; WRD Memorandum 92.59). Paper documents, such as agreements between the well owner and the USGS for use of the well, also are necessary and are stored in well files and field folders.

- Much of the information needed to set up files for existing wells can be obtained from well owners, drillers, records from state or local jurisdictions, and well-construction logs.
- Information that will be needed to set up well files for new wells is recorded by field personnel as the new well is installed (Lapham and others, 1997).

RULE OF THUMB:
Before starting fieldwork—Make sure the NWIS file is established.
After fieldwork—Update NWIS files promptly.

1.3.2.A NWIS Files

Within the NWIS system, well information, ground-water levels, and water-quality data are stored in three data bases: the Ground-Water Site Inventory (GWSI), Quality of Water Data (QWDATA), and the Automatic Data Processing System (ADAPS). All wells for which data are stored must be identified by an electronic record in NWIS.

- GWSI primarily contains (1) descriptive information about the site and well and (2) noncontinuous water-level data. Specific information entered into GWSI is used to create an NWIS site file.
- QWDATA contains results of water-quality analyses, noncontinuous water-level data, and other data related to water-quality analysis.
- ADAPS contains continuous records of water levels and water quality.

The minimum information required for establishing electronic files in GWSI and QWDATA is shown in table 1-4. Individual studies and District offices may have additional data-storage requirements. For example, the GUNIT (geologic unit) code provides important information for ground-water studies.

When creating or updating a GWSI site-file record, fill in information that is needed by, or useful to, the study, in addition to the required information shown in table 1-4.

Table 1-4. Minimum information required for electronic storage of site and ground-water-quality data in the U.S. Geological Survey National Water Information System (NWIS)

[GWSI, Ground-Water Site Inventory; QWDATA, Quality of Water Data]

Information required for creation of a ground-water file in NWIS[1,2] (GWSI)		
Data description	**Component (C) number for data entry into GWSI**	**Example (Description of code)**
Agency code	C4	USGS
Station Identification Number (Latitude/longitude/sequence no.)	C1	394224075340501
Station Name		
Latitude	C12	KE Be 61
Longitude	C9	394224
Station locator sequence number	C10	0753405
District/User	C815	01
State	C6	24 (Maryland)
County	C7	10 (Delaware)
Agency Use	C8	003 (Sussex)
Station Type	C803	A (Active)
Data Reliability	C802	6 (Well)
Site Type	C3	C (Field Checked)
Use of site	C2	W (Well)
	C23	O (Observation)

Information required for storage of sample analyses in the water-quality file of NWIS (QWDATA)[1]		
Data description	**Alpha parameter code**	**Sample data (Description of code)**
Agency code	AGNCY	USGS
Station Identification Number	STAID	394224075340501
Sample Medium	MEDIM	6 (ground water)
Sample Type	STYPE	2 (blank sample)
Hydrologic ("Hydro") Event	EVENT	9 (routine sample)
Hydrologic ("Hydro") Condition	HSTAT	A (not determined)
Date (year/month/day)	DATES	19880909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields from those shown are available in NWIS and QWDATA that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether a non-USGS agency collected the data.

[2]From Ground-Water Site Schedule Form 9-1904-A, May 1991. Also refer to Mathey (1991) and Garcia and others (1997).

1.3.2.B
Well Files

A well file also must be established for each well selected or installed for the study or in a data network. At the outset of the study, it is useful to refer to a checklist of the items and types of information needed for the well file (fig. 1-3).

WELL-INFORMATION CHECKLIST, Page 1 of 2

Project name and identification number: _____
Latitude-longitude: _____ Sequence number: _____
Other site or well ID: _____ Station name: _____

Indicate well type: Public, Domestic, Commercial, Industrial, Irrigation, Observation, Monitoring, Other _____

Item in well file	Date item filed
Criteria for well selection or installation	
Ground-Water Site Inventory (GWSI) data entered into National Water Information System (NWIS)	
Paper copy of GWSI form	
Copies of agreement to complete activity (for example, drilling or sampling) _____	
List agreements _____	
Copies of field forms and logs:	
Well-drilling record	
Driller's log	
Lithologic log	
Cuttings	
Cores	
Aquifer tests: (list types) _____	
Geophysical logs: (list types) _____	
Well-construction record	
Well-development record	
Well-maintenance checks: (list types) _____	
Well-location information:	
Latitude-longitude and method of determination	
Well-location map(s)	
Site-sketch map	
Written description of location	
Well-casing elevation (elevation, and method and date of determination)	
Photographs of well and vicinity (with measuring/sampling points identified)	
Land use/land cover form (Lapham and others, 1997)	

Figure 1-3. Example of a well-information checklist for a well file and field folder.

WELL-INFORMATION CHECKLIST, Page 2 of 2

Item in well file	Date item filed
Water-quality records for each sampling event (for example, purging, field measurements, field forms, sampling history) and copies of laboratory analyses requested	_____
Water-level measurements - current:	_____
Water-level measurements - historical:	_____
Record of well leveling (survey)	_____
Pumping schedule/history	_____
Type of pump in well and location of intake	_____

Description of measuring point for water levels: _____

Description of collection point for samples from

Supply wells _____

Monitoring wells _____

Other information (for example, geologic unit, aquifer name):

Figure 1-3. Example of a well-information checklist for a well file and field folder—*Continued.*

The well file is the repository of the information compiled for the well, and it should contain documentation for site selection, well inventory, well installation, and sample collection.

- Include well-construction information to the extent that it is available (Lapham and others, 1997).
- Include water-quality information, hydrogeologic field forms and logs, and plots of water-quality data and other hydrologic, geologic, geochemical, or geophysical information available for the well or field site.
- Include a log of well-maintenance and well-integrity checks and tests, geophysical logs and surveys, results of aquifer tests, analyses of cores or cuttings of geologic materials, and analyses from previously collected samples from the well or from a nearby well.

1.3.2.C
Field Folders

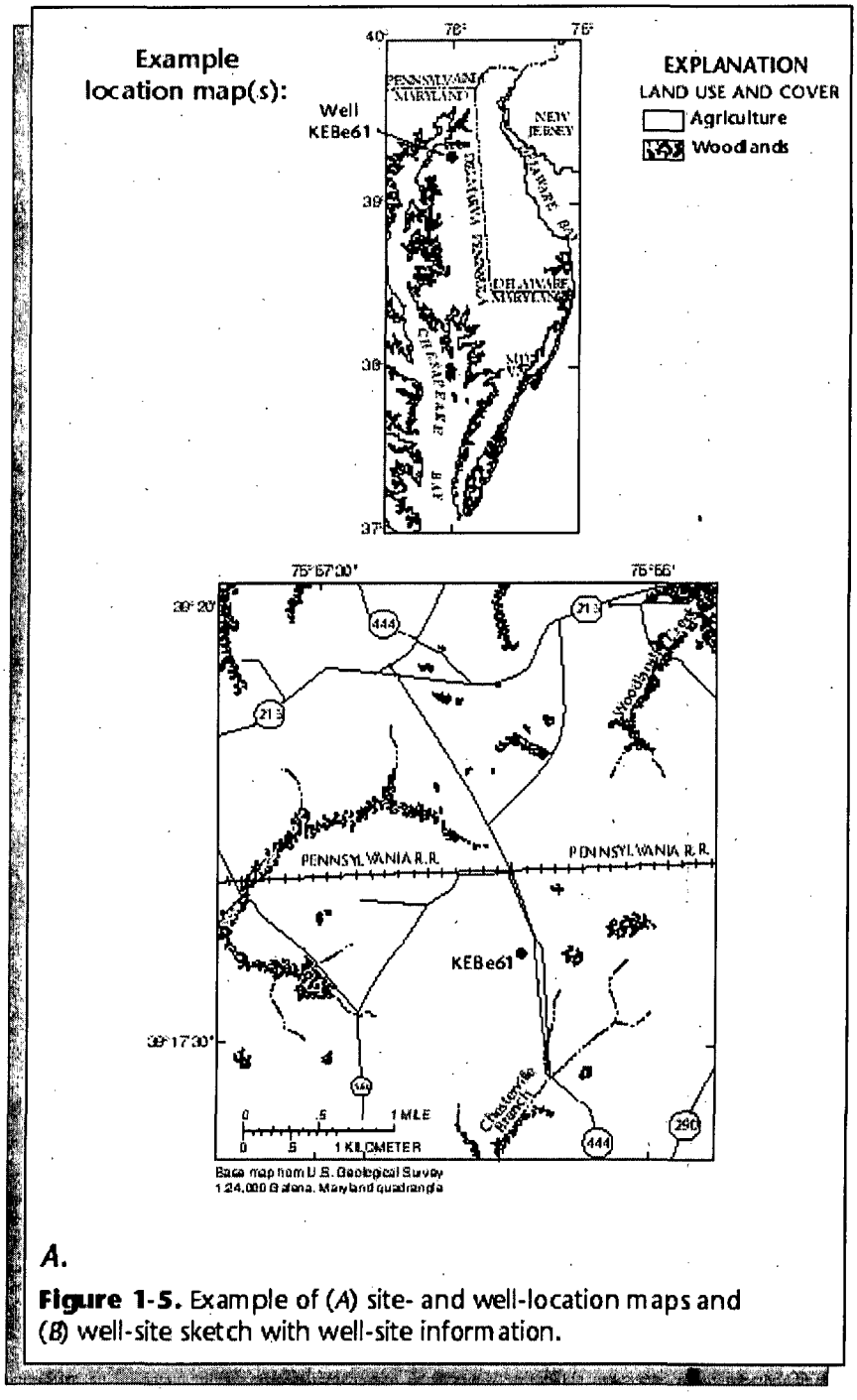
Selected information related to the well file and electronic records is kept in a field folder. The field folder contains information needed by personnel to locate and gain access to the site and to collect and process ground-water samples. The field folder should be taken along on each visit to the well for reference at the field site. The generic contents of a field folder are listed in the field folder checklist

(fig. 1-4). Examples of site-location maps and a site sketch are shown in figure 1-5.

Field-folder checklist: ground-water quality		
	Item	Comments
	Forms (new forms and (or) examples of completed forms): • Permission forms—must be signed by proper authority. • Analytical Services Request form(s). • Ground-water field form and well-inventory form.	
	Equipment and supplies checklists.	
	Field-techniques manuals.	
	Site location and description: • Maps showing location and identification number of well(s). • Name of landowner, tenant, or other responsible party. • Site access instructions (call owner; get keys or tools needed for security gate, well house, well protective casing). • Photographs and land use/land cover form to document site conditions. • Well dimensions and construction.	
	Sampling schedule and instructions: • Laboratory analyses, codes, and bottle types • Preservation requirements. • Quality-control samples. • Location of sampler intake during sample collection. • Pumping rate for purging and sampling.	
	Purging instructions: • Number of well volumes. • Rate of pumping; containment and discharge of purge water. • Location of sampler intake during purging. • Field measurements and stability protocols. • Previous field-measurement and purge-volume records. • Place to discharge excess water.	
	Water-level measurements: • Location of measuring point. • Previous records from well.	
	Safety information: • Nearest emergency facilities; home phone number of supervisor. • Diagram of where to park, placement of flags and cones. • Traffic conditions; location of power lines. • Environmental hazards such as weather and animals.	
	Ancillary information: • Geologic section(s). • Hydrologic section(s).	

	• Borehole geophysical logs.	
	Shipping instructions: • Mailing labels; location of nearest post office or shipping agent. • Ice or holding time requirements.	

Figure 1-4. Checklist for contents of ground-water sampling field folder.



A.

Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch with well-site information.

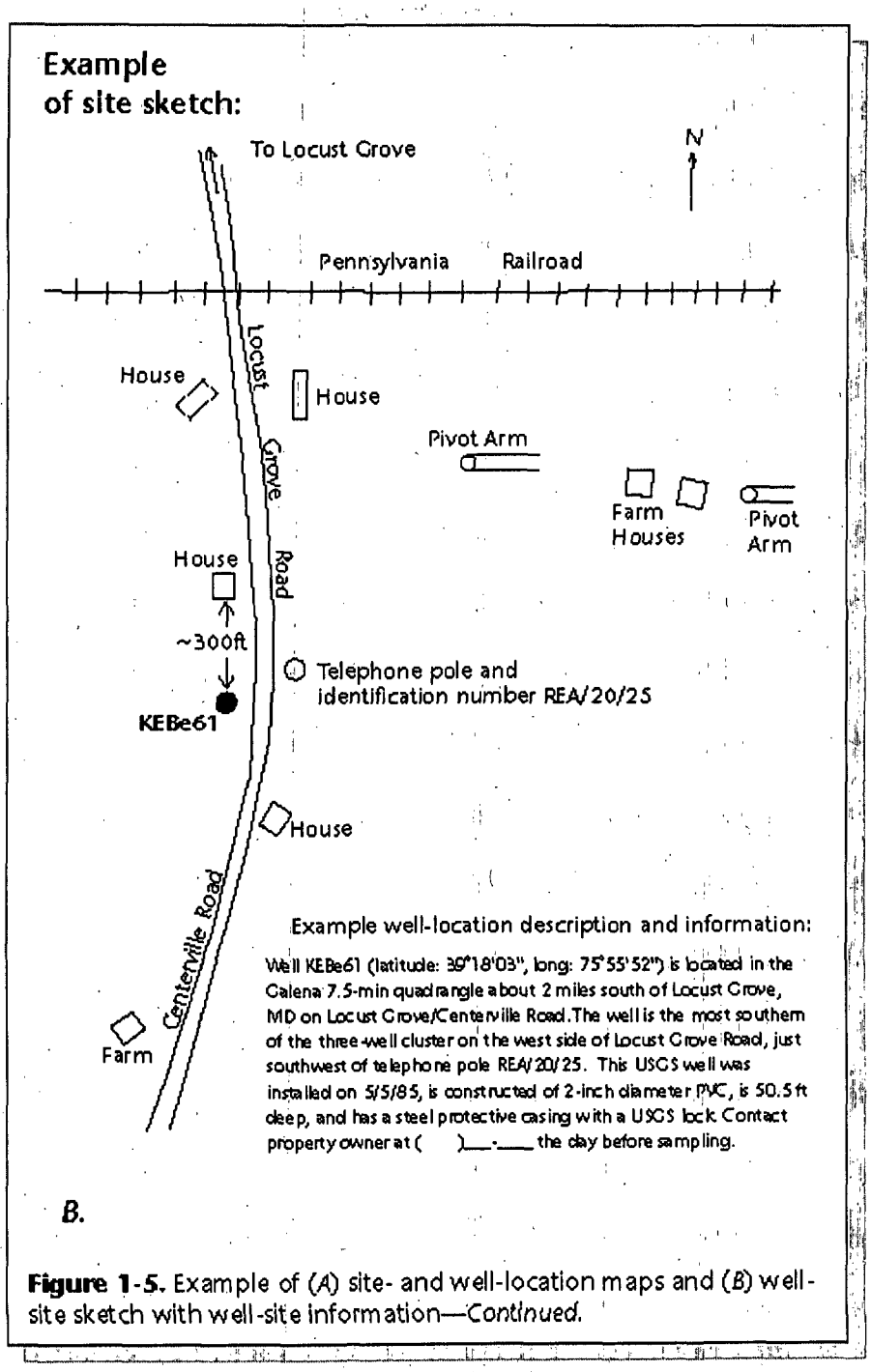


Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch with well-site information—*Continued.*

⇨ Selected references and internal documents
⇧ Return to Section 1.2 Surface water
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Section 1.3.pdf

1.3
GROUND WATER

Ground water is sampled from various types of existing wells or wells installed specifically for a study.

- **Water-supply wells** are wells that are installed primarily for supply of public, irrigation, domestic, commercial, or industrial water and usually are equipped with a dedicated high-capacity pump. The term "supply well" is used in this publication.
- **Observation wells** are wells or piezometers that are installed (usually without a dedicated pump) for the purpose of collecting hydrologic data. The term generally has been applied to wells installed to observe and determine hydrologic characteristics of an aquifer (Lapham and others, 1997).
- **Monitor wells** are observation wells that are installed specifically for assessment of physical, chemical, and biological characteristics of the aquifer. Low-capacity portable pumps are commonly used for sampling, but monitoring wells can be equipped with a dedicated pump. The term "monitoring well" is used in this publication.

Information is compiled about the well and well site during site-reconnaissance visits, well installation, and subsequent data-collection efforts at the site. This information is used to help select the well(s) needed for study. The ground-water site inventory is compiled in the office and verified in the field. In an office inventory, the study team identifies existing wells or well sites and compiles background information and available records for those wells. The field inventory is completed during reconnaissance trips in which well location is verified, additional information is collected, and the suitability of the site for study objectives is determined. For each well, the inventory of site and well information is entered into the NWIS water-quality (QWDATA) and ground-water site inventory (GWSI) data bases and is added to the file created for the well (well file).

1.3.1
SITE RECONNAISSANCE AND WELL SELECTION

Field personnel critically evaluate existing and installed wells to determine whether they will yield samples that are representative of the environment targeted for study.

As a member of the study team:

- Be prepared to participate in office- and field-related aspects of selecting and installing wells (see Lapham and others, 1997, for details).

- Be familiar with study objectives and requirements for data collection and quality.
- Be familiar with considerations for well selection and well installation (summarized in table 1-2).

Information gathered from a site reconnaissance visit can help determine whether an existing well or a proposed well-installation site meets the criteria established by the study. Site reconnaissance visits also ensure efficient field operations and could be a critical factor in site selection or rejection. These site visits commonly are needed to verify the location and condition of wells, evaluate site characteristics, and make modifications to the site and adjustments to sampling plans to allow sampling to proceed. Before leaving for the site, determine the activities that are to be completed and make the necessary preparations (table 1-3).

Keep in mind the primary concerns for water-quality studies:

- The sample must represent the system intended for study.
- Sample integrity must be maintained.

Site visits also can be used to identify areas of ground-water recharge and discharge, test field equipment, test well-purging and sampling procedures, conduct aquifer tests, make preliminary field measurements, and identify the presence of target analytes.

Review safety plans and procedures before leaving for the field.

Table 1-2. Considerations for well selection and well installation

[Modified from Lapham and others, 1997]

Well location
• Location conforms to the study's network design for areal and depth distribution. • Land-use/land-cover characteristics, if relevant, are consistent with study objectives. • Site is accessible for equipment needed for well installation and sample collection.
Hydrogeologic unit(s)
• Hydrogeologic unit(s) that contribute water to the well can be identified. • Depth and thickness of targeted hydrogeologic unit(s) are known or can be determined. • Yield of water is adequate for sampling (typically, a minimum of 1 gallon per minute).
Well records, description, design, materials, and structure
• Available records (for example, logs of well drilling, completion, and development) have sufficient information to meet the criteria established by the study. • Borehole or casing/screen diameter is adequate for equipment. • Depth to top and bottom of sample-collection (open or screened) interval is known (to determine area contributing water to well). • Length of well screen is proportional to the vertical and areal scale of investigation. • Well has only one screened or open interval, if possible. (Packers can be used to isolate the interval of interest, but packers might not completely isolate zones in unconsolidated or highly fractured aquifers. If packers are used, materials of construction must be compatible with analytes to be studied.) • Top of well screen is several feet below mean annual low-water table to reduce chances of well going dry and to

avoid sampling from unsaturated intervals.
- Filter pack is of a reasonable length (a long interval compared with length of screened or open interval usually results in uncertainty as to location of the source of water to well).
- Well-construction materials do not leach or sorb substances that could alter ambient target-analyte concentrations.
- Well-structure integrity and communication with the aquifer are sound. (Checks include annual depth-to-bottom measurements, borehole caliper and downhole-camera video logs, and aquifer tests.)

Pump type, materials, performance, and location of sampler intake

- Supply wells have water-lubricated turbine pumps rather than oil-lubricated turbine pumps. (Avoid suction-lift, jet, or gas-contact pumps, especially for analytes affected by pressure changes, exposure to oxygen, or that partition to a gas phase.)
- Pump and riser-pipe materials do not affect target-analyte concentrations.
- Effects of pumping rate on measurements and analyses have been or will be evaluated.
- Sampler intake is ahead of water treatments, pressure tanks, or holding tanks.

Table 1-3. Example of site-reconnaissance activities

Before the site visit
Review considerations for well selection and installation (summarized in table 1-2).
Review background information collected.
Obtain permission to gain access to the site and to collect samples from the well.
Update well files: record changes in ownership and land use.
Contact utility companies (gas, water, and electric) before digging or drilling.
Determine whether the pump may or may not be removed from well by field personnel. (Owner's permission is required to remove a pump—you could be liable for damage to pump or well.)
Be sure that you get information needed about the site that could interfere with or interrupt sampling. For example, • Hours of pump operation and scheduled downtime • Pumping rate or rates • Holding tanks or chemical treatments • Electrical service to the site • Scheduled maintenance for pumps or related equipment • Scheduled site maintenance, such as painting, construction, and defoliation • Seasonal water-level declines that make the well unusable • Times of denied access; for example, no access while the owner is out of town • Special site-access needs; for example, clearance with a site owner or site operator, keys to unlock access to the site, animals • Restrictions on the location
Record conditions that could compromise study objectives, including potential point or nonpoint sources of contamination. For example, • Nearby wells that could affect well hydraulics • Condition of well—for example, rusting or punctured casing, poor surface seal • Land use and land cover or changes in land use and land cover • Application of salt on nearby roads during winter, or application or use of herbicides and pesticides • Landfills or other waste-management facilities • Industrial, commercial, and agricultural complexes and discharges
During the site visit

Measure water level in each well. Record water-level data on the appropriate form(s).

Identify potential difficulties with the type of equipment and sample-collection methodology to be used. (Note that sampling plans will have to be modified accordingly.)

Update field folders.

- Note site conditions that could affect the quality of data collected from that well.
- Note change(s) in land use.

Verify well identification number and make sure that it is clearly and permanently labeled.

- Check that identification corresponds with what is in the field folder and on site and location maps
- Correct any mistakes or uncertainty about well identification and well location.

Verify type of pump, well diameter, and use of holding tanks, pressure tanks, chemical treatments.

- Check whether oil is floating on the water column in a well equipped with an oil- lubricated pump.
- Make sure that the downhole treatment system is turned off before collecting water samples.
- Determine if a portable pump or another intended sampling device is suitable for use.

Establish optimum pumping rate(s) for purging and sample collection and decide where to route excess discharge.

- Adjust pumping rate to ensure adequate purging of the well without entrainment of atmospheric gases due to excessive drawdown.
- Route water away from the well to prevent (1) creating muddy and slippery conditions and (2) damage to or defacement of the property to which you were granted access.

Check that well structure is intact

- Wells used for ground-water studies should be "sounded" annually to check whether depth to bottom corresponds with well construction information or whether the well is filling with loose materials (U.S. Geological Survey, 1980; Lapham and others, 1997). A decrease in depth to bottom could indicate that the well casing is collapsing, or that there is a breach or corrosion of well screen or casing, or that the well is improperly designed to retain aquifer materials.
- Borehole caliper and downhole-camera video logs can identify a damaged or broken well casing. A downhole camera can identify a plugged screen or accumulation of sediment in the well.
- Aquifer tests, such as slug tests, can be used to check the hydraulic connection between the well and the aquifer. Aquifer tests, however, are generally beyond the scope of site reconnaissance.
- The surface seal of a USGS monitoring well should be intact and the well should be capped. Concrete pad should be repaired if cracked or separated from outer casing. A tight-fitting well cap should have a small ventilation hole.

Check well access for sample-collection points.

- Sample-collection points need to be near the wellhead, ahead of where water enters pressure tanks, holding tanks, or treatment systems.
- At wells where an access point close to the well is not available, it might be possible to install a hose bibb or tap at the wellhead. Because it usually is not possible to control the pumping rate of a supply well, the field person may need to set up a hose-and-valve system to control the rate at which water is sampled and to reduce the likelihood of backflow of water stored in plumbing lines.

Check well access for water-level measurements. The construction of some supply wells makes water-level measurements difficult or impossible.

- Although it is often possible to slip a weighted steel or electric well tape below the pump to get a water-level measurement, the pump can be damaged if the weight or tape becomes entangled in the pump. The weight should be connected so that it will snap off of the tape under stress.
- Water levels can be estimated through the air line on some wells.

- Sometimes field personnel are permitted to remove the pump from the well to get a measurement; however, pump removal can be difficult, time consuming, and potentially unsafe, and could damage the pump.
- A note should be made in the well file if there is no access for a depth measurement.

1.3.2 INFORMATION FOR NATIONAL WATER INFORMATION SYSTEM (NWIS) FILES, WELL FILES, AND FIELD FOLDERS

USGS policy requires specific information on ground-water sampling sites to be stored in NWIS (Edwards and others, 1987; Hubbard, 1992; WRD Memorandum 92.59). Paper documents, such as agreements between the well owner and the USGS for use of the well, also are necessary and are stored in well files and field folders.

- Much of the information needed to set up files for existing wells can be obtained from well owners, drillers, records from state or local jurisdictions, and well-construction logs.
- Information that will be needed to set up well files for new wells is recorded by field personnel as the new well is installed (Lapham and others, 1997).

RULE OF THUMB:
Before starting fieldwork—Make sure the NWIS file is established.
After fieldwork—Update NWIS files promptly.

1.3.2.A NWIS Files

Within the NWIS system, well information, ground-water levels, and water-quality data are stored in three data bases: the Ground-Water Site Inventory (GWSI), Quality of Water Data (QWDATA), and the Automatic Data Processing System (ADAPS). All wells for which data are stored must be identified by an electronic record in NWIS.

- GWSI primarily contains (1) descriptive information about the site and well and (2) noncontinuous water-level data. Specific information entered into GWSI is used to create an NWIS site file.
- QWDATA contains results of water-quality analyses, noncontinuous water-level data, and other data related to water-quality analysis.
- ADAPS contains continuous records of water levels and water quality.

The minimum information required for establishing electronic files in GWSI and QWDATA is shown in table 1-4. Individual studies and District offices may have additional data-storage requirements. For example, the GUNIT (geologic unit) code provides important information for ground-water studies.

When creating or updating a GWSI site-file record, fill in information that is needed by, or useful to, the study, in addition to the required information shown in table 1-4.

Table 1-4. Minimum information required for electronic storage of site and ground-water-quality data in the U.S. Geological Survey National Water Information System (NWIS)

[GWSI, Ground-Water Site Inventory; QWDATA, Quality of Water Data]

Information required for creation of a ground-water file in NWIS[1,2] (GWSI)

Data description	Component (C) number for data entry into GWSI	Example (Description of code)
Agency code	C4	USGS
Station Identification Number (Latitude/longitude/sequence no.)	C1	394224075340501
Station Name		
Latitude	C12	KE Be 61
Longitude	C9	394224
Station locator sequence number	C10	0753405
District/User	C815	01
State	C6	24 (Maryland)
County	C7	10 (Delaware)
Agency Use	C8	003 (Sussex)
Station Type	C803	A (Active)
Data Reliability	C802	6 (Well)
Site Type	C3	C (Field Checked)
Use of site	C2	W (Well)
	C23	O (Observation)

Information required for storage of sample analyses in the water-quality file of NWIS (QWDATA)[1]

Data description	Alpha parameter code	Sample data (Description of code)
Agency code	AGNCY	USGS
Station Identification Number	STAID	394224075340501
Sample Medium	MEDIM	6 (ground water)
Sample Type	STYPE	2 (blank sample)
Hydrologic ("Hydro") Event	EVENT	9 (routine sample)
Hydrologic ("Hydro") Condition	HSTAT	A (not determined)
Date (year/month/day)	DATES	19880909
Time (standard 24-hour clock time)	TIMES	1530 hrs
Analysis Status	ASTAT	H (initial entry)
Analysis Source	ASRCE	9 (USGS laboratory and field)

[1]Numerous additional data fields from those shown are available in NWIS and QWDATA that can be useful for data analysis or mandatory for meeting study objectives; for example, indicating whether a non-USGS agency collected the data.

[2]From Ground-Water Site Schedule Form 9-1904-A, May 1991. Also refer to Mathey (1991) and Garcia and others (1997).

1.3.2.B
Well Files

A well file also must be established for each well selected or installed for the study or in a data network. At the outset of the study, it is useful to refer to a checklist of the items and types of information needed for the well file (fig. 1-3).

WELL-INFORMATION CHECKLIST, Page 1 of 2

Project name and identification number: _____
Latitude-longitude: _____ Sequence number: _____
Other site or well ID: _____ Station name: _____

Indicate well type: Public, Domestic, Commercial, Industrial, Irrigation, Observation, Monitoring, Other _____

Item in well file	Date item filed
Criteria for well selection or installation	
Ground-Water Site Inventory (GWSI) data entered into National Water Information System (NWIS)	
Paper copy of GWSI form	
Copies of agreement to complete activity (for example, drilling or sampling) _____	
List agreements _____	
Copies of field forms and logs:	
Well-drilling record	
Driller's log	
Lithologic log	
Cuttings	
Cores	
Aquifer tests: (list types) _____	
_____	
Geophysical logs: (list types) _____	
_____	
Well-construction record	
Well-development record	
Well-maintenance checks: (list types) _____	
_____	
Well-location information:	
Latitude-longitude and method of determination	
Well-location map(s)	
Site-sketch map	
Written description of location	
Well-casing elevation (elevation, and method and date of determination)	
Photographs of well and vicinity (with measuring/sampling points identified)	
Land use/land cover form (Lapham and others, 1997)	

Figure 1-3. Example of a well-information checklist for a well file and field folder.

WELL-INFORMATION CHECKLIST, Page 2 of 2

Item in well file	Date item filed
Water-quality records for each sampling event (for example, purging, field measurements, field forms, sampling history) and copies of laboratory analyses requested	
Water-level measurements - current:	
Water-level measurements - historical:	
Record of well leveling (survey)	
Pumping schedule/history	
Type of pump in well and location of intake	

Description of measuring point for water levels: _____

Description of collection point for samples from

Supply wells _____

Monitoring wells _____

Other information (for example, geologic unit, aquifer name):

Figure 1-3. Example of a well-information checklist for a well file and field folder—*Continued.*

The well file is the repository of the information compiled for the well, and it should contain documentation for site selection, well inventory, well installation, and sample collection.

- Include well-construction information to the extent that it is available (Lapham and others, 1997).
- Include water-quality information, hydrogeologic field forms and logs, and plots of water-quality data and other hydrologic, geologic, geochemical, or geophysical information available for the well or field site.
- Include a log of well-maintenance and well-integrity checks and tests, geophysical logs and surveys, results of aquifer tests, analyses of cores or cuttings of geologic materials, and analyses from previously collected samples from the well or from a nearby well.

1.3.2.C
Field Folders

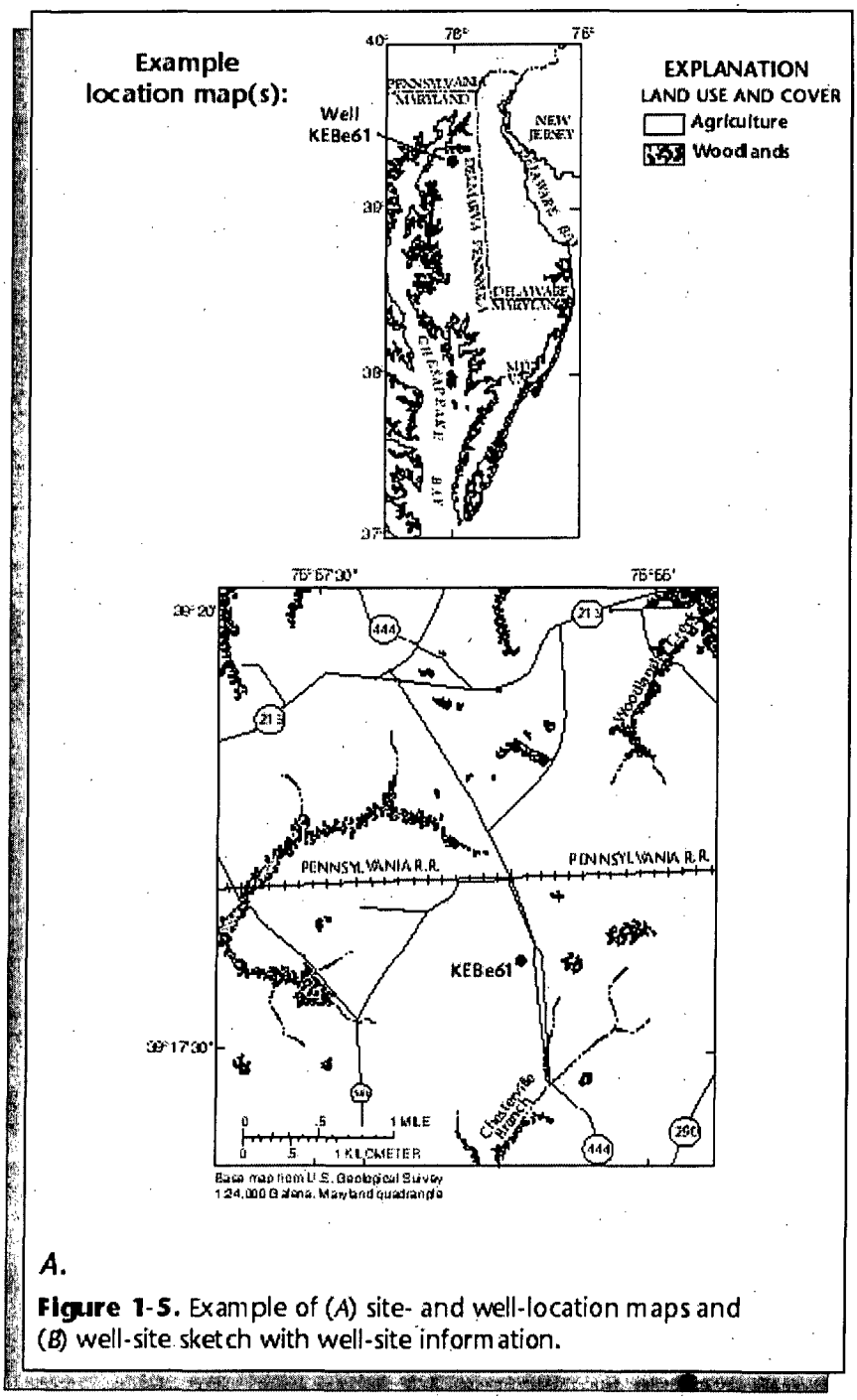
Selected information related to the well file and electronic records is kept in a field folder. The field folder contains information needed by personnel to locate and gain access to the site and to collect and process ground-water samples. The field folder should be taken along on each visit to the well for reference at the field site. The generic contents of a field folder are listed in the field folder checklist,

(fig. 1-4). Examples of site-location maps and a site sketch are shown in figure 1-5.

Field-folder checklist: ground-water quality		
	Item	Comments
	Forms (new forms and (or) examples of completed forms): • Permission forms—must be signed by proper authority. • Analytical Services Request form(s). • Ground-water field form and well-inventory form.	
	Equipment and supplies checklists.	
	Field-techniques manuals.	
	Site location and description: • Maps showing location and identification number of well(s). • Name of landowner, tenant, or other responsible party. • Site access instructions (call owner; get keys or tools needed for security gate, well house, well protective casing). • Photographs and land use/land cover form to document site conditions. • Well dimensions and construction.	
	Sampling schedule and instructions: • Laboratory analyses, codes, and bottle types • Preservation requirements. • Quality-control samples. • Location of sampler intake during sample collection. • Pumping rate for purging and sampling.	
	Purging instructions: • Number of well volumes. • Rate of pumping; containment and discharge of purge water. • Location of sampler intake during purging. • Field measurements and stability protocols. • Previous field-measurement and purge-volume records. • Place to discharge excess water.	
	Water-level measurements: • Location of measuring point. • Previous records from well.	
	Safety information: • Nearest emergency facilities; home phone number of supervisor. • Diagram of where to park, placement of flags and cones. • Traffic conditions; location of power lines. • Environmental hazards such as weather and animals.	
	Ancillary information: • Geologic section(s). • Hydrologic section(s).	

	• Borehole geophysical logs.	
	Shipping instructions: • Mailing labels; location of nearest post office or shipping agent. • Ice or holding time requirements.	

Figure 1-4. Checklist for contents of ground-water sampling field folder.



A.

Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch with well-site information.

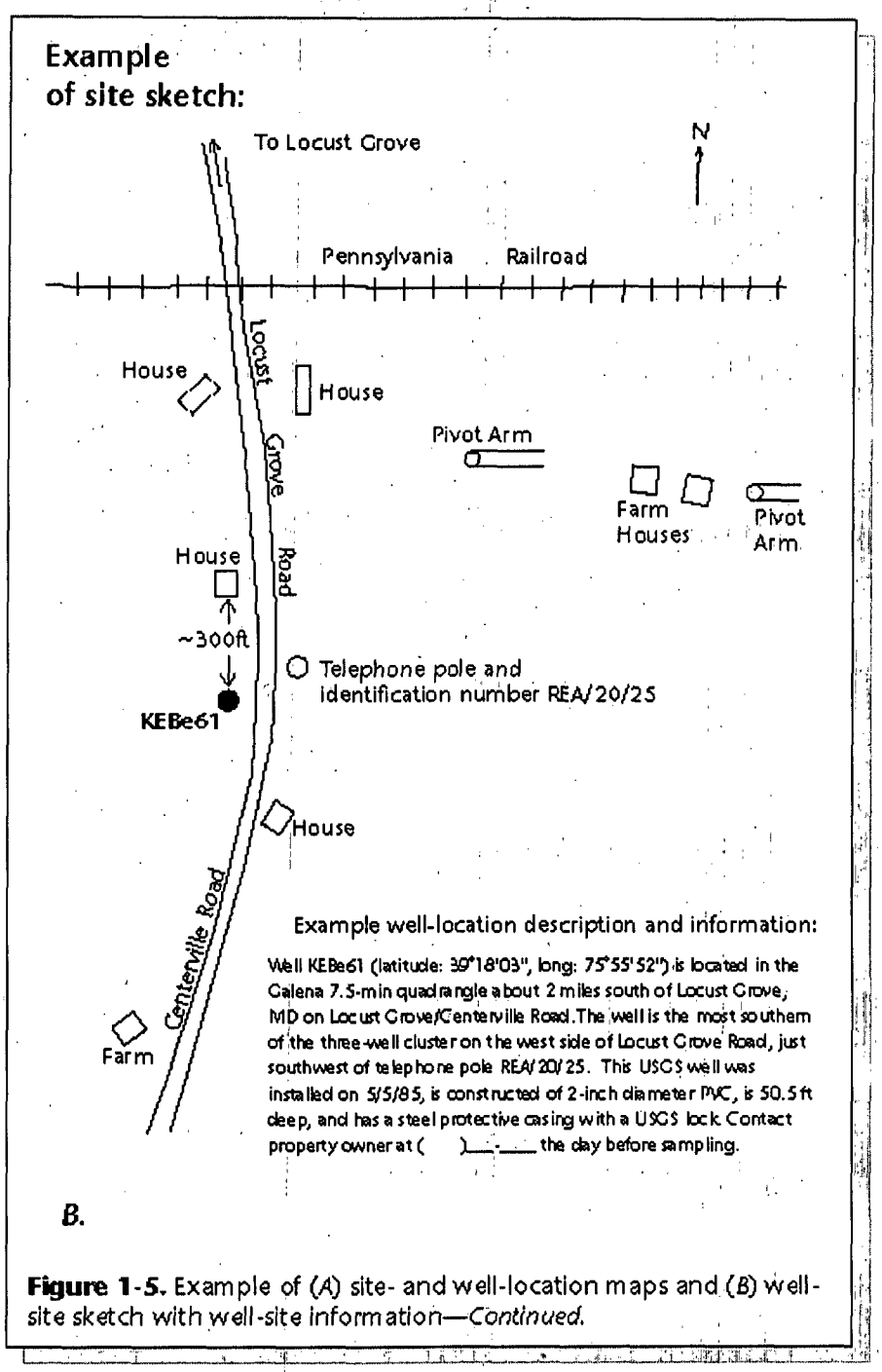


Figure 1-5. Example of (*A*) site- and well-location maps and (*B*) well-site sketch with well-site information—*Continued.*

⇨ Selected references and internal documents
⇧ Return to Section 1.2 Surface water
⇧ Return to Complete Contents for Chapter A1
⇧ Return to Field Manual Complete Contents
⇧ Return to USGS Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 17:44:13 Mon 09 Jul 2001

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data



Chapter A2.

SELECTION OF EQUIPMENT FOR WATER SAMPLING

Revised 2002 by Susan L. Lane, Sarah Flanagan, and Franceska D. Wilde

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

For additional information write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

Copies of this report can be purchased from:
U.S. Geological Survey
Branch of Information Services
Box 25286, Federal Center
Denver, CO 80225

Foreword

The mission of the Water Resources Discipline of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.

(signed)

Robert M. Hirsch
Associate Director for Water

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

Chapters of Section A: *National Field Manual for the Collection of Water-Quality Data*

A1. Preparations for Water Sampling

A2. Selection of Equipment for Water Sampling

A3. Cleaning of Equipment for Water Sampling

A4. Collection of Water Samples

A5. Processing of Water Samples

A6. Field Measurements
- 6.0 General Information and Guidelines
- 6.1 Temperature
- 6.2 Dissolved Oxygen
- 6.3 Specific Electrical Conductance
- 6.4 pH
- 6.5 Reduction-Oxidation Potential (Electrode Method)
- 6.6 Alkalinity and Acid Neutralizing Capacity
- 6.7 Turbidity

A7. Biological Indicators
- 7.0 Five-Day Biochemical Oxygen Demand
- 7.1 Fecal Indicator Bacteria
- 7.2 Fecal Indicator Viruses
- 7.3 Protozoan Pathogens (in preparation)

A8. Bottom-Material Samples

A9. Safety in Field Activities

SELECTION OF EQUIPMENT FOR WATER SAMPLING

A2.

National Field Manual for the Collection of Water-Quality Data

Chapter A2.

	Page
Abstract	7
Introduction	8
Purpose and scope	9
Requirements and recommendations	10
Field manual review and revision	11
Acknowledgments	11

A2. Selection of Equipment for Water Sampling..... 13

2.0 Chemical compatibility with the water sample..... 15
D.B. Radtke, F.D. Wilde, S.L. Lane, and Sarah Flanagan

2.0.1 Equipment materials 17

2.0.2 Disposable gloves 18

2.0.3 Blank water and chemical reagents..... 19

2.1 Sample collection 21
S.L. Lane, Sarah Flanagan, Jacob Gibs, D.B. Radtke,
W.E. Webb, and F.D. Wilde

2.1.1 Surface-water equipment 22

2.1.1.A Isokinetic depth-integrating samplers 22

Hand-held samplers 27

Cable-and-reel samplers 29

2.1.1.B Nonisokinetic samplers 30

Open-mouth samplers..... 31

Thief samplers 33

Single-stage samplers 35

Automatic samplers and pumps 37

2.1.1.C Support equipment 37

2.1.2 Ground-water equipment..... 38

2.1.2.A Pumps 42

Supply-well pumps 42

Monitoring-well pumps..... 46

Well-development pumps..... 52

2.1.2.B Bailers, thief samplers, and passive diffusion bag samplers 54
Bailers and thief samplers 54
Passive diffusion bag samplers 56
2.1.2.C Support equipment 56
2.2. Sample processing 57
S.L. Lane, Sarah Flanagan, F.D. Wilde, M.W. Sandstrom, K.K. Fitzgerald, and D.B. Radtke
2.2.1 Sample splitters 57
2.2.1.A Churn splitter 59
2.2.1.B Cone splitter 62
2.2.2 Processing and preservation chambers 66
2.2.3 Filtration systems 68
2.2.3.A Inorganic constituents 71
Disposable capsule filter 71
Plate-filter assemblies 73
2.2.3.B Organic compounds 76
Metering pump 77
Filtration assemblies 79
Filter material 83
2.2.4 Pump tubing 84
2.3. Field vehicles 89
S.L. Lane, Sarah Flanagan, and D.B. Radtke
2.4. Lists of equipment and supplies 91
S.L. Lane, Sarah Flanagan, and D.B. Radtke
Conversion factors, selected terms, and abbreviations CF–1
Selected references and technical memorandums REF–1
Appendix: Construction of a collapsible sample-processing/preservation chamber APP–1

Illustrations

2-1. Diagrams of isokinetic depth-integrating samplers: (*A*) US DH-81, (*B*) US DH-95, (*C*) US D-95, (*D*) US D-96, and (*E*) US D-99 25

2-2. Diagrams of nonisokinetic open-mouth samplers: (*A*) hand-held open-mouth bottle sampler, (*B*) US WBH-96 weighted-bottle sampler, (*C*) biochemical oxygen demand (BOD) sampler, and (*D*) volatile organic compound (VOC) sampler ... 32

2-3. Diagrams of nonisokinetic thief samplers: (*A*) Kemmerer sampler, (*B*) Van Dorn sampler, and (*C*) double check-valve bailer with bottom-emptying device 34

2-4. Diagram and photograph of a US U-59 sampler: (*A*) single-stage and (*B*) a bank of U-59 samplers installed on a plank post 36

2-5. Diagrams of pumps typically used to obtain water from supply wells: (*A*) centrifugal pump and (*B*) jet pump 43

2-6. Diagrams of Swagelok® perfluoroalkoxy needle valve: (*A*) front view and (*B*) exploded view 45

2-7. Diagrams of pumps typically used for withdrawal of water samples from monitoring wells: (*A*) peristaltic suction-lift pump and (*B-F*) examples of submersible positive-displacement pumps 50

2-8. Photographs of churn sample splitters: (*A*) plastic churn splitter, and (*B*) fluoropolymer churn splitter 59

2-9. Photograph of a cone splitter 62

2-10. Photographs of (*A*) a polyvinyl chloride frame of a processing or preservation chamber, and (*B*) a sample being processed within the chamber 67

2-11. Photograph of a disposable capsule filter with 0.45-micrometer polyethersulfone pleated filter membrane 72

2-12. Photograph of a nonmetallic backflushing plate-filter assembly for 142-millimeter-diameter filter membrane 75

2-13. Photograph of a valveless piston metering pump 77

2-14. Photographs of flexible fluorinated ethylene polypropylene (FEP) tubing: (*A*) convoluted design and (*B*) corrugated design 78

2-15. Photographs of (A) aluminum plate-filter assembly for 142-millimeter-diameter filter disc and (B) PFA filter holder for 47-millimeter-diameter filter 80

2-16. Diagram of a fluorinated ethylene-propylene pressure-filtration assembly for processing samples for analysis of total particulate and dissolved organic carbon 82

Tables

2-1. General guidelines for selecting equipment on the basis of construction material and target analyte(s) 16

2-2. Isokinetic depth-integrating water-quality samplers and sampler characteristics 24

2-3. Prefield checklist for hand-held and cable-and-reel samplers 27

2-4. General requirements and considerations for selecting ground-water sampling equipment (pumps or thief samplers) 40

2-5. Examples of pump capability as a function of well and pump characteristics in a 2-inch-diameter well 49

2-6. Advantages and limitations of sample splitters 58

2-7. Example of six cone-splitter accuracy tests using deionized water 65

2-8. Capsule filter requirements and recommendations for processing of surface-water and ground-water samples 73

2-9. Common varieties and characteristics of fluorocarbon polymer tubing 85

2-10. Support equipment for surface-water sampling 92

2-11. Support equipment for ground-water sampling 93

2-12. Sample-collection equipment for (*A*) surface water and (*B*) ground water 93

2-13. Sample-processing equipment and supplies 95

2-14. Sample-preservation equipment and supplies 98

2-15. Cleaning and quality-control sampling equipment and supplies 99

2-16. Shipping equipment and supplies 100

2-17. Miscellaneous field supplies 101



Chapter A2. SELECTION OF EQUIPMENT FOR WATER SAMPLING

Revised 2002 by **Susan L. Lane, Sarah Flanagan, and Franceska D. Wilde**

Edited by **Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo**

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter of the manual addresses the selection of equipment commonly used by USGS personnel to collect and process water-quality samples.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be posted on the World Wide Web on the USGS page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed March 20, 2003).

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A2 provides information about equipment used to collect and process water samples. Requirements, recommendations, and guidelines are described that pertain to the selection and use of field equipment by USGS personnel. **Formal training and field apprenticeship are needed in order to correctly implement the requirements and recommendations described in this chapter.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" and consists of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" followed by the chapter number (or chapter and section number). For example, NFM 4 refers to chapter 4 on "Collection of Water Samples," and NFM 4.1 refers to the section on surface-water sampling methods.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of chapter 2 of the *National Field Manual* is to provide a description of the requirements, recommendations, and guidelines routinely used for equipment selection in USGS studies involving the collection and processing of water-quality samples. (The terms "required" and "recommended," as used in this report, are explained below under "Requirements and Recommendations.") The information provided covers topics fundamental to the collection and processing of surface-water and ground-water samples that are representative of the ambient environment. This chapter does not attempt to encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. Descriptions of equipment used to collect and process samples for analysis of biological indicators or suspended solids are given in chapters 7 and 8, respectively, of the *National Field Manual.*

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums and other documents that define the policy pertinent to such requirements are referenced in this manual. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplish specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented in permanent and readily accessible records.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given procedure or equipment selection are acceptable on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this chapter to the extent that such documents are available. Specific data-quality requirements, study objectives, or other constraints affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection must be documented. Departure from or modifications to recommended procedures must be quality assured and documented in permanent and readily accessible records.

[1]"District" refers to an organizational unit of the USGS in any of the States or Territories of the United States.

FIELD MANUAL REVIEW AND REVISION

This is Version 2.0 of Chapter A2, "Selection of Equipment for Water Sampling," dated March 2003. Each chapter of the *National Field Manual* is reviewed and revised periodically to correct any errors, incorporate technical advances, and address additional topics. These updated chapters or chapter sections will be reissued in electronic format only. Version 2.0 of this chapter is the first reissue of this report. Subsequent minor changes will be designated as a new version by the number that follows the decimal point. When an NFM chapter incorporates additional topics or major technical changes, the chapter is reissued electronically and reprinted as a new edition. The version or edition number appears in the footer of each page.

To make comments or suggest updates to the NFM, go online to http://pubs.water.usgs.gov/twri9A/ and click on "NFM-GNATS," and then on "Submit a new problem report." Select the "category" by scrolling through the options until you find the chapter and sections that pertain to your report, and fill out the fields indicated. Alternatively, comments or corrections can be sent to nfm-owq@usgs.gov. Newly revised and reissued chapters or chapter sections will be posted on the World Wide Web on the USGS page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed March 20, 2003). This page also contains a link to the NFM "Comments and Errata" page that chronicles changes to each chapter.

ACKNOWLEDGMENTS

The information included in the original and revised versions of chapter 2 of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. D.A. Evans, R.G. Fay, R.T. Iwatsubo, and W.C. O'Neal, whose professional insight, knowledge, and

experience were instrumental in improving the accuracy of the revised version of this chapter, are gratefully acknowledged. The technical content of the original version of this report was enhanced by expertise from B.A. Bernard, Dallas Childers, Jr., T.K. Edwards, G.D. Glysson, J.R. Gray, A.J. Horowitz, H.E. Jobson, K.K. Fitzgerald, J.W. LaBaugh, R.W. Lee, S.W. McKenzie, R.H. Meade, Jr., W.C. O'Neal, R.L. Rickman, S.K. Sando, J.V. Skinner, R.L. Snyder, and Y.E. Stoker. Valuable editorial assistance was provided by I.M. Collies and M.S. Ashman. Production assistance from G.H. Comfort, A.M. Weaver, and M.V. Bonito was instrumental in maintaining the quality of this report.

In addition to the references provided, important source materials included USGS handbooks, manuals, and technical memorandums. The following USGS personnel developed the manuals or protocols that provided the foundation for this *National Field Manual*: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, M.T. Koterba, C.E. Lamb, W.W. Lapham, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

Appreciation is extended to the following companies who granted permission to publish their illustrations in this manual: Bennett Sample Pumps, Inc., Amarillo, Tex.; Cole-Parmer Instrument Company, Vernon Hills, Ill.; Fultz Pumps, Inc., Lewistown, Penn.; Gelman Sciences, Ann Arbor, Mich.; GeoTech Environmental Equipment, Inc., Denver, Colo.; Grundfos Pumps Corporation, Olathe, Kans.; Savillex Corporation, Minnetonka, Minn.; Swagelok Company, Solon, Ohio; Timco Manufacturing Company, Prairie du Sac, Wis.; US Filter/Johnson Screens, St. Paul, Minn.; and Wildlife Supply Company, Saginaw, Mich.

Special thanks go to T.L. Miller and S.K. Sorenson for providing the ongoing support needed to produce and maintain a national field manual for water-quality studies.



Chapter A2. SELECTION OF EQUIPMENT FOR WATER SAMPLING

Revised 2002 by **Susan L. Lane, Sarah Flanagan, and Franceska D. Wilde**

Edited by **Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo**

This chapter provides information to assist field personnel in selecting the sample-collection and -processing equipment[2] that are appropriate for study objectives, data-quality requirements,[3] and site conditions for water-quality investigations. Selection of equipment for collecting or processing water-quality samples depends on the physical constraints and safe operation of the equipment and on its suitability with respect to achievement of study objectives.

[2]Equipment used for field measurements of physical or chemical properties of water (temperature, dissolved oxygen, specific electrical conductance (conductivity), pH, reduction-oxidation potential, alkalinity, and turbidity) is described in NFM 6; equipment used for biological indicator determination is described in NFM 7; equipment used for bottom-material sampling is described in NFM 8; and safety equipment is described in NFM 9.

[3]As used in this publication, the term data-quality requirements refers to that subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the variability (or error brackets) allowable to fulfill the scientific objectives of the study.

Criteria for selecting equipment for water sampling depend on (1) the mechanical constraints of the equipment to perform adequately under given environmental conditions, (2) the adequacy of equipment operation to obtain water-quality samples that represent the environmental conditions of the sample source, and (3) the adequacy of the equipment materials and construction to maintain sample integrity and not to be a source of leaching and sorption of target analytes.

- **Always operate equipment safely.**
- Be thoroughly familiar with requirements for equipment operation and maintenance.
- Be aware of the limitations as well as applications of the equipment with respect to your field site.
- Maintain and test equipment on a regular schedule.

CHEMICAL COMPATIBILITY WITH THE WATER SAMPLE 2.0

By D.B. Radtke, F.D. Wilde, S.L. Lane, and Sarah Flanagan

The materials used to construct and contact equipment can alter sample chemistry (table 2-1). Equipment designed for water-quality work commonly is constructed of a combination of materials, the most inert being used for components that will contact the sample. Nonsample-wetted components and manual contact with sampling equipment also can be a source of sample contamination. Field personnel must wear gloves and use other techniques to minimize potential contamination, implement quality-assurance procedures, and quantify potential effects by analyzing quality-control samples collected using laboratory-certified deionized and blank water.

When planning equipment use, consider having several sets of precleaned equipment available. A clean set of equipment for each sampling site prevents cross contamination between sites, helps to eliminate the need for time-consuming equipment cleaning in the field, and serves as a backup should equipment break or become contaminated.

Check that the equipment to be used will not affect the sample chemistry.

Table 2-1. General guidelines for selecting equipment on the basis of construction material and target analyte(s)

[✓, generally appropriate for use shown; Fl, fluoride; Si, silica; Cr, chromium; Ni, nickel; Fe, iron; Mn, manganese; Mo, molybdenum; $^3H/^3He$, tritium/helium-3; CFC, chlorofluorocarbon; SF-6, sulfur hexafluoride; B, boron]

Construction material for sampling equipment (does not apply to well casing)		Target analyte(s)	
Material	**Description**	**Inorganic**	**Organic**
Plastics[1]			
Fluorocarbon polymers[2] (other varieties available for differing applications)	Chemically inert for most analytes.	✓ (potential source of Fl)	✓ (Sorption of some organics.)
Polypropylene	Relatively inert for inorganic analytes.	✓	Do not use.
Polyethylene (linear)	Relatively inert for inorganic analytes.	✓	Do not use.
Polyvinyl chloride (PVC)	Relatively inert for inorganic analytes.	✓	Do not use.
Silicone	Very porous. Relatively inert for most inorganic analytes.	✓ (potential source of Si)	Do not use.
Nylon	Relatively inert for inorganic analytes.	✓	Do not use. Exception: CFCs
Metals[3]			
Stainless steel, 316-grade (SS 316)	SS 316—metal having the greatest corrosion resistance. Comes in various grades. Used for submersible pump casing.[3]	✓ (potential source of Cr, Ni, Fe, and possibly Mn and Mo, if corroded[4]) Do not use for surface-water sampling: equipment must have a plastic coating (does not apply to submersible pumps).	✓ Do not use if corroded.[4]
Stainless steel, 304-grade (SS 304)	Similar to SS 316, but less corrosion resistant.	Do not use.	✓ Do not use if corroded.[4]
Other metals: brass, iron, copper, aluminum, and galvanized and carbon steels	Refrigeration-grade copper or aluminum tubing are used routinely for collection of $^3H/^3He$, CFC, and SF-6 samples.	**Do not use** (except as noted for isotopes).	✓ Routinely used for CFCs. Do not use if corroded.
Glass			
Glass, borosilicate (laboratory grade) Ceramic	Relatively inert. Potential sorption of analytes.	✓ (glass is potential source of B and Si)	✓

[1]Plastics used in connection with inorganic trace-element sampling must be uncolored or white (Horowitz and others, 1994).
[2]Fluorocarbon polymers include materials such as Teflon®, Kynar®, and Tefzel® that are relatively inert for sampling inorganic or organic analytes.
[3]Most submersible sampling pumps have stainless steel components. One can minimize effects on inorganics samples by using fluorocarbon polymers in construction of sample-wetted components (for example, for a bladder, stator, impeller) to the extent possible.
[4]Corroded/weathered surfaces are active sorption sites for organic compounds and can leach trace elements.

EQUIPMENT MATERIALS 2.0.1

Materials used in equipment can include plastics, glass, ceramics, and metals. Chemical reactivity varies widely within the same group of materials, depending on the chemical composition, the physical configuration, and the manufacturing process. Thus, regarding reactivity with water and most other chemical substances, fluorocarbon polymers are less reactive than plastics such as polyethylene; 316-type stainless steel (SS 316) is less reactive than brass, iron, or galvanized steel (table 2-1). For plastics and metals in general:

- The softer or more flexible forms of any plastic or metal are more reactive than the rigid forms.
- The more polished the surface, the less reactive the material tends to be.

2.0.2 DISPOSABLE GLOVES

Use of disposable, powderless gloves is required when handling equipment for collecting and processing water-quality samples. Wearing gloves serves to protect field personnel from contact with contaminants and chemical preservatives, and protects the sample from contamination transmitted by sample handling.

Although common glove types include those made of vinyl, latex, and nitrile, nitrile is in standard use for USGS sampling work because of its resistance to most of the chemicals to which it typically will be exposed, for the length of exposure (usually under 15 minutes). Field personnel are cautioned that direct contact with materials such as latex or nitrile can cause severe allergic reactions in some individuals and should be monitored.

- Wear powderless nitrile gloves when handling equipment and chemical solutions. **Do not allow the water that enters the sample bottle to contact gloved (or bare) hands.**
- Check the manufacturer's chemical resistance chart for any compound, such as acid, base, or organic solvent, to which the glove might be exposed.

Physical properties to consider when selecting disposable gloves are glove length, slip protection, puncture resistance, heat and flame resistance, cold protection, and comfort. These factors can vary between manufacturers.

Gloves should be inspected visually for defects. Check for tears, punctures, and other flaws that can prevent the glove from being an effective shield. After putting the gloves on, rinse them with water while gently rubbing hands together to remove any surface residue before handling sampling equipment.

BLANK WATER AND CHEMICAL REAGENTS 2.0.3

USGS personnel must use the blank water designated by the USGS National Water Quality Laboratory (NWQL) and available through the Ocala Water Quality and Research Laboratory (OWQRL). Blank water for quality-control samples must have a laboratory-certified analysis to document the chemical composition and chemical concentration. Several grades of blank water are available, and selecting the appropriate grade depends on the sample analysis to be performed.

- **VPBW** (Volatile/Pesticide-Grade Blank Water): Blank water that is suitable for collecting blank samples to be analyzed for volatile organic compounds, pesticides, and all inorganic constituents (major ions, trace elements, and nutrients); purged with nitrogen gas.
  - Shelf life of unopened bottle of VPBW for analysis of volatile organic compounds (VOCs) is 2 weeks after VPBW has been purged of VOCs, and 1 year for other constituents.
  - VPBW also is referred to as N_2-purged Universal Blank Water—see Office of Water Quality Technical Memorandum 2002.14.
- **PBW** (Pesticide-Grade Blank Water): Blank water that is suitable for collecting blank samples to be analyzed for pesticides, major ions, and trace elements.
  - Shelf life of unopened bottle is 1 year after date of laboratory (NWQL) certification.
  - PBW also is referred to as Universal Blank Water when used instead of IBW.
- **IBW** (Inorganic-Grade Blank Water): Blank water that is suitable for collecting blank samples to be analyzed for inorganic trace elements, major ions, and nutrients.

Deionized water (DIW), including ASTM International (formerly known as American Society for Testing and Materials) Type 1 water from other sources, is not an acceptable substitute for the blank water described above. DIW that has been quality-controlled may be used as a cleaning solution, as described in NFM 3.

Unopened bottles of blank water must be stored in a location where there is no exposure to vehicle exhaust, cleaning fluids, or other solvents. No open bottles of blank water are to be stored for later use to collect blank samples to be analyzed for either inorganic or organic analytes.

SAMPLE COLLECTION 2.1

By S.L. Lane, Sara Flanagan, Jacob Gibs,
D.B. Radtke, W.E. Webb, and F.D. Wilde

Guidelines for selecting sample-collection equipment and related supplies differ, depending on the chemical nature of the target analyte and on whether samples are collected for surface water or ground water. Routine use should be made of checklists, field forms (see NFM 6.0.1 and 6.0.2), and logbooks. Examples of checklists for sample-collection equipment and supplies are provided in section 2.4.

A logbook must be maintained that is dedicated to keeping calibration and maintenance records for each field-measurement, field-analysis, and multiparameter instrument. A field book in which the equipment and methods used for project activities and field-site observations are recorded also is strongly recommended. Logbooks and other records documenting field activities may be requisitioned if the project data are a likely candidate for litigation. Documentation of equipment use and extra quality-control analyses are necessary if study objectives or site conditions result in a departure from published USGS required or recommended procedures.

- Logbooks must be bound so that pages are not readily removable (no loose leaf or spiral notebooks), and pages should be preprinted with consecutive numbers.
- Entries in logbooks or on field forms must be in ball-point pen or permanent non-smudge marker (not pencil or liquid ink) and dated.
- Do not erase incorrect entries or mistakes: draw a single line through the mistake and initial and date it.

All equipment should be maintained and tested on a regular schedule (NFM 6). For example, thermistor thermometers should be checked every 3 to 4 months, along with an annual 5-point calibration (NFM 6.1.2). Equipment checks, calibrations, maintenance, and repair must be entered into the logbook.

2.1.1 SURFACE-WATER EQUIPMENT

Study objectives, flow conditions, and structures (such as a bridge, cableway, or boat) from which sample-collection equipment (a sampler) is deployed must be considered when determining which equipment to use. The equipment selected also depends on whether the stream can be waded or not. To determine whether stream depth and velocity are too great to safely wade the stream (NFM 9), follow this rule of thumb:

RULE OF THUMB: Do NOT wade in flowing water when the product of depth (in feet) multiplied by velocity (in feet per second) equals 10 or greater.

Application of this rule varies among individuals according to their weight and stature, and depends on the condition of the streambed.

Two primary types of surface-water samplers are used by the USGS:

- Isokinetic depth-integrating samplers
- Nonisokinetic samplers

2.1.1.A ISOKINETIC DEPTH-INTEGRATING SAMPLERS

An isokinetic depth-integrating sampler is designed to accumulate a representative water sample continuously and isokinetically (that is, stream water approaching and entering the sampler intake does not change in velocity) from a vertical section of a stream while transiting the vertical at a uniform rate (ASTM, 1999; see NFM 4, Appendix A-4-A). Isokinetic depth-integrating samplers are categorized into two groups, based on the method of suspension: hand-held samplers and cable-and-reel samplers.

Types and pertinent characteristics of isokinetic depth-integrating samplers recommended for sampling in flowing water are summarized in table 2-2, illustrated on figure 2-1, and described below. For detailed descriptions of isokinetic depth-integrating samplers, refer to Szalona (1982), Ward and Harr (1990), Horowitz and others (1994), Edwards and Glysson (1999), and Federal Interagency Sedimentation Project at http://fisp.wes.army.mil (accessed March 20, 2003).

For collection of an isokinetic sample, minimum stream velocity must be greater than 1.5 feet per second (ft/s) for a rigid-bottle depth-integrating sampler, or 2.0 ft/s for a US D-96 or US D-99 bag sampler.

The maximum allowable transit rate (R_t) relative to mean velocity (V_m) for a given sampler varies with nozzle size and sample-bottle size (equipment properties were designed using English units; refer to page CF-1 for conversion to metric units) (table 2-2). **Do not exceed the listed R_t/V_m ratio for the given nozzle and bottle size.** A lower R_t/V_m is better for ensuring that a representative velocity-weighted sample is collected, but care must be taken to not overfill the sampler bottle. **Do not exceed the 15 ft (approximately 4.6 meters (m)) maximum depth of deployment for a rigid-bottle sampler.**

Table 2-2. Isokinetic depth-integrating water-quality samplers and sampler characteristics

[R_t, transit rate in feet per second (ft/s); V_m, mean stream velocity in the vertical being sampled, in ft/s; DH, depth-integrating hand-held sampler; PN, polypropylene cap and plastic (Delrin®) nozzle; PFA, perfluoroalkoxy bottle or bag; C&N, cap and nozzle; PC, plastic coated; PT, polypropylene or PFA bottle; PDC, plastic dip coated; D, depth-integrating sampler; P, plastic nozzle; TFE, tetrafluoroethylene nozzle]

Sampler designation	Sampler construction material	Sampler dimensions			Distance of nozzle from bottom, in inches	Suspension method	Maximum calibrated velocity, in feet per second	Maximum depth, in feet	Sampler container size, in liters	Nozzle intake size,[1] in inches	Maximum transit rate ratio,[2] R_t/V_m
		Length (inch)	Width (inch)	Weight (pound)							
US DH-81	PN or PFA-C&N	[3]6.5	3.2	[3]0.5	[4]4	Hand-held (PC)	7.6	15 15 13.3	1 (PT)	3/16 1/4 [1]5/16	0.2 .3 .4
US DH-95	Bronze (PDC) with PN or PFA-C&N	22	6.6	29	4.8	Hand-held or reel and cable	7.4	15 15 13.3	1 (PT)	3/16 1/4 5/16	.18 .32 .4
US D-95	Bronze (PDC) with PN or PFA-C&N	26	6.7	64	4.8	Reel and cable	6.7	15 15 13.3	1 (PT)	3/16 1/4 [1]5/16	.18 .32 .4
US D-96	Bronze (PDC) with P or TFE nozzle	35	8	132	4	Reel and cable	12.5	110 60 39	3 (PFA)	3/16 1/4 5/16	.4 .4 .4
US D-99	Bronze (PDC) with P or TFE nozzles	47	10	275	9.5	Reel and cable	15	220 120 78	6 (PFA)	3/16 1/4 5/16	.4 .4 .4

[1]Nozzle sizes are those recommended for the application shown.
[2]Refer to NFM 4, Appendix A, for maximum transit-rate ranges, and to Office of Surface Water Technical Memorandum 94.05, dated January 31, 1994.
[3]Length, width, and weight will depend on specific bottle dimensions. Weight indicated is for cap and nozzle only. Handle is plastic coated with clear heat-shrinking tubing.
[4]Distance of nozzle from the bottom will depend on specific bottle dimensions.

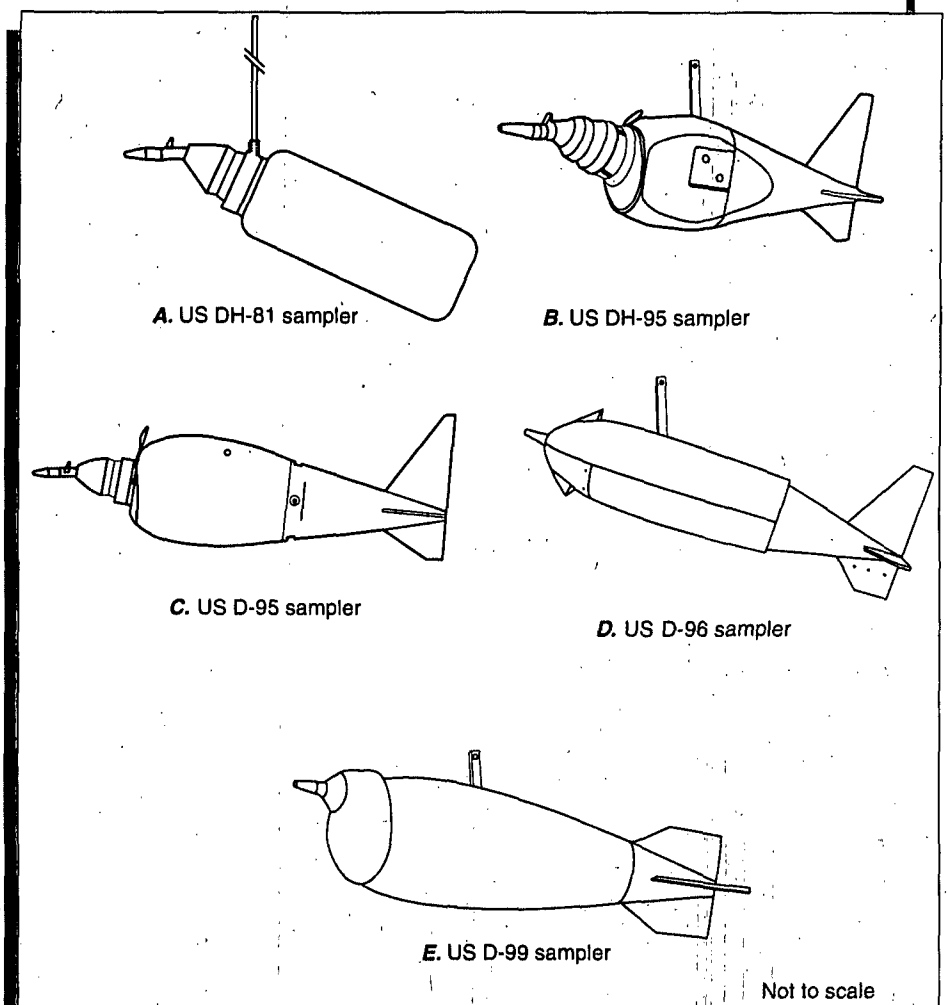


Figure 2-1. Isokinetic depth-integrating samplers: (*A*) US DH-81, (*B*) US DH-95, (*C*) US D-95, (*D*) US D-96, and (E) US D-99. (Illustrations courtesy of Federal Interagency Sedimentation Project, Waterways Experiment Station, Vicksburg, Miss.)

The cap-and-nozzle assembly is available in fluoropolymer and polypropylene materials. The same cap and nozzle can be used for the US DH-81, US DH-95, and US D-95 samplers.

- Use the US DH-81, US DH-95, US D-95, US D-96, or US D-99 samplers (fig. 2-1) to collect samples in flowing waters for all analyses except inorganic gases and volatile organic compounds.
  - Samples of water for determination of trace elements must contact only noncontaminating materials, typically fluorocarbon polymer or polypropylene.
  - Samples of water for determination of organic compounds must contact only noncontaminating materials, typically a metal (such as stainless steel), fluoropolymers or fluorocarbon polymers (such as Teflon®[4]), or ceramics (such as hard-fused microcrystalline alumina).
- Discontinue use of the US DH-48, US DH-59, US DH-76, US D-49, US D-74, US D-77, US D-77 Bag, Frame Bag (FB), US P-61, US P-63, and US P-72 samplers for collecting trace-element samples (refer to Office of Water Quality Technical Memorandum 2002.09 for details): testing indicates that these samplers contaminate samples with measurable concentrations of trace elements.
  - Some of these samplers may be acceptable for major ions, nutrients, and suspended sediments.
  - Collect additional quality-control samples if it is necessary to use any of these samplers (Horowitz and others, 1994).

[4]Teflon is a registered trademark of the DuPont Corporation.

Hand-held samplers

The US DH-81 (fig. 2-1*A*) or US DH-95 (fig. 2-1*B*) sampler is used to collect water samples where flowing water can be waded or where a bridge is accessible and low enough from which to sample. The sampler components (cap, nozzle, and bottle) are interchangeable. Both inorganic and organic samples can be collected with either sampler as long as the construction material of the sampler components (table 2-1) does not affect ambient concentrations of target analytes. Isokinetic depth-integrated samples for bacteria analysis also can be collected with these samplers because the cap, nozzle, and bottle can be autoclaved. All hand-held samplers should be tested and maintained as described on table 2-3. The checklist also applies to cable-and-reel samplers.

Table 2-3. Prefield checklist for hand-held and cable-and-reel samplers

✓	Sampler items	Comment
	Mechanical operation	Test the working condition of the sampler. If tail fin is damaged or broken, sampler will not swim correctly.
	Nozzles	Replace nozzles that have burrs or are damaged. Use only nozzles purchased from the Federal Interagency Sedimentation Project.
	Plastic coating	If plastic coating is damaged or any metal parts are exposed, recoat or touch up with a plastic dip product.
	Sampler is clean	Before field work, clean appropriate parts of the sampler according to procedures described in NFM 3 and store in plastic for transport to the field site.
	Laboratory results from analysis of sampler blank	Make sure the sampler has been quality assured with an annual equipment blank and certified for water-quality use (see NFM 1 and NFM 4).
	Separate sets of sampler components and backup equipment	If at all feasible, for a given field trip when collecting multiple water samples, prepare and use separate sets of sampler bottles, caps, and nozzles for each sampling site. Have backup equipment available on-site.
	Field-cleaning supplies and blank water	If separate sets of sampler components are not available, then clean equipment between sampling sites (see NFM 3) and be prepared to process the number of field blanks needed to document that equipment was adequately cleaned.

When using the US DH-81 (fig. 2-1*A*):

- Use a 3/16-, 1/4-, or 5/16-in. nozzle.
- Make sure that flow velocity exceeds 1.5 ft/s (~0.46 m/s) but does not exceed 7.6 ft/s (~2.32 m/s) (to collect an isokinetic sample).
- Maximum depth of deployment must be within 15 ft (~4.6 m) if using a 3/16- or 1/4-in. nozzle, and within 13.3 ft (~4 m) if using a 5/16-in. nozzle.
- Use caution when sampling in depths that exceed 13.3 ft (~4 m) to avoid overfilling the sampler.

When using the US DH-95 (fig. 2-1*B*):

- Use the 1-L bottle. Use caution when sampling in depths that exceed 13.3 ft (~4 m) to avoid overfilling the sampler.
- To collect an isokinetic sample when using a 3/16-in. nozzle, flow velocity must be between 2.1 to 6.2 ft/s (~0.64 to 1.9 m/s) and depth of deployment should not exceed 15 ft (~4.6 m).
- To collect an isokinetic sample when using a 1/4-in. nozzle, flow velocity must exceed 1.7 ft/s (~0.52 m/s) but be no greater than 7.4 ft/s (~2.25 m/s), and depth of deployment should be within 15 ft (~4.6 m).
- To collect an isokinetic sample when using a 5/16-in. nozzle, flow velocity also should be between 1.7 and 7.4 ft/s (~0.52 and 2.25 m/s), and depth of deployment should not exceed 13.3 ft (~4 m).

Cable-and-reel samplers

Cable-and-reel samplers are used to collect water samples where flowing water should not be waded. These include the US D-95, US D-96, and US D-99 samplers. (Refer to table 2-2 for sampler characteristics and sampling limitations.) Like the hand-held US DH-81 and US DH-95, these cable-and-reel samplers can be used for collecting inorganic and organic samples; however, appropriate sampler components (cap, nozzle, and bottle or bag) must be selected so as not to bias concentrations of target analytes. Isokinetic depth-integrated samples for bacteria analysis also can be collected with these samplers because the cap, nozzle, bottle, and bags can be autoclaved.

The US D-96 Bag sampler uses a perfluoroalkoxy (PFA) or polyethylene bag that is placed in a sliding tray that supports the bag and holds the nozzle holder with nozzle in place. The bag is attached to the nozzle holder with a hook-and-loop strap. The US D-99 Bag sampler uses a 6-L PFA or polyethylene bag that is placed in a chamber behind the nozzle, through an access door.

Metal parts of the US D-95 Bottle sampler and US D-96 Bag and US D-99 Bag samplers must be coated with plastic (for example, Plasti Dip®) and recoated periodically to prevent possible sample contamination from metallic surfaces. **All cable-and-reel samplers should be tested and maintained before use, as described on table 2-3.**

When using the US D-95 Bottle sampler (fig. 2-1*C*):

- Use a 3/16-, 1/4-, or 5/16-in. nozzle. US DH-81 and DH-95 nozzles can be used.
- Make sure that flow velocity exceeds 1.7 ft/s (~0.52 m/s), but no greater than 7.4 ft/s (~2.25 m/s), depending on the nozzle diameter used.
- Use in water less than 13.3 to 15 ft (~4 to 4.6 m) deep (at sea level), depending on the nozzle used and altitude at the site for an isokinetic, depth-integrated sample.

When using the US D-96 Bag sampler (fig. 2-1*D*):

- Use a 3/16-, 1/4- or 5/16-in. nozzle. The nozzles needed are unique to the D-96 sampler and mounts.
- Make sure that flow velocity exceeds 2 ft/s (~0.61 m/s), but is no greater than 12.5 ft/s (~3.8 m/s).
- Use in water with a maximum depth between 39 and 110 ft (~11.9 and 33.5 m), depending on nozzle diameter for an isokinetic, depth-integrated sample.
- Water temperature must be at or greater than 4°C. The sampler has been tested at temperatures of 39°F (4°C) and found to function properly.

When using the US D-99 Bag sampler (fig. 2-1*E*) **for isokinetic sampling:**

- Use a 3/16-, 1/4- or 5/16-in. nozzle and mount (do not use a 1/8-in. nozzle that is designed for the D-99 sampler).
- Make sure that flow velocity exceeds 3.0 ft/s (~0.9 m/s).
- Use in water with a maximum depth between 78 and 220 ft (~23.8 and 67 m), depending on nozzle diameter, for an isokinetic, depth-integrated sample.
- Water temperature must be at or greater than 4°C.

2.1.1.B NONISOKINETIC SAMPLERS

Nonisokinetic samplers are sampling devices in which the sample enters the device at a velocity that differs from ambient stream velocity. All of the isokinetic samplers described in 2.1.1.A can be used to collect depth-integrated, although nonisokinetic, samples, when used beyond the minimum and maximum ranges of velocity and depth (table 2-2). As with all samplers, the materials that contact the sample must not bias concentrations of target analytes by sorbing or leaching target analytes.

Open-mouth samplers

Open-mouth samplers used for the collection of water samples include the hand-held bottle, the weighted-bottle sampler, the biochemical oxygen demand (BOD) sampler, and the volatile organic compound (VOC) sampler (fig. 2-2).

- **The hand-held bottle sampler** is the simplest type of open-mouth sampler. A bottle is dipped to collect a sample (fig. 2-2*A*) where depth and velocity are less than the minimum requirements for depth-integrating samplers.
- **The weighted-bottle sampler** is available in stainless steel (US WBH-96) (fig. 2-2*B*) or polyvinyl chloride. The weighted-bottle sampler can be used to collect samples where flow velocities are less than the minimum requirement for isokinetic depth-integrating samplers and where the water body is too deep to wade. An open bottle is inserted into a weighted holder that is attached to a handline for lowering. Sampling depth is restricted by the capacity of the bottle and the rate of filling.
- **The BOD sampler and the VOC sampler** (fig. 2-2*C-D*), respectively, are open-mouth samplers designed to collect nonaerated samples.
  - The BOD sampler accommodates 300-milliliter (mL) glass BOD bottles specifically designed to collect samples for dissolved-oxygen determination (American Public Health Association and others, 1992, p. 4-99).
  - The VOC sampler is specifically designed to collect nonaerated samples in 40-mL glass septum vials for determination of volatile organic compounds.

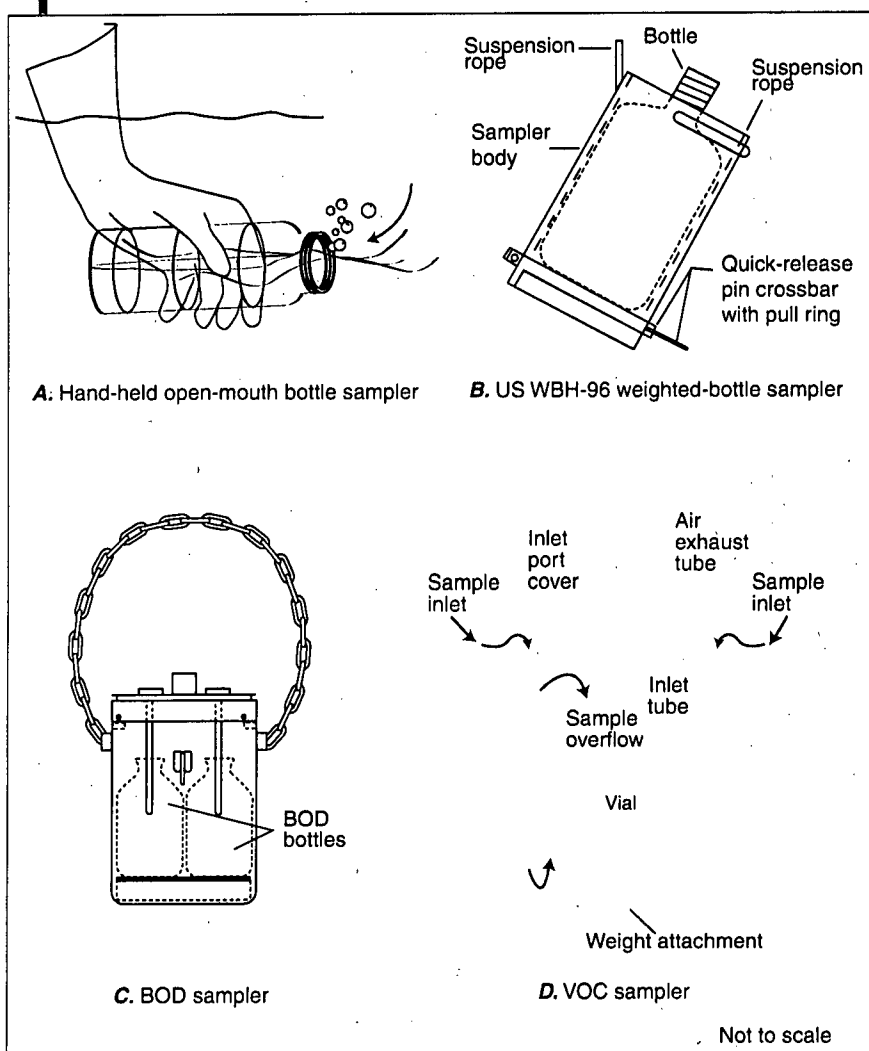


Figure 2-2. Nonisokinetic open-mouth samplers: (*A*) hand-held open-mouth bottle sampler, (*B*) US WBH-96 weighted-bottle sampler, (*C*) biochemical oxygen demand (BOD) sampler, and (*D*) volatile organic compound (VOC) sampler. (*A*, from U.S. Environmental Protection Agency, 1982b; *B*, courtesy of Federal Interagency Sedimentation Project, Waterways Experiment Station, Vicksburg, Miss.; *C*, published with permission of Wildlife Supply Company; *D*, from Shelton, 1997.)

Thief samplers

Thief samplers are used to collect instantaneous discrete samples. Thief samplers have been used primarily to collect samples from lakes, reservoirs, and some areas of estuaries. Smaller versions, designed to collect ground-water samples, also have been used in still and flowing surface water. The most commonly used thief samplers are the Kemmerer sampler, Van Dorn sampler, and double check-valve bailer with bottom-emptying device (fig. 2-3). These samplers are available in various sizes, mechanical configurations, and in various types of construction material (such as stainless steel, glass, polyvinyl chloride, fluorocarbon polymer). Disposable fluorocarbon polymer bailers also are available. For descriptions of additional thief samplers, see U.S. Environmental Protection Agency (1982b), Ward and Harr (1990), and American Public Health Association and others (1992) or consult the manufacturer of environmental sampling equipment.

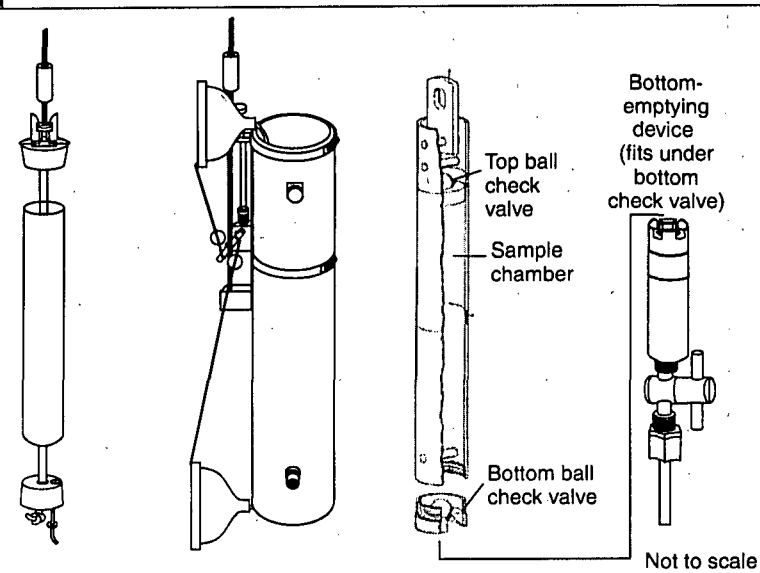


Figure 2-3. Nonisokinetic thief samplers: (*A*) Kemmerer sampler, (*B*) Van Dorn sampler, and (*C*) double check-valve bailer with bottom-emptying device. (*A-B*, from *Standard Methods for Examination of Water and Wastewater*, 18th Edition. Copyright 1992 by the American Public Health Association, the American Water Works Association and the Water Environment Federation. Used with permission. *C*, published with permission of Timco Mfg. Inc.)

Single-stage samplers

Single-stage samplers such as the US U-59 (fig. 2-4*A*) are designed to obtain suspended-sediment samples from streams at remote sites or at streams where rapid changes in stage make it impractical to use a conventional isokinetic depth-integrating sampler. Single-stage samplers can be mounted above each other to collect samples from different elevations or times as streamflow increases and the hydrograph rises (fig. 2-4*B*). (Edwards and Glysson, 1999.)

- **The US U-59** is a sample container mounted to collect a water sample as stage rises above the sampler intake.
  - The vertical-intake sampler is used to sample streams carrying sediments finer than 0.062 millimeter (mm). The vertical intake is less likely to become clogged or fouled by floating solid materials compared to a horizontal-type intake.
  - The horizontal-intake sampler is used to sample streams carrying sediment coarser than 0.062 mm.
- **The US U-73,** which can be used to sample water during either rising or falling stage, is constructed to provide some protection form trash or other solids that could clog or foul the intake.

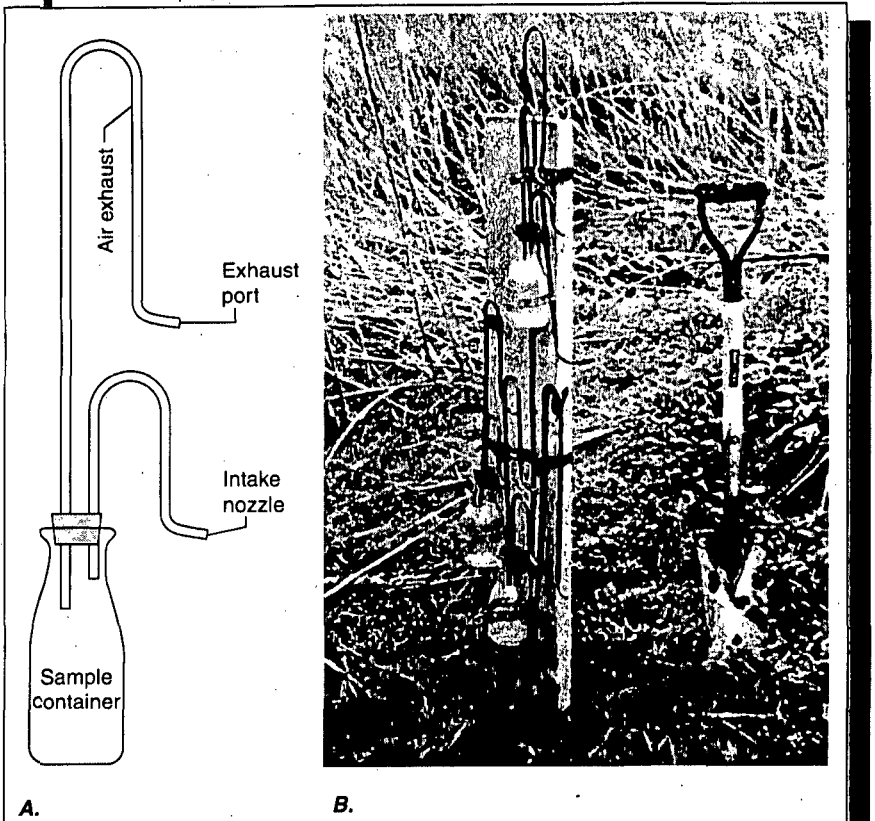


Figure 2-4. US U-59 sampler: (*A*) single stage, and (*B*) a bank of U-59 samplers installed on a plank post. (A, from Edwards and Glysson, 1999; B, photograph by J.C. Mundorff.)

Automatic samplers and pumps

Automatic pumping samplers (autosamplers) with fixed-depth intake(s)[5] are sometimes used to collect samples at remote sites; from ephemeral, small streams; or from urban storm drains where stage rises quickly (American Public Health Association and others, 1992; Edwards and Glysson, 1999). These samplers can be programmed to collect samples at preset time intervals or at selected stages, thus reducing the personnel requirements for time-intensive sampling. Whenever automatic samplers or pumps are used, the sample is considered to be a point-integrated sample.

Pumps used for water sampling are grouped into two general categories: suction-lift pumps and submersible pumps. Pumps can be used to collect water samples from lakes, reservoirs, and estuaries (Radtke and others, 1984; Radtke, 1985; Ward and Harr, 1990). Suction-lift and submersible pumps are described in section 2.1.2, "Ground-Water Equipment."

SUPPORT EQUIPMENT 2.1.1.C

Much of the equipment used to measure streamflow also can be used as support equipment when collecting water samples in water bodies that cannot be waded. Examples of commonly used support equipment are listed in section 2.4.

Clean Hands/Dirty Hands techniques described in NFM 4 are required when sampling for trace elements (Horowitz and others, 1994) and are recommended as a general practice in sample collection, particularly when using heavy-duty support equipment.

[5]Automatic pumping samplers are available through commercial manufacturers, such as American Sigma, ISCO, and Manning.

Use of a vertical transit rate pacer, such as the US VTP-99, can help to ensure an accurate flow-weighted sample, after the appropriate transit rate has been determined (Edwards and Glysson, 1999, p. 53–60). Once programmed, the pacer produces an audible signal for pacing the raising and lowering of either hand-held or mechanically hoisted samplers. The pacer is small enough to be carried in a shirt pocket, and the tone is audible for several feet in a quiet environment. The US VTP-99 can be used with a miniature phone-type monaural headphone jack; neither the jack nor the headphones are supplied. Tables for using the pacer when sampling with either a hand-held sampler or type "A," "B," or "E" reel can be found in the publication "Using the US VTP-99 vertical transit rate pacer."[6]

Exercise great care to avoid sample contamination when using support equipment to handle samplers for collecting trace-element samples.

2.1.2 GROUND-WATER EQUIPMENT

The type of sampler or sampling system selected depends on the type and location of well, depth to water from land surface, physical characteristics of the well, ground-water chemistry, and the analytes targeted for study. Selecting the appropriate equipment for collecting ground-water samples is important in order to obtain data that will meet study objectives and data-quality requirements. Ground-water sampling equipment is available from commercial sources. Support equipment (for example, tubing, valves, manifolds) is available commercially or, for USGS personnel, through the Hydrologic Instrumentation Facility (HIF).

[6]The publication is available at the URL http://fisp.wes.army.mil/Instructions%20US%20VTP-99%20990722.pdf (accessed March 20, 2003).

Ground water most commonly is collected using either pumps designed specifically for water sampling from monitoring wells, pumps installed in supply wells, or a bailer or other point or thief-type sampler.[7] General considerations for selecting ground-water equipment are listed in table 2-4.

- Monitoring wells: Samplers can be portable, dedicated, or permanently installed in the well.
  - — Portable equipment is commonly used at multiple well sites and cleaned after each use.
  - — Portable samplers and sample tubing commonly are dedicated to be used only at a site with large contaminant concentrations.
  - — Some types of portable equipment can be installed in a well for the duration of the monitoring program. Remove the sampler periodically for cleaning.
- Supply wells (for domestic, public (municipal), industrial or commercial, and agricultural use): Equipment selection is limited as such wells normally are equipped with permanent, large-capacity pumps.
  - — Choice of equipment usually depends on well configuration and type of pump installation (permanent or temporary).
  - — Modifications to the well and ancillary equipment attached at the wellhead are necessary in some cases (see section 2.1.2.A.)

[7]Additional categories of sampling equipment not described in this report include multilevel collection systems (LeBlanc and others, 1991; Smith and others, 1991; Gibs and others, 1993); samplers designed to collect ground water under natural-gradient flow conditions (Margaritz and others, 1989); and pump-and-packer systems.

Table 2-4. General requirements and considerations for selecting ground-water sampling equipment (pumps or thief samplers)

Requirements	Considerations
Construction materials	• Is the sampler constructed from materials that (initially or over time) could leach targeted analytes? If left in the well, is the sampler constructed of materials that will degrade appreciably within the lifetime of the study? • Can the sampler be cleaned? Can it withstand the level of decontamination needed and subsequently produce clean equipment blanks?
Operation, capabilities, and limitations	• Could operation of the sampler compromise sample integrity with respect to study objectives or data quality? For example, does the sampler heat or aerate the sample, or subject it to negative pressure, leading to volatilization of purgeable organic compounds, oxidation of target analytes, or changes in partial pressure of carbon dioxide or other gases? • Is the sampler capable of evacuating standing water (that is, can it be used for purging in addition to sample collection)? • Is the sampler capable of providing flow or sample volumes sufficient for sample collection and in a manner that minimizes suspension of sediments or colloids that could bias chemical measurements? • Is the sampler mechanically capable of withdrawing formation water from the desired depth?
Power requirements	• What are the power requirements of the sampler or the manner in which it will be deployed? Will it require electrical power (alternating or direct current), gasoline or other fuel-powered generators, or compressed gas such as air or nitrogen? • Will the capacity of the power source be sufficient to allow the sampler to run continuously throughout purging and sample collection? • Could the power source contaminate samples? (For example, gasoline-powered generators or compressors are a potential source of volatile organic compounds.) • Could the fuel be changed to a noncontaminating type (for example, convert a gasoline-powered generator to propane fuel)?
Transport	• Is the sampler easily transported to remote sites and rugged enough for field use?
Sampler repair	• Can the sampler be repaired in the field?
Availability and cost	• Are the available samplers suitable for study use? Are funds available to purchase, operate, and maintain the sampler? • Are funds available to purchase a spare pump head? This would allow for continuous use of a sampling pump while one pump head is being repaired.

Sampling equipment must not be a source of contamination or otherwise affect analyte concentration (table 2-1). Of specific importance for ground-water sampling is a potential change in ground-water chemistry due to atmospheric exposure.

- Select equipment that minimizes sample aeration.
- Select equipment that will not leach or sorb significant concentrations of the target analytes, with respect to data-quality requirements.
  - Samplers that tested successfully[8] for inorganic constituents[9] were the Grundfos Redi-Flo2®, Fultz SP-300, Bennett, and several bladder pumps (with Teflon® bladders), submersible pumps, and double check-valve fluorocarbon polymer bailers.
  - Samplers tested that achieved a greater than 95-percent recovery of volatile organic compounds were Grundfos Redi-Flo2®, Fultz SP-300, bladder pumps, and the Bennett pump. Recovery for double check-valve fluorocarbon polymer bailers was less than 95 percent (U.S. Geological Survey, 1992a, b).

Choice of equipment is constrained by many factors, including equipment construction and specifications. For example, it is necessary to consider the power requirements, lift capability, and discharge capacity of submersible pumps. Ideal equipment for sample collection might not exist, and compromise is often necessary. **Field personnel must understand the application, advantages, disadvantages, and limitations of the available equipment with respect to study objectives and site characteristics, and must document how any compromises made might affect the data and data-quality objectives.**

---

[8]Unpublished results of testing by the USGS confirmed that commonly used sampling equipment does not, in general, affect sample concentrations of inorganic constituents or organic compounds (U.S. Geological Survey Office of Water Quality, written commun., 1994). (The samplers tested were precleaned and fitted with new, cleaned tubing and had fluorocarbon polymer interior parts, where available.)

[9]Trace-element concentrations in blank samples processed through these samplers were within the margin of analytical variability at a method reporting level of 1 microgram per liter.

2.1.2.A PUMPS

Pumps transport water from depth to land surface either by suction lift or positive pressure.[10] The pumping mechanism for most suction-lift pumps (peristaltic, jet, and some nonsubmersible centrifugal pumps) is at land surface. Positive-pressure pumps (helical rotor, gear, bladder, piston, inertial submersible, and centrifugal) are grouped together as submersible pumps because they are placed below static water level.

Supply-well pumps

Jet (venturi) pumps and above land-surface centrifugal pumps (fig. 2-5), as well as high-capacity submersible pumps and turbine pumps are common in domestic, municipal, and other supply wells.

- Be aware that large- and small-capacity pumps used in supply wells can affect analyte concentrations. (See NFM 1 and Lapham and others, 1997.)
  - — Erroneous data produced as a result of using these pumps are most likely for dissolved gases, VOCs, and reduction-oxidation (redox) chemical species.
  - — Oil in the water column is common for oil-lubricated pumps.
  - — Chemical treatment systems, pressure tanks, and holding tanks can compromise sample integrity.

[10]For more detailed information on pumps, refer to manufacturers' instructions and specifications and to U.S. Environmental Protection Agency (1982b), Morrison (1983), Driscoll (1986), Imbrigiotta and others (1988), Ward and Harr (1990), American Public Health Association and others (1992), Gibs and others (1993), Sandstrom (1995), Koterba and others (1995), and Edwards and Glysson (1999).

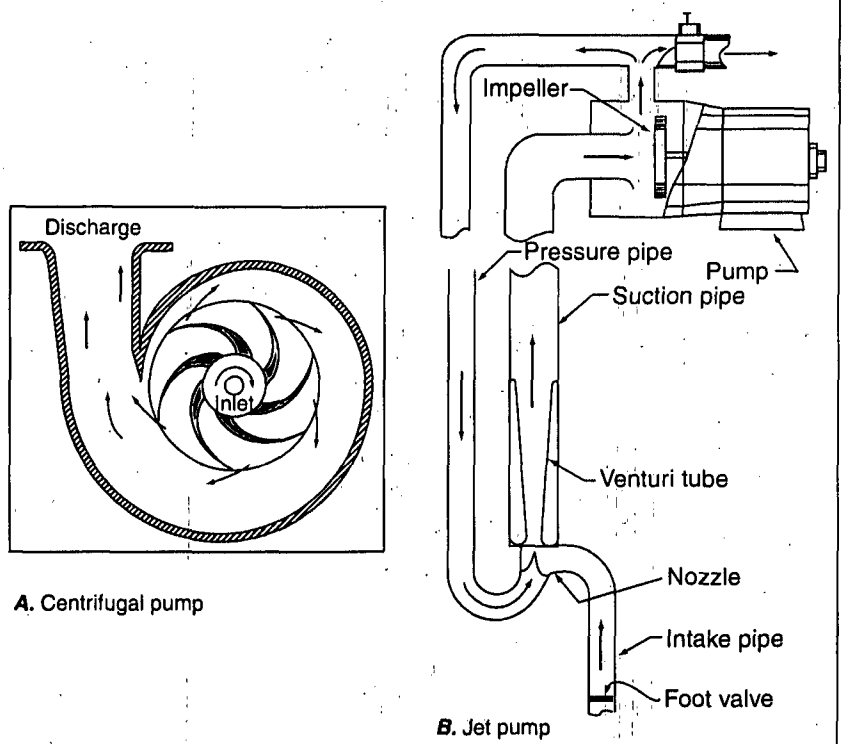
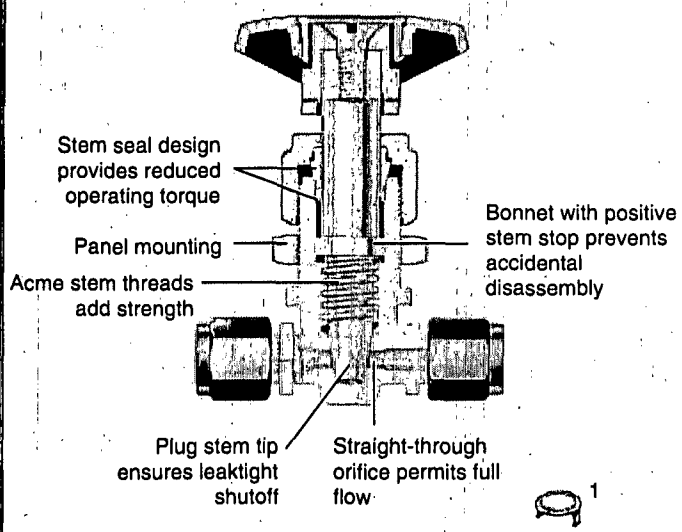


Figure 2-5. Pumps typically used to obtain water from supply wells: (*A*) centrifugal pump, and (*B*) jet pump. (From Driscoll, 1986, and published with permission of US Filter/Johnson Screens.)

- Install a hookup system for transfer of sample from the wellhead to the chamber or area where samples will be processed (NFM 4 and 5). Clean such equipment of oils and other manufacturing and shipping residues (NFM 3) before use.
  - Ensure that the point of sample discharge from the hookup system on supply wells is ahead of chemical treatments or holding tanks. Obtain permission to modify the discharge point by installing a spigot or other plumbing appropriate to preserve the quality of the sample, if possible. Otherwise, do not use the well. The spigot or other plumbing also must be cleaned before use.
  - Install an anti-backsiphon device in line with the hookup system.
  - Install an optional needle valve with flow-regulating capabilities in line with the hookup system (fig. 2-6*A*).

A. Swagelok® PFA Needle Valve number PFA-4RPS8 (fits 1/2-inch tubing)



B. Materials of Construction

Component	Material Grade/ASTM Specification
1 Handle insert	PFA 440-HP/ D3307
2 Screw	
3 Handle	
4 Packing nut	
5 Upper packing	
6 *Lower packing*	
7 *Stem stop*	
8 Panel nut	
9 *Stem*	
10 *Body, ferrules*	
11 Nut	
Lubricant	PTFE based

Wetted components listed in *italics*.

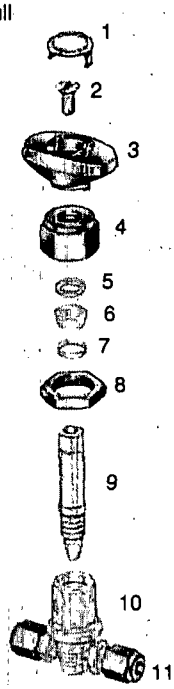


Figure 2-6. Swagelok® perfluoroalkoxy needle valve: (*A*) front view and (*B*) exploded view.

Monitoring-well pumps

Suction-lift and positive-displacement pumps are commonly used to collect water samples from monitor (monitoring) wells. Field personnel should consider the criteria and guidelines listed in tables 2-4 and 2-5 when selecting a pump for sampling from monitoring wells.

- Suction-lift pumps create a vacuum in the intake line that draws the sample up to land surface (fig. 2-7*A*).
  - — The vacuum can result in the loss of dissolved gases and VOCs.
  - — Intake tubing could diffuse atmospheric gases sufficiently to affect some target analytes unless thick-walled low-diffusion tubing is used.
  - — Use of a peristaltic pump (1- to 2-L/min pumping rate) is limited to wells in which depth to water is less than about 25 ft (approximately 9 m). The operational lift may be as small as 20 ft.
  - — Peristaltic pumps have the advantages of few moving parts, easily replaceable tubing and heads, and portability.
  - — Provided that data quality is not compromised, properly operated peristaltic pumps can be used to obtain samples from shallow wells, especially those that produce small volumes of water.
- Submersible pumps (positive pressure or other types of positive-displacement pumps) designed specifically for collection of water samples from monitoring wells generally are preferred because they do not create a vacuum (fig. 2-7*B–F*).

- In general, do not use submersible pumps for well development. This can ruin the pump, shorten its functional life, or damage smooth internal surfaces, causing leaching of target analytes.
  - Install an anti-backsiphon device in-line to prevent backflow from contaminating the ground water.
  - Select suitable materials for sample line, sample-line connectors (see "Pump Tubing," section 2.2.4), and sample-line reels (see "Support Equipment," section 2.1.2.C, and "Lists of Equipment and Supplies," section 2.4) for use with portable submersible pumps.
- The suitability and application of commonly used submersible pumps depends on pump and well characteristics and on practical constraints (tables 2-4 and 2-5). It is necessary to determine that:
  - the rate of pumping is suitable for a given lift (table 2-5),
  - the maximum lift of the pump at the water surface is greater than the lift to land surface,
  - the power source and pump characteristics are sufficient to allow the pump to run continuously throughout purging and sample collection,
  - the height of the water column must be at least 5 ft above the top of the submersible pump (to avoid setting the pump intake too close to the bottom of the well), and
  - the pumping rate will not cause excessive drawdown, resulting in intersection of the water level with the well screen or open interval or causing the well to go dry.

- The pump used to purge and sample the well generally is not appropriate for well development or redevelopment (Lapham and others, 1997). Using a pump designed for sample collection as a well-development tool can shorten the pump life or damage smooth internal surfaces, causing leaching of target analytes. If the well should be redeveloped in preparation for collecting a representative sample, two options that are available include use of an inertial lift pump or use of an air-suction lift pump.

Portability and repairability are important logistical considerations when selecting a pump. All the pumps shown in figure 2-7 are made for transport to and from the field, but fuel or electrical power requirements make some more awkward to transport and operate at remote sites than others (not shown is the inertial-lift pump, which has no fuel or electrical power requirement when operated manually). Ruptured bladders for bladder pumps can be replaced easily in the field. Fluorocarbon polymer impellers used in gear pumps are easily abraded and can be ruined by particulate-laden water. Such impellers can be replaced in the field, but usually with some difficulty. Submersible centrifugal pumps and piston pumps generally are not easily repaired in the field and can be awkward to transport, but include features such as variable-speed capability that make them favored for many applications. When selecting a pump for sampling, consider purchasing an additional pump head (the submerged motor component) since most repairs involve the pump head. The pump heads for some pump types or models (such as the Fultz pump) are constructed for quick connect and disconnect, to ease pump head replacement under field conditions.

Table 2-5. Examples of pump capability as a function of well and pump characteristics in a 2-inch-diameter well

[Table modified from Koterba and others (1995), p. 18-19. ft, foot; gal, gallon; TDH, total dynamic head; gal/min, gallon per minute; ~, approximately; ---, not available]

Well characteristics			Pump characteristics			
			Example: Fultz SP-300 (lift capacity is exceeded at ~150 ft)		Example: Grundfos RediFlo2® (lift capacity is exceeded at ~260 ft)	
Water-column height (ft)	Lift or TDH[1] (ft)	Three-well-volume purge protocol[2] (gal)	Pumping rate at lift or TDH shown (gal/min)	Maximum volume after 2 hours pumping[3] (gal)	Pumping rate at lift or TDH shown (gal/min)	Maximum volume after 2 hours pumping (gal)
20	25	10	1.0	120	7.0	840
40	160	20	---	---	~4.8	538

[1]In these examples, the lift is equivalent to TDH and is estimated as the depth to water in the well (see Koterba and others, 1995, for explanation).
[2]Standard procedure is to purge a minimum of three well volumes while monitoring field measurements (NFM 4, NFM 6): purge volume = V=0.0408HD^2, where H is water-column height (in feet) and D is the well diameter (in inches).
[3]Maximum pumped volume is calculated from the pumping rate for a given pump system (from manufacturer's specifications) at the lift (or TDH) multiplied by an assumed total purging time of 2 hours (see Koterba and others, 1995).

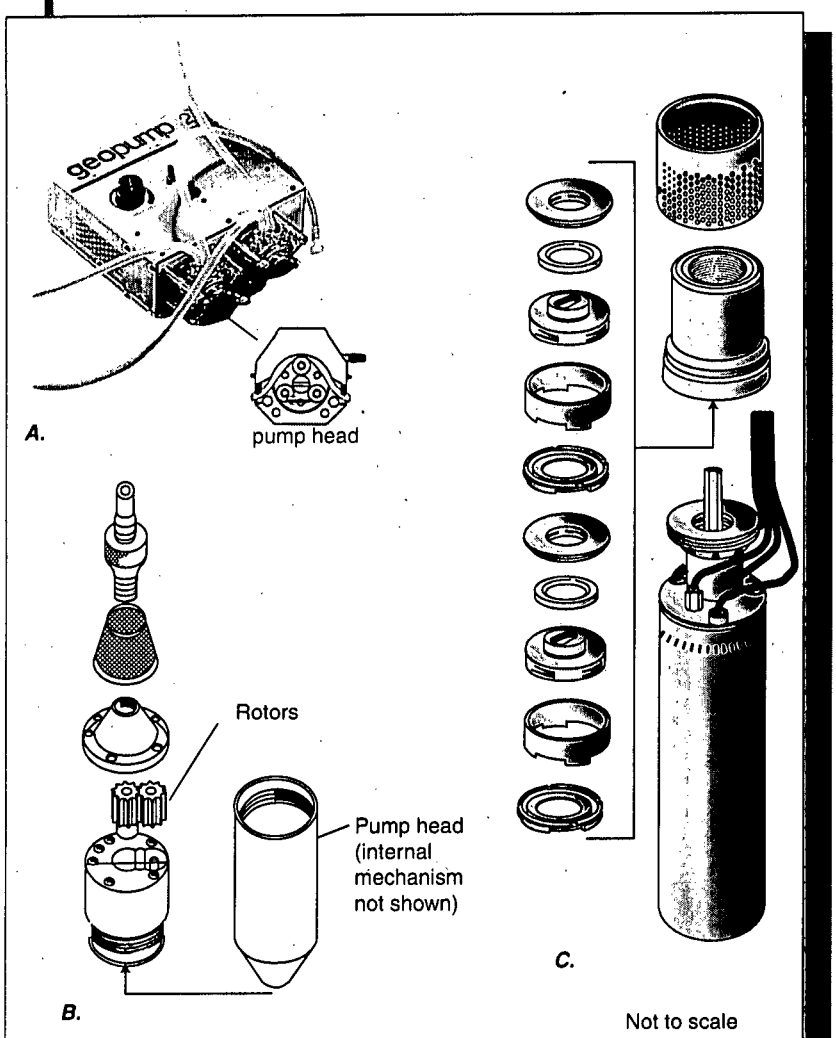


Figure 2-7. Pumps typically used for withdrawal of water samples from monitoring wells: (*A*) peristaltic suction-lift pump and (*B-F*) examples of submersible positive-displacement pumps. (*A*) peristaltic pump showing detail of pump head, (*B*) electrical gear or rotor pump, (*C*) electrical centrifugal impeller pump showing detail of impeller assembly. (Illustrations published with permission: *A*, GeoTech Environmental Equipment, Inc., with pump head from Cole-Parmer Instrument Company; *B*, Fultz Pumps, Inc.; *C*, Grundfos Pumps Corporation.)

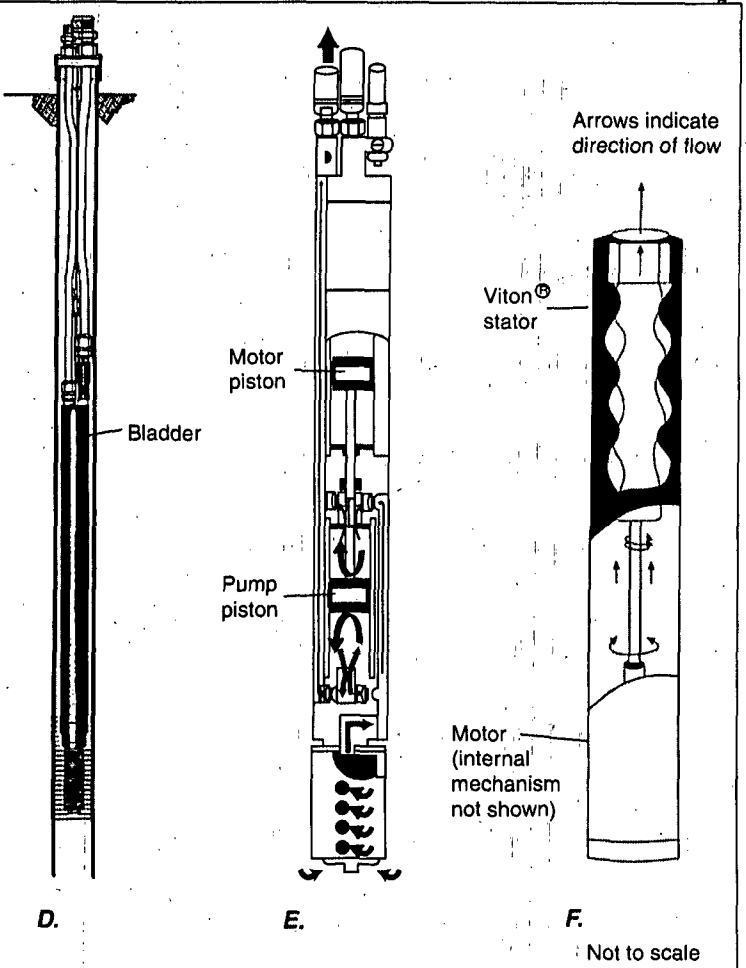


Figure 2-7. Pumps typically used for withdrawal of water samples from monitoring wells: (*A*) peristaltic suction-lift pump, and (*B-F*) examples of submersible positive-displacement pumps—*Continued.* (*D*) bladder pump, (*E*) reciprocating piston pump, and (*F*) progressive cavity pump. (Illustrations published with permission: *D* and *F*, GeoTech Environmental Equipment, Inc.; *E*, Bennett Sample Pumps, Inc.)

Well-development pumps

Wells need to be developed after construction to remove sediment and other debris at the bottom of the well and to improve hydraulic connection to the aquifer. Wells might need to be redeveloped after long periods of inactivity before water-quality samples are collected. Sounding of the well (confirming the well depth) may indicate that the well should be redeveloped in preparation for collecting a representative sample. The pump used to purge and sample the well, in general, is not appropriate for well development or redevelopment (Lapham and others, 1997).

- Use of inertial pumps fitted with a surge block (for example, the Waterra Inertial Pump, Model 404), is an effective and easily operated method for well development or redevelopment. The Waterra Pump consists of a riser tube (5/8-in. or 1.58-cm outer diameter (OD) polyethylene or similar tubing) with a one-way valve at the bottom of the tubing and a surface hand- or mechanical-pumping mechanism. The valve allows water to enter the tubing as it is pushed downwards, and retains the column of water when the riser tube is pulled upward again. Adding a surge block to the riser tube and valve creates a strong churning effect that helps to remove sediment that collected at the bottom of the well. Such a pump works well in silty/sandy environments, and can be successfully operated in wells with depths ranging up to 100 ft (~30.6 m) when using a hand pump, 200 ft (~61 m) when using a pump powered by an electric motor, and 250 ft (~76 m) when using a pump powered by a gasoline motor.

- Another inexpensive option to consider in well development is to use inexpensive disposable plastic (clear or white) tubing with a suction-lift pump. This method, however, is limited to shallow wells with water table depths less than 25 ft (~7.6 m) from the land surface. To aid in removing sediments from the bottom of the well, add a surge block and one-way valve to the bottom of the tubing as described above. The tubing can be physically raised and lowered, producing a purging effect. To prevent cross-contamination of wells, new tubing, surge block, and valve should be used for each well that is developed or redeveloped.

- Wells can also be developed by the air-lift or gas-lift method. This method is not recommended for shallow wells, but may be the only method available for very deep wells, especially for wells that approach 2,000 ft (~610 m) in depth. In this method, compressed air is forced down the well and replaces the water and debris in the casing. The displaced water and debris in the well casing is then forced up and out of the well. **However, care must be taken to ensure that air is not forced from the well screen into the surrounding aquifer system. Air introduced into the aquifer can change its geochemistry, either temporarily or permanently.**

2.1.2.B BAILERS, THIEF SAMPLERS, AND PASSIVE DIFFUSION BAG SAMPLERS

Use of a bailer or other thief sampler disturbs the water column, especially when it is raised and lowered repeatedly, and is not recommended for this reason. The disturbance can result in stirring up or mobilizing particulate matter, including colloidals or mineral precipitates that are artifacts of well construction and are not part of the ambient ground-water flow. This, in turn, can result in analysis of substantially greater than ambient concentrations of trace elements and hydrophobic organic compound(s). This is not a concern with passive diffusion bags.

Bailers and thief samplers

Bailers can have some necessary and useful applications, even though they are not generally recommended for ground-water sampling. Bailers are the only option available for sampling some ground-water systems, especially at great depth. Use of a bailer is preferred at sites where concentrations of contaminants are extremely large, because bailers are easier to clean (some are disposable and therefore do not require cleaning) and less expensive to replace than pumps. The following recommendations apply in situations where bailers are the only reasonable choice for sampling wells.

- Select bailers with double check valves (fig. 2-3*C*), to ensure that a point sample has been collected and to help prevent sample aeration. The material of choice normally is fluorocarbon polymer (Teflon®) because it can be used when sampling for both organic and inorganic analytes, and can be readily cleaned.
- Consider using disposable fluorocarbon polymer bailers at sites where concentrations of contaminants are large. Discard disposable equipment after one use.
- Use a bottom-emptying device through which the rate of sample flow can be controlled. Place the bailer into a holding stand while emptying sample from the bailer through the bottom-emptying tube.
- Use either fluorocarbon polymer-coated or colorless (white) polypropylene line for lowering the sample; keep the line on a reel. Polypropylene is easy to clean and inexpensive, and can be discarded after one use.

Specialized sealed downhole samplers, grouped loosely under the thief-sampler category (fig. 2-3), are designed to capture and preserve in situ ground-water conditions by precluding sample aeration and pressure changes from sample degassing (escape of VOCs) or outgassing (escape of inorganic gases). Such sampling equipment includes syringe samplers (Gillham, 1982), true thief samplers (Ficken, 1988), samplers using hermetic isolation methods (Gibs and others, 1993; Torstensson and Petsonk, 1988), chlorofluorocarbon (CFC) samplers (Busenberg and Plummer, 1992), and a combined well-bore flow and depth-dependent water sampler (Izbicki and others, 1999).

Passive diffusion bag samplers

Water-filled passive diffusion bag (PDB) samplers are suitable for obtaining samples to be analyzed for selected volatile organic compounds (VOCs).[11] A typical PDB sampler consists of a low-density polyethylene (LDPE) lay-flat tube closed at both ends and containing deionized water. The sampler is positioned at the target horizon of the well by attachment to a weighted line or fixed pipe. Sampler construction and application are described in Vroblesky (2001).

2.1.2.C SUPPORT EQUIPMENT

The support equipment used during ground-water sampling depends on the type and size of the pump or sampler used, field conditions, and depth to water or to sampling interval in the well. A reel should be used for efficient and clean deployment of the sample line. Commonly used support equipment is listed in section 2.4. A detailed description of the various types of support equipment is beyond the scope of this manual.

[11]PDBs are not suitable when collecting samples to be analyzed for inorganic ions, methyl-*tert*-butyl, acetone, or phthalates, and have limited applicability for other non-VOCs.

SAMPLE PROCESSING 2.2

By S.L. Lane, Sara Flanagan, M.W. Sandstrom, K.K. Fitzgerald, F.D. Wilde, and D.B. Radtke

Water samples must be processed as quickly as possible after collection. The equipment most commonly used for sample processing includes sample splitters, disposable capsule filters, filtration assemblies, solid-phase extraction systems, and chambers in which samples are processed and treated with chemical preservatives. Having several sets of cleaned processing equipment on hand is recommended. The equipment and supplies commonly used to process surface-water and ground-water samples are listed in section 2.4.

SAMPLE SPLITTERS 2.2.1

The collection of surface water generally results in a single composite sample. A ground-water sample generally is not collected as a composite; instead, the sample is pumped directly into separate bottles for designated analyses. There are exceptions. For example, ground water withdrawn using a bailer or thief sampler can be collected as a composite sample, provided that sample integrity for the analytes of interest can be maintained.

A composite sample often is subdivided (split) into subsamples for analysis. Each whole-water subsample should contain suspended and dissolved concentrations of target analytes that are virtually equal to those in every other subsample. Use of polypropylene/polyethylene (plastic) churn splitters, the fluorocarbon polymer churn splitter, and the cone splitter are discussed in sections 2.2.1.A and 2.2.1.B, respectively. Testing and comparative data between the splitters are described in Capel and Larson (1996), Horowitz and others (2001), and in Office of Water Quality Technical Memorandum 97.06. Advantages and limitations among the fluoropolymer churn splitter, plastic churn splitter, and cone splitter are shown in table 2-6.

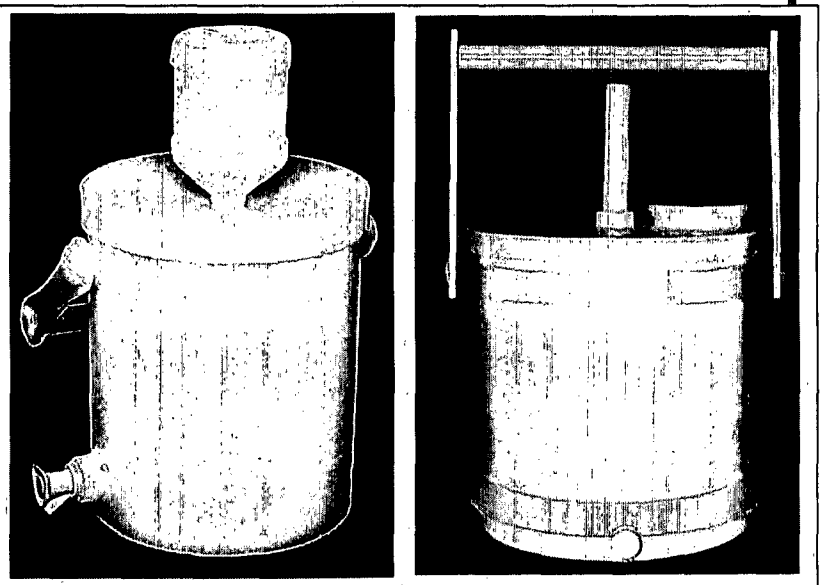
Table 2-6. Advantages and limitations of sample splitters

[L, liter; mg/L, µm, micrometer; milligrams per liter; mL, milliliters; >, greater than; ≤, less than or equal to]

Splitter	Advantages	Limitations
Fluoropolymer churn splitter	Can be used to process samples for both inorganic and non-volatile organic analyses. Simple to operate. Easy to clean. No modification of the splitter design is necessary.	Although it can be used to split samples with particle sizes ≤ 250 µm and suspended-sediment concentrations ≤ 1,000 mg/L, splitting accuracy becomes unacceptable for particle sizes >250 µm and suspended-sediment concentrations >1,000 mg/L. Sample volumes less than 4 L or greater than 13 L cannot be split for whole-water subsamples from this 14-L churn. Samples for bacteria determinations are not to be taken from a churn splitter because the splitter cannot be autoclaved.
Plastic (non-fluorocarbon polymer) churn splitter	Simple to operate. Easy to clean.	Plastic (nonfluorocarbon polymer) churn splitters must not be used to composite samples for determination of organic compounds. Although it can be used to split samples with particle sizes ≤ 250 µm and suspended-sediment concentrations ≤ 1,000 mg/L, splitting accuracy becomes unacceptable for particle sizes >250 µm and suspended-sediment concentrations >1,000 mg/L. When using the 14-L churn, sample volumes that total less than 4 L or greater than 13 L cannot be split for whole-water subsamples. Requires a modified spigot and construction of a funnel assembly. Samples for bacteria determinations are not to be taken from a churn splitter because the splitter cannot be autoclaved.
Fluorocarbon-polymer cone splitter	Used to process samples with suspended-sediment concentrations from 0 to 10,000 mg/L. Samples containing sediment particles ranging in size from very fine clay and silt (1 to 10 µm) to sand-size particles (250 µm) can be split. Samples as small as 250 mL can be split into 10 equal subsamples. Samples greater than 13 L can be processed. Can be used to process samples for both inorganic and nonvolatile organic analyses.	Accuracy of the volume equivalents must be verified before using a new or modified cone splitter. Splitter is awkward to operate and clean in the field. Sample is vulnerable to contamination from atmospheric sources or from improper operation. Splitting accuracy for sediment particles >250 µm or sediment concentrations >10,000 mg/L must be quantified by the user. Samples for bacteria determinations are not to be processed through the cone splitter because the splitter cannot be adequately sterilized. The cone splitter must be level for proper operation.

CHURN SPLITTER 2.2.1.A

The churn splitter is available in either polypropylene and polyethylene plastic (fig. 2-8*A*) or in fluoropolymer plastic (fig. 2-8*B*). Both churn types come in the 14-L size, but the plastic churn also is available in an 8-L size. Splitter advantages and limitations are described in table 2-6. The 8- or 14-L plastic churn splitter is recommended to composite and split surface-water samples for inorganic analyses. The 14-L fluoropolymer churn splitter is recommended to composite and split samples for either inorganic or nonvolatile organic analyses.



A. *B.*

Figure 2-8. Churn sample splitters: (*A*) Plastic churn splitter (from Capel and Larson, 1996) and (*B*) Fluoropolymer churn splitter (from Federal Interagency Sedimentation Project Catalog: accessed December 9, 2002, at http://fisp.wes.army.mil/Catalog%20Page%20US%20SS-1.htm).

- **Trace-element samples:** Do not collect or extract samples for trace-element analyses from a metal container. Use either the plastic or fluoropolymer churn splitter.
- **Organic carbon samples:** Use only the fluoropolymer churn to collect or extract samples for organic-compound analysis. Stainless steel and glass containers also can be used to composite samples for dissolved organic compound analysis. Do not use a plastic churn or container.
- **Churn covering:** To keep the entire churn-splitter assembly clean during sampling and prevent potential contamination, the churn splitter is placed inside two pliable, clear plastic bags (double bagged). These bags should be large enough to completely enclose the churn splitter, including funnel and churn handle, with enough excess material so that the bag openings can be gathered, folded over, and kept closed.
- **Churn carrier:** The carrier is a white plastic container, with lid, large enough to hold the double-bagged churn splitter assembly.
  - The lid of the carrier serves both as a seal for the carrier and as a windbreak when the collected subsample is poured into the churn funnel.
  - The purpose of the carrier is to minimize contamination during transport. In exposed areas, such as bridges and roadways, the carrier can protect against atmospheric sources of contamination, particularly material from motor vehicles.
- **Volume of sample needed:**
  - Subsamples totaling 10 L can be withdrawn from the 14-L churn for whole-water analysis, whereas subsamples totaling 5 L can be withdrawn from the 8-L churn for whole-water analysis.

- Do not use the 4 L remaining in the 14-L churn and the 3 L remaining in the 8-L churn for total, total recoverable, or suspended-material subsamples. However, the sample mixture remaining in either churn can be used for filtered subsamples for the determination of dissolved constituents.

The spigot and lid of the plastic churn splitter must be modified, as described below:

- The original spigot contains a metal spring that introduces a potential source of metal contamination and should be replaced (Horowitz and others, 1994). Purchase the modified spigot from OWQRL, or replace the metal spring with a piece of tubing as follows:

  (1) Cut a 7/8-in. length of 6424-03 Masterflex® tubing. This length is very important to ensure proper operating of the modified spigot. Cut the tubing with a utility knife or something that will cut a straight edge; if edge is jagged, water may leak past the button and possibly contaminate samples.

  (2) Pop button off spigot with a small-blade screwdriver (or push the button in and pull the shaft away from the back).

  (3) Slide the tubing over the sleeve on the inside of the button.

  (4) Slide the tubing that is now attached to the button over the stopper shaft, and compress until the button locks into place.

- Funnel assembly for plastic churn lid: To meet requirements for trace-element sampling, a funnel assembly is inserted into a 1-in.-(2.54 cm-)diameter hole drilled through the lid of the churn splitter (fig. 2-8).

  - The funnel is used when pouring whole-water samples into the churn splitter so that the churn lid can be left on, thus minimizing exposure of the composite sample to atmospheric contamination.

  - To make the funnel assembly, cut the top section (at the shoulder line) from a 1-L polypropylene sample bottle and insert it into the hole drilled in the churn lid. Cut the bottom two-thirds from a 1-L Nalgene® or other larger diameter sampler bottle and use as a funnel cap.

2.2.1.B CONE SPLITTER

The cone splitter is a pour-through device constructed entirely of fluorocarbon polymers (fig. 2-9), and thus can be used to process samples for inorganic and nonvolatile-organic analytes. **The cone splitter may be used to process samples with particle sizes ≤250 micrometers (μm) and suspended-sediment concentrations ≤10,000 milligrams per liter (mg/L) (table 2-6).** The primary function of the cone splitter is to divide the sample simultaneously into as many as 10 equal-volume samples. Some cone splitters have a 2-mm mesh screen in the reservoir funnel to retain large debris, such as leaves and twigs, that could clog or interfere with the splitting process. Below the funnel is a short standpipe that directs sample water in a steady stream, into a splitting chamber that contains a notched, cone-shaped splitting head with 10 equally spaced exit ports around its base. There should be no ridges, benches, or surfaces inside the splitting chamber that could retain material or interfere with the splitting process. The cone splitter is supported either by tripod legs or with an adjustable clamp and stand.

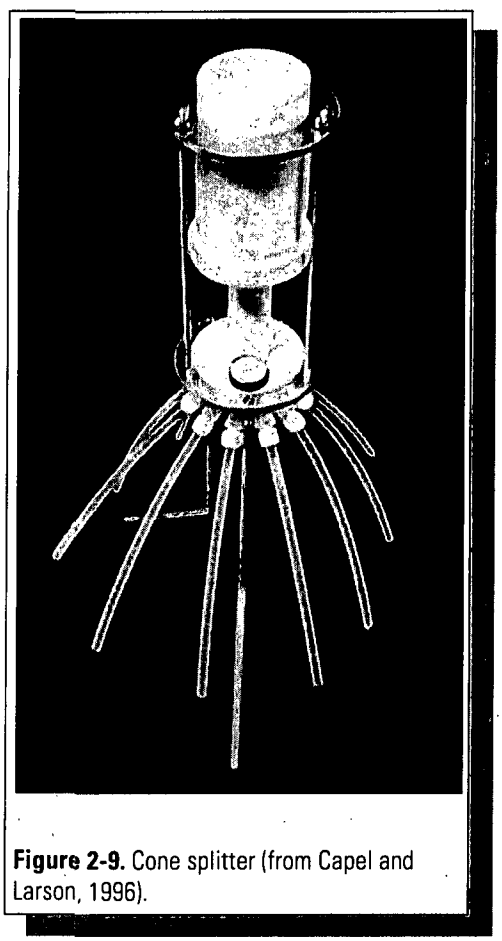


Figure 2-9. Cone splitter (from Capel and Larson, 1996).

The cone splitter is built to very close tolerances in order to achieve accurate and reliable operation. Bias to data can result from splitter imperfections or improper operation; therefore, calibration and proper use is necessary when processing samples.

Before using a new or modified cone splitter, test the splitter to be used as follows (Office of Water Quality Technical Memorandum 80.17):

1. Inspect the cone splitter housing and outlet ports. They should be smooth and symmetrical without any visible burrs or chips. **The cone splitter must be clean.**
2. Place the cone splitter on a stable platform or bench. **The splitter must be level for proper operation.** Use a bull's-eye level to check leveling and recheck during use; the level will change as personnel move inside the field vehicle.
3. Connect 10 discharge tubes to the outlet ports. The tubes must be the same length, and as short as possible. Label the outlets from 1 to 10.
   - All tubes must be pushed in as far as possible to the machined surface in the Swagelok® fitting in the cone-splitter ports. The ends should be flush with the bottom of the inside of the port.
   - Tubes need only extend into the receiving containers sufficiently to prevent spillage.
   - Tubes must not extend in so far that the ends become submerged.
4. Wet the cone splitter by pouring several liters of deionized water through it.
   - Lightly tap the system to dislodge adhering water drops, then discard the water.
   - Place an empty sample bottle under each outlet tube.
5. Accurately measure 3 L of deionized water into a 1-gallon narrow-mouth plastic bottle.
6. Rapidly invert the 1-gallon bottle over the reservoir, letting deionized water flow out as fast as possible. For proper operation, the standpipe must be discharging at its full flowing capacity.
7. After all deionized water has passed through the splitter, tap the assembly several times to dislodge adhering water drops.

Check for spills and leaks. If any are observed, stop the test, correct the problem, and repeat steps 1-7.

8. Measure the volumes of the 10 subsamples carefully, within an accuracy of ±1.0 mL. Record the volumes for each outlet on a form similar to table 2-7.
9. Repeat the test a minimum of three times. Use the same initial volume for each test.

Calculate and document the results of the cone-splitter accuracy test as follows:

1. Referring to the example in table 2-7, calculate the mean volume of each subsample ($\bar{x}$) and standard deviation (S_x):

$$\bar{x} = \frac{\Sigma x_i}{n} \text{ and}$$

$$S_x = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}},$$

where

x_i is the measured volume for each subsample and

n is the number of subsamples (outlet ports).

2. Calculate the standard deviation in percent (E_x):

$$E_x = \frac{S_x}{x} \times 100.$$

3. Calculate the error for each subsample (E_i):

$$E_i = \frac{x_i - x}{x} \times 100.$$

4. Compute the mean standard error ($\overline{E_{\bar{x}}}$) for the three tests and document the maximum and minimum errors (E_i) for all tests in field notes.
5. If data-quality requirements warrant, note the error patterns for individual outlets to determine which outlets produce consistent bias and label them with their mean percent bias error. Depending on the objectives of the sampling effort, this pattern of error may not be of concern.

A cone splitter is considered acceptable for sample processing if the mean standard error ($\overline{E_{\bar{x}}}$) for the three tests is 3 percent or less, and no individual error (E_i) exceeds ±5 percent.

Table 2-7. Example of six cone-splitter accuracy tests using deionized water

[Modified from Office of Water Quality Technical Memorandum 80.17]

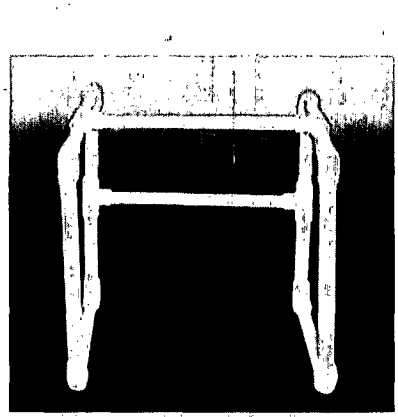
Test number	1		2		3		4		5		6		Averages	
Initial sample weight (grams)	2,499.4		2,499.5		2,499.5		2,499.5		2,499.5		2,499.4			
Outlet number	Outlet volume (x_i)	Percent (E_i)	Outlet volume (x_i)	Percent (E_i)	Outlet volume (x_i)	Percent (E_i)	Outlet volume (x_i)	Percent (E_i)	Outlet volume (x_i)	Percent (E_i)	Outlet volume (x_i)	Percent (E_i)	Mean volume (x_i)	Percent (E_i)
1	248.4	-0.5	249.5	-0.1	247.4	-0.9	248.1	-0.7	247.8	-0.8	249.2	-0.2	248.4	-0.5
2	246.8	-1.2	246.8	-1.2	245.6	-1.6	248.4	-.6	246.3	-1.4	246.7	-1.2	246.8	-1.2
3	249.4	-.1	251.0	.5	250.6	.4	251.1	.5	249.8	0	248.7	-.4	250.1	.1
4	250.7	.4	252.6	1.1	252.5	1.1	251.3	.6	251.8	.8	250.5	.3	251.6	.7
5	248.1	-.6	248.3	-.6	249.8	0	249.3	-.2	250.2	.2	248.1	-.6	249.0	-.3
6	252.2	1.0	250.3	.2	252.7	1.2	252.0	.9	252.7	1.2	250.6	.4	251.8	.8
7	245.7	-1.6	246.2	-1.4	246.0	-1.5	246.3	-1.4	246.6	-1.3	245.9	-1.5	246.1	-1.5
8	252.7	1.2	254.2	1.8	252.9	1.3	253.3	1.4	253.1	1.3	254.6	2.0	253.5	1.5
9	248.7	-.4	247.3	-1.0	247.5	-.9	247.1	-1.1	248.2	-.6	249.5	-.1	248.0	-.7
10	253.9	1.7	252.1	.9	251.8	.8	250.6	.3	251.7	.8	253.0	1.3	252.0	1.0
Final sample weight	2,496.6		2,498.3		2,496.8		2,497.5		2,498.2		2,496.8		2,497.4	
Sample loss	2.8		1.2		2.7		2.0		1.3		2.6			
Mean weight ($\bar{x}$)	249.7		249.8		249.7		249.8		249.8		249.7		249.8	
Standard deviation (S_x)	2.7		2.7		2.8		2.3		2.5		2.7			
Error percent (E_x)	1.1		1.1		1.1		.9		1.0		1.1			

2.2.2 PROCESSING AND PRESERVATION CHAMBERS

Working within sample-processing and -preservation chambers reduces the possibility of random atmospheric contamination during sample bottling, filtering, and preserving with chemical reagents. **Use of these chambers is required for samples for trace-element analyses** (Horowitz and others, 1994), and is recommended for most other analytes, such as major and minor inorganic ions and organic compounds. The processing chamber serves as a collection chamber into which sample water is pumped and either filtered or directly collected in sample bottles. There is no standard design for either fixed or portable chambers; however, to prevent contamination of inorganic samples with metals, the materials used in their construction should be either nonmetallic or completely covered by or embedded in nonmetallic material. Although bench testing of plastic chamber components, including the clear plastic cover, revealed no emission of volatile organic substances, this can be further substantiated by analyzing an ambient blank for VOC analysis that is collected within the chamber(s).

Fixed sampling chambers typically are enclosures that are permanently installed in a field vehicle for the sole purpose of sample collection/processing and preservation and must not be used as a storage area. Fixed and portable chambers need to be cleaned between uses. The portable chamber illustrated is inexpensive and easily constructed with ≤1/2-in.-diameter white polyvinyl chloride (PVC) pipe or tubes, which are used to support a transparent plastic-bag covering (fig. 2-10; Appendix). The transparent bag forms a protective tent within which to work while collecting, processing, or preserving samples. Another option is to purchase or construct a fixed or portable glove box. The glove box should have no metal parts to which a sample for metals analysis might be exposed. Use glove boxes that can be filled with an inert gas such as nitrogen or argon when samples need to be strictly isolated from contact with atmospheric gases.

- The processing chamber either sits over a fixed or portable sink or contains a basin to which a waste-disposal funnel or hose has been attached, allowing excess water to drain readily to waste. The sample tubing is inserted through a hole in the top of the chamber, and can be connected to a filtration device inside the chamber.
- The preservation chamber also consists of the frame and bag cover, but without provision for sample tubing. The bottled sample is passed from the processing chamber into the preservation chamber, in which chemical treatment is added to the sample. A suitable container placed inside the preservation chamber is needed in which spent preservative ampoules are contained (see NFM 5).



A.



B.

Figure 2-10. Example of (*A*) a polyvinyl chloride frame of a processing or preservation chamber, and (*B*) a sample being processed within the chamber. (*A*, Photograph by B.A. Bernard; *B*, photograph by Jacob Gibs.)

Use of separate chambers for sample collection/processing and sample preservation generally is the most efficient approach. Space permitting, multiple preservation chambers can be used, each dedicated to a specific chemical treatment. Otherwise, use of a single preservation chamber dictates a change in the bag covering for each change in chemical treatment.

If there is insufficient space in which to set up both the processing and preservation chambers, the processing-chamber frame can also function as a preservation-chamber frame provided that the cover is changed before sample preservation, is clipped to the outside of the chamber frame rather than supported over the frame, and is changed every time the preservation procedure requires a change in gloves (NFM 5).

2.2.3 FILTRATION SYSTEMS

Filtration separates particulate substances (solid-phase and biological materials) from the solute or aqueous phase of a water sample. Water samples are filtered for analysis of inorganic constituents, organic compounds, and biological materials to help determine the environmental fate and quantify the transport of these target analytes. Additional information relevant to selection of filtration systems can be found in Kennedy and others (1976), Ward and Harr (1990), Horowitz and others (1994), Koterba and others (1995), and in NFM 5.

For surface-water applications, the most common filtration system consists of a reversible, variable-speed battery-operated peristaltic pump or a metering pump that forces the whole-water sample through tubing into a filtration assembly. For ground water, the sample ordinarily is pumped through a sample line directly into a disposable capsule filter or other filtration assembly. If the sample is collected by bailer, the sample is bottom-emptied through fluorocarbon-polymer tubing and either is composited in a churn or other vessel first or is transferred directly to the filtration assembly by means of a peristaltic pump. Some bailers can be directly connected to a filtration device and hand-pump system.

TECHNICAL NOTE: Separation of solid from aqueous phases can be achieved by methods other than filtration, and data requirements may dictate the need for an alternative method such as centrifugation, ultracentrifugation, dialysis or lipid-membrane separation, or reverse-flow osmosis and tangential-flow filtration.

The filtration assembly and filter material to be used depends on the class of target analyte(s) (table 2-8), as discussed below.

- Inorganic Samples—The filter membrane (filter) for filtering samples for analysis of inorganic constituents typically comprises material such as polyethersulfone, cellulose nitrate, or polycarbonate polymer. Polyethersulfone is the membrane material used in the disposable capsule filter that currently is in routine use by the USGS water-quality program.
- Organic Samples—Samples for organic-compound analysis are filtered through discs composed of glass fiber (microfiber) material. Organonitrogen-herbicide samples also can be filtered through disposable nylon membranes (Sandstrom, 1995). The membrane material described above for inorganic samples should not be used for organic samples.
- Organic-Carbon Samples—Samples to be analyzed for dissolved organic carbon either can be filtered through glass-microfiber filter (GF/F) discs or through the disposable capsule (polyethersulfone) filter; the choice of filter depends on study objectives and protocols. Any sample to be analyzed for total particulate carbon (TPC) must be filtered through a GF/F disc.

A filtered sample is defined operationally by the nominal pore size of the filter (membrane or disc).

- The filter pore size selected depends on study objectives, data requirements, and industry standards.

- The standard pore sizes of filters used by the USGS are:
  - 0.7μm for pesticides, most other organic compounds, and some bacteria (NFM 7).
  - 0.45 μm for inorganic constituents (including major ions, radiochemicals, and trace elements), some bacteria (NFM 7), and dissolved organic carbon.
  - 0.2 μm or less for trace-element samples to be analyzed for some geochemical applications and interpretive studies and for nutrient samples for which exclusion of bacteria at the 0.2-μm threshold is desirable.
- See NFM 7 for a description of filters for biological analysis.

INORGANIC CONSTITUENTS 2.2.3.A

The standard device for filtering samples for analysis of inorganic constituents is the disposable capsule filter, which has replaced routine use of the plate-filter assembly for most applications (table 2-8). **Construction materials of filtering systems must not be a source of sample contamination with respect to the substances for which the sample will be analyzed.**

Disposable capsule filter

The protocol for filtering a sample for analysis of inorganic constituents requires using a disposable capsule filter[12] such as the Pall-Gelman AquaPrep 600 ground-water sampling capsule with pleated polyethersulfone (Supor®) filter membrane material (hereafter referred to as "capsule filter") (fig. 2-11).

g

[12]The disposable capsule filter with polyethersulfone membrane also may be used for processing samples for analysis of dissolved organic carbon (section 2.2.3.B, NFM 5.2.2.C).

Horowitz and others (1994) concluded that the disposable capsule filter would not be a probable source of sample contamination for inorganic constituents, including trace elements, major ions, nutrients, stable isotopes, and radiochemicals (**table 2-8**) if prerinsed with a minimum of 1,000 mL (1 L) of inorganic-grade blank water.

- Capsule filters are sealed units; hence, the likelihood of contamination is reduced because the filter membrane is not handled.
- The surface area of the capsule-filter membrane is roughly three times that of the 142-mm plate filter and is less subject to clogging.
- Cleaning the filtration device is not necessary because each capsule filter is discarded after one use.
- OWQRL checks the quality of each lot of capsule filters and provides a certificate of analysis with each filter.

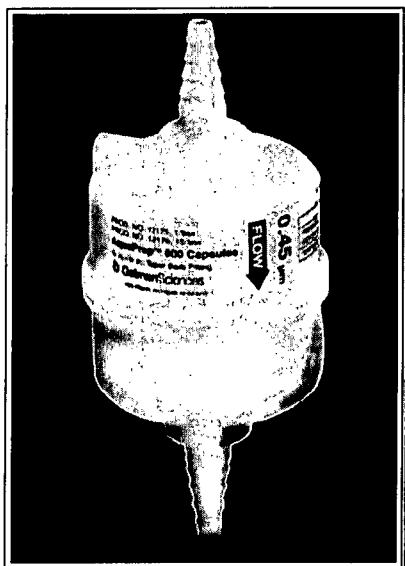


Figure 2-11. Disposable capsule filter with 0.45-µm polyether- sulfone pleated filter membrane (published with permission of Gelman Sciences).

Do not reuse filters—discard the disposable polyethersulfone capsule filter after each sample.

Table 2-8. Capsule filter requirements and recommendations for processing of surface-water and ground-water samples

[Table modified from Horowitz and others (1994) and includes only those constituents evaluated in the experiments described in the reference and in Office of Water Quality Technical Memorandum 2000.08]

Disposable capsule filter *required*[1]		Disposable capsule filter *recommended*[2]
Aluminum	Lead	Anions (chloride, sulfate)
Antimony	Lithium	Calcium
Barium	Manganese	Magnesium
Beryllium	Molybdenum	Nutrients (nitrogen, phosphorus)
Boron	Nickel	Radiochemicals (excluding radon gas)
Cadmium	Silver	Silica
Chromium	Thallium	Sodium
Cobalt	Uranium	Strontium
Copper	Zinc	Dissolved organic carbon
Iron		

[1]The requirements for surface-water sampling described in Horowitz and others (1994) are generally applicable to ground-water studies.
[2]*The plate-filter method is acceptable, contingent on use of equipment-cleaning protocols (NFM 3) and project* data objectives.

Plate-filter assemblies

Before 1994, the most common filtration assembly used for USGS studies for filtering inorganic samples was the nonmetallic backflushing plate-filter assembly designed to hold a 142-mm filter. Because this method allows greater exposure of the sample to the air and because the assembly is time-consuming to field clean, this equipment generally is not recommended for routine filtering of inorganic samples (table 2-8).

- Types of plate-filter assemblies available for inorganic samples include:
  - Fluorocarbon polymer filtration assembly designed for 47-mm-diameter filters; can be used for in-line filtering of inorganic or organic samples by using an appropriate filter membrane.
  - Plastic vacuum filtration assembly for a 47-mm-diameter filter; used with either a hand vacuum pump or a peristaltic pump.
  - Plastic backflushing assembly, available for 142-mm- and 293-mm-diameter filters (no longer in common use for USGS studies) (fig. 2-12).

- A smooth-tipped plastic forceps is needed to transfer the filter to the plate of the filter assembly. Kennedy and others (1976) give detailed instructions for use of the plate-filter assembly.

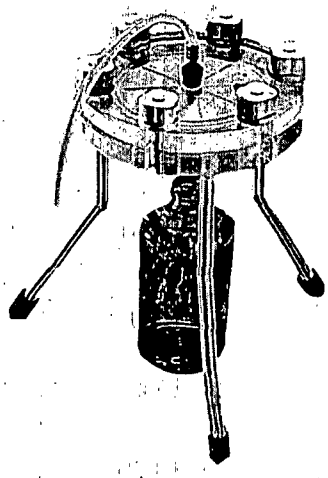


Figure 2-12. Nonmetallic backflushing plate-filter assembly for 142-millimeter-diameter filter membrane. (Illustration reproduced with permission of Gelman Sciences.)

2.2.3.B ORGANIC COMPOUNDS

Filtering whole-water samples isolates suspended solid-phase substances from the aqueous phase, thus allowing separate determinations of organic compounds in each phase. Filtering also helps to preserve samples for organic determinations by removing microorganisms that could degrade compounds in the sample (Ogawa and others, 1981).

- Hydrophobic compounds are analytes that preferentially partition to particulate matter. Filtering concentrates particulate matter on the disc (filter), enhancing extraction efficiency and lowering analytical detection limits. This is especially useful for whole-water samples with small concentrations of suspended material and for which large volumes of sample (4 to 40 L) must be filtered to provide an analyzable mass of suspended materials.
- Hydrophilic compounds are analytes that are water soluble. Filtering is used to remove suspended material or other particulate matter from the water sample, to identify concentrations of dissolved analytes, and to remove any solid-phase substances containing constituents that could interfere with the analysis and that could be co-extracted with target analytes.

Equipment needed to filter samples for determination of trace organic compounds, such as pesticides, is described in detail in Sandstrom (1995) and includes a positive displacement pump, an aluminum plate-filter assembly (or other appropriate or designated filtration assembly), the filter, and metal forceps. All equipment and components used for filtering whole-water samples for trace organic determinations should be made of materials (a) that will not contaminate the sample or sorb analytes, and (b) that can withstand organic cleaning solvents without being damaged. Such materials include stainless steel or aluminum, fluorocarbon polymer, glass, and nonporous ceramics (hard-fused microcrystalline alumina). Use of plastics, rubber, oils, and other lubricants is to be avoided because it can result in sample contamination, analytical interference, and (or) sorptive losses.

Metering pump

The valveless piston metering pump consists of a pump head with a reciprocating piston driven by a 12-volt direct current (DC), variable-speed motor (fig. 2-13). It has a delivery rate of up to 500 mL per minute.

The pump head and all wetted parts are constructed of ceramic, fluorocarbon polymer, or stainless steel components, which are resistant to organic solvents. These pumps can tolerate some suspended materials in the sample being pumped, but large concentrations of suspended materials can cause excessive wear of pump parts and strain on the pump motor.

The ceramic piston and shaft of these pumps will break if motor amperage exceeds 4 amps. To avoid this, either a 4-amp DC circuit breaker connected in-line with the pump power line, or an alternating to direct current converter with 4-amp maximum output, should be used.

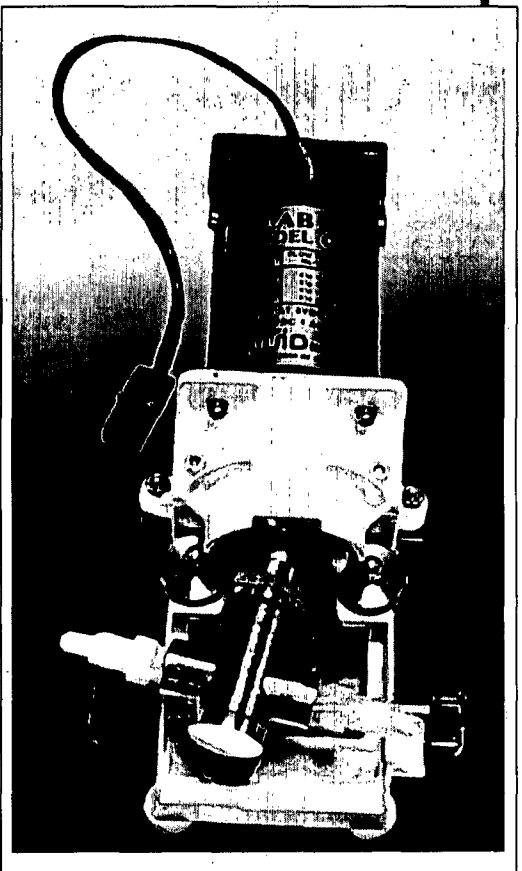
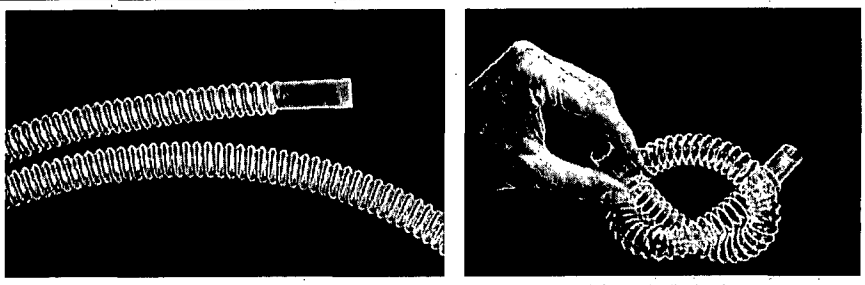


Figure 2-13. Valveless piston metering pump. (Photograph by B.A. Bernard, 1998).

The pump and filtration assembly are connected by 1/4-in.-diameter convoluted fluorinated ethylene polypropylene (FEP) tubing (fig. 2-14) with appropriate fittings. The convoluted tubing does not crimp when bent.



A. Convoluted (spiral) design

B. Corrugated (parallel) design

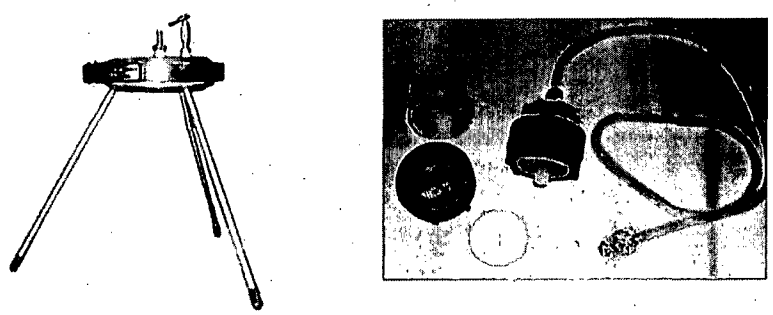
Figure 2-14. Flexible fluorinated ethylene polypropylene (FEP) tubing: (*A*) convoluted design and (*B*) corrugated design. (Published with permission of Cole-Parmer Instrument Company: *A*, Copyright 1992. *B*, Copyright 1987. Cole-Parmer does not warrant these illustrations to be current, accurate, or suitable for any purpose.)

Filtration assemblies

The filtration equipment described below includes various types of plate-filter assemblies. Their use depends on the analysis to be requested or the field method selected. Plate-filter assemblies are available for filters with disc diameters ranging from 13 to 293 mm. The size selected is determined by the sample volume to be filtered and by the concentration of suspended materials in the sample. When collecting samples for analysis of organo-nitrogen herbicides and dissolved organic carbon, filtration options include specific types of disposable capsule filters.

- **Trace organic compounds:** Typical plate-filter assemblies used for pesticides and other selected trace organic analytes include either the three-legged aluminum (or stainless steel) plate-filter assembly (fig. 2-15*A*) or the PFA in-line filter-holder assembly (fig. 2-15*B*). The aluminum plate-filter assembly consists of two machined aluminum or stainless steel plates (designed to contain a 142-mm-diameter filter) held together by locking bolts or a locking ring.
  - The plates have fluorocarbon polymer-coated silicone or Viton® O-rings set in grooves to seal the filtration assembly. A stainless steel screen on the lower plate supports the filter. A valve is built into the upper plate to exhaust trapped air. Connectors are built into the center of the top and bottom plates so that inlet and outlet fluorocarbon polymer tubing can be attached.

— Teflon® in-line filter-holder assembly: PFA filtration assembly with Tefzel® ETFE clamp nut holds a 47-mm-diameter GF/F (0.7-µm nominal pore size). (Similar assemblies are available currently from commercial manufacturers, such as Savillex, Cole-Parmer, and Berghof.)



A. Aluminum plate-filter assembly ***B.*** PFA filter holder

Figure 2-15. (*A*) Aluminum plate-filter assembly for 142-millimeter-diameter filter disc and (*B*) PFA filter holder for 47-millimeter-diameter filter. (Cole-Parmer EW-06621-40 PFS filter holder shown. *Photograph published with permission of GeoTech* Environmental Equipment, Inc.)

- **Organonitrogen herbicides:** Samples for analysis of organonitrogen herbicides may be filtered using an in-line 25-mm disposable nylon filter unit (nylon filter), as explained in the indented items that follow. (Alternatively, either a plate-filter assembly or PFA in-line filter-holder assembly can be used, as described above under "Trace organic compounds"). Although filtration devices made of plastic components should not be used to process water-sediment samples for determination of organic compounds, the nylon filter has been approved and is an efficient option for a specific solid-phase extraction (SPE) method for samples for organonitrogen-herbicide analysis (Sandstrom and others, 1994).

  — The in-line disposable nylon filter consists of a 25-mm-diameter nylon membrane, nominal 0.45-µm pore diameter, enclosed in a nylon housing with Luer-Lok inlet and outlet fittings. **The nylon filter must be discarded after one use.**

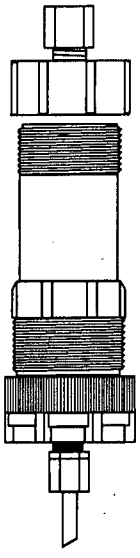
  — For detailed information regarding tubing connectors and other equipment needed for the nylon filter, and on how to connect the nylon filter to the sampling system, refer to NFM 5 and Sandstrom and others (1994).

  — The 25-mm filter unit is appropriate for the SPE method because the required volume of filtered sample is only about 100 mL.

- **Dissolved and particulate carbon:** Dissolved organic carbon (DOC) samples are processed through either a Savillex florinated ethylenepropylene (FEP) pressure-filtration assembly, or a disposable Supor® capsule filter, depending on other carbon analyses required (NFM 5.2.2.C). Total particulate carbon (TPC) samples are processed through a Savillex pressure filtration assembly (fig. 2-16), loaded with a baked 25-mm, 0.7-micron pore size, glass-microfiber filter (GF/F) on a 25-mm stainless steel or polysulfone filter-support screen.

- Either a hand-pressure pump or a peristaltic pump fitted with clean tubing can be used to move the TPC and particulate inorganic carbon (PIC) sample through the Savillex filtration assembly. Pressure can also be exerted using organic-free nitrogen gas in a pressure tank with a regulator.
- A persitaltic pump or submersible ground-water pump can be used to move the DOC sample through the capsule filter.

A detailed description of the methods and equipment needs for carbon-analysis sampling can be found in NFM 5.2.2.C, "Procedures for processing samples for carbon analysis." See also the equipment lists provided below in section 2.4.



Fluorocarbon polymer filter assembly

Figure 2-16. Fluorinated ethylene-propylene pressure-filtration (FEP) assembly for processing samples for analysis of total particulate carbon and dissolved organic carbon. (Published with permission from the Savillex Corporation.)

Filter material

Tortuous-path depth filters made of borosilicate glass fibers are used to filter most samples for organic determination because the material is basically inert, can withstand organic solvents, and can withstand laboratory preparation (being baked at 450°C). **Membrane filters (cellulose, polycarbonate, or polyethersulfone polymers) commonly used to process samples for determination of nutrients and other inorganic constituents are not suitable for filtering samples for most organic determinations,** mainly because they are not resistant to organic solvents used to preclean the sampling and processing equipment. DOC samples, however, may be processed through the polyethersulfone capsule filter (disposable Supor® filter) (NFM 5) if study objectives permit.

- Use glass microfiber filters (GF/F) with 0.7-µm nominal pore size that has been baked at 450°C for at least 2 hours. (USGS personnel can obtain baked 142-mm- and 25-mm-diameter GF/F from OWQRL.) The 25-mm GF/F is used in the Savillex filtration assembly.
- Use only filters without binders. (Acrylic resin binders might leach from the filter and contaminate samples, or might not be completely combusted when baked at 450°C.) Binder-free glass-fiber filters are available in various diameters ranging from 13 to 293 mm.
- For the filter material used in processing organonitrogen herbicides and dissolved organic carbon see the previous section on "Filtration assemblies." For the DOC sample, use a 25-µm, 0.7-mm GF/F if the Savillex unit is used.

2.2.4 PUMP TUBING

Pump tubing refers to the sample lines used with peristaltic, metering, and submersible pumps. Field personnel are cautioned to evaluate possible artifacts in a sample associated with pump tubing and tubing connections. For filtering ground-water samples that are pumped directly from the well to a filtration assembly, C-Flex® or fluorocarbon polymer tubing is generally recommended.

- Tubing connectors and connections that contact the sample should be made of inert material, to the extent possible. Stainless steel connections must be the highest grade available (SS 316). If flexible copper, aluminum, or stainless steel tubing is used for chlorofluorocarbon (CFC) sampling, it should be refrigeration grade. Such fittings ordinarily are delivered with coatings of machining lubricants, which must be removed by cleaning before use.
  - Greaseless fittings can be ordered. Fluorocarbon polymer, silicone, C-Flex® pump tubing commonly are used with portable submersible pumps and with peristaltic or metering pumps. Use of a fluorocarbon polymer material generally is recommended because fluorocarbon polymers are relatively inert with respect to many inorganic and organic analytes (table 2-9).

- Silicone tubing is suitable when sampling for inorganic analytes only, and only after appropriate cleaning (see NFM 3).
  - Measurable concentrations of silica (0.09 to 0.24 mg/L) have been detected in blank samples passed through silicone tubing (Horowitz and others, 1994). These concentrations are likely to be significant only if low ionic-strength water is being sampled.
  - Silicone tubing was not designed for use with acids.
  - Silicone tubing is gas permeable and very sorptive of organic compounds.

Table 2-9. Common varieties and characteristics of fluorocarbon polymer tubing

FEP (fluorinated ethylene polypropylene) • Most transparent • Best abrasion resistance • High flexibility • Least expensive of the Teflon® varieties
PFA (perfluoroalkoxy) • Less transparent than FEP • Virtually nonporous (nonpermeable) • Most expensive of the Teflon® varieties
PTFE (polytetrafluoroethylene) • Least transparent; milky to white • Most flexible • Midpriced between FEP and PFA
Kynar® (polyvinylidene fluoride) • Translucent • Not very flexible • Less expensive than the Teflon® varieties
Tefzel® (Ethylene tetrafluoroethylene) • Withstands higher pressure than Teflon® • Most expensive

- C-Flex® tubing is made from a thermoplastic elastomer and is suitable for use when sampling for all inorganic analytes and DOC.
  - C-Flex® is relatively resistant to acid. Acid resistance is a factor because dilute hydrochloric acid is required in some cleaning procedures (see NFM 3).
  - C-Flex® is less permeable to gas than silicone tubing.
- Fluorocarbon polymer tubing is recommended when sampling for most inorganic and organic analytes. Fluorocarbon polymer tubing is available in corrugated and convoluted, as well as in straight-wall configurations (fig. 2-14).
  - Fluorocarbon polymer tubing premolded to the shape of the pump head is available.
  - Convoluted fluorocarbon polymer tubing is flexible and easy to handle. Attach convoluted tubing to each end of the premolded tubing.
  - Fluorocarbon polymer tubing sheathed in another plastic is available at lower cost but is not recommended because the fluorocarbon polymer twists, constricts, and readily cracks.

- Polyvinyl chloride (PVC) tubing (Tygon®) is suitable for inorganic samples only, and must be appropriately cleaned prior to contact with inorganic samples.
  - PVC tubing can be washed with dilute acid.
  - PVC tubing has the lowest gas permeability of any peristaltic pump tubing.
  - When used with a peristaltic pump, PVC tubing has a shorter life than silicone, C-Flex®, or Norprene®.
  - PVC tubing may leach plasticizers.
- Nylon, polyethylene, and polypropylene are all inexpensive, rigid tubing that can withstand high pressure and are suitable for sampling inorganic analytes. Nylon tubing is more resistant to organic compounds than other plastic tubing, but has not been tested as a source of trace-element or organic-compound contamination.

- Norprene® tubing is made from a thermoplastic elastomer (a polypropylene base with USP mineral oil) and is suitable when sampling for inorganic analytes only. It must be appropriately cleaned prior to contact with samples collected for inorganic analysis. (Norprene® tubing has the longest life of any manufacturer-recommended tubing material.)
  - Norprene® tubing can be washed with dilute acid.
  - Norprene® tubing may leach USP mineral oil.
  - For use with a peristaltic pump.
  - The gas permeability of Norprene® tubing is lower than that of silicone tubing and greater than that of PVC tubing.

FIELD VEHICLES 2.3

By S.L. Lane, Sarah Flanagan, and D.B. Radtke

Water samples should be processed within vehicles that are designed, designated, prepared, and dedicated for that purpose. If a multiple-use vehicle must be used for water-quality work, then use of portable processing and preservation chambers is mandatory, and additional quality-control samples must be collected to document that the quality of the data has not been compromised. Contamination of some target analytes is much more likely when multiple-use vehicles are used for collection of water-quality data.

Whether using a field vehicle dedicated for water-quality work or a multi-use vehicle, every effort must be made to keep the work area clean and to eliminate sources of sample contamination.

- Keep metallic objects, such as surface-water and ground-water sampling support equipment, out of the inorganic sample-processing and -preservation area.
- Install a dustproof barrier between the vehicle's cab and the sample-processing and -preservation area.
- Cover metallic surfaces (cabinets or shelving that cannot be replaced) with plastic sheeting. Replace the sheeting periodically.
- Store chemical substances so that chemical fumes will not enter the sample-processing and -preservation area.
- If transporting a nitrogen tank, make sure the tank is fastened securely to the vehicle with a bracket. Gas-supply outfits sell brackets specially designed for gas tanks/cylinders.

For additional discussions of field-vehicle recommendations and requirements, refer to Horowitz and others (1994), Shelton (1994), and Koterba and others (1995).

CAUTION: Store acids, bases, and solvents in separate storage areas so that the chemicals cannot mix if a spill occurs (NFM 9).

LISTS OF EQUIPMENT AND SUPPLIES 2.4

By S.L. Lane, Sarah Flanagan, and D.B. Radtke

Checklists of the equipment and supplies commonly used to collect and process water samples are provided in the tables that follow (tables 2-10 through 2-17) to aid field personnel in selecting equipment needed to prepare for a water-quality field trip. These lists are not exhaustive and should be modified to meet specific study needs. Many of the items listed are explained in greater detail in other NFM chapters, as indicated. Refer to other chapters of this *National Field Manual* series for lists of equipment and supplies for field measurements (NFM 6), biological indicators (NFM 7), and bottom-material samples (NFM 8). Equipment must be cleaned and tested before field work begins (NFM 3).

Do not forget backup equipment.

Table 2-10. Support equipment for surface-water sampling

[A detailed description of the various types of support equipment is beyond the scope of this manual; refer to Corbett and others (1943), Buchanan and Somers (1969), and Rantz and others (1982).]

Cranes		
✓	Type	Sampler maximum recommended weight (pounds)
	Type A	100
	Type E	300[1]
	Bridge board	50
	Other	

Crane Bases		
✓	Type	Sampler maximum recommended weight (pounds)
	Three-wheel	100
	Four-wheel	150

✓	Miscellaneous
	Battery or hydraulic power motor system for B-56 or E-53 reel
	Hanger bars, connectors, and pins for connecting sampler to cable
	Counterweights for four-wheel crane base
	Safety equipment (flotation jacket, cable cutter, bridge safety plan, traffic cones, and warning signs)
	Vertical transit rate pacer (US VTP-99)
	Other

Reels[2]						
✓	Reel	Cable diameter (inches)	Maximum weight (pounds)	Cable capacity (feet)	Brake	Operation type
	A-55	0.084 .10	50 100	95 80	No	Hand
	B-56	.10 .125	150 200	144 115	Yes	Hand or power
	E-53	.10 .125	150 300	206 165	Yes	Power
	Other					

[1]CAUTION: As of this publication date, a 275- to 300-pound sampler has not been tested for use with 275- to 300-pound weights.
[2]Selection of type of reel should be based largely on maximum cable length needed and weight of sampler that must be supported.

Table 2-11. Support equipment for ground-water sampling

✓	Ground-water support equipment
	Handline or manual/power reel with line
	Tripod assembly with manual or power reel
	Wellhead guide for flexible sample line to pump
	Wheeled carts to transport portable sampling equipment
	Energy source for reels and pumps (batteries, compressor, or generator)
	Other

Table 2-12. Sample-collection equipment for (*A*) surface water and (*B*) ground water

[NFM, *National Field Manual for the Collection of Water-Quality Data*]

✓	(*A*) Surface-water-quality sample collection (refer to NFM 4)
	Weighted bottle and handline (plastic or stainless steel) bottle
	US D-95 (plastic dipped) Bottle (1 liter) Nylon or fluorocarbon polymer nozzle[1] (3/16, 1/4, or 5/16 inch) and cap
	US DH-81 (handle and collar) Nylon or fluorocarbon polymer nozzle[1] (3/16, 1/4, or 5/16 inch) and cap Plastic or fluorocarbon polymer bottle (0.5 or 1 liter)
	US DH-95 (plastic dipped) Bottle (1 liter) Nylon or fluorocarbon polymer nozzle[1] (3/16, 1/4, or 5/16 inch) and cap
	US D-96 Bag and US D-96-A1 (plastic dipped) Slotted bottle (plastic) Nylon or fluorocarbon polymer nozzle[1] (3/16, 1/4, or 5/16 inch) and cap PFA (perfluoroalkoxy) bag
	US D-99 Bag (plastic coated) Nylon or fluorocarbon polymer nozzle[1] (3/16, 1/4 or 5/16 inch) PFA bag
	Crane with 3- or 4-wheel base and counterweights
	Reel, hanger bars, and pins
	Current meter for US DH-95, US D-95, US D-96, US D-96-A1, and US D-99
	Bridge board and reel
	Plastic sheeting with weighted corners to cover bridge rail, 2 millimeters thick
	Vertical transit rate pacer
	Biochemical Oxygen Demand sampler
	Volatile Organic Compound sampler
	Thief sampler
	Pumping sampler(s)
	Other

Table 2-12. Sample-collection equipment for (*A*) surface water and (*B*) ground water—*Continued*

✓	(*B*) Ground-water-quality sample collection (refer to NFM 4)
	Positive-displacement submersible pump, discharge line, and reel
	Water-supply-well sample line and garden-hose threaded adaptor
	Thief-type sampler. (Examples: bailer, single or double-check valve, and bottom emptying device)
	Suction-lift pump (peristaltic or centrifugal)
	Antibacksiphon device
	Sample-water manifold to split sample water flow
	Flowthrough chamber for field-measurement electrodes (pH, conductivity, dissolved oxygen, water temperature, oxidation/reduction)
	Tubing, appropriate for type of pump and target analytes
	Tubing connectors, compatible with tubing and target analytes
	Water-level measuring tape, steel or electric, and bleach solution[2]
	Water-level indicator (blue chalk for steel tape)
	Weight, to attach to water-level measuring tape or sample line. **Do not use lead.** Use stainless steel or other relatively noncontaminating material.
	Power source for pump or reel; batteries for electronic sounder
	Graduated bucket (to measure rate of discharge) and stopwatch
	Containers for disposal of purge water
	Flow controller for sampling pump
	Plastic sheeting, 2 millimeters or thicker
	Other

[1] Use only nozzles purchased from the Federal Interagency Sedimentation Project.
[2] If measuring water level from a drinking-water well, decontaminate equipment by dipping the wetted section into a 10-percent bleach/water solution, followed by rinsing with deionized water. Dry the steel tape to prevent rusting.

Table 2-13. *Sample-processing equipment and supplies*

[NFM, *National Field Manual for the Collection of Water-Quality Data;* L, liter; mm, millimeter; µm, micrometer; in., inch; g, gram; mL, milliliter]

✓	Sample splitters (refer to NFM 5)
	Plastic churn splitter, 8 L or 14 L, modified spigot and funnel (NFM 2.2.1.A) (inorganic analytes) Fluoropolymer churn splitter, 14 L (organic and (or) inorganic analytes) Modified spigot or Master Flex 6424-03 tubing to modify metal-spring spigots
	Churn carrier
	Cone splitter • Splitting chamber for cone splitter • Bull's-eye bubble level and shims for cone splitter
	Large clear plastic bags: protective • Covering for transporting clean churn splitter or cone splitter
	Subsample bottle kits for whole-water samples
	Other: Gloves (powderless, disposable nitrile)
✓	**Filtration systems for inorganics (refer to NFM 5)**
	Peristaltic pump and batteries
	Pump tubing for ground-water and peristaltic pump (C-Flex™, silicone, fluorocarbon polymer)
	Filtration assembly (disposable capsule, plate-type, other)
	Filter membranes and discs (various diameters, pore sizes, and materials)
	Forceps (plastic or ceramic)
	Subsample bottle kits for filtered inorganic samples
	Deionized water: Inorganic grade blank water (IBW) or Universal blank water (UBW)
	Other: Gloves (powderless, disposable nitrile)
✓	**Filtration systems for organics (refer to NFM 5)**
	Plate-filter assembly, aluminum or stainless steel, for 13-, 142-, or 293-mm-diameter filter disc or PFA filter holder for 47-mm-diameter filter disc
	Filter disc, borosilicate glass fiber (GF/F), 0.7-µm pore size, baked 142-mm, or 13-, 47-, or 293-mm-diameter filter disc, as required
	Pump, ceramic piston valveless metering, with fluorocarbon polymer convoluted tubing or ground-water pump tubing, and batteries
	Filtration assembly, 25-mm-diameter, in-line, with disposable nylon filter
	Subsample bottle kits
	Volatile/pesticide-grade blank water (VPBW)
	Pesticide-grade blank water (PBW)
	Forceps (metal or ceramic)
	Other: Gloves (powderless, disposable nitrile)
✓	**Miscellaneous processing equipment and supplies**
	Sample processing chamber; supply of transparent plastic covers (bags) for portable chamber and disposable nonpowdered gloves to handle equipment.
	Other: Gloves (powderless, disposable nitrile)

Table 2-13. Sample-processing equipment and supplies—*Continued*

✓	
	Filtration system for carbon analysis (refer to NFM 5)
	Fluorocarbon-polymer filtration assembly and baked glass-microfiber filter discs (25 mm, 0.7-µm pore size)
	Disposable capsule filter for dissolved organic carbon sample analysis, if consistent with study protocols and objectives
	Hand pressure or peristaltic pump
	C-flex tubing with in-line 0.2-µm air filter
	Cylinder, graduated, glass
	Holding stand, ring, and medium three-prong clamp
	Forceps, stainless steel
	Whirl-Pak bags (6 ounce and 18 ounce)
	Aluminum foil squares
	Cooler and ice
	Organic grade water
	Power source for pump (battery, generator, other)
	Other: Gloves (powderless, disposable nitrile)
✓	**Solid-phase extraction (SPE) system (refer to NFM 5)**
	Valveless piston metering pump (ceramic) with fluorocarbon polymer convoluted tubing
	Fluorocarbon polymer tubing, 1/8-in. outside diameter
	Various tubing fittings, adaptors, connectors, and unions
	Portable balance, 1 to 6,000 g
	Graduated glass cylinders
	Beaker (plastic), 1,000 mL
	Spike mixture and micropipette kit
	Surrogate mixture and micropipette kit
	SPE column (C-18 or Carbopac-B™); checklist and reporting form
	Methanol, ascorbic acid, sodium chloride, and pesticide-grade organic water, all in fluorocarbon polymer dispenser bottles
	Gloves (powderless, disposable nitrile)
	Stopwatch
	Aluminum foil

Table 2-13. Sample-processing equipment and supplies—*Continued*

✓	**Tritium/Helium-3 ($^3H/^3He$) age dating sampling system (see NFM 5)**
	Copper sample tubes; two tubes per well[1]
	500-mL safety-coated glass bottle with polycone seals
	Back-pressure-valve assembly[2]
	• Whitey valve SS-1RS6, 3/8-in. stainless steel valve • Swagelok 3/8-in. nylon ferrule sets, NY-600 set (10 each set) • A small length of 3/8-in. clear tubing (allows you to watch for air bubbles)
	Reducing union to connect sample line to 3/8-in. sample tube
	Socket wrench with 13-mm socket is used to turn the bolts that close the pinch-off clamps
✓	**Passive diffusion bag (PDB) samplers for investigating selected volatile organic compounds (see NFM 5)**
	1- to 2-ft-long low-density polytheylene (LPDE) lay-flat tube[3]
	Polyethylene mesh (sleeve for PDB)
	Deionized water (used to initially fill the PDB before deployment)
	Weighted line or fixed pipe (to hold PDB in place in well)
	Cable ties or stainless steel spring clamps (to hold PDB to weighted line or fixed pipe)
	Heat source to seal ends of PDB

[1] Obtain information online at Reston Chlorofluorocarbon Laboratory by completing a Sample Tube Request Form (http://water.usgs.gov/lab/cfc) (accessed 5-12-2003). Samples are shipped to Lamont-Doherty Earth Observatory in Palisades, NY, for analysis.
[2] NWQL Technical Memorandum 97.04S provides photographs and diagrams of sampling equipment.
[3] Vroblesky (2001) includes photographs of sampling equipment and deployment.

Table 2-14. Sample-preservation equipment and supplies

[NFM, *National Field Manual for the Collection of Water-Quality Data*; N, normal; HCl, hydrochloric acid]

✓	Preservation equipment and supplies (refer to NFM 5)
	Preservation chamber(s)
	Chamber covers (large, transparent bags)
	Waste containers for spent preservative ampoules, dedicated for each chemical used
	Chemical reagents (such as nitric, hydrochloric, and sulfuric acids) and project requirements for sample preservation for the analytes targeted and analytical method selected. Note that although several analytes might require the same type of acid preservative, the normality, volume, and grade specified by the laboratory may differ; it is important to follow explicit laboratory directives concerning the chemical treatment of a sample.
	Nitric acid (analytical grade)
	6N ultrapure hydrochloric acid vial (for mercury sample)
	Sulfuric acid
	HCl for volatile organic compound sample
	Phosphoric acid/cupric sulfate
	Sodium hydroxide
	Ascorbic acid
	Zinc acetate
	Phytoplankton kit
	Radon kit
	Cooler, ice or chilling agent
	Other: for example, apron, goggles, gloves (powderless, disposable nitrile)

Table 2-15. Cleaning and quality-control sampling equipment and supplies

[NFM, *National Field Manual for the Collection of Water-Quality Data;* FEP, fluorinated ethylene polypropylene]

✓	General cleaning equipment and supplies (refer to NFM 3)
	Basins or standpipes (clear or white plastic, fluorocarbon polymer, stainless steel)
	Brushes (nonmetallic, clear or white)[1]
	Detergent, laboratory phosphate-free (0.1 to 2 percent by volume)
	Tap water
	Deionized water, District-produced or equivalent (ASTM International Type 1) (Office of Water Quality Technical Memorandum 92.01), distilled water purchased from commercial supplier
	Wash bottles
	Material Safety Data Sheet for each chemical to be used
	Sealable plastic bags without color closure strips and large plastic storage bags
	Other safety equipment, for example • Laboratory coat or apron • Goggles • Gloves • Eyewash station • Acid spill kit; solvent spill kit • Safety shower
✓	**Inorganic constituents**
	Hydrochloric acid, analytical grade (5 percent by volume)
	Neutralization container and marble chips
	Wash bottle for hydrochloric acid
	Inorganic-grade blank water (IBW) (National Water Quality Technical Memorandum 92.01) (Office of Water Quality Technical Memorandum 2002.14)[2]
	Large plastic bags (clear or white)
	Plastic sheeting (clear or white)

Table 2-15. Cleaning and quality-control sampling equipment and supplies—*Continued*

[NFM, *National Field Manual for the Collection of Water-Quality Data;* FEP, fluorinated ethylene polypropylene]

✓	Organic Compounds
	Methanol, pesticide grade[3]
	Waste container, methanol[3]
	Wash bottle, methanol (FEP-grade plastic)[3]
	Aluminum foil
	Fluorocarbon polymer bags/sheeting
	Pesticide- or volatile-grade blank water (PBW or VPBW)[2]
	Deionized water, district-produced or equivalent (ASTM International Type 1)

[1] Restaurant-supply stores are an excellent source for these types of brushes.
[2] Refer to Office of Water Quality Technical Memorandum 2002.14 for description of a universal blank water. USGS personnel should obtain blank water from OWQRL "One-Stop Shopping" Web site using the following item numbers:
IBW - Q378 FLD
Universal blank water - N1580 or N1570
VPBW - N1580 or N1570
PBW - N1590 or N1600
[3] Methanol supplies must not be used for contact with samples for organic carbon analysis.

Table 2-16. Shipping equipment and supplies

[NFM, *National Field Manual for the Collection of Water-Quality Data*]

✓	Shipping equipment and miscellaneous shipping supplies (refer to NFM 5)
	Coolers, 1 to 5 gallon
	Boxes (sturdy)
	Packing material (foam sleeves, bubble wrap)
	Ice
	Large plastic bags for lining coolers and boxes
	Sample-bottle labels
	Analytical Services Request (ASR) form
	Return-address label and account number
	Sealable plastic bag for forms and return label
	Tape, fiber
	Shipping label (forms)

Table 2-17. Miscellaneous field supplies

[NFM, *National Field Manual for the Collection of Water-Quality Data*]

✓	Miscellaneous field supplies (refer to NFM 5)
	Notebook and pen (indelible ink)
	Field instruments (NFM 6; Office of Water Quality Technical Memorandum 94.02)
	Calibration logbook for each instrument (NFM 6)
	Field folder(s) with station, site, and well information and permission form
	Field documentation forms
	Calculator and extra batteries
	Watch
	Tagline
	Stopwatch and headset for discharge measurement
	Hip boots
	Chest waders
	Rain gear
	Personal flotation device
	Traffic safety vest, cones, signs, warning lights
	First aid kit
	Highway emergency kit
	Tool kit
	Tape (electrical, fiber, fluorocarbon polymer, other)
	Plastic-coat spray
	Fire extinguisher
	Flashlight with extra batteries
	Backup batteries for sampling devices
	Keys to sampling site, security locks, and vehicle (extra set)
	Weather report
	Field trip itinerary (copy to supervisor); sampling and safety plans, Job Hazard Analysis form
	Cellular phone or two-way radio
	Camera with extra film and batteries
	Work gloves
	Shovel, ice chisel/auger
	Boat, motor, gasoline, oil, paddle, oars
	Drinking water
	Soap (antibacterial)
	Paper towels (lint free)
	Safety plan(s) (NFM 9)
	Map(s)
	Locations and phone numbers of hospitals and other emergency facilities (NFM 9)
	USGS photo ID should be with all field personnel at all times in the field.
	Other

CONVERSION FACTORS, SELECTED TERMS, AND ABBREVIATIONS

CONVERSION FACTORS

Multiply*	By	To obtain
inch (in.)	25.4	millimeter (mm)
square inch (in^2)	645.16	square millimeter (mm^2)
foot (ft)	0.3048	meter (m)
gallon (gal)	3.785	liter (L)
pound, avoirdupois (lb)	0.4536	kilogram
meter (m)	3.281	foot
centimeter (cm)	0.3937	inch
micrometer (μm)	3.9372×10^{-5}	inch
millimeter (mm)	0.03937	inch
liter (L)	0.2642	gallon
milligrams per liter (mg/L)	0.5841	grains per gallon
milliliter (mL)	0.0338	ounce, fluid
milliliter (mL)	2.64×10^{-4}	gallon
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois
gram (g)	0.03527	ounce, avoirdupois
kilogram (kg)	2.205	pound

***Example:** 1 in. x 25.4 = 25.4 mm.

Vertical datum: Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88). (The term "sea level" is no longer used to express vertical datum in publications of the Water Resources Discipline of the U.S. Geological Survey.)

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$

SELECTED TERMS

Analyte (target analyte): "Substances being determined in an analysis" (from Bennett, Harry, ed., 1986). The term "target analyte" is used in this report to refer to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured properties such as temperature, conductivity, dissolved-oxygen concentration, pH, Eh, alkalinity, color, or turbidity.

Fluorocarbon polymers and fluoropolymers: Fluorocarbon polymers (polyfluorocarbons) or fluoropolymers are composed of monomers (smallest repeating compound segment of polymer) consisting of carbon, fluorine, hydrogen, and, for one polymer, oxygen. The fluoropolymers have tradenames that include, for example, Teflon® and Tefzel® (ethylene tetrafluoroethylene) (products of the DuPont Company) and Kynar® (a polyvinylidene fluoride, a product of the Atofina Chemicals Company). Common types of fluoropolymers include FEP (fluorinated ethylene polypropylene), PFA (perfluoroalkoxy), PTFE (polytetrafluoroethylene), and PVDF (polyvinylidene fluoride). Each fluorocarbon polymer has different chemical and physical properties; however, all are relatively nonreactive chemically at ambient temperatures and do not leach monomers.

Trace element(s): For the purpose of this report and to maintain consistency with common usage, the term "trace element(s)" is used to refer to metals and other elements such as arsenic, antimony, selenium, and tellurium that usually are present in natural surface- and ground-water systems in concentrations less than 1 mg/L (modified from Hem, 1985). Common usage of this term, as defined above, is inexact and not rigorous with respect to the aqueous chemistry discipline.

Whole water: Water as sampled from its source and not subjected to filtration or other phase-separation process. Common synonymous terms include: raw (water) sample and unfiltered (water) sample.

SELECTED SYMBOLS

~	approximately
>	greater than
≤	less than or equal to
±	plus or minus

ABBREVIATIONS

BOD	biochemicaloxygen demand
CFC	chlorofluorocarbon
DC	direct current
DIW	distilled/deionized water
DOC	dissolved organic carbon
ETFE	ethylene-tetrafluorethylene
ft/s	feet per second
FEP	fluorinated ethylene polypropylene
gal/min	gallon per minute
GF/F	glass microfiber filters
HIF	USGS Hydrologic Instrumentation Facility, Stennis Space Center, Mississippi
IBW	inorganic-grade blank water
L/min	liter per minute
lb/in^2	pounds per square inch
mg/L	milligramsper liter
NFM	*National Field Manual for the Collection of Water-Quality Data*
NWQL	USGS National Water Quality Laboratory
OWQRL	Ocala Water Quality and Research Laboratory
PBW	pesticide-grade blank water (water certified free of pesticide compounds)
PDB	passive diffusion bag sampler
PFA	perfluoroalkoxy

ABBREVIATIONS—*Continued*

PIC	particulate inorganic carbon
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
SPE	solid-phase extraction
SS	stainless steel
TPC	total particulate carbon
TWRI	Techniques of Water-Resources Investigations
USGS	U.S. Geological Survey
USP	United States Pharmacopeia
VOC	volatile organic compounds
VPBW	volatile/pesticide grade blank water

SELECTED REFERENCES AND TECHNICAL MEMORANDUMS

SELECTED REFERENCES FOR SELECTION OF EQUIPMENT FOR WATER SAMPLING

American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, variously paged.

Ammex Corportation, 2002, The Ammex glove guide, accessed June 13, 2002, at www.ammex.com.

ASTM, 1999, Annual book of ASTM standards--Standard guide for sampling fluvial sediment in motion: West Conshohocken, PA, v. 11.02, p. 498-515.

Bennett, Harry, ed., 1986, Concise chemical and technical dictionary (4th ed.): New York, Chemical Publishing Co., 1,271 p.

Buchanan, T.J., and Somers, W.P., 1969, Discharge measurements at gaging stations: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. A8, 65 p.

Busenberg, E., and Plummer, L.N., 1992, Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age-dating tools—Example, the alluvium and terrace system of central Oklahoma: Water Resources Research, v. 28, no. 9, p. 2257–2283.

Capel, P.D., and Larson, S.J., 1996, Evaluation of selected information on splitting devices for water samples: U.S. Geological Survey Water-Resources Investigations Report 95-4141, 103 p.

Capel, P.D., Nacionales, F.C., and Larson, S.J., 1995, Precision of a splitting device for water samples: U.S. Geological Survey Open-File Report 95-293, 6 p.

Cole-Parmer, on-line catalog accessed March 11, 2003, at http://www.coleparmer.com

Corbett, D.M., and others, 1943, Stream-gaging procedure—a manual describing methods and practices of the Geological Survey: U.S. Geological Survey Water-Supply Paper 888, 245 p.

Driscoll, F.G., 1986, Groundwater and wells (2d ed.): St. Paul, Minn., Johnson Filtration Systems, Inc., 1,089 p.

Edwards, T.K., and Glysson, D.G., 1999, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 89 p.

Federal Interagency River Basin Committee, Subcommittee on Sedimentation, 1952, The design of improved types of suspended sediment samplers—Inter-Agency Report 6: Minneapolis, Minn., St. Anthony Falls Hydraulics Laboratory, 5 p.

Federal Interagency Sedimentation Project, accessed July 12, 2002, at http://fisp.wes.army.mil

Federal Interagency Sedimentation Project [catalog], US SS-1 fluoropolymer "churn" sample splitter: accessed December 9, 2002, at http://fisp.wes.army.mil/Catalog%20Page%20US%20SS-1.htm

Federal Interagency Sedimentation Project, Operating instructions for the US D-96 depth-integrating collapsible bag suspended-sediment sampler: accessed December 12, 2002, at http://fisp.wes.army.mil/Operators_Manual_US_D-96_020709.pdf.

Federal Interagency Sedimentation Project, Operator's manual for the US DH-81 depth-integrating suspended-sediment sampler: accessed December 12, 2002, at http://fisp.wes.army.mil/Operators_Manual_for_the_US_DH-81_010612.pdf.

Federal Interagency Sedimentation Project, Using the US VTP-99 vertical transit rate pacer: accessed December 12, 2002 at http://fisp.wes.army.mil/Instructions%20US%20VTP-99%20990722.pdf.

Federal Interagency Sedimentation Project, 2000, Report LL, Development of the US D-95 suspended-sediment sampler: accessed December 12, 2002, at http://fisp.wes.army.mil/000619%20Report%20LL,%20US%20D-95.pdf.

Federal Interagency Sedimentation Project, 2000, Report MM, Development of the US DH-95 suspended-sediment sampler: accessed December 12, 2002, at http://fisp.wes.army.mil/000619%20Report%20MM,%20US%20DH-95.pdf.

Federal Interagency Sedimentation Project, 2000, Sampling with the US D-95 depth-integrating suspended-sediment sampler: accessed December 12, 2002 at http://fisp.wes.army.mil/Instructions%20US%20D-95%20000608%20.pdf.

Federal Interagency Sedimentation Project, 2001, Report PP, The US D-96—An isokinetic suspended-sediment/water-quality collapsible-bag sampler: accessed December 12, 2002, at http://fisp.wes.army.mil/011114%20Report%20PP,%20US%20D-96.pdf.

Federal Interagency Sedimentation Project, 2002, The US XD-99™: accessed December 12, 2002, at http://fisp.wes.army.mil/In_Development_US_XD-99.htm

Ficken, J.R., 1988, Recent development of downhole water samplers for trace organics, *in* Collins, A.G., and Johnson, A.I., eds., Ground-water contamination—field methods: Philadelphia, American Society for Testing and Materials Special Technical Publication 963, p. 253–257.

Gibs, Jacob, Brown, G.A., Turner, K.S., MacLeod, C.L., Jelinski, J.C., and Koehnlein, S.A., 1993, Effects of small-scale vertical variations in well-screen inflow rates and concentrations of organic compounds on the collection of representative ground-water-quality samples: Ground Water, v. 31, no. 2, p. 201–208.

Gillham, R.W., 1982, Syringe devices for ground-water sampling: Ground Water Monitoring Review, v. 2., no. 2, p. 36-39.

Harte, P.T., Brayton, M.J., Ives, Wayne, 2000, Use of passive diffusion samplers for monitoring volatile organic compounds in ground water: U.S. Geological Survey Fact Sheet 088-00, 4 p.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.

Horowitz, A.J., Smith, J.J., and Elrick, K.A., 2001, Selected laboratory evaluations of the whole-water sample-splitting capabilities of a prototype fourteen-liter Teflon® churn splitter: U.S. Geological Survey Open-File Report 01-386, 12 p.

Imbrigiotta, T.E., Gibs, Jacob, Fusillo, T.V., Kish, G.R., and Hochreiter, J.J., 1988, Field evaluation of seven sampling devices for purgeable organic compounds in ground water, *in* Collins, A.G., and Johnson, A.I., eds., Ground-water contamination—field methods: Philadelphia, American Society for Testing and Materials Special Technical Publication 963, p. 258–273.

Izbicki, John, Christensen, Allen, and Hanson, Randy, 1999, U.S. Geological Survey combined well-bore flow and depth-dependent water sampler: U.S. Geological Survey Fact Sheet 196-99, 2 p.

Keith, L.H., 1988, Principles of environmental sampling: Washington, D.C., American Chemical Society, ACS Professional Reference Book, 458 p.

Keith, L.H., ed., 1991, Compilation of EPA's sampling and analysis methods: Chelsea, Mich., Lewis Publishers, 803 p.

Kennedy, V.C., Jenne, E.A., and Burchard, J.M., 1976, Backflushing filters for field processing of water samples prior to trace-element analysis: U.S. Geological Survey Open-File Report 76-126, 12 p.

Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95-398, 69 p.

_____1997, Guidelines and standard procedures for studies of ground-water quality—selection and installation of wells, and supporting documentation: U.S. Geological Survey Water-Resources Investigations Report 96-4233, 110 p.

LeBlanc, D.R., Garabedian, S.P., Hess, K.M., Gelhar, L.W., Quadri, R.D., Stollenwerk, K.G., and Wood, W.W., 1991, Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts. 1. Experimental design and observed tracer movement: Water Resources Research, v. 27, no. 5, p. 895–910.

Margaritz, Mordeckai, Wells, Mona, Amiel, A.J., and Ronen, Daniel, 1989, Application of a multi-layer sampler based on the dialysis cell technique for the study of trace metals in groundwater: Applied Geochemistry, v. 4, p. 617–624.

Morrison, R.D., 1983, Ground water monitoring technology—Procedures, equipment and applications: Prairie Du Sac, Wis., TIMCO Manufacturing, Inc., 111 p.

Norris, J., 1988, Techniques for sampling surface and industrial waters—Special considerations and choices, *in* Keith, L.H., ed., Principles of environmental sampling: Washington, D.C., American Chemical Society, p. 247–253.

Ogawa, I., Junk, G.A., and Scev, H.J., 1981, Degradation of aromatic compounds in groundwater, and methods of sample preservation: Talanta, v. 28, p. 725–729.

Plumb, R., Jr., 1981, Procedures for handling and chemical analysis of sediment and water samples: Vicksburg, Miss., U.S. Army Corps of Engineers Waterways Experiment Station, Environmental Laboratory, Technical Report EPA/CE-81-1, p. 3-73 to 3-76.

Radtke, D.B., 1985, Sediment sources and transport in Kings Bay and vicinity, Georgia and Florida, July 8-16, 1982: U.S. Geological Survey Professional Paper 1347, 120 p.

Radtke, D.B., Buell, G.R., and Perlman, H.A., 1984, Limnological studies of West Point Reservoir, Georgia-Alabama: U.S. Army Corps of Engineers Water Quality Management Study Technical Report, COE SAM/PDEE -84/004, 527 p.

Rantz, S.E, and others, 1982, Measurement and computation of streamflow, volume 1, measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, 284 p.

Sandstrom, M.W., 1995, Filtration of water-sediment samples for the determination of organic compounds: U.S. Geological Survey Water-Resources Investigations Report 95-4105, 13 p.

Sandstrom, M.W., Wydoski, D.S., Schroeder, M.P., Zamboni, J.L., and Foreman, W.T., 1994, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of organonitrogen herbicides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 91-519, 26 p.

Sarkis, Karen, 2000, Protecting hands against chemical exposures: Occupational Hazards, accessed May 12, 2003, at http://www.findarticles.com

Savillex Corporation, 1994, Teflon PFA, molded products for science and industry: Minnetonka, Minn., Catalog 15, 24 p.

Savillex Corporation, online catalog accessed March 11, 2003, at http://www.savillex.com

Shelton, L.R., 1997, Field guide for collecting samples for analysis of volatile organic compounds in stream water for the National National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 97-401, 14 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 94-455, 42 p.

Smith, R.L., Harvey, R.W., and LeBlanc, D.R., 1991, Importance of closely spaced vertical sampling in delineating chemical and microbiological gradients in groundwater studies: Journal of Contaminant Hydrology, v. 7, p. 285–300.

Szalona, J.J., 1982, Development of a bag-type suspended-sediment sampler: Minneapolis, Minn., St. Anthony Falls Hydraulics Laboratory, Federal Inter-Agency Sedimentation Project, Report Y, 32 p.

Torstensson, Bengt-Arne, and Petsonk, A.M., 1988, A hermetically isolated sampling method for ground-water investigations, *in* Collins, A.G., and Johnson, A.I., eds., Ground-water contamination—field methods: Philadelphia, American Society for Testing and Materials Special Technical Publication 963, p. 274–289.

University of California, Davis Environmental Health and Safety, 2002, Safety net#50, Guidelines for the selection of chemical-resistant gloves, accessed June 12, 2002, at http://www.ehs.ucdavis.edu/sftynet

U.S. Environmental Protection Agency, 1980, Samplers and sampling procedures for hazardous waste stream: Cincinnati, Ohio, Municipal Environmental Research Laboratory, EPA 600/2-80-018, 70 p.

_____1982a, Sampling protocols for collecting surface water, bed sediment, bivalves, and fish for priority pollutant analysis: Washington, D.C., Office of Water Regulations and Standards Monitoring and Data Support Division, EPA 68-01-6195, variously paged.

_____1982b, Handbook for sampling and sample preservation of water and wastewater: Cincinnati, Ohio, Environment Monitoring and Support Laboratory, EPA 600/4-82-029, 402 p.

_____1983, Addendum to handbook for sampling and sample preservation of water and wastewater: Cincinnati, Ohio, Environment Monitoring and Support Laboratory, EPA 600/4-82-029, 28 p.

_____1987, A compendium of Superfund field operations methods: Washington, DC., Office of Emergency and Remedial Response, EPA 540-P-87/001, 508 p.

_____1989, Soil sampling quality assurance user's guide: Las Vegas, Nev., Environment Monitoring Systems Laboratory, EPA 600/8-89-046, 268 p.

U.S. Geological Survey, 1978, Sediment, chap. 3 *in* U.S. Geological Survey, National handbook of recommended methods for water-data acquisition: p. 3-1 to 3-100.

_____1984, Chemical and physical quality of water and sediment, chap. 5 *in* U.S. Geological Survey, National handbook of recommended methods for water-data acquisition: p. 5-1 to 5-194.

_____1992a, Indiana District tests ground-water sampling devices, *in* WRD Instrument News, Debra Tracey, ed.: Stennis Space Center, Miss., Hydrologic Instrumentation Facility, no. 57, p. 1.

U.S. Geological Survey, 1992b, Ground-water sampler testing in a standpipe system, *in* WRD Instrument News, Debra Tracey, ed.: Stennis Space Center, Miss., Hydrologic Instrumentation Facility, no. 59, p. 6.

_____Techniques of Water Resources Investigations Reports, accessed December 12, 2002, at http://water.usgs.gov/pubs/twri/

Vroblesky, D.A., 2001, User's guide for polyethylene-based passive diffusion bag samplers to obtain volatile organic compound concentrations in wells—Part 1—Deployment, recovery, data interpretation, and quality control and assurance: U.S. Geological Survey Water-Resources Investigations Report 01-4060, 18 p.

Vroblesky, D.A., ed., 2001, User's guide for polyethylene-based passive diffusion bag samplers to obtain volatile organic compound concentrations in wells—Part 2—Field Tests: U.S. Geological Survey Water-Resources Investigations Report 01-4061, variously paged.

Ward, J.R., and Harr, C.A., eds., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90-140, 71 p.

Winterstein,T.A., and Stefan, H.G., 1983, Suspended sediment sampling in flowing water, laboratory study of effects of nozzle orientation, withdrawl rate and particle size: Minneapolis, Minn., University of Minnesota, St. Anthony Falls Hydraulic Laboratory External Memorandum M-168, 97 p.

TECHNICAL MEMORANDUMS OF THE U.S. GEOLOGICAL SURVEY, WATER DISCIPLINE

Office of Water Quality, Office of Surface Water, and National Water Quality Laboratory Technical Memorandums are available electronically on the Internet through the USGS Web site on the World Wide Web. The site address (URL) is http://water.usgs.gov/admin/memo/ (accessed January 8, 2003).

Water Quality

Memo No.	Title	Date
qw78.06	WATER QUALITY: Field filtering of water samples for chemical analysis	April 5, 1978
qw80.17	EQUIPMENT AND SUPPLIES: New sample splitter for water-quality samples	July 3, 1980
qw92.01	Distilled/Deionized Water for District Operations	December 20, 1991
qw94.02	EQUIPMENT: Discontinuance of field use of mercury liquid-in-glass thermometers	November 22, 1993
qw97.06	Comparison of the suspended-sediment splitting capabilities of the churn and cone splitters	May 5, 1997
qw2000.05	Particulate organic carbon	April 28, 2000
qw2000.08	New method for particulate carbon and particulate nitrogen	June 1, 2000
qw2002.09	Water-quality field methods phaseout of US D-77 and Frame-type samplers	January 25, 2002
qw2002.14	Availability of universal blank water for inorganic and organic analyses	April 18, 2002

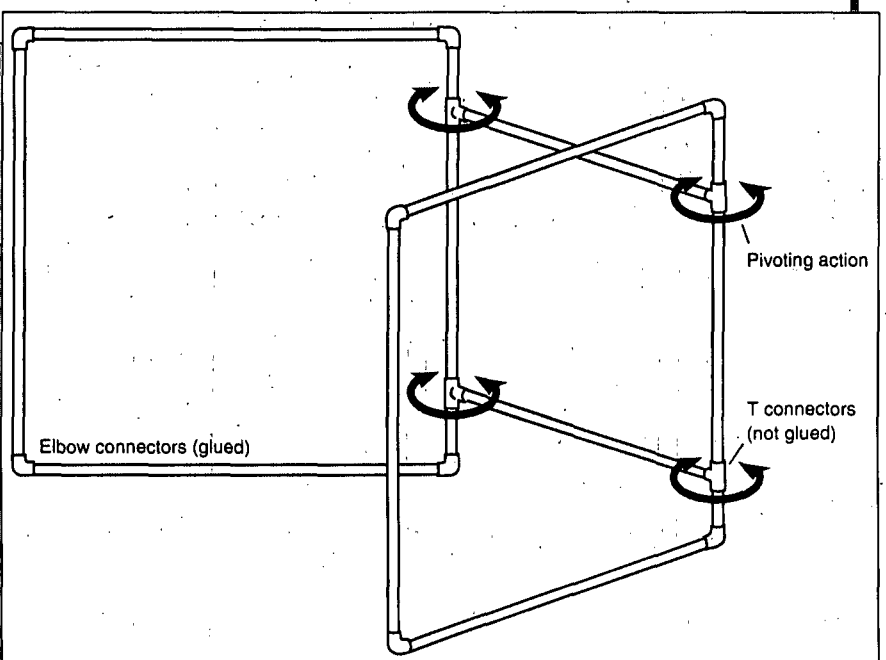
Surface Water

Memo No.	Title	Date
sw94.05	Maximum sampling depths and transit rates for suspended sediment and water-quality samplers	January 31, 1994

National Water Quality Laboratory (NWQL)

Memo No.	Title	Date
92.01	Availability of equipment blank water for inorganic and organic analysis	March 25, 1992
97.04S	Collection, processing, and analysis of ground-water samples for tritium/helium-3 dating	April 7, 1997

APPENDIX: CONSTRUCTION OF A COLLAPSIBLE SAMPLE-PROCESSING/PRESERVATION CHAMBER



This frame can be pulled apart at the 4 joints that are left unglued, and will swivel or fold at these joints. Schedule 40 polyvinyl chloride pipes can be used for greater rigidity. Dimensions of chamber depend on its use (processing or preservation) and the space available in the vehicles.

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data



Chapter A3. CLEANING OF EQUIPMENT FOR WATER SAMPLING

Edited by
F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo



U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, *Secretary*

U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, *Acting Director*

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

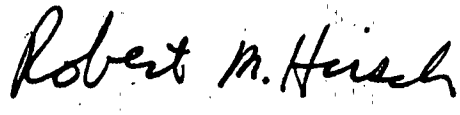
For additional information
write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192
ISBN = 0-607-90850

Copies of this report can be
purchased from:
U.S. Geological Survey
Information Services
Box 25286, Federal Center
Denver, CO 80225

Foreword

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.



Robert M. Hirsch
Chief Hydrologist

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

Chapters of Section A: National Field Manual for the Collection of Water-Quality Data

A1. Preparations for Water Sampling

A2. Selection of Equipment for Water Sampling

A3. Cleaning of Equipment for Water Sampling

A4. Collection of Water Samples

A5. Processing of Water Samples

A6. Field Measurements
- 6.0 General Information and Guidelines
- 6.1 Temperature
- 6.2 Dissolved Oxygen
- 6.3 Specific Electrical Conductance
- 6.4 pH
- 6.5 Reduction-Oxidation Potential (Electrode Method)
- 6.6 Alkalinity and Acid Neutralizing Capacity
- 6.7 Turbidity

A7. Biological Indicators
- 7.1 Fecal Indicator Bacteria
- 7.2 Five-Day Biochemical Oxygen Demand

A8. Bottom-Material Samples

A9. Safety in Field Activities

---

[1]Bold type indicates published chapters and chapter sections, and shaded type indicates chapters and chapter sections that are in preparation.



CLEANING OF EQUIPMENT FOR WATER SAMPLING

A3.

National Field Manual for the Collection of Water-Quality Data

Chapter A3.

Page

Abstract 5

Introduction 5

Purpose and scope 6

Requirements and recommendations 7

Field manual review and revision 8

Acknowledgments 8

A3. Cleaning of Equipment for Water Sampling 9

3.1 Supplies for equipment cleaning 11
D.B. Radtke, A.J. Horowitz, and M.W. Sandstrom

3.2 Cleaning procedures 15
A.J. Horowitz and M.W. Sandstrom

3.2.1 Cleaning of equipment used to sample for inorganic constituents 17

3.2.2 Cleaning of equipment used to sample for organic compounds 25

3.3 Specific procedures for cleaning selected types of equipment 31
A.J. Horowitz, M.W. Sandstrom, and F.D.Wilde

3.3.1 Inorganic-sample bottle cleaning procedures 31

3.3.2 Churn splitter cleaning procedures 32

3.3.3 Cone splitter cleaning procedures..... 34

3.3.4 Filtration equipment cleaning procedures..... 36

3.3.4.A Disposable capsule filter cleaning procedure 36

3.3.4.B Plate-filter assembly cleaning procedure 37

3.3.4.C Pressure-filter assembly cleaning procedure 40

3.3.5 Sample tubing cleaning procedures..... 42

3.3.6 Processing and preservation chambers and flowthrough chamber cleaning procedures 44

3.3.7 Radon sampler cleaning procedure 45

3.3.8 Surface-water sampler cleaning procedures..... 46

3.3.9 Ground-water sampler cleaning procedures..... 49

3.3.9.A Cleaning of bailers and other nonpumping samplers..... 50

3.3.9.B Cleaning of submersible pumps and submersible-pump tubing 50

3.4 Quality control for equipment-cleaning procedures..... 61
A.J. Horowitz, M.W. Sandstrom, and F.D. Wilde

Conversion factors and abbreviations CF–1

Selected references and internal documents.....REF–1

Publications on Techniques of Water-Resources Investigations.....TWRI–1

Illustrations

3-1. Diagram showing general sequence for cleaning equipment before sampling for inorganic and (or) organic analytes 16

3-2. Diagram showing office-laboratory cleaning procedures for equipment used to sample for inorganic constituents 18

3-3. Diagram showing field-site cleaning procedures for equipment used to sample for inorganic constituents 18

3-4. Diagram showing cleaning procedures for equipment used to sample for organic compounds 25

3-5. Diagram showing cleaning procedures for submersible pumps 51

3-6. Estimation of cleaning-solution volumes for standpipe, pump, and pump tubing 56

3-7. Sequence of sample collection to obtain the equipment blank 65

Table

3-1. Supplies for cleaning equipment used for water-sampling activities 12



Chapter A3. CLEANING OF EQUIPMENT FOR WATER SAMPLING

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* provides protocols and guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. Chapter A3 describes procedures for cleaning the equipment used to collect and process water samples and for assessing the efficacy of the equipment-cleaning process. This chapter is designed for use with the other chapters of this field manual.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect data on the Nation's surface-water and ground-water resources. Chapter A3 describes procedures for cleaning the

equipment used to collect and process samples of surface water and ground water and procedures for assessing the efficacy of the equipment-cleaning process.

The *National Field Manual* is Section A of Book 9 of the USGS publication series Techniques of Water-Resources Investigations (TWRI). Each chapter of this manual is published as a separate report. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual.* Other chapters and sections of other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the specific chapter and (or) section number. For example, general information on field measurements of ground water is covered in section 6.0.2 of Chapter A6, "Field Measurements," and would be cited as NFM 6.0.2.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to *(1)* establish and communicate scientifically sound methods and procedures, *(2)* provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, *(3)* encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The equipment-cleaning procedures presented in this chapter are adequate for routine environmental conditions. A modification of the cleaning procedures might be required, for example, in order to decontaminate equipment adequately after sampling at sites where analyte concentrations are large. Modifications to the standard procedures described in this chapter must be documented and quality controlled.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that a specific USGS Office of Water Quality (OWQ) policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and District[1] or other professional personnel, as appropriate. Technical memorandums or other unpublished documents that define the policy pertinent to such requirements are cited in this chapter. Personnel are instructed to use required equipment or procedures as described in this chapter. Departure from or modifications to the stipulated requirements that might be necessary to accomplish specific data-quality requirements or study objectives must be based on referenced research and good field judgment and must be quality assured and documented.

Recommended (recommend, recommended, or recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given procedure or equipment selection are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

[1]**District** refers to a water-data collecting organizational unit of the USGS located in any of the States or Territories of the United States.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Please send comments or corrections to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to nfm-owq@usgs.gov). Information regarding the status and any errata of this and other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications Section of the following website: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>.

ACKNOWLEDGMENTS

The information in this chapter of the *National Field Manual* is based principally on the work of Sandstrom (1990), Horowitz and others (1994), Shelton (1994), and Koterba and others (1995).

The editors wish to thank and pay tribute to R.W. Lee and S.W. McKenzie, who were responsible for final technical review and who contributed to the accuracy, quality, and usability of this report. We would like to express appreciation to the following colleague reviewers for helping to improve this report: H.D. Ardourel, B.A. Bernard, K.K. Fitzgerald, D.S. Francy, S.R. Glodt, V.J. Kelly, S.L. Lane, S.K. Sando, C.A. Silcox, and W.R. White. The editors are indebted to I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone for their valuable editorial contributions, and to C.T. Mendelsohn, L.E. Menoyo, and A.M. Weaver, whose production assistance was instrumental in maintaining the quality of the report.

Special thanks go to T.L. Miller, whose encouragement and faith in this project has been instrumental to its achievement; and to D.A. Rickert and J.R. Ward, who provided the support needed to produce a national field manual for water-quality studies.



A3. CLEANING OF EQUIPMENT FOR WATER SAMPLING

Equipment cleaning (decontamination): Applying cleaning solutions to the surfaces of equipment or using other nondestructive procedures (such as steam cleaning) to remove foreign substances that could affect the concentrations of analytes in samples.

USGS policy requires that equipment for water samples be properly cleaned before contacting the sample and that the effectiveness of cleaning procedures be quality controlled (Sandstrom, 1990; Horowitz and others, 1994; Koterba and others, 1995). The goal of equipment cleaning is to help ensure that the equipment is not a source of foreign substances that could affect the ambient concentrations or chemistry of target analytes in samples. Standard procedures are described in this chapter for when, where, and how to clean equipment constructed of various materials and to collect equipment blanks and field blanks for quality control. Space is commonly dedicated in an office laboratory for equipment cleaning and for storage of cleaning supplies. In this report this work space can include the Field Service Unit or other dedicated office space.

- Clean all sample-collection and sample-processing equipment before use.
  - Manufacturing residues must be removed from new equipment.
  - Dust and any other foreign substances must be removed from equipment that has been in storage.
  - Substances adhering to equipment from previous sampling must be removed.
- Prevent cross contamination between sampling sites by rinsing equipment with deionized water (DIW) while equipment is still wet, and then clean equipment as prescribed in this chapter before transporting it to the next site.
- Do not substitute field rinsing with sample water for the equipment-cleaning procedures described in this chapter.
- Collect equipment blanks and field blanks for quality control. A minimum of one equipment blank per year is required for each piece of equipment. The frequency of collecting blanks normally is based on study objectives and site conditions.

To help prevent sample and site contamination, be sure to use properly cleaned equipment.

SUPPLIES FOR EQUIPMENT CLEANING 3.1

By D.B. Radtke, A.J. Horowitz, and M.W. Sandstrom

The supplies commonly used to clean sample-collection and sample-processing equipment are listed in table 3-1. Cleaning supplies are to be stored in a contaminant-free cabinet. Follow safety instructions regarding the storage of chemical reagents (NFM 9).

Before gathering the cleaning supplies, check the construction materials (for example, metal, glass, or plastic) of washbasins and other cleaning items relative to the samples to be collected.

- **For analysis of inorganic constituents**—Basins, brushes, and other items used for cleaning should be constructed of a suitable nonmetallic material such as uncolored or white polypropylene, polyethylene, or other plastic. **Do not use cleaning agents or items that might leach or sorb metals if the equipment to be cleaned will be used for samples to be analyzed for trace elements.**
- **For analysis of organic compounds**—Basins and other cleaning items can be constructed of metal, glass, or plastic materials. Stainless steel is recommended if methanol will be used. **Do not use cleaning agents or items that might leach, sorb, or leave residues of organic substances that could bias or interfere with the analysis.**

CAUTION: Refer to Material Safety Data Sheets (MSDS) before handling any chemicals.

- **Wear appropriate safety gloves, glasses, and apron when working with corrosive and oxidizing solutions.**
- **When using chemicals, work in a well-ventilated area.**

Table 3-1. Supplies for cleaning equipment used for water-sampling activities

[ACS, American Chemical Society; DIW, distilled/deionized water; µS/cm, microsiemens per centimeter at 25 degrees Celsius; PBW, pesticide-grade blank water; VBW, volatiles and pesticide-grade blank water; IBW, inorganic-grade blank water; L, liter; cm, centimeter; TOC, total organic carbon; DOC, dissolved organic carbon; SOC, suspended organic carbon; NFM, *National Field Manual*; PVC, polyvinyl chloride; IBW, inorganic-grade blank water]

Item	Description and Comments
Acid solution[1]	Hydrochloric: ACS trace-element grade (5 percent by volume in DIW). Nitric: ACS trace-element grade (10 percent by volume in DIW).
Aluminum foil	Organics only: Heavy duty, for work surfaces and equipment.
Bags, plastic or fluorocarbon polymer	Sealable bags with uncolored closure strips, various sizes. Recyclable trash bags are recommended for large equipment storage.
Noncolored plastic sheeting	Clean sheeting used to provide a clean work surface.
Brushes and sponges	Uncolored; plastic components needed for inorganic work.
Distilled/deionized water (DIW)	Maximum specific electrical conductance, 1 µS/cm (usually District produced; Office of Water Quality Memorandum 92.01).
Office-produced organic-grade deionized water	Usable only as a cleaning solution and only as specified in the text. Must not be used to substitute for PBW or VBW.[2]
Detergent	Nonphosphate laboratory soap (for example, Liquinox™).
Gloves, disposable	Powderless, noncolored vinyl, latex, or nitrile (latex or nitrile for use with methanol), assorted sizes.
Inorganic-grade blank water (IBW)[2]	Blank water with certificate of analysis prepared and (or) quality assured by the analyzing laboratory. IBW is required for blank samples.
Jerricans or carboys	For waste solutions and as neutralization container. Neutralization container: 25- to 30-L, polyethylene, wide-mouth, with layer of marble chips. Methanol waste container: Appropriate for flammable liquid.
Methanol	ACS pesticide grade. Methanol is the organic solvent in common use for equipment cleaning, but study requirements might dictate use of a different ACS pesticide-grade solvent.
Neutralization materials	Marble landscape chips (1- to 2-cm chips recommended).[3]
Pesticide-grade blank water (PBW)[2]; volatile-grade blank water (VBW)[2]	Blank water prepared and (or) quality assured by the analyzing laboratory; required for collecting blank samples as follows: PBW for pesticide analysis; VBW for volatile compounds analysis and pesticide analysis; and either PBW or VBW for TOC, DOC, and SOC analyses.
Safety equipment and guidelines (NFM 9)	For example, Material Safety Data Sheets (MSDS), safety glasses, chemical spill kit, apron, emergency phone numbers.

Table 3-1. Supplies for cleaning equipment used for water-sampling activities—*Continued*

Item	Description and Comments
Standpipes for submersible pump	Plastic, glass, or other suitable material; for example, pipette jars or capped PVC casing; one standpipe labeled for blank water and one each for each cleaning solution. (Do not use PVC for methanol.)
Tapwater	If quality is questionable, substitute DIW. Tapwater is more effective for initial and rapid removal of detergent residue.
Tissues	Laboratory grade, lint free, various sizes (for example, Kimwipes™).
Washbasins	One washbasin for each cleaning solution; white or uncolored. Plastic, nonleaching. (Stainless steel is required for methanol.)
Wash bottles (dispenser or squeeze)	Labeled to indicate contents (for example, ACID, DIW, TAP). Fluorocarbon polymer needed for methanol, PBW, VBW, and IBW.

[1]Hydrochloric acid is required if analyzing for nitrogen species; otherwise, nitric acid is acceptable.
[2]PBW and VBW can be obtained from the USGS National Water Quality Laboratory (NWQL). IBW can be obtained from the USGS Quality of Water Service Unit.
[3]Agricultural limestone, soda ash, baking soda, and crushed shells are not recommended (Horowitz and others, 1994).

CAUTION: Methanol is extremely flammable and potentially explosive, emits noxious fumes, and is absorbed through the skin. Observe safety practices when handling methanol or other organic solvents.

- **Wear safety gloves, glasses, and apron.**
- **Work in a well-ventilated area and away from an open flame or sparks.**
- **Make sure that all electrically powered equipment is grounded; alternating current equipment must have a ground-fault interrupter.**
- **Inspect electrical wiring for cuts, breaks, or abrasions where the metal wire is exposed.**
  - **Exposed wires can cause sparks if a short to ground occurs.**
  - **Replace faulty wires—do not rely on fixing with electrical tape.**

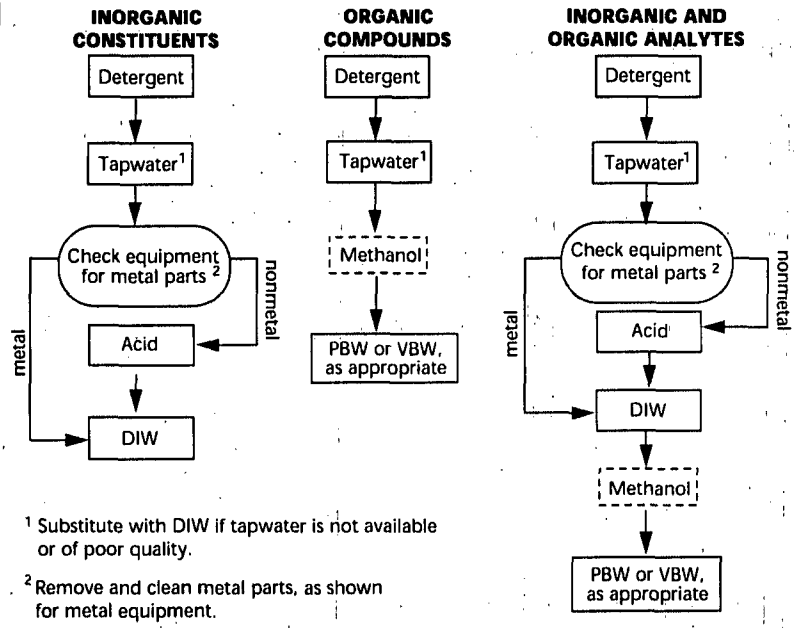
CLEANING PROCEDURES 3.2

By A.J. Horowitz and M.W. Sandstrom

Equipment should be cleaned in an area protected from airborne or other sources of contamination. Procedures to remove contaminants to concentrations below the targeted method-detection levels can vary, depending on the cleaning supplies used, the type of equipment being cleaned, the solubility and concentration of contaminant(s), and the length of time equipment is exposed to contaminant(s). **Examine equipment-blank and field-blank data to determine whether adjustments to the cleaning protocol are needed (section 3.4).**

The cleaning procedure to be used depends on the type(s) of water samples that will be collected and processed. Figure 3-1 summarizes the sequence of cleaning procedures for equipment used to collect samples for inorganic and (or) organic analytes (Sandstrom, 1990; Horowitz and others, 1994; and Koterba and others, 1995).

- **Inspect equipment for stains, cuts, or abrasions. Replace parts as needed.**
  - Replace chipped or cracked glassware.
  - Replace bent sampler nozzles or samplers with bent fins (surface-water samplers).
  - Replace tubing if mold, mildew, or imbedded sediment cannot be removed.
  - Replace cracked or severely crimped O-rings.
  - Repair pump intakes and antibacksiphons that have loose or missing screws.
  - Check the flow manifold and sample tubing to ensure that valves and quick-connect fittings are in good working order; repair or replace as necessary to eliminate any problems.
  - Recoat chipped surface-water samplers with epoxy paint or "plasti-coat." Such samplers must be recoated before use.



[1] Substitute with DIW if tapwater is not available or of poor quality.

[2] Remove and clean metal parts, as shown for metal equipment.

EXPLANATION

DIW	Distilled/deionized water
methanol	Current protocol includes methanol rinse for most types of equipment except that used with samples for organic-carbon analyses. . SAFETY ALERT: Methanol is highly flammable; fumes can be hazardous to human health.
PBW	Pesticide-grade blank water
VBW	Volatiles- and pesticide-grade blank water

Figure 3-1. *General sequence for cleaning equipment before sampling for inorganic and (or) organic analytes.*

- **Rinse equipment with DIW directly after use while equipment is still wet and before cleaning procedures are implemented.**
- **Place cleaned equipment in doubled storage bags.**

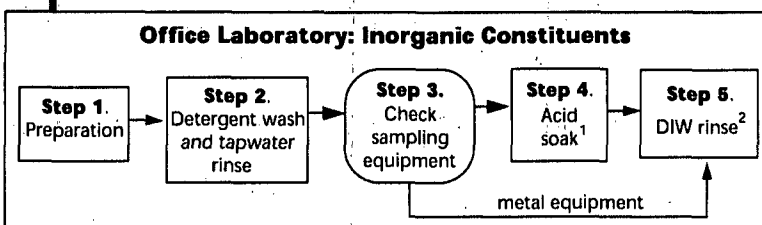
Do not allow collection and processing equipment to sit uncleaned in a field vehicle or elsewhere between field trips.

CLEANING OF EQUIPMENT USED TO SAMPLE FOR INORGANIC CONSTITUENTS 3.2.1

Cleaning of equipment used to collect and process water for analysis of inorganic constituents involves a five-step office-laboratory procedure or a five-step field-site procedure. These procedures are effective for cleaning equipment exposed to water containing concentrations of as much as 50,000 µg/L of iron, 5,000 µg/L each of manganese and zinc, 400 µg/L of copper, 125 µg/L of cobalt, and large concentrations of the other trace elements (Horowitz and others, 1994). The cleaning procedures are summarized in figures 3-2 and 3-3. (These procedures do not apply to field-measurement instruments—see NFM 6.)

Equipment should be cleaned periodically in the office laboratory, where complete disassembly is more practical and more thorough procedures are possible. Compared to cleaning at the field site, cleaning procedures carried out in the office laboratory involve longer exposure of equipment to cleaning solutions, more frequent change of cleaning solution, and greater volumes of rinse water.

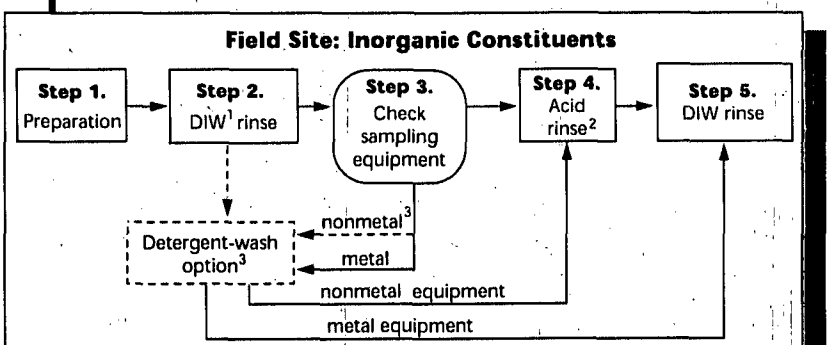
- To minimize field cleaning of equipment between sampling sites, preclean a separate set of equipment for each site.



[1] Acid soak used for nonmetal equipment.

[2] DIW = deionized water (table 3-1).

Figure 3-2. Office-laboratory cleaning procedures for equipment used to sample for inorganic constituents.



[1] DIW = deionized water (table 3-1).

[2] Acid rinse used for nonmetal equipment.

[3] Detergent wash is routine only for field cleaning of submersible pumps, metal equipment components, or excessively contaminated equipment.

Figure 3-3. Field-site cleaning procedures for equipment used to sample for inorganic constituents.

- If individual or dedicated sets of equipment for each field site are not available or cannot be precleaned, clean the equipment onsite and process additional field blanks during each field trip (Horowitz and others, 1994; Koterba and others, 1995).

- Return excessively contaminated equipment to the office laboratory for rigorous cleaning before reuse.

- After cleaning, document completion of and any modifications to the cleaning procedures.

Equipment-cleaning procedures for inorganic constituents

Standard procedures for office-laboratory and field-site cleaning of equipment used to collect and process samples for analysis of inorganic constituent are described below and summarized in figures 3-2 and 3-3. Not all the steps listed apply to all equipment, however. For example,

- Omit detergent step when cleaning plastic bags for surface-water samplers.

- Omit acid step when cleaning submersible pumps, the churn-splitter spigot, or other equipment constructed of stainless steel or other metallic material.

- Omit detergent and acid steps when cleaning sample bottles.

Be sure to check the specific procedures for sample bottles and other selected equipment listed in section 3.3 before proceeding with the office-laboratory and field-site procedures.

Step 1. Preparation at the office laboratory or field site (figs. 3-2 and 3-3).

a. Prepare a contaminant-free space for cleaning and drying the cleaning supplies and sample-collection and sample-processing equipment.

   i. Gather the cleaning supplies, the equipment to be cleaned, and the plastic bags or other material with which to wrap the cleaned equipment. Check table 3-1 for the cleaning supplies needed.

   ii. Place clean plastic sheeting over the work surface.

   iii. Put on disposable, powderless gloves[2], a laboratory coat or apron, and safety glasses.

   iv. Prepare the detergent solution, using a nonphosphate, laboratory-grade detergent.

   - **Office laboratory** (fig. 3-2). Use 0.1- to 2-percent solution, volume-to-volume (v/v), using a higher concentration for dirtier equipment.
   - **Field site** (fig. 3-3). Use 0.1- to 0.2-percent solution, v/v.

   v. Prepare the acid solution, using a 5-percent v/v dilution of ACS trace-element-grade hydrochloric acid (HCl) in DIW.

   - **Add the acid to the water**, not water to acid (NFM 9).
   - If nitric acid (HNO_3) will be used, prepare a 10-percent solution (v/v) of ACS trace-element-grade acid in DIW.

   vi. Label each washbasin, standpipe, and wash bottle to indicate the solution it will contain. Use a black waterproof marker.

   vii. Unwrap the equipment to be cleaned and discard the storage bags. Change gloves.

b. Clean the items used to clean the equipment.

   i. Fill washbasins and (or) standpipes with the nonphosphate detergent solution. Put wash bottles, scrub brushes, and other small items used for cleaning into a washbasin. **Soak for 30 minutes.**

   ii. Scrub interior and exterior sides of basins and standpipes with soft scrub brushes. Fill wash bottles with a soapy solution and shake vigorously.

---

[2]Refers to laboratory gloves that are nonpowdered on the inside and intended for disposal after one use. Glove materials must be appropriate for the work to be carried out and the solutions and equipment to be contacted. For example, vinyl gloves are appropriate for most sampling activities but not when working with methanol or other organic solvents.

iii. Rinse all items thoroughly with tapwater to remove detergent residue. No detergent bubbles should appear when fresh tapwater is agitated in the basin, standpipe, or wash bottle.

iv. Rinse washbasins with DIW.

v. Pour 5-percent HCl (or 10 percent HNO_3) solution into washbasins, standpipes, and wash bottles. Soak for 30 minutes. **Do not soak items with metal parts (exposed or hidden) in an acid solution.**

vi. Discard used acid solution into a neutralization container containing a bottom layer of marble chips (Step 4d).

vii. Rinse washbasins, standpipes, and wash bottles with DIW. Dispose of DIW using directions in Step 4d.

c. Disassemble sample-collection and sample-processing equipment. Change gloves.

- Submersible pumps should be disassembled periodically for office cleaning, but they are not usually disassembled for field cleaning.
- Processing and preservation chamber frames should be cleaned periodically using office-laboratory cleaning procedures. Field cleaning is needed only if the cover is slipped over the frame instead of being clipped to the inside of the frame.

Step 2. Detergent wash and tapwater rinse—Office laboratory (fig. 3-2).

a. Place small equipment parts into washbasin labeled for detergent and fill with a 0.1- to 2-percent solution of nonphosphate laboratory detergent. The amount of detergent depends on the hardness of the tapwater and the degree to which the equipment is dirty or contaminated.

b. Soak equipment and tubing for 30 minutes: fill tubing with solution and keep submerged.

c. Scrub exterior and interior of equipment surfaces to the extent possible, using a firm sponge or soft brush to remove any adhering material such as oil and grease, sediment, algae, and chemical deposits. Pay particular attention to grooves and crevices, O-rings, nozzles, and other spaces where inorganic or organic materials might be trapped. Change gloves.

d. Rinse equipment thoroughly with warm tapwater to remove detergent residue. Equipment rinsing is completed when no soap bubbles appear after the rinse water is agitated. Change gloves.

Step 2. DIW rinse and detergent-wash option—Field site (fig. 3-3).

For the DIW rinse:

a. Rinse equipment and tubing with DIW. Pay particular attention to removing material from grooves and crevices, O-rings, nozzles, and places where materials might be trapped. Note that equipment should already have had one DIW rinse directly after contact with sample water and before the equipment had a chance to dry.

b. Change gloves. Proceed to field detergent-wash option only for metal equipment components or for equipment that has become excessively contaminated.

For the detergent-wash option:

A field detergent wash is used for between-site cleaning of submersible pumps, metal components of equipment, or for equipment that has become greasy or otherwise coated and requires detergent to remove foreign materials; specific instructions for submersible pumps are given in section 3.3.9.

a. Place small equipment, tubing, and parts into basin labeled "detergent" and fill with a 0.1- to 0.2-percent detergent solution. Soak for about 10 minutes, or keep equipment assembled and circulate the solution through pump tubing for 5 to 10 cycles.

b. Scrub equipment surfaces with a firm sponge or soft brush to remove any adhering material such as oil and grease, sediment, algae, or chemical deposits. Pay particular attention to grooves and crevices, O-rings, nozzles, and other places where materials might be trapped. Change gloves.

c. Rinse equipment thoroughly with tapwater to remove detergent residue. Use DIW if tapwater is unavailable or is suspected of having a quality so poor as to contaminate the equipment. If necessary, use a wash bottle filled with DIW or tapwater to rinse hard-to-reach places; pump tapwater through assembled equipment for five or more tubing volumes. Equipment rinsing is complete when no soap bubbles appear after agitating the rinse water. If nonmetal equipment has been detergent-washed, go to Step 4.

d. Place equipment into acid-solution washbasin. Change gloves.

Step 3. Check equipment—Office laboratory and field site (figs. 3-2 and 3-3).

— Nonmetal equipment or equipment with removable metal parts: remove any metal parts and go to Step 4.

— Metal equipment components or excessively contaminated equipment: go to Step 2, detergent-wash option at the field site and then to Step 5, DIW rinse.

Step 4. Acid soak/rinse—Office laboratory and field site (figs. 3-2 and 3-3).

For equipment constructed primarily of glass or fluorocarbon polymer or some other plastic, soak (office laboratory) or rinse (field site) in a 5-percent (v/v) HCl solution to remove any remaining organic films and inorganic deposits.

> TECHNICAL NOTE: A 10-percent (v/v) HNO_3 solution can be used instead of HCl if samples to be collected with the equipment will not be analyzed for nitrogen species.

CAUTION: Wear safety glasses and other protective apparel when working with acids.

a. Place nonmetal equipment and tubing into the washbasin labeled "acid solution."

b. **Office laboratory.** Fill basin with dilute HCl solution (see TECHNICAL NOTE above). Soak equipment and tubing for 30 minutes. Carefully swirl the acid solution several times during the 30-minute soak to enhance removal of mineral encrustations.

c. **Field site.** Using a wash bottle filled with 5-percent HCl solution (see TECHNICAL NOTE above), rinse exterior of equipment and tubing. Pump acid solution through the equipment and tubing, using a peristaltic pump.

d. Carefully pour or pump the used acid solution into a neutralization container with marble chips covering the bottom (table 3-1). Do not reuse the acid solution.

   - Do not fill the neutralization container more than three-fourths full of acid solution.
   - Ventilate container and workspace to allow for safe escape of carbon dioxide gas during dissolution of marble chips.

- Check the solution pH periodically using narrow range pH indicator strips. Neutralization is complete when the solution pH is greater than 6.0 or the original DIW pH.
- Discard the neutral solution, as appropriate.
- Rinse the container with tapwater but retain any undissolved marble chips. Replenish chips to form a layer on the bottom of the neutralization container.

Step 5. DIW rinse—Office laboratory or field site (figs. 3-2 and 3-3).

a. Place equipment into the cleaned washbasin labeled DIW. Change gloves.

b. **Office laboratory.** Rinse exterior and interior of each piece of equipment and tubing thoroughly with DIW and place on a clean surface to dry or into a clean IBW washbasin if blank samples will be collected to quality control the cleaning procedures.

c. **Field site.** Pump DIW through equipment.

d. Pour or discharge DIW rinse water into neutralization container. Change gloves.

e. Continue DIW rinsing until rinse-water pH is greater than 6.0 or the original DIW pH.

f. Allow equipment to air dry in an area free from potential airborne contaminants.

Storage of clean equipment

- Place dry, clean equipment inside doubled plastic bags. For small equipment, parts, and tubing, use sealable plastic bags.
- Place the churn splitter and funnel into doubled plastic bags and then place churn splitter inside of the churn carrier.

Clean equipment at the sampling site while equipment is still wet and before leaving for the next site.

CLEANING OF EQUIPMENT USED TO SAMPLE FOR ORGANIC COMPOUNDS 3.2.2

Nearly identical procedures are used in the office laboratory and at the field site to clean equipment used to sample for organic compounds. The office laboratory provides an environment in which equipment can be cleaned over an extended time using greater volumes of cleaning and rinsing solutions than in the field. The five-step cleaning procedure summarized in figure 3-4 is described in this section. If inorganic constituents also will be sampled for, check the sequence of cleaning solution to be used as shown in figure 3-1 before proceeding.

- Preclean a separate set of equipment for each site in order to avoid field cleaning of equipment between sampling sites. Always rinse equipment with DIW directly after use, however.
- If individual or dedicated sets of equipment for each field site are not available or cannot be precleaned, field clean equipment before moving to the next sampling site and process additional field blanks for each field trip (Koterba and others, 1995).
- Collect additional field blanks after cleaning equipment that was exposed to high levels of contamination (NFM 4) and before the equipment is reused for environmental sampling.

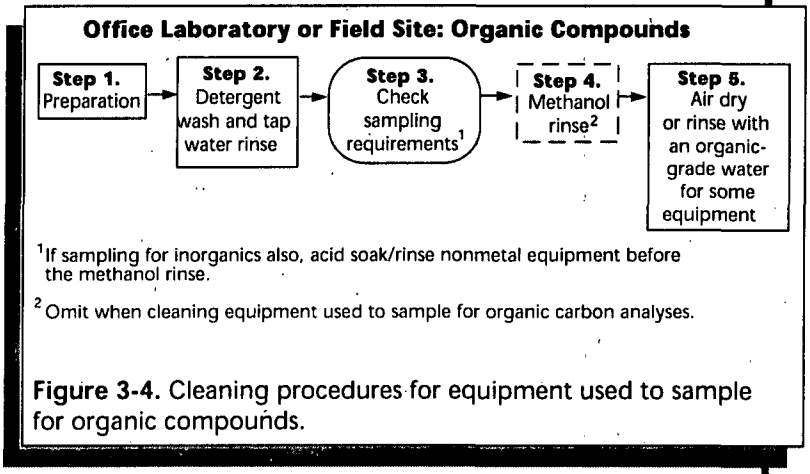


Figure 3-4. Cleaning procedures for equipment used to sample for organic compounds.

Equipment-cleaning procedure for organic compounds

Standard procedures for office-laboratory and field-site cleaning of equipment used to collect and process samples for organic-compound analysis are described below and summarized in figure 3-4. Not all the steps listed apply to all equipment, however. For example,

- **Omit any cleaning procedure for sample bottles for organic compounds.** Bottles for organic analyses arrive from the laboratory capped and ready for use and should not be rinsed by field personnel. Discard bottles if received uncapped.
- **Omit the methanol rinse when cleaning the equipment used to collect and process samples for total, dissolved, and suspended organic carbon (TOC, DOC, SOC).** If equipment (such as a submersible pump) that has been in contact with methanol or other organic solvent must be used for TOC, DOC, or SOC sampling, flush the equipment with copious quantities of sample water before collecting the sample; collection of a blank sample for DOC quality control is recommended.

Be sure to check the specific procedures for selected equipment listed in section 3.3 before proceeding with the office-laboratory and field-site procedures.

Step 1. Preparation (fig. 3-4).

a. Prepare a contaminant-free space for cleaning and drying the cleaning supplies and sample-collection and sample-processing equipment.

   i. Gather the cleaning supplies, the equipment to be cleaned, and clean storage bags and aluminum foil with which to wrap the cleaned equipment. (Check table 3-1 for the cleaning supplies needed.)

   ii. Cover the cleaning area with aluminum foil or fluorocarbon polymer sheeting.

iii. Put on disposable, powderless gloves,[3] a laboratory coat or apron, and safety glasses. **Gloves provide protection from direct contact with solvents only for a limited period of time.**

iv. Prepare the detergent solution, using nonphosphate laboratory-grade detergent. A 0.1- to 0.2-percent (v/v) solution is normally of sufficient strength, unless equipment is very oily or greasy. **Do not use greater than a 0.2-percent solution for field cleaning.**

b. Clean the items used to clean the equipment.

i. Label each washbasin, standpipe, and wash bottle with a black waterproof marker to indicate the solution it will contain.

ii. Follow Steps 2–5, listed below, to clean the washbasins, standpipes, wash bottles, and other items to be used for equipment cleaning.

c. Disassemble sample-collection and sample-processing equipment. Submersible pumps should be disassembled periodically for office cleaning but usually are not disassembled for field cleaning.

[3]Refers to laboratory gloves that are nonpowdered on the inside and intended for disposal after one use. Glove materials must be appropriate for the work to be carried out and the solutions and equipment to be contacted. For example, vinyl gloves are appropriate for most sampling activities but not when working with methanol or other organic solvents. Use solvent-resistant gloves when cleaning with organic solvents. Latex or nitrile disposable, powderless gloves are appropriate when using methanol.

Step 2. Detergent wash and tapwater rinse (fig. 3-4).

a. Place small equipment parts into washbasin labeled for detergent. Fill washbasin with a 0.2-percent solution of nonphosphate, laboratory-grade detergent. (The specific concentration of detergent solution depends on how contaminated the equipment might be and on the hardness of the tapwater.) Change gloves.

- ***Office laboratory.*** *Soak equipment in detergent solution* for 10 to 30 minutes.
- ***Field site.*** Rinse equipment exterior and interior with detergent solution.

b. Scrub the exterior and interior of equipment surfaces to the extent possible, using a firm sponge or soft brush to remove any adhering material such as oil and grease, sediment, algae, or chemical deposits. Pay particular attention to removing material from areas where inorganic or organic materials might be trapped, *such as grooves and crevices, O-rings, and nozzles.*

c. Place equipment into tapwater washbasin.

d. Rinse equipment thoroughly with tapwater to remove detergent residue. Use an organic-grade water (PBW, VBW, or office-produced) if tapwater is unavailable or is of a quality so poor as to contaminate the equipment. If necessary, use a wash bottle filled with organic-grade water or tapwater to rinse hard-to-reach places. Equipment rinsing is complete if no detergent bubbles appear when rinse water is agitated. Change gloves.

Step 3. Check sampling requirements (fig. 3-4).

a. If samples will be collected for organic analysis only, go to Step 4.

b. If samples will be collected for inorganic analysis in addition to organic analysis, follow the procedure for the acid wash and DIW rinse before proceeding with the methanol rinse (see figs. 3-1 and 3-4).

Step 4. Methanol rinse[4] (fig. 3-4).

a. Change to gloves that are chemically resistant to any solvent being used. Place cleaned equipment into a clean stainless steel or organic-solvent-resistant washbasin. Methanol-rinse area must be outside of the field vehicle and away from the sample-processing site. **Sample-collection, -processing, and -preservation areas must remain free of solvent vapors.**

CAUTION: Use methanol or other organic solvents sparingly and work under a fume hood or in a well-ventilated area, away from where an open flame or sparks can occur. Wear safety gloves, glasses, and apron.

b. Use pesticide-grade methanol (or appropriate organic solvent) dispensed from a methanol fluorocarbon-polymer wash bottle (office laboratory) or pumped through tubing (field site) (see TECHNICAL NOTE below).

i. Rinse equipment exterior and interior with a minimum amount of methanol.

ii. Rinse interior of pump tubing with methanol.

- Do not rinse exterior of pump tubing with methanol.
- **Do not rinse pump tubing with methanol or any organic solvent if TOC, DOC, or SOC samples will be withdrawn through that tubing.**

[4]Current (1998) cleaning protocol dictates the use of methanol to remove contaminants from equipment to be used to collect samples for analysis of organic compounds.

iii. Place equipment components and tubing on a clean aluminum foil surface.

iv. Pour or discharge used methanol (or other organic solvent) into an appropriate waste container for flammable liquids (Water Resources Division Memorandum 94.007). Change gloves. Dispose of gloves used for methanol rinse appropriately.

TECHNICAL NOTE: Rinse with dichloromethane or hexane if the methanol rinse is not sufficient to clean equipment contaminated with excessive concentrations of hydrophobic organic compounds. If rinsing with dichloromethane or hexane, use pesticide-grade solutions, wear nitrile gloves, and use only on dry equipment (dichloromethane and hexane are not soluble in water). Do not rinse equipment with any organic solvent if equipment will be used for TOC, DOC, or SOC samples.

Step 5. Air dry equipment or rinse with organic-grade water (fig. 3-4).

a. Allow methanol-rinsed equipment to air dry in an area free from dust and potential airborne contaminants (place an aluminum foil tent loosely over the drying equipment).

b. If it is not practical for the methanol to evaporate from the interior of equipment components or sample tubing, either

- dry by blowing clean, filtered, inert gas through equipment; or
- rinse methanol from equipment with pesticide-grade or volatile-grade blank water, dispensed from a wash bottle or pumped with a valveless fluid metering pump.

Storage of clean equipment

Cover all equipment orifices with aluminum foil or fluorocarbon polymer bags, then place equipment into sealable storage bags. Isolate equipment used to collect trace-element samples from aluminum foil.

SPECIFIC PROCEDURES FOR CLEANING SELECTED TYPES OF EQUIPMENT 3.3

By A.J. Horowitz, M.W. Sandstrom, and F.D. Wilde

The equipment-cleaning steps described in sections 3.2.1 and 3.2.2 apply to most, but not all, equipment. This section describes the cleaning procedures needed for specific equipment for which the general protocols are modified or do not apply, or for which more detailed instructions might be useful. Wear appropriate disposable, powderless gloves throughout each cleaning procedure, changing gloves with each change in cleaning solution and as described in section 3.2.

INORGANIC-SAMPLE BOTTLE CLEANING PROCEDURES 3.3.1

Bottles for samples to be analyzed for inorganic constituents include translucent colorless polyethylene, opaque brown polyethylene, and transparent glass bottles. Translucent polyethylene bottles that were acid rinsed at the laboratory should arrive capped with colorless, translucent plastic caps. Glass bottles for samples for mercury analysis also are acid rinsed and should arrive capped.

- **Discard acid-rinsed bottles that are received uncapped.**
- A cleaning procedure is required for bottles that will contain samples to be analyzed for trace elements and is recommended for bottles that will contain samples to be analyzed for major ions and nutrients.

Before leaving for the field, clean polyethylene and glass sample bottles, including acid-rinsed bottles, as described in the steps that follow:

1. Put on powderless, vinyl gloves.
2. Fill each bottle about one-quarter full of DIW and cap.
3. Shake vigorously and decant DIW.

4. Repeat the DIW rinse (Steps 2 and 3 above) two more times.
5. Following the last rinse, fill each bottle half full with DIW and cap the bottle.
6. Rinse exterior of bottle with DIW and dry with lint-free laboratory tissue.
7. Store bottles in doubled plastic bags.

3.3.2 CHURN SPLITTER CLEANING PROCEDURES

Plastic churn splitters are used primarily for samples to be analyzed for inorganic constituents (NFM 2). Avoid the need to field-clean the churn splitter by using a separate, precleaned churn splitter at each field site to be sampled, if possible.

When using the detergent wash/tapwater rinse for the churn splitter—Office-laboratory procedure (fig. 3-2, Step 2):

1. Fill churn splitter through the funnel with detergent solution.
2. Soak for 30 minutes.
3. Scrub interior and exterior surfaces with a soft brush, taking care not to abrade the surface.
4. Pay particular attention to cleaning the paddle and the area around the spigot.
5. Make sure spigot and funnel are free of sediment, including fine particulates (clay), organic matter, and stains.
6. Drain some of the cleaning solution through the spigot before discarding the remaining solution.
7. Fill churn through the funnel splitter about one-third full with tapwater; swirl and shake churn vigorously to remove detergent residues. Allow tapwater to pass through the spigot.
8. Repeat rinse procedure until no bubbles remain in rinse water after the water is agitated.

When using the acid rinse for the churn splitter—Office-laboratory or field-site procedures (figs. 3-2 and 3-3, Step 4):

1. Do not allow acid solution to contact the outside of churn splitter, or the churn spigot.

2. Do not pass acid solution through the spigot.

3. Decant acid solution by pouring out of the top of the churn into the neutralization container.

When using the DIW rinse for the churn splitter—Office-laboratory or field-site procedures (figs. 3-2 and 3-3, Step 5):

1. Fill the churn splitter through the funnel with DIW to about one-third full.

2. Swirl the DIW vigorously and pour it out of the top of the churn into the neutralization container.

3. Repeat the fill-and-swirl procedures of 1 and 2 above at least twice, checking the pH of the DIW after each swirl with narrow-range pH indicator strips.

4. **Pass a portion of the DIW through the spigot only after the DIW pH equals or is greater than either 6.0 or the pH of the DIW before acidification. Pour the rest of the DIW into the neutralization container.**

For storage of a cleaned churn splitter—Office-laboratory or field-site procedures:

1. Package a clean, dry churn splitter in two new plastic bags and loosely tie or secure with a nonmetal clip. If a churn splitter must be packaged while wet, use within 1 to 3 days and (or) keep chilled to prevent bacterial growth.

2. Place entire package into the churn carrier.

3.3.3 CONE SPLITTER CLEANING PROCEDURES

The fluorocarbon-polymer cone splitter (NFM 2) is appropriate for splitting samples for inorganic or organic analyses. When cleaning the cone splitter (Office of Water Quality Technical Memorandum 97.03), pay particular attention to removing foreign material from threaded and hard-to-access parts. Field cleaning can be minimized by having separate, precleaned cone splitters available for each site and by keeping a supply of clean tubes to replace the used tubes for each site to be sampled.

When inorganic constituents will be analyzed in samples processed through the cone splitter:

Office laboratory. Follow the steps as described for figure 3-2.

Field site. Referring to figure 3-3:

1. Prepare the field site as described in section 3.2.1. Put on disposable, powderless gloves.
2. Rinse the splitter thoroughly with deionized water.
3. Inspect the cone splitter. If it looks dirty, is suspected of being contaminated, or was allowed to dry between field sites without a thorough DIW rinse, or if the splitter will be used for sampling both inorganic and organic analytes, use the detergent-wash option. Change gloves.
4. Acid rinse by passing 1 L of 5-percent HCl solution through the cone splitter. Collect used acid solution into a neutralization container. Change gloves.
5. Rinse the cone splitter with at least 3 L of deionized water. Collect the rinse solution into a neutralization container. Change gloves.
6. Allow the cone splitter to dry and then store in a clean plastic bag. Seal the bag and store in a second plastic bag or plastic storage container for transport to the next site. A cone splitter that is packaged into bags while wet should be used within 1 to 3 days and (or) kept chilled to prevent bacterial growth.

When organic compounds will be analyzed in samples processed through the cone splitter (fig. 3-4):

Office Laboratory. Follow the steps described for figure 3-4.

Field Site.

1. Prepare site as described in section 3.2.2. Put on appropriate disposable, powderless gloves; if a solvent will be used, select gloves that will withstand contact with the solvent.
2. Detergent wash and rinse equipment as described for figure 3-4.
3. Check equipment and sampling requirements. If splitter will also be used for inorganics sampling, follow acid-rinse directions before rinsing with methanol or other organic solvent.
4. Proceed with the methanol (or other organic solvent) rinse, if required (section 3.2.2).
   - **Do not use any organic solvent if the cone splitter will contact samples for analysis of TOC, DOC, or SOC.**
   - If samples processed through a splitter will be analyzed for TOC, DOC, or SOC, rerinse the splitter thoroughly to completely remove residues from the detergent wash. Use PBW, VBW, or other organic-grade water for the final rinse if complete methanol evaporation is impractical. If the cone splitter will not be used to process samples for inorganic constituents at the next site, wrap nozzle and other orifices in aluminum foil.

For storage of a cleaned cone splitter:

1. Allow the cone splitter to air dry.
2. Place the cone splitter into a clean plastic bag and seal.
3. Store in a second plastic bag or plastic storage container for transport to the next site.

If a cone splitter must be packaged while wet, use within 1 to 3 days and (or) keep chilled to prevent bacterial growth.

3.3.4 FILTRATION EQUIPMENT CLEANING PROCEDURES

Filtration equipment includes disposable capsule filters and various plate-filter and pressure-filter assemblies. Cleaning procedures for these types of equipment are described below.

3.3.4.A Disposable Capsule Filter Cleaning Procedure

The disposable capsule filter has a one-time use for processing samples to be analyzed for inorganic constituents but must be cleaned before use. The filter can be prerinsed in the office laboratory instead of at the field site as long as it is kept chilled and used in less than 1 day. After filtering the sample, clean or replace the sample-delivery tubing and discard the capsule filter. The cleaning procedure described below comprises sufficient cleaning of the filter for analysis of inorganic constituents at the parts-per-billion (ppb) concentration level (Horowitz and others, 1994).

To clean the disposable capsule filter, pump 1 L of DIW to the filter through precleaned tubing (section 3.3.5) as follows (refer to NFM 5.2.1.A for additional instructions):

1. Use Clean Hands/Dirty Hands techniques described in NFM 4. Remember: the Dirty Hands team member performs operations that are outside of the processing chamber and the Clean Hands team member performs operations that are inside the chamber. Put on disposable, powderless gloves.

2. In a processing chamber, remove the capsule filter from the protective bags. Attach pump tubing to the inlet connector of the capsule filter, keeping the tubing as short as possible. **Make sure the direction of flow through the capsule filter matches the direction-of-flow arrow on the side of the filter.**

3. Pump 1 L of DIW through the capsule filter; discharge waste rinse water through a sink funnel or to a toss bottle.
   - Operate the pump at a low speed.
   - Hold the capsule filter so the arrow is pointing up at an acute angle from the horizontal plane. (This expels trapped air from the capsule; do not allow water to spray onto chamber walls.)
4. Remove tubing from the DIW reservoir and continue to operate the pump in the forward, mid-range speed position to drain as much of the DIW that remains in the capsule filter as possible. While the pump is operating, shake the capsule filter to help remove any entrained DIW.
5. Detach the capsule filter from the peristaltic pump tubing, put into a clean, sealable plastic bag, and store chilled until ready for use at the next site.

Plate-Filter Assembly Cleaning Procedure 3.3.4.B

To clean filtration equipment used for samples to be analyzed for inorganic or organic analytes, consult sections 3.2.1 and 3.2.2, respectively. Use Clean Hands/Dirty Hands techniques, as appropriate (NFM 4).

- **Preclean in the office laboratory** one plate-filter assembly per site to be sampled, if possible, in order to save the time that would be needed to clean the plate-filter assembly during the field effort.
- **During the detergent wash and (or) DIW rinse,** pay particular attention to grooves and crevices, O-rings; and support structures for the filter, where sediment or organic matter might be lodged. Detergent wash and DIW rinse the pressure valve.
- **Remove and discard the used filter at the field site;** rinse the filter assembly immediately with DIW while still wet from filtering the sample, even if a clean filter assembly is available for the next site.

When field cleaning the plastic plate-filter assembly:

1. Disassemble the plate-filter assembly inside the processing chamber while it is still wet from the sample water and while wearing disposable, powderless gloves.

   a. Remove the used filter media carefully to avoid spilling any of the filter cake.

   b. Place the filter media into a sealable plastic bag. Seal and pass the bag out of the chamber. Change gloves.

2. DIW rinse all components of the plate-filter assembly, including the exterior and interior of the tubing and the pressure valve, dispensing the DIW from a wash bottle. Pay particular attention to grooves and crevices, O-rings, and support structures for the membrane filter, where inorganic or organic materials might be lodged. Change gloves.

3. Inspect the plastic plate-filter assembly. Use the detergent-wash option described in figure 3-3 (Step 2) if the filter assembly looks dirty, is suspected of being contaminated, or was allowed to dry after use without first rinsing thoroughly with deionized water.

4. Reassemble the plate-filter assembly, reattaching the piece of tubing to the outlet of the filter assembly and placing the discharge end of the tube through the drain or disposal funnel in the bottom of the processing chamber to the acid-neutralization container. Reconnect the filter assembly to the peristaltic pump with the sample tubing. Change gloves.

5. To acid rinse the plate-filter assembly, pump 1 L of 5-percent HCl solution (or 10-percent HNO_3^- solution) through the plate-filter assembly. Check that the acid solution is being discharged into the acid-neutralization container. Alternately squeeze and release the tubing at the outlet to force the acid solution to cover and rinse all interior surfaces of the filtration assembly. (Be careful not to force tubing from the outlet by squeezing tubing for too long.)

6. To DIW rinse the plate-filter assembly, pump 2 L of deionized water through the assembly, using the same squeeze-and-release method described above in 5 for the acid rinse. Ensure that all the rinse water is being discharged to the acid-neutralization container. After confirming that the pH of the acid rinse solution is greater than 6.0 or the original pH of the DIW, appropriately discard solutions from the neutralization container.

7. For storage, place the cleaned plate-filter assembly and tubing into clean double bags for temporary storage until use at the next site. If wet when bagged, store for no longer than 24 hours and (or) chill to prevent bacterial growth. The filter assembly must be dry if stored for more than 24 hours.

Always remove the used filter media from the plate-filter assembly before cleaning and storage.

When field cleaning the aluminum plate-filter assembly, use the general cleaning instructions in section 3.2.2 for figure 3-4, as follows:

1. Inspect the aluminum (or stainless steel) plate-filter assembly for damage or excessive contamination and replace if necessary.

2. Wearing disposable, powderless gloves, prepare the area to be used for cleaning the plate-filter assembly by lining the table or counter surface with aluminum foil.

3. Disassemble the filter assembly and remove the used glass-fiber filter media carefully to avoid spilling any of the filter cake. Place used filter media into a sealable plastic bag, seal the bag, and put aside for disposal. Place components of the plate-filter assembly and tubing into a washbasin for detergent. Change gloves.

4. Detergent wash by using a 0.1- to 0.2-percent nonphosphate-detergent solution. Scrub each component of the filter assembly with a soft brush to remove any adhering material such as oil and grease, sediment, algae, or chemical deposits. Pay particular attention to grooves and crevices, O-rings, and support structures for the glass-fiber filter, where inorganic or organic materials might be lodged. Pump detergent solution through tubing. Place components of the plate-filter assembly onto a clean, aluminum-foil-covered surface.

5. Discard detergent solution from basin, rinse basin with tapwater, and place components of the plate-filter assembly into the basin. Change gloves.

6. Rinse each component thoroughly to remove detergent residue, paying particular attention to grooves and crevices. Use a wash bottle filled with DIW or tapwater to rinse hard-to-reach places. Place rinsed components onto a dry section of clean aluminum foil or basin. Change gloves. If the assembly will be rinsed with

methanol or other organic solvent, change to disposable, solvent-resistant gloves, and place components of the filter assembly into a clean, solvent-resistant washbasin.

7. Rinse plate-filter assembly components with pesticide-grade methanol or an equivalent grade for other organic solvents. Do not methanol rinse any tubing or filtration assembly to be used for collecting or processing samples for TOC, DOC, or SOC analysis. The instructions for the methanol rinse apply also for use of any other organic solvent. **Rinse the equipment with methanol while outside of the field vehicle and downwind of sampling activity.**

   a. Dispense methanol from a fluorocarbon-polymer wash bottle. Rinse all sample-contacting surfaces of filter-assembly components and tubing over a solvent-resistant basin or waste container. ***Methanol-laced rinse water must be collected into an appropriate waste container designed for flammable liquids.***

   b. Place methanol-rinsed equipment components onto a clean aluminum foil surface to air dry. (Cover equipment components loosely with an aluminum foil tent, if concerned about airborne contaminants.)

8. Reassemble the plate-filter assembly. Wrap nozzles with aluminum foil and seal filter assembly in plastic bags. Double bag for transport or for long-term storage.

3.3.4.C Pressure-Filter Assembly Cleaning Procedure

The cleaning procedures described in section 3.2.2 for figure 3-4 do not apply to the filtration assembly used for samples to be analyzed for DOC and SOC. The filtration assembly for processing organic-carbon samples is a gas-pressurized apparatus constructed of either stainless steel or fluorocarbon-polymer material.

- **Do not bring the pressure-filter assembly in contact with methanol or other organic solvent or organic-solvent vapors.**
- In general, office-produced organic-grade water that is prepared by being passed through appropriate columns to remove organic compounds is of adequate purity for cleaning this equipment. PBW or VBW also can be used. Office-produced organic-grade water, however, must not be substituted for blank samples.

▶ **Do not clean the pressure-filter assembly with detergent.** Exception: see Step 3 below.

When using office-laboratory or field-site cleaning procedures for cleaning the pressure-filter assembly:

1. Wearing disposable, powderless gloves, disassemble the pressure-filter assembly before it dries and place components into a clean washbasin. Change gloves.

2. Using office-produced organic-grade water, thoroughly rinse the pressure-filter assembly and place it into a washbasin or onto a clean surface. Generally, these steps are sufficient to field clean the pressure-filter assembly.

   - If necessary, use a soft-bristled toothbrush to remove sediment, chemical deposits, and other foreign material from threaded components, gaskets, O-rings, support screens, grooves, and nozzles. Take care not to scratch or mar inner surfaces when scrubbing.

   - Rinse the pressure-filter assembly thoroughly with office-produced organic-grade water or PBW or VBW.

3. If the pressure-filter assembly is very dirty or contaminated, clean as follows:

   a. Disassemble and soak assembly for at least 1 hour in a 0.1-percent solution of nonphosphate laboratory-grade detergent.

   b. Scrub with a soft-bristled toothbrush, as described above in 2.

   c. Rinse repeatedly with office-produced organic-grade water, being sure to remove all traces of detergent.

4. Place all components of the pressure-filter assembly onto aluminum foil and allow to air dry thoroughly under a protective aluminum foil tent.

5. Reassemble the pressure-filter assembly, wrap nozzles in aluminum foil, and seal in a storage bag.

Do not use methanol or other organic solvents on the equipment used to filter samples for organic-carbon analyses.

3.3.5 SAMPLE TUBING CLEANING PROCEDURES

Cleaning procedures are described below for the tubing and nozzles used with peristaltic and valveless metering pumps. Cleaning procedures for submersible pump tubing are described in section 3.3.9.B. Wear appropriate, disposable, powderless gloves throughout the cleaning process, changing gloves with each change in cleaning solution as indicated throughout section 3.2.

- Preclean the number of tubing sections needed at each site in the office laboratory rather than recleaning tubing in the field, in order to save time during field work. Place into doubled plastic bags and store tubing dry or store wet tubing chilled to prevent bacterial growth. If bacterial growth is present, reclean tubing before use.
- Use disposable tubing if possible, especially at contaminated sites, to avoid the cleaning process and prevent the possibility of cross contamination.

When using office-laboratory or field-site procedures for cleaning plastic (including fluorocarbon-polymer) sample tubing used for samples to be analyzed for inorganic constituents, follow the general sequence of procedures described for figures 3-2 or 3-3, and those described for filtration assemblies (section 3.3.4).

To summarize the key steps for figures 3-2 or 3-3:

1. Pump 1 L of 5-percent HCl solution through the tubing, discharging the used acid solution into a neutralization container. Pinch and release tubing near tubing outlet while pumping the acid through to ensure that all interior surfaces are acid rinsed.
2. Pump 2 L of DIW through tubing, using the same pinch-and-release method. Discharge used DIW to an acid-neutralization container, and check that the rinse-water pH is greater than 6.0 or the original DIW pH.
3. Discard neutralized solutions appropriately.
4. Clean stainless steel connections or metal tubing using detergent-wash and tapwater/DIW rinse procedures.

When using office-laboratory or field-site procedures for cleaning tubing for organic-compound samples:

Follow the general sequence of procedures described for figures 3-1 and 3-4. Proceed with the methanol rinse after the detergent wash and tapwater rinse. If samples also will be collected for inorganic-constituent analysis, however, acid rinse nonmetallic tubing and components after the detergent wash/tapwater rinse and before continuing to the methanol rinse. When cleaning sample tubing:

1. Pump 1 L of nonphosphate, laboratory-grade detergent solution through tubing, followed by sufficient tapwater or DIW to remove detergent residue. Pinch and release tubing near tubing outlet while pumping the solution to ensure that all interior surfaces are cleaned.
2. Place discharge end of tubing from peristaltic or valveless metering pump over methanol waste container.
   - Pass one tubing volume of methanol through the same pump system used for filtration, using the same pinch-and-release method.
   - Short sections of tubing can be held over the waste container while dispensing the methanol from a fluorocarbon-polymer wash bottle instead of pumping the methanol through the tubing.
   - **Do not methanol rinse tubing to be used for samples for TOC, DOC, or SOC analysis.**
3. Store tubing in doubled plastic bags.

CAUTION: Do not use methanol around equipment that can create electrical sparks (see section 3.3.9.B).

3.3.6 PROCESSING AND PRESERVATION CHAMBERS AND FLOWTHROUGH CHAMBER CLEANING PROCEDURES

Processing and preservation chambers used to protect samples from atmospheric contamination generally are portable and are assembled at the field site. Large, clear plastic bags usually are clipped to the inside of the frame rather than stretched over the frame. Plastic clips are used to hold the cover tightly in place. When the bag is clipped to the inside, it is not necessary to field clean the chamber frame.

The flowthrough chamber, used when monitoring ground-water field measurements, is connected inline to the pump sampler. The flowthrough chamber should be kept free of sediment and dirt or deposits on the chamber walls. Air dry and store the chambers in sealable plastic bags.

When cleaning the processing and preservation chambers:

Office laboratory. Clean the frame of portable chambers in the office with detergent solution, then rinse thoroughly with tapwater and dry and store in plastic bags.

Field site. Frames require regular cleaning after each use at a site if chamber covers are stretched over the outside of the frame rather than clipped to the frame.

1. Discard the used bag.
2. Wipe the chamber frame with DIW.
3. Replace chamber cover only when the next samples are ready to be processed.
4. If the processing chamber is a fixed installation, clean out any spilled sample water, solid materials, or wash solutions, and swab down the inside using deionized water and lint-free laboratory tissue.
5. Use detergent solution followed by a thorough tapwater or DIW rinse if a spill has contaminated the chamber.
6. Store chamber frames in plastic bags.

When cleaning the flowthrough chamber:

1. Clean the flowthrough chamber in the office laboratory with detergent solution and rinse thoroughly with tapwater, followed by DIW. **Do not use acid solution or methanol.**
2. If the flowthrough chamber needs to be field cleaned, remove measurement sensors and clean with a dilute detergent solution; rinse thoroughly with tapwater followed by DIW.

RADON SAMPLER CLEANING PROCEDURE 3.3.7

Soak radon samplers in a detergent solution for 10 minutes and rinse thoroughly with tapwater to remove detergent residue; follow with three to five rinses with DIW. **Do not use methanol.** Air dry the radon sampler and store in doubled plastic bags.

3.3.8 SURFACE-WATER SAMPLER CLEANING PROCEDURES

Disassemble surface-water samplers for cleaning and follow the sequence of procedures described in section 3.2 and figures 3-2, 3-3, or 3-4, as appropriate.

When using office-laboratory procedures for cleaning surface-water samplers:

1. Periodically disassemble samplers for office-laboratory cleaning. **Discard the bag sampler bag after one use**—do not attempt to scrub or detergent wash the used bag. Prepare cleaning solutions, cleaning equipment, and cleaning area as described in section 3.2.

2. Soak components in detergent solution for 30 minutes. Put on appropriate disposable, powderless gloves. Scrub components with a soft brush or sponge and rinse thoroughly (section 3.2.1 or 3.2.2). Change gloves.

3. Check the sequence of cleaning procedures shown in figure 3-1.

   a. If the sampler is used for sampling inorganic constituents, soak each nonmetallic component in a 5-percent trace-metal-grade HCl solution for 30 minutes, followed by copious rinsing with DIW (section 3.2.1). **Acid rinse only nonmetal parts.** Change gloves.

      - Acid must not contact the metal collar on the DH-81 sampler.
      - Make sure that the nozzle is unscrewed from the cap.

   b. If the sampler is used for collecting organic-compound samples, rinse each component with pesticide-grade methanol dispensed from a fluorocarbon-polymer wash bottle and allow to air dry (section 3.2.2). **Do not methanol rinse tubing or components that will contact TOC, DOC, or SOC samples.** Change gloves.

4. If collecting an equipment blank (section 3.4), change gloves and rinse each component with the appropriate blank water before collecting the blank sample.

5. Reassemble the sampler. If the sampler is dedicated to sampling for organic compounds, double wrap the sampler nozzle in aluminum foil. Place the sampler into double plastic bags and seal for storage and transport.

When using field-site procedures for cleaning surface-water samplers:

1. Unwrap precleaned washbasins (one for each cleaning solution to be used).

2. Disassemble the used sampler into its component parts (bottle, cap, nozzle) so that all of the pieces can be thoroughly wetted with the various rinses. **Discard the previously used bag-sampler bag** (do not attempt to clean it for reuse).

3. Wearing appropriate disposable gloves, thoroughly rinse the sampler components with DIW. Use a stream of DIW from the wash bottle, if required.

4. Check whether target analytes are inorganic constituents, organic compounds, or both. Review figure 3-1 for the appropriate cleaning sequence.

   a. If a sampler will be used for collecting samples for analysis of inorganic constituents only, change gloves and

      i. Thoroughly rinse the sampler components with tapwater or DIW.

      ii. Acid rinse nonmetallic components over a container using a stream of dilute acid solution from the appropriate wash bottle, if required.

      iii. Thoroughly rerinse the sampler components with DIW over the same washbasin, if possible (see section 3.2.1). Change gloves.

      iv. Place each component on a clean, plastic surface. Pour used acid solution and DIW rinse water into neutralization container.

      v. Check the pH of the solution in the neutralization container. Discard when solution pH is greater than 6.0 or the original DIW pH. Change gloves.

   b. If a sampler will be used for collecting samples for analysis of organic compounds only, change gloves and

      i. Detergent wash, then rinse sampler components thoroughly with tapwater or DIW until agitated rinse water produces no more suds. Change to solvent-resistant gloves.

      ii. Rinse sampler components with pesticide-grade methanol (section 3.2.2), collecting the used methanol into an appropriate container for safe storage until appropriate disposal is arranged.

iii. Place each component on a clean, aluminum-foil-covered surface to air dry and cover loosely with an aluminum foil tent, if airborne contaminants are a concern. Change gloves.

c. If sampler will be used for collecting samples for both organic and inorganic analyses, change gloves and

i. Proceed with a detergent wash and thorough tapwater and (or) DIW rinse.

ii. Acid rinse and DIW rinse nonmetallic components, as described above, discarding used solutions appropriately. Change to solvent-resistant gloves.

iii. Rinse with methanol, if needed, as described above.

iv. Place cleaned items on a clean plastic surface to air dry.

5. Reassemble sampler. If the sampler is dedicated to sampling for organic compounds, double-wrap sampler nozzle in aluminum foil. Place sampler into doubled plastic bags for storage and transport.

Do not use methanol or other organic solvents on equipment used to collect organic-carbon samples.

GROUND-WATER SAMPLER CLEANING PROCEDURES 3.3.9

Ground water is sampled with nonpumping samplers (such as bailers, syringe samplers, and the Kemmerer sampler) and with pumping samplers (such as peristaltic and valveless metering pumps and submersible pumps). Office-laboratory cleaning procedures are used before a sampler is used for the first time, after the sampler has been in long-term storage, and whenever the sampler has become excessively contaminated. Field-site cleaning procedures are used after sampling at a field site and before proceeding to the next sampling site. Caveats and modifications that apply to the general office-laboratory and field-site cleaning procedures (section 3.2) are described in this section. The cleaning procedures used should be documented on field forms.

The rinse with methanol, or other organic solvent, is appropriate only for samplers being used to collect samples for organic-compound analysis. **Solvents are never used to clean equipment when sampling for TOC, DOC, or SOC.** Dispose of used methanol and all other cleaning solutions appropriately.

> TECHNICAL NOTE: Sampler components made of fluorocarbon-polymer plastic generally can withstand a solvent rinse with methanol. Check with the manufacturer before using an organic solvent on pump components constructed of any other plastic material.

3.3.9.A Cleaning of Bailers and Other Nonpumping Samplers

Office-laboratory procedure. Clean nonpumping samplers in a designated area of the office laboratory. Follow the procedures described for figures 3-2 and 3-4, as appropriate for equipment used to sample for inorganic constituents or organic compounds, respectively.

Field-site procedure. Follow the field-site cleaning procedures described for figures 3-3 and 3-4, as appropriate for equipment used to sample for inorganic constituents or organic compounds, respectively.

- Rinse the outside of the sampler with DIW directly after use.
- After filling the sampler with each cleaning solution, shake the sampler vigorously and drain solution through the bottom-emptying device, spigot, or nozzle of the sampler.
- If the sampler looks very dirty or is contaminated, disassemble and clean sampler components using the office-laboratory procedure.

3.3.9.B Cleaning of Submersible Pumps and Submersible-Pump Tubing

The general sequence shown in figure 3-5 is appropriate for cleaning most submersible pumps. The field-site cleaning procedure (described below after the office-laboratory procedure) is sufficient for routine cleaning of the pump in most cases. Collection of blank samples for quality control must be included as a standard protocol for every study in order to document and ensure the efficacy of the cleaning procedure for the field conditions encountered.

- ▶ Fluorocarbon-polymer tubing used to collect water containing large concentrations of volatile organic compounds (VOCs) can be difficult to clean adequately.

- Collect additional blanks if VOC concentrations in last sample collected through the tubing were greater than 500 µg/L.
- Pump tubing should be replaced rather than cleaned if VOC concentrations in last sample exceeded about 700 µg/L.

▶ Most submersible pumps have a stainless steel casing and other metal parts and should not be acid rinsed.

- To clean pumps that are excessively contaminated, a dilute acid rinse followed by copious water rinsing can be used occasionally without damaging the pump.
- Repeated rinsing with dilute acid solution can pit or corrode the pump's stainless steel surface. If the surface appears dulled, the pump must not be used for collecting trace-metal samples.

▶ Lubrication water inside water-lubricated pumps (for example, the Grundfos RediFlo2™) can become contaminated and cause contamination of subsequent samples. Replace the lubrication water with VBW each time after sampling and when cleaning the pump. Follow manufacturer's instructions.

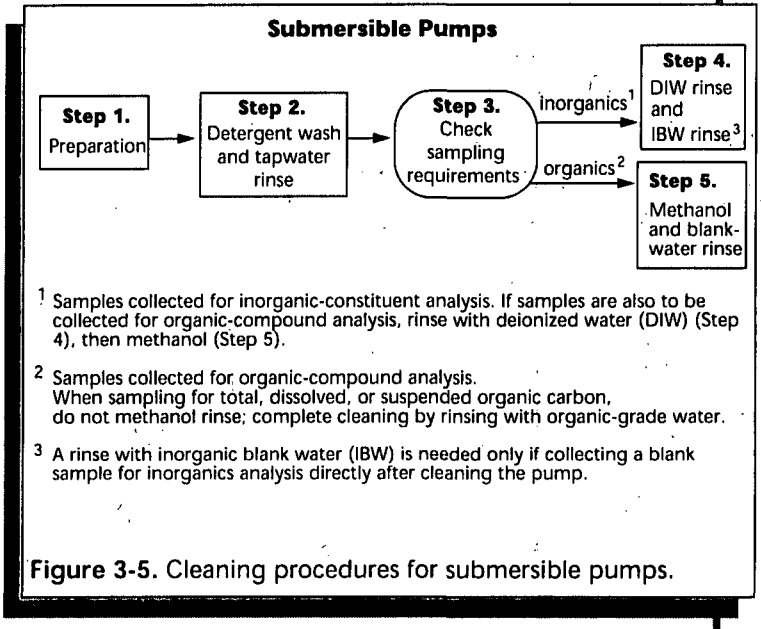


Figure 3-5. Cleaning procedures for submersible pumps.

Office-laboratory pump-cleaning procedure:

Use office-laboratory procedures about once a year and more frequently if results of the pump blank or other information indicate that the pump is contaminated.

Step 1. Preparation.

a. Wearing appropriate gloves, prepare several gallons of a laboratory-grade nonphosphate detergent solution (about 0.1 or 0.2 percent, v/v; use up to 2-percent solution for excessively contaminated pump systems).

b. Preclean washbasins and standpipes (section 3.2).

c. Place pump into sink or waste basin and scrub exterior surfaces with soft brush and detergent solution; rinse thoroughly with tapwater.

d. Disassemble the pump and place components into a detergent-solution washbasin.

Step 2. Detergent wash and tapwater rinse pump components and tubing.

a. Soak pump components in the detergent solution for 30 minutes.

b. Scrub pump components with soft sponge or brush.

c. Rinse thoroughly with tapwater.

d. Raise discharge end of tubing above the rest of the tubing. Using a peristaltic or valveless fluid metering pump, fill the pump tubing with fresh detergent solution until solution rises to the end of the tubing. Plug the tubing end(s).

e. After 30 minutes remove plug from discharge end of tubing and flush detergent solution from tubing by pumping copious amounts of tapwater through the tubing. Change gloves.

Step 3. Check sampling requirements.

— If pump will be used for collecting samples for inorganic-constituent analysis, reassemble the pump and go to Step 4.

— Complete Step 4 if pump will be used for collecting samples for analysis of both inorganic and organic analytes before proceeding to Step 5.

— If the pump will be used for collecting samples for organic-compound analyses only, go to Step 5.

Step 4. DIW rinse.

a. Place pump components into DIW washbasin and dispense DIW from a wash bottle to thoroughly rinse all pump components.

b. Using a peristaltic pump and appropriate clean tubing, pump DIW through the sample tubing to rinse.

c. Reassemble pump and connect pump tubing. Change gloves.

d. If collecting equipment blanks to verify that the pump has been adequately cleaned (section 3.4):

i. Rinse a clean standpipe dedicated to blank water with blank water.

ii. Insert pump into blank-water standpipe only after pump exterior has been rinsed with blank water or air dried after the methanol rinse.

iii. Pour IBW into the standpipe and pump at least one tubing volume to waste before collecting the blank sample.

Step 5. Rinse with blank water followed by a methanol rinse.

a **Change to latex or nitrile gloves.** Put pump components into solvent-resistant washbasin.

b. Working under a fume hood, dispense methanol (or appropriate solvent) from a fluorocarbon-polymer wash bottle to rinse each pump component and the exterior pump casing. Collect the used solvent into a nonflammable container for storage until disposal.

- **Do not reuse methanol or other solvents.**
- **Work under a fume hood, if possible, or in a well-ventilated area outside of the office laboratory, as methanol fumes can contaminate other equipment.**

c. Place methanol-rinsed components on a clean, aluminum foil surface and allow the pump components and casing to completely air dry before reassembling the pump (see section 3.2.2).

d. Using a valveless fluid metering pump and fluorocarbon-polymer tubing, pump about 2 L of methanol through sample tubing and to the methanol waste container.

e. Reassemble the pump and connect the pump tubing. Change gloves and dispose of the methanol-contaminated gloves appropriately.

f. Pour an organic-grade water (PBW or VBW) into a clean PBW/VBW standpipe. Insert pump and pass about two tubing volumes of organic-grade blank water (PBW or VBW) through the pump and tubing to waste.

CAUTION: Pumping methanol or other flammable solvents through an electrical pump system could be dangerous in the event of sparks. Methanol emits noxious fumes and is absorbed through the skin. Wear a mask, safety glasses, and other protective apparel to protect yourself when working with organic solvents.

Field-site cleaning procedure for submersible pumps and pump tubing:

Step 1. Preparation.

a. Preclean the standpipes (one standpipe for each cleaning solution to be used, as described in 3.2.1). The standpipes need to be of sufficient height to supply necessary head for proper pump operation. Separate standpipes are designated for detergent solution and tapwater rinse, DIW rinse, methanol rinse, and blank water (IBW/PBW/VBW). Double-bag each cleaned standpipe for transport to the field site.

b. Estimate the volumes of cleaning solutions and blank water that will be needed for the field effort (refer to fig. 3-6).

c. Prepare the volumes of cleaning solutions needed for the field effort, using appropriate bottles for short-term storage and transport.

The volume of storage in tubing, V_s, of a set of pump-reel and extension tubing can be estimated[1,2] as follows:

$$V_s = [(L_p \times C_p) + (L_e \times C_e) + V_{sp}] \times C_{sp}$$

where,

V_s is volume of storage in tubing, in gallons
L_p is length of pump-tubing segment being cleaned, in feet
L_e is length of extension tubing, in feet
C_p (or C_e) = 0.023 liter per foot for a 3/8-inch inside-diameter (ID) tubing
or = 0.041 liter per foot for a 1/2-inch ID tubing
V_{sp} is volume of solution needed to fill standpipe to minimum level required to operate pump, in liters[1]
C_{sp} = 0.264 gallon per liter.

Examples

Given:

1. L_p - sample-wetted tubing segment is 100 feet for a pump-reel system that has a 1/2-inch ID tubing;
2. L_e - two, 10-foot, 3/8-inch-ID pieces of extension tubing, one running from pump-reel outlet to sample collection chamber, and another running from chamber back to pump-reel (return-flow tubing to standpipe); and
3. V_{sp} - minimum volume[1] of solution required in standpipe to operate pump is 0.8 liter.

To estimate the volume of detergent solution needed for the detergent wash cycle:

$$V_s = [(100 \times 0.041) + (20 \times 0.023) + 0.8] \times 0.264 = 1.4 \text{ gallons}$$

The volume of office-produced deionized water needed to displace detergent solution and the volume of laboratory-produced organic-grade blank water needed to displace 2 liters of methanol just pumped into a system, ideally, would each be estimated to equal V_s[1,2].

[1]Estimate assumes no mixing of two solutions and ignores potential for detergent to adhere to tubing walls. Outflow from the discharge end of tubing should be checked for sudsing to determine that detergent has been removed.

[2]Estimate assumes no mixing at interface of two solutions and ignores potential for methanol to adhere to tubing walls. It is recommended that an additional 0.1 gallon (~ 0.4 liter) of blank water (pesticide-grade blank water or volatile-grade blank water) be used for each 10 feet of tubing to remove methanol residues from sample-wetted sections of tubing. Thus in the example above, another 1.1 (= (100 + 10) x (0.1/10)) gallons (4.2 liters) of blank water would be pumped from the system. This implies a total of about 2.5 (= 1.4 + 1.1) gallons (9.6 liters) of blank water would be used to remove methanol from the equipment setup.

[3]The minimum volume corresponds to the level of solution in the standpipe, which, if maintained, allows pump to operate without introducing air through the pump intake. Once this level is reached, remove pump, and measure this volume.

Figure 3-6. Estimation of cleaning-solution volumes for standpipe, pump, and pump tubing. [From Koterba and others, 1995, table 24.]

Step 2. Detergent wash and tapwater rinse.

a. Put on disposable, powderless gloves (usually vinyl). Rest pump in a washbasin or pail partially filled with detergent solution and clean exterior of pump and tubing with a soft brush. Rinse thoroughly with tapwater. (DIW can be substituted for tapwater, but is less efficient in detergent removal and requires a greater volume of water than tapwater.)

b. Place pump into standpipe, add detergent solution to level above pump intake, and route intake and discharge end of pump tubing to the standpipe.

c. Begin pumping:

   i. Record the pumping rate.

   ii. Record the time it takes to fill the sample tubing.

   iii. Calculate the time it takes for a segment of solution to complete one cycle (fig. 3-6).

d. Circulate detergent solution for about three cycles through the tubing and back to the standpipe. If possible, pump detergent solution through tubing at alternating high and low speeds, and (or) introduce air segments between aliquots of the detergent solution to increase cleaning efficiency.

e. Remove the discharge end of tubing from the standpipe and pump about two tubing volumes of detergent solution to waste, adding fresh solution to the standpipe as needed. Remove pump from standpipe.

f. Rinse detergent from standpipe with tapwater until sudsing stops.

g. Rinse pump exterior with tapwater. Place rinsed pump into standpipe; add tapwater/DIW to level above pump intake. Begin pumping through sample tubing. Do not recirculate rinse water, but add water as needed to maintain water level above pump intake. Continue for five or more tubing volumes. Direct rinse water to waste, away from the vicinity of the wellhead and sampling area and (or) contain as required for disposal.

h. Collect rinse water into a small bottle and stop the pump. Shake the bottle—if sudsing is observed in the rinse water, continue the rinse procedure until no suds appear in the rinse water. Change gloves.

Step 3. Check sampling requirements.

— If a pump will be used to collect samples for inorganic-constituent analysis, go to Step 4.

— Complete Step 4 if a pump will be used to collect samples for analysis of both inorganic and organic analytes and go to Step 5.

— If a pump will be used to collect samples for organic-compound analysis only, go to Step 5.

Step 4. DIW rinse.

A separate DIW rinse is not required if DIW was substituted for tapwater.

a. Use a clean DIW-dedicated standpipe, not the tapwater standpipe, and rinse with DIW. Rinse pump exterior with DIW to remove any detergent residue. Place pump into the DIW standpipe and add DIW to level above pump intake. Change gloves.

b. Start pumping DIW. Rinse DIW through sample tubing without recirculating, using about 3 tubing volumes of DIW. Keep the DIW level above pump intake.

c. Collect DIW rinse water in a clean bottle, shake, and check for suds. Continue to DIW rinse until rinse water is free of suds.

d. If collecting field blanks to verify that the pump has been adequately cleaned (section 3.4):

   i. Change gloves. Rinse clean blank-water standpipe with IBW. Rinse pump exterior with blank water.

   ii. Place pump into the standpipe and add IBW to cover the pump intake.

   iii. Turn on pump and displace any water residing in the pump and tubing. Continue pumping IBW for one tubing volume before collecting the blank sample.

Step 5. Methanol rinse.

Make certain that the pump or other nearby electrically powered equipment is grounded, the power cord is intact, and potential sources of sparks do not exist before rinsing pump with methanol.

TECHNICAL NOTES:

- Inspect the integrity of the seals and O-rings on the pump-motor/pump-body housing. Water inside the motor housing may indicate that methanol vapors could enter the motor. Direct-current motors inherently spark because of the commutator ring. AC motors might spark if the insulation is frayed or burnt on the motor windings or any associated wiring.

- If flammable liquids are required for cleaning electrical pump systems, use extreme caution. Vapors from solvents such as methanol can ignite if a disruption in the motor lead-insulation system occurs in the vapor-enriched zone. (Ignition from a spark from an AC induction-type motor in good operating condition is not a concern if rated as using the National Electrical Code (NEC) at Class 1, Group D.[5])

a. Change to latex or nitrile gloves. Wear safety glasses and apron. Work in a well-ventilated area outside of the field van and downwind of the sampling area.

b. Place pump into a clean, dedicated, solvent-resistant standpipe and route discharge end of sample tubing to a methanol waste container. Add methanol solution to level above pump intake.

c. Pump about 2 L of methanol through sample tubing into methanol waste container, keeping the level of solution above pump intake. The operator should stand back from the pump as a safety precaution in the event that an electrical spark ignites the methanol. Carefully put any unused methanol from bottom of standpipe into methanol waste container. Let methanol in the standpipe evaporate to dryness. Change gloves.

---

[5]NEC Class 1; Group D: Areas in which flammable gases or vapors may be present in the air in sufficient quantities to be explosive; atmospheres such as acetone, alcohol, ammonia, benzene, benzol, butane, gasoline, hexane, lacquer solvent vapors, naphtha, natural gas, propane, or gas or vapors of equivalent hazard (Cole-Parmer Instrument Company, 1997).

d. Rinse pump exterior with organic-grade water and place pump into standpipe. Add organic-grade water to the standpipe to push the methanol out of the tubing and into the methanol waste container. Pump at least an additional 0.1 gallon (about 0.38 L) of organic-grade water through the system for every 10 ft (about 3.05 m) of methanol-wetted tubing to the methanol waste container after used methanol is collected.

TECHNICAL NOTE: The recommended organic-grade water is PBW or VBW (supplied by NWQL for blank samples). Office-produced organic-grade water might not be of adequate purity, especially after being stored, and its use requires collection of additional blank samples for quality control (see section 3.4).

e. Repeat d above with blank water (PBW or VBW) pumped from a blank-water standpipe if blank samples will be collected for analysis of organic compounds.

Use of methanol is not recommended as a routine procedure for field cleaning of the pump. A methanol rinse is most safely accomplished as an office-laboratory procedure.

Storage of the cleaned submersible pump and tubing:

1. Place pump into two clean, noncontaminating storage bags and close bags.
2. Cover the pump reel and tubing with doubled plastic bags or sheeting for transport to the next site.

For long-term storage (longer than 3 days), the pump and exterior and interior of the tubing must be dry before being placed into plastic bags. Tubing can be dried by blowing filtered air or filtered (inert) gas through the tubing. If tubing cannot be dried, store chilled to prevent bacterial growth. If bacterial growth has occurred, reclean before use.

QUALITY CONTROL FOR EQUIPMENT-CLEANING PROCEDURES 3.4

By A.J. Horowitz, M.W. Sandstrom, and F.D. Wilde

Quality-control samples are required for any sampling and analysis program. Without quality-control information, the quality of the environmental data collected can be neither evaluated nor qualified. If the user has no means of knowing the associated errors, the data cannot be interpreted properly.

The purpose for obtaining quality-control (QC) samples following equipment cleaning is to ensure that the equipment and the procedures used for cleaning the equipment do not contaminate or otherwise affect the environmental samples that were or will be collected. The QC sample used to assess the adequacy of cleaning procedures before field work commences is called the equipment blank.

- **Blank water**. Blank water is used to develop specific types of QC samples (National Water Quality Laboratory Memorandum 92.01). The water is a solution that is free of analyte(s) of interest at a specified detection level. USGS personnel are required to use blank water that has been analyzed and certified to be of a specific grade and composition.
  - Use IBW to collect blank samples for analysis of inorganic constituents.
  - Use PBW to collect blank samples for analysis of pesticides. (Do not use PBW when collecting samples for VOC analysis.)
  - Use VBW to process blank samples for analysis of VOCs. VBW is also suitable as a blank sample for pesticide analysis.
  - Use PBW or VBW as the quality-control sample for total and dissolved organic-carbon analysis (TOC and DOC). This cannot be documented as a blank sample because neither PBW nor VBW is certified to be free of organic carbon.

- **Equipment blank.** An equipment blank is blank water that is processed under controlled conditions in the office laboratory by being passed sequentially through each component of the sample processing and collection equipment. **An equipment blank represents an entire sampling system (fig.3-7) and is required:**
  - Annually.
  - When a cleaning procedure is followed for the first time.
  - When new equipment will be used for the first time.

To fulfill equipment-blank requirements:

1. Allow enough time in the study workplan to collect the annual equipment blank, complete laboratory analyses, and review analytical results before field work for the study commences.
2. Process the annual equipment blank in a clean, controlled environment in the office laboratory, after the equipment has been cleaned using office-laboratory procedures.
3. Analyze the annual equipment-blank data before collecting and processing the first water-quality sample of either the fiscal year or the study.
   - If the equipment-blank data indicate that the equipment does not introduce contaminants that will bias study results, sampling can proceed.
   - If the equipment-blank data indicate unacceptable concentrations of analytes of interest, the cause must be identified and the equipment or cleaning procedures must be changed or modified before sampling can proceed.

Plan ahead: Assess equipment-blank data before environmental samples are collected.

- **Field blank.** The field blank is blank water that is processed at the field site by being passed sequentially through each component of the equipment being used to collect environmental samples. The procedure for processing the field blank, like the equipment blank, can also result in a set of sequentially collected blank samples (fig. 3-7) (Horowitz and others, 1994). Other types of blank samples also are collected at the field site (NFM 4). **At least one field blank per sampling run is recommended; the numbers and distribution of QC samples depend on study objectives, the target analytes, and site conditions.**

  - Process field blanks through clean equipment.
  - If equipment is used at several sites during a field trip, process a field-equipment blank after the last sample has been collected and again after the equipment has undergone the prescribed field-cleaning procedures.
  - If multiple sets of office-cleaned equipment are used during a field trip, process a field blank at any site during the course of the trip. In this case, the blank must be processed before sampling to avoid contaminating the blank with residues from an environmental sample.
  - Process field blanks onsite and under the same conditions as the environmental sample.

Before filling the QC sample bottle with the appropriate blank water:

1. Check that sample bottles are clean, are the correct type, and are labeled correctly.
2. Check the certificate of analysis for the lot of blank water to be sure that it is appropriate for quality control of target analytes.
3. Record the date and lot number of the IBW, PBW, and (or) VBW used and of the preservative used. To the extent possible, use preservative from the same lot number for an entire sampling trip for both the environmental and quality-control samples.
4. Rinse sample bottles for inorganic constituents three times with a small quantity of the blank water.

Use the following strategy for QC data collection and analysis:

1. For inorganic-constituent samples, initially send only the final equipment-blank sample for the routine inorganic blank-sample analysis or for inorganic analytes targeted by the study.

   - Archive the remaining sequentially processed blank samples (fig.3-7) until the inorganic-constituent analysis of the equipment-blank sample has been received.

   - Do not archive blank samples for organic-compound analysis.

2. Check the analytical results for the equipment blank and field blanks as soon as possible and before the next field trip.

   - If analytical results indicate that the equipment is clean within acceptable limits, the equipment may be used for field work without additional testing or analysis.

   - **Use of equipment is not recommended if analysis of the equipment blank sample indicates greater than acceptable analyte concentrations.**

3. Additional QC data collection and (or) analysis is required if the equipment blank has greater than acceptable analyte concentrations.

   - **For inorganic-sample analysis.** Submit the rest of the sequential blank samples for laboratory analysis and use the analytical results from the sequential blank samples to identify potential source(s) of contamination. Modify equipment-cleaning procedures if contamination can be remedied by a change in cleaning procedure. Repeat collection of equipment blanks until the blank data verify that the equipment is suitable for use.

   - **For organic-sample analysis.** Modify the equipment cleaning procedure if the source of contamination is known or suspected and contamination can be remedied by a change in cleaning procedure. If the source of contamination is not known, reclean equipment using office-laboratory procedures and collect and analyze blanks for each part of the sampling system that could be a source of contamination. Repeat collection of equipment blanks until the blank data verify that the equipment is suitable for use.

The equipment blank is the last sample of a set of sequentially processed blanks collected in the office laboratory and documents the suitability of the equipment for the samples that are to be collected and analyzed. **Field blanks** are collected in the field in the same manner as the equipment blank but document the effectiveness of the field-cleaning procedures plus any ambient contamination.

- Surface water: collect the series of five sequential blank samples listed below for routine surface-water sampling.
- Ground water: collect the source-solution blank (Sample 1) and either a sampler blank (Sample 2) or pump blank (Sample 4) (depending on the type of sampling device being used) along with the filter blank (Sample 5) .

Sample 1. SS blank	**Source solution (SS)** Put on disposable gloves. Pour the IBW, PBW, or VBW directly into appropriate SS blank-sample bottle.[1] Add chemical treatment and (or) chill, as required for the analytes of interest.
Sample 2. Sampler blank	**SS + Sampler** Bottle or bag sampler: Fill sampler container with SS; attach sampler cap and nozzle; decant sample into blank-sample bottle through the nozzle. Preserve sample (add chemical treatment and (or) chill) as required (NFM 5). Bailer or thief sampler: Fill sampler with SS; install bottom-emptying device; empty sample into blank-sample bottle through the bottom-emptying device. Preserve sample, as required. Submersible or nonsubmersible pumps: Go to Sample 4 (Pump blank).
Sample 3. Splitter blank	**SS + Sampler + Splitter**[2] If a cone or churn splitter is used, decant remainder of the SS into sampler container, and then through splitter (through nozzle or bottom-emptying device). Refill sampler container with SS to fill churn with 3 to 5 liters of water. Alternatively, pour enough SS from samplers through cone splitter to fill splitter-blank bottle. Collect SS into blank-sample bottle through churn spigot or cone-splitter exit port(s). Preserve sample, as required.
Sample 4. Pump blank	**SS + Sampler + Splitter + Pump** Nonsubmersible pump (peristaltic, vacuum, or valveless metering pump): Secure intake end of clean pump tubing into churn splitter or into a subsample split with the cone splitter. Pump some sample to waste to rinse tubing, and fill pump-blank bottle directly from the discharge end. Preserve sample, as required. Submersible pump: Place pump in blank-water standpipe and fill standpipe with enough SS to cover pump intake and allow for drawdown. Start pump at low pumping rate, discharge 0.5 liter of SS to waste, then fill blank-sample bottle with SS. Preserve sample, as required.
Sample 5. Filter or equipment blank	**SS + Sampler + Splitter + Pump + Filter** Pump SS through a prerinsed filtration assembly (plate filter or capsule filter); pump the first aliquot to waste and then pump SS directly into the blank-sample bottle. Preserve sample, as required.

[1]Process the source-solution blank in the protected environment of the office laboratory only, not in the field (NFM 4).

[2]For ground-water quality control: A splitter blank is included if a cone splitter is used; a standpipe blank often is collected if a submersible pump is used.

Figure 3-7. Sequence of sample collection to obtain the equipment blank

CONVERSION FACTORS AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
meter	3.281	foot
milliliter (mL)	0.06102	$inch^3$ or cubic inch
liter (L)	0.2642	gallon
microgram (µg)	3.53×10^{-8}	ounce

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$

ABBREVIATIONS

DIW	deionized water
DOC	dissolved organic carbon
HCl	hydrochloric acid
HNO_3	nitric acid
IBW	inorganic-grade blank water, laboratory-certified free of trace elements and other inorganic constituents
µg/L	micrograms per liter
µS/cm	microsiemens per centimeter at 25°C
MSDS	Material Safety Data Sheet
NFM	*National Field Manual for the Collection of Water-Quality Data*
NWQL	National Water Quality Laboratory of the U.S. Geological Survey
OWQ	Office of Water Quality of the U.S. Geological Survey
PBW	pesticide-grade blank water, certified free of pesticide organic compounds by the NWQL
PVC	polyvinyl chloride
QC	quality control
QWSU	Quality of Water Service Unit
SOC	suspended organic carbon
SS	source solution
TOC	total organic carbon
TWRI	Techniques of Water-Resources Investigations
URL	Uniform Resource Locator
USGS	U.S. Geological Survey
VBW	volatiles-grade blank water, certified free of volatile compounds by the NWQL
v/v	volume to volume

SELECTED REFERENCES AND INTERNAL DOCUMENTS

SELECTED REFERENCES FOR CLEANING OF EQUIPMENT FOR WATER SAMPLING

American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, variously paged.

American Society for Testing and Materials, 1990, Standard practice for decontamination of field equipment used at nonradioactive waste sites: Philadelphia, Pa., no. D 5088-90, 3 p.

Capel, P.D., and Larson, S.J., 1996, Evaluation of selected information on splitting devices for water samples: U.S. Geological Survey Water-Resources Investigations Report 95-4141, 103 p.

Cole-Parmer Instrument Company, 1997, 97-98 Catalog: Vernon Hills, Ill., Cole-Parmer Instrument Company, 1416 p.

Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.

Ivahnenko, Tamara, Szabo, Zoltan, and Hall, G.S., 1996, Use of an ultra-clean sampling technique with inductively coupled plasma-mass spectrometry to determine trace-element concentrations in water from the Kirkwood-Cohansey aquifer system, Coastal Plain, New Jersey: U.S. Geological Survey Open-File Report 96-142, 37 p.

Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95-398, 69 p.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1997, Guidelines and standard procedures for studies of ground-water quality—selection and installation of wells, and supporting documentation: U.S. Geological Survey Water-Resources Investigations Report 96-4233, 110 p.

Mudroch, Alena, and Azcue, J.M., 1995, Manual of aquatic sediment sampling: Boca Raton, Fla., Lewis Publishers Inc., 219 p.

Mudroch, Alena, and MacKnight, S.D., eds., 1994, Handbook of techniques for aquatic sediments sampling; Boca Raton, Fla., Lewis Publishers Inc., 236 p.

Sandstrom, M.W.,1990, Sampling requirements for organic contaminants, *in* American Water Works Association Annual Conference: Cincinnati, Ohio, Management Challenges of New Monitoring Requirements for Organic Chemicals, American Water Works Association Seminar Proceedings, p. 71-85.

Sandstrom, M.W., 1995, Filtration of water-sediment samples for the determination of organic compounds: U.S. Geological Survey Water-Resources Investigations Report 95-4105, 13 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.

Shelton, L.R., and Capel, P.D., 1994, Guidelines for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 94-458, 20 p.

Internal Documents

Office of Water Quality, National Water Quality Laboratory, and Water Resources Division numbered memorandums are available electronically on the Internet through the USGS Home Page on the World Wide Web. The site address (URL) is

http://water.usgs.gov/lookup/get?techmemo.

Water Quality

Memo No.	Title	Date
qw 92.01	Distilled/Deionized Water for District Operations	Dec. 20, 1991
qw 97.03	Protocols for Cleaning a Teflon Cone Splitter to Produce Contaminant-Free Subsamples for Subsequent Determinations of Trace Elements	Feb. 7, 1997

National Water Quality Laboratory (NWQL)

Memo No.	Title	Date
92.01	Technology Transfer—Availability of Equipment Blank Water for Inorganic and Organic Analysis	Mar. 25, 1992

Water Resources Division

Memo No.	Title	Date
wrd 94.007	Safety--Storage, Transportation, Handling and Disposal of Methyl Alcohol	Dec. 3, 1993

PUBLICATIONS ON TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The material is grouped under major subject headings called books and is further divided into sections and chapters. For example, Section A of Book 9 (Handbooks for Water-Resources Investigations) pertains to collection of water-quality data. The chapter, which is the unit of publication, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises.

The Techniques of Water-Resources Investigations (TWRI) reports listed below are for sale by the U.S. Geological Survey, Branch of Information Services, Box 25286, Federal Center, Denver, CO 80225 (authorized agent of the Superintendent of Documents, Government Printing Office). Prepayment is required. Remittance should be sent by check or money order payable to the U.S. Geological Survey. Prices are not included because they are subject to change. Current prices can be obtained by writing to the above address. When ordering or inquiring about prices for any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations." An updated list of TWRI reports can be found by accessing the World Wide Web url: http://water.usgs.gov/lookup/get?TWRI.

Book 1. Collection of Water Data by Direct Measurement

Section D. Water Quality

1-D1. Water temperature—influential factors, field measurement, and data presentation, by H.H. Stevens, Jr., J.F. Ficke, and G.F. Smoot: USGS—TWRI Book 1, Chapter D1. 1975. 65 pages.

1-D2. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents, by W.W. Wood: USGS—TWRI Book 1, Chapter D2. 1976. 24 pages.

Book 2. Collection of Environmental Data

Section D. Surface Geophysical Methods

2-D1. Application of surface geophysics to ground-water investigations, by A.A.R. Zohdy, G.P. Eaton, and D.R. Mabey: USGS—TWRI Book 2, Chapter D1. 1974. 116 pages.

2-D2. Application of seismic-refraction techniques to hydrologic studies, by F.P. Haeni: USGS—TWRI Book 2, Chapter D2. 1988. 86 pages.

Section E. Subsurface Geophysical Methods

2-E1.Application of borehole geophysics to water-resources investigations, by W.S. Keys and L.M. MacCary: USGS—TWRI Book 2, Chapter E1. 1971. 126 pages.

2-E2.Borehole geophysics applied to ground-water investigations, by W.S. Keys: USGS—TWRI Book 2, Chapter E2. 1990. 150 pages.

Section F. Drilling and Sampling Methods

2-F1.Application of drilling, coring, and sampling techniques to test holes and wells, by Eugene Shuter and W.E. Teasdale: USGS—TWRI Book 2, Chapter F1. 1989. 97 pages.

Book 3. Applications of Hydraulics

Section A. Surface-Water Techniques

3-A1.General field and office procedures for indirect discharge measurements, by M.A. Benson and Tate Dalrymple: USGS—TWRI Book 3, Chapter A1. 1967. 30 pages.

3-A2.Measurement of peak discharge by the slope-area method, by Tate Dalrymple and M.A. Benson: USGS—TWRI Book 3, Chapter A2. 1967. 12 pages.

3-A3.Measurement of peak discharge at culverts by indirect methods, by G.L. Bodhaine: USGS—TWRI Book 3, Chapter A3. 1968. 60 pages.

3-A4.Measurement of peak discharge at width contractions by indirect methods, by H.F. Matthai: USGS—TWRI Book 3, Chapter A4. 1967. 44 pages.

3-A5.Measurement of peak discharge at dams by indirect methods, by Harry Hulsing: USGS—TWRI Book 3, Chapter A5. 1967. 29 pages.

3-A6.General procedure for gaging streams, by R.W. Carter and Jacob Davidian: USGS—TWRI Book 3, Chapter A6. 1968. 13 pages.

3-A7.Stage measurement at gaging stations, by T.J. Buchanan and W.P. Somers: USGS—TWRI Book 3, Chapter A7. 1968. 28 pages.

3-A8.Discharge measurements at gaging stations, by T.J. Buchanan and W.P. Somers: USGS—TWRI Book 3, Chapter A8. 1969. 65 pages.

3-A9.Measurement of time of travel in streams by dye tracing, by F.A. Kilpatrick and J.F. Wilson, Jr.: USGS—TWRI Book 3, Chapter A9. 1989. 27 pages.

3-A10.Discharge ratings at gaging stations, by E.J. Kennedy: USGS—TWRI Book 3, Chapter A10. 1984. 59 pages.

3-A11.Measurement of discharge by the moving-boat method, by G.F. Smoot and C.E. Novak: USGS—TWRI Book 3, Chapter A11. 1969. 22 pages.

3-A12.Fluorometric procedures for dye tracing, Revised, by J.F. Wilson, Jr., E.D. Cobb, and F.A. Kilpatrick: USGS—TWRI Book 3, Chapter A12. 1986. 34 pages.

3-A13.Computation of continuous records of streamflow, by E.J. Kennedy: USGS—TWRI Book 3, Chapter A13. 1983. 53 pages.

3-A14.Use of flumes in measuring discharge, by F.A. Kilpatrick and V.R. Schneider: USGS—TWRI Book 3, Chapter A14. 1983. 46 pages.

3-A15.Computation of water-surface profiles in open channels, by Jacob Davidian: USGS—TWRI Book 3, Chapter A15. 1984. 48 pages.

3-A16.Measurement of discharge using tracers, by F.A. Kilpatrick and E.D. Cobb: USGS—TWRI Book 3, Chapter A16. 1985. 52 pages.

3-A17.Acoustic velocity meter systems, by Antonius Laenen: USGS—TWRI Book 3, Chapter A17. 1985. 38 pages.

3-A18.Determination of stream reaeration coefficients by use of tracers, by F.A. Kilpatrick, R.E. Rathbun, Nobuhiro Yotsukura, G.W. Parker, and L.L. DeLong: USGS—TWRI Book 3, Chapter A18. 1989. 52 pages.

3-A19.Levels at streamflow gaging stations, by E.J. Kennedy: USGS—TWRI Book 3, Chapter A19. 1990. 31 pages.

3-A20.Simulation of soluble waste transport and buildup in surface waters using tracers, by F.A. Kilpatrick: USGS—TWRI Book 3, Chapter A20. 1993. 38 pages.

3-A21.Stream-gaging cableways, by C. Russell Wagner: USGS—TWRI Book 3, Chapter A21. 1995. 56 pages.

Section B. Ground-Water Techniques

3-B1. Aquifer-test design, observation, and data analysis, by R.W. Stallman: USGS—TWRI Book 3, Chapter B1. 1971. 26 pages.

3-B2.Introduction to ground-water hydraulics, a programed text for self-instruction, by G.D. Bennett: USGS—TWRI Book 3, Chapter B2. 1976. 172 pages.

3-B3.Type curves for selected problems of flow to wells in confined aquifers, by J.E. Reed: USGS—TWRI Book 3, Chapter B3. 1980. 106 pages.

3-B4.Regression modeling of ground-water flow, by R.L. Cooley and R.L. Naff: USGS—TWRI Book 3, Chapter B4. 1990. 232 pages.

3-B4.Supplement 1. Regression modeling of ground-water flow—Modifications to the computer code for nonlinear regression solution of steady-state ground-water flow problems, by R.L. Cooley: USGS—TWRI Book 3, Chapter B4. 1993. 8 pages.

3-B5.Definition of boundary and initial conditions in the analysis of saturated ground-water flow systems—An introduction, by O. L. Franke, T.E. Reilly, and G.D. Bennett: USGS—TWRI Book 3, Chapter B5. 1987. 15 pages.

3-B6.The principle of superposition and its application in ground-water hydraulics, by T.E. Reilly, O.L. Franke, and G.D. Bennett: USGS—TWRI Book 3, Chapter B6. 1987. 28 pages.

3-B7.Analytical solutions for one-, two-, and three-dimensional solute transport in ground-water systems with uniform flow, by E.J. Wexler: USGS—TWRI Book 3, Chapter B7. 1992. 190 pages.

Section C. Sedimentation and Erosion Techniques

3-C1.Fluvial sediment concepts, by H. P. Guy: USGS—TWRI Book 3, Chapter C1. 1970. 55 pages.

3-C2.Field methods for measurement of fluvial sediment, by T.K. Edwards and G.D. Glysson: USGS—TWRI Book 3, Chapter C2. 1998. 80 pages.

3-C3.Computation of fluvial-sediment discharge, by George Porterfield: USGS—TWRI Book 3, Chapter C3. 1972. 66 pages.

Book 4. Hydrologic Analysis and Interpretation

Section A. Statistical Analysis

4-A1.Some statistical tools in hydrology, by H.C. Riggs: USGS—TWRI Book 4, Chapter A1. 1968. 39 pages.

4-A2.Frequency curves, by H.C. Riggs: USGS—TWRI Book 4, Chapter A2. 1968. 15 pages.

Section B. Surface Water

4-B1.Low-flow investigations, by H.C. Riggs: USGS—TWRI Book 4, Chapter B1. 1972. 18 pages.

4-B2.Storage analyses for water supply, by H.C. Riggs and C.H. Hardison: USGS—TWRI Book 4, Chapter B2. 1973. 20 pages.

4-B3.Regional analyses of streamflow characteristics, by H.C. Riggs: USGS—TWRI Book 4, Chapter B3. 1973. 15 pages.

Section D. Interrelated Phases of the Hydrologic Cycle

4-D1.Computation of rate and volume of stream depletion by wells, by C. T. Jenkins: USGS—TWRI Book 4, Chapter D1. 1970. 17 pages.

Book 5. Laboratory Analysis

Section A. Water Analysis

5-A1.Methods for determination of inorganic substances in water and fluvial sediments, by M.J. Fishman and L.C. Friedman, editors: USGS—TWRI Book 5, Chapter A1. 1989. 545 pages.

5-A2.Determination of minor elements in water by emission spectroscopy, by P.R. Barnett and E.C. Mallory, Jr.: USGS—TWRI Book 5, Chapter A2. 1971. 31 pages.

5-A3.Methods for the determination of organic substances in water and fluvial sediments, edited by R.L. Wershaw, M.J. Fishman, R.R. Grabbe, and L.E. Lowe: USGS—TWRI Book 5, Chapter A3. 1987. 80 pages.

5-A4.Methods for collection and analysis of aquatic biological and microbiological samples, by L.J. Britton and P.E. Greeson, editors: USGS—TWRI Book 5, Chapter A4. 1989. 363 pages.

5-A5.Methods for determination of radioactive substances in water and fluvial sediments, by L.L. Thatcher, V.J. Janzer, and K.W. Edwards: USGS—TWRI Book 5, Chapter A5. 1977. 95 pages.

5-A6.Quality assurance practices for the chemical and biological analyses of water and fluvial sediments, by L.C. Friedman and D.E. Erdmann: USGS—TWRI Book 5, Chapter A6. 1982. 181 pages.

Section C. Sediment Analysis

5-C1.Laboratory theory and methods for sediment analysis, by H. P. Guy: USGS—TWRI Book 5, Chapter C1. 1969. 58 pages.

Book 6. Modeling Techniques

Section A. Ground Water

6-A1.A modular three-dimensional finite-difference ground-water flow model, by M. G. McDonald and A. W. Harbaugh: USGS—TWRI Book 6, Chapter A1. 1988. 586 pages.

6-A2.Documentation of a computer program to simulate aquifer-system compaction using the modular finite-difference ground-water flow model, by S.A. Leake and D.E. Prudic: USGS—TWRI Book 6, Chapter A2. 1991. 68 pages.

6-A3.A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 1: Model Description and User's Manual, by L. J. Torak: USGS—TWRI Book 6, Chapter A3. 1993. 136 pages.

6-A4.A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 2: Derivation of finite-element equations and comparisons with analytical solutions, by R.L. Cooley: USGS—TWRI Book 6, Chapter A4. 1992. 108 pages.

6-A5.A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 3: Design philosophy and programming details, by L.J. Torak: USGS—TWRI Book 6, Chapter A5, 1993. 243 pages.

6-A6.A coupled surface-water and ground-water flow model (MODBRANCH) for simulation of stream-aquifer interaction by E.D. Swain and Eliezer J. Wexler: USGS—TWRI Book 6, Chapter A6, 1996. 125 pages.

Book 7. Automated Data Processing and Computations

Section C. Computer Programs

7-C1.Finite difference model for aquifer simulation in two dimensions with results of numerical experiments, by P.C. Trescott, G.F. Pinder, and S.P. Larson: USGS—TWRI Book 7, Chapter C1. 1976. 116 pages.

7-C2.Computer model of two-dimensional solute transport and dispersion in ground water, by L.F. Konikow and J.D. Bredehoeft: USGS—TWRI Book 7, Chapter C2. 1978. 90 pages.

7-C3.A model for simulation of flow in singular and interconnected channels, by R.W. Schaffranek, R.A. Baltzer, and D.E. Goldberg: USGS—TWRI Book 7, Chapter C3. 1981. 110 pages.

Book 8. Instrumentation

Section A. Instruments for Measurement of Water Level

8-A1.Methods of measuring water levels in deep wells, by M.S. Garber and F.C. Koopman: USGS—TWRI Book 8, Chapter A1. 1968. 23 pages.

8-A2.Installation and service manual for U.S. Geological Survey manometers, by J.D. Craig: USGS—TWRI Book 8, Chapter A2. 1983. 57 pages.

Section B. Instruments for Measurement of Discharge

8-B2.Calibration and maintenance of vertical-axis type current meters, by G.F. Smoot and C.E. Novak: USGS—TWRI Book 8, Chapter B2. 1968. 15 pages.

Book 9. Handbooks for Water-Resources Investigations

Section A. National Field Manual for the Collection of Water-Quality Data

9-A1.Preparations for water sampling, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo: USGS—TWRI Book 9, Chapter A1. 1998. Variously paged.

9-A2.Selection of equipment for water sampling, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A2. 1998. Variously paged.

9-A3. Cleaning of equipment for water sampling, by F.D. Wilde, D.B., Radke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A3. 1998. Variously paged.

9-A6.Field measurements, by F.D. Wilde and D.B. Radtke, editors: USGS—TWRI Book 9, Chapter A6. 1998. Variously paged.

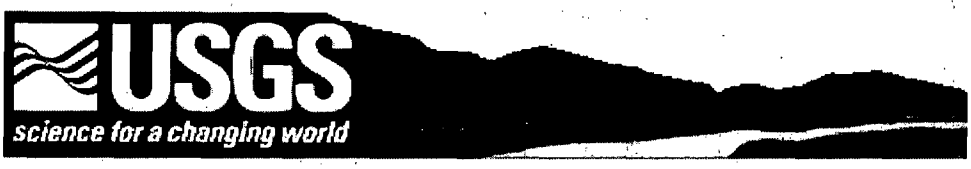
9-A7.Biological indicators, by D.N. Myers and F.D. Wilde, editors: USGS—TWRI Book 9, Chapter A7. 1997. Variously paged.

9-A8.Bottom-material samples, by D.B. Radtke: USGS—TWRI Book 9, Chapter A8. 1998. Variously paged.

9-A9.Safety in field activities, by S.L. Lane and R.G. Fay: USGS—TWRI Book 9, Chapter A9. 1998. Variously paged.

ISBN 0-607-90850-5





Water Resources--Office of Water Quality

This document is also available in pdf format: *Complete pdf for Chapter A4*

- **Comments/errata page**
- **Citation Information**

CHAPTER A4. COLLECTION OF WATER SAMPLES

Cover/Title Page
Back of Title Page
Foreword

Abstract
Introduction

Purpose and scope
Requirements and recommendations
Field manual review and revision
Acknowledgments

A4 Collection of Water Samples
Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo, editors

4.0 Techniques to prevent sample contamination
F.D. Wilde and D.B. Radtke

4.1 Surface-water sampling: collection methods at flowing-water and still-water sites
W.E. Webb, D.B. Radtke, and R. T. Iwatsubo

4.2 Ground-water sampling: preparations and purging methods at water-supply wells and monitoring wells
Jacob Gibs and F.D. Wilde

4.3 Quality-control samples
F.D. Wilde, T.L. Schertz and D.B. Radtke

Conversion factors, selected terms, and abbreviations

Selected references and internal documents

Publications on Techniques of Water-Resources Investigations

Appendix

Appendix A4-A. Transit rate and volume guidelines for isokinetic sampling
Appendix A4-B. Quality-control samples collected by field personnel for water-quality studies
Appendix A4-C. Examples from the National Water-Quality Assessment Program related to protocols for collecting blank samples at ground-water sampling sites

⇨ Abstract
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

http://water.usgs.gov/owq/FieldManual/chapter4/Ch4_contents.html
Privacy Statement || Disclaimer || Accessibility

USGS

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data



Chapter A4. COLLECTION OF WATER SAMPLES

Edited by
F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo

USGS

⇨Titlepage
⇧Return to Chapter A4 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

USGS

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

For additional information write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

Copies of this report can be purchased from:
U.S. Geological Survey
Information Services
Box 25286, Federal Center
Denver, CO 80225

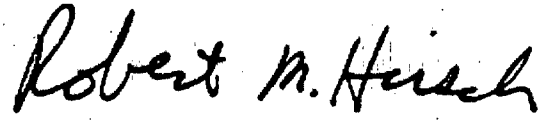
⇨Foreword
⇧Return to Chapter A4 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

USGS

Foreword

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.



Robert M. Hirsch
Chief Hydrologist

⇧Return to Chapter A4 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

USGS

Water Resources--Office of Water Quality

This document is also available in pdf format: abstract.pdf

National Field Manual

CHAPTER A4. COLLECTION OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data that are used to assess the quality of the Nation's surface-water and ground-water resources. This chapter provides information and addresses appropriate methods for the collection of surface-water, ground-water, and associated quality-control samples. Among the topics covered are procedures to prevent sample contamination; instructions for collecting isokinetic, depth-integrated samples from streams; and guidelines and criteria for purging wells in preparation for collecting samples from ground water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A4 provides information about the collection of water samples for investigations and assessments of environmental water quality. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this chapter.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual* . Other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to Chapter A6 on "Field Measurements" and NFM 6.4 refers to the section on field measurement of pH.

The procedures described in this chapter represent protocols that are generally applicable to USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter of the *National Field Manual* is to provide field personnel and other interested parties with a description of the requirements, recommendations, and guidelines routinely used in USGS studies involving the collection of water-quality samples. The information provided covers topics fundamental to the collection of water samples that are representative of the ambient environment. The information provided does not attempt to encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. Also beyond the scope of this chapter is discussion of procedures to collect samples for analysis of suspended or biological materials.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District' or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

⇨ Section 4.0 Contents
⇧ Return to Chapter A4 Contents
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

USGS

Water Resources--Office of Water Quality

This document is also available in pdf format: abstract.pdf

National Field Manual

CHAPTER A4. COLLECTION OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data that are used to assess the quality of the Nation's surface-water and ground-water resources. This chapter provides information and addresses appropriate methods for the collection of surface-water, ground-water, and associated quality-control samples. Among the topics covered are procedures to prevent sample contamination; instructions for collecting isokinetic, depth-integrated samples from streams; and guidelines and criteria for purging wells in preparation for collecting samples from ground water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A4 provides information about the collection of water samples for investigations and assessments of environmental water quality. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this chapter.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual* . Other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to Chapter A6 on "Field Measurements" and NFM 6.4 refers to the section on field measurement of pH.

The procedures described in this chapter represent protocols that are generally applicable to USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter of the *National Field Manual* is to provide field personnel and other interested parties with a description of the requirements, recommendations, and guidelines routinely used in USGS studies involving the collection of water-quality samples. The information provided covers topics fundamental to the collection of water samples that are representative of the ambient environment. The information provided does not attempt to encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. Also beyond the scope of this chapter is discussion of procedures to collect samples for analysis of suspended or biological materials.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District' or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

⇨ Section 4.0 Contents
⇧ Return to Chapter A4 Contents
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

USGS

Water Resources--Office of Water Quality

This document is also available in pdf format: abstract.pdf

National Field Manual

CHAPTER A4. COLLECTION OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data that are used to assess the quality of the Nation's surface-water and ground-water resources. This chapter provides information and addresses appropriate methods for the collection of surface-water, ground-water, and associated quality-control samples. Among the topics covered are procedures to prevent sample contamination; instructions for collecting isokinetic, depth-integrated samples from streams; and guidelines and criteria for purging wells in preparation for collecting samples from ground water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A4 provides information about the collection of water samples for investigations and assessments of environmental water quality. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this chapter.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual* . Other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to Chapter A6 on "Field Measurements" and NFM 6.4 refers to the section on field measurement of pH.

The procedures described in this chapter represent protocols that are generally applicable to USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter of the *National Field Manual* is to provide field personnel and other interested parties with a description of the requirements, recommendations, and guidelines routinely used in USGS studies involving the collection of water-quality samples. The information provided covers topics fundamental to the collection of water samples that are representative of the ambient environment. The information provided does not attempt to encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. Also beyond the scope of this chapter is discussion of procedures to collect samples for analysis of suspended or biological materials.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

⇨ Section 4.0 Contents
⇧ Return to Chapter A4 Contents
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

USGS

Water Resources--Office of Water Quality

This document is also available in pdf format: abstract.pdf

National Field Manual

CHAPTER A4. COLLECTION OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data that are used to assess the quality of the Nation's surface-water and ground-water resources. This chapter provides information and addresses appropriate methods for the collection of surface-water, ground-water, and associated quality-control samples. Among the topics covered are procedures to prevent sample contamination; instructions for collecting isokinetic, depth-integrated samples from streams; and guidelines and criteria for purging wells in preparation for collecting samples from ground water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A4 provides information about the collection of water samples for investigations and assessments of environmental water quality. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this chapter.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual* . Other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to Chapter A6 on "Field Measurements" and NFM 6.4 refers to the section on field measurement of pH.

The procedures described in this chapter represent protocols that are generally applicable to USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter of the *National Field Manual* is to provide field personnel and other interested parties with a description of the requirements, recommendations, and guidelines routinely used in USGS studies involving the collection of water-quality samples. The information provided covers topics fundamental to the collection of water samples that are representative of the ambient environment. The information provided does not attempt to encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. Also beyond the scope of this chapter is discussion of procedures to collect samples for analysis of suspended or biological materials.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

⇨ Section 4.0 Contents
⇧ Return to Chapter A4 Contents
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

USGS

Water Resources--Office of Water Quality

This document is also available in pdf format: abstract.pdf

National Field Manual

CHAPTER A4. COLLECTION OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data that are used to assess the quality of the Nation's surface-water and ground-water resources. This chapter provides information and addresses appropriate methods for the collection of surface-water, ground-water, and associated quality-control samples. Among the topics covered are procedures to prevent sample contamination; instructions for collecting isokinetic, depth-integrated samples from streams; and guidelines and criteria for purging wells in preparation for collecting samples from ground water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A4 provides information about the collection of water samples for investigations and assessments of environmental water quality. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this chapter.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual* . Other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to Chapter A6 on "Field Measurements" and NFM 6.4 refers to the section on field measurement of pH.

The procedures described in this chapter represent protocols that are generally applicable to USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter of the *National Field Manual* is to provide field personnel and other interested parties with a description of the requirements, recommendations, and guidelines routinely used in USGS studies involving the collection of water-quality samples. The information provided covers topics fundamental to the collection of water samples that are representative of the ambient environment. The information provided does not attempt to encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. Also beyond the scope of this chapter is discussion of procedures to collect samples for analysis of suspended or biological materials.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

⇨ Section 4.0 Contents
⇧ Return to Chapter A4 Contents
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

USGS

Water Resources--Office of Water Quality

This document is also available in pdf format: Chapter A4.pdf

COLLECTION OF WATER SAMPLES A4

This chapter of the *National Field Manual* describes standard USGS methods (sampling strategies, techniques, requirements, and recommendations) for routine collection of representative water samples. A representative sample is one that typifies the ambient targeted characteristics of the media of interest at the time of collection. Obtaining representative samples is of primary importance for an accurate description of the environment. In order to collect a representative sample that will yield the information required, (1) study objectives, including data-quality requirements,[2] must be understood in the context of the water system to be sampled and (2) artifacts of the sampling process must be minimized.[3] Field personnel must be alert to conditions that could compromise the quality of a sample.

- **Think contamination!** To ensure the integrity of the sample, be aware of possible sources of contamination. Contamination introduced during each phase of sample collection (and processing is additive and usually is substantially greater than contamination introduced elsewhere in the sample-handling and -analysis process. **Collect sufficient quality-control samples.**
- **Collect a representative sample.** Use appropriate procedures and quality-assurance measures tha ensure sample representativeness and integrity and that meet study criteria.

Before field work begins, review the preparations for water sampling described in NFM 1 and the safety requirements described in NFM 9. Sampling plans should be prepared and reviewed in advance. Some programs require chain-of-custody documentation and (or) a prescribed format for sampling and safety plans (SAPs).

- **Never compromise the safety of field personnel.**
- **Become thoroughly familiar with sample processing requirements (NFM 5) before proceeding to collect water samples.**
- **Keep clear and precise field records.** Implement the methods described in this chapter conscientiously and consistently, as appropriate to study objectives and site conditions. **Any departure from standard methods needs to be documented, quality assured, and reported with the data and interpretation of the data.**

Sample collection forms a continuum with sample processing, and information in this chapter (such as collecting quality-control samples) overlaps to some extent with the information in NFM 5 for processing of water samples.

---

[2]As used in this report, data-quality requirements refer to that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the variability allowable to fulfill the scientific objectives of the study.

[3]The degree to which a sample can be considered representative of a water body depends on many interrelated factors including, for example, temporal and spatial homogeneity of the water body, sample size, and the method and manner of sample collection.

⇨Section 4.0
⇧Return to Abstract
⇧Return to Chapter A4 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data



Chapter A4. COLLECTION OF WATER SAMPLES

Edited by
F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

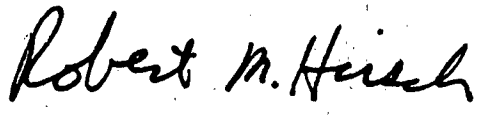
For additional information write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

Copies of this report can be purchased from:
U.S. Geological Survey
Information Services
Box 25286, Federal Center
Denver, CO 80225

Foreword

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a National Field Manual is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.



Robert M. Hirsch
Chief Hydrologist

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

Chapters of Section A: National Field Manual for the Collection of Water-Quality Data

A1. Preparations for Water Sampling

A2. Selection of Equipment for Water Sampling

A3. Cleaning of Equipment for Water Sampling

A4. Collection of Water Samples

A5. Processing of Water Samples

A6. Field Measurements
- 6.0 General Information and Guidelines
- 6.1 Temperature
- 6.2 Dissolved Oxygen
- 6.3 Specific Electrical Conductance
- 6.4 pH
- 6.5 Reduction-Oxidation Potential (Electrode Method)
- 6.6 Alkalinity and Acid Neutralizing Capacity
- 6.7 Turbidity

A7. Biological Indicators
- 7.1 Fecal Indicator Bacteria
- 7.2 Five-Day Biochemical Oxygen Demand

A8. Bottom-Material Samples

A9. Safety in Field Activities

COLLECTION OF WATER SAMPLES A4.

National Field Manual for the Collection of Water-Quality Data

Chapter A4.

Page

Abstract 7

Introduction 8

Purpose and scope 8

Requirements and recommendations 9

Field manual review and revision 10

Acknowledgments 11

A4. Collection of Water Samples 13

4.0 Techniques to prevent sample contamination 15
F.D. Wilde and D.B. Radtke

4.0.1 Clean-sampling procedures 17

4.0.2 Field rinsing of equipment 19

4.0.2.A Surface-water bottle samplers and bag samplers 19

4.0.2.B Churn splitter 20

4.0.2.C Cone splitter 20

4.0.2.D Ground-water samplers 21

4.0.3 Avoiding exchange of sample with atmospheric gases 22

4.1 Surface-water sampling: collection methods at flowing-water and still-water sites 23
W.E. Webb, D.B. Radtke, and R.T. Iwatsubo

4.1.1 Flowing-water sites 24

4.1.1.A Isokinetic, depth-integrated sampling methods 25

Equal-width-increment (EWI) method 30

Equal-discharge-increment (EDI) method 39

Single vertical at centroid-of-flow (VCF) method 47

4.1.1.B Nonisokinetic dip, discrete, and pump sampling methods 49

4.1.2 Still-water sites 56

4.2 Ground-water sampling: preparations and purging methods at water-supply wells and monitoring wells 61
Jacob Gibs and F.D. Wilde

4.2.1 Water-supply wells 74

4.2.2 Monitoring wells 80

4.3 Quality-control samples 91
F.D. Wilde, T.L. Schertz, and D.B. Radtke

4.3.1 Blank samples 93

4.3.1.A Source-solution, equipment, trip, and other prefield blanks 94

4.3.1.B Ambient and field blanks 95

Ambient blanks 96

Field blanks 97

4.3.2 Replicate samples 99

4.3.2.A Concurrent replicate samples 99

4.3.2.B Sequential replicate samples 100

4.3.2.C Split replicate samples 100

4.3.3 Spike samples 101

4.3.4 Reference samples 102

4.3.5 Blind samples 103

Conversion factors, selected terms, and abbreviations CF–1

Selected references and internal documents.....REF–1

Publications on Techniques of Water-Resources Investigations.....TWRI–1

Appendix A4-A. Transit rate and volume guidelines for isokinetic sampling.....APP–A1

Tables showing:

1a. Isokinetic transit rates for a 1-liter bottle sampler with a 3/16-inch nozzle APP–A3

1b. Isokinetic transit rates for a 1-liter bottle sampler with a 1/4-inch nozzle APP–A5

1c. Isokinetic transit rates for a 1-liter bottle sampler with a 5/16-inch nozzle APP–A7

2a. Isokinetic transit rates for a 3-liter bottle sampler with a 1/4-inch nozzle APP–A9

2b. Isokinetic transit rates for a 3-liter bottle sampler with a 5/16-inch nozzle APP–A11

3a. Minimum volumes for isokinetic sampling with a bag sampler APP–A13

3b. Isokinetic transit rates for a 3-liter bag sampler with a 1/4-inch nozzle APP–A15

3c. Isokinetic transit rates for a 3-liter bag sampler with a 5/16-inch nozzle APP–A17

Appendix A4-B. Quality-control samples collected by field personnel for water-quality studies APP–B1

Appendix A4-C. Examples from the National Water-Quality Assessment Program related to protocols for collecting blank samples at ground-water sampling sites APP–C1

1. Example of procedure to estimate and collect field volumes of blank solutions APP–C2

2. Example of procedure to collect blank samples with a submersible pump APP–C3

Illustrations

4-1. Relation between intake velocity and sediment concentration for isokinetic and nonisokinetic collection of water samples that contain particulates greater than 0.062 millimeters 27

4-2. Equal-width-increment method for collection of water samples 31

4-3. Equal-discharge-increment method for collection of water samples 40

4-4. Discharge-measurement field notes used to determine the equal-discharge-increment centroid locations based on cumulative discharge and far-midpoint stationing 43

4-5. Example of a manifold used for well purging and sample collection 64

4-6. Estimation of purge volume and purge time 71

4-7. Example of field form for a record of well purging 72

4-8. Example of procedure for collecting field blanks and associated blank samples 98

Tables

4-1. Good field practices for collection of water-quality samples 16

4-2. Clean Hands/Dirty Hands techniques for water-quality sampling 18

4-3. Uses and advantages of equal-width-increment and equal-discharge-increment sampling methods 29

4-4. Considerations for maintaining the integrity of ground-water samples 66

4-5. Advantages and disadvantages of collecting water samples from supply wells with permanently installed pumps 74



Chapter A4. COLLECTION OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data that are used to assess the quality of the Nation's surface-water and ground-water resources. This chapter provides information and addresses appropriate methods for the collection of surface-water, ground-water, and associated quality-control samples. Among the topics covered are procedures to prevent sample contamination; instructions for collecting isokinetic, depth-integrated samples from streams; and guidelines and criteria for purging wells in preparation for collecting samples from ground water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (requirements and recommendations) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A4 provides information about the collection of water samples for investigations and assessments of environmental water quality. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this chapter.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual* . Other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to Chapter A6 on "Field Measurements" and NFM 6.4 refers to the section on field measurement of pH.

The procedures described in this chapter represent protocols that are generally applicable to USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, (3) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter of the *National Field Manual* is to provide field personnel and other interested parties with a description of the requirements, recommendations, and guidelines routinely used in USGS studies involving the collection of water-quality samples. The information provided covers topics fundamental to the collection of water samples that are representative of the ambient environment. The information provided does not attempt to encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. Also beyond the scope of this chapter is discussion of procedures to collect samples for analysis of suspended or biological materials.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual* , the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that, on the basis of research and (or) consensus, the USGS Office of Water Quality recognizes one or several acceptable alternatives for selecting equipment or procedures. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the alternatives must be based on referenced research and good field judgment, and reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be mailed to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to nfm-owq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found near the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials included USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

Contributions that improved the technical quality of this document were provided by the following colleagues: H.D. Ardourel, B.A. Bernard, R.W. Boulger, Jr., K.K. Fitzgerald, S.R. Glodt, G.D. Glysson, J.R. Gray, H.E. Jobson, J.W. LaBaugh, A.H. Mullin, W.C. O'Neal, C.J. Patton, R.L. Rickman, S.K. Sando, M.W. Sandstrom, R.L. Snyder, and W.R. White. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn and A.M. Weaver was instrumental in enhancing the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.



A4. COLLECTION OF WATER SAMPLES

This chapter of the *National Field Manual* describes standard USGS methods (sampling strategies, techniques, requirements, and recommendations) for routine collection of representative water samples. A representative sample is one that typifies the ambient targeted characteristics of the media of interest at the time of collection. Obtaining representative samples is of primary importance for an accurate description of the environment. In order to collect a representative sample that will yield the information required, (1) study objectives, including data-quality requirements,[2] must be understood in the context of the water system to be sampled and (2) artifacts of the sampling process must be minimized.[3] Field personnel must be alert to conditions that could compromise the quality of a sample.

- **Think contamination!** To ensure the integrity of the sample, be aware of possible sources of contamination. Contamination introduced during each phase of sample collection (and processing) is additive and usually is substantially greater than contamination introduced elsewhere in the sample-handling and -analysis process. **Collect sufficient quality-control samples.**
- **Collect a representative sample.** Use appropriate procedures and quality-assurance measures that ensure sample representativeness and integrity and that meet study criteria.

[2]As used in this report, data-quality requirements refer to that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the variability allowable to fulfill the scientific objectives of the study.

[3]The degree to which a sample can be considered representative of a water body depends on many interrelated factors including, for example, temporal and spatial homogeneity of the water body, sample size, and the method and manner of sample collection.

Before field work begins, review the preparations for water sampling described in NFM 1 and the safety requirements described in NFM 9. Sampling plans should be prepared and reviewed in advance. Some programs require chain-of-custody documentation and (or) a prescribed format for sampling and safety plans (SAPs).

- **Never compromise the safety of field personnel.**
- **Become thoroughly familiar with sample processing requirements (NFM 5) before proceeding to collect water samples.**
- **Keep clear and precise field records.** Implement the methods described in this chapter conscientiously and consistently, as appropriate to study objectives and site conditions. **Any departure from standard methods needs to be documented, quality assured, and reported with the data and interpretation of the data.**

Sample collection forms a continuum with sample processing, and information in this chapter (such as collecting quality-control samples) overlaps to some extent with the information in NFM 5 for processing of water samples.

TECHNIQUES TO PREVENT SAMPLE CONTAMINATION 4.0

By F.D. Wilde and D.B. Radtke

Contamination of water samples can be prevented by planning the order in which sites will be sampled and by recognizing potential sources of contamination. NFM 1 provides information on reconnaissance of field sites. Sites should be sampled in the order of least to greatest potential for equipment fouling or contamination. The cleanest sites are often those that are in pristine environments, in areas where concentrations of dissolved solids are low, or upstream or upgradient from known or suspected sources of contamination.

The most common causes of sample contamination during sample collection include poor sample-handling techniques, atmospheric input, inadequately cleaned equipment, and use of equipment constructed of materials inappropriate for the analytes targeted for study. Contamination of samples from these sources can be prevented or minimized by adhering to good field practices (table 4-1). Use of Clean Hands/Dirty Hands sampling techniques is described in section 4.0.1, along with other clean-sampling procedures. Field rinsing of equipment to be used to collect and process samples is described in section 4.0.2. The considerations and planning required for collecting ground-water or other samples that contain gases are described in section 4.0.3. Collection of equipment blanks and field blanks is necessary to help identify potential sources of sample contamination (section 4.3). The same equipment that is used to collect (and/or process) environmental samples is to be used to collect (and/or process) blank samples.

Sample at sites with the least contamination or lowest chemical concentrations first.

Table 4-1. *Good field practices for collection of water-quality samples*

[Modified from "Rules for Trace-Metal Sampling" by Howard Taylor, U.S. Geological Survey, written communication, 1992; NFM, *National Field Manual for the Collection of Water-Quality Data*]

- Be aware of and record potential sources of contamination at each field site.
- Wear appropriate disposable, powderless gloves:
  - Change gloves before each new step during sample collection (and processing).
  - Avoid hand contact with contaminating surfaces (such as equipment, coins, food).
- Use equipment constructed of materials that are relatively inert with respect to the analytes to be collected (NFM 2).
- Use only equipment that has been cleaned according to prescribed procedures (NFM 3).
- Field rinse equipment, but only as directed. Some equipment for some analytes should not be field rinsed.
- Use correct sample-handling procedures:
  - Minimize the number of sample-handling steps.
  - Use Clean Hands/Dirty Hands techniques (table 4-2) as required for parts-per-billion trace-element sampling. Adapt Clean Hands/Dirty Hands techniques for other sample types, as appropriate. Obtain training for and practice field techniques under supervision before collecting water samples.
- Collect (and process) samples in enclosed chambers so as to minimize contamination from atmospheric sources.
- Collect a sufficient number of appropriate types of quality-control samples.
- Follow a prescribed order for collecting samples.

CLEAN-SAMPLING PROCEDURES 4.0.1

Clean-sampling procedures (sometimes called the parts-per-billion or ppb protocol) involve (1) using equipment that is constructed of noncontaminating materials (NFM 2) and that has been cleaned rigorously before field work and between field sites (NFM 3); (2) handling equipment in a manner that minimizes the chance of altering ambient sample composition; (3) handling samples in a manner that prevents contamination; and (4) routinely collecting quality-control (QC) samples. Clean Hands/Dirty Hands (*CH/DH*) techniques separate field duties and dedicate one individual (designated as Clean Hands) to tasks related to direct contact with the sample. *CH/DH* techniques are summarized on table 4-2. Implementation of this protocol requires hands-on training and field-team coordination.[4] **The field team must be trained in and practice these procedures before using them to collect samples.**

Clean-sampling procedures, including *CH/DH* techniques, were developed for collecting (and processing) samples vulnerable to contamination.

- **Requirement:** Clean-sampling procedures (such as *CH/DH* techniques) are required when collecting samples for analysis of metals and other inorganic trace elements (hereafter referred to collectively as trace elements), as follows:
  - For trace elements with ambient concentrations at or near 1 µg/L.
  - For iron, aluminum, or manganese with ambient concentrations to about 200 µg/L.
- **Recommendation:** Clean-sampling procedures are recommended when collecting samples for analysis of most trace elements with concentrations to about 100 µg/L.

[4]A detailed description of Clean Hands/Dirty Hands techniques can be found in Horowitz and others (1994). Clean Hands/Dirty Hands techniques also are included in procedures for equipment cleaning (refer to NFM 3) and sample processing (refer to NFM 5).

▶ **Recommendation:** Clean-sampling techniques are recommended when collecting samples for analysis of trace-organic compounds and major inorganic elements, particularly when the target analyte could be subject to contamination from field or laboratory procedures at a level that could exceed data-quality requirements.

Table 4-2. Clean Hands/Dirty Hands techniques for water-quality sampling

- Clean Hands/Dirty Hands techniques require two or more people working together.
- At the field site, one person is designated as Clean Hands (*CH*) and a second person as Dirty Hands (*DH*). Although specific tasks are assigned at the start to *CH* or *DH*, some tasks overlap and can be handled by either, as long as the prescribed care is taken to prevent contaminating the sample.
- Both *CH* and *DH* wear appropriate disposable, powderless gloves during the entire sampling operation and change gloves frequently, usually with each change in task. (Wearing multiple layers of gloves allows rapid glove changes.) **Gloves must be appropriate to withstand any acid, solvent, or other chemical substance that will be used or contacted.**
- *CH* takes care of all operations involving equipment that contacts the sample; for example, *CH*
  - Handles the surface-water sampler bottle.
  - Handles the discharge end of the surface-water or ground-water sample tubing.
  - Transfers sample to churn or cone splitter.
  - Prepares a clean work space (inside vehicle).
  - Sets up processing and preservation chambers.
  - Places equipment inside chambers (for example, sample bottles, filtration and preservation equipment).
  - Works exclusively inside chambers during collection/processing and preservation.
  - Changes chamber covers, as needed.
  - Sets up field-cleaning equipment and cleans equipment.
- *DH* takes care of all operations involving contact with potential sources of contamination; for example, *DH*
  - Works exclusively exterior to processing and preservation chambers.
  - Prepares and operates sampling equipment, including pumps and discrete samplers, peristaltic pump switch, pump controller, manifold system.
  - Operates cranes, tripods, drill rigs, vehicles, or other support equipment.
  - Handles the compressor or other power supply for samplers.
  - Handles tools such as hammers, wrenches, keys, locks, and sample-flow manifolds.
  - Handles single or multiparameter instruments for field measurements.
  - Handles the churn carrier, including outer protective bags.
  - Handles stream-gaging or water-level equipment.
  - Sets up and calibrates field-measurement instruments.
  - Measures and records water levels and field measurements.

FIELD RINSING OF EQUIPMENT 4.0.2

Most equipment used for sample collection and processing is field rinsed with the water to be sampled just before the water samples are collected (some exceptions are described below). The purposes of field rinsing are to condition, or equilibrate, the equipment to the sample environment and to help ensure that all cleaning-solution residues have been removed before sampling begins.[5] The Clean Hands team member is responsible for field rinsing the equipment whenever *CH/DH* techniques are used. Field-rinsing procedures are summarized below for sampling devices and for sample-compositing and sample-splitting equipment. Field-rinsing procedures are discussed in detail in Horowitz and others (1994) and Koterba and others (1995).

Field rinsing of equipment does not substitute for equipment cleaning.

Surface-Water Bottle Samplers and Bag Samplers 4.0.2.A

Sampling devices used to collect water samples from surface water are described in NFM 2. A bottle- or bag-type sampler is used for most routine sampling in streams. If a pump sampler will be used, refer to section 4.1.2, step 4B.

To field rinse a surface-water sampler:

1. Put on appropriate disposable, powderless gloves (gloves).
2. Partially fill and rinse the sampler with the water to be sampled (rinse water). Avoid getting sand in the rinse water.
3. Shake or swirl and then drain the rinse water from the sampler through the nozzle. (For bag samplers, the bag must be removed from the sampler to properly discard final rinse water.)

[5]Cleaning procedures and subsequent collection of the equipment blank are described in NFM 3.

4.0.2.B Churn Splitter

Surface-water samples commonly are composited in a churn splitter that has a funnel attached to the lid (NFM 2 and NFM 5.1.1.A).

To field rinse the churn splitter:

1. Put on gloves.
2. Pour 2 to 4 L of rinse water from the sampler into the churn splitter (churn) through the top funnel.
3. Remove the churn from the churn carrier, leaving the outer plastic bag inside the carrier. Move the churn disk up and down several times to ensure that the inside of the churn is thoroughly wetted, then swirl the rinse water vigorously in the churn.
4. Pierce a hole through the inner plastic bag to expose the churn spigot and drain the rinse water through the spigot. **If sand is present**, swirl water vigorously in the churn, open the plastic bag, and partially lift the churn cover to pour the rinse water out of the top of the churn. (Draining the rinse water through the spigot will not adequately remove sand.)
5. After the rinse water has been drained from the churn, rotate the churn in the plastic bag so that the spigot is no longer exposed. Place the inner plastic bag holding the churn into an outer plastic bag and place into the churn carrier.

4.0.2.C Cone Splitter

The cone splitter is required for specific site conditions (NFM 5.1.1.B) and is the sample splitter of choice for some water-quality data-collection programs.

To field rinse the cone splitter:

1. Put on gloves.
2. Uncover the splitter reservoir and pour or pump 2 to 4 L of rinse water into the cone-splitter reservoir.
3. Lightly tap the splitter to dislodge adhering water drops. Discard rinse water.
4. Cover the splitter.

Ground-Water Samplers 4.0.2.D

Samples of ground water from monitoring wells generally are collected using either a submersible pump, a peristaltic or valveless metering pump, or a point sampler such as a bailer, thief sampler, or syringe (NFM 2).

To field rinse a ground-water sampler:

1. Put on gloves.
2. Lower the sampler carefully through the water column in the well to the selected depth interval for sampling. **When lowering the sampler, take care to minimize disturbance to the water column and to sediments at the bottom of the well.**
   - If using a pump sampler, run water continuously through the pump and sample tubing to the waste container to achieve the equivalent volume of three equipment rinses. Field rinsing is accomplished with well purging, provided that the well will be purged with the same equipment to be used for sample withdrawal.
   - If using a bailer or other point sampler, follow the same procedure as for the surface-water bottle sampler (section 4.0.2.A).
3. Discard or contain the purge water used for field rinsing, as appropriate. Comply with waste-disposal regulations if water contaminated with toxic levels of chemicals is withdrawn from the well.

4.0.3 AVOIDING EXCHANGE OF SAMPLE WITH ATMOSPHERIC GASES

Collection of environmental samples from water bodies for which concentrations of dissolved gases differ significantly from atmospheric concentrations might require special field equipment or procedures. Water bodies isolated from the atmosphere or with dissolved-oxygen concentrations substantially less than that of air can be found in surface-water systems but are more common in ground-water systems. For such sites, exposure of the sample to the atmosphere can increase dissolved-oxygen concentrations, causing reduced metal ions to oxidize and precipitate as a hydroxide (for example, oxidation of iron species from ferrous (Fe^{+2}) to ferric (Fe^{+3}) iron). Precipitation of the iron or other metal hydroxide before or during filtration results in lower concentrations of iron and co-precipitating metals in the analyzed sample than are ambient in the ground water. Examples of nonmetal analytes for which atmospheric exposure can compromise sample integrity include volatile organic compounds (VOCs), pH, alkalinity, chlorofluorocarbons (CFCs), and some bacteria. Equipment and procedures should be selected that minimize contact with the atmosphere or minimize the effect of pressure changes from the source of the sample to the point of field measurement or sample processing. **In general, to maintain sample integrity for environments of limited atmospheric circulation:**

- Use pump and tubing conveyances that minimize entrainment of atmospheric gases or use equipment designed to collect and contain sample in situ.
- Use inline flowthrough sample-collection and sample-processing systems (NFM 6.2.2).
- Transport samples that need to be processed at the surface inline to a chamber filled with an inert gas such as nitrogen. This prevents oxidation but does not prevent degassing.

SURFACE-WATER SAMPLING: COLLECTION METHODS AT FLOWING-WATER AND STILL-WATER SITES 4.1

By W.E. Webb, D.B. Radtke, and R.T. Iwatsubo

The methods used to collect surface-water samples depend not only on flow characteristics of the surface-water body but also on the following considerations: safety of field personnel (NFM 9); nature of streamflow; field-measurement profiles (NFM 6); temporal and spatial heterogeneity; physical setting; ecological characteristics; weather conditions; fluvial-sediment transport; target analytes; point and nonpoint sources of contamination; and study objectives, including data-quality requirements. Each sampling site needs to be examined and sampled in a manner that minimizes bias caused by the collection process and that best represents the environmental conditions at the time of sampling.

The field team should be thoroughly familiar with procedures and requirements described in the *National Field Manual* and Office of Water Quality Technical Memorandum 99.02[6] before beginning field work. Standard references that provide descriptions of surface-water sampling techniques include: Federal Inter-Agency Sedimentation Project (1986), Ward and Harr (1990), and Edwards and Glysson (1998). Study requirements for quality control (QC) must be checked and previous QC data examined before field work begins.

- The field team should review requirements and procedures for collection of equipment blanks, field blanks, concurrent samples, and other relevant QC samples before beginning field work (section 4.3).
- The field team should be adequately staffed and equipped. For example, additional personnel and equipment are required for collection of concurrently collected samples (concurrent replicate samples, section 4.3).

[6]The technical memorandums referenced in this manual are available on the World Wide Web; see "Selected References and Internal Documents" for memorandum titles, dates, and the Web site address.

4.1.1 FLOWING-WATER SITES

Flowing streamwater is collected using either isokinetic, depth-integrating or nonisokinetic sampling methods. Isokinetic, depth-integrating methods are designed to produce a discharge-weighted (velocity-weighted) sample; that is, each unit of stream discharge is equally represented in the sample (Office of Water Quality Technical Memorandum 99.02). The analyte concentrations determined in a discharge-weighted sample are multiplied by the stream discharge to obtain the discharge of the analyte.

Collection of an isokinetic, depth-integrated, discharge-weighted sample is standard procedure; however, site characteristics, sampling-equipment limitations, or study objectives constrain how a sample is collected and could necessitate use of other methods. If the QC plan calls for collection of concurrent samples, then the relevant procedures must be reviewed and the appropriate equipment prepared (section 4.3).

Nonisokinetic sampling methods, such as those involving use of an automated point sampler, generally do not result in a discharge-weighted sample unless the stream is completely mixed laterally and vertically. Thus, the analytical results cannot be used to directly compute analyte discharges.

Document the sampling method used on the appropriate field form for each sample.

Isokinetic, Depth-Integrated Sampling Methods 4.1.1.A

Collection of isokinetic, depth-integrated samples involves using either an equal-width-increment (EWI) or equal-discharge-increment (EDI) sampling method. The EWI or EDI methods usually result in a composite sample that represents the discharge-weighted concentrations of the stream cross section being sampled. The EWI and EDI methods are used to divide a selected cross section of a stream into increments having a specified width. The term **vertical** refers to that location within the increment at which the sampler is lowered and raised through the water column. EWI verticals are located at the midpoint of each width increment. EDI verticals are located at the centroid, a point within each increment at which stream discharge is equal on either side of the vertical.

Isokinetic samplers usually are used to obtain a discharge-weighted sample along the stream cross section. When using an isokinetic sampler there should be no change in velocity (speed and direction) as the sample enters the intake (fig. 4-1). If properly implemented, EDI and EWI methods should yield identical results. The uses and advantages of each method are summarized below and in table 4-3.

- Collect isokinetic, depth-integrated samples by using a standard depth- and width-integrating method if analysis of a representative sample from a cross section of flowing water is required for discharge computations. Appendix A4-A and Edwards and Glysson (1998, figures 39-43), provide detailed information about isokinetic, depth-integrating transit rates for collecting samples.

- For isokinetic sampling, the mean velocity of the vertical that is sampled must exceed the minimum-velocity requirement of an isokinetic sampler—the minimum velocity requirement is either 1.5 ft/s for a bottle sampler or 3 ft/s for a bag sampler (Appendix A4-A; NFM 2).
  - The transit rate (the rate at which the sampler is lowered or raised) used to collect an isokinetic, depth-integrated sample is mainly a function of the nozzle diameter of the sampler, volume of the sampler container, stream velocity, and sampling depth (Appendix A4-A; NFM 2). Note that water temperature can affect isokinetic sampling. For example, bag samplers do not work isokinetically in water temperatures that are less than about 7 °C.
  - An error in concentrations of suspended particulates coarser than 62 mm can be significant when the velocity of the sample entering the nozzle and the stream velocity differ significantly. The velocity of the sample entering the nozzle also can be affected by the transit rate: too fast a transit rate will cause a sampler to undersample sand-sized particulates (Edwards and Glysson, 1998).
  - The transit rate must be kept constant during sampler descent through a vertical and also during sampler ascent through a vertical. Although not necessary, usually the same transit rate is used for raising the sampler as was used for lowering the sampler through a given vertical.

RULE OF THUMB: For isokinetic, depth-integrating sampling, do not exceed the designated maximum transit rate.

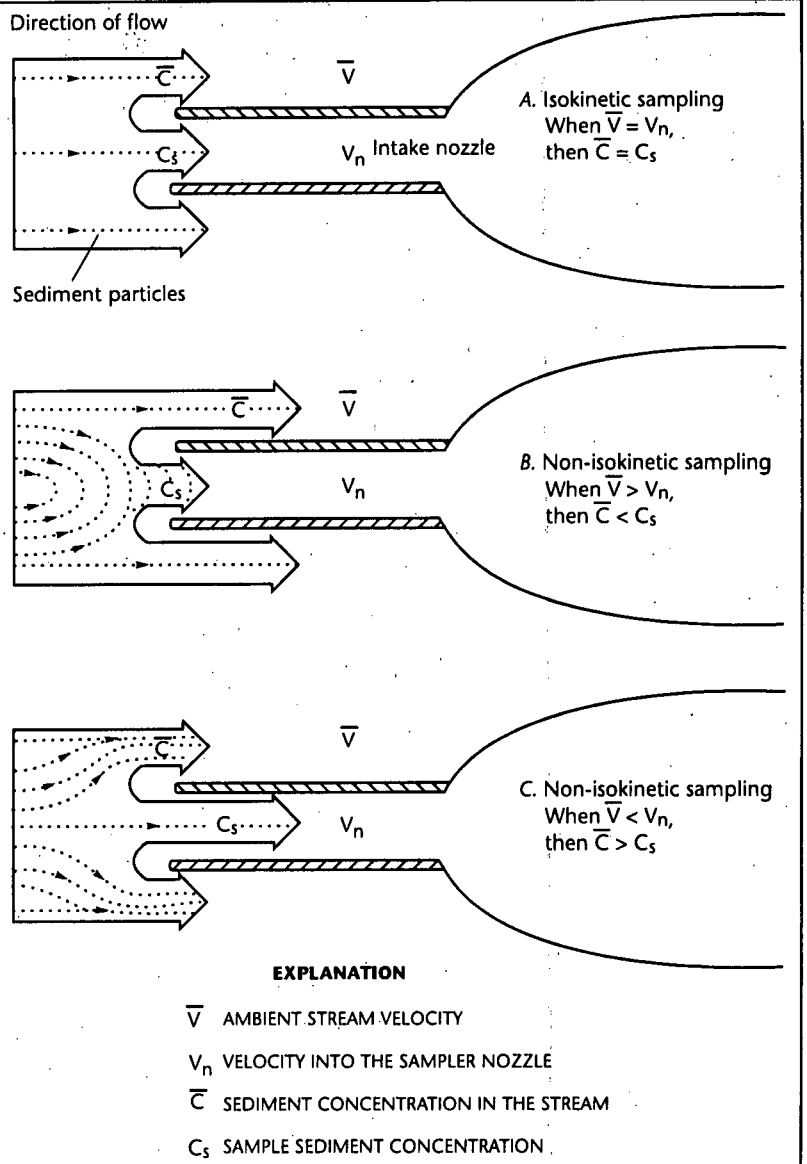


Figure 4-1. Relation between intake velocity and sediment concentration for isokinetic and nonisokinetic collection of water samples that contain particulates greater than 0.062 millimeters (modified from Edwards and Glysson, 1998, p. 13).

The number of increments needed in order to get a discharge-weighted sample at a site is related primarily to data objectives (for example, the accuracy needed) and how well-mixed or heterogeneous the stream is with respect to the physical, chemical, and biological characteristics of the cross section. The recommended number of increments for EWI and EDI methods are discussed in the sections to follow. Edwards and Glysson (1998) describe a statistical approach for selecting the number of increments to be used, based on sampling error and suspended-sediment characteristics.

Selecting the number of increments

- Examine the variation in field-measurement values (such as specific electrical conductance, pH, temperature, and dissolved oxygen) along the cross section (NFM 6).
- Consider the distribution of streamflow (discharge), suspended-materials concentration and particle-size distribution, and concentrations of other targeted analytes along the cross section. Consider whether the distribution or analyte concentrations will change during sample collection.
- Consider the type of sampler that will be used and the volume of sample that will have to be collected for the analysis of the target analytes.
- Avoid side-channel eddies. EDI and EWI methods cannot be used at locations with upstream eddy flow.

Table 4-3. Uses and advantages of equal-width-increment (EWI) and equal-discharge-increment (EDI) sampling methods

EWI method	Advantages of the EWI method
EWI is used when information required to determine locations of sampling verticals for the EDI method is not available, and (or) the stream cross section has relatively uniform depth and velocity. **Use EWI whenever:** • The location of EDI sampling verticals changes at the same discharge from one sampling time to another. This situation occurs frequently in streams with sand channels.	• EWI method is easily learned and implemented for sampling small streams. • Generally, less time is required onsite if the EWI method can be used and information required to determine locations of sampling verticals for the EDI method is not available.
EDI method	**Advantages of the EDI method**
EDI is used when information required to determine locations of sampling verticals for the EDI method is available. **Use EDI whenever:** • Small, nonhomogeneous increments need to be sampled separately from the rest of the cross section. The samples from those verticals can be analyzed separately or appropriately composited with the rest of the cross-sectional sample. (Have the sampling scheme approved.) or • Flow velocities are less than the isokinetic transit-rate range requirement. A discharge-weighted sample can be obtained, but the sample will not always be isokinetic. or • The EWI sampling method cannot be used. For example, isokinetic samples cannot be collected because stream velocities and depths vary so much that the isokinetic requirements of the sampler are not met at several sampling verticals. or • Stage is changing rapidly. (EDI requires less sampling time than EWI, provided the locations of the sampling verticals can be determined quickly.)	• Fewer increments are necessary, resulting in a shortened sampling time (provided the locations of sampling verticals can be determined quickly and constituents are adequately mixed in the increment). • Sampling during rapidly changing stages is facilitated by the shorter sampling time. • Subsamples making up a sample set may be analyzed separately or may be proportionally composited with the rest of the cross-sectional sample. • The cross-sectional variation in constituent discharge can be determined if subsample bottles are analyzed individually. • A greater range in velocity and depths can be sampled isokinetically at a cross section. • The total composite volume of the sample is known and can be adjusted before sampling begins.

Equal-width-increment (EWI) method

For the EWI sampling method, the stream cross section is divided into a number of equal-width increments (fig. 4-2). Samples are collected by lowering and raising a sampler through the water column at the center of each increment. (This sampling location is referred to as the vertical.) The combination of the same constant transit rate used to sample at each vertical and the isokinetic property of the sampler results in a discharge-weighted sample that is proportional to total streamflow.

- **Isokinetic sampling is required for the EWI method.** Use isokinetic, depth-integrating sampling equipment (NFM 2).
  - **Use the same size sampler container (bottle or bag) and nozzle** at each of the sampling verticals (fig. 4-2).
  - **Collect samples using the same transit rate** at each vertical during descent and ascent of the sampler. The transit rate must be constant and within the operational range of the sampler (Appendix A4-A).
- Composite the subsamples from all verticals in a churn splitter or process subsamples through the cone splitter (NFM 5).

Do not use EWI when stream velocities are less than the minimum velocity required for the isokinetic sampler selected:

- **1.5 ft/s for the bottle sampler**
- **3 ft/s for the bag sampler**

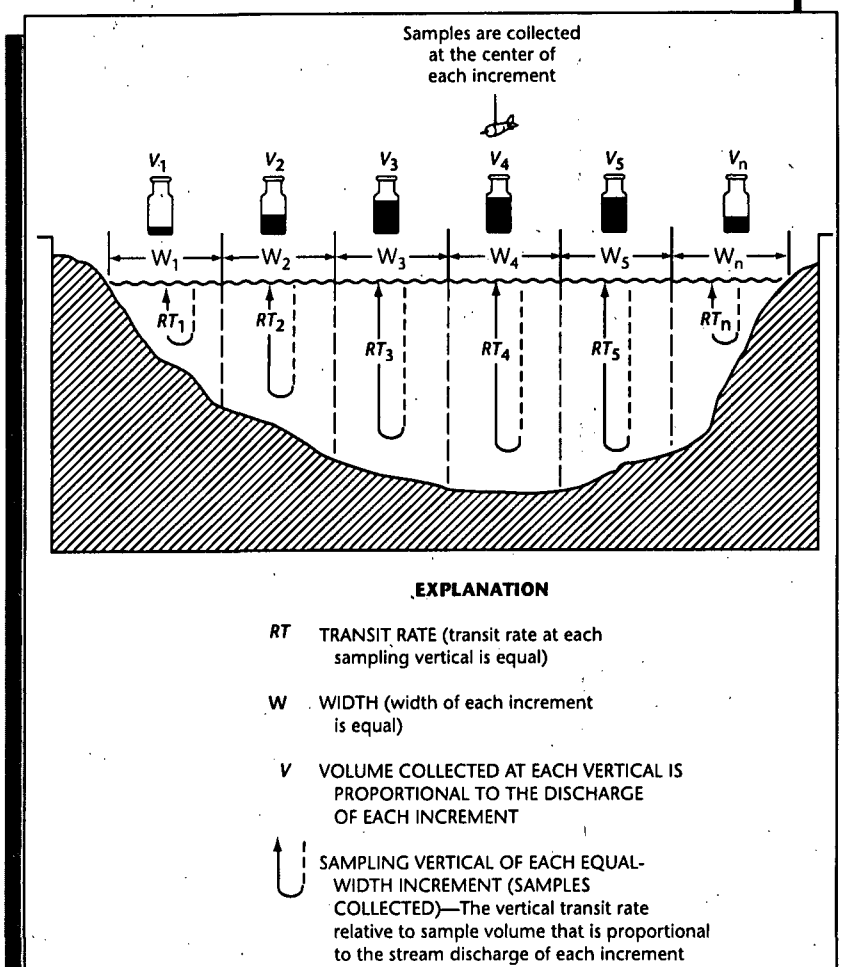
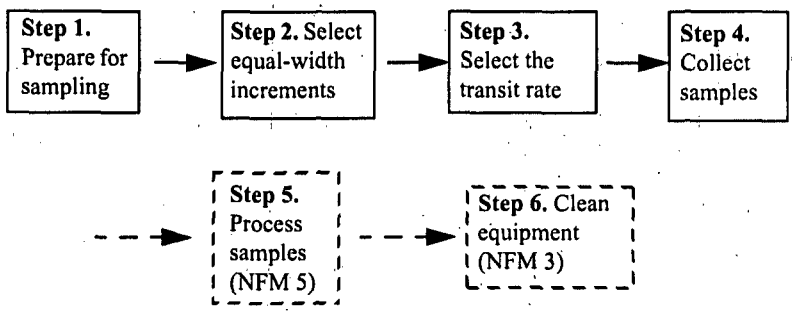


Figure 4-2. Equal-width-increment method for collection of water samples (modified from Edwards and Glysson, 1998).

Guidelines for the EWI sampling method



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies.

Step 1. Prepare for sampling[7]

a. Upon arrival at the field site, set out safety equipment such as traffic cones and signs. Park vehicle in a location and direction so as to prevent sample contamination from vehicle emissions.

b. Assemble sampling equipment and set up a clean work space.

- **Organic compounds**. Select equipment with fluorocarbon polymer, glass, or metal components if components will directly contact samples to be analyzed for organic compounds. **Do not use plastics other than fluorocarbon polymers.**
- **Inorganic constituents**. Select equipment with components made of fluorocarbon polymer or other relatively inert and uncolored plastics or glass if components will directly contact samples to be analyzed for inorganic constituents. **Do not use metal or rubber components for trace-element sampling.**
- **Microbiological analyses**. Collect samples for microbiological analyses using equipment and techniques described in NFM 7.

[7]Preparations for water sampling are described in NFM 1, 2, and 3. Consult NFM 5 for sample processing, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material sampling and NFM 9 for field safety.

Step 2. Select the number and width of equal-width increments.

a. Visually inspect the stream from bank to bank and longitudinally, observing velocity, width, and depth distribution, and apparent distribution of sediment and aquatic biota along the cross section. Note and document the location of stagnant water, eddies, backwater, reverse flows, areas of faster than normal flow, and piers or other features along the cross section.

b. Determine stream width from a tagline or from distance markings on a bridge railing or cableway.

c. At sites with little sampling history, measure and record the cross-sectional variation of field measurements (such as specific electrical conductance, pH, temperature, and dissolved oxygen). Review the magnitude of the variations along the cross section.

d. Determine the width of the increment. To obtain the number of increments, divide the stream width by the increment width. **The number of increments must be a whole number.** Increment width is based on study objectives, variation in field measurements and flow, and stream-channel characteristics along the cross section.

   - Collect the subsample at the center of each equal-width increment (the vertical).
   - If the subsample does not represent the mean value for that increment, decrease the increment width until the mean value for the increment is represented. This will increase the number of increments sampled.

e. Locate the first sampling vertical at a distance of one-half of the selected increment width from the edge of the water. Locate all the other verticals at the center of each remaining equal-width increment along the cross section.

   Example:

   - If a stream 56 ft wide has been divided into 14 increments of 4 ft each, the first sampling vertical would be 2 ft from the water's edge and subsequent verticals would be at 6, 10, 14 ft from the water's edge, and so forth.
   - Even if streamflow is divided, as in a braided channel, equal-width increments must be identical from channel to channel, and the same constant transit rate must be used at each vertical.

f. Make slight adjustments to sampling locations, if necessary, to avoid sampling where the flow is affected by a pier or other obstruction.

TECHNICAL NOTE: Sampling near or downstream from large in-stream obstructions such as bridges and piers could result in artificially elevated concentrations of suspended sediments if the sampler is immersed in an eddy that is caused by the obstruction. If it is necessary to include an eddy in the cross section to be sampled, consider treating the eddy as a solid obstruction: subtract the eddy width from that of the total cross section, and determine the width of the increments based on the remaining stream width.

RULE OF THUMB

When selecting the number of equal-width increments:

- Cross-sectional width ≥ 5 ft—use a minimum of 10 equal-width increments.
- Cross-sectional width <5 ft—use as many increments as practical, but equally spaced a minimum of 3 in. apart.

Equipment limitations also constrain the number of increments selected; for example:

- When using a D-95 at maximum depth with a 14-L churn splitter, EWI samples can be collected at approximately 14 verticals. If an 8-L churn splitter is used, samples can be collected at approximately 10 verticals.
- When using a D-77 and a 14-L churn splitter, the maximum average depth must not exceed 5 ft when samples are collected at 10 verticals.

Step 3. Select the transit rate.

a. Refer to Appendix A4-A for guidelines for determining the transit rates for collecting isokinetic, depth-integrated samples. Unless the mean velocity is actually determined, use the trial-and-error method to determine the minimum transit rate.

b. Locate the equal-width increment containing the largest discharge (largest product of depth times velocity) by sounding for depth and either measuring or estimating velocity. At the vertical for this increment, use of the minimum transit rate results in the maximum allowable filling of the sampler bottle or bag during one vertical traverse.

c. Determine the minimum transit rate at this vertical for the type of sampler (bottle or bag), size of sampler nozzle, and the desired sample volume.

- Approximate the mean velocity of the vertical in feet per second by timing a floating marker (such as a peanut) as it travels a known distance. (A known length of flagging tape tied to the cable where the sampler is attached often is used to measure the distance.) Divide the distance (in feet) by the time (in seconds) and multiply by 0.86.
- Make sure that the transit rate does not exceed the maximum allowable transit rate to be used at any of the remaining verticals along the cross section. This can be determined by sampling the slowest increment. **If the minimum volume of sample (relative to depth of the vertical) is not collected at this vertical, then the EWI method cannot be used at this cross section to collect a discharge-weighted sample (Appendix A4-A).**

Guidelines for selecting the transit rate for EWI sampling

- **The descending and ascending transit rate must be constant in each direction and must be the same for each vertical along the cross section.**
- **Do not exceed the maximum allowable transit rate if using EWI.** If the transit rate must exceed the maximum allowable rate, use EDI instead of EWI.
- The transit rate selected must be sufficiently rapid to keep from overfilling the sampler. The sampler is overfilled when the water surface in the sampler container is above the bottom edge of the nozzle when the sampler is held in the sampling position.
- The same size sampler nozzle and container must be used at all verticals along the cross section.
- If the total volume collected will exceed the recommended volume for the churn splitter, then a cone splitter must be used.

Step 4. Collect samples.

The sample-collection procedure is the same whether you are wading or using the reel-and-cable suspension method. **Use *CH/DH* techniques, as required (section 4.0.1). Always follow safety procedures (NFM 9).**

a. Move to the first vertical (midpoint of first EWI near edge of water) and field rinse equipment (section 4.0.2).

b. Record start time and gage height.

c. Lower field-rinsed sampler at the predetermined constant transit rate until slight contact is made with the streambed. **Do not pause** upon contacting the streambed. Raise the sampler immediately at the same constant transit rate until sampler completes the vertical traverse.

- Take care not to disturb the streambed by bumping the sampler on it; bed material may enter the nozzle, resulting in erroneous data.
- Do not overfill the sampler container. Overfilling results in a sample that is not isokinetic and that could be enriched with heavy particulates because of secondary circulation of water through the sampler (from nozzle through air exhaust). This enrichment will result in an artificially increased sediment concentration and will bias particle-size distribution toward heavier and larger particulates.
- Do not underfill the sampler container (Appendix A4-A). Underfilling will result in a sample that is not isokinetically collected because the maximum transit rate has been exceeded.
- If the required volume cannot be collected, use the EDI method to obtain discharge-weighted samples.

d. Inspect each subsample as it is collected, looking for overfilling or underfilling of the sampler container and (or) the presence of anomalously large amounts of particulates that might have been captured because of excessive streambed disturbance during sample collection. **If you note any of these conditions, discard the sample, making sure there are no residual particulates left in the container, and resample.**

e. Move sampling equipment to the next vertical. Maintain the selected transit rate. The volume of the subsample can vary considerably among verticals. Subsamples can be collected at several verticals before emptying the sampler container, as long as the maximum volume of sample in a bottle or bag sampler has not been exceeded. If the container is overfilled, it is necessary to resample.

TECHNICAL NOTE: The tables in Appendix A4-A apply to the first complete round-trip transit starting with an empty sampler container. These tables cannot be used if the sampler is not emptied between verticals.

f. Continue to the next vertical until no more samples can be collected without overfilling the sampler container. Empty the subsample into a field-rinsed churn or cone splitter and repeat sample collection in the same manner until subsamples have been collected at all the verticals.

- If the total volume of the subsamples to be collected will exceed the operational capacity of the churn, select from the following options: use either a sampler with a smaller bottle or a bag sampler with a smaller nozzle; or use a cone splitter; or use the EDI method, if appropriate.
- To ensure that all particulates are transferred with the sample, swirl the subsample gently to keep particulates suspended and pour the subsample quickly into the churn or cone splitter.
- Sample EWI verticals as many times as necessary to ensure that an adequate sample volume is collected as required for analysis, **but sample at each vertical an equal number of times.** (The composite cross-sectional sample will remain proportional to flow at the time of sampling.)
- If flow is stable during sampling, then multiple samples can be collected at each vertical during a single traverse along the cross section. If flow is changing, however, study objectives should determine whether to collect multiple samples at each vertical during a single traverse or to collect one sample at each vertical during multiple traverses along the cross section. Document on field forms the method used.

g. Record the following information after all samples have been collected:

- Sampling end time.
- Ending gage height.
- All field observations and any deviations from standard sampling procedures.

Step 5. Process Samples → Refer to NFM 5.

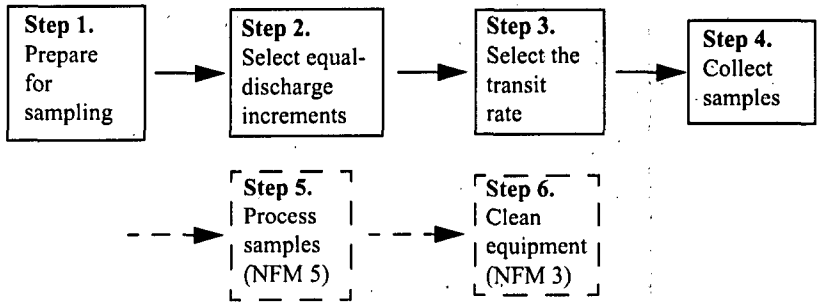
Step 6. Clean Equipment → Refer to NFM 3.

- If the sampler will not be reused during a field trip, rinse sampler components with deionized water before they dry and place them into a plastic bag for transporting to the office laboratory to be cleaned.
- If the sampler will be reused during the field trip, rinse the components with DIW while still wet from sampling and then field-clean while at the sampling site using the prescribed procedures (NFM 3). Reassemble the sampler.
- Collect a field blank, if required, after sampling equipment has been cleaned at the sampling site.
- Place the cleaned sampler into a plastic bag and seal for transport to the next site.

Equal-discharge-increment (EDI) method

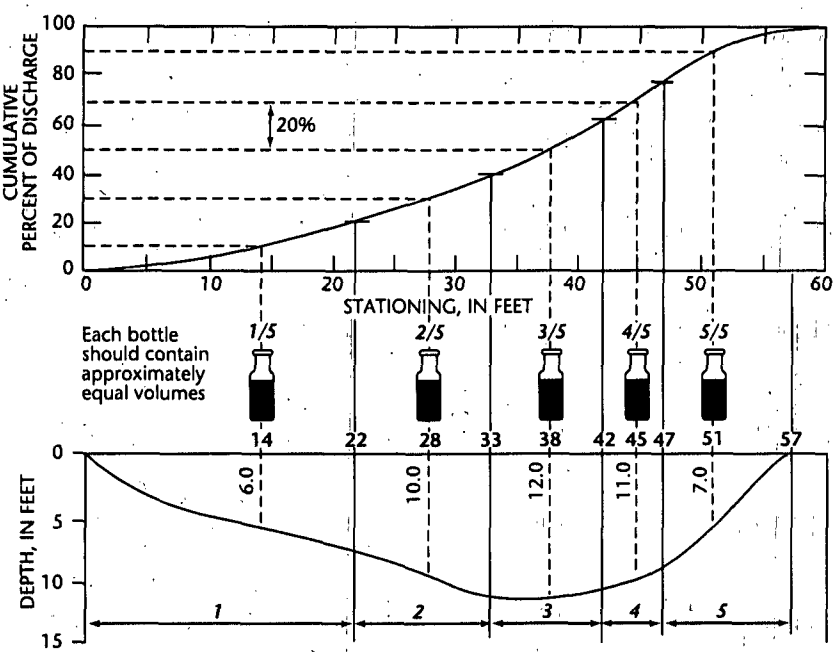
The objective of the EDI method is to collect a discharge-weighted sample that represents the entire flow passing through the cross section by obtaining a series of samples, each representing equal volumes of stream discharge. The EDI method requires that flow in the cross section be divided into increments of equal discharge. Equal-volume, depth-integrated samples are collected at the centroid of each of the equal-discharge increments along the cross section (fig. 4-3). Centroid is defined as that point in the increment at which discharge is equal on both sides of the point.

Guidelines for the EDI sampling method



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies.

Example: Sampler D77; nozzle size, 5/16 inches ID; 3 Liter sample bottle; width 57 feet; maximum depth 12 feet; maximum velocity, 5.0 ft/s; width of section containing 20 percent of flow is variable, 5 to 22 feet; 20 percent of flow per section will give 5 sampling verticals; transit rate variable, 0.3 to 1.7 ft/s.



Sampling vertical bottle/ number	Percent discharge	Increment centroid from left edge of water, in feet	Increment depth, in feet	Velocity, in feet per second	Transit rate to give 2.7 liters, in feet per second
1/5	20	14	6	2.5	0.16
2/5	20	28	10	3.0	.33
3/5	20	38	12	3.1	.41
4/5	20	45	11	6.1	.72
5/5	20	51	7	4.8	.37

Figure 4-3. Equal-discharge-increment method for collection of water samples (modified from Bruce Ringen, U.S. Geological Survey, written commun., 1978).

Step 1. Prepare for sampling for inorganic and organic analytes.[8]

a. Upon arrival at the field site, set out safety equipment such as traffic cones and signs. Park vehicle in a location and direction so as to prevent sample contamination from vehicle emissions.

b. Assemble equipment needed and set up a clean work space.

- **Organic compounds**. Select equipment with fluorocarbon polymer, glass, or metal components if components will directly contact samples to be analyzed for organic compounds. **Do not use plastics other than fluorocarbon polymers.**
- **Inorganic constituents**. Select equipment with components made of fluorocarbon polymer or other relatively inert and uncolored plastics or glass if components will directly contact samples to be analyzed for inorganic constituents. **Do not use metal or rubber components for trace-element sampling.**
- **Microbiological analyses**. Collect samples for microbiological analyses using equipment and techniques described in NFM 7.

Step 2. Select the number and location of equal-discharge increments.

The number and location of equal-discharge increments should not be determined arbitrarily. Selection of increments for a sampling site is governed by factors described in a, d, and e below.

a. Visually inspect the stream from bank to bank, observing velocity, width, and depth distribution, as well as apparent distribution of sediment and aquatic biota along the cross section. Document location of stagnant water, eddies, backwater, reverse flows, areas of faster than normal flow, and piers or other obstructions along the cross section.

b. Determine stream width from a tagline or from distance markings on bridge railings or on a cableway.

c. At sites with little sampling history—measure, record, and review the cross-sectional variation of field measurements (for example, specific electrical conductance, pH, temperature, and dissolved oxygen).

[8]Preparations for water sampling are described in NFM 1, 2, and 3. Consult NFM 5 for sample processing, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material sampling, and NFM 9 for field safety.

d. Measure discharge at the cross section to be sampled or use an existing EDI graph prepared from current or historical discharge measurements (fig. 4-3) (Edwards and Glysson, 1998). An existing EDI graph can be one prepared for the site that shows, for example, cumulative discharge or cumulative percent of discharge versus stationing.

e. Determine volume of discharge that will be represented in each EDI, based on data objectives for the study, variation in field measurements, flow and stream-channel characteristics along the cross section, and volume of sample required for analyses of target analytes.

f. Divide the cross section into equal-discharge increments.

- When determining the number of increments to be sampled, keep in mind that the subsample collected at the centroid of each EDI must represent the mean streamflow measured for that increment. If mean streamflow for the increment is not represented, increase the number of increments by decreasing the volume represented by each discharge increment until the mean streamflow value for the increment is represented.
- As a guide, a minimum of 4 sampling increments is recommended; the number of increments is usually less than 10.

g. Determine the location of the centroid of flow within each increment from the discharge measurement by (1) constructing a curve using cumulative discharge or cumulative percentage of discharge (fig. 4-3) plotted against cross-section stationing, or (2) determining EDI locations directly from the discharge measurement sheet (fig. 4-4; an explanation of this method and definition of midpoint are described in Edwards and Glysson, 1998.) Centroid-of-flow locations also can be determined from an EDI graph, as described below and in the TECHNICAL NOTE that follows the example below.

Station: 11482500 Redwood Creek at Orick, CA

Far-Mid Point	Dist. from initial point	Width	Depth	Observation depth	Revolutions	Time in seconds	Velocity: At point	Velocity: Mean in vertical	Adjusted for hor. angle or	Area	Discharge: Q	Discharge: Σ Q	
	0	4	0	.6	LE	W	0			0	0	0	
4	8	8	1.00		30	47	1.41			8.0	11.3	11.3	
12	16	8	1.80		30	44	1.51			14.4	21.7	33.0	
20	24	8	2.00		50	44	2.50			16.0	40.0	73.0	62.2
26	32	8	2.00		60	45	2.92			16.0	46.7	119.7	
28	40	8	2.30		50	48	2.29			18.4	42.1	161.8	
36	48	8	2.25		40	44	2.00			18.0	36.0	197.8	186.6
44	56	8	2.25		40	40	2.20			18.0	39.6	237.4	
50	64	8	2.30		40	40	2.20			18.4	40.5	277.9	
52	72	8	2.30		50	45	2.44			18.4	44.9	322.8	311.0
60	80	8	2.20		40	45	1.96			17.6	34.5	357.3	
68	88	8	2.00		40	43	2.05			16.0	32.8	390.1	
74	96	8	1.90		50	47	2.34			15.2	35.6	425.7	
76	104	8	2.00		40	42	2.10			16.0	33.6	459.3	435.4
84	112	8	2.00		40	40	2.20			16.0	35.2	494.5	
92	120	8	1.90		30	43	1.54			15.2	23.4	517.9	
100	128	8	1.80		40	40	2.20			14.4	31.7	549.6	
102	136	8	1.70		50	44	2.50			13.6	34.0	583.6	559.8
108	144	8	1.60		50	44	2.50			12.8	32.0	615.6	
116	152	8	1.00		20	54	.827			8.0	6.6	622.2	
124	160	4	0	.6	RE	W	0			0	0	622.2	
132													
134	160	160								290.4	622.2		
140													
148													
156													
160													

EDI Centroid Location — EDI Cumulative Discharge

Figure 4-4. Discharge-measurement field notes used to determine the equal-discharge-increment centroid locations based on cumulative discharge and far-midpoint stationing (from Edwards and Glysson, 1998, p. 42).

Example:

In this example, each EDI equals 20 percent of discharge.

i. If the stream cross section will be divided into five equal-discharge increments, divide stream discharge by five to determine the discharge increment.

ii. Locate the centroid of the initial EDI where cumulative discharge equals half the discharge increment (10 percent). This is the location of the vertical from which the first subsample is collected.

iii. Locate each of the remaining centroids (four in this example) by adding the discharge increment (20 percent) to the previous centroid discharge (20 + 10 = 30) and determining where that cumulative discharge occurs along the cross section.

iv. The EDI centroids will correspond to locations of 10, 30, 50, 70, and 90 percent of the cumulative discharge along the cross section. In figure 4-3, these percentages of cumulative discharges correspond to locations at 14, 28, 38, 45, and 51 ft from the left edge of the water, whereas in figure 4-4, the centroid locations of the equal-discharge increments are at 26, 50, 74, 102, and 134 ft.

TECHNICAL NOTE: If the stream channel is stable at the cross section to be sampled, graphs of cumulative discharge or percentage cumulative discharge at various stages can be based on historical discharge measurements. Location of EDI centroids can be determined from these EDI graphs so that discharge measurements do not have to be made before each sampling. Linear interpolation based on discharge can be made between curves for different discharges on the EDI graphs. **EDI graphs require periodic verification by being compared to recent discharge measurements.**

Step 3. Select the transit rate.

a. Determine the sampling depth and the mean stream velocity at the centroid of each equal-discharge increment.

b. Determine the transit rate for each centroid that will yield subsamples with approximately the same volume (within 10 percent) using sampling depth, mean stream velocity, and information in Appendix A4-A. When compositing subsamples, the minimum volume for every equal-discharge increment is the minimum volume for the deepest vertical.

Guidelines for selecting the transit rate for EDI sampling

- Collect samples of equal volumes at each centroid. This is required for EDI if the sample will be composited (fig. 4-3). Generally, transit rates vary from centroid to centroid in order to collect equal volumes.
- Keep the transit rate unidirectional, constant, and within the isokinetic transit range of the sampler when collecting isokinetic samples at each centroid.
- **Do not exceed the maximum transit rate** (Appendix 4A-4). The maximum transit rate will be exceeded if the minimum sample volume associated with stream velocity and the selected nozzle and bottle size is not collected. Exceeding the maximum transit rate will affect the concentration of particulates ≥ 0.062 millimeters.

Step 4. Collect samples.

The procedures are the same whether you are wading or using a reel-and-cable suspension method. **Use *CH/DH* techniques, as required (section 4.0.1), and implement safety procedures (NFM 9).**

- ▶ Collect microbiological samples using equipment and techniques as described in NFM 7.
- ▶ Collect subsamples at EDI centroids as many times as necessary to ensure collection of sufficient sample volume for analysis. If the sample is to be composited, care must be taken to obtain approximately the same total volume (± 10 percent) from each EDI centroid so that the composited cross-sectional sample will be proportional to flow at the time of sampling.
- ▶ Stay within the isokinetic transit-rate range of the sampler at each centroid. If flow velocity is less than the isokinetic transit-rate range of the sampler, a discharge-weighted sample still can be obtained by collecting equal volumes at each centroid; however, this sample will not be isokinetic.

a. Move sampling and support equipment to the centroid of the first increment to be sampled. Field rinse the sampling equipment (section 4.0.2) and record sampling start time.

b. Read and record the starting gage height.

c. Lower the sampler at the predetermined transit rate until slight contact is made with the streambed.

   - **Do not pause upon contacting the streambed.** Raise the sampler immediately at a constant transit rate to complete the vertical traverse. The descending transit rate does not have to equal the ascending transit rate, but each rate must be unidirectional, constant, and within the isokinetic transit range of the sampler.
   - Take care not to disturb the streambed with the sampler. Disturbing the streambed could cause bed material to enter the nozzle, resulting in erroneous data.
   - Ensure that the sampler container has not overfilled. Overfilling will result in enrichment of the sample with heavy particulates due to secondary circulation of water through the sampler (from nozzle through air exhaust). This enrichment will result in an artificially increased sediment concentration and will bias particle-size distribution towards heavier and larger particulates.

d. Inspect each subsample, looking for overfilling and (or) the presence of anomalously large amounts of particulates that might have been captured because of excessive streambed disturbance during sample collection. If you note either or both of these conditions, discard the sample, making sure there are no residual particulates left in the container, and resample.

e. Ensure that the sampler container is not underfilled (that the minimum volume indicated in Appendix A4-A has been collected). Underfilling will result in a subsample that is not isokinetically collected—usually because the maximum transit rate has been exceeded.

f. Depending on study objectives, either process and (or) analyze the subsample collected at the initial centroid as a separate sample, composite this subsample with other subsamples collected along the cross section, or split the subsample for further processing.

   - If the total volume of the subsamples that will be collected will exceed the operational capacity of the churn or cone splitter, decrease the number of increments or use an appropriate sampler with a smaller bottle or with a bag with a smaller nozzle.
   - Ensure that all particulates in the sampler bottle or bag are transferred with the sample by swirling the sample gently to keep particulates suspended, and quickly pouring the sample into the churn or cone splitter.

g. Move equipment to the next vertical.

- Determine the transit rate for this vertical. If the subsamples are composited, the total volume collected at each centroid must be equal.
- Repeat procedures, steps 4 c-f.
- Repeat this process at the remaining verticals along the cross section.

h. Record the following information after all samples have been collected:

- Sampling end time.
- Ending gage height.
- All field observations and any deviations from standard sampling procedures.

Step 5. Process samples → Refer to NFM 5.

Step 6. Clean equipment → Refer to NFM 3.

- If the sampler will not be reused during a field trip, rinse the components with deionized water before they dry and place them into a plastic bag for transport to the office laboratory to be cleaned.
- If the sampler will be reused during the field trip, rinse the components with DIW while still wet from sampling, and then follow the prescribed cleaning procedures while at the sampling site (NFM 3). Reassemble the sampler.
- Collect a field blank, if required, after sampling equipment has been cleaned at the sampling site.
- Place cleaned sampler into a plastic bag and seal for transport to the next site.

Single vertical at centroid-of-flow (VCF) method

The VCF method for collecting water samples is identical to the EDI method except that there is one centroid of flow for the stream cross section and therefore only one vertical is sampled. To use this method, the section must be well mixed vertically and laterally with respect to concentrations of target analytes.

Guidelines for the VCF method

1. Measure discharge along the cross section where sampling is to be done. (This is not necessary if the section is stable and accurate historical discharge measurements are available.)
2. Locate the centroid of flow from the discharge measurement.
   - Either (a) construct an EDI graph using cumulative discharge or cumulative percentage of discharge plotted against cross-section stationing (for example, in fig. 4-3, the centroid location is station 38, which corresponds to 50 percent of cumulative flow), or (b) determine centroid location directly from the discharge measurement sheet (for example, in fig. 4-4, the centroid location is station 74).
   - EDI graphs of cumulative discharge at various stages can be based on historical discharge measurements if the stream channel is stable at the cross section to be sampled. The location of centroids can be determined from these EDI graphs so that discharge measurements do not have to be made before each sampling. **EDI graphs require periodic verification.**
3. Examine the cross section for uniformity of appearance.
4. Measure the cross-sectional variation of field measurements (such as specific electrical conductance, pH, temperature, and dissolved oxygen) at sites with little sampling history. Record and review variations along the cross section.
5. Evaluate data from steps 1–4 to decide if the VCF method is appropriate. Use either the EDI or the EWI sampling method if streamflow, field-measurement, or chemical-analysis data do not confirm that the stream section is well mixed vertically and laterally.
6. If the VCF method is used, follow steps 3 and 4 of the instructions for the EDI method for selecting transit rate and collecting samples.
7. **Process samples** → Refer to NFM 5.
8. **Clean equipment** → Refer to NFM 3.

Nonisokinetic Dip, Discrete, and Pump Sampling Methods 4.1.1.B

Most nonisokinetic samplers cannot be used to collect representative discharge-weighted samples from streams transporting sand-size or larger particulates. These samplers have important uses for unattended stream sampling and for sampling to determine constituent occurrence and distribution, but they have limited value for collecting samples used to calculate constituent discharge.

Guidelines for nonisokinetic sampling methods

Use nonisokinetic sampling methods when:

- Velocity of flow is so high that an isokinetic sampler cannot be lowered through the vertical properly and safely.
- Extreme low-flow conditions render use of an isokinetic sampler impractical. For example, when water depth is equal to or less than that of the unsampled zone or when stream velocity is less than the minimum velocity requirement for an isokinetic sampler (1.5 ft/s for bottle samplers, 3 ft/s for bag samplers).
- Automatic pumping samplers are needed for specific situations; for example, time-dependent regulatory monitoring, sampling at remote sites, or sampling of floods or urban runoff when discharge is rapidly changing and a large number of samples are needed from several locations within a relatively short time.
- Periods of extreme cold cause the nozzle or air-exhaust vent to freeze, rendering isokinetic, depth-integrating samplers inoperable.
- Study objectives dictate use of nonisokinetic sampling methods.

Three nonisokinetic sampling methods most commonly used are the dip (weighted-bottle), discrete, and pump methods. Ward and Harr (1990) and Edwards and Glysson (1998) provide detailed information on these sampling methods. General instructions are provided below.

- **Dip sampling method**. Dip sampling involves dipping a narrow-mouthed bottle into a water body. Dip sampling is not recommended for discharge-weighted sampling when it is possible to obtain a depth-integrated, isokinetic sample. **The error introduced by dip sampling can be significant if the target analytes are sorbed onto suspended materials that are not uniformly distributed along the cross section.** Care must be taken to avoid collecting particulates that are resuspended as the result of wading or bumping the sampler on the streambed.
  - To collect a dip sample in water that is too shallow to submerge an isokinetic, depth-integrating sampler, wade to where the sample(s) will be collected and immerse a hand-held, narrow-mouth bottle at the centroid of flow or at multiple locations along a cross section.
  - To sample with a hand-held bottle, stand downstream of the bottle while it is being filled.
  - To collect a dip sample where water is too deep to wade, lower a weighted-bottle sampler at the centroid of flow or at multiple locations along a cross section.
- **Discrete sampling method**. Discrete (point) sampling involves either (1) lowering a sampler to a specified depth and collecting a sample by first opening, then closing the sampler, or (2) using a single-stage sampler, which fills when stream stage rises to a predetermined height.
  - Thief-type samplers are the most common point samplers used for collecting water-quality samples (NFM 2). Although these samplers are designed primarily to sample still waters, they can be adapted for slow-flowing water by attaching them to a weighted line. Samples can be collected at the centroid of flow or at multiple verticals and at selected depths along the cross section.
  - Isokinetic point samplers (for example, the P-61 and P-63 described in Edwards and Glysson, 1998) are available for collecting samples for suspended-sediment concentration and particle-size determination, and for selected chemical constituents. **The P-61 and P-63 samplers are not suitable for collecting samples for trace-metal analyses.**

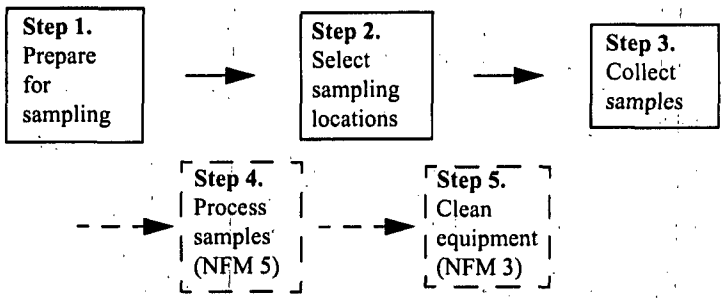
- Single-stage samplers, such as the U-59 (NFM 2) are useful for collecting samples for analysis of sediment and selected chemical constituents at stations located on streams or other locations susceptible to flash floods or where it is otherwise difficult to reach a station to manually collect samples. Before single-stage samplers can be installed, some knowledge of the seasonal stage characteristics of the stream is needed so that an appropriate sequence of samples can be obtained for a given storm season. The stream-stage and flow-velocity characteristics not only affect the design with respect to the vertical spacing of the samplers but also the support necessary for the samplers. These samplers have not been certified as appropriate for collection of uncontaminated trace-element samples.

▶ **Pump sampling method**. Pump sampling involves either suction lift or submersible pump systems designed to collect water-quality samples (NFM 2). Pump systems can be portable or can be permanently installed and automated for sampling.

- Pump samplers generally are not used to collect isokinetic samples because of the difficulty in controlling the sample velocity through the sampler intake relative to the flow rate and direction of suspended particulates in the stream.
- Portable-pump samplers generally are used to collect a point sample by lowering the pump to a selected depth.
- A portable pump also can be used to collect a nonisokinetic, depth-integrated sample by continuous pumping at a constant rate as the intake is being lowered through the vertical.

Collection of useful data, especially with the use of automated pumping samplers, requires intensive planning and quality assurance, including careful site selection, selection of the type and construction material of the sampler, a review of historical hydrologic information, and collection of an adequate number and types of quality-control samples. The physical, chemical, and biological characteristics of the cross section, study objectives, and pump limitations must be considered when determining how and where to collect samples.

Guidelines for nonisokinetic sampling methods



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies.

Step 1. Prepare for sampling for inorganic and organic analytes.[9]

a. Upon arrival at the field site, set out safety equipment such as traffic cones and signs. Park vehicle in a location and direction so as to prevent sample contamination from vehicle emissions.

b. Assemble equipment and set up a clean work space.

- **Organic compounds**. Select equipment with fluorocarbon polymer, glass, or metal components if components will directly contact samples to be analyzed for organic compounds. **Do not use plastics unless they are fluorocarbon polymers.**
- **Inorganic constituents**. Select equipment with components made of fluorocarbon polymer or other relatively inert and uncolored plastics or glass if components will directly contact samples to be analyzed for inorganic constituents. **Do not use metal or rubber components for trace-element sampling.**
- Collect samples to be analyzed for sediment concentration and (or) particle-size distribution using a separate set of clean sample bottles. Sediment samples generally are not field composited.
- Collect bacteria samples using equipment and techniques described in NFM 7.
- Calibrate field instruments as described in NFM 6.

[9]Preparations for water sampling are described in NFM 1, 2, and 3. Consult NFM 5 for sample processing, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material sampling, and NFM 9 for field safety.

Step 2. Select sampling locations.

Review data objectives to ensure they will be met at the sampling location(s) selected. If discharge-weighted samples are needed and the stream section is well mixed with respect to target analytes, locate multiple sampling points along the cross section using the EDI method.

a. Measure discharge at the cross section where samples will be collected.

b. At sites with very little sampling history, measure the variation within each field measurement (specific electrical conductance, pH, temperature, and dissolved oxygen) along the cross section and review these data.

c. Locate the centroid of flow if distribution of streamflow and the field-measurement data indicate that the section is well mixed (refer to the description of the VCF sampling method at the end of section 4.1.1.A, p. 48).

Step 3. Collect samples.

By applying EDI sampling methods and collecting equal-volume samples at the centroid of each equal-discharge increment, a sample can be collected that is discharge weighted but that is not isokinetic.

Using CH/DH techniques, as required (section 4.0.1):

a. Move sampling and support equipment to the first sampling location. Field rinse equipment (section 4.0.2).

b. Record starting gage height and sampling start time.

c. Lower field-rinsed sampler using the method selected.

- If a vertical traverse is made to collect the sample, **do not pause when contact with the streambed occurs**, but raise the sampler immediately until the traverse is completed. Take care not to disturb the streambed with the sampler, as bed material entering the sampler results in erroneous data.
- If a discrete sample is to be collected, lower the sampler to the desired depth, then sample.
- If a pump is used to collect a sample, lower the pump intake to the desired depth and pump about three sample-tubing volumes to field rinse sample tubing before collecting the sample.

d. Move to the next vertical (if more than one vertical will be sampled along the cross section).

   i. Record the time and repeat sample collection as described in step 3c above.

   ii. Inspect each sample, looking for anomalously large amounts of particulates that might have been captured because of excessive streambed disturbance during sample collection. If such a condition is observed, discard the sample, making sure there are no residual particulates left in the container, and resample.

   iii. Depending on data objectives, either composite the samples collected or set aside each sample to be independently processed and analyzed.

   - If pumped samples will be composited, pump the samples directly into the churn splitter.
   - If transferring the subsample to a churn or cone splitter, ensure that all particulates in the sampler are transferred with the sample by swirling the sample gently to keep particulates suspended and pouring the sample quickly into a sample splitter.

e. After all the samples have been collected:

   - Record sampling end time and gage height. For automated samplers, record beginning and ending dates and times for the sampling period.
   - Retrieve samples from automated pumping samplers at the earliest possible time to reduce the chance of chemical or biological alteration of the sample. (Automatic samplers with refrigeration are available to help maintain sample integrity.) Samples collected by automatic samplers generally are composited.
   - Document all field observations and any deviations from standard sampling procedures.

Step 4. Process samples ➜ Refer to NFM 5.

Step 5. Clean equipment ➜ Refer to NFM 3.

- If the sampler will not be reused during a field trip, rinse the sampler components with deionized water before they dry and place them in a plastic bag for transport to the office laboratory to be cleaned.
- If the sampler will be reused during the field trip, rinse the components with DIW while still wet from sampling and then field-clean while at the sampling site using the prescribed procedures (NFM 3). Reassemble the sampler.
- Collect a field blank, if required, after sampling equipment has been cleaned at the sampling site.
- Place the cleaned sampler into a plastic bag and seal for transport to the next site.

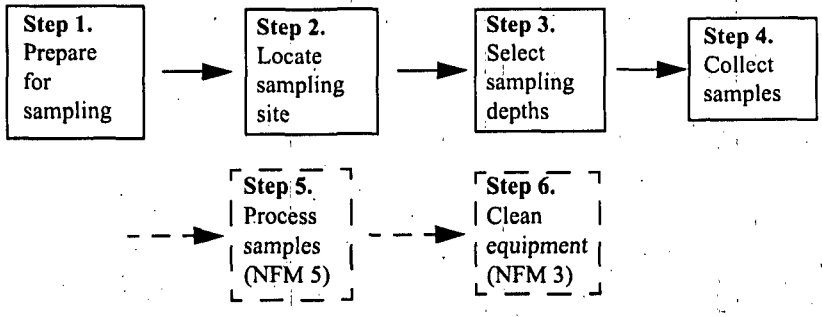
4.1.2 STILL-WATER SITES

In still water, samples generally are collected at multiple sites and at multiple depths. The probability is very small that any still-water body (lake, reservoir, pond, lock, storage pool) is relatively homogeneous with regard to any water-quality characteristic. Therefore, a single site or sampling point generally is not adequate to describe the physical and chemical properties of the water body, or the distribution and abundance of the inhabiting biological community. The number of sampling sites and the depths where samples will be collected depend on study objectives and the physical, chemical, and biological characteristics of the water body (Ward and Harr, 1990).

Thief-type samplers usually are used to collect still-water samples; however, pumping samplers also can be used. A disadvantage of pumping a sample is that if a thin stratum of water is being sampled, water can move radially from unknown depths and distances into the pump.

- Samples must be collected at a known depth.
- Sample integrity must be maintained to the degree possible while samples are being brought to the surface for further processing.

Guidelines for sampling at still-water sites



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies.

Step 1. Prepare for sampling of inorganic and organic analytes.[10]

a. Upon arrival at the field site, set out safety equipment such as traffic cones and signs. Park vehicle so as to prevent sample contamination from emissions.

b. Assemble equipment and set up a clean work space.

- **Organic compounds**. Select equipment with fluorocarbon polymer, glass, or metal components if components will directly contact samples to be analyzed for organic compounds. **Do not use plastics other than fluorocarbon polymers.**
- **Inorganic constituents**. Select equipment with components made of fluorocarbon polymer or other relatively inert and uncolored plastics or glass if components will directly contact samples to be analyzed for inorganic constituents. **Do not use metal or rubber components for trace-element sampling.**
- **Microbiological analyses**. Collect microbiological samples using equipment and techniques described in NFM 7.

Step 2. Locate sampling site.

a. Locate the first sampling site (vertical section) and maintain a sampling platform position at the site.

b. Record depth to bottom.

Step 3. Select sampling depths.

a. Make field measurements (such as specific electrical conductance, pH, temperature, and dissolved oxygen) in situ to obtain a vertical profile of field-measurement variation.

b. Measure light penetration (if applicable).

c. Select and record sampling depth(s) based on study objectives and the variation in field measurements for the vertical.

[10]Preparations for water sampling are described in NFM 1, 2, and 3. Consult NFM 5 for sample processing, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material sampling, and NFM 9 for field safety.

Step 4. Collect samples.

Field rinse sampling equipment first (section 4.0.2). Collect samples by using the procedures listed below under Step 4A for a thief-type sampler and under Step 4B for a pump sampler.

Step 4A. Thief-type sampler.

The instructions listed below are for samplers that operate with an open/close mechanism. If the sampler operates as a point-source bailer, follow a and c-g below. Pulling the bailer up will trigger the upper check valve to seal off the sample from the water overlying the targeted depth.

a. Lower opened sampler to the desired depth while minimizing disturbance of the water column.

b. Isolate the sample by activating the mechanism that closes the sampler.

c. Raise the sampler from the water body.

d. Dispense sample to sample bottle or compositing/splitting device using *CH/DH* techniques, as required or recommended:

- If using a bailer, drain sample through the bottom-emptying device.
- If sample compositing and (or) splitting is required, ensure that all particulates in the sampler are transferred with the sample by swirling the sample gently to keep particulates suspended and pouring the sample quickly into the churn or cone splitter.

e. Repeat the instructions in Step 4A a -d if more sample is needed from the same depth for that vertical section.

f. Repeat the instructions in Step 4A a -e for each depth to be sampled in that vertical section. If a second sample from a different depth or vertical section will be composited, either (1) clean and field rinse the splitter after processing the first sample and before collecting the second sample, or (2) use another clean splitter.

g. Move to the next site if another vertical section will be sampled. Repeat Step 4A a -f.

Step 4B. Pump sampler.

a. Lower the pump or pump-sample tubing (attached to a weighted line) to the desired sampling depth.

b. Turn on the pump and pump about three sample-tubing volumes to field-rinse the pump, tubing, and other sample-collection or -processing equipment. Discard rinse water.

c. Direct sample flow into collection container(s) until sufficient sample volume has been collected.

d. Repeat Step 4B a - c if another depth and (or) vertical section is to be sampled. If a second sample from a different depth or vertical section will be composited, either (1) clean and field rinse the splitter after processing the first sample and before collecting the second sample, or (2) use another clean splitter.

Step 5. Process samples ➜ Refer to NFM 5.

Step 6. Clean equipment ➜ Refer to NFM 3.

- If the sampler will not be reused during a field trip, rinse the sampler components with deionized water before they dry and place them in a plastic bag for transporting back to the office laboratory to be cleaned (NFM 5).
- If the sampler will be reused during the field trip, rinse the components with DIW while still wet from sampling and then field-clean while at the sampling site using the prescribed procedures (NFM 3). Reassemble the sampler.
- Collect a field blank, if required, after sampling equipment has been cleaned at the sampling site.
- Place the cleaned sampler into a plastic bag and seal for transport to the next site.

GROUND-WATER SAMPLING: PREPARATIONS AND PURGING METHODS AT WATER-SUPPLY WELLS AND MONITORING WELLS 4.2

By Jacob Gibs and F.D. Wilde

Collecting samples of ground water that accurately represent aquifer conditions requires sampling appropriate wells using equipment and methods that maintain the integrity of the sample with respect to the physical, chemical, and biological characteristics of interest. Ground-water sample collection involves specific preparations, such as measuring the water level in a well and purging the well of standing water. This chapter (NFM 4) primarily addresses the activities up to the point that the ground-water sample enters a collection/processing chamber. Because purging, sample withdrawal, and sample processing form a continuous process, the information provided in this chapter overlaps somewhat with that in NFM 5. NFM 5 addresses the required and recommended procedures for filling bottles with a water sample (raw or filtered), sample preservation, and other sample-processing activities.

The generic information provided below for withdrawing water from wells is followed by specific information and procedures for sampling from supply wells (section 4.2.1) and monitoring wells (section 4.2.2).

Considerations for collecting representative ground-water samples

Consideration must be given to well type, well construction, sampling equipment, and well-purging and sampling methods to ensure that a representative sample is collected.[11] Field personnel should be aware of the factors that can affect the quality of ground-water samples and are instructed to use appropriate contamination prevention techniques (tables 4-1 and 4-2). It is imperative to review the most recent analyses of blank samples

[11]Ground-water samples collected using passive or natural-gradient methods or from direct-push or cone-penetrometer systems are not addressed in this chapter.

collected through the equipment to be used for sampling before field work begins, and to collect other types of quality-control (QC) samples as a routine part of field work (section 4.3 and Appendixes A4-B and A4-C).

Review any previously collected QC data before field work begins.

- **Well type.** Check the type of well(s) to be sampled before beginning field work. Equipment and sampling methods can differ substantially, depending on the well type (NFM 1).
  - **Supply wells** are designed for domestic, public, industrial/commercial, and irrigation use and commonly are constructed using methods and materials that can affect sample chemistry. (NFM 1 and Lapham and others, 1997, describe selection criteria for supply wells.) Pumps installed in supply wells generally deliver a large volume of water that is subsampled for water quality.
  - **Monitoring wells** are designed and installed principally for the collection of water-quality samples and related data. Samples from monitoring wells are collected either with portable, low-capacity pumps or with other types of sampling devices designed for water-quality work. Sampling devices can be dedicated for use at a well and (or) can be installed permanently or semipermanently.
- **Well construction.** Periodically check the integrity of the well's construction and hydraulic communication with the aquifer: inspect casing with a televiewer, note any changes in depth-to-well-bottom measurements, and run slug tests or aquifer tests (Lapham and others, 1997). Check well integrity only after sample collection is complete or during a nonsampling site visit to avoid stirring up particulates that could cause a bias in analysis of trace metals, polychloride biphenyls (PCBs), or other analytes that tend to associate with particulates. If water from the well is laden with particulates, the well should be redeveloped or purged until turbidity values return to background or near-background levels (normally less than 5 NTU, the threshold for visible turbidity).

- To collect samples that represent a specific zone of an aquifer, the well must be in hydraulic communication with the water-bearing unit of interest and must be isolated or sealed from overlying and underlying units.
- Determine the aquifer interval(s) that yield significant contribution of flow if collecting samples in media with strongly defined paths of preferential flow, such as in fractured rock.
- Review guidelines in NFM 1 and Lapham and others (1997) for selecting the materials, length, and diameter of the well screen and casing, well completion method, and well development method.

▶ **Sampling equipment.** Select and prepare equipment using the guidelines and protocols described in NFM 2, 3, 5, and 6.

- The sample-wetted parts of the equipment must be constructed of materials that will not contaminate the sample or otherwise affect ambient concentrations of target analytes.
- All sampling equipment must be precleaned and quality assured. Equipment-blank analyses should confirm that the equipment to be used is not a source of contamination with respect to concentrations of target analytes. Document in field notes the cleaning and QA procedures used, along with the analytical results for equipment-blank data.
- A flow-splitting manifold constructed of noncontaminating materials is recommended for use at the wellhead for directing pumped sample flow (fig. 4-5).
- The sample tubing should extend into a processing chamber or glove box to avoid sample contamination from the atmosphere. Set up sample chambers before beginning sample collection (a flowthrough chamber for field measurements and processing and preservation chambers for sample filtration and preservation, respectively).

Refer to NFM 6 for detailed instructions on field measurements for conductivity, pH, Eh, temperature, turbidity, dissolved oxygen, and alkalinity.

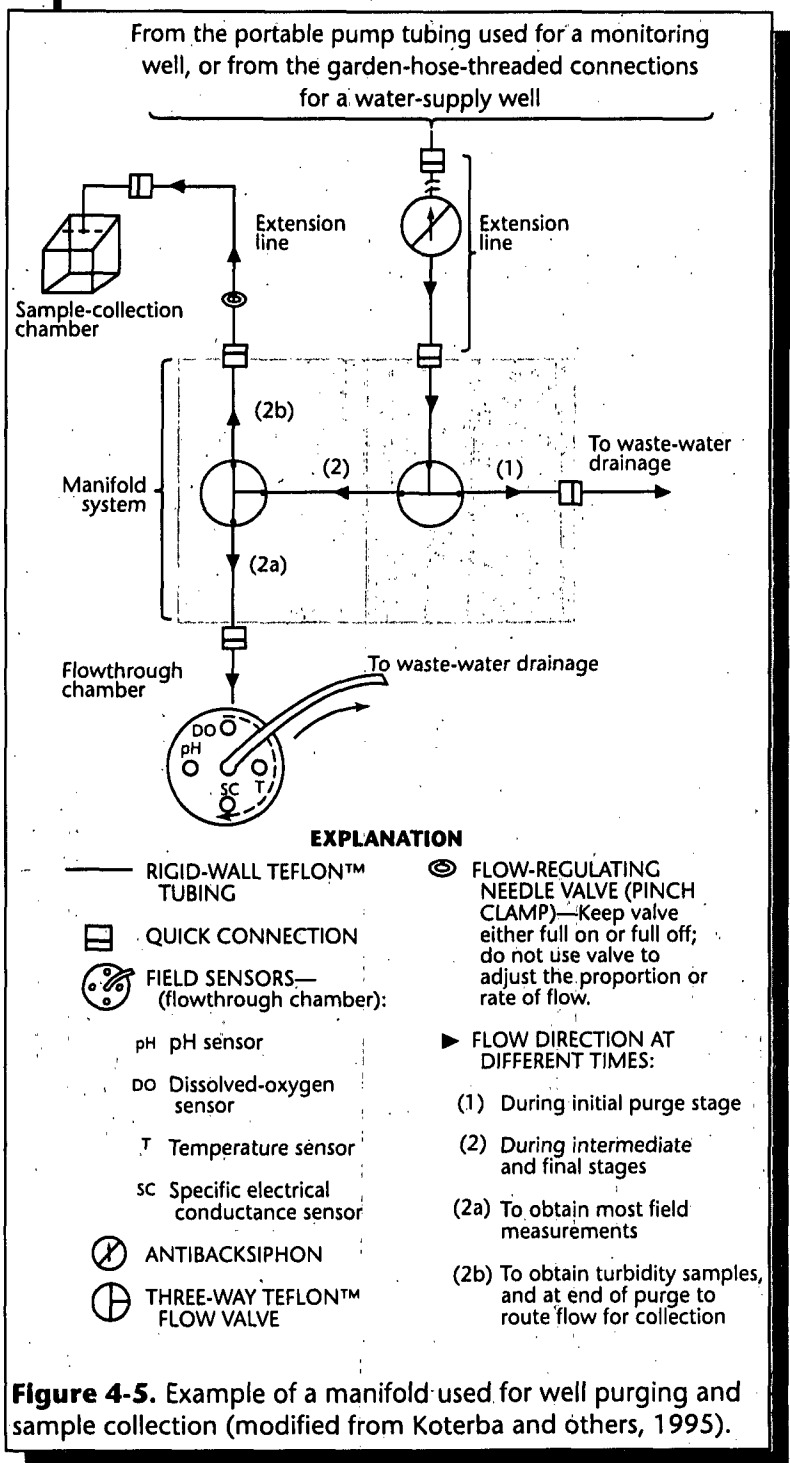


Figure 4-5. Example of a manifold used for well purging and sample collection (modified from Koterba and others, 1995).

✓	Checklist of equipment and supplies used for site setup and sampling at wells
	Antibacksiphon device (one-way or check valve)
	Flow-splitting valve(s) (two- or three-way manifold)
	Keys (for locked facilities)
	Photoionization detector (PID or sniffer)
	Tarp or plastic sheeting to place around well to keep equipment clean
	Tubing to direct waste discharge offsite or into sample container
	Sample processing and preservation chambers in which samples are bottled and treated, respectively
	Airtight flowthrough chamber for field-measurement sensors
	Sample tubing (precleaned, several lengths)
	Sampling device(s) (precleaned, portable equipment or other, as appropriate)
	Stopwatch and calibrated bucket to measure pumping rate
	Threaded fittings, male/female, such as hose-type connectors (precleaned)
	Tools (such as wrenches to remove well cap)
	Water-level measurement equipment

- **Well-purging and sampling methods.** Before selecting and implementing the purging and sampling methods described below, consider how maintaining sample integrity (table 4-4) applies to your specific study and site, making sure to consider:
  - Type and construction of well, and the hydraulic conditions and subsurface geochemistry at the site (Lapham and others, 1997).
  - Study requirements to ensure and determine data quality for target analytes (section 4.3).
  - Specific protocols needed to meet program or study objectives that could require modification of standard methods. Document any deviations from recommended sampling procedures and record field observations in field notes.

Table 4-4. Considerations for maintaining the integrity of ground-water samples

Factors that can compromise sample integrity
• **Time.** Chemical and microbial reactions that affect target-analyte concentration can be rapid.
• **Loss of pressure.** Pressure in ground water can be much greater than atmospheric pressure. As the sample is brought to land surface, depressurization of the sample can cause changes in sample chemistry.
• **Exposure to the atmosphere.** Atmospheric gases and particulates that enter the sample can affect the water chemistry.
• **Leaching or sorption.** Chemical substances can be leached from or sorbed by the equipment that contacts the sample.
• **Temperature.** Ground-water temperature is often lower than the atmospheric temperature at land surface. As the sample is brought to land surface, an increase in temperature can increase chemical reaction rates and microbial activity and cause degassing.
Strategies to maintain sample integrity
• **Plan sampling at sites in a sequence that avoids contamination.** Start with pristine sites or those least contaminated or with lowest concentrations of dissolved solids or target analytes. End at the site with the highest concentrations of target analytes.
• **Purge the well of standing water.** Purge the well to reduce artifacts from well installation or sampler deployment. If possible, pump at a rate that does not overly stress the aquifer, creating drawdown and mobilizing particulates. Protocols for purging and pumping rate can depend on well type and study objectives.
• **Isolate the sample.** Use, for example, processing and preservation chambers.
• **Avoid sample aeration.** Purge the well before sampling; filter in-line; use thick, nonpermeable sample tubing; completely fill filtration assemblies and sample tubing with sample; fill sample bottles from bottom up to overflowing whenever appropriate; handle anoxic water under an inert gas atmosphere, if necessary.
• **Clean equipment.** Sample only with decontaminated equipment and quality assure the efficacy of the cleaning procedures.
• **Collect quality-control samples.** Review the analytical results and adjust field procedures, if necessary, before the next sampling.
• **Avoid temperature changes.** Keep sample tubing as short as possible and shaded from direct sunlight.

Verify the well ID before sampling. Every well must be permanently labeled with its unique ID.

Offsite preparations[12]

Before leaving for the field site, review the types of environmental and QC samples to be collected (check section 4.3 for QC information). QC samples require additional equipment and supplies.

- Prepare the field forms that will be needed (for example, water-level, purging, field-measurement, analytical services request, and chain-of-custody forms). Fill out as much information as possible, including the equipment to be used and numbers and types of samples to be collected.
- Check equipment requirements (NFM 2). When assembling the equipment, test that equipment is in good working condition. Take backup equipment, as appropriate.
  - **Organic-compound samples.** Use fluorocarbon polymer, glass, or metal for any equipment components that will be in contact with samples to be analyzed for organic compounds. Do not use plastics other than fluorocarbon polymers.
  - **Inorganic-constituent samples.** Use fluorocarbon polymer or other relatively inert and uncolored plastics or glass for any equipment components that will be in contact with samples to be analyzed for inorganic constituents. Do not use metal or rubber components for trace-element sampling. Stainless-steel sheathed pumps are generally acceptable, but could leach low concentrations of chromium, molybdenum, nickel, and vandium to the sample. **Collect an equipment blank before sampling to demonstrate the acceptability of the data to be collected.**
- Set up a clean workspace (usually in the water-quality field vehicle) and the sample-processing and -preservation chambers. Place the filter unit and other necessary supplies for sample collection and processing into the processing chamber.

[12]Preparations for water sampling are describe in NFM 1, 2, and 3. Consult NFM 5 for sample processing, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material sampling, and NFM 9 for field safety.

Measuring water levels

The static water level in a well is measured routinely before water samples are withdrawn from the well. Water-level-measurement procedures can differ for supply wells (section 4.2.1) and monitoring wells (section 4.2.2). Detailed procedures for various methods of measuring water levels are documented in U.S. Geological Survey (1980, p. 2-8) and additional information can be obtained from the USGS Office of Ground Water (http://water.usgs.gov/ogw).

- Procedures and equipment for water-level measurement can differ, depending on the type, construction, and design of a well.
- Document in field notes if oil is floating on the water table. Review your equipment-cleaning and sample-collection strategies and revise as needed if oil is present, to prevent contamination of samples. A dual-phase sonde can be used to determine the thickness of the oil layer, as well as the depth to water.
- Water-level measurement may not be possible or accurate in some supply wells (section 4.2.1). Record any measurement problem(s) on field forms.
- Continuous monitoring of water levels is recommended throughout purging of monitoring wells (section 4.2.2).
- Record discrete water-level measurements on field forms.

Purging the well while monitoring field measurements

Standard purge procedure involves removal of at least three well volumes of standing water while monitoring field measurements and water level as a function of time, pumping rate, and the volume of water removed (figs. 4-6 and 4-7). The low-flow (micropurge) and standard purging methods are discussed in the TECHNICAL NOTE below.

- Purging should not cause significant drawdown in monitoring wells; the purge procedure should be modified appropriately if substantial drawdown occurs. Ensure that purging is sufficient to remove water from the annular space surrounding the well casing.
- Field-measurement procedures are described in detail in NFM 6. Collection of water samples is not recommended from a well in which field measurements have not met stability criteria (fig. 4-7).
- **Exceptions to the three-well-volume rule.** Site characteristics or study objectives could require modification of the standard purge procedure by changing the number of well volumes removed or by changing or adding the types of field measurements and analyses. **Document the well-purging procedure used.** When standard purge volumes cannot be removed, (1) sufficient water must be withdrawn from the well to field rinse the sampler and sample tubing, and (2) field measurements must be monitored before collecting samples. Modify the standard purging protocol when:
  - A supply well to be sampled has been pumped continuously or long enough to have removed three casing volumes of water before sampling.
  - The sample-collection interval is sealed with packers (purge the packed interval).
  - Drawdown occurs rapidly but recovery to approximately 90 percent cannot be achieved before samples are collected.
  - Purging probably will disturb sediment at the bottom of the well because the water column is small.
  - The well to be sampled is equipped with a dedicated sampling device and the intake is within the open or screened interval.
  - A purge-minimization device (Schalla, 1996) or low-flow purging techniques are used.

TECHNICAL NOTE:

- **Low-flow (micropurge) purging** procedures are designed to minimize the volume of purge water and are applicable to some studies and sites at which the pump intake is to be located within the screened/open interval and a low rate of flow can be maintained without compromising sample integrity for the target analytes (usually unfiltered trace elements) (Kearl and others, 1992; Puls and Powell, 1992; Puls and Barcelona, 1996). The low-flow method requires either a permanently installed (dedicated) pump capable of low flow rates, or a waiting period of 24 hours after installing and before starting a portable pump.
- **Standard procedure** is to calculate a purge volume using the height of the water column to the bottom of the well, instead of the water-column height to the top of the screen. The greater volume minimizes effects on ground-water chemistry from (1) vertical and (or) horizontal exchange of water in the open or screened interval with the aquifer, and (2) diffusion of oxygen from air above the water column into the column of standing water within the open or screened interval. In addition, the length of the open or screened interval might not be known, while well depth can be measured onsite. The smaller the ratio of length of open or screened interval to total height of water column, the smaller the difference between the low-flow and standard procedures for calculating purge volume and possible effect on water chemistry.

RULE OF THUMB: A sufficient volume has been purged from the well when the variability in sequentially monitored field measurements is within the prescribed criteria for stability.

Well volume = $V = 0.0408\ HD^2$ = ___ gallons, where
V is volume of water in the well, in gallons,
D is inside diameter of well, in inches, and
H is height of water column, in feet

Purge volume = $(n)(V)$ = _____ gallons, where
n is number of well volumes to be removed during purging

Q **= estimated pumping rate = _____ gallons per minute**

Approximate purge time = (purge volume)/*Q* = _____ minutes

Well casing diameter (*D*)	Gallons per foot of casing
1.0	0.04
1.5	.09
2.0	.16
3.0	.37
4.0	.65
4.5	.83
5.0	1.02
6.0	1.47
8.0	2.61
10.0	4.08
12.0	5.88
24.0	23.5
36.0	52.9

Figure 4-6. Estimation of purge volume and purge time.

RECORD OF WELL PURGING

Date: _____ By: _____

STATION ID _____ STATION NAME _____

HEIGHT OF WATER COLUMN_____ DEPTH OF WELL_____

PUMP INTAKE (ft or m below MP): Start_____ End _____

WELL-PURGING METHOD AND PUMP TYPE (describe): _____

_____

TIME	WATER LEVEL below *MP LS	DRAW-DOWN	TEMPER-ATURE	CONDUC-TIVITY	pH	DISSOLVED OXYGEN	TURBID-ITY	APPROX. PUMPING RATE
HR:MIN	*ft or m	*ft or m	°C	µS/cm	standard units	mg/L	*NTU (or FTU)	*gpm or L/min

* Circle the unit used; MP, measuring point; LS, land surface; ft, feet; m, meter; °C, degrees Celsius; mg/L, miligrams per liter; gpm, gallons per minute; L/min, liters per minute.

Well volume = $V = 0.0408\ HD^2$ = ____ gallons. **Purge volume** = $(n)(V)$ = ____ gallons.
V = volume of water in well, in gallons; D = inside well diameter, in inches; H = height of water column, in feet; n = number of well volumes to purge. Well volume is 0.16 gallons per foot for a 2-in. casing diameter.

FIELD MEASUREMENT	STABILITY CRITERIA[1]
pH	± 0.1 standard units
Temperature (T) (in degrees Celsius)	± 0.2°C (thermistor thermometer) ± 0.5°C (liquid-in-glass thermometer)
Specific electrical conductance (SC) (in microsiemens per centimeter at 25 °C)	± 5%, for SC ≤ 100 µS/cm ± 3%, for SC > 100 µS/cm
Dissolved-oxygen concentration (DO) (in milligrams per liter)	± 0.3 mg/L
Turbidity (TBY) (in nephelometric turbidity units or formazin turbidity units; FTU ≈NTU)	± 10%, for NTU < 100 Note: Ambient TBY is ≤ 5 NTU for most ground-water systems

[1]Allowable variation between 5 or more sequential field-measurement values.

Figure 4-7. Example of field form for a record of well purging.

Withdrawing the ground-water sample

If samples are being pumped, start sample collection immediately after final field measurements have been recorded. Refer to sections 4.2.1 and 4.2.2 for guidelines relevant to water-supply wells and monitoring wells, respectively.

- Do not stop the pump after purging, but record the rate of pumping.
- Pump samples from the well through the sample tubing that goes directly into the processing chamber.

If samples will be withdrawn using a thief-type sampler, lower and raise the sampler smoothly at a constant rate, keeping the suspension line clean and off the ground.

- **A bailer or other thief-type sampler is not recommended for trace-element or volatile organic compound (VOC) sampling.**
- Bailing can mobilize particulates and, unless designed for VOC sampling, can allow VOCs to escape. See section 4.2.2, Step 4, under "Nonpumped samples" (p. 88), for additional guidelines if a nonpumping sampling device will be used.

Field Cleaning of Sampling Equipment

If more than one well will be sampled during a field trip, each site and (or) a field vehicle must be set up for onsite cleaning of the sampling equipment. Field personnel should design the most efficient field-cleaning system, appropriate for the sites to be sampled and in accordance with the equipment-cleaning guidelines described in NFM 3.

4.2.1 WATER-SUPPLY WELLS

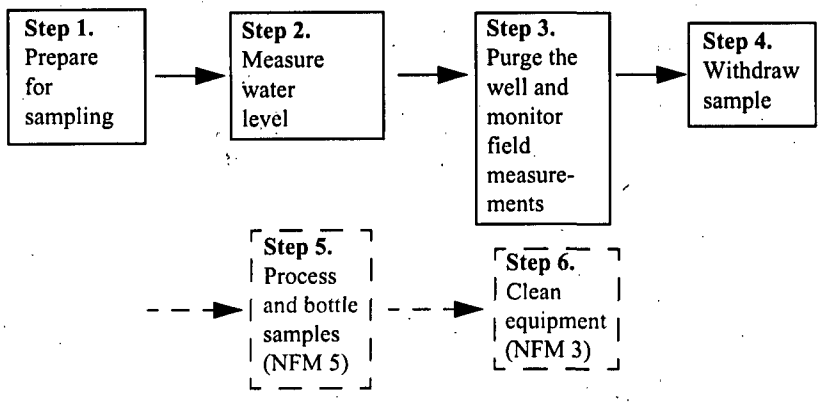
Collection of samples from water-supply wells with permanently installed pumps requires specific considerations, preparations, and precautions. Refer to other NFM chapters for guidelines for reconnaissance and preparations at supply-well sites (NFM 1) and safety precautions (NFM 9). Field personnel should be aware of the potential sources of contamination to samples withdrawn from supply wells (table 4-5; NFM 1).

- Do not sample the well if it is not possible to bypass any holding tank or chemical treatment system.
- Document all field observations and any deviations from standard sampling procedures.
- Obtain permission for access to and collection of samples and data from the well.

Table 4-5. Advantages and disadvantages of collecting water samples from supply wells with permanently installed pumps

Advantages
• Cost of well and pump installation is not a factor. • Samples from domestic and municipal wells (for studies of the quality of potable water supplies) are collected directly from the resource being studied. • Pumps are dedicated to the site; therefore, - cross-contamination of other wells from pumping equipment is not a problem, and - field time and effort otherwise expended in operating and cleaning portable pumps can be allocated to other tasks. • In-service supply wells generally require a minimal amount of purging at the time of sampling.
Disadvantages
• The well and the open or screened intervals might not isolate the aquifer zone where water-quality information is needed. • Materials of construction of well and pump may affect concentrations of the analytes targeted for study. • Pumps with high capacities can alter the water chemistry of a sample if the pump is lubricated with oil. The water chemistry of a sample can also be altered by aeration and degassing caused by high-velocity pumping, suction lift, and cavitation. • Access for water-level measurements might be unavailable; or, access might be indirect (through an air line), thus yielding less accurate measurements.

Protocols and guidelines for sampling from water-supply wells



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies. Implement good field practices and *CH/DH* techniques, as applicable (duties typically performed by Clean Hands (*CH*) and Dirty Hands (*DH*) are indicated in the steps that follow).

Step 1. Prepare for sampling at a supply-well site *(CH/DH)*.

a. Upon arrival, set out safety equipment such as traffic cones and signs. Park vehicle in a position to prevent sample contamination from vehicle and traffic emissions and the prevailing wind.

- Check the well identification number and compare it with the number in the well file and in field notes (NFM 1).
- Assign *CH/DH* tasks.

b. Describe well and site conditions in field notes and (or) on field forms, as appropriate (*DH*).

c. Check site for hazardous conditions (NFM 9) (*DH*).

- Test for toxic fumes if the well is in an enclosed structure or if there is reason to suspect the presence of organic vapors.
- Examine the area for evidence of animal infestation and other potential safety hazards.

d. Calibrate field-measurement instruments (*DH*). (Refer to NFM 6 for instructions.)

e. Spread clean plastic sheeting (for example, a polypropylene tarp) around the well to keep sampling equipment and sample tubing clean. Prepare area to be used for field cleaning of equipment (*DH*). Put on gloves.

f. Set up sample processing and preservation chambers in a clean workspace (usually in the water-quality field vehicle). Change gloves. Place filter unit and other necessary supplies for sample collection and processing into the processing chamber (*CH*).

g. Connect sample tubing as close to the wellhead as possible (*DH*).

   i. Determine the location and method of hookup to the well.

      - There must be no water-storage tanks, holding or pressurization tanks, or chemical disinfection or water-softening systems inline between the pump and tap or faucet to which sample tubing will be attached. Obtain written permission to install a tap to bypass any holding tank or chemical treatment system.
      - Select a faucet without an aerator, or obtain written permission from the owner to remove the aerator.

   ii. Use connectors and sample tubing that are compatible with the target analytes and that will not contaminate the sample. Clean connectors and tubing before use. At highly contaminated sites, it is recommended that this equipment be dedicated to that site or disposable equipment be used. Because connector fittings compatible with existing plumbing can vary, check that you have the size and configuration needed, and carry various sizes as spares.

   iii. Connect a short length of sample tubing (2 to 3 ft) between the tap/faucet fitting and the antibacksiphon valve (*DH*).

   iv. Connect an adequate length of sample tubing from the antibacksiphon valve to manifold; from manifold, connect lines to flowthrough chamber, to processing chamber, and to waste discharge. Keep the discharge end of the sample tubing sealed until use. Keep tubing for sample and field-measurement lines as short as possible and protected from direct sunlight and extreme temperatures.

      - Tubing that transfers sample to the processing chamber must be of noncontaminating material, such as fluorocarbon polymer, and handled by *CH*.

- Tubing connected to a flowthrough chamber for field measurements that is used for that purpose only (not for sample collection) can be of any material, but should be transparent in order to see if bubbles or sediment are entrained in the sample flow (*DH*).
- Tubing that is used solely to discharge purged water or other wastewater can be of any material, but needs to be long enough to direct water away from the work area (*DH*).

Step 2. Measure water level *(DH).*

Procedures and equipment for water-level measurement depend on well type and construction and the presence of nonaqueous liquid phases.

a. Put on gloves if chalking a steel tape. Using a weighted steel or electric tape in a nonpumping well, measure water level to the nearest 0.01 ft (for wells < 200 ft to water); repeat measurement until precision is within 0.02 ft. At deep wells, calculate the compensation factor to account for tape stretching.
   - Care must be taken not to entangle the well tape in the pump discharge pipe or intake.
   - An unweighted tape might be necessary if the weight cannot fit past the pump apparatus.
   - At some supply wells, the water level can only be estimated using the less accurate air-line method.

b. Record water-level measurements on field forms (fig. 4-7) and note any deviations from standard water-level measuring procedures.

Step 3. Purge the well and monitor field measurements *(DH).*

A supply well that is in regular service and that is pumping continuously or that has been operating long enough to have removed three casing volumes of water within several hours of sample collection does not require removal of three well volumes. Sample tubing needs to be flushed with sample and the field measurements monitored before sampling, however. It is recommended that water level in the well should be maintained above the screened or open interval to ensure a representative sample.

- Adjust the flow rate at the pump (preferable) or use a manifold with a flow-regulating valve (needle valve), if possible. The flow-regulating valve is necessary to prevent backpressure and air bubbles from building in the line. **Flow should not be halted or the flow rate changed suddenly during the final phases of purging and sampling.**
- The pump should produce a smooth, solid stream of water without air or gas bubbles and without pump cavitation during field measurements and sample withdrawal.
- **Contain and dispose of purge water as required by Federal, State, or local regulations.** Do not discharge the purge water from one well into another without proper authorization. Discharge the water far enough away from a well or well cluster so as not to affect water quality in the well.

a. Calculate the well volume: **V**olume, in gallons = **(0.0408)** x (**H**eight of water column) x (inside **D**iameter^2 of well, in inches). Note that depth to bottom of well and inside casing diameter must be known to calculate well volume. Begin to calculate the three well volumes after discharging the initial volume of water to waste until sediment is cleared from the flow. Record the start and end times of purging, the purging rate, water levels, and location of pump intake (fig. 4-7).

   - Field personnel could request a site operator or homeowner to start pumping the well before personnel arrive at the site.
   - If the pump is turned off but three well volumes have been removed within 24 hours before sampling, additional purging is not necessary if samples will be analyzed only for concentrations of nutrients or major ions. Purging immediately before sampling is recommended if samples for trace elements and volatile organic compounds will be collected.

b. Open any additional valves or taps/faucets to ensure that the pump will operate continuously and to reduce the possibility of backflow of water stored in ancillary plumbing lines. Keep all principal discharge lines (faucets and tap) open during sample collection that are open during purging. **Flow must not be interrupted during purging, field measurements, or sample collection.**

c. Begin flow through the flowthrough chamber for field measurements. Adjust flow to the chamber (NFM 6) from the pump, if possible, using a manifold with flow-regulating valves. **Do not use a flow-splitting valve to adjust flow rate.**

Once flow is constant, begin monitoring field measurements. (Instructions for monitoring field measurements are provided in NFM 6.)

- To control the flow rate from the manifold, a flow-regulating valve (such as a needle valve) is needed.
- Keep three-way valves either completely open or closed. Partially open three-way valves can create a vacuum and air bubbles and can draw in water that has possibly been in contact with contaminating materials. **Do not use a three-way valve or flow-splitting valve to regulate the flow.**

d. Calculate and record the final pumping rate. When water is flowing through more than one conduit (valve, tap/faucet, manifold lines) calculate the pumping rate by summing the rate of flow through each conduit. **The final pumping rate, used during the final five sets of field measurements, also should be used during sample collection.**

e. As the final well volume is removed, record on field forms at least five sets of field measurements at regularly spaced intervals and check data against stability criteria (fig. 4-7; NFM 6). Recommended measurements include specific electrical conductance, pH, temperature, dissolved oxygen, and turbidity.

Step 4. Withdraw sample (*CH*).

Flow should be constant and uninterrupted during purging and sampling. Regulate flow at the pump (as described below in Step 3).

a. Wearing gloves, check that the sample tubing is properly secured within the processing chamber.

b. Direct sample flow through sample tubing to processing chamber immediately after final field measurements have been recorded.

Step 5. Process sample → Refer to NFM 5.

RULE OF THUMB: The rate of flow for filling sample bottles should not exceed

- **500 mL/min for bottles 250 mL or greater in volume, or**
- **150 mL/min for 40-mL VOC vials.**

Step 6. Clean equipment → Refer to NFM 3.

At highly contaminated sites, use sample tubing that is disposable or dedicated to that site in order to minimize the risk of cross-contamination between wells. Wear gloves while cleaning and handling sampling equipment.

- Rinse sampling equipment with deionized water before the equipment dries.
- Clean equipment to be used at another well during the same field trip after rinsing and before moving to the next site.
- Collect field blanks used to assess equipment-cleaning procedures directly after the sampling equipment has been cleaned in the field or after moving to the next site and before sampling, as dictated by the data-quality requirements of the study (section 4.3).

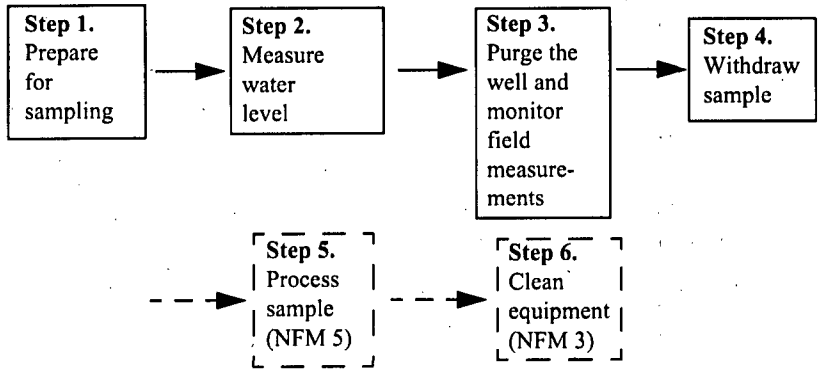
4.2.2 MONITORING WELLS

Ground-water samples commonly are collected from monitoring wells using portable sampling equipment. Sampling equipment can be dedicated for use at a specific well or can be installed permanently for the duration of the study, if using the same equipment for several wells poses a substantial risk of cross contamination.

Check NFM 2 for applications and limitations of various purging and sampling devices (pumps, bailers, and other samplers). Submersible pumps are recommended in general, but site characteristics can place limitations on the practical use of various types of sampling equipment. **If possible, the pump that is used for sampling also should be used for purging.**

- Select equipment that will not alter the chemical composition of the sample with respect to target analytes. Use only clean equipment.
- Several months in advance of sampling, quality assure the sampling equipment selected with an equipment blank(s) to verify that the equipment is suitable for the purpose of the study.
- Obtain permission for access to and collection of samples and data from the well.
- Document all field observations and any deviations from standard sampling procedures.

Protocols and guidelines for sampling from monitoring wells



Be sure that the field effort is adequately staffed and equipped. Check QC requirements before departing—QC samples require additional equipment and supplies. Implement good field practices and *CH/DH* techniques as applicable (duties typically performed by Clean Hands (*CH*) and Dirty Hands (*DH*) are indicated in the steps that follow).

Step 1. Prepare for sampling at a monitoring-well site (*DH/CH*).

a. Set out safety equipment such as traffic cones and signs. Park vehicle in a position to prevent sample contamination from vehicle and traffic emissions and prevailing wind.

- Check well-identification number and compare it with the well file and field notes.
- Assign *CH/DH* tasks to field personnel.

b. Describe well and site conditions in field notes and (or) on field forms, as appropriate (*DH*).

c. Check site for hazardous conditions (NFM 9) (*DH*).

- Test for toxic fumes if the well is in an enclosed structure or if there is reason to suspect the presence of organic vapors.
- Examine the area for evidence of animal infestation and other potential safety hazards.

d. Set up equipment and instruments for field measurements and sample withdrawal (*DH*).

- Keep sample tubing shaded from direct sunlight to minimize changes in the temperature of the sample.
- Calibrate field-measurement instruments (NFM 6).

e. Spread clean plastic sheeting (for example, a polypropylene tarp) on the ground around the well to keep sampling equipment and sample tubing clean (*DH*). Prepare area to be used for field cleaning of equipment. Put on gloves.

f. Set up sample processing and preservation chambers (usually in the water-quality field vehicle). Change gloves. Place filter unit and other necessary supplies for sample collection and processing into the processing chamber (*CH*).

g. Remove cap from well casing and connect manifold to pump (if using a pump) (*DH*). Verify clear access downhole by lowering a section of blank pipe through the depth interval to be sampled and raising it slowly. **Do not drop the pipe or otherwise stir up particulates in the process of lowering and raising the pipe.**

i. Connect the antibacksiphon valve in-line between the pump and manifold. (The antibacksiphon valve is a standard component of some submersible pumps.)

ii. Connect sample tubing to manifold, keeping tubing as short as possible.

iii. From manifold, connect lines to flowthrough chamber, processing chamber, and waste discharge. Keep the discharge end of sample tubing (handled by *CH)* sealed until used. Keep tubing for sample and field-measurement lines as short as possible and protected from direct sunlight and extreme temperatures.

- Tubing that transfers sample to the processing chamber must be of noncontaminating material (*CH*).
- Tubing connected to a flowthrough chamber for field measurements that is used for that purpose only (not for sampling) can be of any material, but should be transparent in order to see if bubbles or sediment are entrained in the flow (*DH*).
- Tubing connected to the manifold that is used solely to discharge purge water or other wastewater can be of any material, but it needs to be long enough to direct water away from the work area (*DH*).

Step 2. Measure water level (*DH*).

Procedures and equipment for water-level measurement depend on well type and construction and the presence of nonaqueous liquid phases.

a. Put on gloves before chalking a steel tape. Using a weighted steel or electric tape in a nonpumping well, record two or more consecutive water-level measurements to the nearest 0.01 ft (for wells of less than 200 ft to water); repeat measurement until precision is within 0.02 ft (U.S. Geological Survey, 1980). At deep wells, calculate the compensation factor to account for tape stretching.

b. Record water-level measurements on field forms (fig. 4-7).

c. Set up a system to measure water levels throughout purging. Electrical tapes or submersible pressure transducers are recommended—repeated measurements with a steel tape can be cumbersome and can generate turbidity in the water column.

RULE OF THUMB: The initial water-column height should be greater than 4 ft plus the length of the sampling device.

Step 3. Purge the well and monitor field measurements (*DH*).

Purge wells with a pump, if possible. Operate pumps in a manner that minimizes turbidity. **Do not use a bailer for purging** unless well characteristics or other constraints exclude other alternatives and the turbidity during and after bailing is less than about 5 NTU or at background level. Measuring water levels is recommended throughout purging to document drawdown and the location of the water level with respect to the screened/open interval and the pump intake.

- Use the same pump equipment for purging that will be used to collect samples, if possible.
- **Avoid refueling or changing equipment, and do not stop the pump during the final phase of purging and sample collection.** Be aware of study objectives and potential sources of contamination. For example, avoid fueling the equipment on the same day that samples are collected for VOC analysis.

- Adjust the flow rate at the pump (preferable) or use a manifold with a flow-regulating valve (needle valve). The flow-regulating valve is necessary to prevent backpressure and air bubbles from building in the tubing.
  - **Pump at a rate that does not significantly lower the water level. The water level should be maintained above the screened or open interval.**
  - **Flow should not be halted or the flow rate changed suddenly during the final phases of purging and sampling.**

TECHNICAL NOTES:

- A dual-pump system often is used when the water table is deeper than 250 ft and (or) a large volume of water must be purged. Position, in series, a submersible turbine or gear pump downhole and a centrifugal pump at the surface.
  - Water discharging from the slow-pumping submersible pump is used for field measurements and sample collection, while the centrifugal pump removes the required volume of purge water at a faster rate. Changes in pumping rate might increase turbidity.
  - Dissolved oxygen, Eh, or turbidity should not be measured while using a dual pumping system. Record measurements while operating only the submersible pump.
- When the water table is less than 25 to 30 ft from land surface, a peristaltic pump sometimes is used for small-diameter wells. A peristaltic pump or other comparable suction device can affect dissolved-oxygen concentrations and Eh measurements unless low-gaseous-diffusion tubing such as Tygon™ is used (NFM 2) .
- An inflatable packer sometimes is set above and below the screened/open interval, with a pump intake located within the screened/open interval.
  - Packers, which can fail to form a complete seal between aquifer intervals, should be used with pressure transducers to indicate whether water is leaking past the packers or short circuiting in the aquifer.
  - The materials of which the packer is made also might affect sample chemistry by leaching or sorbing target analytes.

a. Calculate and record well volume (figs. 4-6 and 4-7) using the static depth to water measured in Step 2, as follows:

   $V=0.0408HD^2$ [**V**olume, in gallons = (0.0408) x (**H**eight of water column, measured in feet as well depth minus water level) x (inside **D**iameter^2 of the well, in inches)]. Note that depth to bottom of well and inside casing diameter must be known to calculate well volume.

b. Lower a submersible pump, followed by a water-level sensor, to the desired location of the pump intake. (The pump position is fixed if the monitoring well has a permanently installed sampling system.) Move the equipment slowly and smoothly through the water column to avoid stirring up particulates. The intake can be either lowered continually while purging to the final depth desired or placed immediately at its final position. **Note that the final pump intake position always is at the point of sample collection.**

   - Position the pump intake at least 3 ft (≈0.9 m) below static water surface and a minimum distance above the top of the screened/open interval of 10 times the well diameter (for example, 20 in. for a 2-in. well diameter), if the sample is to represent the entire screened or open interval of aquifer. The location of the intake might be different if the study objective requires collecting the sample from a point within the screened/open interval or from wells in which packers are installed.
   - Place water-level sensor (electric tapes) a maximum of 1 ft (≈0.3 m) below the water surface.

c. Position the pump intake.

   - **If final intake position is above the screened or open interval, do not exceed 1 ft (≈0.3 m) of drawdown.**
   - **If final intake position is within the screened or open interval, do not exceed 0.5 ft (≈0.15 m) of drawdown.** The final pumping rate should be as slow as necessary to avoid causing turbidity.

d. Start the pump, channeling initial discharge to waste.

- Gradually increase and (or) adjust the pumping rate to limit drawdown to between 0.5 and 1 ft (≈0.15 to ≈0.3 m). Control the flow rate through the field-measurement tubing from the pump, if possible; or use a flow-regulating valve on the manifold. **Do not use a flow-splitting valve to adjust flow rate.**
- Record changes in water level during purging.
- Do not halt or suddenly change the flow rate during the purging/sample collection process. The pump must produce a solid stream of water during field measurements or sample collection. Adjust the pumping rate to eliminate air or gas bubbles or pump cavitation.

e. Do not move the pump during field measurements or sample collection after intake has been set at the final location. **The final depth of pump intake must be the same for making field measurements as for sample collection.**

f. **Discharge water to waste until sediment is cleared from the flow.** Begin flow through the flowthrough chamber for field measurements. Regulate the flow to the flowthrough chamber, as required, for measurements of pH and dissolved oxygen (NFM 6).

g. Record the start time of purging, the pumping rate(s), water levels, and final location of pump intake (fig. 4-7). If water is flowing through more than one conduit (such as valve and manifold lines), calculate flow rate by summing the flow rate through each conduit.

h. Purge a minimum of three well volumes or the purge volume dictated by study objectives. (Check exceptions to the three-well-volume procedure described on p. 69.)

- Record water-level and field measurements and time of measurement throughout purging (fig. 4-7; NFM 6).
- **The final pumping rate toward the end of purging (when stability of five or more sets of field measurements are being monitored) must be the same as the pumping rate during sample collection.**
- Check for special instructions regarding any field-measurement or field-analysis requirements based on study objectives.
- **Contain and dispose of purge water as required by Federal, State, or local regulations.** Do not discharge purge water from one well into another without proper authorization. Discharge the water far enough away from a well or well cluster so as not to affect water quality.

i. Check field-measurement data against stability criteria (fig. 4-7), as instructed in NFM 6. Record the time purging ended and note any deviations from standard well-purging procedures.

Step 4. Withdraw ground water (*CH*).

Put on gloves and begin sample collection immediately after field measurements have been completed.

Pumped samples—

a. Check that sample tubing is properly secured within the processing chamber. Direct the sample flow through sample tubing to the processing chamber.

b. Use the flow-regulating valve on the manifold to adjust sample flow to be smooth and uniform; avoid splashing while filling sample bottles.

c. Go to Step 5.

RULE OF THUMB: The rate of flow for filling sample bottles should not exceed

- **500 mL/min for bottles 250 mL or greater in volume, or**
- **150 mL/min for 40-mL VOC vials.**

Nonpumped samples—

a. Field rinse the sampler and sampler emptying device (and compositing device, if used) three times before collecting the sample. Deploy the sampler so as to minimize disturbance to the water column and aquifer materials.

   i. Use a reel to keep sampler line clean and untangled.

   ii. Lower sampler smoothly, entering water with as little disturbance as possible.

   iii. Allow sampler to fill, then withdraw sampler smoothly.

   iv. Shake water in sampler vigorously to rinse all interior surfaces.

   v. Attach sample-delivery tube or bottom-emptying device to sampler and drain the rinse water through the sampler.

   vi. Repeat rinse procedure at least twice.

b. Repeat (a) i - iii to withdraw ground water for the sample.

> TECHNICAL NOTE: When a device is lowered and raised through the water column, the disturbance to the water column can result in outgassing or degassing of ambient dissolved gases and an increase in concentrations of suspended particulates. Repeated movement of the device through the water column exacerbates these effects and can result in substantial modification of the ambient water composition and chemistry.

c. Composite the bailed sample or set up bailer in an enclosed or protected space.

Step 5. Process sample ➜ Refer to NFM 5.

Step 6. Clean equipment ➜ Refer to NFM 3.

At contaminated sites, use sample tubing that is disposable or dedicated to that site to avoid lengthy field-cleaning procedures and to minimize the risk of cross-contamination between wells.

- Rinse sampling equipment with deionized water before the equipment dries.
- Clean equipment to be used at another well during the same field trip after the DIW rinse and before moving to the next site.
- Collect field blanks used to assess equipment-cleaning procedures directly after the sampling equipment has been cleaned in the field or after moving to the next site and before sampling, as dictated by the data-quality requirements of the study (section 4.3).

QUALITY-CONTROL SAMPLES 4.3

By F.D. Wilde, T.L. Schertz, and D.B. Radtke

Collection of quality-control (QC) samples is a required component of sample collection for water-quality studies. QC samples are collected, usually at the field site, in order to identify, quantify, and document bias and variability in data resulting from the collection, processing, shipping, and handling of samples by field and laboratory personnel. **The bias and variability associated with data must be known so that environmental data can be adequately interpreted** (Horowitz and others, 1994; Koterba and others, 1994; Koterba and others, 1995).

The procedures for collecting QC samples can depend on, or be modified according to, the purpose of the quality-assurance program. Thus, personnel need to understand the purpose for each QC sample to be collected (Appendix A4-B) and how the resulting QC data will be used. The type, number, and distribution of QC samples are determined by the design and data-quality requirements of the study. For any water-quality sampling schedule, personnel must:

- **Be aware that an equipment blank is required at least annually (NFM 3).**
- **Be alert to field conditions** for which blanks or other QC samples should be collected, in addition to those planned. **It is usually best to collect the additional QC samples;** it can be decided later whether to submit them for laboratory analysis.
- **Collect all field QC samples on the same day that environmental samples are collected,** using the same equipment as for environmental samples.

- **Obtain the QC sample solutions needed.**
  - **Blanks.** The source solution needed for blank samples must be produced and certified by a laboratory to have analyte concentrations that do not exceed a specified method detection limit. Review and keep on file the certificate of analysis for each lot of blank water; keep a record of the lot numbers used for each sample.
    - **Inorganic-grade blank water (IBW)** is required for blanks that will be analyzed for inorganic constituents.
    - **Pesticide-grade blank water (PBW) and volatile-grade blank water (VBW)** are required for blanks that will be analyzed for pesticides and volatile organic compounds, respectively. VBW can also be used for pesticide blanks.
    - **VOC trip blanks** must be requested from the laboratory as a separate order and can be shipped with an order for VOC vials.
  - **Replicates and field-matrix spikes.** The surface or ground water being sampled (environmental water) is the solution used for most types of replicates (sequential, split, and concurrent samples) and spikes.
  - **Standards and reference materials.** Standards and reference materials are either artificial or environmental solutions with known and certified analyte concentrations.
    - Reference materials usually are obtained from the National Institute of Standards and Technology (NIST) (http://www.nist.gov).
    - USGS personnel can obtain Standard Reference Water Samples (SRS) from the USGS Branch of Quality Systems (http://btdqs.usgs.gov).
- **Use preservatives from the same lot number** for the environmental and associated QC samples. Record preservative lot number.

- **Label QC sample bottles** with a QA sample-designation code, site identification number, date of sample collection, and an assigned or real time of collection. Identification of specific types of QC samples can follow a study-developed time-coding protocol in which a specific time interval is assigned that pertains only to a specific type of QC sample.
- **Store QC data in an electronic data base devoted to QC data.** For USGS studies, it is recommended that this be an alternative data base within NWIS QWDATA—check for District and (or) program protocols for QC data-storage requirements.

Use Good Field Practices (table 4-1) and Clean Hands/Dirty Hands techniques (table 4-2) when collecting and processing QC samples.

BLANK SAMPLES 4.3.1

The primary purpose of a blank sample is to identify potential sources of sample contamination and assess the magnitude of contamination with respect to concentration of target analytes (Appendix A4-B). There are many possible types of blanks, and the processing procedures described below and in Appendix A4-B address only those most commonly collected. (Additional information can be found in Branch of Quality Systems memorandums 92.01 and 95.01; Sandstrom, 1990; Horowitz and others, 1994; and Koterba and others, 1995, although terminology differs somewhat among these references.) Examples to estimate the volume of blank solutions needed for field QC and blank-collection protocols are given in Appendix A4-C.

4.3.1.A Source-Solution, Equipment, Trip, and Other Prefield Blanks

Prepare the source-solution blank, equipment blank, and trip blank before going to the field for environmental sampling. Wear gloves and conform to other clean-hands practices when working with blank solutions.

- **Source-solution blank.** Collect in a designated clean, draft-free area of the office laboratory, such as under a laminar-flow hood or laminar-flow bench. **Do not collect the source-solution blank in a fume hood.** Submit the sample for analysis along with field-collected samples.
- **Equipment blank.** Collect in a designated clean area of the office laboratory. Collect the equipment blank at least 4 weeks before using the equipment in the field to ensure enough time for chemical analysis and review of the resulting QC data.
- **Trip blank**. Carry the trip blank as received from the laboratory to the field site. Do not open, but store with the environmental samples collected for the same target analytes, and submit for analysis along with the field-collected samples. Record the trip-blank lot number on the NWQL Analytical Services Request (ASR) form submitted with the vial. (The lot number can be found on the box, and is sometimes printed on the label.)

A variety of other types of blank samples that are collected in the controlled office-laboratory environment can be designed to test some aspect of sample handling not related to field activities. Examples of this type of blank (described in Appendix A4-B) include the refrigerator blank, the shelf blank, and the preservation blank.

When working with blank water, wear disposable, powderless gloves and implement clean-sampling techniques.

Ambient and Field Blanks 4.3.1.B

The collection of blank samples, described in this section, addresses onsite (field) processing of blank water in the same environment in which the surface- or ground-water samples are collected and (or) processed.

To prepare for processing blank samples:

1. Label the capped, precleaned sample bottle with the site identification number, laboratory sample designation code (NFM 5), date, and time.
2. Put on gloves. Place each stock container of the blank solution to be used into clean plastic bags.
   - IBW—Required for trace-element, major-ion, and nutrient field-blank analysis.
   - PBW—Required for pesticide field-blank analysis; can be used as a blank for total or dissolved organic carbon (TOC/DOC).
   - VBW—Required for VOC field-blank analysis; can be used as a blank for TOC/DOC and pesticides.
3. If pumping blank water from a standpipe, change gloves and then rinse the precleaned standpipe three times using a small volume of blank solution of the type selected. Keep standpipe covered until use.
4. Change gloves. Place precleaned, labeled sample bottle(s) and the stock of blank solutions to be used into processing chamber.
   - IBW blanks—Discard the deionized water that half fills the precleaned polyethylene sample bottle. Rinse the sample bottle with a small quantity of blank solution and discard rinsate before filling with IBW.
   - PBW or VBW blanks—Do not prerinse the sample bottle. Use glass bottles or vials as received precleaned from the laboratory.

Ambient blanks

Ambient blanks are used to answer questions such as "To what extent could exposure of the sample to its collection and processing environment introduce measurable concentrations of target analytes?" Depending on the site characteristics or conditions being subjected to quality control, different procedures can be used for collecting the ambient blank. Three common procedures are described below. For each procedure, prevent contamination of the source solution and blank sample by capping the respective bottles immediately after use.

Procedure 1. Fill clean sample bottle(s) with the appropriate blank water in the same office-laboratory area in which the source-solution blank is collected, and transport to the field. Place the bottle(s) in the processing or preservation chamber or other area in which the environmental sample(s) are being processed. Open the blank-sample bottle to expose blank sample to the chamber atmosphere for the period of time in which the environmental sample(s) are being processed. Cap the bottle(s) and label appropriately.

Procedure 2. Working within the area being tested (usually the area in which the environmental sample is being collected or processed), pour blank water from the source-solution container directly into the sample bottle. Cap the bottle immediately and label appropriately. The goal is to use similar procedures to expose an identical volume of blank water to the ambient atmospheric conditions as that for collection of sample water.

Procedure 3. While working within the area being tested (such as a field vehicle), fill a clean, wide-mouthed container with the type of blank water desired and leave open to the atmosphere for the entire testing period. Pour the blank water into a clean sample bottle. Cap the bottle and label appropriately. (This type of ambient blank is sometimes referred to as an atmospheric blank.)

Field blanks

Field blanks are collected and processed at the field site in the same manner and using the same equipment as the environmental sample(s). Equipment must be meticulously cleaned for collection of field blanks (NFM 3). Field blanks answer questions such as "Has this component of the equipment system been adequately cleaned?" or "Does this equipment component introduce detectable concentrations of target analytes?" or "Is there carry-over contamination from the previous sampling site?"

- Field blanks can represent equipment components of the sampling system; for example, the sampler blank, splitter blank, filter blank, or pump blank. (The pump blank for ground water often is the same as or analogous to a sampler blank, when a pump is the type of sampler used to withdraw water from its original source.)
- A single field blank that represents the entire sampling system is commonly referred to as the field blank or field-system blank (fig. 4-8 and Appendix A4-B). The field blank is comprised of an aliquot of blank water processed sequentially through each component of the sampling system.

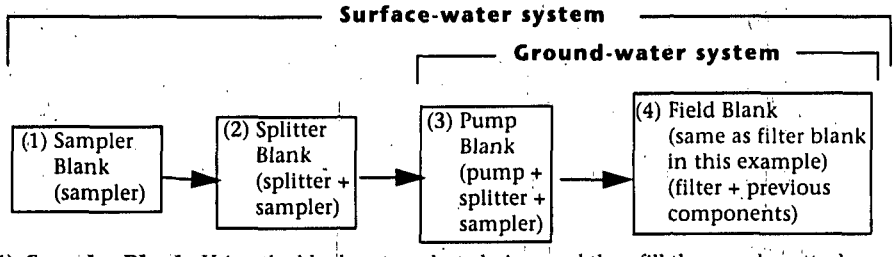
Submit field blanks for laboratory analysis of the same target analytes as the environmental sample(s). If the analytes being quality controlled are inorganic, preserved with acid, and are not time dependent, the sequential blank samples representing components of the sampling system and any associated source-solution and ambient blanks normally can be stored for up to 6 months.

1. If the field-blank data indicate constituent concentrations at acceptable levels, the associated set of sequential blanks can be discarded. (Be sure to use appropriate means for disposing of chemically treated solutions.)
2. If laboratory data indicate greater than acceptable concentrations:
   a. Submit the source-solution blank, ambient blank(s), and equipment-component blank(s) (the sampler blank, splitter blank, pump blank, and so forth) to the laboratory for analysis.
   b. Use the data from equipment-component blank samples to identify the source(s) of contamination detected in the field blank.
   c. **Take appropriate measures to eliminate contamination during future sampling trips.**

EXAMPLE PROCEDURE FOR COLLECTING FIELD BLANKS

A set of blanks can be generated that is associated with the field blank to help determine which equipment component in the system could be a source of contamination. The **field blank** is the final sample that represents all equipment components of the sampling system. After each blank sample is collected, preserve and store sample as required.

- **Follow steps 1 through 4 to process a surface-water field blank.** In this example, the equipment used includes a US D-77 sampler, 8-liter (L) churn splitter, peristaltic pump, and filter assembly.
- **Follow steps 3 and 4 to process a ground-water field blank.** In this example, the equipment used includes a submersible pump and a filter assembly.



(1) Sampler Blank. Using the blank water selected, rinse and then fill the sampler; attach sampler cap and nozzle; pour the required volume through nozzle into sample bottle.

(2) Splitter Blank.[1] *Rinse churn splitter with blank water. Pour the blank water remaining in* the sampler through the sampler nozzle and into the 8-L churn splitter. Refill sampler, repeat until churn contains 3 to 5 L of blank water. Process the required blank-sample volume through the churn spigot into the splitter-blank bottle. (If a cone splitter is used instead of a churn splitter, the blank sample is processed through the exit port tubes.)

(3) Pump Blank.[1]

- **Surface-water example**: Using the peristaltic pump, thread the intake end of clean tubing into churn splitter through the funnel, and cap the funnel loosely. Insert the discharge end of the pump tubing into a processing chamber and pump blank water through the tubing for an initial rinse, discharging rinse water to waste. After the rinse, pump the required volume of blank water from the churn splitter into the pump-blank bottle.
- **Ground-water example:** Rinse a precleaned, noncontaminating standpipe with blank water and discard rinse water. Place submersible pump into the standpipe and pour in blank water—keep water level above the pump intake. Insert discharge end of pump tubing into a processing chamber. Circulate blank water through pump and tubing to rinse, discharging rinse water to waste. Pump the required volume of blank water from the standpipe into the pump-blank bottle.

(4) Field-System Blank (the field blank). The **field blank** in this example is the same as a special type of **filter blank**[1] because the filter assembly is the final component of the equipment system through which the blank is processed. Working in the processing chamber, precondition the filter with blank water (NFM 5).

- **Surface-water example:** Pump the required volume of blank water from the churn splitter through the prerinsed filter assembly into the field-blank bottle.
- **Ground-water example:** Pump the required volume of blank water from the standpipe through the prerinsed filter assembly into the field-blank bottle.

[1]These are special cases of a splitter blank, pump blank, and filter blank, respectively, because the equipment component named is the final component but not the only component contacting the blank sample.

Figure 4-8. Example of procedure for collecting field blanks and associated blank samples.

REPLICATE SAMPLES 4.3.2

The primary purpose of replicate samples is to identify and (or) quantify the variability in all or part of the sampling and analysis system. Replicates—environmental samples collected in duplicate, triplicate, or higher multiples—are considered identical in composition and are analyzed for the same chemical properties. Common types of replicates are described below.

Concurrent Replicate Samples 4.3.2.A

Concurrent replicates are simultaneously collected samples of environmental water used to answer questions such as "What was the variability introduced from collection, processing, shipping, and laboratory handling of the sample?" Concurrent replicates can be designed to assess variability inherent in the system being sampled (Appendix A4-B).

Depending on study objectives, concurrent samples can be collected by using two sampling devices of the same type simultaneously or by filling separate sample-compositing containers concurrently using the same sampling device. The following procedure (from Horowitz and others, 1994) is used at surface-water sites to fill two or more sample-compositing containers (usually churn splitters) and incorporates Clean Hands/Dirty Hands techniques:

1. Complete equipment field-rinsing procedures (section 4.0.2). Label bottles appropriately. Change gloves.
2. At the first vertical of an EWI or EDI section, collect a sample and pour into a field-rinsed churn splitter (section 4.1).
3. Resample the first vertical and pour into the second churn splitter.
4. Move to second vertical, collect sample, and pour into second churn splitter.
5. Resample second vertical and pour into first churn splitter.
6. Collect and pour sample into each churn splitter in this manner for each of the remaining verticals, alternating churn splitters as described in 2-5 listed above.
7. Process and preserve a sample (a) from the first churn, and (b) from the second churn.

4.3.2.B Sequential Replicate Samples

Sequential replicates are samples of environmental water that are collected consecutively instead of simultaneously. Sequential replicates are used to assess variability among samples resulting from collection, processing, shipping, and laboratory procedures conducted at different sampling times. The sequential replicate can be designed to assess sample variability from inhomogeneities in the system being sampled by spacing samples over short or long time periods.

4.3.2.C Split Replicate Samples

Split replicates are samples that are divided into two or more equal subsamples, each of which is submitted to one or more laboratories for the identical analysis. Field-split samples are used to assess variability from sample processing and preservation. Bottles must be appropriately labeled, and the sequence of procedures used must be recorded.

To split a sample into two subsamples after the original has been processed and preserved, use the following procedure (from Horowitz and others, 1994):

1. Wearing disposable, powderless gloves and working inside a processing chamber, start with a full sample bottle of processed (whole-water or filtered) sample.
   - For inorganic samples only, use a bottle rinsed twice with deionized water and then field rinsed with a small volume of processed sample.
   - Do not field rinse bottles for organic samples.
2. Transfer entire contents of first bottle to second bottle, cap second bottle, and thoroughly shake bottle to mix.
3. Pour entire contents of second bottle back into first bottle.
4. Pour one-half of sample from first bottle back into second bottle, then cap both bottles.

To split concurrent replicate samples that were processed through separate compositing devices (such as churn splitters), follow the procedure listed in 1-4 above and label the samples as follows (from Horowitz and others, 1994):

Churn splitter #1: first bottle "Site (X), Sample 1, Split A"
"Site (X), Sample 1, Split B"

Churn splitter #2: first bottle "Site (X), Sample 2, Split A"
"Site (X), Sample 2, Split B"

SPIKE SAMPLES 4.3.3

Spike samples are used to answer questions such as "What loss or gain of target analytes occurred because of water-matrix characteristics; the field processing, shipping, or handling procedures used; holding time; or laboratory analytical procedures?"

Typically, spikes are applied to samples to be analyzed for concentrations of organic compounds. A sample is spiked by adding a mixture of target compounds obtained from the laboratory to an environmental sample after the sample has been processed. **An unspiked environmental sample must accompany each spiked sample.**

Training is required before personnel attempt to spike samples. The spike kits provided to USGS personnel by the NWQL include the spike solution, equipment, and bottle labels, and detailed instructions.

The numbers and types of matrix spikes used depend on the objectives and data-quality requirements of individual studies, as determined by the project chiefs. Although analyses for a set of spike samples—laboratory spike, field spike, and field-spike replicate—provides the most complete information relating to the performance of the analytical method, the data from only laboratory spikes, or perhaps only one field spike, could be sufficient to meet study needs.

When preparing field-spiked samples for pesticides or VOCs, follow the procedure listed below:

1. Keep samples chilled until spiking. Label bottles appropriately.
2. Wearing gloves, spike each of the QC samples with the appropriate volume of the correct NWQL-provided spike solution:
   - Check that the pesticide samples are being spiked with pesticide-spike solution.
   - Check that the VOC samples are being spiked with VOC-spike solution.
3. Chill field-spiked samples to 4 °C or below without freezing, and handle in a manner identical to that of the environmental sample.
4. Record the following information related to the spike sample on field and NWQL Analytical Services Request forms:

   Lot number of spike solution, volume of spike solution, and source of spike solution.

4.3.4 REFERENCE SAMPLES

Standard-reference-water samples (SRS) and reference-material samples are used to answer questions, such as "What are the bias and variability associated with field-handling, shipping, and laboratory procedures?" Reference samples commonly are submitted from the field as blind samples (section 4.3.5) and as split replicate samples (section 4.3.2.C) because the composition is known, eliminating guesswork regarding the accuracy and correctness of the analytical results.

Reference samples with a natural water matrix are currently available to USGS personnel from the USGS Branch of Quality Systems. NIST and some commercial laboratories also supply reference materials.

When preparing reference samples, follow the procedure listed below:

1. **Prepare this sample before leaving for the field site.**
   a. Relabel the reference-sample bottle with the site identification code and a field date and time. The sample should appear as if it is an environmental sample.
   b. Process SRS or reference-material samples in a clean environment in the office laboratory, under a laminar-flow hood or other protective chamber, to avoid atmospheric contamination. **Do not process these QC samples under a fume hood.**
   c. Rinse each sample bottle three times with a small volume of SRS or reference-material sample, fill the bottle with the reference solution, and cap securely.
2. Prepare an ASR form; record the SRS or reference-material sample identification code (from the original container) in field notes.
3. Pack the sample and the accompanying ASR form to take to the field site.
4. Ship SRS or reference-material samples in the same container with the environmental and other QC samples collected at the field site.

BLIND SAMPLES 4.3.5

The source and chemical composition of blind samples are known to the submitter although typically not known to the analyst; therefore, blanks, SRS, or reference material usually are used as blind samples. Blind samples can be designed to answer questions such as "What bias and variability are introduced by procedures used within a single laboratory or among laboratories?" Replicate or spike samples also can be used to answer a similar question.

CONVERSION FACTORS, SELECTED TERMS, AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter
inch (in.)	25.4	millimeter
meter (m)	3.281	foot
micrometer (μm)	3.281×10^{-6}	foot
millimeter (mm)	0.03937	inch
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois
liter (L)	0.2642	gallon
milliliter (mL)	2.64×10^{-4}	gallon

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$

SELECTED TERMS

Accuracy: The degree of agreement of a measured value with the true or expected value of the quantity of concern (Taylor, 1987).

Analyte (target analyte): "Substances being determined in an analysis" (from Bennett, 1986). The term target analyte is used in this report to refer to any chemical or biological substance for which concentrations in a sample will be determined. Target analyte does not include field-measured parameters such as specific electrical conductance, pH, temperature, dissolved oxygen, Eh, alkalinity, color, or turbidity.

Aquifer: "A saturated permeable geologic unit that can transmit significant quantities of water under ordinary hydraulic gradients" (Freeze and Cherry, 1979).

Area-weighted sample: A sample that contains an equal volume from each unit of area sampled.

Bias: Systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system. The error can be positive (indicating contamination) or negative (indicating loss of analyte concentration) (from Taylor, 1987).

Bag samplers: Samplers whose containers are bags that instantly transmit the ambient pressure to the interior of the sample container and do not have opening or closing valves.

Bottle samplers: A rigid sample container that does not instantly transmit the ambient pressure to the interior of the sample container and has neither pressure compensation nor opening and closing valves. Point samplers described in Edwards and Glysson (1998) use rigid bottles but have pressure compensation and opening and closing valves and are not considered bottle samplers for the purposes of this document. **The tables in Appendix A4-A were not designed for use with point samplers.**

Centroid (as used to designate a special case of stream-sampling location for the equal-discharge-increment method): The vertical in the increment at which discharge is equal on both sides of the vertical (G. Douglas Glysson, U.S. Geological Survey, written commun., 1997).

Contaminant: Biological, chemical, or physical substances or properties added to the medium of concern through human activity or natural processes and that corrupt its ambient composition.

Contamination (of water): Corruption of ambient water composition or attributes by the addition of biological, chemical, or physical substances as a result of human activity or natural processes. Addition of such substances can degrade the quality of the water resource.

Data-quality requirements: That subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the variability allowable without compromising achievement of the scientific objectives of the study.

Depth-integrated sample: A sample collected when each vertical portion of the stream depth is represented in the sample in proportion to the desired sampling scheme.

- **Depth integration.** "A method of sampling at every point throughout a given depth (the sampled depth) whereby the water-sediment mixture is collected isokinetically so that the contribution from each point is proportional to the stream velocity at the point. This process yields a sample with properties that are discharge weighted over the sampled depth" (ASTM, 1990).

- **Depth integration for a discharge-weighted sample.** "A discharge-weighted (velocity-weighted) sample of water-sediment mixture collected at one or more verticals in accordance with the technique of depth integration; the discharge of any property of the sample expressible as a concentration can be obtained as the product of the concentration and the water discharge represented by the sample" (ASTM, 1990). For a discharge-weighted sample, the water-sediment mixture is collected isokinetically so that the contribution from each point is proportional to the stream velocity at the point (that is, the sample contains an equal volume from each unit of discharge sampled).

- **Depth integration to collect an area-weighted sample.** The ASTM definition of depth integration does not accommodate the concept of an area-weighted sample. Area weighting is similar in concept to discharge weighting, except that the water-sediment mixture is collected so that the contribution from each point is proportional to the stream area at the point (that is, contains an equal volume from each unit of area sampled). Area-weighted sampling is used to obtain a sample that contains the average concentration of a property that is observed in a cross section. Averaged in situ field measurements of streams are more nearly area weighted than discharge weighted. The product of an area-weighted property concentration and the stream discharge would not yield the discharge of the property unless the stream contained the same property concentration at every point.

Discharge-weighted sample: A sample that contains an equal volume from each unit of discharge sampled.

District: An office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

Equal-width-increment (EWI) and **equal-discharge-increment (EDI) sample-collection methods:** Methods specifically designed to result in the collection of discharge-weighted, depth-integrated, isokinetic samples (Edwards and Glysson, 1998). When either method is used properly, the resulting samples contain the same property concentrations.

Isokinetic sampling: A sample collected in such a way that the water-sediment mixture moves with no change in velocity as it leaves the ambient flow and enters the sampler intake (ASTM, 1990).

Precision: The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions (Taylor, 1987).

Quality Assessment: Overall process of assessing the quality of the environmental data by reviewing the application of the quality-assurance elements and the analysis of the quality-control data.

Quality Assurance (QA): A system of protocols and procedures implemented to meet expected standards of quality needed to fulfill study objectives and control unmeasurable components of a study, such as sampling at the right place and (or) time using the correct equipment and techniques.

Quality Control (QC): A system of activities (such as collection of blank or replicate samples) whose purpose is to assess the quality of environmental data by generating a set of data that will be used to estimate the magnitude of the bias and variability resulting from the procedures used for obtaining the data.

Raw sample: A whole-water (unfiltered) sample that has not been processed through a filter or other phase-separation device.

Transit: To move the sampler from the stream surface to the streambed or from the streambed to the surface.

Transit rate: The rate at which the sampler is passed through the water from the stream surface to the streambed or from the streambed to the surface.

Unsampled zone: The unsampled portion of the sampling vertical, usually assumed to be the zone from the streambed to the sampler intake. Generally, sampler intakes are 4 to 7 inches above the streambed, depending on the kind of sampler used.

Variability: Random error in independent measurements as the result of repeated application of the process under specific conditions.

Vertical: Refers to that location within the increment at which the sampler is lowered and raised through the water column.

ABBREVIATIONS

<	less than
≤	equal to or less than
≥	equal to or greater than
ft/s	feet per second
gal/min	gallon per minute
L/min	liter per minute
µg/L	microgram per liter (equivalent to parts per billion)
mg/L	milligram per liter
mL/min	milliliter per minute
ppb	parts per billion (equivalent to micrograms per liter)
ASR	Analytical Services Request
ASTM	American Society for Testing and Materials
CFC	chlorofluorocarbon
CH/DH	Clean Hands/Dirty Hands
DIW	distilled, deionized water
DOC	dissolved organic carbon
EDI	equal-discharge increment
EWI	equal-width increment
FTU	Formazin turbidity unit
IBW	inorganic-grade blank water
ID	identification number that is unique to a field site, station, or well
NAWQA	National Water-Quality Assessment Program
NFM	*National Field Manual for the Collection of Water-Quality Data*
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
NTU	Nephelometric turbidity unit
NWQL	National Water Quality Laboratory
PBW	pesticide-grade blank water
PCB	polychlorinated biphenyls
QA	quality assurance
QC	quality control
QWSU	Quality Water Service Unit
SRS	Standard reference water sample
TBY	turbidity
TOC	total organic carbon
URL	Uniform Resource Location
USGS	U.S. Geological Survey
VBW	volatiles-grade blank water (is also of pesticide grade)
VCF	single vertical at centroid of flow
VOC	volatile organic compound

SELECTED REFERENCES AND INTERNAL DOCUMENTS

SELECTED REFERENCES FOR COLLECTION OF WATER SAMPLES

American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, p. 1114-1122.

American Society for Testing and Materials (ASTM), 1990, Compilation of ASTM standard definitions (7th ed.): Philadelphia, ASTM, 554 p.

_____1992, ASTM Standards on ground water and vadose zone investigations: Philadelphia, ASTM pub. code 03-418192-38, 166 p.

Arizona Department of Environmental Quality, 1991, Quality assurance project plan: Phoenix, Ariz., Office of Water Quality, 209 p.

Arizona Water Resources Research Center, 1995, Field manual for water quality sampling: Tucson, Ariz., University of Arizona, ADEQ TM-94-3, 51 p.

Backhus, D.A., Ryan, J.N., Groher, D.M., MacFarlane, J.K., and Gschwend, P.M., 1993, Sampling colloids and colloid-associated contaminants in ground water: Ground Water, v. 31, no. 3, p. 466-479.

Baedecker, M.J., and Cozzarelli, I.M., 1992, The determination and fate of unstable constituents of contaminated groundwater, *in* Lesage, Suzanne, and Jackson, R.E., eds., 1992, Groundwater contamination and analysis at hazardous waste sites: New York, Marcel Dekker, p. 425-461.

Bayer, R., Schlosser, P., Bnisch, G., Rupp, H., Zaucker, F., and Zimmek, G., 1989, Performance and blank components of a mass spectrometric system for routine measurement of helium isotopes and tritium by the ^{3}He ingrowth method: Sitzungsberichte der Heidelberger Akademie der Wissenschaften, Mathematisch-naturwissenschaftliche Klasse, Jahrgang 1989, 5, Abhandlung, Springer-Verlag, 42 p.

Bennett, H., ed., 1986, Concise chemical and technical dictionary (4th ed.): New York, Chemical Publishing Co., p. 99.

Busenberg, E., and Plummer, L.N., 1992, Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age-dating tools—Example, the alluvium and terrace system of central Oklahoma: Water Resources Research, v. 28, no. 9, p. 2257-2283.

Busenberg, E., Weeks, E.P., Plummer, L.N., and Bartholemay, R.C., 1993, Age dating ground water by use of chlorofluorocarbons (CCl_3F and CCl_2F_2), and distribution of chlorofluorocarbons in the unsaturated zone, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho: U.S. Geological Survey Water-Resources Investigations Report 93-4054, 47 p.

Edwards, T.K., and Glysson, G.D., 1998, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 80 p.

Ekwurzel, Brenda, Schlosser, Peter, Smethie, W.M., Jr., Plummer, L.N., Busenberg, Eurybiades, Michel, R.L., Weppernig, Ralf, and Stute, Martin, 1994, Dating of shallow groundwater—Comparison of the transient tracers $^{3}H/^{3}He$, chlorofluorocarbons and ^{85}Kr.: Water Resources Research, v. 30, no. 6, p. 1693-1708.

Federal Interagency Sedimentation Project, 1986, Catalog—Instruments and reports for fluvial sediment investigations: Minneapolis, Minnesota, St. Anthony Falls Hydraulics Laboratory, 138 p.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, N.J., Prentice-Hall, 604 p.

Gibs, Jacob, and Imbrigiotta, T.E., 1990, Well-purging criteria for sampling purgeable organic compounds: Ground Water, v. 28, no. 1, p. 68-78.

Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.

Ivahnenko, Tamara, Szabo, Zoltan, and Hall, G.S., 1996, Use of an ultra-clean sampling technique with inductively coupled plasma-mass spectrometry to determine trace-element concentrations in water from the Kirkwood-Cohansey aquifer system, coastal plain, New Jersey: U.S. Geological Survey Open-File Report 96-142, 37 p.

Kearl, P.M., Korte, N.E., and Cronk, T.A., 1992, Suggested modifications to ground water sampling procedures based on observations from the colloidal borescope: Ground Water Monitoring Review, v. 12, no. 2, p. 155-160.

Keith, L.H., 1978, Principles of environmental sampling: Washington, D.C., American Chemical Society ACS Professional Reference Book, 458 p.

Keith, L.H., ed., 1991, Compilation of EPA's sampling and analysis methods: Chelsea, Mich., Lewis Publishers, 803 p.

Koterba, M.T., Dysart, J.E., Phillips, S.W., and Zynjuk, L.D., 1994, Use and value of quality-control data in studies in the Chesapeake Bay Region, *in* Proceedings of the National Symposium on Water-Quality, November 5-11, Chicago, Ill., American Water Resources Association, p. 65-74.

Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95-398, 69 p.

_____ 1997, Guidelines and standard procedures for studies of ground-water quality—selection and installation of wells, and supporting documentation: U.S. Geological Survey Water-Resources Investigations Report 96-4233, 110 p.

Mueller, D.K., Martin, J.D., and Lopes, T.J., 1997, Quality-control design for surface-water sampling in the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 97-223, 14 p.

Nielsen, D.M., ed.,1991, Practical handbook of ground-water monitoring: Chelsea, Mich., Lewis Publishers, 717 p.

Plumb, R., Jr., 1981, Procedures for handling and chemical analysis of sediment and water samples: Vicksburg, Miss., U.S. Army Engineers Waterways Experiment Station Environmental Laboratory, Technical Report EPA/CE-81-1, p. 3-73 - 3-76.

Plummer, L.N., Michel, R.L., Thurman, E.M., and Glynn, P.D., 1993, Environmental tracers for age dating young ground water, *in* Alley, W.M., ed., Regional ground-water quality, chap. 11: New York, Van Nostrand Reinhold, p. 255-294.

Puls, R.W., and Barcelona, M.J., 1989, Ground water sampling for metals analyses: Washington, D.C., U.S. Environmental Protection Agency, Office of Research and Development, EPA Ground Water Issue, EPA/540/4-89/001, 6 p.

_____1996, Low-flow (minimal drawdown) ground-water sampling procedures: Washington, D.C., U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, EPA Ground Water Issue, EPA/540/S-95/504, 12 p.

Puls, R.W., and Powell, R.M., 1992, Acquisition of representative ground water quality samples for metals: Ground Water Monitoring Review, Summer 1992, v. 12, no. 3, p. 167-176.

Rantz, S.E, and others, 1982, Measurement and computation of streamflow, volume 1, Measurement of stage and discharge: U.S. Geological Survey Water Supply Paper 2175, 284 p.

Sandstrom, M.W., 1990, Sampling requirements for organic contaminants, *in* American Water Works Association Annual Conference: Cincinnati, Ohio, Management Challenges of New Monitoring Requirements for Organic Chemicals, American Water Works Association Seminar Proceedings, p. 71-85.

Sandstrom, M.W., 1995, Filtration of water-sediment samples for the determination of organic compounds: U.S. Geological Survey Water-Resources Investigations Report 95-4105, 13 p.

Schalla, R., 1996, Purge water minimization at LEHR: Richland, Wash., Pacific Northwest National Laboratory, PNNL-11406, variously paged.

Schlosser, P., Stute, M., Dorr, H., Sonntag, C., and Munnich, K.O., 1988, Tritium/^{3}He dating of shallow groundwater: Earth and Planetary Science Letters, v. 89, p. 353-362.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.

Solomon, D.K., Schiff, S.L., Poreda, R.J., and Clarke, W.B., 1993, A validation of the ^{3}H/^{3}He method for determining groundwater recharge: Water Resources Research, v. 29, no. 9, p. 2951-2962.

Solomon, D.K., and Sudicky, E.A., 1992, Correction to "Tritium and helium 3 isotope ratios for direct estimation of spatial variations in groundwater recharge": Water Resources Research, v. 28, no. 4, p. 1197.

Szabo, Z., Rice, D.E., Plummer, L.N., Busenberg, E., Drenkard, S., and Schlosser, P., 1996, Age dating of shallow groundwater with chlorofluorocarbons, tritium helium 3, and flow path analysis, southern New Jersey coastal plain: Water Resources Research, v. 32, no. 4, p. 1023-1038.

Taylor, J.K., 1987, Quality assurance of chemical measurements: Chelsea, Mich., Lewis Publishers, 328 p.

U.S. Environmental Protection Agency, 1980, Samplers and sampling procedures for hazardous waste stream: Cincinnati, Ohio, Municipal Environmental Research Laboratory, EPA 600/ 2-80-018, 70 p.

U.S. Environmental Protection Agency, 1982a, Sampling protocols for collecting surface water, bed sediment, bivalves, and fish for priority pollutant analysis: Washington, D.C., Final Draft Report, Office of Water Regulations and Standards Monitoring and Data Support Division.

_____ 1982b, Handbook for sampling and sample preservation of water and wastewater: Environment Monitoring and Support Laboratory, Cincinnati, Ohio, EPA 600/4-82-029, 402 p.

_____ 1983, Addendum to Handbook for sampling and sample preservation of water and wastewater: Cincinnati, Ohio, Environment Monitoring and Support Laboratory, EPA 600/ 4-83-039, 28 p.

_____ 1986, RCRA groundwater monitoring technical enforcement guidance document: Washington, D.C., OSWER - 9950.1.

_____ 1987, A compendium of Superfund field operations methods: Washington, DC., Office of Emergency and Remedial Response, EPA/540-P-87/001, 508 p.

_____ 1990, Monitoring lake and reservoir restoration: Washington, D.C., Office of Water, EPA 440/4-90-007.

_____ 1991, Handbook—ground water, v. II, Methodology: Washington, D.C., EPA/625/6-90/016b, 141 p.

_____ 1992, Consensus method for determining groundwaters under the direct influence of surface water using microscopic particulate analysis (MPA): EPA Region 10.

_____ 1992, Pocket sampling guide for operations of small water systems: Cincinnati, Ohio, Office of Ground Water and Drinking Water, EPA/814-B-92-001, 94 p.

_____ 1993, Preparation of a U.S. EPA Region 9 sample plan for EPA-lead superfund projects: San Francisco, Calif., EPA Region 9, Quality Assurance Management Section, August 1993.

U.S. Geological Survey, 1980, Surface water, chap. 1 *of* National handbook of recommended methods for water-data acquisition: Office of Water Data Coordination, 130 p.

_____ 1980, Ground water, chap. 2 *of* National handbook of recommended methods for water-data acquisition: Office of Water Data Coordination, 130 p.

_____ 1984, Chemical and physical quality of water and sediment, chap. 5 *of* National handbook of recommended methods for water-data acquisition: Office of Water Data Coordination, p. 5-1 to 5-194.

_____ 1992a, Indiana district tests ground-water sampling device, *in* WRD Instrument News, Debra Tracey, ed.: Stennis Space Center, Miss., Hydrologic Instrumentation Facility, no. 57, p. 1.

_____ 1992b, Ground-water sampler testing in a standpipe system, *in* WRD Instrument News, Debra Tracey, ed.: Stennis Space Center, Miss., Hydrologic Instrumentation Facility, no. 59, p. 6.

Ward, J.R., and Harr, C.A., eds., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90-140, 71 p.

Internal Documents

The following Branch of Quality Systems (formerly Branch of Quality Assurance), Office of Water Quality, and National Water Quality Laboratory technical memorandums are available on the World Wide Web at http://water.usgs.gov/lookup/get?techmemo.

Memo No.	Title	Date
	Branch of Quality Systems	
92.01	ADP—Storage of water-quality, quality assurance data in NWIS	February 5, 1990
95.01	ADP—Storage of water-quality quality assurance data in NWIS	October 28, 1994

Memo No.	Title	Date
	Water Quality	
qw92.02	FIELD TECHNIQUES—Field preparation of containers for aqueous samples	December 20, 1991
qw94.16	New preservation techniques for nutrient samples	August 5, 1994
qw95.02	Establishment of U.S. Geological Survey (USGS) Laboratory for determination of chlorofluorocarbons (CFCs) in air and water samples (joint office memo—also available as Office of Ground Water Technical Memorandum 95.02)	December 29, 1994
qw97.03	Protocols for cleaning a Teflon cone splitter to produce contaminant-free subsamples for subsequent determinations of trace elements	February 7, 1997
qw97.06	Comparison of the suspended-sediment splitting capabilities of the churn and cone splitters	May 5, 1997
qw99.02	Guidance for collecting discharge-weighted samples in surface water using an isokinetic sampler	November 3, 1998

Memo No.	Title	Date
	National Water Quality Laboratory	
92.04	Bottles for tritium analyses	August 12, 1992
93.09	Radon. - Discontinuance of duplicate samples for radon-in-water	August 24, 1993
95.04	Shipping samples to the National Water Quality Laboratory	December 2, 1994
95.05	Nitrogen isotope sample preservation for water samples	March 8, 1995
96.05	Collection, processing, and analysis of carbon isotope samples	April 5, 1996
97.04	Tritium/helium dating of ground-water samples available through contract with Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York	April 7, 1997

Memo No.	Title	Date
	Water Resources	
94.008	LEGAL-Agreement forms 9-1482, 9-1482A, and 9-1483	February 18, 1994

PUBLICATIONS ON TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The material is grouped under major subject headings called books and is further divided into sections and chapters. For example, Section A of Book 9 (Handbooks for Water-Resources Investigations) pertains to collection of water-quality data. The chapter, which is the unit of publication, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises.

The Techniques of Water-Resources Investigations (TWRI) reports listed below are for sale by the U.S. Geological Survey, Branch of Information Services, Box 25286, Federal Center, Denver, CO 80225 (authorized agent of the Superintendent of Documents, Government Printing Office). Prepayment is required. Remittance should be sent by check or money order payable to the U.S. Geological Survey. Prices are not included because they are subject to change. Current prices can be obtained by writing to the above address. When ordering or inquiring about prices for any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations." An updated list of TWRI reports can be found by accessing the World Wide Web url: http://water.usgs.gov/lookup/get?TWRI.

Book 1. Collection of Water Data by Direct Measurement

Section D. Water Quality

1-D1. Water temperature—influential factors, field measurement, and data presentation, by H.H. Stevens, Jr., J.F. Ficke, and G.F. Smoot: USGS—TWRI Book 1, Chapter D1. 1975. 65 pages.

1-D2. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents, by W.W. Wood: USGS—TWRI Book 1, Chapter D2. 1976. 24 pages.

Book 2. Collection of Environmental Data

Section D. Surface Geophysical Methods

2-D1. Application of surface geophysics to ground-water investigations, by A.A.R. Zohdy, G.P. Eaton, and D.R. Mabey: USGS—TWRI Book 2, Chapter D1. 1974. 116 pages.

2-D2. Application of seismic-refraction techniques to hydrologic studies, by F.P. Haeni: USGS—TWRI Book 2, Chapter D2. 1988. 86 pages.

Section E. Subsurface Geophysical Methods

2-E1.Application of borehole geophysics to water-resources investigations, by W.S. Keys and L.M. MacCary: USGS—TWRI Book 2, Chapter E1. 1971. 126 pages.

2-E2.Borehole geophysics applied to ground-water investigations, by W.S. Keys: USGS—TWRI Book 2, Chapter E2. 1990. 150 pages.

Section F. Drilling and Sampling Methods

2-F1.Application of drilling, coring, and sampling techniques to test holes and wells, by Eugene Shuter and W.E. Teasdale: USGS—TWRI Book 2, Chapter F1. 1989. 97 pages.

Book 3. Applications of Hydraulics

Section A. Surface-Water Techniques

3-A1.General field and office procedures for indirect discharge measurements, by M.A. Benson and Tate Dalrymple: USGS—TWRI Book 3, Chapter A1. 1967. 30 pages.

3-A2.Measurement of peak discharge by the slope-area method, by Tate Dalrymple and M.A. Benson: USGS—TWRI Book 3, Chapter A2. 1967. 12 pages.

3-A3.Measurement of peak discharge at culverts by indirect methods, by G.L. Bodhaine: USGS—TWRI Book 3, Chapter A3. 1968. 60 pages.

3-A4.Measurement of peak discharge at width contractions by indirect methods, by H.F. Matthai: USGS—TWRI Book 3, Chapter A4. 1967. 44 pages.

3-A5.Measurement of peak discharge at dams by indirect methods, by Harry Hulsing: USGS—TWRI Book 3, Chapter A5. 1967. 29 pages.

3-A6.General procedure for gaging streams, by R.W. Carter and Jacob Davidian: USGS—TWRI Book 3, Chapter A6. 1968. 13 pages.

3-A7.Stage measurement at gaging stations, by T.J. Buchanan and W.P. Somers: USGS—TWRI Book 3, Chapter A7. 1968. 28 pages.

3-A8.Discharge measurements at gaging stations, by T.J. Buchanan and W.P. Somers: USGS—TWRI Book 3, Chapter A8. 1969. 65 pages.

3-A9.Measurement of time of travel in streams by dye tracing, by F.A. Kilpatrick and J.F. Wilson, Jr.: USGS—TWRI Book 3, Chapter A9. 1989. 27 pages.

3-A10.Discharge ratings at gaging stations, by E.J. Kennedy: USGS—TWRI Book 3, Chapter A10. 1984. 59 pages.

3-A11.Measurement of discharge by the moving-boat method, by G.F. Smoot and C.E. Novak: USGS—TWRI Book 3, Chapter A11. 1969. 22 pages.

3-A12.Fluorometric procedures for dye tracing, Revised, by J.F. Wilson, Jr., E.D. Cobb, and F.A. Kilpatrick: USGS—TWRI Book 3, Chapter A12. 1986. 34 pages.

3-A13.Computation of continuous records of streamflow, by E.J. Kennedy: USGS—TWRI Book 3, Chapter A13. 1983. 53 pages.

3-A14.Use of flumes in measuring discharge, by F.A. Kilpatrick and V.R. Schneider: USGS—TWRI Book 3, Chapter A14. 1983. 46 pages.

3-A15.Computation of water-surface profiles in open channels, by Jacob Davidian: USGS—TWRI Book 3, Chapter A15. 1984. 48 pages.

3-A16.Measurement of discharge using tracers, by F.A. Kilpatrick and E.D. Cobb: USGS—TWRI Book 3, Chapter A16. 1985. 52 pages.

3–A17.Acoustic velocity meter systems, by Antonius Laenen: USGS—TWRI Book 3, Chapter A17. 1985. 38 pages.

3–A18.Determination of stream reaeration coefficients by use of tracers, by F.A. Kilpatrick, R.E. Rathbun, Nobuhiro Yotsukura, G.W. Parker, and L.L. DeLong: USGS—TWRI Book 3, Chapter A18. 1989. 52 pages.

3–A19.Levels at streamflow gaging stations, by E.J. Kennedy: USGS—TWRI Book 3, Chapter A19. 1990. 31 pages.

3–A20.Simulation of soluble waste transport and buildup in surface waters using tracers, by F.A. Kilpatrick: USGS—TWRI Book 3, Chapter A20. 1993. 38 pages.

3–A21.Stream-gaging cableways, by C. Russell Wagner: USGS—TWRI Book 3, Chapter A21. 1995. 56 pages.

Section B. Ground-Water Techniques

3–B1. Aquifer-test design, observation, and data analysis, by R.W. Stallman: USGS—TWRI Book 3, Chapter B1. 1971. 26 pages.

3–B2.Introduction to ground-water hydraulics, a programed text for self-instruction, by G.D. Bennett: USGS—TWRI Book 3, Chapter B2. 1976. 172 pages.

3–B3.Type curves for selected problems of flow to wells in confined aquifers, by J.E. Reed: USGS—TWRI Book 3, Chapter B3. 1980. 106 pages.

3–B4.Regression modeling of ground-water flow, by R.L. Cooley and R.L. Naff: USGS—TWRI Book 3, Chapter B4. 1990. 232 pages.

3–B4.Supplement 1. Regression modeling of ground-water flow—Modifications to the computer code for nonlinear regression solution of steady-state ground-water flow problems, by R.L. Cooley: USGS—TWRI Book 3, Chapter B4. 1993. 8 pages.

3–B5.Definition of boundary and initial conditions in the analysis of saturated ground-water flow systems—An introduction, by O. L. Franke, T.E. Reilly, and G.D. Bennett: USGS—TWRI Book 3, Chapter B5. 1987. 15 pages.

3–B6.The principle of superposition and its application in ground-water hydraulics, by T.E. Reilly, O.L. Franke, and G.D. Bennett: USGS—TWRI Book 3, Chapter B6. 1987. 28 pages.

3–B7.Analytical solutions for one-, two-, and three-dimensional solute transport in ground-water systems with uniform flow, by E.J. Wexler: USGS—TWRI Book 3, Chapter B7. 1992. 190 pages.

Section C. Sedimentation and Erosion Techniques

3–C1.Fluvial sediment concepts, by H. P. Guy: USGS—TWRI Book 3, Chapter C1. 1970. 55 pages.

3–C2.Field methods for measurement of fluvial sediment, by T.K. Edwards and G.D. Glysson: USGS—TWRI Book 3, Chapter C2. 1998. 80 pages.

3–C3.Computation of fluvial-sediment discharge, by George Porterfield: USGS—TWRI Book 3, Chapter C3. 1972. 66 pages.

Book 4. Hydrologic Analysis and Interpretation

Section A. Statistical Analysis

4–A1.Some statistical tools in hydrology, by H.C. Riggs: USGS—TWRI Book 4, Chapter A1. 1968. 39 pages.

4–A2.Frequency curves, by H.C. Riggs: USGS—TWRI Book 4, Chapter A2. 1968. 15 pages.

Section B. Surface Water

4–B1.Low-flow investigations, by H.C. Riggs: USGS—TWRI Book 4, Chapter B1. 1972. 18 pages.

4–B2.Storage analyses for water supply, by H.C. Riggs and C.H. Hardison: USGS—TWRI Book 4, Chapter B2. 1973. 20 pages.

4–B3.Regional analyses of streamflow characteristics, by H.C. Riggs: USGS—TWRI Book 4, Chapter B3. 1973. 15 pages.

Section D. Interrelated Phases of the Hydrologic Cycle

4–D1.Computation of rate and volume of stream depletion by wells, by C.T. Jenkins: USGS—TWRI Book 4, Chapter D1. 1970. 17 pages.

Book 5. Laboratory Analysis

Section A. Water Analysis

5–A1.Methods for determination of inorganic substances in water and fluvial sediments, by M.J. Fishman and L.C. Friedman, editors: USGS—TWRI Book 5, Chapter A1. 1989. 545 pages.

5–A2.Determination of minor elements in water by emission spectroscopy, by P.R. Barnett and E.C. Mallory, Jr.: USGS—TWRI Book 5, Chapter A2. 1971. 31 pages.

5–A3.Methods for the determination of organic substances in water and fluvial sediments, edited by R.L. Wershaw, M.J. Fishman, R.R. Grabbe, and L.E. Lowe: USGS—TWRI Book 5, Chapter A3. 1987. 80 pages.

5–A4.Methods for collection and analysis of aquatic biological and microbiological samples, by L.J. Britton and P.E. Greeson, editors: USGS—TWRI Book 5, Chapter A4. 1989. 363 pages.

5–A5.Methods for determination of radioactive substances in water and fluvial sediments, by L.L. Thatcher, V.J. Janzer, and K.W. Edwards: USGS—TWRI Book 5, Chapter A5. 1977. 95 pages.

5–A6.Quality assurance practices for the chemical and biological analyses of water and fluvial sediments, by L.C. Friedman and D.E. Erdmann: USGS—TWRI Book 5, Chapter A6. 1982. 181 pages.

Section C. Sediment Analysis

5–C1.Laboratory theory and methods for sediment analysis, by H. P. Guy: USGS—TWRI Book 5, Chapter C1. 1969. 58 pages.

Book 6. Modeling Techniques

Section A. Ground Water

6–A1.A modular three-dimensional finite-difference ground-water flow model, by M.G. McDonald and A.W. Harbaugh: USGS—TWRI Book 6, Chapter A1. 1988. 586 pages.

6–A2.Documentation of a computer program to simulate aquifer-system compaction using the modular finite-difference ground-water flow model, by S.A. Leake and D.E. Prudic: USGS—TWRI Book 6, Chapter A2. 1991. 68 pages.

6–A3.A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 1: Model Description and User's Manual, by L.J. Torak: USGS—TWRI Book 6, Chapter A3. 1993. 136 pages.

6–A4.A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 2: Derivation of finite-element equations and comparisons with analytical solutions, by R.L. Cooley: USGS—TWRI Book 6, Chapter A4. 1992. 108 pages.

6–A5.A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 3: Design philosophy and programming details, by L.J. Torak: USGS—TWRI Book 6, Chapter A5, 1993. 243 pages.

6–A6.A coupled surface-water and ground-water flow model (MODBRANCH) for simulation of stream-aquifer interaction by E.D. Swain and Eliezer J. Wexler: USGS—TWRI Book 6, Chapter A6, 1996. 125 pages.

Book 7. Automated Data Processing and Computations

Section C. Computer Programs

7–C1.Finite difference model for aquifer simulation in two dimensions with results of numerical experiments, by P.C. Trescott, G.F. Pinder, and S.P. Larson: USGS—TWRI Book 7, Chapter C1. 1976. 116 pages.

7–C2.Computer model of two-dimensional solute transport and dispersion in ground water, by L.F. Konikow and J.D. Bredehoeft: USGS—TWRI Book 7, Chapter C2. 1978. 90 pages.

7–C3.A model for simulation of flow in singular and interconnected channels, by R.W. Schaffranek, R.A. Baltzer, and D.E. Goldberg: USGS—TWRI Book 7, Chapter C3. 1981. 110 pages.

Book 8. Instrumentation

Section A. Instruments for Measurement of Water Level

8–A1.Methods of measuring water levels in deep wells, by M.S. Garber and F.C. Koopman: USGS—TWRI Book 8, Chapter A1. 1968. 23 pages.

8–A2.Installation and service manual for U.S. Geological Survey manometers, by J.D. Craig: USGS—TWRI Book 8, Chapter A2. 1983. 57 pages.

Section B. Instruments for Measurement of Discharge

8–B2.Calibration and maintenance of vertical-axis type current meters, by G.F. Smoot and C.E. Novak: USGS—TWRI Book 8, Chapter B2. 1968. 15 pages.

Book 9. Handbooks for Water-Resources Investigations

Section A. National Field Manual for the Collection of Water-Quality Data

9–A1.Preparations for water sampling, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo: USGS—TWRI Book 9, Chapter A1. 1998. Variously paged.

9–A2.Selection of equipment for water sampling, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A2. 1998. Variously paged.

9–A3. Cleaning of equipment for water sampling, by F.D. Wilde, D.B., Radke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A3. 1998. Variously paged.

9–A4.Collection of water samples, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A4. 1999. Variously paged.

9–A5.Processing of water samples, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A5. 1999. Variously paged.

9–A6.Field measurements, by F.D. Wilde and D.B. Radtke, editors: USGS—TWRI Book 9, Chapter A6. 1998. Variously paged.

9–A7.Biological indicators, by D.N. Myers and F.D. Wilde, editors: USGS—TWRI Book 9, Chapter A7. 1997. Variously paged.

9–A8.Bottom-material samples, by D.B. Radtke: USGS—TWRI Book 9, Chapter A8. 1998. Variously paged.

9–A9.Safety in field activities, by S.L. Lane and R.G. Fay: USGS—TWRI Book 9, Chapter A9. 1998. Variously paged.

APPENDIX A4-A

TRANSIT RATE AND VOLUME GUIDELINES FOR ISOKINETIC SAMPLING

Prepared by Wayne E. Webb,
U.S. Geological Survey, Reston, Va.

The tables in Appendix A4-A apply to the first complete round-trip transit starting with an empty sampler container. **These tables are valid only if the sampler is emptied between verticals.**

Tables showing:

1. Isokinetic transit rates for a 1-liter bottle sampler with a
   a. 3/16-inch nozzle
   b. 1/4-inch nozzle
   c. 5/16-inch nozzle
2. Isokinetic transit rates for a 3-liter bottle sampler with a
   a. 1/4-inch nozzle
   b. 5/16-inch nozzle
3. a. Minimum volumes for isokinetic sampling with a bag sampler
   b. Isokinetic transit rates for a 3-liter bag sampler with a 1/4-inch nozzle
   c. Isokinetic transit rates for a 3-liter bag sampler with a 5/16-inch nozzle

The designations in the **RATE** column of these tables are defined as follows:

full The reeling or transit rate that fills the sampler to its maximum volume.

-10 tip The reeling or transit rate that will result in a volume in the sampler such that if the sampler nozzle is tipped 10 degrees down from the horizontal, no sample will spill from the nozzle.

fastest The reeling or transit rate that is the fastest rate to avoid compression problems in bottle samplers or to not exceed a transit rate that is more than 0.4 times the stream velocity for bag samplers.

The volume designations in these tables are defined as follows:

max vol. The volume that will be in the sampler when the "full" (see definition above) reeling rate or transit rate is used for the specified stream depth and velocity.

-10 vol. The volume that will be in the sampler when the "-10 tip" (see definition above) reeling or transit rate is used for the specified stream depths and velocity.

min vol. The volume that will be in the sampler when the "fastest" (see definition above) reeling or transit rate is used for the specified stream depth and velocity.

APPENDIX A4-A—Table 1a. Isokinetic transit rates for a 1-liter bottle sampler with a 3/16-inch nozzle

[Transit rates in feet per second; Depth is (water depth) - (unsampled zone); max, maximum; vol, volume; min, minimum; mL, milliliter; --, not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
1	full	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.05	0.06	0.07	0.08	0.09	1,050	919
1	-10 tip	0.02	0.03	0.03	0.04	0.05	0.05	0.06	0.07	0.08	0.10	0.11	0.12	798	667
1	fastest	0.12	0.17	0.21	0.25	0.29	0.33	0.37	0.41	0.50	0.58	0.66	0.74	131	--
2	full	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.12	0.14	0.17	0.19	1,050	807
2	-10 tip	0.04	0.05	0.07	0.08	0.10	0.11	0.12	0.14	0.16	0.19	0.22	0.25	798	555
2	fastest	0.13	0.18	0.22	0.27	0.31	0.36	0.40	0.45	0.54	0.63	0.72	0.81	243	--
3	full	0.05	0.06	0.08	0.09	0.11	0.12	0.14	0.16	0.19	0.22	0.25	0.28	1,050	711
3	-10 tip	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.25	0.29	0.33	0.37	798	459
3	fastest	0.14	0.19	0.24	0.29	0.34	0.38	0.43	0.48	0.58	0.67	0.77	0.87	339	--
4	full	0.06	0.08	0.10	0.12	0.14	0.17	0.19	0.21	0.25	0.29	0.33	0.37	1,050	628
4	-10 tip	0.08	0.11	0.14	0.16	0.19	0.22	0.25	0.27	0.33	0.38	0.44	0.49	798	376
4	fastest	0.15	0.21	0.26	0.31	0.36	0.41	0.46	0.51	0.62	0.72	0.82	0.93	423	--
5	full	0.08	0.10	0.13	0.16	0.18	0.21	0.23	0.26	0.31	0.36	0.41	0.47	1,050	555
5	-10 tip	0.10	0.14	0.17	0.20	0.24	0.27	0.31	0.34	0.41	0.48	0.54	0.61	798	303
5	fastest	0.16	0.22	0.27	0.33	0.38	0.44	0.49	0.55	0.66	0.77	0.88	0.99	496	--
6	full	0.09	0.12	0.16	0.19	0.22	0.25	0.28	0.31	0.37	0.43	0.50	0.56	1,050	490
6	-10 tip	0.12	0.16	0.20	0.25	0.29	0.33	0.37	0.41	0.49	0.57	0.65	0.74	798	238
6	fastest	0.17	0.23	0.29	0.35	0.41	0.47	0.52	0.58	0.70	0.81	0.93	1.05	561	--

APPENDIX A4-A—Table 1a. Isokinetic transit rates for a 1-liter bottle sampler with a 3/16-inch nozzle—*Continued*

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
7	full	0.11	0.14	0.18	0.22	0.25	0.29	0.33	0.36	0.43	0.51	0.58	0.65	1,050	432
7	-10 tip	0.14	0.19	0.24	0.29	0.33	0.38	0.43	0.48	0.57	0.67	0.76	0.86	798	180
7	fastest	0.18	0.25	0.31	0.37	0.43	0.49	0.55	0.62	0.74	0.86	0.99	1.11	618	--
8	full	0.12	0.17	0.21	0.25	0.29	0.33	0.37	0.41	0.50	0.58	0.66	0.75	1,050	380
8	-10 tip	0.16	0.22	0.27	0.33	0.38	0.44	0.49	0.54	0.65	0.76	0.87	0.98	798	129
8	fastest	0.19	0.26	0.32	0.39	0.45	0.52	0.58	0.65	0.78	0.91	1.04	1.17	670	--
10	full	0.16	0.21	0.26	0.31	0.36	0.41	0.47	0.52	0.62	0.72	0.83	0.93	1,050	292
10	-10 tip	0.20	0.27	0.34	0.41	0.48	0.54	0.61	0.68	0.82	0.95	1.09	1.23	798	40
10	fastest	0.22	0.29	0.36	0.43	0.50	0.57	0.65	0.72	0.86	1.00	1.15	1.29	759	--
12	full	0.19	0.25	0.31	0.37	0.43	0.50	0.56	0.62	0.75	0.87	0.99	1.12	1,050	218
12	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
12	fastest	0.24	0.31	0.39	0.47	0.55	0.63	0.71	0.78	0.94	1.10	1.25	1.41	832	--
14	full	0.22	0.29	0.36	0.43	0.51	0.58	0.65	0.72	0.87	1.01	1.16	1.30	1,050	156
14	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
14	fastest	0.26	0.34	0.43	0.51	0.60	0.68	0.77	0.85	1.02	1.19	1.36	1.53	894	--
15	full	0.23	0.31	0.39	0.47	0.54	0.62	0.70	0.78	0.93	1.09	1.24	1.40	1,050	129
15	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
15	fastest	0.27	0.35	0.44	0.53	0.62	0.71	0.80	0.89	1.06	1.24	1.42	1.59	922	--

APPENDIX A4-A—Table 1b. Isokinetic transit rates for a 1-liter bottle sampler with a 1/4-inch nozzle

[Transit rates in feet per second; Depth is water depth - unsampled zone; max, maximum; vol, volume; min, minimum; mL, milliliter; --, not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
1	full	0.03	0.04	0.05	0.06	0.06	0.07	0.08	0.09	0.11	0.13	0.15	0.17	1,050	918
1	-10 tip	0.04	0.05	0.06	0.07	0.08	0.10	0.11	0.12	0.15	0.17	0.19	0.22	798	667
1	fastest	0.22	0.29	0.37	0.44	0.51	0.59	0.66	0.73	0.88	1.03	1.17	1.32	132	--
2	full	0.06	0.07	0.09	0.11	0.13	0.15	0.17	0.18	0.22	0.26	0.29	0.33	1,050	806
2	-10 tip	0.07	0.10	0.12	0.15	0.17	0.19	0.22	0.24	0.29	0.34	0.39	0.44	798	555
2	fastest	0.24	0.32	0.40	0.48	0.56	0.63	0.71	0.79	0.95	1.11	1.27	1.43	243	--
3	full	0.08	0.11	0.14	0.17	0.19	0.22	0.25	0.28	0.33	0.39	0.44	0.50	1,050	710
3	-10 tip	0.11	0.15	0.18	0.22	0.25	0.29	0.33	0.36	0.44	0.51	0.58	0.65	798	458
3	fastest	0.26	0.34	0.43	0.51	0.60	0.68	0.77	0.85	1.02	1.19	1.36	1.54	340	--
4	full	0.11	0.15	0.18	0.22	0.26	0.29	0.33	0.37	0.44	0.52	0.59	0.66	1,050	626
4	-10 tip	0.15	0.19	0.24	0.29	0.34	0.39	0.44	0.48	0.58	0.68	0.77	0.87	798	375
4	fastest	0.27	0.36	0.46	0.55	0.64	0.73	0.82	0.91	1.09	1.28	1.46	1.64	423	--
5	full	0.14	0.18	0.23	0.28	0.32	0.37	0.41	0.46	0.55	0.64	0.74	0.83	1,050	553
5	-10 tip	0.18	0.24	0.30	0.36	0.42	0.48	0.54	0.61	0.73	0.85	0.97	1.09	798	301
5	fastest	0.29	0.39	0.49	0.58	0.68	0.78	0.87	0.97	1.17	1.36	1.55	1.75	497	--
6	full	0.17	0.22	0.28	0.33	0.39	0.44	0.50	0.55	0.66	0.77	0.88	0.99	1,050	488
6	-10 tip	0.22	0.29	0.36	0.44	0.51	0.58	0.65	0.73	0.87	1.02	1.16	1.31	798	236
6	fastest	0.31	0.41	0.52	0.62	0.72	0.82	0.93	1.03	1.24	1.44	1.65	1.86	562	--

APPENDIX A4-A—Table 1b. Isokinetic transit rates for a 1-liter bottle sampler with a 1/4-inch nozzle—*Continued*

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
7	full	0.19	0.26	0.32	0.39	0.45	0.52	0.58	0.64	0.77	0.90	1.03	1.16	1,050	430
7	-10 tip	0.25	0.34	0.42	0.51	0.59	0.68	0.76	0.85	1.02	1.19	1.36	1.52	798	178
7	fastest	0.33	0.44	0.55	0.65	0.76	0.87	0.98	1.09	1.31	1.53	1.74	1.96	620	--
8	full	0.22	0.29	0.37	0.44	0.52	0.59	0.66	0.74	0.88	1.03	1.18	1.32	1,050	378
8	-10 tip	0.29	0.39	0.48	0.58	0.68	0.77	0.87	0.97	1.16	1.36	1.55	1.74	798	126
8	fastest	0.34	0.46	0.57	0.69	0.80	0.92	1.03	1.15	1.38	1.61	1.84	2.07	672	--
10	full	0.28	0.37	0.46	0.55	0.64	0.74	0.83	0.92	1.10	1.29	1.47	1.66	1,050	288
10	-10 tip	0.36	0.48	0.61	0.73	0.85	0.97	1.09	1.21	1.45	1.69	1.94	2.18	798	37
10	fastest	0.38	0.51	0.63	0.76	0.89	1.01	1.14	1.27	1.52	1.78	2.03	2.28	761	--
12	full	0.33	0.44	0.55	0.66	0.77	0.88	0.99	1.10	1.32	1.55	1.77	1.99	1,050	214
12	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
12	fastest	0.42	0.55	0.69	0.83	0.97	1.11	1.25	1.39	1.66	1.94	2.22	2.50	836	--
14	full	0.39	0.52	0.64	0.77	0.90	1.03	1.16	1.29	1.55	1.80	2.06	2.32	1,050	152
14	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
14	fastest	0.45	0.60	0.75	0.90	1.05	1.20	1.36	1.51	1.81	2.11	2.41	2.71	898	--
15	full	0.41	0.55	0.69	0.83	0.97	1.10	1.24	1.38	1.66	1.93	2.21	2.48	1,050	124
15	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
15	fastest	0.47	0.63	0.78	0.94	1.10	1.25	1.41	1.57	1.88	2.19	2.50	2.82	926	--

APPENDIX A4-A—Table 1c. Isokinetic transit rates for a 1-liter bottle sampler with a 5/16-inch nozzle

[Transit rates in feet per second; Depth is water depth - unsampled zone; max, maximum; vol, volume; min, minimum; mL, milliliter; --, not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
1	full	0.04	0.06	0.07	0.09	0.10	0.12	0.13	0.14	0.17	0.20	0.23	0.26	1,049	918
1	-10 tip	0.06	0.08	0.09	0.11	0.13	0.15	0.17	0.19	0.23	0.26	0.30	0.34	800	668
1	fastest	0.34	0.46	0.57	0.69	0.80	0.92	1.03	1.15	1.38	1.61	1.84	2.07	132	--
2	full	0.09	0.12	0.14	0.17	0.20	0.23	0.26	0.29	0.35	0.40	0.46	0.52	1,049	806
2	-10 tip	0.11	0.15	0.19	0.23	0.26	0.30	0.34	0.38	0.45	0.53	0.60	0.68	800	557
2	fastest	0.37	0.50	0.62	0.74	0.87	0.99	1.12	1.24	1.49	1.74	1.98	2.23	243	--
3	full	0.13	0.17	0.22	0.26	0.30	0.35	0.39	0.43	0.52	0.60	0.69	0.78	1,049	709
3	-10 tip	0.17	0.23	0.28	0.34	0.40	0.45	0.51	0.57	0.68	0.79	0.91	1.02	800	460
3	fastest	0.40	0.53	0.67	0.80	0.93	1.07	1.20	1.33	1.60	1.87	2.13	2.40	340	--
4	full	0.17	0.23	0.29	0.35	0.40	0.46	0.52	0.58	0.69	0.81	0.92	1.04	1,049	626
4	-10 tip	0.23	0.30	0.38	0.45	0.53	0.60	0.68	0.75	0.91	1.06	1.21	1.36	800	376
4	fastest	0.43	0.57	0.71	0.86	1.00	1.14	1.28	1.43	1.71	2.00	2.28	2.57	424	--
5	full	0.22	0.29	0.36	0.43	0.50	0.58	0.65	0.72	0.86	1.01	1.15	1.29	1,049	552
5	-10 tip	0.28	0.38	0.47	0.57	0.66	0.75	0.85	0.94	1.13	1.32	1.51	1.70	800	303
5	fastest	0.46	0.61	0.76	0.91	1.06	1.21	1.37	1.52	1.82	2.13	2.43	2.73	497	--
6	full	0.26	0.35	0.43	0.52	0.60	0.69	0.78	0.86	1.04	1.21	1.38	1.55	1,049	487
6	-10 tip	0.34	0.45	0.57	0.68	0.79	0.91	1.02	1.13	1.36	1.58	1.81	2.04	800	238
6	fastest	0.48	0.64	0.81	0.97	1.13	1.29	1.45	1.61	1.93	2.26	2.58	2.90	562	--

APPENDIX A4-A—Table 1c. Isokinetic transit rates for a 1-liter bottle sampler with a 5/16-inch nozzle—*Continued*

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume- min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
7	full	0.30	0.40	0.50	0.60	0.71	0.81	0.91	1.01	1.21	1.41	1.61	1.81	1,049	429
7	-10 tip	0.40	0.53	0.66	0.79	0.92	1.06	1.19	1.32	1.58	1.85	2.11	2.38	800	180
7	fastest	0.51	0.68	0.85	1.02	1.19	1.36	1.53	1.70	2.04	2.38	2.73	3.07	620	--
8	full	0.35	0.46	0.58	0.69	0.81	0.92	1.04	1.15	1.38	1.61	1.84	2.07	1,049	377
8	-10 tip	0.45	0.60	0.75	0.91	1.06	1.21	1.36	1.51	1.81	2.11	2.42	2.72	800	128
8	fastest	0.54	0.72	0.90	1.08	1.26	1.44	1.62	1.80	2.16	2.51	2.87	3.23	672	--
10	full	0.43	0.58	0.72	0.86	1.01	1.15	1.29	1.44	1.73	2.01	2.30	2.59	1,049	287
10	-10 tip	0.57	0.75	0.94	1.13	1.32	1.51	1.70	1.89	2.26	2.64	3.02	3.40	800	38
10	fastest	0.59	0.79	0.99	1.19	1.39	1.59	1.78	1.98	2.38	2.77	3.17	3.57	762	--
11	full	0.47	0.63	0.79	0.95	1.11	1.27	1.42	1.58	1.90	2.22	2.53	2.85	1,049	219
11	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
11	fastest	0.60	0.80	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	830	--
12	full	0.52	0.69	0.86	1.04	1.21	1.38	1.55	1.73	2.07	2.42	2.76	3.11	1,049	143
12	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
12	fastest	0.60	0.80	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	906	--
13	full	0.56	0.75	0.94	1.12	1.31	1.50	1.68	1.87	2.24	2.62	2.99	3.37	1,049	68
13	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
13	fastest	0.60	0.80	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	981	--

APPENDIX A4-A—Table 2a. Isokinetic transit rates for a 3-liter bottle sampler with a 1/4-inch nozzle

[Transit rates in feet per second; Depth is water depth - unsampled zone; max, maximum; vol, volume; min, minimum; mL, milliliter; --, not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
2	full	0.02	0.03	0.03	0.04	0.05	0.05	0.06	0.07	0.08	0.10	0.11	0.12	2,832	2,120
2	-10 tip	0.02	0.03	0.04	0.05	0.06	0.06	0.07	0.08	0.09	0.11	0.13	0.14	2,457	1,745
2	fastest	0.08	0.11	0.14	0.16	0.19	0.22	0.24	0.27	0.33	0.38	0.43	0.49	712	--
3	full	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.12	0.14	0.16	0.18	2,832	1,840
3	-10 tip	0.04	0.05	0.06	0.07	0.08	0.09	0.11	0.12	0.14	0.17	0.19	0.21	2,457	1,465
3	fastest	0.09	0.12	0.15	0.18	0.20	0.23	0.26	0.29	0.35	0.41	0.47	0.53	992	--
4	full	0.04	0.05	0.07	0.08	0.10	0.11	0.12	0.14	0.16	0.19	0.22	0.25	2,832	1,597
4	-10 tip	0.05	0.06	0.08	0.09	0.11	0.13	0.14	0.16	0.19	0.22	0.25	0.28	2,457	1,222
4	fastest	0.09	0.13	0.16	0.19	0.22	0.25	0.28	0.31	0.38	0.44	0.50	0.56	1,235	--
5	full	0.05	0.07	0.09	0.10	0.12	0.14	0.15	0.17	0.20	0.24	0.27	0.31	2,832	1,383
5	-10 tip	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.24	0.28	0.31	0.35	2,457	1,009
5	fastest	0.10	0.13	0.17	0.20	0.23	0.27	0.30	0.33	0.40	0.47	0.53	0.60	1,449	--
6	full	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.25	0.29	0.33	0.37	2,832	1,195
6	-10 tip	0.07	0.09	0.12	0.14	0.17	0.19	0.21	0.24	0.28	0.33	0.38	0.42	2,457	820
6	fastest	0.11	0.14	0.18	0.21	0.25	0.28	0.32	0.35	0.42	0.50	0.57	0.64	1,637	--
7	full	0.07	0.10	0.12	0.14	0.17	0.19	0.21	0.24	0.29	0.33	0.38	0.43	2,832	1,028
7	-10 tip	0.08	0.11	0.14	0.17	0.19	0.22	0.25	0.28	0.33	0.39	0.44	0.50	2,457	653
7	fastest	0.11	0.15	0.19	0.22	0.26	0.30	0.34	0.37	0.45	0.52	0.60	0.67	1,804	--

APPENDIX A4-A—Table 2a. Isokinetic transit rates for a 3-liter bottle sampler with a 1/4-inch nozzle—*Continued*

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
8	full	0.08	0.11	0.14	0.16	0.19	0.22	0.25	0.27	0.33	0.38	0.44	0.49	2,832	878
8	-10 tip	0.09	0.13	0.16	0.19	0.22	0.25	0.28	0.31	0.38	0.44	0.50	0.57	2,457	503
8	fastest	0.12	0.16	0.20	0.24	0.28	0.32	0.36	0.40	0.47	0.55	0.63	0.71	1,954	--
9	full	0.09	0.12	0.15	0.18	0.21	0.25	0.28	0.31	0.37	0.43	0.49	0.55	2,832	743
9	-10 tip	0.11	0.14	0.18	0.21	0.25	0.28	0.32	0.35	0.42	0.50	0.57	0.64	2,457	368
9	fastest	0.12	0.17	0.21	0.25	0.29	0.33	0.37	0.42	0.50	0.58	0.67	0.75	2,089	--
10	full	0.10	0.14	0.17	0.20	0.24	0.27	0.31	0.34	0.41	0.48	0.55	0.61	2,832	620
10	-10 tip	0.12	0.16	0.20	0.24	0.28	0.31	0.35	0.39	0.47	0.55	0.63	0.71	2,457	246
10	fastest	0.13	0.17	0.22	0.26	0.31	0.35	0.39	0.44	0.52	0.61	0.70	0.79	2,212	--
12	full	0.12	0.16	0.20	0.25	0.29	0.33	0.37	0.41	0.49	0.57	0.65	0.74	2,832	408
12	-10 tip	0.14	0.19	0.24	0.28	0.33	0.38	0.42	0.47	0.57	0.66	0.75	0.85	2,457	33
12	fastest	0.14	0.19	0.24	0.29	0.33	0.38	0.43	0.48	0.57	0.67	0.76	0.86	2,424	--
14	full	0.14	0.19	0.24	0.29	0.33	0.38	0.43	0.48	0.57	0.67	0.76	0.86	2,832	229
14	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
14	fastest	0.16	0.21	0.26	0.31	0.36	0.42	0.47	0.52	0.62	0.73	0.83	0.93	2,603	--
15	full	0.15	0.20	0.26	0.31	0.36	0.41	0.46	0.51	0.61	0.72	0.82	0.92	2,832	149
15	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
15	fastest	0.16	0.22	0.27	0.32	0.38	0.43	0.49	0.54	0.65	0.76	0.86	0.97	2,683	--

APPENDIX A4-A—Table 2b. Isokinetic transit rates for a 3-liter bottle sampler with a 5/16-inch nozzle

[Transit rates in feet per second; Depth is water depth - unsampled zone; max, maximum; vol, volume; min, minimum; mL, milliliter; not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
2	full	0.03	0.04	0.05	0.06	0.07	0.09	0.10	0.11	0.13	0.15	0.17	0.19	2,830	2,118
2	-10 tip	0.04	0.05	0.06	0.07	0.09	0.10	0.11	0.12	0.15	0.17	0.20	0.22	2,461	1,749
2	fastest	0.13	0.17	0.21	0.25	0.30	0.34	0.38	0.42	0.51	0.59	0.68	0.76	712	--
3	full	0.05	0.06	0.08	0.10	0.11	0.13	0.14	0.16	0.19	0.22	0.26	0.29	2,830	1,837
3	-10 tip	0.06	0.07	0.09	0.11	0.13	0.15	0.17	0.18	0.22	0.26	0.29	0.33	2,461	1,468
3	fastest	0.14	0.18	0.23	0.27	0.32	0.36	0.41	0.46	0.55	0.64	0.73	0.82	993	--
4	full	0.06	0.09	0.11	0.13	0.15	0.17	0.19	0.21	0.26	0.30	0.34	0.38	2,830	1,593
4	-10 tip	0.07	0.10	0.12	0.15	0.17	0.20	0.22	0.25	0.29	0.34	0.39	0.44	2,461	1,224
4	fastest	0.15	0.20	0.24	0.29	0.34	0.39	0.44	0.49	0.59	0.68	0.78	0.88	1,237	--
5	full	0.08	0.11	0.13	0.16	0.19	0.21	0.24	0.27	0.32	0.37	0.43	0.48	2,830	1,379
5	-10 tip	0.09	0.12	0.15	0.18	0.21	0.25	0.28	0.31	0.37	0.43	0.49	0.55	2,461	1,010
5	fastest	0.16	0.21	0.26	0.31	0.36	0.42	0.47	0.52	0.62	0.73	0.83	0.94	1,451	--
6	full	0.10	0.13	0.16	0.19	0.22	0.26	0.29	0.32	0.38	0.45	0.51	0.58	2,830	1,190
6	-10 tip	0.11	0.15	0.18	0.22	0.26	0.29	0.33	0.37	0.44	0.52	0.59	0.66	2,461	820
6	fastest	0.17	0.22	0.28	0.33	0.39	0.44	0.50	0.55	0.66	0.77	0.88	0.99	1,641	--
7	full	0.11	0.15	0.19	0.22	0.26	0.30	0.34	0.37	0.45	0.52	0.60	0.67	2,830	1,021
7	-10 tip	0.13	0.17	0.21	0.26	0.30	0.34	0.39	0.43	0.52	0.60	0.69	0.77	2,461	652
7	fastest	0.18	0.23	0.29	0.35	0.41	0.47	0.53	0.58	0.70	0.82	0.93	1.05	1,809	--

APPENDIX A4-A—Table 2b. Isokinetic transit rates for a 3-liter bottle sampler with a 5/16-inch nozzle—*Continued*

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00		
8	full	0.13	0.17	0.21	0.26	0.30	0.34	0.38	0.43	0.51	0.60	0.68	0.77	2,830	870
8	-10 tip	0.15	0.20	0.25	0.29	0.34	0.39	0.44	0.49	0.59	0.69	0.79	0.88	2,461	501
8	fastest	0.18	0.25	0.31	0.37	0.43	0.49	0.55	0.62	0.74	0.86	0.99	1.11	1,960	--
9	full	0.14	0.19	0.24	0.29	0.34	0.38	0.43	0.48	0.58	0.67	0.77	0.86	2,830	734
9	-10 tip	0.17	0.22	0.28	0.33	0.39	0.44	0.50	0.55	0.66	0.77	0.88	0.99	2,461	365
9	fastest	0.19	0.26	0.32	0.39	0.45	0.52	0.58	0.65	0.78	0.91	1.04	1.17	2,096	--
10	full	0.16	0.21	0.27	0.32	0.37	0.43	0.48	0.53	0.64	0.75	0.85	0.96	2,830	610
10	-10 tip	0.18	0.25	0.31	0.37	0.43	0.49	0.55	0.61	0.74	0.86	0.98	1.10	2,461	241
10	fastest	0.20	0.27	0.34	0.41	0.48	0.54	0.61	0.68	0.82	0.95	1.09	1.22	2,220	--
12	full	0.19	0.26	0.32	0.38	0.45	0.51	0.58	0.64	0.77	0.90	1.02	1.15	2,830	396
12	-10 tip	0.22	0.29	0.37	0.44	0.52	0.59	0.66	0.74	0.88	1.03	1.18	1.32	2,461	26
12	fastest	0.22	0.30	0.37	0.45	0.52	0.60	0.67	0.74	0.89	1.04	1.19	1.34	2,435	--
14	full	0.22	0.30	0.37	0.45	0.52	0.60	0.67	0.75	0.90	1.05	1.19	1.34	2,830	215
14	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
14	fastest	0.24	0.32	0.40	0.48	0.57	0.65	0.73	0.81	0.97	1.13	1.29	1.45	2,615	--
15	full	0.24	0.32	0.40	0.48	0.56	0.64	0.72	0.80	0.96	1.12	1.28	1.44	2,830	135
15	-10 tip	--	--	--	--	--	--	--	--	--	--	--	--	--	--
15	fastest	0.25	0.34	0.42	0.50	0.59	0.67	0.76	0.84	1.01	1.18	1.34	1.51	2,695	--

APPENDIX A4-A—Table 3a. Minimum volumes for isokinetic sampling with a bag sampler

[The volumes listed below are the minimum volumes that must be collected in a bag sampler to have not exceeded 0.4 times the mean stream velocity. Generally, bag samplers must be operated in water warmer than 7 degrees Celsius and where the velocity is greater than 3 feet per second.]

Water depth minus unsampled zone, in feet	Minimum volume (in milliliters) for the nozzle diameter (inch) shown [1]		
	3/16 inch	1/4 inch	5/16 inch
1	27	48	75
2	54	96	151
3	81	145	226
4	109	193	301
5	136	241	377
6	163	289	452
7	190	338	528
8	217	386	603
9	244	434	678
10	271	483	754
11	298	531	829
12	326	579	904
13	353	627	980
14	380	675	1,055
15	407	724	1,131
20	543	965	1,507
25	678	1,206	1,884
30	814	1,447	2,262
35	950	1,688	2,638
40	1,085	1,930	3,015
45	1,221	2,171	3,392
50	1,357	2,412	3,769
55	1,492	2,653	4,146
60	1,629	2,894	4,524
65	1,764	3,136	4,899
70	1,899	3,377	5,276
75	2,035	3,618	5,653

APPENDIX A4-A—Table 3a. Minimum volumes for isokinetic sampling with a bag sampler—*Continued*

Water depth minus unsampled zone, in feet	Minimum volume (in milliliters) for the nozzle diameter (inch) shown [1]		
	3/16 inch	1/4 inch	5/16 inch
80	2,171	3,859	6,030
85	2,306	4,100	6,407
90	2,442	4,342	6,784
95	2,578	4,583	7,161
100	2,713	4,824	7,537
120	3,257	5,789	9,045
140	3,799	6,754	10,552
160	4,342	7,718	12,060
180	4,884	8,683	13,567
200	5,427	9,650	15,075

[1] Minimum volume = area of nozzle x time in water x mean stream velocity in vertical; minimum volume in milliliters = 15 x 3.14 x 2.54 cubed x nozzle diameter, in inches squared x depth, in feet.

APPENDIX A4-A—Table 3b. Isokinetic transit rates for a 3-liter bag sampler with a 1/4-inch nozzle

[Transit rates in feet per second; Depth is water depth - unsampled zone; max, maximum; vol, volume; min, minimum; mL, milliliter; --, not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00	10.00	12.00		
6	full	0.11	0.13	0.16	0.18	0.20	0.22	0.27	0.31	0.36	0.40	0.44	0.53	2,607	2,318
6	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	290	--
8	full	0.15	0.18	0.21	0.24	0.27	0.30	0.36	0.41	0.47	0.53	0.59	0.71	2,607	2,221
8	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	386	--
10	full	0.19	0.22	0.26	0.30	0.33	0.37	0.44	0.52	0.59	0.67	0.74	0.89	2,607	2,125
10	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	483	--
12	full	0.22	0.27	0.31	0.36	0.40	0.44	0.53	0.62	0.71	0.80	0.89	1.07	2,607	2,028
12	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	579	--
14	full	0.26	0.31	0.36	0.41	0.47	0.52	0.62	0.73	0.83	0.93	1.04	1.24	2,607	1,931
14	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	676	--
16	full	0.30	0.36	0.41	0.47	0.53	0.59	0.71	0.83	0.95	1.07	1.19	1.42	2,607	1,835
16	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	773	--
18	full	0.33	0.40	0.47	0.53	0.60	0.67	0.80	0.93	1.07	1.20	1.33	1.60	2,607	1,738
18	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	869	--
20	full	0.37	0.44	0.52	0.59	0.67	0.74	0.89	1.04	1.19	1.33	1.48	1.78	2,607	1,642
20	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	966	--
22	full	0.41	0.49	0.57	0.65	0.73	0.81	0.98	1.14	1.30	1.47	1.63	1.96	2,607	1,545
22	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,062	--

APPENDIX A4-A—Table 3b. Isokinetic transit rates for a 3-liter bag sampler with a 1/4-inch nozzle—*Continued*

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00	10.00	12.00		
24	full	0.44	0.53	0.62	0.71	0.80	0.89	1.07	1.24	1.42	1.60	1.78	2.13	2,607	1,449
24	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,159	--
26	full	0.48	0.58	0.67	0.77	0.87	0.96	1.16	1.35	1.54	1.73	1.93	2.31	2,607	1,352
26	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,255	--
28	full	0.52	0.62	0.73	0.83	0.93	1.04	1.24	1.45	1.66	1.87	2.07	2.49	2,607	1,255
28	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,352	--
30	full	0.56	0.67	0.78	0.89	1.00	1.11	1.33	1.56	1.78	2.00	2.22	2.67	2,607	1,159
30	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,449	--
35	full	0.65	0.78	0.91	1.04	1.17	1.30	1.56	1.81	2.07	2.33	2.59	3.11	2,607	917
35	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,690	--
40	full	0.74	0.89	1.04	1.19	1.33	1.48	1.78	2.07	2.37	2.67	2.96	3.56	2,607	676
40	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,931	--
45	full	0.83	1.00	1.17	1.33	1.50	1.67	2.00	2.33	2.67	3.00	3.33	4.00	2,607	435
45	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	2,173	--
50	full	0.93	1.11	1.30	1.48	1.67	1.85	2.22	2.59	2.96	3.33	3.70	4.44	2,607	193
50	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	2,414	--
53	full	0.98	1.18	1.37	1.57	1.77	1.96	2.36	2.75	3.14	3.53	3.93	4.71	2,607	48
53	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	2,559	--

APPENDIX A4-A—Table 3c. Isokinetic transit rates for a 3-liter bag sampler with a 5/16-inch nozzle

[Transit rates in feet per second; Depth is water depth - unsampled zone; max, maximum; vol, volume; min, minimum; mL, milliliter; --, not applicable]

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00	10.00	12.00		
2	full	0.06	0.07	0.08	0.09	0.10	0.12	0.14	0.16	0.19	0.21	0.23	0.28	2,604	2,453
2	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	151	--
4	full	0.12	0.14	0.16	0.19	0.21	0.23	0.28	0.32	0.37	0.42	0.46	0.56	2,604	2,302
4	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	302	--
6	full	0.17	0.21	0.24	0.28	0.31	0.35	0.42	0.49	0.56	0.63	0.70	0.83	2,604	2,151
6	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	453	--
8	full	0.23	0.28	0.32	0.37	0.42	0.46	0.56	0.65	0.74	0.83	0.93	1.11	2,604	2,000
8	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	604	--
10	full	0.29	0.35	0.41	0.46	0.52	0.58	0.70	0.81	0.93	1.04	1.16	1.39	2,604	1,849
10	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	755	--
12	full	0.35	0.42	0.49	0.56	0.63	0.70	0.83	0.97	1.11	1.25	1.39	1.67	2,604	1,698
12	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	906	--
14	full	0.41	0.49	0.57	0.65	0.73	0.81	0.97	1.14	1.30	1.46	1.62	1.95	2,604	1,547
14	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,057	--
16	full	0.46	0.56	0.65	0.74	0.83	0.93	1.11	1.30	1.48	1.67	1.86	2.23	2,604	1,396
16	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,208	--
18	full	0.52	0.63	0.73	0.83	0.94	1.04	1.25	1.46	1.67	1.88	2.09	2.50	2,604	1,245
18	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,359	--

APPENDIX A4-A—Table 3c. Isokinetic transit rates for a 3-liter bag sampler with a 5/16-inch nozzle—*Continued*

Depth (in feet)	Rate	Mean stream velocity in vertical (feet per second)												Max. vol. -10 vol. min. vol.	Volume-min. vol. (mL)
		2.50	3.00	3.50	4.00	4.50	5.00	6.00	7.00	8.00	9.00	10.00	12.00		
20	full	0.58	0.70	0.81	0.93	1.04	1.16	1.39	1.62	1.86	2.09	2.32	2.78	2,604	1,094
20	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,509	--
22	full	0.64	0.77	0.89	1.02	1.15	1.28	1.53	1.79	2.04	2.30	2.55	3.06	2,604	943
22	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,660	--
24	full	0.70	0.83	0.97	1.11	1.25	1.39	1.67	1.95	2.23	2.50	2.78	3.34	2,604	792
24	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,811	--
26	full	0.75	0.90	1.06	1.21	1.36	1.51	1.81	2.11	2.41	2.71	3.01	3.62	2,604	642
26	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	1,962	--
28	full	0.81	0.97	1.14	1.30	1.46	1.62	1.95	2.27	2.60	2.92	3.25	3.90	2,604	491
28	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	2,113	--
30	full	0.87	1.04	1.22	1.39	1.57	1.74	2.09	2.43	2.78	3.13	3.48	4.17	2,604	340
30	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	2,264	--
32	full	0.93	1.11	1.30	1.48	1.67	1.86	2.23	2.60	2.97	3.34	3.71	4.45	2,604	189
32	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	2,415	--
34	full	0.99	1.18	1.38	1.58	1.77	1.97	2.37	2.76	3.15	3.55	3.94	4.73	2,604	38
34	fastest	1.00	1.20	1.40	1.60	1.80	2.00	2.40	2.80	3.20	3.60	4.00	4.80	2,566	--
35	full	--	--	--	--	--	--	--	--	--	--	--	--	--	--
35	fastest	--	--	--	--	--	--	--	--	--	--	--	--	--	--

APPENDIX A4-B

QUALITY-CONTROL SAMPLES COLLECTED BY FIELD PERSONNEL FOR WATER-QUALITY STUDIES

Prepared by F.D. Wilde, U.S. Geological Survey, Reston, Va.; T.L. Schertz, U.S. Geological Survey, Lakewood, Colo.; and S.W. McKenzie, U.S. Geological Survey, Portland, Oreg.

Appendix A4-B—Quality-control samples collected by field personnel for water-quality studies

[Common types of QC samples are described in this table; the list is not comprehensive. Some terms, descriptions, and purposes for quality-control samples have been compiled and modified from Sandstrom (1990), Horowitz and others (1994), Shelton (1994), Koterba and others (1995), unpublished course notes from "Quality-Control Sample Design and Interpretation," and the following Branch of Quality Systems Technical Memorandums: 90.03, 92.01, 95.01; QC, quality control; Blank-water abbreviations [1]: PBW, pesticide-grade blank water; VBW, volatile-grade blank water, IBW, inorganic-grade blank water]

BLANKS[2] Quality-control samples used to assess possible source(s) and (or) magnitude of sample contamination		
Sample type	**General description[3]**	**Purpose[3]**
Ambient blank	Blank water that is exposed to the identical collection and processing areas and time period as environmental samples. The blank water is transferred from the stock-solution container to the same type of bottle used for an environmental sample. The specific mode of exposure to the atmosphere is determined by the QC objective. **Examples:** (*a*) The blank water is transferred to a sample bottle while in the sample-processing chamber used for environmental samples. (*b*) Container such as a sample bottle is prefilled with blank water, opened while in the processing chamber, and exposed to the chamber atmosphere throughout the processing of environmental samples.	Determine analyte concentrations present in the environmental sample that could be attributed to exposure of sample to the ambient atmosphere in which samples are collected, processed, and analyzed. Referring to the general description: Example (*a*) is used to assess concentrations after processing the blank in a manner that mimics collection of the environmental sample. Example (*b*) is used to indicate the maximum analyte concentration that would result from prolonged sample exposure to ambient conditions.
Source-solution blank	Stock solution of PBW, VBW, or IBW that is transferred to a sample bottle in an area of the office laboratory within a controlled atmosphere that is relatively clean and protected with respect to target analytes.	Determine the source of water used for blanks and the degree to which the composition of blank solution could have changed (with respect to target analytes) from time of laboratory certification to time of use.
Trip blank	A sample bottle filled at the laboratory with VBW, PBW, or IBW (usually VBW) that remains unopened and is carried to the field and is stored and shipped with the environmental samples.	Determine whether shipping, storage, and field transport can be a source of sample contamination or cross-contamination.

Appendix A4-B—Quality-control samples collected by field personnel for water-quality studies—*Continued*

BLANKS[2] —Continued Quality-control samples used to assess possible source(s) and (or) magnitude of sample contamination		
Sample type	**General description[3]**	**Purpose[3]**
Equipment blank In this example, the sample referred to as the equipment blank is the same as the filter blank, as the filter assembly is the last component of this sampling-equipment system.	Blank water that is passed sequentially through each component of the equipment system to be used for collecting and processing environmental samples and resulting in a single final blank sample. • Differs from a field blank in that the equipment blank is processed under controlled conditions in an office laboratory and before equipment will be used for field work. Collected annually, unless equipment is in constant use and regularly quality controlled. • Often results in collecting a series of blank samples sequentially, each sample of which represents a different component or combined components of the equipment system used. The blanks generated in such a series are a special case of the generic term that identified the QC sample type. For example, if processing a water sample through a DH-77 sampler, churn splitter, peristaltic pump, and filter assembly, in that order, the following set of samples could be collected to be associated with the equipment blank: - Sampler blank (blank water processed through the DH-77 sampler. - Splitter blank (blank water processed through the sampler and then through a churn splitter). - Pump blank (blank water processed through the sampler, churn splitter, and then through a peristaltic pump system). - Filter blank (blank water processed through the sampler, churn splitter, peristaltic pump system, and through the filter assembly).	• Identify effects of the equipment system used to collect and process samples on analyte concentrations. • Verify adequacy of equipment-cleaning procedures (NFM 3). • Relating to components of the equipment system, assess potential of sample contamination and adequacy of equipment-cleaning procedures associated with each component of the equipment system to be used for field work.

Appendix A4-B—Quality-control samples collected by field personnel for water-quality studies—*Continued*

BLANKS[2]—Continued Quality-control samples used to assess possible source(s) and (or) magnitude of sample contamination		
Sample type	**General description[3]**	**Purpose[3]**
Field-blank system ("The field blank"—see fig. 4-8)	Blank water that is passed through the entire sampling equipment system onsite and subjected to identical collection, processing, preservation, transportation, and storage procedures and laboratory handling as for environmental samples. An identical sequence of procedures is followed as for the equipment blank. • The field blank is processed onsite through clean equipment on the same day as environmental samples: (*a*) directly after the equipment has been field cleaned and before leaving for the next site (NFM 3) or (*b*) at the next site, just before environmental samples for that site are processed. • A set of blanks can be processed and associated with the field blank, analogous to the equipment blank.	Determine the concentrations of target analyte(s) that could be present in environmental sample attributable to field procedures for equipment cleaning and sample handling. Results include effects from laboratory handling. Examples related to (*a*) and (*b*) under General description: (*a*) Check the adequacy of field cleaning procedures (demonstrate that equipment was adequately decontaminated after previous use) (NFM 3); (*b*) Identify contamination of sampling equipment while in transport from office to field site or between field sites, and ambient field conditions at the field site.
Sampler blank	Blank water processed through the same sampler used for environmental samples. (Blanks processed through pump samplers usually are designated pump blanks.)	• Identify effects of sampler on analyte concentrations. • Verify adequacy of cleaning procedures (NFM 3).
Splitter blank	Blank water processed through the same sample-splitting device used to collect or to process environmental samples (such as a churn splitter, cone splitter, or manifold system).	• Identify effects of splitter on analyte concentrations. • Verify adequacy of cleaning procedures (NFM 3).
Pump blank	Blank water processed through the pump-and-tubing system used for environmental samples.	• Identify effects of pump on analyte concentrations. • Verify adequacy of cleaning procedures (NFM 3).
Filter blank	Blank water processed through the filter assembly used for environmental samples. If the filter blank is to represent the same filter media, blank is processed prior to environmental samples.	• Identify effects of filtration assembly on analyte concentrations. • Verify adequacy of cleaning procedures, if a plate or cartridge assembly is used—see NFM 3.

Appendix A4-B—Quality-control samples collected by field personnel for water-quality studies—*Continued*

BLANKS[2] —Continued Quality-control samples used to assess possible source(s) and (or) magnitude of sample contamination		
Sample type	**General description[3]**	**Purpose[3]**
Preservation blank	Blank water that is transferred to a sample bottle and chemically treated with a preservative in an area protected from atmospheric contamination (usually, the office laboratory). The preservative used is from the same lot number used for other QC and environmental samples.	Determine the potential for and magnitude of sample contamination from the chemical treatment to be used to preserve the environmental sample.
Shelf blank ("Hold" blank)	Blank water that is transferred into the same type of bottle used for an environmental sample (usually in the protected environment of the office laboratory) and stored adjacent to stored environmental samples for the same length of time.	Determine the potential for and magnitude of sample contamination from sample storage in a designated area for a designated length of time.
Refrigerator blank	Blank water that is transferred into a sample bottle (usually in the protected environment of the office laboratory) and stored adjacent to environmental samples in a refrigerated area for the same length of time.	Determine the potential for and magnitude of sample contamination from sample refrigeration for a designated length of time.

Appendix A4-B—Quality-control samples collected by field personnel for water-quality studies—*Continued*

REPLICATE AND VARIABILITY SAMPLES Quality-Control Samples Used To Assess Field and Laboratory Variability		
Sample type	**General description[3]**	**Purpose[3]**
Replicates (duplicates, triplicates, etc., of sequential, split, concurrent, or other type of replicate)	A set of samples that are collected close in time and space and in a manner so that the samples are thought to be representative of the ambient water composition at the time of collection.	Depending upon its type, a replicate is used to determine variability in some part of the sample collection, processing, and analysis system.
Concurrent replicates	Samples obtained by collecting simultaneously with two or more samplers or by using one sampler and alternating collection of samples into two or more compositing containers (Horowitz and others, 1994).	• Identify and (or) quantify the variability in the system being sampled. • Analysis includes the variability introduced from collection, processing, shipping, and laboratory handling and analysis of the sample.
Sequential replicates	Samples that are collected one after the other and considered virtually identical in composition.	• Identify and (or) quantify the variability introduced from collection, processing, shipping, and laboratory handling and analysis. • Can be designed to indicate temporal variability resulting from consecutive collection of samples.

Appendix A4-B—Quality-control samples collected by field personnel for water-quality studies—*Continued*

REPLICATE AND VARIABILITY SAMPLES —Continued Quality-Control Samples Used To Assess Field and Laboratory Variability		
Sample type	**General description[3]**	**Purpose[3]**
Split replicates	Samples obtained by dividing one sample into two or more subsamples either before or after sample processing and preservations **each of the subsamples is to be analyzed for concentrations of the same constituents or compounds**. Examples: (*a*) A processed and treated sample in a sample bottle is split into two or more aliquots and subjected to identical handling and analysis. (*b*) Environmental water is passed through a splitting device (such as a cone splitter or T-valve) from which subsamples are collected simultaneously and subjected to identical handling and analysis. (*c*) Environmental water is collected into a compositing device from which subsamples are collected sequentially and subjected to identical handling and analysis.	• Assess variability for a given sample matrix. • Compare differences in analyses obtained from the same or separate laboratories. • Analysis includes any variability from splitting and other sample-processing procedures, shipping, and laboratory handling and analysis of the sample.
Reference sample	A laboratory-prepared solution or material whose composition is certified for one or more properties so that it can be used to assess a measurement method or for assigning concentration values of specific analytes.	Tests for bias and variability of the laboratory measurement process.
Spike sample	Environmental ("field-matrix spikes") or reference-material sample to which a spike solution has been added in known concentrations and in a manner that does not substantially change the original sample matrix. **Spike solution** is a solution having laboratory-certified concentrations of selected analytes and that is added in known quantities to a sample. [4]	Assess the recovery of target analytes relative to the actual conditions to which samples have been exposed; quantify effects of sample-matrix interferences and analyte degradation on analyte recovery.

Appendix A4-B—Quality-control samples collected by field personnel for water-quality studies—*Continued*

REPLICATE AND VARIABILITY SAMPLES—Continued Quality-Control Samples Used To Assess Field and Laboratory Variability		
Sample type	**General description[3]**	**Purpose[3]**
Blind sample	A sample (typically, reference material) submitted for laboratory analysis with composition known to the submitter but unknown (blind) to the analyst. Every blind sample analyzed should have an associated reference to the source and the preparation procedure.	Test for bias and variability of the laboratory measurement process.

[1]Blank water is a solution that is free of analyte(s) of interest at a specified detection limit and that is used to develop specific types of QC samples. USGS personnel are required to use blank water that has been analyzed and certified to be of a specific grade. Order IBW from the QWSU in Ocala, Fla., via <Ocalaman@usgs.gov>. Order PBW and VBW from NWQL in Arvada, Colo. via <densuppl@usgs.gov>.

[2]Blanks for trace-element analysis have a unique NWQL schedule of analysis, different from that of the environmental sample.

[3]The description of a QC sample depends to some extent on the purpose for which it is collected. The purpose for the QC sample can govern the mode of its collection, processing, and treatment, and the equipment to which it is exposed. Purposes for a specific type of QC sample are varied.

[4]Obtain spike solutions in spike kits for pesticide and volatile organic compound analyses supplied by NWQL.

APPENDIX A4-C

EXAMPLES FROM THE NATIONAL WATER-QUALITY ASSESSMENT PROGRAM RELATED TO PROTOCOLS FOR COLLECTING BLANK SAMPLES AT GROUND-WATER SAMPLING SITES

Modified from Koterba and others, 1995

APPENDIX A4-C. —Table 1. Example of procedure to estimate and collect field volumes of blank solutions

[Modified from Koterba and others, 1995 and based on protocols of the National Water-Quality Assessment Program. Updated information is available on the World Wide Web at the following URL: http://wwwrvares.er.usgs.gov/nawqa/OFR95-399.html. DIW, District deionized water with specific electrical conductance less than 1.0 microsiemens per liter; VBW, volatiles-organic-grade blank water; PBW, pesticide-grade blank water; IBW, inorganic-grade blank water; DOC, dissolved (filtered) organic carbon; gal, gallons; L, liters; ≈, approximately; NWQL, National Water Quality Laboratory; QWSU, Quality of Water Service Unit (Ocala, Fla.); SC, NWQL analytical schedule; LC, NWQL analyte code]

Assumptions: Submersible pump was used to collect the ground-water samples. Equipment just used to collect ground-water samples has been decontaminated, and, except for the pump intake being in a standpipe, is set up on site in the same manner as it was for the collection of ground-water samples.

Blank-solution types and estimate of volumes required[1]

Field blank(s) desired	Required blank-solution type	Minimum volume in gal (L)	Comments
VOCs and DOC[1] or pesticides and DOC	VBW PBW[1]	1.5 (≈6)	Waste 0.5 gal, then collect field blanks; can use DIW to force last of VBW (or PBW) through the system.
VOCs, DOC[1] and pesticides	VBW	2.0 (≈8)	Waste 0.5 gal, then collect field blanks; can use DIW to force last of VBW or PBW through the system.
Major ions and nutrients, or trace elements	IBW	1.0 (≈4)	Waste 0.5 gal, then collect field blanks; can use DIW to force last of the IBW needed through the system.
Major ions and nutrients and trace elements	IBW	1.5 (≈6)	Waste 0.5 gal, then collect field blanks; if necessary, use DIW to force last of the IBW needed through the system.
Combinations of the organics and inorganics above	VBW/PBW and IBW	1.5 to 2.0 (≈6 to ≈8) 1.0 to 1.5 (≈4 to ≈6)	Waste 0.5 gal of the VBW or PBW, then collect organic field blanks. Use IBW to push the VBW or PBW through the system. Waste 0.5 gal. of IBW, then collect inorganic field blanks, using DIW to push the IBW through the system.

[1] NWQL-PBW can not be used for VOC field blanks. Select VBW or PBW for DOC field blanks only after reviewing certification forms of the lot numbers available. A solution blank sample of water from the same lot of NWQL water is used for DOC field blank and poured directly into DOC 125-mL amber sample bottle. Record the lot number of the water used for the solution blank on the ASR form.

APPENDIX A4-C.—Table 2. Example of procedure to collect blank samples with a submersible pump

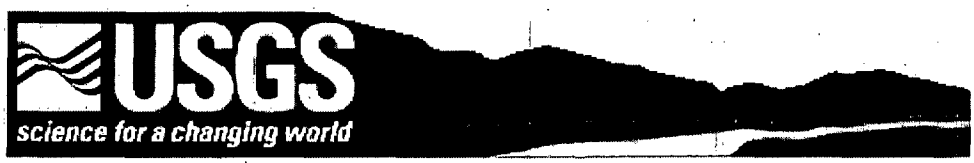
[Modified from Koterba and others (1995). Updated information is available on the World Wide Web at the following URL: http://wwwrvares.er.usgs.gov/nawqa/OFR95-399.html. DIW, deionized water; VBW, volatiles-grade blank water; PBW, pesticide-gradeblankwater; IBW, inorganic-gradeblankwater; VOC, volatileorganiccompound; QC, quality control]

General Field-Blank Collection Procedure[1]
1. Divide field team duties . Three-person team recommended—two people collect samples in a manner similar to that used to collect ground-water samples; the third person adds blank water to standpipe and controls flow through system, as needed, to facilitate field blank collection.
2. Check flow set-up—from standpipe to sample collection/processing chamber, ensure that adequate volumes of DIW and the required blank water are within easy reach of person stationed at standpipe and arranged in order of collection: VBW first, PBW next, IBW last.
3. Set low flow rate—Once pumping is initiated, set flow (on basis of measurement at chamber outflow) to about 0.1 gal. (500 mL) per minute or less to avoid wasting blank water (150 mL/min or less is recommended for filling VOC vials).
4. Collect blank solutions in prescribed sequence—As solutions are changed, pump operator should change to clean gloves, empty residual solution from standpipe, rinse pump intake and standpipe, individually, at least three times each, with the next solution. Attempt to pump air segment into pump line before adding next solution to standpipe to mark change in solution type.
• If air segment can not be used to mark the end of one solution and the beginning of the next, then determine the change in solutions on the basis of the storage volume in line divided by the pumping rate to estimate the time it takes for the solution to travel from the standpipe to the collection/processing chamber.
• Pass about 0.5 gallons (approximately 2 L) of blank solution to waste before collecting the QC sample, regardless of whether air segments or timed flow or both are used to assess when the solution arrives at the collection chamber.
• Use one type of water to force the last of another type from the sample tubing after all samples that require that blank-water type have been collected, in order to limit the amount of blank water left in the sample tubing.

[1]**Assumptions:** Submersible pump was used to collect the ground-water samples. Organic and inorganic field blanks will be collected. Equipment just used to collect ground-water samples has been cleaned, and, except for the pump intake being in a standpipe instead of a well, is set up on site in the same manner as it was for the collection of ground-water samples. Standpipe has just been cleaned and subsequently rinsed with VBW. If only inorganic field blanks will be collected, rinse the cleaned standpipe with IBW and modify steps 2-4 accordingly.

ISBN 0-607-92183-8





Water Resources--Office of Water Quality

This document is also available in pdf format:

View pdf for Chapter A5, version 2 (4/2002) and the following updates:
Revised section 5.6.1.C is not incorporated in the above pdf file for Chapter 5. View 5.6.1.C (vers. 2.1)
New section 5.6.1.F is not incorporated in the above file for Chapter 5. View 5.6.1.F.
New section 5.6.4.A is not incorporated in the above file for Chapter 5. View 5.6.4.A.
Address any comments or suggestions to nfm-owq@usgs.gov.

- ***Comments/errata page***
- ***Citation Information***

CHAPTER A5. (Version 2.1, 4/2004) PROCESSING OF WATER SAMPLES

Cover/Title Page
Back of Title Page
Foreword

Abstract
Introduction

Purpose and scope
Requirements and recommendations
Field manual review and revision
Acknowledgments

A5 Processing of water samples
Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo, editors

5.0 General information
D.B. Radtke and F.D. Wilde

5.1 Raw samples
D.B. Radtke, A.J. Horowitz, J. Gibs, and F.D. Wilde

5.2 Filtered samples
D.B. Radtke, A.J. Horowitz, and M.W. Sandstrom

5.3 Solid-phase extraction of pesticides
M.W. Sandstrom

5.4 Sample preservation
D.B. Radtke

5.5 Handling and shipping of samples
D.B. Radtke

5.6 Summary of sample-collection and sample-processing procedures for specific analytes
F.D. Wilde and Jacob Gibs
*Section 5.6.1.C, Phenols, has been revised in this section to create version 2.1 of chap. A5.
*New section. View new section 5.6.1.F, "Wastewater, Pharmaceutical, and Antibiotic Compounds" (pdf)
*New section. View new section 5.6.4.A, "Arsenic Speciation" (pdf)

Conversion factors, selected terms, abbreviations, and chemical symbols and formulas

Selected references and internal documents

Publications on Techniques of Water-Resources Investigations

Appendix

Appendix A5-A. Sample-designation codes and a summary of field-processing requirements for analyses of organic compounds in water

Appendix A5-B. Sample-designation codes and a summary of field-processing requirements for analyses of inorganic constituents in water

Appendix A5-C. Sample-designation codes and a summary of field-processing requirements for analyses of stable isotopes and radiochemicals in water

Appendix A5-D. Procedures for processing samples for analysis of dissolved and suspended organic carbon using a silver filter and gas-pressurized filtration apparatus (Note: Appendix A5-D has been added to Chapter A5, Version 2 (4/02) and contains the text for the Version 1 section 5.2.2.C.)

⇨Abstract
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Privacy Statement || Disclaimer || Accessibility
Page last modified: Apr 15, 2004 imc
URL: http://water.usgs.gov/owq/FieldManual/chapter5/html/Ch5_contents.html

Users with visual disabilities can visit this site for conversion tools and information to help make PDF files accessible.

Version History:
(Version 1 of Chapter A5 has been archived at the following Web address:
http://water.usgs.gov/owq/FieldManual/chapter5-Archive/html/Ch5_contents.html)
(Version 2 has been updated to Version 2.1 with changes to section 5.6.1.C, "Phenols." The archive of 5.6.1.C, version 2, is at http://water.usgs.gov/owq/FieldManual/chapter5-Archive/pdf/5.6.1.C-v2.pdf)

USGS

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data



Chapter A5. PROCESSING OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

USGS
science for a changing world

⇨Titlepage
⇧Return to Chapter A5 Contents Page
⇧ Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Chapter A5 (Version 2, 4/02)

USGS

U.S. DEPARTMENT OF THE INTERIOR

GALE A. NORTON, Secretary

U.S. GEOLOGICAL SURVEY

Charles G. Groat, Director

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

For additional information write to:

Chief, Office of Water Quality

U.S. Geological Survey

12201 Sunrise Valley Drive

Mail Stop 412

Reston, VA 20192

Copies of this report can be purchased from:

U.S. Geological Survey

Information Services

Box 25286, Federal Center

Denver, CO 80225

⇨ Foreword
⇧ Return to Chapter A5 Contents Page
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

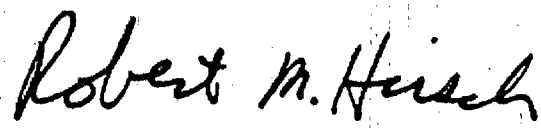
Chapter A5 (Version 2, 4/02)

USGS

Foreword

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.



Robert M. Hirsch
Chief Hydrologist

⇧Return to Chapter A5 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Chapter A5 (Version 2, 4/02)

USGS

Water Resources--Office of Water Quality

National Field Manual
CHAPTER A5. PROCESSING OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction for pesticide analyses; sample preservation; and sample handling and shipping.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (required and recommended procedures) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A5 describes methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction; sample preservation; and sample handling and shipping. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. A list of TWRI publications is included at the end of this report. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to chapter A6 on "Field Measurements" and NFM 6.4 refers to the section in Chapter A6 on field measurement of pH.

The procedures described in this chapter represent protocols that are applicable to most USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published along with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter on processing water samples is to provide field personnel and other interested parties with a description of the required and recommended procedures routinely used in USGS studies to composite, subsample, filter, preserve, and ship surface-water and ground-water samples to the USGS National Water Quality Laboratory (NWQL) for analysis. The sample processing procedures presented can be applied to the majority of samples that are analyzed routinely by NWQL for inorganic constituents and organic compounds. Samples that require special analysis or samples that are to be sent to other laboratories for analysis might require different processing procedures, the protocols for which are beyond the scope of this chapter.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements[2] or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

[2]As used in this report, data-quality requirements are that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the allowable variability that fulfill study objectives.

⇨Section 5.0 Contents
⇧Return to Chapter A5 Contents
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages
Chapter A5, Version 2 (4/02)

USGS

Water Resources--Office of Water Quality

National Field Manual
CHAPTER A5. PROCESSING OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction for pesticide analyses; sample preservation; and sample handling and shipping.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (required and recommended procedures) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A5 describes methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction; sample preservation; and sample handling and shipping. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. A list of TWRI publications is included at the end of this report. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual.* Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to chapter A6 on "Field Measurements" and NFM 6.4 refers to the section in Chapter A6 on field measurement of pH.

The procedures described in this chapter represent protocols that are applicable to most USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published along with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter on processing water samples is to provide field personnel and other interested parties with a description of the required and recommended procedures routinely used in USGS studies to composite, subsample, filter, preserve, and ship surface-water and ground-water samples to the USGS National Water Quality Laboratory (NWQL) for analysis. The sample processing procedures presented can be applied to the majority of samples that are analyzed routinely by NWQL for inorganic constituents and organic compounds. Samples that require special analysis or samples that are to be sent to other laboratories for analysis might require different processing procedures, the protocols for which are beyond the scope of this chapter.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements[2] or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

[2]As used in this report, data-quality requirements are that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the allowable variability that fulfill study objectives.

⇨Section 5.0 Contents
⇧Return to Chapter A5 Contents
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages
Chapter A5, Version 2 (4/02)

USGS

Water Resources--Office of Water Quality

National Field Manual
CHAPTER A5. PROCESSING OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction for pesticide analyses; sample preservation; and sample handling and shipping.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (required and recommended procedures) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A5 describes methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction; sample preservation; and sample handling and shipping. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. A list of TWRI publications is included at the end of this report. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual.* Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to chapter A6 on "Field Measurements" and NFM 6.4 refers to the section in Chapter A6 on field measurement of pH.

The procedures described in this chapter represent protocols that are applicable to most USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published along with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter on processing water samples is to provide field personnel and other interested parties with a description of the required and recommended procedures routinely used in USGS studies to composite, subsample, filter, preserve, and ship surface-water and ground-water samples to the USGS National Water Quality Laboratory (NWQL) for analysis. The sample processing procedures presented can be applied to the majority of samples that are analyzed routinely by NWQL for inorganic constituents and organic compounds. Samples that require special analysis or samples that are to be sent to other laboratories for analysis might require different processing procedures, the protocols for which are beyond the scope of this chapter.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements[2] or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

[2]As used in this report, data-quality requirements are that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the allowable variability that fulfill study objectives.

⇨Section 5.0 Contents
⇧Return to Chapter A5 Contents
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages
Chapter A5, Version 2 (4/02)

USGS

Water Resources--Office of Water Quality

National Field Manual
CHAPTER A5. PROCESSING OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction for pesticide analyses; sample preservation; and sample handling and shipping.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (required and recommended procedures) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A5 describes methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction; sample preservation; and sample handling and shipping. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. A list of TWRI publications is included at the end of this report. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual.* Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to chapter A6 on "Field Measurements" and NFM 6.4 refers to the section in Chapter A6 on field measurement of pH.

The procedures described in this chapter represent protocols that are applicable to most USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published along with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter on processing water samples is to provide field personnel and other interested parties with a description of the required and recommended procedures routinely used in USGS studies to composite, subsample, filter, preserve, and ship surface-water and ground-water samples to the USGS National Water Quality Laboratory (NWQL) for analysis. The sample processing procedures presented can be applied to the majority of samples that are analyzed routinely by NWQL for inorganic constituents and organic compounds. Samples that require special analysis or samples that are to be sent to other laboratories for analysis might require different processing procedures, the protocols for which are beyond the scope of this chapter.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements[2] or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

[2]As used in this report, data-quality requirements are that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the allowable variability that fulfill study objectives.

⇨Section 5.0 Contents
⇧Return to Chapter A5 Contents
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages
Chapter A5, Version 2 (4/02)

USGS

Water Resources--Office of Water Quality

National Field Manual
CHAPTER A5. PROCESSING OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction for pesticide analyses; sample preservation; and sample handling and shipping.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (required and recommended procedures) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A5 describes methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction; sample preservation; and sample handling and shipping. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. A list of TWRI publications is included at the end of this report. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to chapter A6 on "Field Measurements" and NFM 6.4 refers to the section in Chapter A6 on field measurement of pH.

The procedures described in this chapter represent protocols that are applicable to most USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published along with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter on processing water samples is to provide field personnel and other interested parties with a description of the required and recommended procedures routinely used in USGS studies to composite, subsample, filter, preserve, and ship surface-water and ground-water samples to the USGS National Water Quality Laboratory (NWQL) for analysis. The sample processing procedures presented can be applied to the majority of samples that are analyzed routinely by NWQL for inorganic constituents and organic compounds. Samples that require special analysis or samples that are to be sent to other laboratories for analysis might require different processing procedures, the protocols for which are beyond the scope of this chapter.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements[2] or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to

nfmowq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U. S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

The editors and authors wish to pay tribute to R.W. Lee and S.W. McKenzie, who provided final technical review, and who contributed significantly to the accuracy, quality, and usability of this report. Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

---

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

[2]As used in this report, data-quality requirements are that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the allowable variability that fulfill study objectives.

⇨Section 5.0 Contents
⇧Return to Chapter A5 Contents
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages
Chapter A5, Version 2 (4/02)

USGS

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter A5.pdf

PROCESSING OF WATER SAMPLES A5

Edited by Fanceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

Sample processing forms a continuum with sample collection (NFM 4) and involves the compositing, subsampling (splitting), filtration, solid-phase extraction, preservation, and shipment of samples. Samples are most vulnerable to sampling artifacts, contamination, incorrect chemical treatment, and mislabeling during sample processing. Samples must be processed as soon as possible after collection.[3]

Sample processing: the measures taken to prepare and preserve a water sample as or after it is collected and shipped for laboratory analysis.

---

[3]Consult NFM 4 for collection of water samples, and in addition, NFM 1 for field preparations, NFM 2 for equipment selection, NFM 3 for equipment cleaning, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material samples, and NFM 9 for field safety.

⇨Section 5.0
⇧Return to Abstract
⇧Return to Chapter A5 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Chapter A5, Version 2 (4/02)

USGS

Water Resources--Office of Water Quality

This document is also available in pdf format:

Complete pdf for Section 5.0--General Information

National Field Manual

5.0 GENERAL INFORMATION

By D.B. Radtke and F.D. Wilde

5.0.1 Preparatory procedures

5.0.2 Sequence for processing samples

5.0.3 Field rinsing of bottles used to contain samples for analysis of inorganic constituents

Table

5-1. Recommended sequence for processhing samples

5-2. Directions for field rinse of bottles used to contain samples for inorganic-constituent analysis

Section 5.0

Return to Abstract Page

Return to Chapter A5 Contents Page

Return to Field Manual Complete Contents

Return to Water Quality Information Pages

USGS

Water Resources--Office of Water Quality

PREPARATORY PROCEDURES 5.0.1

Use of the procedures described in this section will help to avoid mistakes and preserve sample integrity. Protocols that are applicable to most sampling efforts for surface water are described in detail in Horowitz and others (1994). Koterba and others (1995) describe the protocols for ground-water sampling that were designed for the National Water-Quality Assessment (NAWQA) Program; these protocols are generally applicable to the routine collection of ground-water samples. Field personnel are responsible for being familiar with any specific sampling protocols that might be required for their studies and programs, especially those that differ from the routine procedures covered by this field manual. For example, field procedures, bottle type, and sample preservation requirements differ for samples collected as part of the USEPA Drinking Water Program (National Water Quality Laboratory Technical Memorandum 97.05[4]).

- To minimize delays in sample processing, calibrate field instruments (NFM 6), and set up processing equipment and supplies in the work area before collecting the sample.
- Clean-sampling procedures are recommended as a general practice when processing raw samples, particularly those for analysis of trace levels of inorganic and organic analytes.
- **Clean-sampling procedures such as Clean Hands/Dirty Hands techniques (NFM 4) are required when collecting samples to be filtered for analysis of trace elements** (Office of Wate Quality Technical Memorandum 94.09; Horowitz and others, 1994; Koterba and others, 1995).
- **When using Clean Hands/Dirty Hands techniques:**
  - Designate the Clean Hands (CH) person and the Dirty Hands (DH) person before field work begins (table 4-2 in NFM 4).
  - **CH duties**: Has the only contact with the sample bottle; transfers sample from sampler to splitter; filters, extracts, and preserves sample.
  - **DH duties**: Operates sampling equipment and manages any contact with potential sources of contamination (for example, the churn carrier and pumps).
  - **CH and DH**: Both must wear appropriate disposable, powderless gloves (vinyl, latex, or nitrile for inorganic work; latex or nitrile for organic work).
- **Check sample-designation codes and processing requirements for each sample.** Requirement depend on program and laboratory protocols, study objectives, and data-quality requirements. Laboratory codes and processing requirements are summarized in Appendixes A5-A, B, and C.
  - **Organic analytes**. Identify the bottle requirement by checking the sample designation code (see in-text table below and Appendix A5-A). Use only containers that arrive clean, baked, and capped. **Discard any bottles that arrive uncapped**.
  - **Inorganic and radiochemical analytes**. Identify the bottle requirement by checking the sample designation code (see in-text table below and Appendixes A5-B and A5-C). For example, samples to be acidified must be collected in bottles that arrive from the laboratory acid rinsed and capped; **discard any acid-rinsed bottles that arrive uncapped**. Prerinse all bottles used for nutrients, major-ion, and trace-element samples with deionized water (DIW) before sampling. Field rinse bottles with the water to be sampled, if a field rinse is

specified (section 5.0.3 and Appendixes A5-B and A5-C).

Common organic-compound sample-designation codes for the National Water Quality Laboratory of the U.S. Geological Survey

[Refer also to Appendix A5-A. ml, milliliters; °C, degrees Celsius]

Sample designation code	Bottle description and sample preservation
VOC	40-mL amber glass vials, laboratory cleaned and baked, for analysis of volatile organic compound sample (VOC or VOA); sample chilled to or below 4°C without freezing. Some programs require chemical treatment.
GCC	1-L amber, glass bottle, laboratory cleaned and baked, for various types of pesticides and organic-compound samples other than VOCs; sample chilled to or below 4°C without freezing.
TOC, DOC	125-mL amber glass bottle, laboratory cleaned and baked, for total (TOC) or dissolved (DOC) organic carbon; sample chilled to 4°C or below without freezing.

Common inorganic-constituent sample-designation codes of the National Water Quality Laboratory of the U.S. Geological Survey

[Refer also to Appendix A5-B and A5-C. mL, milliliter; <, less than; °C, degrees Celsius; L, liter]

Sample designation code	Bottle description and sample preservation
RA, FA	250-, 500-, or 1,000-mL polyethylene bottles, acid-rinsed, capped, to be filled with raw (RA) or filtered (FA) samples and acidified with nitric acid to pH <2.
RU, FU	250-, 500-, or 1,000-mL polyethylene bottles, uncapped, to be filled with untreated raw (RU) and filtered (FU) samples.
FCC	125-mL polyethylene bottles, uncapped, to be filled with filtered (FCC, brown bottle) sample for nutrient analysis and chilled to or below 4°C without freezing.
WCA, FCA	125-mL polyethylene bottles, uncapped; to be filled with raw (WCA, uncolored bottle) or filtered (FCA, brown bottle) sample for nutrient analysis, treated with sulfuric acid, and chilled to or below 4°C without freezing.
RAM, FAM	250-mL glass bottles, acid-rinsed, capped, to be filled with raw (RAM) or filtered (FAM) sample for mercury analysis, and treated with nitric acid/potassium dichromate solution.
FAR	1-L polyethylene bottles, acid rinsed, capped, to be filled with filtered (FAR) samples for radiochemical analysis and treated with nitric acid to pH <2.

- **Clean equipment and supplies as directed in NFM 3.**
  - -- **Organic analytes.** All containers arrive precleaned and baked from the laboratory. **Do not prerinse or field rinse these glass bottles or vials.** Samples to be analyzed for organic compounds are hereafter referred to as organic-compound samples.
  - -- **Inorganic analytes.** Prerinse bottles with DIW and store half filled with DIW. This procedure is required for all FA samples with target analytes at parts-per-billion (ppb) concentrations, and is recommended for all samples to be analyzed for inorganic constituents (hereafter referred to as inorganic-constituent samples) that also require field-rinsed bottles.
- **Set up a clean work area** at the field site for sample processing. (An appropriate area includes, for example, a mobile laboratory, a water-quality field vehicle (NFM 2), or clean space in a building near the sampling site.)
  - -- Protect the area from airborne sources of contamination such as dust, vehicle emissions, and vapors from inorganic chemicals and organic solvents.
  - -- Spread sheeting over the area where samples are to be processed. For inorganic-constituent samples, use plastic sheeting. For organic-compound samples, use aluminum foil.
- **Prevent direct contact with potential source(s) of contamination.**
  - -- Exclude airborne particulates by processing samples onsite in processing and preservation chambers.
  - -- Handle anoxic samples rapidly and under an inert gas atmosphere (NFM 4.0.3).
  - -- Keep hands gloved and away from potential sources of contamination while processing samples. While filling the sample bottle, the sample must not come in contact with gloved hands.
- **Keep sample-processing equipment covered** with a clean, noncontaminating material when not in use; keep sample bottles capped and covered or bagged.

---

[4]The technical memorandums referenced in this manual are available on the Word Wide Web; see "Selected References and Internal Documents" for memorandum titles, dates, and the Web Site address.

⇨Section 5.0.2
⇧Return to 5.0
⇧Return to Chapter A5 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

USGS

Water Resources--Office of Water Quality

SEQUENCE FOR PROCESSING SAMPLES 5.0.2

The order of sample collection, processing, and preservation for specific analytes should be determined before beginning field work and adhered to consistently. The recommended sequence for sample collection and processing is based on logistics for maintaining sample integrity and differs for ground-water and surface-water sampling. The recommended sequence can be modified, depending on the types of samples to be collected and on data objectives. In general, process samples in the order indicated on table 5-1.

- For ground-water sampling, the amount of well purging might affect concentrations of VOCs measured in the ground-water samples (Gibs and Imbrigiotta, 1990). Therefore, VOC samples are collected first.
- When sampling either surface water or ground water for inorganic analyses,
  - -- Filter trace-element samples first, as prescribed and explained in section 5.2 and in Horowitz and others (1994).
  - -- Next, filter nutrient, major ion, and other inorganic-constituent samples having concentrations that will not be appreciably affected as nominal pore size of the filter media decreases.
  - -- Filter the alkalinity sample (NFM 6) with the other anions.
- When composite samples of surface water are processed, samples for analysis of organic compounds usually are processed first and are taken from a noncontaminating compositing device separate from that for inorganic-constituent samples, unless a cone splitter is used (section 5.1).

Table 5-1. Recommended sequence for processing samples

1. Organic compounds—Raw (wholewater or unfiltered) samples first, followed by filtered samples. **Do not field rinse bottles.** Chill immediately a. Volatile organic compounds (VOCs). b. Pesticides, herbicides, polychlorinated biphenyls (PCBs) and other agricultural and industrial organic compounds.
2. Total organic carbon (TOC), dissolved organic carbon (DOC),[1] and suspended organic carbon (SOC). Chill immediately.
3. Inorganic constituents, nutrients, radiochemicals, isotopes: **For ground water,** filtered samples first, followed by raw samples. **For surface water,** raw samples first, followed by filtered samples. (Field rinse each bottle, as required.) a. Trace metals. b. Separate-treatment constituents (such as mercury, arsenic, selenium) and major cations. c. Major anions, alkalinity, and nutrients. Chill nutrients immediately. d. Radiochemicals and isotopes. (Bottle-rinse, filtration, and preservation requirements depend on analysis to be performed (section 5.6 and Appendix A5-C.)[2])
4. Radon and chlorofluorocarbons.[2] Do not rinse bottle.
5. Microorganisms (NFM 7).

[1]TOC and DOC samples can be collected whenever most appropriate for the specific field operation.
[2]Radon and chlorofluorocarbon and most isotope samples are collected outside of the processing chamber.

⇨ Section 5.0.3
⇧ Return to 5.0.1
⇧ Return to Contents for 5.0--General Information
⇧ Return to Chapter A5 Contents Page
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data



Chapter A5. PROCESSING OF WATER SAMPLES

Edited by Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

For additional information write to:

Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Box 25286, Federal Center
Denver, CO 80225

Foreword

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.

Robert M. Hirsch

Robert M. Hirsch
Chief Hydrologist

Book 9
Handbooks for Water-Resources Investigations

Chapters of Section A, *National Field Manual for the Collection of Water-Quality Data*

A1. Preparations for Water Sampling

A2. Selection of Equipment for Water Sampling

A3. Cleaning of Equipment for Water Sampling

A4. Collection of Water Samples

A5. Processing of Water Samples

A6. Field Measurements
- 6.0 General Information and Guidelines
- 6.1 Temperature
- 6.2 Dissolved Oxygen
- 6.3 Specific Electrical Conductance
- 6.4 pH
- 6.5 Reduction-Oxidation Potential—Electrode Method
- 6.6 Alkalinity and Acid Neutralizing Capacity
- 6.7 Turbidity

A7. Biological Indicators
- 7.1 Fecal Indicator Bacteria
- 7.2 Five-Day Biochemical Oxygen Demand

A8. Bottom-Material Samples

A9. Safety in Field Activities

5.1 Raw samples 23
D.B. Radtke, A.J. Horowitz, J. Gibs, and F.D. Wilde

5.1.1 Composites and subsamples 23

5.1.1.A Churn-splitter procedure 24

5.1.1.B Cone-splitter procedure 27

5.1.2 Ground water: pumped and bailed samples 31

5.2 Filtered samples 37
A.J. Horowitz, M.W. Sandstrom, and J. Gibs

5.2.1 Inorganic constituents 38

5.2.1.A Capsule-filter procedure 40

5.2.1.B Plate-filter procedure 48

5.2.2 Organic compounds 51

5.2.2.A Plate-filter procedure 53

5.2.2.B Capsule-filter procedure for processing samples for analysis of organonitrogen herbicides (optional) 59

5.2.2.C Procedures for processing samples for carbon analysis[1] **(Revised 1/2002)** 61

5.3 Solid-phase extraction of pesticides 75
M.W. Sandstrom

5.3.1 Solid-phase extraction by C-18 column 77

5.3.2 Solid-phase extraction by Carbopak-B™ column 82

5.4 Sample preservation 89
D.B. Radtke

5.4.1 Chilling 89

5.4.2 Chemical treatment 91

[1]Section 5.2.2.C (revised 1/2002) was rewritten to reflect changes in methodology. The original version of 5/99, with minor changes, appears as Appendix A5-D.

Foreword

The mission of the Water Resources Division of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government and scientific agencies, and the general public. Reliable and objective data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that data collected are of the quality required to fulfill our mission.

Robert M. Hirsch

Robert M. Hirsch
Chief Hydrologist

Book 9
Handbooks for Water-Resources Investigations

Chapters of Section A, *National Field Manual for the Collection of Water-Quality Data*

A1. Preparations for Water Sampling

A2. Selection of Equipment for Water Sampling

A3. Cleaning of Equipment for Water Sampling

A4. Collection of Water Samples

A5. Processing of Water Samples

A6. *Field Measurements*
- 6.0 General Information and Guidelines
- 6.1 Temperature
- 6.2 Dissolved Oxygen
- 6.3 Specific Electrical Conductance
- 6.4 pH
- 6.5 Reduction-Oxidation Potential—Electrode Method
- 6.6 Alkalinity and Acid Neutralizing Capacity
- 6.7 Turbidity

A7. Biological Indicators
- 7.1 Fecal Indicator Bacteria
- 7.2 Five-Day Biochemical Oxygen Demand

A8. Bottom-Material Samples

A9. Safety in Field Activities



PROCESSING OF WATER SAMPLES A5.

National Field Manual for the Collection of Water-Quality Data

Chapter A5.

Page

Abstract 7

Introduction 7

Purpose and scope 8

Requirements and recommendations 9

Field manual review and revision 10

Acknowledgments 11

A5. Processing of Water Samples 13

5.0 General information 13
D.B. Radtke and F.D. Wilde

5.0.1 Preparatory procedures 15

5.0.2 Sequence for processing samples 19

5.0.3 Field rinsing of bottles used to contain samples for analysis of inorganic constituents 20

5.1 Raw samples 23
D.B. Radtke, A.J. Horowitz, J. Gibs, and F.D. Wilde

5.1.1 Composites and subsamples 23

5.1.1.A Churn-splitter procedure 24

5.1.1.B Cone-splitter procedure 27

5.1.2 Ground water: pumped and bailed samples 31

5.2 Filtered samples 37
A.J. Horowitz, M.W. Sandstrom, and J. Gibs

5.2.1 Inorganic constituents 38

5.2.1.A Capsule-filter procedure 40

5.2.1.B Plate-filter procedure 48

5.2.2 Organic compounds 51

5.2.2.A Plate-filter procedure 53

5.2.2.B Capsule-filter procedure for processing samples for analysis of organonitrogen herbicides (optional) 59

5.2.2.C Procedures for processing samples for carbon analysis[1] **(Revised 1/2002)** 61

5.3 Solid-phase extraction of pesticides 75
M.W. Sandstrom

5.3.1 Solid-phase extraction by C-18 column 77

5.3.2 Solid-phase extraction by Carbopak-B™ column 82

5.4 Sample preservation 89
D.B. Radtke

5.4.1 Chilling 89

5.4.2 Chemical treatment 91

[1]Section 5.2.2.C (revised 1/2002) was rewritten to reflect changes in methodology. The original version of 5/99, with minor changes, appears as Appendix A5-D.

5.5 Handling and shipping of samples 95
D.B. Radtke

5.5.1 Labeling sample bottles 95

5.5.2 Filling out an Analytical Services Request form 96

5.5.3 Packaging samples 98

5.5.4 Shipping samples 101

5.6 Summary of sample-collection and sample-processing procedures for specific analytes 103
F.D. Wilde and Jacob Gibs

5.6.1 Common organic compounds 103

5.6.1.A Volatile organic compounds 104

5.6.1.B Semivolatile organic compounds, pesticides, organonitrogen herbicides, polychlorinated biphenyls 105

5.6.1.C Phenols 106

5.6.1.D Carbon **(Revised 1/2002)** 106

5.6.1.E Methylene blue active substances and oil and grease 107

5.6.2 Major ions and trace elements 108

5.6.2.A Major and minor cations and trace elements 108

5.6.2.B Nutrients (Nitrogen and Phosphorus) **(Revised 1/2002)** 109

5.6.2.C Anions 110

5.6.3 Stable isotopes and radiochemicals 111

5.6.3.A Carbon ($^{13}C/^{12}C$ and ^{14}C) 111

5.6.3.B Hydrogen ($^{2}H/^{1}H$) and oxygen ($^{18}O/^{16}O$) 113

5.6.3.C Nitrogen ($^{15}N/^{14}N$) 114

5.6.3.D Sulfur ($^{34}S/^{32}S$) 114

5.6.3.E Radium 226 and radium 228 116

5.6.3.F Uranium (U-234, U-235, U-238) 116

5.6.3.G Gross radioactivity 116

5.6.3.H Tritium 117

5.6.3.I Radon-222 118

5.6.3.J Tritium/helium-3 ($^{3}H/^{3}He$) 119

5.6.3.K Chlorofluorocarbons (CFC-11, CFC-12, CFC-113) 122

Conversion factors, selected terms, abbreviations, and chemical formulas CF-1

Selected references and internal documents REF-1

Publications on Techniques of Water-Resources Investigations TWRI-1

Appendix A5-A. Sample-designation codes and a summary of field-processing requirements for analyses of organic compounds in water APP-A-1

Appendix A5-B. Sample-designation codes and a summary of field-processing requirements for analyses of inorganic constituents in water APP-B-1

Appendix A5-C. Sample-designation codes and a summary of field-processing requirements for analyses of stable isotopes and radiochemicals in water APP-C-1

Appendix A5-D. Procedures for processing samples for analysis of dissolved and suspended organic carbon using a silver filter and gas-pressurized filtration apparatus **(Added 1/2002)** APP-D-1

Illustrations

5-1. An equipment system suitable for filtering samples for analysis of organic compounds 54

5-2. Worksheet for C-18 solid-phase extraction of pesticides 78

5-3. Worksheet for Carbopak-B™ solid-phase extraction of pesticides 84

5-4. Request form for equipment, instructions, and analysis of chlorofluorocarbon samples 126

Tables

5-1. Recommended sequence for processing samples 20

5-2. Directions for field rinse of bottles used to contain samples for inorganic-constituent analysis 21

5-3. Field cleaning and conditioning procedures for media used to filter samples for inorganic-constituent analysis 39

5-4. Field conditioning requirements for media used to filter samples for organic-compound analysis 52

5-5. Equipment for filtration of water-sediment samples for determination of organic compounds 53

5-6a. Equipment and supplies used to process samples for analyses of total particulate carbon and particulate inorganic carbon using the pressure-filtration method 63

5-6b. Equipment and supplies used to process samples for analyses of total particulate carbon and particulate inorganic carbon using the vacuum-filtration method 64

5-6c. Equipment and supplies used to process samples for analyses of dissolved organic carbon method 65

5-6d. Guidelines for selecting the volume needed for filtration of samples for analysis of suspended and particulate organic carbon 66

5-7. Checklist of general equipment and supplies required for broad-spectrum pesticide analysis by onsite solid-phase extraction 76

5-8. Equipment and supplies used for collection of samples for chlorofluorocarbon analysis 128



Chapter A5. PROCESSING OF WATER SAMPLES

Edited by **Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo**

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols and provides guidelines for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter addresses methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and bailed samples and subsamples; sample filtration; solid-phase extraction for pesticide analyses; sample preservation; and sample handling and shipping.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is <http://water.usgs.gov/lookup/get?newpubs>.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to assess the quality of our Nation's water resources. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* describes protocols (required and recommended procedures) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A5 describes methods to be used in processing water samples to be analyzed for inorganic and organic chemical substances, including the bottling of composite, pumped, and

bailed samples and subsamples; sample filtration; solid-phase extraction; sample preservation; and sample handling and shipping. **Formal training and field apprenticeship are necessary in order to implement correctly the procedures described in this manual.**

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. A list of TWRI publications is included at the end of this report. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*. Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to chapter A6 on "Field Measurements" and NFM 6.4 refers to the section in Chapter A6 on field measurement of pH.

The procedures described in this chapter represent protocols that are applicable to most USGS studies involving the collection of water-quality data. Modification of required and recommended procedures to fulfill study objectives or to enhance data quality must be documented and published along with the data and data interpretation.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

The purpose of this chapter on processing water samples is to provide field personnel and other interested parties with a description of the required and recommended procedures routinely used in USGS studies to composite, subsample, filter, preserve, and ship surface-water and ground-water samples to the USGS National Water Quality Laboratory (NWQL) for analysis. The sample processing procedures presented can be applied to the majority of samples that are analyzed routinely by NWQL for inorganic constituents and organic compounds. Samples that require special analysis or samples that are to be sent to other laboratories for analysis might require different processing procedures, the protocols for which are beyond the scope of this chapter.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual*, the terms **required** and **recommended** have USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and have been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other internal documents that define the policy pertinent to such requirements are referenced in this chapter. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements[2] or study objectives must be based on referenced research and good field judgment, and be quality assured and documented.

[1]District refers to an office of the USGS, Water Resources Division, located in any of the States or territories of the United States.

[2]As used in this report, data-quality requirements are that subset of data-quality objectives pertaining to the analytical detection level for concentrations of target analytes and the allowable variability that fulfill study objectives.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given equipment selection or procedure are acceptable on the basis of research and (or) consensus. Specific data-quality requirements, study objectives, or other constraints might affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives must be based on referenced research and good field judgment. Reasons for the selection should be documented. Departure from or modifications to recommended procedures must be quality assured and documented.

FIELD MANUAL REVIEW AND REVISION

Chapters of the *National Field Manual* will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Comments or corrections can be sent to NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or direct electronic mail to nfm-owq@usgs.gov). Information regarding the status and any errata of this or other chapters can be found at the beginning of the electronic version of each chapter, located in the Publications section of the following Web site: http://water.usgs.gov/lookup/get?owq.

Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey," at http://water.usgs.gov/lookup/get?newpubs.

ACKNOWLEDGMENTS

The information included in this chapter of the *National Field Manual* is based on existing manuals, various reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials include USGS handbooks, manuals, and technical memorandums. The editors and authors wish to acknowledge the following individuals in the USGS who developed the field and training manuals that provided the foundation for information on the collection and processing of water samples: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Kirkland, L.R. Kister, J.R. Knapton, C.E. Lamb, R.F. Middelburg, J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The technical content of this report was enhanced by expertise from H.D. Ardourel, B.A. Bernard, R.W. Brenton, A.D. Bumgartner, M.R. Burkhardt, R.W. Carmody, B.F. Connor, T.B. Coplen, II, J.H. Eychaner, K.K. Fitzgerald, D.S. Francy, J.R. Garbarino, S.R. Glodt, J.A. Kammer, V.J. Kelly, J.W. LaBaugh, S.L. Lane, W.D. Lanier, R.W. Lee, D.K. Mueller, A.H. Mullin, C.J. Patton, L.N. Plummer, D.L. Rose, S.K. Sando, M.P. Schroeder, C.A. Silcox, A.H. Welch, W.R. White, and D.S. Wydoski. These scientists contributed significantly to the accuracy, quality, and usability of this report. Valuable editorial assistance was provided by I.M. Collies, C.M. Eberle, B.B. Palcsak, and Chester Zenone. Production assistance from C.T. Mendelsohn, A.M. Weaver, and L.E. Menoyo was instrumental in maintaining the quality of this report.

Special thanks go to T.L. Miller, whose encouragement and faith in this project was instrumental to its achievement, and to D.A. Rickert and J.R. Ward for providing the support needed to produce a national field manual for water-quality studies.

This page left blank intentionally.



PROCESSING OF WATER SAMPLES A5.

Edited by **Franceska D. Wilde, Dean B. Radtke, Jacob Gibs, and Rick T. Iwatsubo**

Sample processing forms a continuum with sample collection (NFM 4) and involves the compositing, subsampling (splitting), filtration, solid-phase extraction, preservation, and shipment of samples. Samples are most vulnerable to sampling artifacts, contamination, incorrect chemical treatment, and mislabeling during sample processing. Samples must be processed as soon as possible after collection.[3]

Sample processing: the measures taken to prepare and preserve a water sample as or after it is collected and shipped for laboratory analysis.

GENERAL INFORMATION 5.0

By **D.B. Radtke and F.D. Wilde**

How samples are processed depends on the targeted analytes and the intended use of the data. Processing procedures for some analytes might require modification of standard processing procedures, as described in section 5.6. **Equipment components must be made of materials that (1) will not contribute or sorb target analytes to or from the water sample, and (2) can withstand cleaning solutions.**

[3]Consult NFM 4 for collection of water samples, and in addition, NFM 1 for field preparations, NFM 2 for equipment selection, NFM 3 for equipment cleaning, NFM 6 for field measurements, NFM 7 for biological indicators, NFM 8 for bottom-material samples, and NFM 9 for field safety.

This page left blank intentionally.

PREPARATORY PROCEDURES 5.0.1

Use of the procedures described in this section will help to avoid mistakes and preserve sample integrity. Protocols that are applicable to most sampling efforts for surface water are described in detail in Horowitz and others (1994). Koterba and others (1995) describe the protocols for ground-water sampling that were designed for the National Water-Quality Assessment (NAWQA) Program; these protocols are generally applicable to the routine collection of ground-water samples. Field personnel are responsible for being familiar with any specific sampling protocols that might be required for their studies and programs, especially those that differ from the routine procedures covered by this field manual. For example, field procedures, bottle type, and sample preservation requirements differ for samples collected as part of the USEPA Drinking Water Program (National Water Quality Laboratory Technical Memorandum 97.05[4]).

- To minimize delays in sample processing, calibrate field instruments (NFM 6), and set up processing equipment and supplies in the work area before collecting the sample.
- Clean-sampling procedures are recommended as a general practice when processing raw samples, particularly those for analysis of trace levels of inorganic and organic analytes.
- **Clean-sampling procedures such as Clean Hands/ Dirty Hands techniques (NFM 4) are required when collecting samples to be filtered for analysis of trace elements** (Office of Water Quality Technical Memorandum 94.09; Horowitz and others, 1994; Koterba and others, 1995).

[4]The technical memorandums referenced in this manual are available on the World Wide Web; see "Selected References and Internal Documents" for memorandum titles, dates, and the Web Site address.

- **When using Clean Hands/Dirty Hands techniques:**
  - Designate the Clean Hands (CH) person and the Dirty Hands (DH) person before field work begins (table 4-2 in NFM 4).
  - **CH duties**: Has the only contact with the sample bottle; transfers sample from sampler to splitter; filters, extracts, and preserves sample.
  - **DH duties**: Operates sampling equipment and manages any contact with potential sources of contamination (for example, the churn carrier and pumps).
  - **CH and DH**: Both must wear appropriate disposable, powderless gloves (vinyl, latex, or nitrile for inorganic work; latex or nitrile for organic work).
- **Check sample-designation codes and processing requirements for each sample.** Requirements depend on program and laboratory protocols, study objectives, and data-quality requirements. Laboratory codes and processing requirements are summarized in Appendixes A5-A, B, and C.
  - **Organic analytes**. Identify the bottle requirement by checking the sample designation code (see in-text table below and Appendix A5-A). Use only containers that arrive clean, baked, and capped. **Discard any bottles that arrive uncapped**.
  - **Inorganic and radiochemical analytes**. Identify the bottle requirement by checking the sample designation code (see in-text table below and Appendixes A5-B and A5-C). For example, samples to be acidified must be collected in bottles that arrive from the laboratory acid rinsed and capped; **discard any acid-rinsed bottles that arrive uncapped**. Prerinse all bottles used for nutrients, major-ion, and trace-element samples with deionized water (DIW) before sampling. Field rinse bottles with the water to be sampled, if a field rinse is specified (section 5.0.3 and Appendixes A5-B and A5-C).

Common organic-compound sample-designation codes for the National Water Quality Laboratory of the U.S. Geological Survey

[Refer also to Appendix A5-A. ml, milliliters; °C, degrees Celsius]

Sample designation code	Bottle description and sample preservation
VOC	40-mL amber glass vials, laboratory cleaned and baked, for analysis of volatile organic compound sample (VOC or VOA); sample chilled to or below 4°C without freezing. Some programs require chemical treatment.
GCC	1-L amber, glass bottle, laboratory cleaned and baked, for various types of pesticides and organic-compound samples other than VOCs; sample chilled to or below 4°C without freezing.
TOC, DOC	125-mL amber glass bottle, laboratory cleaned and baked, for total (TOC) or dissolved (DOC) organic carbon; sample chilled to 4°C or below without freezing.

Common inorganic-constituent sample-designation codes of the National Water Quality Laboratory of the U.S. Geological Survey

[Refer also to Appendix A5-B and A5-C. mL, milliliter; <, less than; °C, degrees Celsius; L, liter]

Sample designation code	Bottle description and sample preservation
RA, FA	250-, 500-, or 1,000-mL polyethylene bottles, acid-rinsed, capped, to be filled with raw (RA) or filtered (FA) samples and acidified with nitric acid to pH <2.
RU, FU	250-, 500-, or 1,000-mL polyethylene bottles, uncapped, to be filled with untreated raw (RU) and filtered (FU) samples.
FCC	125-mL polyethylene bottles, uncapped, to be filled with filtered (FCC, brown bottle) sample for nutrient analysis and chilled to or below 4°C without freezing.
WCA, FCA	125-mL polyethylene bottles, uncapped; to be filled with raw (WCA, uncolored bottle) or filtered (FCA, brown bottle) sample for nutrient analysis, treated with sulfuric acid, and chilled to or below 4°C without freezing.
RAM, FAM	250-mL glass bottles, acid-rinsed, capped, to be filled with raw (RAM) or filtered (FAM) sample for mercury analysis, and treated with nitric acid/potassium dichromate solution.
FAR	1-L polyethylene bottles, acid rinsed, capped, to be filled with filtered (FAR) samples for radiochemical analysis and treated with nitric acid to pH <2.

- **Clean equipment and supplies as directed in NFM 3.**
  - **Organic analytes.** All containers arrive precleaned and baked from the laboratory. **Do not prerinse or field rinse these glass bottles or vials.** Samples to be analyzed for organic compounds are hereafter referred to as organic-compound samples.
  - **Inorganic analytes.** Prerinse bottles with DIW and store half filled with DIW. This procedure is required for all FA samples with target analytes at parts-per-billion (ppb) concentrations, and is recommended for all samples to be analyzed for inorganic constituents (hereafter referred to as inorganic-constituent samples) that also require field-rinsed bottles.
- **Set up a clean work area** at the field site for sample processing. (An appropriate area includes, for example, a mobile laboratory, a water-quality field vehicle (NFM 2), or clean space in a building near the sampling site.)
  - Protect the area from airborne sources of contamination such as dust, vehicle emissions, and vapors from inorganic chemicals and organic solvents.
  - Spread sheeting over the area where samples are to be processed. For inorganic-constituent samples, use plastic sheeting. For organic-compound samples, use aluminum foil.
- **Prevent direct contact with potential source(s) of contamination.**
  - Exclude airborne particulates by processing samples onsite in processing and preservation chambers.
  - Handle anoxic samples rapidly and under an inert gas atmosphere (NFM 4.0.3).
  - Keep hands gloved and away from potential sources of contamination while processing samples. While filling the sample bottle, the sample must not come in contact with gloved hands.
- **Keep sample-processing equipment covered** with a clean, noncontaminating material when not in use; keep sample bottles capped and covered or bagged.

SEQUENCE FOR PROCESSING SAMPLES 5.0.2

The order of sample collection, processing, and preservation for specific analytes should be determined before beginning field work and adhered to consistently. The recommended sequence for sample collection and processing is based on logistics for maintaining sample integrity and differs for ground-water and surface-water sampling. The recommended sequence can be modified, depending on the types of samples to be collected and on data objectives. In general, process samples in the order indicated on table 5-1.

- For ground-water sampling, the amount of well purging might affect concentrations of VOCs measured in the ground-water samples (Gibs and Imbrigiotta, 1990). Therefore, VOC samples are collected first.
- When sampling either surface water or ground water for inorganic analyses,
  - Filter trace-element samples first, as prescribed and explained in section 5.2 and in Horowitz and others (1994).
  - Next, filter nutrient, major ion, and other inorganic-constituent samples having concentrations that will not be appreciably affected as nominal pore size of the filter media decreases.
  - Filter the alkalinity sample (NFM 6) with the other anions.
- When composite samples of surface water are processed, samples for analysis of organic compounds usually are processed first and are taken from a noncontaminating compositing device separate from that for inorganic-constituent samples, unless a cone splitter is used (section 5.1).

Table 5-1. Recommended sequence for processing samples

1. Organic compounds—Raw (wholewater or unfiltered) samples first, followed by filtered samples. **Do not field rinse bottles.** Chill immediately a. Volatile organic compounds (VOCs). b. Pesticides, herbicides, polychlorinated biphenyls (PCBs) and other agricultural and industrial organic compounds.
2. Total organic carbon (TOC), dissolved organic carbon (DOC),[1] and suspended organic carbon (SOC). Chill immediately.
3. Inorganic constituents, nutrients, radiochemicals, isotopes: **For ground water,** filtered samples first, followed by raw samples. **For surface water,** raw samples first, followed by filtered samples. (Field rinse each bottle, as required.) a. Trace metals. b. Separate-treatment constituents (such as mercury, arsenic, selenium) and major cations. c. Major anions, alkalinity, and nutrients. Chill nutrients immediately. d. Radiochemicals and isotopes. (Bottle-rinse, filtration, and preservation requirements depend on analysis to be performed (section 5.6 and Appendix A5-C.)[2])
4. Radon and chlorofluorocarbons.[2] Do not rinse bottle.
5. Microorganisms (NFM 7).

[1]TOC and DOC samples can be collected whenever most appropriate for the specific field operation.
[2]Radon and chlorofluorocarbon and most isotope samples are collected outside of the processing chamber.

5.0.3 FIELD RINSING OF BOTTLES USED TO CONTAIN SAMPLES FOR ANALYSIS OF INORGANIC CONSTITUENTS

Most polyethylene sample bottles and only those glass sample bottles that are designated for analysis of inorganic constituents (inorganics bottles) are field rinsed as described in table 5-2. Check Horowitz and others (1994) and the laboratory requirements (summarized in Appendixes A5-B and A5-C) for more detailed discussions of field rinsing. **The field-rinse water normally is the same as the water that will fill the sample bottle: use wholewater sample for raw (unfiltered) samples and filtrate for filtered samples.**

- If the volume of sample obtained for processing is limited, DIW of the appropriate quality may be substituted as the rinse solution for the first two of the three required rinses.
- Wear disposable, powderless gloves while processing samples.

Check analyte requirements before field rinsing bottles. For example, DO NOT field rinse glass bottles that are designated for analysis of organic compounds.

Table 5-2. Directions for field rinse of bottles used to contain samples for inorganic-constituent analysis

[DIW, deionized water; mL, milliliters]

Bottle Preparation
• If bottles were previously rinsed and half-filled with DIW[1], discard DIW and rinse once only with the water to be sampled. Use filtrate for filtered samples and wholewater for raw samples.
• If bottles were not prerinsed with DIW, rinse twice with DIW onsite, followed by one field rinse with the water to be sampled (use only 25-mL filtrate for bottle rinse for the filtered sample[1,2]).
Field-Rinse Technique
1. Put on disposable, powderless gloves.
2. Fill sample bottle about 1/10 full of rinse water. Cap bottle.
3. Shake the bottle vigorously to rinse all interior surfaces.
4. Discard rinse water by swirling the solution out of the bottle.
5. Shake off adhering droplets.

[1]Required for filtered trace-element samples (Horowitz and others, 1994).
[2]Refer to section 5.2.1.A for detailed guidance relating to surface-water and ground-water samples.

(Blank page)

RAW SAMPLES 5.1

By D.B. Radtke, A.J. Horowitz, Jacob Gibs, and F.D. Wilde

Raw samples, commonly referred to as wholewater or unfiltered samples, are collected directly into the appropriate type of sample bottle from the sampling device (such as a submersible pump, sample-compositing device, peristaltic pump, or cone splitter). It is recommended that this sample collection take place within a processing chamber, especially if analyte concentrations are expected to be near the detection limit, to prevent contamination from airborne sources.

- Equipment must be clean before samples are collected and processed.
- Disposable, powderless gloves must be worn throughout sample collection and processing. In order to withstand the solvents or chemicals that could be contacted, vinyl gloves are adequate for inorganic work, but use of organic solvents for organic work requires latex or nitrile gloves.

COMPOSITES AND SUBSAMPLES 5.1.1

Surface-water samples normally are composited and processed through sample splitting (subsampling) devices (NFM 2). Ground-water samples are not composited but are pumped either directly through a splitter or through a filtration assembly (filter assembly) into sample bottles, unless a bailer or other thief-type sampler is used to collect the sample. Inorganic-constituent samples usually are composited in the churn splitter, and organic-compound samples commonly either are composited in a 20-L glass, fluorocarbon polymer, or metal container, or are processed through a cone splitter.

Only the Clean Hands person fills sample bottles with water withdrawn from the churn or cone splitter (NFM 4).

Two types of water-sample splitters commonly used by the USGS are the polypropylene churn splitter (churn) and the fluorocarbon polymer cone splitter (cone).[5] Each splitter has specific advantages and disadvantages (NFM 2.2.1). By convention, the churn usually is used only for inorganic-constituent (and possibly for suspended organic carbon) samples. The churn is constructed of plastic materials that can potentially affect concentrations of other organic compounds. The cone is constructed of fluorocarbon polymer material and can be used for either inorganic-constituent or organic-compound samples. **Program or study protocols might dictate which equipment to use.**

- Either the churn or cone splitter can be used for splitting raw samples with suspended-sediment concentrations up to 1,000 mg/L.
- Only the cone splitter can be used for splitting raw samples with suspended-sediment concentrations up to 10,000 mg/L (Office of Water Quality Technical Memorandum 97.06).
- The splitting accuracy of the cone splitter is unknown for suspended-sediment concentrations between 10,000 to 100,000 mg/L (Office of Water Quality Technical Memorandum 97.06), but data are available that indicate the splitting accuracy of the cone is unacceptable at concentrations of 100,000 mg/L or more.

5.1.1.A Churn-Splitter Procedure

Subsamples collected from the composite sample in a churn splitter must be processed according to the specific procedures described below, using Clean Hands/Dirty Hands (CH/DH) techniques as applicable.

1. Assemble sample-processing equipment and supplies on a clean work surface.
   - Put on appropriate, disposable, powderless gloves (gloves). (Wearing multiple pairs of gloves at one time provides an efficient means of changing gloves quickly.)

[5]Consult the following references for more detailed information about the churn and cone splitters: Office of Water Quality Technical Memorandums 76.24-T, 80.17, 94.13, and 97.06; Capel and others (1995); and Capel and Larson (1996).

- If hand contact is made with a potential contaminant, remove the outer (contaminated) gloves before continuing with sample processing.
- For CH/DH techniques: Remove churn splitter and inner bag from churn carrier. Leave the churn carrier and outer bag outside the processing area (vehicle or building).

2. Place all prelabeled wholewater or suspended-material bottles within easy reach of the churn spigot.
3. Churn the composite sample at a uniform rate by raising and lowering the disk inside the churn splitter with smooth, even strokes.
   - When churning, the disk should touch bottom on every stroke, and the stroke length should be as long as possible without breaking water surface. **Do not break the surface of the water.**
   - **The churning rate should be about 9 inches per second (in/s).** If the churning rate is significantly greater than 9 in/s, or if the disk breaks the surface of the water, excessive air is introduced into the sample and could affect dissolved gases, bicarbonate, pH, and other characteristics of the sample.
   - Inadequate churning can result in withdrawal of nonrepresentative wholewater or suspended-material samples.
4. Pre-mix the composite sample by churning for about 10 strokes to uniformly disperse suspended material before subsampling.
5. **Raw subsample.** Withdraw the raw subsamples for wholewater or suspended-materials analyses first.
   - Withdraw an adequate volume of sample water for the field rinse while continuing to churn.
   - **Withdraw the first subsample.** The first subsample withdrawn from the churn should be the largest volume required (usually a 1-L sample).
   - Do not interrupt the churning/subsampling process, if possible. If an interruption occurs, reestablish the churning rate and remix the sample by churning ten strokes before resuming subsampling.
   - As the volume of composite sample in the churn decreases, adjust the stroke length to maintain a churning rate of about 9 in/s and avoid breaking the surface of the water being sampled.

6. Check requirements for sample preservation. **For raw samples that require chemical treatment ⇨ Go to section 5.4.**
   - For raw samples that require chilling without chemical treatment(s)—Pack samples in ice or refrigerate as quickly as possible. Maintain at or below 4°C without freezing (section 5.4).
   - For raw samples that do not require chilling or chemical treatment—Set samples aside in a clean area for shipping to the laboratory (section 5.5).
7. **Filtered samples ⇨ Go to section 5.2.** After wholewater or suspended-material subsampling is complete, use the remainder of the composite sample in the churn for filtered samples.
8. Empty the churn after the required number of samples has been processed.
   - If the churn will be reused during the field trip, disassemble and field clean onsite while still wet, as described in NFM 3.
   - If the churn will not be reused during that trip, rinse with DIW before it dries out, place it in a plastic bag and in the churn carrier to be transported back to the office laboratory for cleaning.
9. Document on field forms and in field notes the types of samples collected and the splitting procedures used.

A field blank might be required after all sampling and processing equipment has been field cleaned (NFM 4.3).

TECHNICAL NOTES: Subsamples totaling 10 L and 5 L can be withdrawn from the 14-L and 10-L churn, respectively, for samples for wholewater analysis. The sample volume remaining in either churn may be used for filtered samples.

The churn splitter is used to split samples with particle sizes ≤ 250 µm and suspended-sediment concentrations ≤1,000 mg/L. Splitting accuracy becomes unacceptable at particle sizes > 250 µm and concentrations > 1,000 mg/L.

Cone-Splitter Procedure 5.1.1.B

Inorganic-constituent and organic-compound samples can be split using a fluorocarbon polymer (Teflon™) cone splitter. Although the cone splitter is used primarily for simultaneous distribution of surface-water samples into bottles, the cone also can be used similarly for a bailed or composited ground-water sample. The sample is poured into the splitter from the sampling device or transferred from a noncontaminating compositing container. If used for splitting pumped ground-water samples, the sample is pumped directly into the cone splitter.

1. Put on appropriate, disposable, powderless gloves (gloves). Remove cone splitter from protective covering.
2. Prepare a processing area that is protected from dust and fumes. Preferably, the cone splitter is installed in a processing chamber or covered with a large plastic bag.
3. Install cone splitter (see NFM 2, fig. 2-10, for a labeled diagram). **The cone splitter is built to close tolerances to achieve accurate and reliable operation and requires the following:**
   - **Use a bull's-eye level to level the cone splitter: this is critical for accurate performance.**
   - All tubes exiting the cone splitter must be the same length, as short as possible, and precleaned. Organic-compound samples require fluorocarbon polymer tubing. Carry a separate set of tubes for each site, and clean all sets on return to the office laboratory. If extra tubes are not available, do not reuse tubes for multiple sites without first cleaning them.
   - Push tubes as far as possible into the fittings on the splitter.

Minimize atmospheric contamination—Cover the cone splitter and sample bottles during the sample splitting process and when not in use.

4. Field rinse cone splitter and the appropriate sample bottles with the water to be sampled. **Do not field rinse laboratory-cleaned and baked glass bottles.**
   a. Open cover to access cone-splitter reservoir. (Flap or access slots for hands can be cut into the plastic bag covering the splitter.)
   b. Transfer 2 to 4 L of the sample into the cone-splitter reservoir. Some splitter reservoirs may be retrofitted with a funnel to ease pouring.
   c. Close cover and lightly tap splitting system to dislodge adhering water drops. Discard rinse water.
   d. Field rinse bottles for raw samples (RA, RU, and so on) with wholewater sample. Do not use the water sample previously processed through the cone splitter; follow directions in table 5-2.
5. Place bottles for raw samples under outlet tubes. Complete splitting procedure first with bottles for organic-compound samples, next with bottles for inorganic-constituent samples.
   - Place outlet tubes into sample bottles to prevent spilling. **Outlet tubes should not extend beyond the neck of the sample bottle. Do not submerge the ends of outlet tubes in the sample.**
   - Outlet tubes can be combined to collect various combinations of volumes of the original sample. Make sure no back pressure results from restrictions of water and air flow if combining outlet tubes into a single bottle.
   - Direct sample discharge from unused outlet tubes to waste.
6. Pour (or pump) sample into cone splitter. If hand contact is made with a potential contaminant while using CH/DH techniques, remove outer contaminated glove(s) or put on a new pair of gloves before transferring sample to cone splitter.
   a. Gently shake or agitate sample for at least 10–15 seconds to resuspend any particulate matter present in sampler bottle or discrete sampler (such as a bailer).

b. Transfer sample to cone-splitter reservoir (some splitter reservoirs may be retrofitted with a funnel to ease filling).

- Open cone-splitter cover and invert sampler or compositor containing sample over splitter reservoir. (If using a bailer, empty through bottom-emptying device. If using a pump, hold sample line over the cone-splitter reservoir and pump sample directly into the cone splitter.)
- First, collect organic-compound samples into clean, baked glass bottles (Appendix A5-A).
- Next, collect inorganic-constituent samples into cleaned and field-rinsed polyethylene bottles or as designated (Appendix A5-B or A5-C).

c. Maintain a head of water above the splitter standpipe to prevent air from entering the splitting block while rapidly transferring the sample. **Do not spill any of the sample when pouring or pumping it into the cone splitter.**

d. For proper operation, the splitter standpipe must be discharging at full-flowing capacity.

- **Never overfill sample bottle.**
- **Always transfer the entire composite sample into cone splitter** for thorough distribution into the sample bottles.

7. **When splitting the samples, avoid exposing samples to direct sunlight or freezing conditions.** During sample splitting, the temperature of samples from the cone splitter should remain constant.
8. Close cone-splitter cover.
9. After flow has stopped, lightly tap the cone splitter to dislodge adhering drops.
10. Remove sample bottles and cap them immediately.
11. **To obtain smaller subsample volumes**, position bottles at cone outlet ports and pour a sample from the preceding set of split samples into the cone splitter. **For inorganics only, remember to rinse each new set of polyethylene sample bottles with DIW and sample as previously directed** (sections 5.0.1 and 5.0.3).

12. If multiple passes through the cone are required, randomize the ports selected. This minimizes bias from differences in ports caused by manufacturing processes.
13. Check requirements for sample preservation. **For samples that require chemical treatment ⇨ Go to section 5.4.**
    - For raw samples that require chilling without chemical treatment(s)—Pack samples in ice or refrigerate as quickly as possible. Maintain samples at or below 4°C without freezing (section 5.4).
    - For raw samples that do not require chilling or chemical treatment—Set samples aside in a clean area for shipping to the laboratory (section 5.5).
14. **Filtered samples ⇨ Go to section 5.2.** Remember to use only sample filtrate for the bottle field rinse.
15. Clean cone splitter, following instructions in NFM 3.
    - Disassemble and clean in the field before reusing. Field cleaning between sites must be done onsite while the cone splitter is still wet.
    - If the cone splitter will not be reused immediately, rinse with DIW and place in a plastic bag for transporting back to the office laboratory for cleaning.
16. Document on field forms and in field notes the types of samples collected and the splitting procedures used.

A field blank might be required after sampling and processing equipment has been field cleaned (NFM 4.3).

GROUND WATER: PUMPED AND BAILED SAMPLES 5.1.2

Steps for filling bottles with raw sample pumped from water-supply wells and monitoring wells are described in this section (refer also to section 5.6 and Appendixes A5-A, A5-B, and A5-C). The equipment needed and the procedures required to purge a well and withdraw the sample are described in NFM 2 and NFM 4, respectively, and are only briefly described below.

The recommended method for withdrawing ground-water samples from conventional supply or monitoring wells is to use a submersible or peristaltic pump and to pump the sample directly to a processing chamber (or to a glove box filled with inert gas).[6] Ground-water samples collected using a bailer or other discrete sampling device can be processed either as described under 5.1.1 (composites and subsamples) or within a processing chamber (or glove box), as described later in this section.

Only the Clean Hands person fills the sample bottle inside of the sample-processing chamber (NFM 4).

Collect/process equipment blanks, field blanks, replicates, and other types of quality-control (QC) samples periodically (NFM 4.3 and Appendix A4-B of NFM 4). The frequency, number, types, and distribution of QC samples are determined ahead of time according to the study workplan. Nevertheless, in the event of unforeseeable field conditions (for example, dust storms, new point source(s) of contamination, or application of agricultural or other chemicals), **field personnel must judge whether to process additional QC samples.**

- Replicates of environmental samples—Fill bottles one after the other (NFM 4.3).
- Field blanks—Process according to the study quality-assurance plan or as needed (NFM 4.3).

[6]Wells or devices constructed to obtain samples under natural flow gradient (passive) conditions are not addressed in this report.

Processing of samples

The steps listed below for processing raw ground-water samples are based on the assumption that both organic-compound and inorganic-constituent samples will be collected. Before proceeding, check section 5.6 for analyte requirements.

- Prelabel bottles with site identification, sample designation, date, and time (section 5.5 and NFM 1).
- Process samples in the order recommended for sample collection listed on table 5-1. This helps to limit overpurging of volatile compounds, reduce airborne contamination and cross contamination among samples and sites, and minimize discrepancies in the ionic mass balance.
- When pumping the sample, do not stop the pump or interrupt flow to the processing chamber during sampling. The rate of flow during sampling should remain constant throughout processing and be the same as the rate of flow while making final field measurements at the end of purging (NFM 4, NFM 6).

To process ground-water samples for organic-compound analyses:

1. Put on appropriate (latex or nitrile), disposable, powderless gloves (gloves). Cover bench or table with a sheet of aluminum foil to make a clean work surface.
2. Assemble necessary equipment and supplies on the clean work surface, and remove aluminum foil wrapping from precleaned equipment. Attach processing chamber cover. (Processing of organic-compound samples within a chamber is not mandatory but is recommended.)
3. Check requirements for treatment of the sample(s) collected.
   - If collecting a VOC sample that will be acidified—Test for the number of drops of HCl needed to lower sample pH to ≤ 2 using 40 mL of the final purge water. Dispense the HCl from a dropper bottle.
   - All samples processed for organic-compound analysis are to be chilled to 4°C or below without freezing.
4. Place bottles and other equipment needed for processing raw samples into processing chamber. If collecting samples for VOCs, place only VOC vials and VOC equipment in the chamber.

5. Withdraw samples from the well.

If using a pump—

a. Purge wells first, preferably with the same pump to be used for withdrawing the samples. Consult NFM 4.2 for purging procedures.

b. Check that the discharge end of sample line from the pump or manifold is secured in the processing chamber.

c. Direct sample flow through the sample line into the processing chamber (NFM 4.2).

- Waste initial sample through chamber drain for the sample-line rinse; do not let sample spray onto chamber cover—change chamber cover if this happens.
- Check for air bubbles in the sample line; tap the line or make adjustments to remove any air from the line.
- Flow should appear smooth and uniform (with no splashing) and should not exceed 150 mL/min when filling 40-mL VOC vials or 500 mL/min for larger bottles.

If using a bailer—

a. Purge wells first, using a pump (NFM 4.2). Do not purge wells with a bailer unless absolutely necessary.

b. Set up holding stand, as appropriate.

c. Lower the sampler (after field rinse) smoothly into the well; cause as little disturbance to the water column as possible. Follow analogous directions as those for sampler field rinsing (NFM 4.0.2.A).

d. After reaching the sampling depth within the screened or open interval, collect sample by raising the sampler smoothly (minimizing disturbance to water column). Keep the deployment line clean and untangled as sampler is lowered and raised.

e. Place sampler into holding stand and insert sample-delivery tube/device.

> TECHNICAL NOTE: Sampling from wells with a bailer or other discrete sampling device is not recommended if target analytes (such as trace elements and hydrophobic organic compounds) are those that typically associate or partition to particulates because deployment of bailers or other point-source samplers usually stirs up or otherwise mobilizes particulates. Fine-grained and colloidal-sized particulates can persist in the water column, causing a potential for bias.

6. Collect all raw organic-compound samples into designated bottles.
   a. Fill VOC vial from bottom of vial to overflowing without entraining air bubbles. Leave a convex meniscus. If sample will not be acidified, cap vial securely, invert, and check for air bubbles. **Follow directions in section 5.6.1.A.**
   b. If acidification of the sample is required,
      - The preservative can be added to VOC samples while samples are inside the processing chamber as long as the chemical treatment will not affect any subsequent samples to be collected for analysis of organic compounds. Otherwise, acidify VOC samples in a preservation chamber.
      - Add 1 to 5 drops of HCl to the sample (sections 5.4 and 5.6). Usually two drops of HCl are sufficient to lower the pH of the VOC sample to ≤ 2. Cap vial securely, invert, and check for air bubbles. If air bubbles are present, discard the vial and start again.
      - Change cover of processing chamber and change gloves.
   c. Place remaining raw organic-compound sample bottles into processing chamber. Fill bottles directly from the sample line to the shoulder of each bottle (section 5.6.1.B).
7. For filtered organic-compound samples:
   a. Place aluminum plate-filter assembly into chamber for pesticides and other filtered organic-compound samples. Change gloves.
   b. Load the filter, connect the plate-filter assembly, and field rinse the filter as directed in section 5.2.2.A.
   c. After following filtration directions in section 5.2.2.A, pass bottles out of chamber for DH handling.
8. After processing raw and filtered organic-compound samples:
   a. Fill sample bottle with DIW and label "temperature-check sample" to accompany chilled organic-compound samples.
   b. Remove the equipment used to process the samples and pass to DH.
   c. Discard chamber cover.
   d. Remove aluminum foil covering from work bench.
9. **Sample preservation ⇨ Go to section 5.4.**

Process ground-water samples for inorganic-constituent and remaining analyses:

1. Direct flow of pumped sample away from the processing chamber. Change to vinyl or latex, disposable, powderless gloves (gloves).
2. Cover bench or table with a plastic sheet to make a clean work surface. Change processing chamber cover. Assemble equipment and supplies needed on the clean work surface. Remove plastic wrapping from pre-cleaned equipment. Change gloves.
3. **For filtered inorganic-constituent, nutrient, radiochemical, and isotope samples:**
   a. Place filtration equipment, sample bottles (prelabeled), and other supplies and equipment for filtered inorganic-constituent samples into processing chamber. Change gloves.
   b. Connect filtration equipment as directed in section 5.2.1.
   c. Resume sample flow to the chamber.
      - Check for air bubbles in the sample line; tap line or make adjustments to remove air from the line.
      - Flow should be smooth and uniform—about 500 mL/min to fill sample bottles without splashing.
   d. Collect all filtered inorganic-constituent samples first, as directed in section 5.2.1.
4. Disconnect the filter assembly. Change gloves.
5. **Raw inorganic-constituent, nutrient, radiochemical, and isotope samples:**
   a. Place prelabeled bottles for raw samples into the processing chamber. Change gloves.
   b. Field rinse bottles with raw sample (section 5.1, table 5-1).
   c. Collect samples into designated bottles.
   d. Place bottles outside of chamber. Change gloves.
6. Remove equipment, discarding chamber cover appropriately.
7. **Sample preservation ⇨ Go to section 5.4.**
8. **Radon and CFC samples ⇨ Go to section 5.6.**

Blank page

FILTERED SAMPLES 5.2

By D.B. Radtke, A.J. Horowitz, and M.W. Sandstrom

Filtration is the physical process used to separate the particulate and aqueous fractions of a water sample. Samples are filtered for several purposes; for example, to remove microorganisms in order to help preserve ambient analyte concentrations, to remove suspended materials that interfere with specified analytical procedures, and to determine chemical speciation and fractionation of trace elements for geochemical studies.

Study objectives and the analytes targeted for study dictate the filtration method and equipment to be used. Ambient concentrations of filtered analytes typically can be near the limit of detection; therefore, field personnel must pay strict attention to possible sources of contamination from sampling and processing equipment, construction material of the chamber frame and of the filtration equipment, and the way the equipment is handled. (Equipment and supplies used to filter water samples are described in detail in NFM 2.)

- Check the composition and pore size of the filter medium and the effective filtration area of the filter; these can affect the quality and accuracy of the data and can compromise data-quality requirements.
- To minimize airborne contamination,
  - Filter samples within a processing chamber.
  - Add chemical treatments to samples within a separate preservation chamber.

Filter samples during or immediately after sample collection.

5.2.1 INORGANIC CONSTITUENTS

Most filtration systems currently used by the USGS are appropriate for filtering wholewater samples, if the limitations of each system are taken into account. **Standard USGS procedure is to filter inorganic-constituent wholewater samples through a 0.45-micrometer (µm) pore-size disposable capsule filter.** Filtration through media with pore sizes other than 0.45 µm or with other equipment (such as tangential-flow devices) depends on the use and interpretation of the data and can yield substantially different results for trace-element concentrations.

Data-quality requirements for interpretive studies of ground-water and surface-water chemistry can dictate filtering the sample through a nominal pore size of ≤ 0.2 µm. The quality-assurance procedures used for samples filtered through the 0.45-µm nominal-pore-size capsule, plate, or other filtration equipment also are required for the ≤ 0.2-µm filters. If concentrations of target analytes are analyzed at sub-parts-per-billion levels, more stringent QA/QC measures are needed. Such samples can be filtered through a plate filter or other filtration equipment (for example, a 47-mm-diameter vacuum-filter unit) as long as the equipment used is approved by the study or program, data-quality requirements are met, and additional quality-control samples are collected. For additional information on filtration artifacts, procedures, and equipment, see Kennedy and others (1976), Salonen (1979), McCarthy (1988), McCarthy and Zachara (1989), Puls and Barcelona (1989), Ward and Harr (1990), Horowitz and others (1992, 1994), Williams and others (1993), Robards and others (1994), and Koterba and others (1995).

Cleaning and conditioning of various filter media used for inorganic constituents are summarized in table 5-3. Contamination during sample filtration can be reduced by following the instructions given for cleaning, conditioning, and handling of the filter media.

Table 5-3. Field cleaning and conditioning procedures for media used to filter samples for inorganic-constituent analysis

[µm, micrometer; mL, milliliter; sample, the water to be sampled; µg/L, microgram per liter; mm, millimeter; HNO_3, 1 molar solution of ultrapure-grade nitric acid; HCl, 1 molar solution of ultrapure-grade hydrochloric acid; nutrients, nitrogen and phosphorus species; DIW, District- or laboratory-produced deionized water of known quality, ASTM Type-1 grade or better; IBW, laboratory-produced inorganic-grade blank water; *N*, normal; >, greater than]

Description	Filter media	Field cleaning/ conditioning	Application
Disposable capsule filter[1] (Polypropylene)	Polysulfone, pleated membrane, 0.45-µm or 0.2-µm pore size	Clean with 1,000 mL DIW and remove residual DIW[2] Condition with 25 mL sample	Major ions and nutrients; trace elements with concentrations > 1 µg/L; radiochemicals and isotopes
Plate filter — 142 mm (Polycarbonate or acrylic)	Cellulose nitrate, tortuous path (0.45 and 0.1 µm are most commonly used pore sizes)	Clean with 500 mL DIW and extract residual DIW Condition with 100 mL sample	Major ions and nutrients; trace elements if concentrations > about 100 µg/L
Cartridge or hand-pressure filter assembly—47 mm (Polypropylene or fluorocarbon polymer)	Cellulose nitrate, tortuous path (0.45, 0.2, and 0.1 µm are most commonly used pore sizes)	Clean with 100 mL DIW and remove residual DIW Condition with 20 mL IBW or 10 mL sample	Major ions and nutrients; trace elements with concentrations at about 1 µg/L or greater
Cartridge or hand-pressure filter assembly—47 mm (Fluorocarbon polymer)	Polycarbonate (such as Nuclepore), direct path (0.40 and 0.1 µm are most commonly used pore sizes)	Soak in HNO_3 rinse with IBW.[3] Remove residual IBW Condition with 20 mL IBW or 10 mL sample	Major ions and nutrients; trace elements with concentrations at about 1 µg/L or greater

[1]Example: Gelman Sciences 12175 (0.45 µm); 600 square-centimeter filtration area. Other disposable capsule filters are available that have different effective filtration area, media type, and media pore size.

[2]For trace-metal analyses at nanogram-per-liter concentration levels, first acid rinse with 500 mL of 1-*N* HCl (polysulfone membranes cannot withstand HNO_3).

[3]Substitute HCl for HNO_3 if sampling includes nutrients.

- Before filtering, designate one member of the processing team as Clean Hands (CH) and another member as Dirty Hands (DH) if using the CH/DH method (NFM 4).
- Wear appropriate, disposable, powderless gloves throughout the process. Vinyl gloves are adequate for inorganic-constituent sampling.
- Filter the samples within a processing chamber to minimize the possibility of contamination.

5.2.1.A Capsule-Filter Procedure

The capsule filter is a disposable, self-contained unit composed of a pleated filter medium encased in a plastic housing that can be connected in-line to a sample-delivery system (such as a submersible or peristaltic pump) that generates sufficient pressure (positive or negative) to force water through the filter. Filter media are available in several other pore sizes, but 0.45 µm is the pore size used routinely for most studies at this time. The capsule filter is required for most studies when filtering samples for trace-element analysis and is recommended when filtering samples for major-ion or other inorganic-constituent analyses.

The following instructions implement Clean Hands/Dirty Hands (CH/DH) techniques and the other QA procedures that are required for trace-element samples with analyte concentrations at the parts-per-billion (ppb) level and that are recommended as good field practice for all samples.

- The DH team member performs operations that are outside of the processing chamber and the CH team member performs operations inside the chamber. DH and CH must wear appropriate disposable, powderless gloves (gloves).
- Preclean capsule filters (step 5 below) before leaving for the field to save field time.

Fill bottles for filtered samples in this sequence: FA (trace elements) → FAM (mercury) → FA and FU (major ions) → FCC or FCA (nutrients) → FAR and all other samples.

To prepare the work space, sample bottles, and capsule filter:

1. CH/DH: Put on one or several layers of gloves.
2. *CH*: Assemble processing chamber, attach chamber cover, and change gloves. Place capsule filter and sample bottles into chamber, and run discharge end of peristaltic pump tubing into the chamber. Open DIW[7] container and cover it with a plastic bag to prevent contamination from airborne particulates.
3. *CH/DH*: (*CH*) Insert intake end of peristaltic pump tubing through the plastic covering and into a l-L container of DIW.
   a. (*DH*): Attach tubing to peristaltic pump head and pump DIW to fill tubing.
   b. Discharge waste rinse water through a sink funnel or a toss (waste) bottle.
4. Discard DIW stored in DIW-prerinsed sample bottles. If sample bottles were not DIW-prerinsed by field personnel:
   a. Wearing gloves, rinse off exterior of each bottle.
   b. Pour DIW into bottle until about one-tenth full.
   c. Cap bottle and shake vigorously about five times.
   d. Uncap and empty bottle.
   e. Repeat b–d of step 4 twice (for a total of three times).
   f. Recap bottles until ready to field rinse.

[7]Office of Water Quality Technical Memorandum 92.01 describes the quality required of the deionized water.

5. **Clean the capsule filter.** If the capsule filter was precleaned, go to the sections that follow on "To filter a composite sample" or "To filter a pumped sample," as appropriate. The steps below comprise sufficient precleaning of the filter for inorganic analytes at the parts-per-billion (ppb) concentration level. More rigorous precleaning procedures that include rinsing with trace-metal-grade hydrochloric acid are required for samples containing ppb concentrations of target analytes (table 5-3). **Only CH touches those portions of tubing that will be in direct contact with the DIW or capsule filter.**

   a. *CH*: In the processing chamber, remove capsule filter from protective bags.

      - Attach pump tubing to inlet connector of capsule filter, keeping tubing as short as possible. **Make sure direction of flow through capsule filter matches the direction-of-flow arrow on the side of the capsule.**
      - To help minimize aeration of the sample (usually for ground-water samples), secure a short length of clean fluorocarbon polymer tubing onto capsule filter outlet to extend into the sample bottle so the bottle can be filled from the bottom up.

   b. *CH/DH*: Pump 1 L of DIW through capsule filter; discharge waste rinse water through a sink funnel or to a toss bottle.

      - *DH* operates the pump at a low speed.
      - *CH* inverts the capsule filter so the arrow on the housing is pointing up. (This expels trapped air from the capsule during initial filling; do not allow water to spray onto the chamber walls.)

   c. *DH*: Remove tubing from DIW reservoir and continue to operate pump in forward mid-range speed position to drain as much of the DIW that remains in the capsule filter as possible. While pump is operating, shake capsule filter to help remove any entrained DIW.

   d. *CH*: Detach capsule filter from peristaltic pump tubing, put it into a clean, sealable plastic bag, and place in a corner of the processing chamber until ready for use.

Filtration procedures differ somewhat, depending on how the sample is collected. If the sample is collected using discrete collection equipment, such as the surface-water bag or bottle sampler or ground-water bailer, use the procedures described below in "To filter a composite sample." If the sample is collected by pumping it directly from the source, use the procedures described below in "To filter a pumped sample." Ground-water samples usually are not collected as a composite. If samples are to be withdrawn from

a well using a bailer, consider using a bailer to which the capsule filter or other filtration device can be connected inline to the bailer bottom-emptying device. Pouring a sample from the top of the bailer into another receptacle aerates the sample and therefore is not a generally recommended procedure for processing ground-water samples.

To filter a composite sample (generally for surface water):

1. Field rinse peristaltic pump tubing with the water to be sampled.
   a. *CH:* Rinse the outside of each end of the peristaltic pump tubing.
   b. *CH*: Transfer intake end of peristaltic pump tubing into composite sample. If a churn splitter is used, transfer intake end of peristaltic pump tubing through churn funnel and reseal plastic bag around the tubing.
   c. *DH*: Start peristaltic pump to slowly pump sufficient sample to completely fill pump tubing.
   d. *CH*: Discard rinse water through the sink funnel or into a toss bottle or other receptacle and dispose of appropriately. Prevent water from ponding in the processing chamber.
   e. *DH*: Stop peristaltic pump after tubing is field rinsed.
2. Field rinse capsule filter:
   a. *CH*: Remove cleaned capsule filter from plastic bag and attach discharge end of the peristaltic pump tubing to the inlet connector on the capsule filter.
      - A clean, small plastic hose clamp may be used to secure the discharge end of the tubing to the capsule filter inlet connector.
      - Check that the direction of sample flow through the capsule filter matches the direction of the arrow on the capsule.
   b. *DH:* Operating the pump at low speed, pump sample through the tubing to the capsule filter.
   c. *CH:* Turn capsule filter so that the outlet is pointing up (arrow on capsule housing is pointing up) and flow of the sample forces trapped air out of the capsule filter while it is filling. **Do not let sample spray onto chamber cover.**
      - The chamber cover must be changed if sample has sprayed onto it.
      - If some water that sprayed onto the chamber cover has dripped into the sample bottle, discard the bottle, change the cover, and collect a new sample.

d. *DH:* Stop the peristaltic pump as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.

> TECHNICAL NOTE: The goal is to minimize clogging the filter medium with suspended materials by minimizing the volume of sample that will be used to field-rinse the filter.

1. Collect sample filtrate.
   a. *CH*: Check that there is a tight connection between the pump tubing and the capsule filter.

      DH: Check that the intake tube is properly inserted in the sample and start the pump.

      CH: Collect a maximum of 25 mL of the water to be sampled as it discharges through the filter. **Do not exceed 25 mL.**

      CH: Field rinse a precleaned 250-mL FA bottle for trace-element sample only with sample filtrate.

      DH: Stop the pump in time to prevent losing filtrate to waste.

      CH: Cap bottle, shake vigorously, and then discard rinse water into appropriate receptacle.

   b. *DH:* Start pump and resume flow from pump to the filter.

      CH: **Filter only the next 200 mL of the sample** into the trace-element FA bottle (fill to top of upper lip of standard 250-mL polyethylene bottle). Cap bottle securely and set aside for chemical treatment.

   c. *DH:* Stop the pump after the trace-element FA bottle is filled.

   d. If a filtered mercury sample is required, restart pump and repeat steps 3a–c, substituting a FAM bottle for the FA bottle.

   e. *CH:* Field rinse any remaining sample bottles for inorganic analyses. **Use no more than a total of 100 mL of filtrate per capsule filter to field rinse any remaining bottles for filtered sample.**

   f. Fill remaining bottles in the following order: (1) major cations, (2) nutrients and major anions (including alkalinity), (3) radiochemicals (Appendix A5-A), and (4) stable isotopes. Cap each bottle immediately after filling.

To filter a pumped sample (usually ground water):

Ground-water samples usually are withdrawn from a well by means of a submersible pump. Note that this method might be appropriate for some surface-water samples. The capsule filter or other filter assembly is connected inline with the sample tubing in order to collect samples directly from the well.

- When sampling ground water, DH should check that the turbidity values recorded at the end of purging have remained stable. Equipment changes or adjustments that disrupt sample flow can affect sample turbidity and should be avoided. If sample flow is disrupted, pump for several minutes until ambient turbidity values are reestablished.
- **Maintain a smooth, uniform flow.** Do not stop pump or divert flow from capsule filter or other filter assembly during bottle field rinse or filtration, if possible.

  TECHNICAL NOTE: If using a three-way valve, changing the setting to divert the flow of sample being pumped to the filter with a submersible pump can cause air bubbles to form, can air-block the filtration equipment, and can cause changes in pumping rate that could result in increased turbidity. These effects should be avoided to preserve sample integrity; therefore, flow to the filter should not be stopped until all filtration is complete.

1. Field rinse the capsule filter with sample water:
   a. *CH:* Ensure that the sample line is full of sample and free of bubbles; then attach the discharge end of the sample line to the inlet connector on the capsule filter.
      - Practice your technique for attaching the capsule filter to the tubing carrying flowing water so that water does not spray onto chamber walls.
      - Check that the direction of flow matches the direction of the arrow on the capsule.
   b. *DH:* Adjust the sample flow through the sample line to the capsule filter, keeping a slow rate of flow.
   c. *CH*: Turn the capsule filter so the outlet is pointing up (arrow on capsule housing is pointing up) and the flow of sample forces trapped air out while the capsule filter is filling.
      - Do not allow water to spray onto chamber walls.
      - The capsule filter should be full of sample. No air should be left in the capsule filter.

d. Field rinse bottles for inorganic-constituent filtered samples with sample filtrate (section 5.0.3). Use bottles that were already rinsed three times with DIW. Determine whether the potential clogging of pores in the filter medium is of concern for your samples (see TECHNICAL NOTE below).

CH: Fill a 250-mL FA bottle for trace elements with 25 mL of sample filtrate; cap, shake vigorously, and discard rinse water into appropriate receptacle.

CH: Fill a FA bottle for trace elements with about 200 mL of sample filtrate (to top of upper lip of 250 mL bottle). Cap bottle and set aside for chemical treatment.

CH: If a mercury sample is required, field rinse and fill a FAM bottle using the same procedure as for the 250-mL FA bottle.

CH: Field rinse remaining bottles, trying to use no more than an additional 100 mL of sample filtrate.

> TECHNICAL NOTE: Depending on sample turbidity and composition, the nominal pore size of filter media tends to decrease as the volume of sample passed through the filter increases because pores are clogged by sediment loading or mineral precipitation on the filter (Horowitz and others, 1994). Ground water with turbidity ≤5 NTU should not affect filter pore size appreciably. To minimize the chance of filter clogging, limit the volume of sample passed through the filter by eliminating the field rinse—be sure that you use clean bottles and fill them one after the other. For ground-water sampling, do not stop the pump during the field-rinse and sampling process.

e. *CH:* Collect sample filtrate immediately into any remaining bottles in the following sequence (flow rate should be slow enough to avoid splashing sample out of the bottle): (1) major cations, (2) major anions and nutrients (including alkalinity sample for field titration), (3) radiochemicals (check Appendix A5-A for bottle-rinse and filtration requirements), (4) stable isotopes.

f. *CH:* Cap each bottle immediately.

Rinse FA, FU, FAM, FCA, and FCC bottles with filtered sample—not with raw sample.

After collecting filtered samples:

1. *CH*: If samples require chemical treatment, place FA bottles in the preservation chamber and go to section 5.4.
2. For filtered samples that do not require chemical treatment:
   a. *CH*: Set samples outside processing chamber.
   b. *DH*: Check that information on the bottle label is correct and complete.
   c. *DH:* Pack samples that require chilling in ice or refrigerate immediately.
   d. *DH:* Pack remaining samples for shipping (section 5.5).
3. Rinse all reusable equipment with DIW immediately—before equipment dries.
   - *CH*: If equipment will be reused at another site before returning to the office, rinse immediately with DIW and field clean tubing and other sample-wetted parts of the equipment using the prescribed cleaning procedures (NFM 3).
   - *CH*: If equipment or tubing will not be reused before returning to the office, rinse immediately with DIW and store rinsed tubing and equipment in plastic bags for office or laboratory cleaning.
4. **Discard the capsule filter after filtering each sample—do not reuse.**
5. Document the filtration procedures used on field forms and in field notes.

Use of the 0.45-µm disposable capsule filter for trace-element samples is required for many USGS programs.

5.2.1.B Plate-Filter Procedure

The filtering procedure using a 142-mm-diameter plastic plate-filter assembly is described below. The procedure remains basically the same for plate-filter assemblies of different diameters.

Prepare and precondition plate-filter assembly:

The following instructions pertain to either a 142-mm-diameter or a 47-mm-diameter plastic plate-filter assembly and require that the assembly components have been rigorously cleaned (NFM 3). To avoid recleaning in the field, prepare a set of filtration equipment for each well or surface-water sampling station. (Ignore Step 3 below if plate-filter assembly has been rinsed in the office.)

1. *CH*: Put on gloves. In a processing chamber, open a clean plate-filter assembly and load with the filter.
   a. Using nonmetallic forceps, place the bottom retaining screen on the base of the filter assembly. **Do not interchange bottom and top retaining screens.**
   b. Place the filter on top of bottom retaining screen using clean, blunt plastic or ceramic forceps. Do not touch the filter with hands (gloved or ungloved).
      - Be sure that only one filter is transferred from its original container directly to the plate of the filter assembly. Take care not to transfer the paper liner that separates each filter.
      - The filter should never be removed from the original container until each is transferred to the plate-filter assembly for use. (Exception: polycarbonate (Nuclepore) filter medium is precleaned with acid solution. If transferring one of these, hold the filter with forceps and rinse off acid with inorganic blank water (IBW) dispensed from wash bottle.)
   c. Using forceps, place the top retaining screen on top of the filter.

      TECHNICAL NOTE: If filtering sediment-laden water, a prefilter can be placed between the filter and the top retaining screen.

   d. Dispense 10 to 20 mL of DIW from a wash bottle onto the filter.

e. Close the plate-filter assembly by aligning the top and bottom plates and lightly tightening the plastic bolts, followed by finger tightening opposite pairs of bolts. **Overtightening can cause the plate-filter assembly to warp and leak.** Check that O-rings are in place before closing the assembly. Change gloves.

2. *DH/CH*: Pass the discharge end of the pump tubing through the hole in the side or top of the processing chamber. **Only the CH team member touches sections of tubing that will be in direct contact with the plate-filter assembly.**
   - Keep tubing as short as practical.
   - Attach a short piece of clean tubing to outlet connector of plate-filter assembly.
3. *DH/CH*: Rinse the plate-filter assembly with DIW, using a peristaltic pump, as follows (**rinsing must be repeated each time a clogged filter is replaced with a new filter**):
   a. *CH/DH*: Place intake end of peristaltic pump tubing into a 500-mL container of DIW. Turn pump on low speed.
   b. *CH*: Open the air-vent valve on top of the plate-filter assembly. Tilt the filter assembly slightly to the side and squeeze the outlet tube closed to force trapped air out through the vent. Release the outlet tube. (Venting trapped air is necessary because air bubbles will reduce the effective filtering area by preventing sample from passing through the filter.)
   c. *CH*: Close valve when top is filled with sample.
   d. *CH*: Pump sample through the plate-filter assembly and discard this field-rinse water through the sink funnel or into the toss bottle to prevent the water from ponding in the bottom of the processing chamber.
   e. *CH/DH*: Remove intake end of the pump tubing from the DIW container and continue to pump, draining as much of the remaining DIW from the plate-filter assembly as possible.
4. If using a peristaltic pump to transfer the sample to the processing chamber (go to step 5 if sample delivery is with a submersible ground-water pump):
   a. *CH*: Rinse intake end of the peristaltic pump tubing with the water to be sampled.
   b. *CH*: Transfer intake end of the peristaltic pump tubing into the container of sample. If a churn splitter is used, transfer the intake end through the churn funnel and reseal the plastic bag around the tubing.

c. *CH*: Remove peristaltic pump tubing from the inlet connector of the plate-filter assembly and hold the end of the tubing over the sink funnel or toss bottle.

d. *DH/CH*: Start the peristaltic pump in the forward position at slow speed and pump sufficient sample to fill and rinse all pump tubing. Stop the pump after the tubing is rinsed.

5. *CH*: Attach the discharge end of the peristaltic-pump or submersible pump tubing to the inlet connector of the plate-filter assembly.
   - Keep tubing as short as practical.
   - A clean, small, plastic hose clamp can be used to secure the discharge tubing to the inlet connector.
6. *DH*: Start sample flow to the plate-filter assembly.
7. *CH*: Vent trapped air and rinse plate-filter assembly as instructed in steps 3 b–d above.
   - If using a peristaltic pump, turn pump on low speed.
   - If using a submersible pump, maintain a slow and steady flow rate.
8. *CH*: Rinse appropriate sample bottles once with filtrate. Filter no more than 100 mL of sample for the final rinse of all sample bottles that require rinsing.
9. Filter samples, filling bottles in the following order, as applicable to study objectives and sample designation:
   a. Trace elements

      TECHNICAL NOTE: Study objectives and data-quality requirements govern procedures to be used if the filtered trace-element sample is to reflect concentrations of analytes in true solution (the dissolved fraction). Such interpretive studies of ground-water or surface-water chemistry commonly use ≤0.1-µm filter media and plate-filter assembly or a tangential flow method of phase separation. Note that any deviation from the standard procedure for collecting filtered trace-element samples through the 0.45-µm capsule filter must be documented and reported with the analytical results.

   b. Major cations
   c. Nutrients, major anions, and alkalinity sample
   d. Radiochemicals
   e. Isotopes

10. *CH*: If the filter medium clogs before the needed volume of water is filtered, carefully remove the filter and replace with a new filter. Repeat steps 1 through 7. Cap each bottle immediately after filling.
11. **If samples require chemical treatment ⇨Go to section 5.4.**
12. *DH*: After filtration,
    a. Check that information on the bottle label is complete and set the samples aside for shipping (section 5.5). Samples that must be chilled need to be refrigerated or packed in ice as quickly as possible and maintained at 4°C without freezing.
    b. Disconnect and disassemble the plate-filter assembly. **Discard the used filter.**
    c. Rinse all equipment with DIW immediately after use and before it dries. Equipment that has dried after sampling without being rinsed or cleaned needs to be cleaned vigorously with a detergent and rinsed with DIW before the next use. Nonmetallic equipment must also be acid rinsed.
    d. Put rinsed tubing in a plastic bag for cleaning at the office laboratory.
    e. If equipment is to be used at the next site, field clean all the equipment using the procedures described in NFM 3. Field cleaning between sampling sites is carried out while still at the sampling site.
13. Document on field forms and in field notes any modifications to the filtration procedures used.

ORGANIC COMPOUNDS 5.2.2

Standard procedure for phase separation of general trace-organic compounds involves the use of a stainless steel or aluminum 142- (or 293-) mm-diameter plate-filter assembly with glass-fiber filter media and a valveless piston or fluorocarbon polymer diaphragm-head metering pump (section 5.2.2.A). Equipment and procedures differ when filtering samples for dissolved and suspended organic carbon (section 5.2.2.C) and optionally for organonitrogen herbicide analyses (section 5.2.2.B). Required conditioning for filter media is discussed below and summarized in table 5-4.

Table 5-4. Field conditioning requirements for media used to filter samples for organic-compound analysis

[mm, millimeter; mL, milliliter; PBW, pesticide-grade blank water; sample, the water to be sampled; methanol, pesticide-grade methanol; DIW, deionized water]

Filtration equipment *Application*	Construction materials	Filter media	Filter cleaning and conditioning[1]
Plate-filter assemblies: 142 or 293 mm *General trace organic compounds*	Stainless steel or aluminum	Glass-fiber filter[2]	Wet with PBW: 10-20 mL (142 mm) or 50-75 mL (293 mm) Condition with 100-125 mL sample
Disposable capsule filter: 25 mm *Organonitrogen herbicides*	Polypropylene	Nylon	Rinse with 10 mL of methanol No conditioning
Pressure filter apparatus: 47 mm *Dissolved and suspended organic carbon*	Stainless steel or fluorocarbon polymer	Silver metal	Rinse with 100 mL PBW or District-prepared organic-grade DIW Condition with 10-15 mL sample

[1]Do not reuse filters.

[2]Use only glass-fiber filters that have been adequately baked.

The procedures for filtering samples for analysis of trace-organic compounds, including volatile organic compounds, pesticides, and base-neutral compounds, are summarized from Sandstrom (1995). CH/DH techniques and associated QA procedures for inorganic analytes with parts-per-billion concentrations are not required for organic analytes but are recommended as good field practices to maintain the integrity of sample chemistry. Field personnel must wear disposable, powderless gloves (gloves). These gloves must be able to withstand any solvents or other chemicals that will be used during sample processing and equipment cleaning. Equipment and supplies used to filter different types of organic compounds are described in NFM 2. Additional information about organic-compound filtration can be found in Ward and Harr (1990), Manning and others (1994), Shelton (1994), and Koterba and others (1995).

Plate-Filter Procedure 5.2.2.A

Read through the procedures described in Sandstrom (1995) and presented in tables 5-4 and 5-5 and in figure 5-1. Obtain the equipment needed (table 5-5), test equipment operation, and collect an equipment blank if needed. Filtering samples for organic-compound analysis inside a processing chamber and using Clean Hands (CH)/Dirty Hands (DH) techniques is not mandatory but is recommended.

Table 5-5. Equipment for filtration of water-sediment samples for determination of organic compounds

[Modified from Sandstrom (1995); FEP, fluorinated ethylene-propylene; mm, millimeter; mL/min, milliliter per minute; L, liter; µm, micrometer; °C, degree Celsius]

Item	Description of equipment
	Container for unfiltered sample. Clean, laboratory-grade glass bottles with fluorocarbon polymer-FEP-lined lids.
	Fluorocarbon polymer-FEP tubing, 6.35-mm outside diameter.
	Union, 6.35-mm tube (Swagelok Company, Solon, Ohio, No. SS-400-6 or equivalent).
	Fluorocarbon polymer-FEP convoluted tubing, 6.35-mm outside diameter (Cole-Parmer Instrument Company, Chicago, Ill., No. L-06486-02 or equivalent).
	Tube fitting, 6.35-mm diameter tube to 6.35-mm diameter pipe thread (Swagelok Company, Solon, Ohio, No. SS-400-1-4 or equivalent).
	Pump, ceramic-piston, valveless, with 12-volt direct current motor, capable of pumping from 0 to 500 mL/min (Fluid Metering, Inc., Oyster Bay, N.Y., Model QB-1 CSC or equivalent).
	Battery, 12-volt direct current.
	Tube fitting, 6.35-mm diameter tube to 9.53-mm diameter pipe thread (Swagelok Company, Solon, Ohio, No. SS-400-1-6 or equivalent).
	In-line plate-filter assembly, aluminum (or stainless steel), 142-mm diameter (Geotech Environmental Equipment Inc., Denver, Colo., No. 0860 or equivalent).
	Glass-microfiber filter media, binder-free, 142-mm diameter, 0.7-µm nominal pore size (Whatman Inc., Clifton, N.J., GF/F grade, No. 1825C142 or equivalent). Note: The filters must be baked at 400°C for at least 2 hours and kept wrapped in aluminum foil before use.
	Bottle for filtered samples, amber borosilicate glass, 1 L with fluorocarbon polymer-FEP-lined cap.
	Fluorocarbon polymer-FEP squeeze (wash) bottle for organic-grade blank water.
	Stainless-steel forceps for handling the filters.

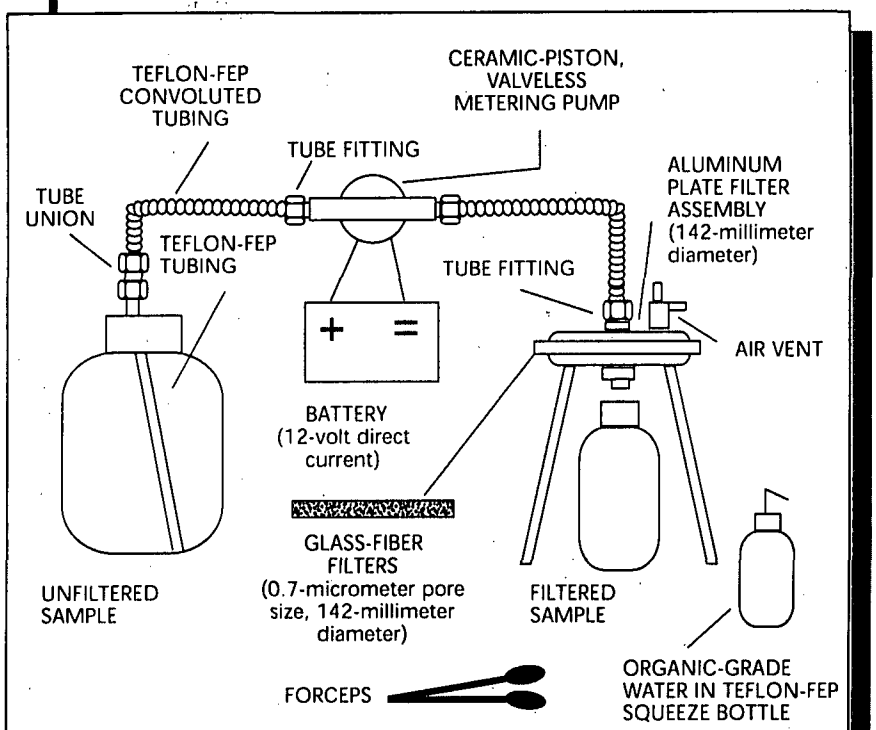


Figure 5–1. An equipment system suitable for filtering samples for analysis of organic compounds (from Sandstrom, 1995).

To filter sample for analysis of general trace-organic compounds in solution:

1. *CH/DH*: Wear appropriate (latex or nitrile) gloves throughout sample processing. Change gloves after setting up equipment. (Wearing several layers of gloves can save time.)
2. *CH*: Load the filter onto the plate-filter assembly within the processing chamber.
   a. Open precleaned plate-filter assembly.
   b. Place one stainless steel support screen on the base of the plate-filter assembly—Use stainless steel forceps.
   c. Place one clean 0.7-µm pore-size glass microfiber filter on top of the screen. **Do not touch the filter with fingers; use stainless steel forceps.**
   d. Wet the filter with a few drops of pesticide-grade blank water (PBW) from a fluorocarbon polymer wash bottle to help keep the filter in place as the unit is assembled.

e. Close plate-filter assembly—Align top and bottom plates. **Lightly tighten** the locking bolts or locking ring. Attach a short length of fluorocarbon polymer tubing to the outlet of the plate-filter assembly to channel filtrate to a toss bottle, sink funnel, or drain.

f. Add 10 to 20 mL of PBW rinse water through the inlet in the upper plate to wet the filter completely before tightening the clamps. (This rinse also helps prevent damage to the filter: a dry filter might rupture when the plate-filter assembly is tightened.)

g. Tighten the locking bolts or ring by hand. **Overtightening can cause the plate-filter assembly to warp and leak and the filter to rupture.**

3. *CH/DH*: Rinse the pump tubing (from a metering pump) or the sample tubing (from a submersible ground-water pump) with the water to be sampled. Discard rinse water into a sink funnel or toss bottle.

4. Set up the pump for filtration.

- *CH*: If using a metering pump, place intake end of tubing into the container holding the sample. Attach discharge end of pump tubing to the inlet connector of the plate-filter assembly. Use a stainless steel compression fitting of the appropriate size to secure the discharge hose to the inlet connector.
- *CH*: If using a submersible pump, attach discharge end of the sample tubing from the pump to the plate-filter assembly, keeping tubing as short as practical. Use a stainless steel compression fitting of the appropriate size to secure the discharge hose to the inlet connector.

5. *CH*: Rinse and condition the filter. The total volume of sample passed through the filter, including rinse water, needs to be accurately determined to ±1 mL and recorded in the field notes.

a. Turn on the metering pump at low speed or open the sample tubing from the submersible pump and operate at a low flow rate.

b. Open the air-vent valve located on top of the plate-filter assembly. Tilt the assembly slightly to the side to allow all trapped air to escape (vent).

c. Close the air-vent valve when water discharges through the valve.

d. Pass 100 mL of sample through the filter to remove any residual liquids from the cleaning or prewetting procedures. If concentration of organic compounds in suspended-material phase is to be determined:

   i. Capture the rinse water in a dry, clean, graduated cylinder.

   ii. Measure and record the actual volume of sample passed through the filter.

e. Discard rinse water to a sink funnel or toss bottle.

6. *DH*: Tare the weight of a clean, baked, glass sample bottle. (First check to see if this is required for the analytical procedures to be used.)
   a. Set up, level, zero, and check the accuracy of the balance with a reference weight. Record accuracy in field notes.
   b. Tare the weight of a dry, clean, capped 1-L amber bottle, and record the weight. Remove the bottle cap.
7. Filter and weigh each sample. (Do not field rinse baked, glass sample bottles.)
   a. *CH*: Resume the flow of sample through the plate-filter assembly.
   b. *CH*: Place the appropriate sample bottle under the outlet of the plate-filter assembly.
   c. *CH*: Collect approximately 1 L of filtered sample for each analytical schedule, but leave headspace in each bottle. If the filter medium becomes too clogged to proceed, go to step 13 below.
   d. *DH*: Cap the bottle(s) and pass sample(s) out of chamber. Wipe the bottle dry with a lint-free laboratory tissue, such as Kimwipe™, to remove any condensation from the outside of the sample bottle.
   e. *DH*: Weigh and record the amount of sample filtered (total weight minus tare weight of bottle).
   f. Chill samples immediately and maintain at or below 4°C without freezing for shipment to the laboratory (section 5.5).

8. *CH*: Remove as much water as possible from the inside of the plate-filter assembly by using the metering pump to pump air through the sample tubing, or by pulling water out through the outlet nozzle with a peristaltic pump, or by using a syringe to apply positive air pressure to the inlet connector. This removes any residual sample and prevents spilling the water-sediment slurry when the plate-filter assembly is disassembled.
9. *CH*: If sediment collected on the filter is to be analyzed for organic compounds:
   a. Carefully disassemble the top of the plate-filter assembly.
   b. Using metal forceps, carefully fold the filter in half and then in half again (quarters).
   c. Transfer the filter to a baked, wide-mouth glass jar with a fluorocarbon-polymer-lined cap.
   d. Record on the jar label and on field forms the total volume of sample that passed through the filter.
   e. Chill and maintain the sediment sample at or below 4°C for shipment to the laboratory (section 5.5)
10. *DH/CH*: If sediment on the filter will not be analyzed, disassemble the top of the plate-filter assembly and remove the filter with forceps. Discard the filter appropriately. Rinse the plate-filter assembly components and tubing immediately after the filter has been removed.
11. *DH/CH*: **If the equipment is to be used at a subsequent site, field clean all equipment while equipment is still wet and before going to the next site.** Clean with detergent solution, rinse with DIW, and final rinse with methanol—do not use methanol on equipment used for TOC, DOC, or SOC samples (NFM 3). If the plate-filter assembly will not be reused before returning to the office, rinse all components with DIW. Put rinsed components and tubing in a resealable bag for cleaning at the office laboratory.
12. Document on field forms and in field notes the filtration procedures used.

13. **If the filter medium becomes clogged before the required volume of sample has been collected,** stop the metering pump or divert the sample flow from the submersible pump (see TECHNICAL NOTE below) and replace the filter with a new filter as indicated in steps a through f below.

> TECHNICAL NOTE: Diverting the flow of sample being pumped with a submersible pump by use of a three-way valve can result in a temporary increase in turbidity (NFM 4). Allow turbidity to clear after reestablishing flow through the sample tubing and to the plate-filter assembly.

a. Remove as much water as possible from inside the plate-filter assembly. The stainless-steel or aluminum plate-filter assembly does not have an upper support screen, so the filter cannot be backflushed. Remove the inlet tubing to the metering pump from the sample and either attach tubing from a peristaltic pump to the outlet and pull residual water out, or use a syringe to apply positive air pressure to the inlet connector.

b. Remove the clogged filter with forceps. **If sediment collected on a filter is to be analyzed for organic compounds, follow directions in step 9.**

c. Load the plate-filter assembly with a new filter and reassemble the unit as described in step 2.

d. Prepare the filter as described in steps 2f and 5a–d, allowing the first 125 mL of sample to remove any sediment particles that may have moved below the filter during the replacement procedure. Use a graduated cylinder to measure volume.

e. Record the volume of sample rinsed through the plate-filter assembly if sediment collected on the filter is to be analyzed for organic compounds. Volume accuracy should be ± 1 mL.

f. Place a tared sample bottle under the plate-filter assembly outlet, resume the flow of sample through the filter, and continue to collect the sample filtrate.

Capsule-Filter Procedure for Processing Samples for Analysis of Organonitrogen Herbicides (Optional) 5.2.2.B

The capsule-filter procedure for filtering samples for organonitrogen-herbicide analysis described below is provided if the option to process these samples onsite is selected. The steps that follow are taken from Sandstrom (1995), which includes more detailed instructions and description of the equipment, including the 25-mm-diameter disposable nylon-media filter capsule (nylon filter):

1. Before leaving for the field site, clean the nylon filter.
   a. Put on appropriate, disposable, powderless gloves (gloves).
   b. Place intake end of the metering pump tubing into the methanol.
   c. Pump about 10 mL through the nylon filter to a used-methanol disposal container.

CAUTION: Do the following if using methanol or other organic solvent:

- **Work under a fume hood or in a well-ventilated area, NOT in the field vehicle.**
- **Wear protection against skin and eye contact and do not inhale fumes.**
- **Collect methanol rinse waste into proper disposal containers and dispose of according to local regulations.**

2. At the field site, cover the field bench or table with a sheet of aluminum foil or Teflon™ to prepare a clean work surface.
3. Place equipment and supplies on the clean work surface. Remove foil or other wrapping from precleaned equipment. Change gloves.
4. Remove the nylon filter from the plastic bag. Rinse the discharge end of the pump tubing with methanol. Discard used methanol to a proper waste container. Attach the metering-pump tubing to the capsule inlet; keep tubing as short as possible.
5. If filtering with a metering pump, transfer the intake end of the pump tubing to the sample. If using a submersible pump to collect the ground-water sample, redirect the sample flow to and from the nylon filter as needed, using a manifold flow-valve system.
6. Purge air from the sample tubing. Before connecting the nylon filter, allow ground-water sample to flow through the tubing at a very low rate. This will require just a few milliliters of sample if a metering pump is used. With sample flowing, connect tubing to the nylon filter. (Use a Luer™ connector of appropriate size to secure the discharge hose to the inlet connector.)
7. Collect at least 100 mL of filtrate in a 125-mL baked amber glass sample bottle. Do not completely fill the bottle. Allow 2–3 cm of headspace. The headspace leaves space for matrix spike standards to be added (if required) and prevents sample loss if the sample freezes.
8. If the nylon filter medium becomes clogged before a sufficient amount of sample has been filtered, replace it with a new nylon filter and repeat steps 6 and 7 until at least 100 mL have been collected.
9. When filtering is complete, cap the bottle firmly. Chill and maintain the sample at or below 4°C without freezing during storage and shipment to the laboratory (section 5.5).
10. Discard the nylon filter. Field clean the pump and tubing as described in NFM 3 before using the equipment at the next site.
11. Document on field forms and in field notes the filtration procedures used.

Procedures for Processing Samples for Carbon Analysis 5.2.2.C

Standard methods are described in this section for processing a sample for analysis of (1) total particulate carbon (TPC), particulate inorganic carbon (PIC), and particulate organic carbon (POC)[1]; and (2) dissolved organic carbon (DOC). The specific method to be used depends on the target analyte and the choice of filter type and filtration equipment, which are to be documented on field forms and in field notes.

- **TPC (Total Particulate Carbon), PIC (Particulate Inorganic Carbon), and POC (Particulate Organic Carbon).** Filtration of the sample requires a 25-mm glass-microfiber filter (see *UPDATE* below). Particulate organic carbon is determined by subtracting the laboratory-analyzed concentrations of particulate inorganic carbon from total particulate carbon; that is, POC = TPC - PIC.
- **DOC (Dissolved Organic Carbon).** Filtration of the sample requires either a disposable capsule unit with a polysulfone pleated filter or a 25-mm glass-microfiber filter (GF/F) (see *UPDATE* below).

> ***UPDATE:*** The NFM-5/99 version of this section (5.2.2.C) entitled "Gas-Pressurized Filter Procedures for Processing Samples for Analysis of Dissolved and Suspended Organic Carbon," which was based on a field method using silver filters, has been moved to Appendix A5-D. That method is no longer used in USGS studies as a standard procedure because of the decreasing availability of the silver filters (Office of Water Quality Technical Memorandum 2000.08).

[1]POC, determined by a calculation, is distinguished from the suspended organic carbon (SOC) analysis, which is determined by direct analysis of organic carbon residue on a silver filter. USEPA method 440.0 is used for laboratory analysis of the TPC and PIC samples and also provides direct determination of total particulate nitrogen (TPN) concentration.

Equipment and equipment-cleaning procedures

The equipment needed to process samples for analysis of TPC and PIC depends on whether the pressure-filtration method (table 5-6a) or the vacuum-filtration method (table 5-6b) will be used. The equipment options for processing samples for analysis of DOC are given in table 5-6c. (Refer to Appendix A5-D if the silver-filter method will be used to process samples for analysis of TOC, SOC (suspended organic carbon), or DOC.)

Equipment should be cleaned while still wet from sampling, preferably before leaving the field site. Immediately after each use, rinse the carbon-processing equipment at least three times with DIW and store it in a plastic bag until sampling is complete and there is time to clean the equipment using USGS standard procedures.

- Clean the carbon-collection and carbon-processing equipment according to the standard procedures described in NFM 3.3.4.C. **Do not use methanol or any other organic solvent to clean this equipment** (see TECHNICAL NOTE).
- If it is necessary to return to the office before cleaning the equipment, be sure to field rinse the equipment onsite immediately after use and then place it in a clean plastic bag for transport.
- After the equipment has been cleaned, double-wrap all apertures and the filter apparatus with aluminum foil and store them inside a sealable plastic bag for transport to the next site or storage in the office.

> TECHNICAL NOTE: Periodically check the NFM Comments and Errata page (http://water.usgs.gov/owq/FieldManual/mastererrata.html)under Chapters A3 and A5 for an update or any changes in equipment-cleaning procedures. If a circumstance arises in which methanol-cleaned equipment must be used to collect samples for DOC analysis, it is necessary to (1) record and report the total volume of water that has passed through the equipment before the DOC sample is collected, (2) collect a field blank sample for laboratory analysis by passing organic-grade blank water through the equipment, (3) collect a source-water blank for laboratory analysis, and (4) compare the laboratory results of carbon concentrations for the environmental and quality-control samples and document the results in field notes and in any report in which the DOC data are presented.

Table 5-6a. Equipment and supplies used to process samples for analysis of total particulate carbon and particulate inorganic carbon using the pressure-filtration method

[FEP, fluorinated ethylene-propylene; DOC, dissolved organic carbon; mm, millimeter; µm, micrometer; °C, degrees Celsius; mL, milliliter; in, inch; oz, ounce; lbs/in^2, pounds per square inch; mg/L, milligrams per liter; VOC, volatile organic compound]

Item	Description/Comments	Supplier or USGS One Stop Shopping Item Number[1]
FEP pressure-filtration apparatus (DOC-25)	Holds a 25-mm filter	Q444FLD
Ring stand and clamp	Holds the DOC-25 filtration unit	Open market
Filter, in-line vent, 50 mm	0.2-µm pore size; pre-filter to remove airborne particulates	Q445FLD
Peristaltic pump	Adjustable flow rate	Open market
C-Flex tubing	For use with pump	Q432FLD or Open market
Precombusted (baked) glass-microfiber filters (GF/F)	25 mm, 0.7-µm pore size, laboratory-baked at 400°C (3 filters are required)	Q441FLD
Metal forceps, two pair	Standard metal forceps for handling filter media	Q347BACT
Glass cylinder	100-mL graduated cylinder, cleaned	Open market
Aluminum foil squares	6 in x 6 in	Q443FLD
Whirl-Pak bags	6 oz	Q22FLD
Whirl-Pak bags	18 oz	Q21FLD
Aluminum foil	Heavy duty	Open market
Cooler and ice	Standard; check with shipper for size and weight restrictions	Open market
Replacement filter-support screen	25 mm, either stainless steel or polysulfone	Pall Gelman Laboratory Part nos. 79791 or 87265
Pressure gage (optional)	Glycerin-filled, 0-30 lb/in^2, to be inverted into side of a plastic tee that is positioned in-line between the peristaltic pump and the DOC-25 filtration unit.	Cole Parmer catalog no. P-07370-70 or equivalent
Organic grade water (if using this method for DOC processing)	Laboratory analysis of the water must certify a concentration of organic carbon that is less than the long-term laboratory reporting limit for DOC (currently <0.16 mg/L). Check the laboratory analysis for the lot number to confirm that it can be used.	N1590 (Pesticide-grade blank water) or N1580 (VOC-grade blank water)

[1]The equipment designated by the letters Q or N preceding a unique number is supplied exclusively for USGS studies through the USGS internal One Stop Shopping. The USGS performs quality-control checks for such equipment. Such equipment can be obtained for non-USGS studies on the open market or other source specified by the user. "Open market" designates equipment to be obtained from a retail or other vendor.

Table 5-6b. Equipment and supplies used to process samples for analysis of total particulate carbon and particulate inorganic carbon using the vacuum-filtration method

[mL, milliliter; mm, millimeter; µm, micrometer; °C, degrees Celsius; in, inch; oz, ounce; FEP, florinated ethylene-propylene]

Item	Description/Comments	Supplier or USGS One Stop Shopping Item Number[1]
Filtration flask	Polypropylene, 500 or 1,000 mL	Open market
Filter funnel	Polysulfone, 25 mm with 200-mL reservoir[2]	Open market
Peristaltic pump or hand pump	Adjustable flow rate	Open market
C-Flex tubing	For use with pump	Q432FLD or Open market
Baked glass-microfiber filters (GF/F)	25 mm, 0.7-µm pore size, laboratory-baked at 400°C (3 filters are required)	Q441FLD
Metal forceps, 2 pair	Standard metal forceps for handling filter media	Q347BACT
Glass cylinder	100-mL graduated cylinder	Open market
Aluminum foil squares	6 in x 6 in	Q433FLD
Whirl-Pak bags	6 oz	Q22FLD
Whirl-Pak bags	18 oz	Q21FLD
Aluminum foil	Heavy duty	Open market
Cooler and ice	Standard: check with shipper for size and weight restrictions	Open market

[1]The equipment designated by the letters Q or N preceding a unique number is supplied exclusively for USGS studies through the USGS internal One Stop Shopping. The USGS performs quality-control checks for such equipment. Such equipment can be obtained for non-USGS studies on the open market or other source specified by the user. "Open market" designates equipment to be obtained from a retail or other vendor.

[2]The filter-support screen can be replaced with a stainless-steel screen like the one used in the FEP pressure-filtration apparatus. Contact Pall Gelman Laboratory, 600 Wagner Road, Ann Arbor, MI, 48103-9019; phone (734) 665-0651.

Do not use methanol or any other solvent to clean TPC or DOC equipment (NFM 3).

Table 5-6c. Equipment and supplies used to process samples for analysis of dissolved organic carbon

[µm, micrometer; GF/F, glass microfiber filter; mm, millimeter; °C, degrees Celsius; FEP, florinated ethylene-propylene; oz, ounce; mL, milliliter; DOC, dissolved organic carbon; <, less than; mg/L, milligrams per liter; *N*, normal; VOC, volatile organic compound]

Item	Description and Comments	Supplier or USGS One Stop Shopping Item Number[1]
Gelman Sciences Supor capsule filter	Pleated polysulfone filter medium, in disposable polypropylene casing, 0.45-µm pore size	Q398FLD
----------or----------	----------or----------	----------or----------
Precombusted (baked) glass microfiber filters (GF/F)	25-mm diameter, 0.7-µm nominal pore size, laboratory baked at 400°C FEP pressure-filtration apparatus or filtration flask with funnel and associated equipment is required, as indicated in table 5-6a and table 5-6b, respectively	Q441FLD
4-oz amber glass bottle, baked	Bottles (125 mL) supplied for DOC samples have been pre-cleaned and baked at 400°C and quality-controlled to meet a detection limit criterion for organic carbon of <0.1 mg/L	Q28FLD
Sulfuric acid (H_2SO_4) preservative	4.5*N*-H_2SO_4, supplied in 1-mL vials	Q438FLD
Organic-grade water	Laboratory analysis of the water must certify a concentration of organic carbon that is less than the long-term laboratory reporting limit for DOC (currently <0.16 mg/L). Check the laboratory analysis for the lot number to confirm that it can be used.	N1590 (Pesticide-grade blank water) or N1580 (VOC-grade blank water)
Aluminum foil	Heavy duty	Open market
Cooler and ice	Standard; check with shipper for size and weight restrictions	Open market
Foam bottle sleeve	Individual bottles are slipped into foam sleeves to protect from breakage.	Q137FLD

[1]The equipment designated by the letters Q or N preceding a unique number is supplied exclusively for USGS studies through the USGS internal One Stop Shopping. The USGS performs quality-control checks for such equipment. Such equipment can be obtained for non-USGS studies on the open market or other source specified by the user. "Open market" designates equipment to be obtained from a retail or other vendor.

TPC, PIC, and POC sample processing

The sample-processing options described below involve use of either the pressure-filtration or vacuum-filtration method. The equipment and supplies needed are listed in tables 5-6a and 5-6b, respectively. Particulate analytes (TPC, PIC, POC, SOC) are reported in units of mass per volume (milligrams per liter), and therefore **the volume of sample passed through each filter must be measured accurately and recorded on the field form and the Analytical Services Request (ASR) form.**

- The amount of water to be filtered to obtain a sufficient quantity of material for the analysis depends on the suspended-sediment concentration and/or on the concentration of humic and other substances (such as organic and inorganic colloids).
- A graph of the historical stream stage plotted against suspended-materials concentration can aid in estimating concentrations of suspended materials. Suspended-material concentrations can be used to help select the volume of sample to be filtered for a POC determination (table 5-6d).
- Record the filtrate volume passed through each filter used for particulate analysis. **This is critical for calculation of POC concentrations.**

Table 5-6d. Guidelines for selecting the volume needed for filtration of samples for analysis of suspended and particulate organic carbon
[Guidelines are based on sand-sized materials; other physical property factors and chemical composition were not taken into account; mg/L, milligrams per liter; mL, milliliters; >, greater than]

Approximate concentration of suspended materials (mg/L)	Volume of sample to be filtered (mL)
1 - 30	250
30 - 300	100
300 - 1,000	30
> 1,000	10

For TPC and PIC samples, be sure to record the total volume of water that passed through each GF/F filter.

To process samples for analysis of TPC and PIC:

1. **Sampling location and collection:** Study objectives and site characteristics determine where the sample will be collected. Follow guidelines for (1) preventing sample contamination as described in NFM 4.0, (2) using the appropriate isokinetic or nonisokinetic method as described in NFM 4.1, and (3) preparing composites and subsamples or discrete samples as described in NFM 5.0 through 5.1.1.[2] Avoid the use of methanol-rinsed equipment.

2. Select one of the following three options. (Note that the actual volume of sample needed is determined by the concentration of particulates for the specific site and not by the bottle volume.)

   - **Collect a discrete sample with a weighted bottle sampler at centroid of flow** (see NFM 4, section 4.1.1.A, VCF method)—Load the sampler with baked 125-mL DOC bottles or a 1-L baked pesticide bottle, depending on the type of sampler being used. Cap all bottles securely after they are filled with sample.

   - **Collect, composite, and process the sample through a cone splitter**—Using procedures described in 5.1.1.B, collect the TPC/PIC subsample from the methanol-free cone splitter into a baked, 1-L pesticide bottle or into three to four baked 125-mL DOC bottles. Cap all bottles securely.

   - **Collect, composite, and process the sample through a churn splitter**—Using procedures described in 5.1.1.A, collect the TPC/PIC subsample from the churn splitter into a baked, 1-L pesticide bottle or into three to four baked 125-mL DOC bottles. Cap all bottles securely.

     TECHNICAL NOTE: An experiment to test the effect of sand in the polyethylene churn splitter on particulate carbon concentrations showed that, under most sampling conditions, the abrasion of material from the churn by sand particles will result in negligible bias in the analytical results. Caution is recommended in situations where very large concentrations of sand particles coincide with carbon concentrations that are close to the analytical minimum reporting limit (MRL).

[2]The guidelines described were designed for stream sampling. These procedures can be adapted for the collection of TPC, PIC, and TPN in ground-water samples, if necessary.

ALERT! Do not field rinse the baked DOC or pesticide bottles.

3. Cover the bench or table with a sheet of aluminum foil to make a clean work surface. Put on disposable, powderless gloves. Assemble necessary equipment and supplies on the clean work surface.
   a. Fold into thirds the aluminum foil square(s) into which the filters will be placed.
   b. To remove airborne particulates, attach an in-line, 0.2-µm pore-size filter to the inlet side of a dry pump hose between the filtration apparatus and the peristaltic or hand pump.
   c. Attach pump tubing to pump.
   d. Remove the aluminum foil wrapping from the equipment.
   e. Change gloves.
4. Prepare the filtration apparatus.
   - **Pressure-filtration method:**
     a. Open the bottom of the DOC-25 filtration unit.
     b. Using metal forceps, place a 25-mm, 0.7-µm pore size, GF/F onto the support screen in the base of the DOC-25 apparatus.
     c. Push the bottom white ring that holds the filter base up against the filter unit and screw it onto the base of the filtration-apparatus barrel by screwing the blue top ring down onto the bottom white ring.
        - Finger-tighten only. Turning the bottom white ring will cause the outer edge of the filter to be cut off, making removal of the filter difficult.
        - Take care not to wrinkle or tear the GF/F.
     d. Place the DOC-25 apparatus into the ring-stand clamp. Place a bottle or beaker under the DOC-25 filtration unit.
     e. Shake the sample vigorously to suspend all particulate matter and immediately pour an aliquot of the sample into the barrel of the DOC-25 apparatus. While pouring, ensure that the particulates remain suspended.
     f. Screw the top part of the DOC-25 apparatus onto the barrel and attach the peristaltic pump tubing.

- **Vacuum-filtration method:**

  a. Place the filter funnel on the filter flask.

  b. Lift the top part of the filter funnel.

  c. Using metal forceps, place the GF/F onto the base of the filter funnel. **Make sure the filter is not wrinkled or torn.**

  d. Place the top part of the filter funnel back on the base.

  e. Shake the sample vigorously to suspend all particulate matter and immediately pour an aliquot of the sample into the filter funnel. While pouring, swirl sample to ensure that the particulates remain suspended (top of filter flask can be covered with aluminum foil while swirling sample).

  f. Attach the pump tubing from the peristaltic pump or hand pump to the vacuum flask.

5. Apply pressure (pressure filtration) or suction (vacuum filtration) to start the flow of sample water through the filtration apparatus.

   - If using a peristaltic pump to pressurize the DOC-25, install a pressure gage in the line.

     a. Do not exceed about 15 lbs. of pressure.

     b. During pumping, a drop in pressure will signal when the last of the sample water has passed through the filter.

6. After an aliquot of sample has been filtered, tap the bottom of the filter apparatus and increase the pressure slightly to dislodge the remaining drops of sample water. When no more filtrate comes out:

   a. Depressurize the filtration apparatus carefully.

      – **Pressure-filtration method**: Remove the tubing to release the pressure and then remove the top of the DOC-25 apparatus. Check that there is no water on the filter and that the filter is covered with particulates. The particulate cake should not be extremely thick.

      – **Vacuum-filtration method**: Remove the foil cover and look into the top of the filter funnel. Check that there is water on the filter and that the filter is covered with particulates.

   b. If the filter is dry but not covered with particulates, add another aliquot of sample by repeating steps 4e-f, 5, and 6a until the filter is loaded to capacity. **It is important that all the water in the barrel be passed through the GF/F, leaving the filter "dry."**

   c. After the filter is dry and covered with particulates, go to step 7.

7. Pour the filtrate into a graduated cylinder and measure and record the volume on the field form and on the "Comments to NWQL" line of the ASR form.

8. Using organic-grade water, rinse any remaining particles from the sides of the DOC-25 barrel or the sides of the filtration funnel. **Do not include the rinse water in the measured volume.**

9. Discard filtrate. **Do not send this filtrate to the laboratory for analysis of DOC.**

10. After all the organic-grade water filtrate has passed through the DOC-25 filtration unit:

    a. Remove the DOC-25 apparatus from the ring stand.

    b. Continue pumping, rotating the DOC-25 apparatus at a slight angle while tapping the side of the filtration unit to evacuate any remaining water droplets that are clinging to the sides of the filtration unit. This procedure moves droplets toward the center of the filter surface for final passage through the filter.

    c. The procedure is complete when filtrate droplets are entirely evacuated and have passed through the filter-holder funnel.

11. After completing the rinse, depressurize the filtration apparatus. Change gloves.

12. Lift the top off the filter funnel to check that the filter is dry before proceeding to carefully remove the bottom of the DOC-25 apparatus.

    a. Open the previously folded aluminum foil square and place it on the clean work surface.

    b. Gently remove the filter from the filter holder with metal forceps. Do not touch the filter with your fingers. Using two metal forceps:

        i. Place the filter so that it is centered on one of the creases in the aluminum foil square; start the fold with the forceps, then press the foil down on top of the filter to complete the fold.

        ii. Fold it in half with suspended material on the inside. Do not lose any suspended material.

Wear safety glasses when pressurizing or depressurizing a filter apparatus.

13. Repeat steps 4-12 two more times until a total of three filters (two for TPC and one for PIC) have been processed.

    - **If the same volume of sample water was filtered through all three filters,** place them all, side by side, into one aluminum-foil envelope.
    - **If different volumes have been filtered,** use either three separate, properly labeled aluminum foil envelopes or use a single packet and write the volume for each filter on the outside of the foil in which each of the filters is located.

14. Close the other flap of the aluminum foil, turning the ends up carefully.

    i. Label the aluminum foil envelope(s) with site identification, date and time, total filtered volume of sample, laboratory sample-designation code, and the laboratory schedule requested.

    ii. Do not use tape and, if a preprinted label is used, do not let it wrap around the ends of the envelope. (The envelope will be opened and used at the laboratory when drying the filters.)

15. Place labeled aluminum foil envelope(s) into small (6 oz) Whirl-Pak bag(s) and seal the bag(s).

16. Place the 6-oz Whirl-Pak bag(s) inside a large (18 oz) Whirl-Pak bag and seal the large bag.

17. Place the 18-oz Whirl-Pak package into an ice-filled cooler and maintain the samples at or below 4°C during storage and shipment to the laboratory.

For TPC and PIC analyses, record the TOTAL volume of sample that passed through each filter.

DOC sample processing

The sample-processing options described below involve filtering the sample either through a GF/F and pressure-filtration apparatus (the pressure-filtration method), or through a capsule filter (the capsule-filter method) (Office of Water Quality Technical Memorandum 2000.08). The pressure-filtration and capsule-filter methods are described below and the equipment needed for each method is listed in tables 5-6a and 5-6c, respectively. The silver-filter method and equipment are described in Appendix A5-D.

- Use organic-grade water when collecting an equipment blank or field blank for quality control. Organic-grade water is deionized water that has been certified by laboratory analysis of the lot to have an organic-carbon concentration that is less than the laboratory reporting limit (currently at 0.16 mg/L for DOC).
- Each equipment or field blank designated for carbon analysis should be accompanied by a source blank collected from the same lot of organic-grade water as is used for the equipment and field blanks.

  TECHNICAL NOTE: A laboratory study to compare the results of the DOC analysis in same-source water that was filtered through 0.45-µm pore-size silver-filter media, the Gelman 0.45-µm Supor™ capsule filter, and 0.7-µm GF/F determined no statistically significant differences in DOC concentrations (Charles Patton and George Aiken, U.S. Geological Survey, written commun., 2001).

- USGS designations and preservation treatment for various filtered samples are listed below. The general order of preservation is to acidify all samples requiring HCl treatment first, followed by those for H_2SO_4 treatment if nutrient samples are to be acidified, and then those for HNO_3 treatment. Wholewater samples are preserved along with their filtered counterparts. The chamber cover is changed with each change in the acid treatment.
  - FAM: filtered, acidified with HCl, for mercury analysis.
  - FCC: filtered and chilled to ≤ 4 °C for nitrogen and phosphorus nutrient analysis.
  - FCA: filtered, acidified with H_2SO_4, and chilled to ≤ 4 °C for nitrogen and phosphorus nutrient analysis.
  - DOC: filtered, acidified with H_2SO_4, for dissolved organic carbon analysis.
  - FA: filtered, acidified with HNO_3, for trace-element and major-cation analysis.
  - FAR: filtered, acidified with HNO_3, for radiochemical analysis.

Capsule-filter method:

1. Collect samples. Set up a clean capsule filter and sample bottle(s) within a protective chamber using the Clean Hands method (NFM 4.0.1).

   a. **Surface Water:** Follow guidelines for (1) preventing sample contamination as described in NFM 4.0, (2) using the appropriate isokinetic or nonisokinetic method as described in NFM 4.1, (3) preparing composites and (or) subsamples or discrete samples as described in NFM 5.0 through 5.1.1, and (4) equipment selection and quality control as described in the TECHNICAL NOTE below.

   b. **Ground Water:** Follow standard guidelines for (1) well purging (NFM 4.2), (2) sampling (NFM 4.0, 4.2, 5.0, and 5.1.2), and (3) equipment selection and quality control as described in the TECHNICAL NOTE below. Use a clean bailer that has not contacted methanol if other sampling equipment has been methanol-rinsed. Sample collection and filtration can be conducted in the same protective chamber.

   TECHNICAL NOTE: Process the DOC sample after other filtered samples have been processed. To prevent methanol contamination of the sample, do not use methanol-rinsed collection and processing equipment, and use a new capsule filter. Collection and analysis of field-blank and source-blank samples is recommended. If methanol-rinsed equipment must be used, collection of these blanks to correlate with each DOC sample is required, regardless of the volume of water passed through the system before DOC sample collection. Taking these quality-control measures does not remove the possibility of methanol contamination of the sample, however.

2. Change gloves. Place a 125-mL baked glass amber bottle under the capsule filter outlet.

   - Do not field rinse the DOC bottle.
   - Do not splash sample water.
   - Pass 1 L of **organic-grade water** (certified for organic-carbon concentration of less than the laboratory reporting limit through the capsule filter). If collecting a quality-control sample, go to step 3.
   - Pass at least 1 L of **sample water** through the capsule filter before collecting the DOC sample.

3. Fill the bottle to its shoulder.

4. Cap the bottle and transfer it to the preservation chamber.

5. Change gloves. Open the DOC bottle in the preservation chamber. Add the contents of a 1-mL H_2SO_4 vial to the DOC sample.
6. Cap the DOC bottle securely. Shake the sample bottle vigorously to mix the sample and H_2SO_4.
7. Remove the DOC bottle from the preservation chamber.
8. Check that the bottle is labeled correctly and completely. Place the bottle in a foam sleeve and then into an ice-filled shipping container.
9. Maintain the sample at or below 4°C without freezing (NFM 5.5).

Pressure-filtration method:

1. Collect sample(s).
   a. **Surface Water:** Follow guidelines for (1) preventing sample contamination as described in NFM 4.0, (2) using the appropriate isokinetic or nonisokinetic method as described in NFM 4.1, (3) preparing composites and (or) subsamples or discrete samples as described in NFM 5.0 through 5.1.1, and (4) equipment selection and quality control as described in the TECHNICAL NOTE below.
   b. **Ground Water:** Follow standard guidelines for (1) well purging (NFM 4.2), (2) sampling (NFM 4.0, 5.0, and 5.1.2), and (3) equipment selection and quality control as described in the TECHNICAL NOTE below.

TECHNICAL NOTE: To prevent methanol contamination of the sample, avoid using methanol-rinsed collection and processing equipment. If methanol residue is a concern, process the DOC sample either before introduction of any methanol-rinsed equipment or well after the work area has been cleared of methanol-rinsed equipment and methanol fumes. Collection and analysis of field-blank and source-blank samples is recommended. If methanol-rinsed equipment must be used, collection of these blanks to correlate with each DOC sample is required, recording the volume of water passed through the system before DOC sample collection. Taking these quality-control measures does not remove the possibility of methanol contamination of the sample, however.

2. Cover the bench or table with a sheet of aluminum foil to make a clean work surface. Assemble the necessary equipment on the clean work surface, wearing disposable powderless gloves.

   a. When using the DOC-25 filtration apparatus, remove airborne particulates as follows: attach an in-line, 0.2-µm pore-size filter (table 5-6a) to the inlet side of a dry pump hose or to the outlet between the peristaltic pump and the DOC-25 unit. If attaching the DOC-25 on the inlet side, be sure to dedicate a piece of tubing for the sole purpose of channeling air flow.

   b. Remove the aluminum foil wrapping from the precleaned equipment.

   c. Change gloves.

3. Prepare the filtration apparatus:

   a. Remove the bottom barrel of the filtration apparatus.

   b. With metal forceps, place a clean GF/F filter onto the support screen in the base of the filtration apparatus. **Make sure that the filter medium is not wrinkled or torn.**

   c. Push the bottom white ring that holds the filter base up against the filter unit and screw it onto the base of the filtration-apparatus barrel by screwing the blue top ring down onto the bottom white ring.

      - Finger-tighten only. Turning the bottom white ring will cause the outer edge of the filter to be cut off, making removal of the filter difficult.
      - Take care not to wrinkle or tear the GF/F.

   d. Open the top of the filtration-apparatus barrel and fill with approximately 100 mL of wholewater sample.

      - **For water with high concentrations of suspended materials** (usually in surface water), collect the sample into a clean baked glass bottle, cap it securely, place it on ice, and allow the suspended materials to settle; then, pour 100 mL of the clear supernatant into the filter barrel.
      - **For surface water,** the 100-mL wholewater sample can be either a subsample collected from the churn or cone splitter or the supernatant from the bottle(s) used in the weighted-bottle sampler.
      - **For ground water,** the 100-mL wholewater sample is collected directly from the pump discharge unless turbidity is high. For turbid samples, follow the procedure described above for water with high concentrations of suspended materials.
      - **For a quality-control sample,** use organic-grade blank water.

e. Screw the top part of the filter apparatus onto the barrel and attach the pump tubing.

f. Apply pressure, regulated to less than 15 lb/in^2, to start the flow of sample water through the filter apparatus.

g. Place a 125-mL clean, baked glass bottle under the discharge tube of the filtration apparatus. **Do not field rinse the DOC bottle.**

h. Fill the DOC bottle to the shoulder with sample filtrate.

- If the filter clogs before 100 mL of sample for DOC analysis can be filtered, depressurize the filtration unit, empty the remaining volume of wholewater sample from the barrel, and remove the clogged GF/F filter.
- Using clean metal forceps, replace the old filter with a new GF/F filter, following the directions from steps 3b-g above for a pressure-filtered DOC sample.

4. After the DOC sample bottle has been filled to the shoulder, cap the bottle and transfer it to the preservation chamber.

5. Depressurize and dismantle the filtration apparatus, discarding the used GF/F filter(s). Clean the apparatus immediately (while still wet), following the USGS procedures prescribed in NFM 3.3.4.C. If the apparatus cannot be field-cleaned immediately, it must be cleaned the same day it is used and before being reused—rinse it copiously with DIW and place it into a plastic bag so that it will not dry before being cleaned.

6. Change gloves before working in the preservation chamber.

7. In the preservation chamber, open the DOC bottle. Add the contents of a 1-mL vial containing 4.5*N* H_2SO_4 preservative.

8. Cap the DOC bottle securely and shake vigorously to mix the sample. Remove the DOC sample bottle from the preservation chamber.

9. Check that the bottle is labeled correctly and completely. Place the bottle into a foam sleeve and into an ice-filled shipping container (see NFM 5.5 for correct shipping procedures).

10. Maintain the sample at or below 4°C without freezing (NFM 5.5).

Wear safety glasses when pressurizing or depressurizing the filter apparatus.

11. To collect a QC sample:

    a. Use the same carbon-processing equipment after it has been cleaned (see step 5, above).

    b. Label bottles.

    c. Change gloves.

    d. Working in a clean processing chamber, process a sample of organic-grade water through the cleaned carbon-sampling and carbon-processing equipment, following the steps prescribed in steps 2-4 above. Cap securely and pass the bottle to the preservation chamber.

    e. Follow steps 6-10 above for sample preservation, handling, and shipping.

    f. Depressurize and dismantle the filtration apparatus, discarding the used filter(s). Allow the apparatus components to air dry in a clean chamber. Cover the apertures of the dry apparatus with aluminum foil and place in a clean, sealable plastic bag for storage.

Never increase the pressure in a filter apparatus to greater than 15 lb/in^2 in order to increase the rate of filtration.

SOLID-PHASE EXTRACTION OF PESTICIDES 5.3

By **M.W. Sandstrom**

Samples collected for analysis of dissolved pesticides can be processed at the laboratory or onsite through a column containing pesticide-specific sorbents. Onsite solid-phase extraction (SPE) is useful, especially at remote sites, because pesticides isolated on the sorbent are less susceptible to degradation than when in water. Also, the SPE cartridges are less expensive to ship than water samples. However, onsite SPE is not required, and in some situations, laboratory SPE might be preferred.

All SPE methods require that the water sample be filtered (section 5.2.2.A) as soon as possible after collection. General equipment and supply needs for SPE for a broad-spectrum analysis of pesticides are listed in table 5-7 and general instructions are given in sections 5.3.1 and 5.3.2. More detailed information on SPE methods and procedures can be found in Sandstrom and others (1992), Sandstrom (1995), Zaugg and others (1995), Lindley and others (1996), and Werner and others (1996).

- Filter the environmental sample (section 5.2.2.A): this is necessary to prevent blockage of the SPE column by particulate material.
- Process the pesticide sample through an SPE column within 4 days of collection.
- Determine the reagents needed for the SPE method to be used (for example, conditioning solution, surrogate solution, and field-matrix spike solution).

Table 5-7. Checklist of general equipment and supplies required for broad-spectrum pesticide analysis by onsite solid-phase extraction

[SPE, solid-phase extraction; mm, millimeter; µL, microliter; µm, micrometer; mL, milliliter; NWQL, National Water Quality Laboratory]

✓	General equipment and supplies[1]	Description	Number required
	Aluminum foil	Heavy duty	1 box
	Blank water[2]	Pesticide grade (NWQL)	4 L
	Filter media	Glass microfiber, 147-mm diameter, 0.7-µm pore diameter, precleaned[3]	1 per sample
	Detergent, nonphosphate laboratory	0.2-percent solution	4 L
	Glass bores	Disposable, for 100-µL micropipet	ample supply
	Gloves, disposable	Powderless, latex or nitrile, assorted sizes	ample supply
	Graduated cylinder or beaker	50 mL, glass	2
	Luer™ connector[2], Tefzel™ male	P-625	1 or more
	Metering pump, valveless, piston-type	FMI Model RHB OCKC	1
	Methanol	Pesticide grade (NWQL)	4 L
	Micropipet	Fixed volume (100 µL)	1 or more
	Nut and union[2], Tefzel™	P-623	1 or more
	Plastic beaker	1 L, for collecting extracted water	1 or more
	Plate-filter assembly	147-mm diameter, aluminum or stainless steel	1
	Portable balance	(Check method for weight requirements.)	1
	Sample bottles[3] and vials (40 mL)[2]	Amber glass, precleaned	1 per sample
	SPE column adapter[2]	(Check method requirements)	1 or more
	SPE columns, precleaned[2]	C-18: Analyticum™ C-18, 500 mg; Carbopak-B™, 500 mg; Other: as required	1 or more of each, as required
	SPE solutions[2]	(Check method requirements for conditioning, surrogate, and spike solutions)	as required by method
	Stopwatch	Standard	1
	Wash bottle, fluorocarbon polymer	250 mL, for methanol	1
	Wash bottle, fluorocarbon polymer	250 mL, for pesticide-grade water	1

[1]Filtration equipment and supplies are described in section 5.2.2.A, table 5-5, and figure 5-1.

[2]Supplies are ordered by USGS personnel through E-mail to NWQL-DENSUPPL.

[3]Supplies are ordered by USGS personnel from the Ocala Water-Quality Research Laboratory in Ocala, Fla.

SOLID-PHASE EXTRACTION BY C-18 COLUMN 5.3.1

The C-18 SPE column is used for samples that will be analyzed by capillary column gas chromatography/mass spectrophotometry with selected ion monitoring using NWQL schedule 2010 for a broad spectrum of pesticides.[8] Detailed descriptions of the method and laboratory and field extraction procedures are found in Zaugg and others (1995). For C-18 SPE processing, obtain a precleaned Analytichem™ SPE column (500 mg) and the other supplies and equipment described in the spike kit available from the NWQL (table 5-7).

Quality-control samples are required as an integral part of the sampling program.

- Process an initial field blank and then after about every 10 to 20 samples.
  - Use pesticide-grade blank water (PBW, obtained from the laboratory).
  - Process the blank in the same manner as you process the environmental water sample.
- Process a field matrix spike about every 20 samples. When processing a field matrix spike:
  - Collect duplicate samples.
  - Use a 100-µL micropipet to add the spike solution (mixture) to one of the duplicate samples. The concentration of spike solution can vary, depending on availability and the needs of the study (1 ng/µL concentration is commonly used at this time). Follow the instructions provided with the spike kit.
  - Add the surrogate to every spiked sample and an associated unspiked sample.
  - Record lot number and concentration of spike mixture on the NWQL Schedule 2010 Reporting Form (worksheet) (fig. 5-2).

[8]C-18 solid-phase extraction method is used for isolation and concentration of 41 pesticides and pesticide metabolites with concentrations of 4 mg/L or less in natural water samples (atrazine, alachlor, cyanazine, and metolachlor have upper concentration limits of 20 mg/L) (Zaugg and others, 1995).

Schedule 2010 Field Extraction Checklist and Reporting Form
U.S. Geological Survey/National Water Quality Laboratory
Solid-Phase Extraction and GC/MS Analysis Filtered Water

Station ID or Unique Number: _____ Station Name _____
Date: _____ Time: _____ Collector: _____
Telephone Number of Collector: _____
Comments: _____

NWQL INFORMATION

❑ SPE Column — Brand or Type: _____
Lot #: _____
Dry weight (wt.): _____ grams (g)

ON-SITE INFORMATION

❑ Filter Sample (0.7-µm glass fiber filter)
Prior to filtration record bottle tare wt.: _____ g

❑ SPE column Conditioning
Methanol (2 mL): _____ milliliters (mL)
Pesticide-grade water (2 mL): _____ mL

(DO NOT LET COLUMN GO DRY ONCE CONDITIONING STARTED)

❑ Sample — Sample + bottle wt: _____ g
– Bottle tare wt: _____ g
= Sample wt: _____ g
Add methanol conditioner (1% of sample wt.): _____ mL
Sample + bottle + methanol: _____ g

❑ Surrogate — Solution ID: _____
Volume added (100 µL): _____ µL

❑ QA Samples – Spike Mixture
Solution ID: _____
Volume added (100 µL): _____ µL

❑ Sample through column _____ g
Sample + plastic beaker _____ g
Plastic beaker _____ g

❑ Flow Rate (= Sample wt. extracted/Time) _____ g
Start time _____ hr:min
Finish time _____ hr:min

❑ Remove excess water. Write station ID,date,time, on column. Store in 40-mL vial @ 4°C.

NWQL INFORMATION

Lab ID: _____ Set#: _____ Date Received _____

❑ Dry Column with N_2 or CO_2: Date:
Pressure: _____ lb/in^2
Time: _____ min
Dry SPE column wt.: _____ g

❑ SPE Elution _____ Date: _____
Add 1.8 mL elution solvent _____ mL

❑ Internal Standard (PAH-dn mixture in toluene keeper)
Solution ID: _____
Volume added (100mL): _____ mL

❑ Evaporate solvent - nitrogen
Pressure: _____ lb/in^2
Time: _____ min

Analysis: Instrument ID: _____ Date: _____
Comments:

Figure 5-2. Worksheet for C-18 solid-phase extraction of pesticides.

Prepare to process samples onsite using the C-18 SPE column:

1. Cover a bench or table with a sheet of aluminum foil to make a clean work surface. Put on appropriate disposable, powderless gloves.
2. Collect and split samples using the appropriate procedures (NFM 4; NFM 5.1; Sandstrom and others, 1995). Filter the samples as instructed in section 5.2.2. Wear gloves (usually latex or nitrile) during sample collection and processing.
3. Set up the necessary equipment and supplies and assemble them on the clean work surface. Remove the aluminum foil wrapping from the precleaned equipment.
4. Record the sampling site information, the lot number and dry weight of the C-18 SPE column, and the surrogate solution identification number on the Schedule 2010 worksheet (fig. 5-2).
5. Change gloves.
6. Tare the weight of a clean amber glass 1-L sample bottle and a 1-L plastic beaker to the nearest gram using an analytical balance and record the weights on the Schedule 2010 worksheet.

Extract the sample:

Use the appropriate surrogate solution mixture supplied by the NWQL for the C-18 SPE method with each environmental sample.

SAMPLE EXTRACTION SHOULD BE COMPLETED ONSITE, IF POSSIBLE. If onsite extraction is not possible, extract the sample within 4 calendar days of collecting the sample.

1. Condition the SPE column:
   a. Pipet 2 mL of pesticide-grade methanol into the C-18 SPE column and allow it to flow through the column by gravity. Collect the methanol rinse in a proper container for disposal.
   b. Remove any excess methanol by rinsing approximately 2 mL of PBW, by gravity, through the column. The rinse water/ methanol mixture must be disposed of according to local, State, or Federal regulations.

c. **Do not allow the SPE column to go dry once the conditioning has started.**

- If the column goes dry, repeat the conditioning process.
- To keep the column from drying out once the conditioning has started, maintain water in the C-18 SPE column by replacing water that drained through the column. Alternatively, attach an on/off valve-to-column outlet to prevent complete draining before the sample is extracted.

2. Following the filtration instructions for general organic compounds (5.2.2.A or Sandstrom, 1995), pass about 1 L of sample through the a glass microfiber filter into the tared bottle, leaving about 2 cm of headspace.
3. Weigh the filled bottle and record the weight on the worksheet (fig. 5-2).
4. Add about 10 mL of methanol to the filtered sample using the bottle-top dispenser or a volumetric pipet. Weigh and record the sample-plus-methanol weight on the worksheet.
5. Add the surrogate solution contained in the 2-mL amber screw-cap vial to the filtered sample as follows (refer to Spike Kit Instruction Manual for detailed information and instructions on use of a micropipet):
   a. Withdraw the surrogate solution from the 2-mL amber screw-cap vial using a clean 100-µL micropipet and a clean glass bore.
   b. Insert the tip of the glass bore into the sample bottle below the surface of the sample, and depress the plunger to deliver the surrogate to the sample. (Tip the bottle on its side, if necessary, to reach below the surface of the sample with the glass bore.)
   c. Keeping the plunger depressed, swirl pipetor in water several times and then withdraw the micropipet from the bottle. Release the plunger, then remove the used glass bore from the micropipet and discard properly.
   d. Rinse the fluorocarbon polymer tip of the micropipet with methanol.
   e. Add the field-matrix spike as dictated by the study's quality-assurance plan, as required.
   f. Cap and swirl the sample to mix the sample + surrogate. (For spiked samples, mix sample + surrogate + spike solution.)
   g. If a duplicate will be submitted for analysis, repeat steps 5a–f on the duplicate sample.

6. Extract the sample through the SPE column using a metering pump fitted with 3.18 mm (1/8 in.) fluorocarbon polymer tubing with appropriate connectors (Sandstrom, 1995; NFM 2).
   a. Insert clean tubing from the inlet side of the pump into the sample bottle.
   b. Turn on the pump, flush air from the tubing (be careful to minimize any sample discharge from the end of the tubing), and then attach the outlet side of the tubing to the small end of the SPE column.
   c. Invert the SPE column to drain any remaining conditioning water left in the SPE column reservoir.
   d. Begin extraction by pumping the sample through the column at a rate of 20 to 25 mL/min and collect the extracted water into the tared 1-L plastic beaker.
7. After the sample has been pumped through the SPE column, turn the pump off and disconnect the column.
8. Remove excess sample from the SPE column using a syringe with 10 to 20 mL of air to push excess sample into a plastic beaker.
9. Weigh the beaker containing the volume of sample extracted through the SPE column. Subtract the tare weight of the beaker from the weight of the beaker plus the extracted sample and record this weight on the worksheet.
10. Write the sample identification number and the sampling date and time on the side of the SPE column. Place the SPE column into a 40-mL glass or plastic shipping ampoule and wrap it in aluminum foil.
11. Finish filling out the worksheet (fig. 5-2). Wrap the completed worksheet around the shipping ampoule and secure it with a rubber band or tape. Place in a sealable plastic bag.
12. Chill the SPE column immediately and maintain between 4°C and 25°C during storage and shipping.
13. Keep a copy of the worksheet for the field folder.

14. Field clean all equipment, including the pump and tubing, immediately after use and before going to the next site (NFM 3).
    a. Rinse thoroughly with about 50 mL of a 0.2-percent solution of a phosphate-free laboratory detergent, followed by about 50 mL of tap water (or DIW) to remove the detergent.
    b. Final rinse with about 30 to 50 mL of methanol. Collect used methanol into an appropriate container for disposal.
15. After cleaning, wrap all the equipment apertures with aluminum foil.

Ship the SPE column to the laboratory immediately. Elution from the SPE column must be completed within 7 days of extraction.

5.3.2 SOLID-PHASE EXTRACTION BY CARBOPAK-B™ COLUMN

The Carbopak-B™ method currently (November 1998) is used for NWQL schedule 2051, which is for analysis of a broad spectrum of field-extracted pesticides.[9] Detailed descriptions of the method and the laboratory and field-extraction procedures can be found in Werner and others (1996). General equipment needs for solid-phase extraction are listed in table 5-7. For Carbopak-B™ SPE processing, obtain the SPE column, Carbopak-B™, 500 mg, precleaned; surrogate mixture and field-matrix spike-solution mixture for Carbopak-B™ SPE and PBW; ascorbic acid solution, 10 g/L; and reagent-grade sodium chloride (NaCl) 10 g/sample.

[9]The Carbopak-B™ method is graphitized carbon-based solid-phase extraction used with a high-performance liquid chromatographic analytical method for determining 41 pesticides and pesticide metabolites that are not readily amenable to gas chromatography or other high-temperature analytical techniques (Werner and others, 1996).

Quality-control samples are required as an integral part of the sampling program.

- Process a field blank with the first sample. Process additional field blanks about every 10 to 20 samples:
  - Use pesticide-grade blank water (PBW).
  - Process the blank in the same manner as the environmental water sample.
- Process field-matrix spikes about every 20 samples. When processing a field-matrix spike:
  - Use a 100-µL micropipet to add the field-matrix-spike solution to two of the triplicate samples. Follow the instructions provided in the spike kit.
  - Add the surrogate to every matrix-spiked sample and associated unspiked sample.
  - Record lot number and concentration of spike-solution mixture on the NWQL Schedule 2051 worksheet (fig. 5-3).

Before beginning field work, prepare an ascorbic acid solution in the office laboratory:

Each Carbopak-B™ requires 15 mL of ascorbic acid solution. Check that you have the volume needed before leaving for the field site(s).

The ascorbic acid solution must remain capped and chilled unless in use. The shelf life of the solution is 28 days—discard if shelf life has been exceeded or if the solution has been left uncapped or unchilled.

1. Place a tared, 1-L amber glass pesticide bottle (cleaned at the NWQL) on an analytical balance and fill to 500 g with PBW (pesticide-grade organic-free water purchased from NWQL DENSUPPL).
2. Empty a 5-g vial of ascorbic acid into the 500 g of PBW to obtain a 10-g/L ascorbic acid solution. Cap immediately and shake to dissolve.
3. Label the bottle with the date and preparer's name, contents of the solution, and the concentration of ascorbic acid.
4. Refrigerate the solution immediately and keep chilled until ready for field use. Transport to the field on ice in a foam sleeve.

Schedule 2051 Field Extraction Checklist and Reporting Sheet Solid-Phase Extraction, HPLC Analysis, Filtered Water

Station ID or Unique Number: _____
Station Name: _____
Date: _____
Time: _____
Collector: _____

❑ Filter Sample	0.7-µm glass fiber filter		
❑ SPE Cartridge Conditioning	Ascorbic acid solution [15 mL]	_____	mL
❑ Sample	Sample + bottle weight	_____	g
	– bottle tare weight	_____	g
	= sample weight	_____	g
❑ Surrogate	Solution lot number	_____	
	Volume added	_____	µL
– QA Samples Spike Mixture	Solution lot number	_____	
	Volume added	_____	µL
❑ Sample through Cartridge	Sample + plastic beaker	_____	g
	– plastic beaker	_____	g
	= volume of sample extracted	_____	mL
❑ Flow Rate	Start time	_____	hr:min
	Stop time	_____	hr:min

❑ Write Station ID Number and Sampling Date on Cartridge

❑ Remove Excess Water

❑ Replace Cartridge in Shipping Container and Store @ 4°C

❑ Comments:

Figure 5–3. Worksheet for Carbopak-B™ solid-phase extraction of pesticides.

Prepare to process samples onsite using the Carbopak-B™ column:

1. Put on disposable, powderless gloves during sample collection and processing. Cover a bench or table with a sheet of aluminum foil to make a clean work surface.
2. Collect and split samples using the procedures described in NFM 4 and NFM 5.1 (refer also Sandstrom and others, 1995; Werner and others, 1996).
3. Set up the equipment and assemble supplies on the clean work surface. Remove the aluminum foil wrapping from equipment.
4. Begin to fill out the NWQL Schedule 2051 worksheet (fig. 5-3), recording the type, lot number, and dry weight of the Carbopak-B™ SPE column.
5. Put on a new pair of gloves.
6. Tare the weight of a clean amber glass, 1-L sample bottle and a 1-L plastic beaker to the nearest gram using an analytical balance. Record the weight on the worksheet provided with each column.
7. Following the filtering instructions for general organic compounds (section 5.2.2.A or Sandstrom, 1995), filter about 1 L of sample through a glass microfiber filter into the tared bottle, leaving about 2 cm of headspace.
8. Weigh the filled bottle and record the weight on the worksheet (fig. 5-3).
9. Calculate and record the sample weight.

Extract the sample:

When extracting the sample, be sure to use the appropriate surrogate solution mixture supplied by the NWQL for the Carbopak-B™ SPE method. Add surrogate solution to all samples including field blanks, replicates, and field-matrix spikes.

Sample extraction must take place within 4 days of sample collection.

1. Withdraw surrogate mixture using a clean 100-µL micropipet and glass bore (detailed instructions on the use of a micropipet are included in the NWQL spike kit).
2. Insert the tip of the glass bore below the surface of the sample in the sample bottle and depress the plunger to deliver the surrogate mixture. (Tip the bottle, if necessary, to reach below the surface of the sample with the micropipet tip.) Keeping the plunger depressed, swirl sample with the pipetor several times and then withdraw the micropipet. Release plunger, then remove and discard the used glass bore.
3. Leave approximately 2 cm of headspace for the addition of NaCl.
4. Rinse the tip of the micropipet with methanol.
5. Add 10 g of NaCl to each sample. Cap and swirl the sample.
6. Process field-matrix spikes, if dictated by the study's quality-assurance plan. To process spikes, set aside three subsamples and spike two of the three subsamples with spike-solution mixture obtained from the NWQL spike kit. Follow the instructions provided with the kit.
7. Fill a clean glass graduated cylinder or beaker with 15 mL of ascorbic acid solution.
8. Using a metering pump fitted with 1/8-in. fluorocarbon polymer tubing and appropriate connectors:
   a. Turn on the pump.
      - Adjust the pump flow rate to deliver about 20 to 25 mL/min (1 drop per second).
      - Test the flow rate by pumping the cleaning solution into a graduated cylinder or beaker and timing with a stopwatch.
   b. Attach the outlet end of the pump tubing to the SPE-column adapter.
   c. Remove the SPE column from the shipping container and attach to the adapter. (The open end of the SPE column should fit tightly over the adapter; make sure the column is sealed completely against the lip of the adapter to create a leak-proof seal.)
   d. Place the inlet end of the pump tubing into 15 mL of ascorbic acid and pump the ascorbic acid solution through the column at a rate of 20 to 25 mL/min.
9. After all ascorbic acid solution has been pumped through the column, continue to pump air through the column for 1 minute. The conditioned column is now ready for sample extraction. **Extract sample onto the column within 8 hours of conditioning with ascorbic acid.**

10. Insert the inlet end of the pump's fluorocarbon polymer tubing into the sample bottle to begin sample extraction.
11. Pump sample through the Carbopak-B™ SPE column at a rate of 20 to 25 mL/min and collect extracted water in tared 1-L plastic beaker.
12. After the sample has been pumped through the column, turn off the pump and disconnect the SPE column.
13. Remove excess sample from the SPE column by using a syringe with 10 to 20 mL of air to push the excess sample into the tared, 1-L plastic beaker.
14. Weigh the beaker with the volume of sample processed through the SPE column (subtract tare weight of beaker from weight of beaker plus sample) and record the weight of the sample processed through the column on the worksheet (fig. 5-3).
15. Write the station identification number and the sampling date and time on the side of the SPE column and place the SPE column in a shipping container (40-mL glass or plastic ampoule). Complete the worksheet, wrap it around the shipping ampoule, and secure it with a rubber band or tape. Place SPE-column sample in a sealable bag. Keep a copy of the worksheet for the field folder.
16. Chill the SPE-column immediately and maintain at 4°C during storage and shipping.

Ship the SPE column to the laboratory immediately. Elution from the SPE column must be completed within 7 calendar days of extraction.

17. Field clean all equipment including the pump and tubing immediately after use (NFM 3) and before going to the next site. Rinse thoroughly with about 50 mL of a 0.2-percent solution of phosphate-free laboratory detergent, followed by about 50 mL of tap water or DIW to remove the detergent. Final rinse with 30 to 50 mL of methanol. Collect methanol rinse into an appropriate container. After cleaning, wrap all equipment apertures with aluminum foil.

SAMPLE PRESERVATION 5.4

By **D.B. Radtke**

Sample preservation is the measure or measures taken to prevent reduction or loss of target analytes. Analyte loss can occur between sample collection and laboratory analysis because of physical, chemical, and biological processes that result in chemical precipitation, adsorption, oxidation, reduction, ion exchange, degassing, or degradation. Preservation stabilizes analyte concentrations for a limited period of time. Some samples have a very short holding time. **Verify that time-dependent samples were received in proper condition, at the correct temperature, and that holding times were not exceeded by contacting the laboratory.**

Some samples must be preserved by filtration (section 5.3) and (or) chilling and (or) chemical treatment (Appendixes A5-A through A5-C). The preservation required for a given sample is described by the analyzing laboratory; for the NWQL, consult the laboratory for sample-preservation instructions.

- Before going to the field site and again at the field site:
  - Check the sample-designation code required for each sample.
  - Check sample requirements for chilling and chemical treatment.
  - Check with the laboratory and make note of holding time restrictions.

CHILLING 5.4.1

Immediately following sample collection and processing, samples that require chilling must be packed in ice or placed in a refrigerator and maintained at 4°C or less, without freezing, until analyzed.

- Check that there is sufficient headspace in the sample bottle to allow for sample expansion.
- Put foam sleeves around samples in glass bottles before packing them in ice.

- **Include a temperature check sample in the shipping container.**
  - Fill a polyethylene bottle with tap water, cap it securely, and label it "Temperature Check Sample," along with the site identification and the date(s) and time(s) of sampling and shipping.
  - Prepare a self-addressed, stamped postcard that is labeled "Temperature Check Sample report." The postcard should include the site information, date(s) and time(s) of sampling and shipping, and a space for the laboratory to record the arrival temperature of the check sample.
  - Put the postcard into the sealable plastic bag with the ASR form. The laboratory will record the temperature of the check sample upon arrival and will complete the card and return it to the sender.
  - Use this information to document that samples were maintained at 4°C or less.

Pack a temperature-check sample with other chilled samples.

Chilled Samples

[This list of samples that require chilling is not comprehensive—check with the analyzing laboratory. These samples must be refrigerated or placed on ice immediately and maintained at or below 4 degrees Celsius without freezing.]

Chemical classification	USGS sample-designation codes[1]
Organic compounds	VOC, GCC, TOC, DOC, SOC, RCB, LC0052, SH 2010, SH 2051, SH 2001, SH 2050
Nutrients	WCA, FCA, FCC
Chemical Oxygen Demand (COD)	LC 2144
Cyanide	LC 0880, LC 0023
$^{15}N/^{14}N$	RUS; LC 1717, LC 1718
^{14}C	RUR/RUS; LC 1199

[1]These sample-designation codes are unique to the USGS and are subject to change.

CHEMICAL TREATMENT 5.4.2

Chemicals used for sample preservation depend on the target analyte (Appendixes A5-A, A5-B, and A5-C). The most frequently used chemical preservatives by the USGS are provided in individual ampoules and contain one of the following: ultrapure nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), or phosphoric acid/copper sulfate ($H_3PO_4/CuSO_4$). The National Water Quality Laboratory can provide a complete list of sample treatments, along with sample designations and container requirements. The preservatives are procured from QWSU and come with a quality-control certificate of analysis for selected constituents. Keep the certificate of analysis in the study data file to help with future interpretation of quality-control and environmental data.

Take steps to minimize sample contamination and maximize safety during the preservation process (Horowitz and others, 1994; Shelton, 1994; Koterba and others, 1995; Timme, 1995). Note that a chemical preservative for one sample may be a source of contamination for another. To help reduce contamination during the preservation process and ensure proper handling of chemicals:

- Work inside a preservation chamber (only the Clean Hands person works inside the chamber). **Change gloves and the cover of the portable preservation chamber each time a different type of chemical treatment is used.** Clean Hands/Dirty Hands techniques must be used for parts-per-billion levels of trace elements and are recommended for use in general and as appropriate for the study.
- Use preservatives packaged in individual ampoules for routine preservation. Be aware that preservatives dispersed from dropper-type bottles or automatic pipets could become contaminated and could result in the contamination of subsequent samples.
- Use the grade of preservative appropriate to meet data-quality requirements. (Check the certificate of analysis for the method detection limit and the concentration of the target analytes of interest.)

- Always store preservatives in separate, sealed containers, preferably away from each other, and away from environmental and quality-control samples.
- Store spent preservative ampoules, containers, and supplies separately in closed and labeled containers (such as screw-cap bottles) until they can be disposed of properly.
  - Use a separate ampoule-waste container for each type of chemical preservative.
  - Store used gloves and chamber covers in a closed container, such as a pail with a lid, until proper disposal can be arranged.
- Follow a prescribed order in which samples are to be preserved (the recommended order is described in the steps below).

CAUTION: Before handling any chemical, refer to the Material Safety Data Sheet (MSDS) for safety precautions. Wear appropriate gloves, safety glasses, and apron when working with corrosive or oxidizing solutions.

For chemical treatment and handling of samples, follow the recommended sequence and procedure described in the steps that follow:

1. Put on appropriate disposable, powderless gloves.
2. Set up preservation chambers and assemble equipment and solutions in the order in which they will be used. If nitric acid is the only chemical preservative being used, the processing chamber can be used as a preservation chamber after all the filtered samples have been removed from the chamber.
3. Rinse the outside of each preservative ampoule with DIW and dry with a laboratory-grade, lint-free paper towel (for example, Kimwipe™).
4. For organic-compound samples:
   a. Change gloves.

b. Place inside the preservation chamber the required organic-compound samples, chemical preservatives (treatments), and ampoule-waste containers. Common treatments include hydrochloric acid, sulfuric acid, or phosphoric acid/copper sulfate. **(VOC samples that are to be chemically treated can have the acid preservative added to the sample within the processing chamber as long as subsequent samples are not contaminated *(section 5.1.2 and Appendix A5-A).***

c. Change gloves.

d. Uncap the sample bottle and dispense the appropriate chemical treatment into the sample. Place any spent ampoule into the appropriate ampoule-waste container.

e. Immediately recap the sample bottle and invert the bottle about five times to mix. **Vials with septum-lined caps for VOC must have no headspace.**

f. Repeat steps b, c, and d for each type of chemical treatment, if necessary, changing gloves and chamber cover each time. Make sure there is headspace in all glass bottles except for the vials for volatile organic compounds (VOC).

g. Chill all organic samples (treated and untreated) immediately and maintain them at 4°C during storage and shipment to the laboratory (section 5.5).

5. For inorganic-constituent samples:

a. Change gloves.

b. Change the chamber cover. Set up additional preservation chambers, if practical. (For example, one chamber for nitric acid treatments and a separate one for potassium dichromate treatment.)

- Transfer samples requiring chemical treatment to the preservation chamber.
- Place the first preservative and its waste container inside the chamber.
- Change gloves.

c. Add chemical treatments to samples in the following order:

i. Major, minor, and trace cation samples: Add contents of the vial containing 2 mL of 6N ultrapure HCl to the sample(s) designated RAM or FAM (Appendix A5-B). Place the spent ampoule into the HCl vial waste container.

ii. Mercury sample(s): Add contents of the $HNO_3/K_2Cr_2O_7$ ampoule to the sample(s) designated RAM or FAM (Appendix A5-B). Place the spent ampoule into the $HNO_3/K_2Cr_2O_7$ ampoule waste container.

iii. Change chamber cover and change gloves.

iv. Nutrient samples designated WCA or FCA (Water Quality Technical Memorandum 99.04):

- Place sample bottles into chamber.
- Add contents of the 1-mL 4.5-normal H_2SO_4 ampoule to 125-mL samples designated as WCA or FCA (Appendix A5-B). Place the spent ampoule into the H_2SO_4 ampoule waste container.
- Chill samples to 4°C or below without freezing immediately after adding the sulfuric acid.

v. Change chamber cover and gloves. Place bottles requiring other acid treatments into the chamber, along with the necessary chemicals and chemical-waste containers. Add the hydrochloric or other acid treatments to the samples. Place spent ampoules in appropriate waste containers.

vi. Remaining samples (Appendixes A5-B and A5-C): Change the chamber cover and change gloves for each type of treatment (for example, zinc acetate, sodium hydroxide, copper sulfate).

d. Tighten the cap on the bottle immediately after adding the chemical treatment and invert about five times to mix.

- Chilled samples must be put on ice and shipped to the laboratory immediately.
- Emptied ampoules must be stored in designated waste or recycle containers.

6. Disassemble and clean the chamber frame.
   a. Remove the disposable cover from the chamber and the work area.
      - Collapse the plastic cover while outside of the field vehicle.
      - Tie a knot in the cover to close it.
      - Dispose of the cover as regulations require.
   b. Clean the chamber frame, if necessary.
7. Document in field notes the preservation procedures and chemical treatments used.
8. Spent ampoules should be collected and, at the end of each field trip, disposed of according to Federal, State, and local regulations. (The District safety officer and water-quality specialists can be consulted for proper ampoule-disposal methods.)

HANDLING AND SHIPPING OF SAMPLES 5.5

By **D.B. Radtke**

Samples should be packaged and shipped to the laboratory for analysis as soon as possible. Generally, the shorter the time between sample collection/processing and sample analysis, the more reliable the analytical results will be. Before shipping samples to the laboratory:

- Check that sample bottles are labeled correctly.
- Complete an Analytical Services Request (ASR) form.
- Pack samples carefully in the shipping container to prevent bottle breakage, shipping container leakage, and sample degradation. Check that the bottle caps are securely fastened.

Protocols for labeling, documenting, and packaging samples established by the receiving laboratory must be followed. **Obtain authorization from the laboratory before shipping highly contaminated or potentially hazardous samples for analysis.** A summary of procedures for shipping samples to the NWQL is outlined below. Office of Water Quality Technical Memorandum 92.06 and National Water Quality Laboratory Technical Memorandum 95.04 give detailed instructions on shipping procedures.

LABELING SAMPLE BOTTLES 5.5.1

Each sample bottle must be correctly labeled with the station identification number, date, time, and sample designation. Sample designation is established by the laboratory. Laboratory codes that are added or deleted from the analytical schedule requested should be recorded on the ASR forms that accompany the samples—**not on the sample bottles.**

1. Label each bottle with a permanent, waterproof marker, or use preprinted labels that will remain securely attached to the bottles, even if they become wet.

2. Write legibly and include as a minimum the following information:
   - Station identification number.
   - Date and time of sample collection.
   - Sample designation code (Appendixes A5-A through A5-C).

A bottle with an unreadable label or no label is a wasted sample.

5.5.2 FILLING OUT AN ANALYTICAL SERVICES REQUEST FORM

Each set of samples must include an Analytical Services Request (ASR) form. To ensure correct processing of samples, the information recorded on the ASR form must correspond to each sample in the shipment.

- **Never send a sample to the NWQL without an ASR form** (forms are available through DENSUPPL).
- **Information recorded on ASR forms must be legible** and completed in permanent ink or by computer.

Fill out the ASR form as follows, including as much information about the sample(s) as possible:

1. Record mandatory information:
   - Station identification number and (or) unique number
   - Telephone number at which field personnel who collected the samples can be reached
   - Name of study chief and (or) field personnel
   - State and District user codes
   - Project account number
   - Date and time at beginning of field trip
   - Schedules and laboratory codes of the analytical work requested for submitted samples

2. Record the Sample Medium, Analysis Status, Analysis Source, Hydrologic Condition, Sample Type, and Hydrologic Event information. This information is mandatory if the analytical results are to be stored in the USGS National Water Information System (NWIS) data base.
3. Record the field-measurement values of specific electrical conductance (conductivity), pH, and field alkalinity (or acid neutralizing capacity).
4. In the comments section of the form, add information that needs to be brought to the laboratory's attention. **Be sure to note if the samples are potentially hazardous or highly contaminated so that proper precautions can be taken by laboratory personnel.**
5. At the bottom of the ASR form, list the total number of sample bottles for each sample-designation code.
6. To prevent water damage to paperwork accompanying samples to the laboratory (such as the ASR form and the temperature-check postcard), place all paperwork inside two sealable plastic bags. In coolers, tape the bags containing the paperwork to the underside of the lid.
7. Keep a copy of the completed ASR forms in the study files.

Add a bold cautionary note to the ASR form if samples could contain hazardous concentrations of contaminants.

5.5.3 PACKAGING SAMPLES

When packaging samples for shipment to the laboratory, remember that all bottles must be protected from breaking (especially glass bottles) and (or) leaking. The laboratory usually will return with the cooler reusable packing materials such as mesh bags, foam sleeves, and bubble wrap. Plastic bags and cardboard boxes will not be returned. **Do not use foam peanuts or vermiculite.**

When packaging samples:

1. Make sure bottle labels are waterproof and that information is legible.
2. Tighten all bottle caps to prevent leakage.
3. Line all shipping containers, including those without ice, with doubled heavy-duty plastic bags.
4. Use adequate packing material to prevent bottle breakage.
   - Ship all glass bottles in foam sleeves or wrap them with bubble wrap.
   - Enclose each sleeved FAM and RAM bottle in two sealable plastic bags.
   - Pack bottles so that they do not touch each other.

Sample integrity must be maintained. Ship samples with enough ice to keep chilled at 4°C or below without freezing until the sample is logged in at the laboratory.

5. Pack samples designated for chilling in coolers.
   a. Use insulated ice chests (coolers) (1- to 5-gallon sizes are recommended). Larger volumes of chilled samples can be sent in coolers as long as the carrier's maximum weight and size restrictions are not exceeded. **Do not use broken or leaky coolers.**
   b. Pack samples designated for chilling with ice.
      - The volume of ice should be equal to or greater than the volume occupied by samples (twice the volume of ice to samples is recommended during warm temperatures).
      - The amount of ice necessary will vary depending on the length of time in transit and ambient air temperature. Chilling the cooler and samples prior to shipment is recommended in hot weather.
      - **Do not use blue ice or other types of commercial refreezing containers that have freezing points below 0°C.** This can cause bottles to freeze and result in ruined samples or broken bottles.
      - Enclose ice and samples in doubled plastic bags. **Do not mix ice with water-absorbent packing materials.**
   c. Seal cooler spouts or drains, preferably with silicone or epoxy.
6. Samples not requiring chilling can be shipped in heavy-duty cardboard boxes but may also be shipped in coolers.

DO NOT USE

— foam peanuts or vermiculite as packing material.

— dry ice to keep samples chilled.

7. When shipping multiple sets of samples in the same container, label each set of sample bottles with a different letter of the alphabet (A, B, C) so that bottles of each sample set will have the same letter.
   - Print the letter in the upper right-hand corner of the ASR form for that particular sample set.
   - Place all bottles from a sample set into a separate bag (such as plastic or mesh) or bind with a rubber band to keep them together.

8. All bottles for a particular schedule should be sent in the same shipping container, with some exceptions. Samples that do not need to be chilled can be packed and shipped in the cooler with chilled samples, provided the following exceptions do not apply. The ASR form must list only those samples that are being shipped with that form. On the ASR form, delete laboratory codes of any sample bottles not included in the same shipping container.
   - **Exception: Do not ship nutrient samples with samples that were treated with HNO_3.**
   - **Exception:** Do not ship FAM and RAM samples in the same container as FA or RA samples when requesting sample analysis for potassium and (or) chromium concentrations.
9. After samples and ice (if required) are placed in doubled plastic bags, close each bag separately with a knot.
10. Inside coolers:
    - Include a return address shipping label with the ASR form. This label must include a street address (not a post office box number), an account number, and the USGS District User Code (to bill return-shipping charges).
    - Label the inside of each cooler and cooler lid with a current return address and telephone number, using a permanent waterproof marker.
11. Include the ASR form for each sample set shipped in each cooler or box.
    - Remember to place the ASR form and temperature-check postcard into two sealable plastic bags to prevent water damage.
    - Tape the plastic bag containing the ASR form(s) and temperature-check card to the underside of the cooler lid, or place the sealed paperwork on top of samples packed in a cardboard box.

SHIPPING SAMPLES 5.5.4

Whenever possible, ship samples to the laboratory on the day of collection. Check laboratory hours of operation—keep in mind that the laboratory might not receive samples on Saturdays, Sundays, or holidays. The integrity of chilled samples sent late on a Thursday or on a Friday could be compromised if not received by the laboratory in time to be unpacked and refrigerated. Check planned arrival time before selecting the carrier service.

- No carrier service will accept or deliver leaky boxes or coolers. Securely tape the outside of shipping containers to prevent leaking and to maintain container integrity.
- Do not exceed maximum weight and size restrictions set by the carrier service.
- When shipping a single set of samples in multiple containers, mark the outside shipping label with the number of containers being shipped (such as 1 of 2, 2 of 2).
- Comply with the carrier service's requirements for meeting U.S. Department of Transportation regulations for transporting hazardous substances.
- **Identify samples that require special shipping procedures:**
  - Send chilled samples to the laboratory by the fastest means possible.
  - Some samples require special handling and shipping (such as radon and CFC samples). Contact the laboratory for specific instructions.
  - Obtain authorization from the laboratory before sending any highly contaminated or potentially hazardous samples to the laboratory for analysis.

Document date of sample shipment on the copy of each ASR form. Keep a copy in study files.

SUMMARY OF SAMPLE-COLLECTION AND SAMPLE-PROCESSING PROCEDURES FOR SPECIFIC ANALYTES 5.6

By F.D. Wilde and Jacob Gibs

Collection methods, equipment needs, and preservation requirements for specific analytes can change over time, owing to advancements in knowledge and technology. Any major changes to sample collection and processing procedures will be announced on the USGS Office of Water Quality Web site (http://water.usgs.gov/lookup/get?owq/) or as a technical memorandum (http://water.usgs.gov/lookup/get?techmemo/). Consult NWQL or the District water-quality specialist for instructions related to the collection, processing, or analysis of solid materials, gases, biota, and any other analytes not described in this manual. Chemical formulas used in this section are spelled out in "Conversion Factors, Selected Terms, Abbreviations, and Chemical Formulas."

COMMON ORGANIC COMPOUNDS 5.6.1

Sample bottles for organic-compound analyses are precleaned and baked at the laboratory and should be received capped. Collect and process samples within processing and preservation chambers, as appropriate, and while wearing disposable, powderless latex or nitrile gloves. In general, change gloves between each collection and processing step and with each new sample type. After collection and processing, check that the information is correct on the bottle label. Place the filled glass sample bottle in a foam sleeve and chill sample to 4°C or below without freezing.

- Most samples for organic-compound analysis are collected in 1-L amber glass bottles, leaving headspace in case of sample expansion (Appendix A5-A).

- Samples for glyphosphate analysis are collected in 40-mL vials, leaving headspace in case of sample expansion.
- Volatile organic compounds are collected in 40 mL baked glass vials without headspace.

Do not field rinse bottles prepared for organic-compound samples.

5.6.1.A Volatile Organic Compounds (VOCs)

Label baked 40-mL amber glass vials as "VOC." Collect three vials per sample for ground water and four vials per sample for surface water.

- **Do not use tape on the vials.** Tape causes the autosampler to jam.
- **Do not aerate the sample.** Samples with air bubbles must be discarded.

TECHNICAL NOTE: **Some programs, such as NPDES and NAWQA, require treatment of VOC samples by adding HCl.** To determine the number of HCl drops needed to lower sample pH to ≤2 before collecting the sample, collect a test sample toward the end of purging and pour 40 mL of the sample into a beaker or spare VOC vial. Check the pH (use narrow-range pH indicator strips such as pHydrion™) after each addition of 2, 3, and 4 drops. Do not use pH indicator strips that are old or expired.

To collect VOC samples:

1. Insert the fluorocarbon polymer discharge line from the pump or the bailer emptying device to the bottom of the vial; flow should be smooth and uniform (between 100 and 150 mL/min).
   - If the vial was supplied with chemical treatment, do not fill vial to overflowing.
   - If no chemical treatment will be added or if the treatment will be added after the vial is filled, allow sample to overflow the vial in order to help purge air from the sample.
2. Slowly withdraw the discharge line from the bottle; slide the discharge line to the side of the vial as the line is about to clear the vial so as to avoid breaking the water surface. Leave a convex meniscus.

3. Add chemical treatment (HCl) to sample if required by the program and if the HCl is not already in the vial. Add 2 to 5 drops (see TECHNICAL NOTE above) of 1:1 HCl:H_2O, drop by drop, to the filled vial to lower the pH to ≤2. Dispense the HCl from a fluorocarbon polymer dropper bottle. **Do not add more than 5 drops of HCl.**
4. If residual chlorine is present, add 25 mg of ascorbic acid to the vial in addition to the HCl.
5. Replace the vial cap immediately. Do not allow the samples to degas. The fluorocarbon polymer (white) side of the septum in the cap should contact the sample.
6. Invert the vial and tap the vial to release any bubbles. Check carefully for gas bubbles in the sample. If gas bubbles are present, discard the sample vial and resample. If degassing of the samples makes excluding bubbles impossible, record this on the field forms and the laboratory ASR form and report an estimate of the relative volume of bubble(s) in the sample.
7. Protect the sample from sunlight. Chill and maintain at 4°C or below without freezing.

Semivolatile Organic Compounds (Base-Neutral Acids), Pesticides, Organonitrogen Herbicides, Polychlorinated Biphenyls (PCBs) 5.6.1.B

Label 1-L baked glass bottles as "GCC." Add the laboratory code, if required. Certain analytical schedules require a filtered sample (check with the laboratory for processing and bottle requirements).

1. Fill to the shoulder of the bottle directly from the sampling, splitting, or filtering device.
2. Be sure to leave headspace in the bottle.
3. Chill and maintain at 4°C or below without freezing.

Instructions for field solid-phase extraction (SPE) of pesticides are provided in section 5.3. Field SPE is an alternative method for processing samples for pesticide analysis and should be considered in situations where transporting glass bottles, shipping weight, or holding/shipping times pose a problem. Field SPE samples usually are extracted after most other onsite activities are completed or by a third team member because equipment setup, sample extraction, and equipment cleaning can be quite time consuming.

5.6.1.C Phenols

Label 1-L baked amber glass phenol bottle as "LC0052."

1. Fill the bottle with raw sample directly from the sampling or splitting device.
2. Leave a small headspace in the bottle.
3. Add 2 mL of 8.5 percent H_3PO_4 to a 1-L sample to achieve pH 4, and 10 mL of $CuSO_4$ to a 1-L sample (100 g/L).
4. Chill and maintain at or below 4°C without freezing.

5.6.1.D Carbon

Particulate organic and inorganic carbon[10]***:***

1. Label the samples for Total Particulate Carbon (TPC) as "LC2606" and for Particulate Inorganic Carbon (PIC) as "LC2608." Note that the concentration of Particulate Organic Carbon (POC, LC2611) is calculated as the difference between TPC and PIC.
2. Refer to the detailed instructions given in section 5.2.2.C for processing the TPC and PIC samples.

Raw (TOC) sample:

1. Use 125-mL baked glass bottles. Label the sample for total organic carbon "LC114."
2. Pour, discharge, or pump the raw sample directly into the sample bottle, up to the shoulder of the bottle (leave headspace).

[10]The analysis for total particulate nitrogen (TPN), LC2607, is performed on the TPC sample upon request.

Filtered (DOC) and suspended (SOC) samples:

1. Label the DOC sample as follows: (a) "LC2612" if processed through a Supor capsule filter; (b) "LC2613" is processed through a GF/F; and (c) "LC113" if processed through a silver filter.
2. Refer to the detailed instructions given in section 5.2.2.C for processing DOC using either the capsule or GF/F filtration procedures. Fill the 125-mL baked glass bottle to the shoulder—allow enough heasdspace for the addition of 4.5*N* H_2SO_4 and the expansion of the chilled sample. Refer to the instructions given in Appendix A5-D if using the silver-filter procedure.
3. Label the SOC sample as "LC305." Refer to the detailed instructions given in Appendix A5-D for the silver-filter procedure. LC305 is available only as a custom analysis.

Methylene Blue Active Substances (MBAS) and Oil and Grease 5.6.1.E

MBAS:

1. Label a 250-mL polyethylene bottle as "RCB."
2. Field rinse the bottle and fill with raw sample.
3. Chill and maintain at 4°C or below without freezing.

Oil and grease:

1. Label a 1-L baked amber glass bottle as "LC0127."
2. Do not field rinse; fill with raw sample, leaving a small headspace.
3. Add approximately 2 mL of sulfuric acid to reach a pH <2.
4. Chill and maintain at 4°C or below, without freezing.

MAJOR IONS AND TRACE ELEMENTS 5.6.2

Bottles (including acid-rinsed polyethylene and glass bottles) used to collect samples for analysis of major ions and trace elements should be rinsed and partially filled with DIW before they are used at the field site, as instructed in NFM 3. Exceptions apply when collecting samples for analysis of isotopes or radiochemicals—consult the isotope laboratory. Collect and process samples within processing and preservation chambers, as appropriate, and while wearing appropriate (for example, vinyl) disposable, powderless gloves. In general, change gloves between each collection and processing step. After collection and processing, check the bottle label for correct information and place glass bottles into foam sleeves.

- Use acid-rinsed bottles (for cations) only if they arrive capped with colorless translucent caps. Do not use any acid-rinsed bottles that are received uncapped.
- Before going to the field, first rinse and then half fill each bottle with DIW as described in NFM 3.
- Discard DIW from bottles at the field site before field rinsing and (or) sampling.
- **Field rinse the inside of sample bottles and bottle caps with sample** (table 5-2; Appendix A5-B). Use filtrate to rinse the bottles that will contain filtered sample.

5.6.2.A Major and Minor Cations and Trace Elements

Use of Clean Hands/Dirty Hands techniques and good field practices are required for samples with parts-per-billion concentrations of trace elements and are recommended for all samples.

Raw samples:

1. Label acid-rinsed polyethylene bottles as "RA" for major and minor cations and most trace-element samples. Label bottles with the laboratory schedule, as appropriate.
   - Arsenic, antimony, and selenium analyses—Label bottles as "RAH." (Some samples are designated "USEPA"—check with the laboratory.)
   - Mercury samples—Label glass bottles as "RAM."
   - USEPA drinking water samples—Label bottles as described in NWQL Technical Memorandum 97.05 or as directed.
2. Field rinse and fill sample bottles directly from the sample-collection or processing device.
3. Add chemical treatment, as specified by the analyzing laboratory.
   - Major and minor cations and trace elements: Add HNO_3 to lower sample pH to <2.
   - Mercury: Add contents of vial containing 2 mL of 6*N* ultrapure HCl.

Filtered samples:

1. Label acid-rinsed polyethylene bottles as "FA" for most trace-element samples, including arsenic, antimony, and selenium. Check NWQL Technical Memorandum 97.05 for requirements for USEPA drinking water samples.
   Exception: Mercury—Label the acid-rinsed 250-mL glass bottles as "FAM."
2. Field rinse and fill sample bottles directly from the filter assembly. Refer to section 5.2 for filtration instructions.

3. Add chemical treatment, if specified by the analyzing laboratory.
   - Major and minor cations and trace elements: Add HNO_3 to lower sample pH to <2.
   - Mercury: Add contents of vial containing 2 mL of 6*N* ultrapure HCl.

Nutrients (Nitrogen and Phosphorus) 5.6.2.B

Refer to Office of Water Quality Technical Memorandums 94.16, 99.04 and 2000.08 for the most recent changes to collecting and processing nutrient samples. See 5.6.1.D and 5.2.2.C for processing of a Total Particulate Nitrogen (TPN) sample, LC2607.

Raw samples:

1. Label bottles as follows:
   - "WCA" for raw samples to be treated with H_2SO_4 (125-mL translucent bottles are preferable).
   - "ERC" for raw samples collected for the USEPA Drinking Water Program (refer to National Water Quality Laboratory Technical Memorandum 97.05 or contact the laboratory for instructions).

   A clean, graduated cylinder may be used when the volume of sample to be filtered is less than 64 mL.
2. Field rinse and fill the sample bottles directly from the sampler or sample splitting device.
3. Add a chemical treatment to WCA and ERC samples, as appropriate.
4. Chill WCA and ERC samples immediately and maintain at 4°C or below without freezing.

Filtered samples:

1. Label bottles as follows:
   - FCC" for filtered samples (125-mL brown bottles).
   - FCA" for filtered samples to be treated with H_2SO_4 (125-mL brown bottles).
2. Field rinse and fill sample bottles directly from the capsule filter or other filter assembly.

- **Use of 0.45-µm pore-size filter media is the standard to date for State or Federal programs that regulate drinking water and for routine water-quality studies for which consistency with historical nutrient data is necessary.** +
- Use of 0.2-µm pore-size filter media is recommended for studies for which exclusion of bacteria from the sample is desirable, and inconsistency with historical data is not an issue. Prefilter sediment-laden samples through 0.45-µm filter media. Record the filter pore size used, if other than 0.45 µm, under the comments section on the field form and ASR forms.

3. Add chemical treatment to FCA samples. (FCC samples do not require chemical treatment.)
4. Chill FCC and FCA samples immediately and maintain at 4°C or below without freezing.

5.6.2.C Anions

Label polyethylene bottles as "FU" (filtered untreated). Process alkalinity samples for field titration using the same steps as for other anions (with the exception of ANC samples) (NFM 6).

1. Refer to section 5.2 for filtration instructions. +
2. Field rinse and fill sample bottles directly from the capsule filter (or filter assembly).
3. Do not add chemical treatment.

Exceptions:

- **Cyanide**—Label the 250-mL polyethylene bottle as "LC0880" for filtered sample and as "LC0023" for raw sample. **Cyanide requires addition of NaOH to raise the pH to >12.**
- **ANC** (acid neutralizing capacity)—Do not filter the ANC sample. Label sample bottle as "RU" (NFM 6).

+

TABLE ISOTOPES AND RADIOCHEMICALS 5.6.3

Isotopes and radiochemicals generally are not processed in a processing or preservation chamber, unless samples are being handled in a glove box. Wear appropriate, disposable, powderless gloves when collecting and processing samples.

Leave enough air space (at least 2 cubic centimeters) if glass bottles are used and the sample will be chilled to allow for the expansion of water samples unless instructed otherwise (Appendix A5-C). Close the polyseal cap tightly and seal with wax or plastic tape, or as directed below for the specific isotope or radiochemical.

Carbon ($^{13}C/^{12}C$ and ^{14}C) 5.6.3.A

Do not let the sample contact air. Filter the sample along with other inorganic-constituent samples if particulates are visible. **Samples without particulates do not require filtration or chemical treatment** (NWQL Technical Memorandum 96.05). If ^{13}C will be collected by direct precipitation in the field using ammoniacal $SrCl_2$, then the precipitates must be submitted as washed, dried, homogenized powders. **The laboratory will not accept bottles with ammoniacal $SrCl_2$ in solution.**

Samples for $^{13}C/^{12}C$ analysis:

1. Label a 1-L glass bottle as "$^{13}C/^{12}C$, RUS," and the laboratory code or schedule number (as requested by the laboratory).
2. Filter the sample if particulates are visible. Establish a closed path from the sample source through the filter and to the bottle to exclude air from the collection system.
3. When filling the bottle, fill from the bottom of the bottle and allow an overflow of two to three bottle volumes. Cap the sample immediately.

Samples for ^{14}C analysis:

The sample must provide a minimum of 5 mg dissolved inorganic carbon (DIC) per sample container.

1. Label bottles as "^{14}C, RUS/RUR," and the appropriate laboratory schedule number. Check with the laboratory and refer to NWQL Technical Memorandum 96.05 for bottling and other field requirements for samples to be analyzed for ^{14}C.
2. Collect sample in duplicate. Filter the sample if particulates are visible. Establish a closed path from the sample source, through the filter, to the bottle to ensure that air is excluded from the collection system.
3. Fill sample container.
   - For samples with ^{14}C content greater than or equal to 5-percent modern carbon, fill the bottle from the bottom of the bottle, allowing an overflow of 2 to 3 bottle volumes. This helps to purge air from the sample. Cap the bottle immediately. For potentially low ^{14}C concentrations, (<10 percent modern carbon) or if relatively long filtration time is required, flush the headspace above the water sample with nitrogen while filling the bottle.
   - For samples with ^{14}C content less than 5-percent modern carbon, use a stainless steel collection vessel, such as a Whitey™ Sample cylinder No. 304L-HDF4, with stainless steel valves on each end. Flush with several liters of filtrate from the bottom of the cylinder up and close the cylinder, leaving no headspace.
4. Archive a duplicate sample and store in the dark, chilled to 4°C or below without freezing.
   - Secure container caps with electrical tape.
   - Record the sample pH and alkalinity on the sample bottle.

Hydrogen ($^{2}H/^{1}H$) and Oxygen ($^{18}O/^{16}O$) 5.6.3.B

Hydrogen and oxygen isotope samples can be collected together in one bottle. Use either a 60-mL clean glass bottle or a 250-mL polyethylene bottle. Label the bottles as "RUS, SH 1142." Use caps with polyseal conical inserts. **To request bottles with appropriate caps, send E-mail to isotopes@usgs.gov.**

- Do not field rinse bottles.
- Do not add chemical treatment.
- Samples may be either raw or filtered.

1. Fill bottle to overflowing directly from the sampler or sample splitting device (raw sample) or from the capsule filter or other filter assembly (filtered sample).
2. If filling a glass bottle, fill to overflowing and then decant the sample until the water level is at the bottle shoulder. Cap the bottle immediately
3. If filling a polyethylene bottle, fill to overflowing and cap the bottle immediately, leaving no headspace. Do not use polyethylene bottles if the sample will be held or archived.

5.6.3.C Nitrogen ($^{15}N/^{14}N$)

Collect filtered, untreated sample (**do not use mercuric chloride**) in a 1-L amber or foil-wrapped glass or high-density polyethylene bottle. Use a polyseal bottle cap. Refer to National Water Quality Technical Memorandum 95.05.

1. Label the bottles as "RUS" and with the appropriate laboratory code (LC 1717, for $^{15}N/^{14}N$ as ammonia; LC 1718, for $^{15}N/^{14}N$ as nitrate; or LC 1921, for $^{15}N/^{14}N$ as nitrate plus ammonia).
2. Fill the bottle to the shoulder directly from the capsule filter or other filter assembly.
3. Put the glass sample bottle into a foam sleeve and keep it chilled at or below 4°C without freezing. Ship overnight, per shipping instructions in NWQL Technical Memorandum 95.04.

5.6.3.D Sulfur ($^{34}S/^{32}S$)

Dissolved sulfide and sulfate are collected and processed separately, according to the directions given in Carmody and others (1998).

1. Label the bottles as "RUS" and with the appropriate laboratory code or schedule number.
2. Send questions to the following E-mail address: <isotopes@usgs.gov>. Special equipment, chemical reagents, and training are needed in order to collect these samples properly.
   Sulfate: Procedures and equipment differ for processing the sulfate sample, depending on whether sulfate concentrations are less than 20 mg/L or equal to or greater than 20 mg/L. Onsite estimation of sulfate concentration is described in Carmody and others (1998).
   - When a water sample from which dissolved sulfate will be collected for isotopic analysis also contains dissolved sulfide (greater than 0.01 mg/L), the sulfide should be removed by nitrogen stripping to avoid contamination of the sulfate sulfur by oxidized sulfide sulfur with very different isotopic composition.

- Sulfate in water with concentrations of greater than 20 mg/L sulfate is collected by precipitating $BaSO_4$ from an acidified sample (up to 2-L volume). $BaSO_4$ can be precipitated and filtered in the laboratory or in the field.
- Anion exchange resin can be used to collect sulfate from samples in which sulfate concentrations are less than 20 mg/L.

Sulfide: Determine if dissolved sulfide (H_2S) is present by its distinctive rotten-egg odor. Measure H_2S concentration with a field spectrophotometer.

- Measurement of dissolved sulfide concentrations greater than 0.6 mg/L with a field spectrophotometer has been problematic.
- An alternative method for samples with dissolved sulfide concentration greater than about 0.5 mg/L is to collect the dissolved sulfide by direct precipitation of Ag_2S by adding $AgNO_3$ to the sample. Care must be taken to add sufficient $AgNO_3$ to precipitate all the sulfide present, or the sulfide sample will be fractionated.
- A method for collection of dissolved sulfide by nitrogen stripping and precipitation of Ag_2S in an $AgNO_3$ trap has been tested and found to cause a small fractionation of the isotopic composition of the sulfide. Two approaches are recommended to minimize this fractionation: (1) collect sulfide by nitrogen stripping for 3 hours or more to minimize the amount of sulfide left in the carboy and, thus, the fractionation produced; and (2) determine the kinetic fractionation factor (α) for the collection apparatus and use this α to calculate the original sulfur isotopic composition of the dissolved sulfide in the ground water from Ag_2S collected for a short time (about 30 minutes).

5.6.3.E Radium 226 and Radium 228

Label acid-rinsed polyethylene bottle(s) as "FAR" and add the appropriate laboratory code ("LC 794" for radon-226 and "LC 1364" for radon-228). Bottle-size requirements depend on analytical method or schedule.

1. Filter the sample using the procedures for inorganic-constituent samples, and fill the sample bottle to the shoulder directly from the capsule filter or other filter assembly.
2. Add reagent-grade HNO_3 to preserve sample to pH <2. **Do not substitute HCl for HNO_3.**

5.6.3.F Uranium (U-234, U-235, U-238)

Label 1-L acid-rinsed polyethylene bottle(s) as "FAR, SH 1130." Check with the laboratory for bottle requirements for the analysis requested.

1. Filter the sample and fill the sample bottle to the shoulder directly from the capsule filter or other filter assembly.
2. Add reagent-grade HNO_3 to preserve the sample to pH <2. **Do not substitute HCl for HNO_3.**

5.6.3.G Gross Radioactivity

Label 1-L acid-rinsed polyethylene bottle(s) as "FAR" (filtered sample) for the gross alpha and the gross beta analyses and with the appropriate laboratory schedule number. The laboratory schedule requested depends on the concentration of total dissolved solids in the sample.

1. Filter the sample.
2. Fill the sample bottle to the shoulder directly from the capsule filter or other filter assembly.
3. Add reagent-grade HNO_3 to preserve the sample to pH <2. **Do not substitute HCl for HNO_3.**

Tritium 5.6.3.H

Label a 1-L bottle as "RUR" and add the appropriate laboratory code. (High density polyethylene bottles are preferred; a glass bottle with a polyseal cap may be used. Refer to National Water Quality Technical Memorandum 92.04.)

- Do not place tritium samples near watches or other devices with luminescent dials. Do not store sample near tritium sources (for example, glowing clocks, watches, signs).
- **Do not field rinse sample bottles.**

1. Fill bottle with raw, untreated sample. The bottle should be dry before being filled. It might be desirable to flush the bottle with a filtered, inert gas such as argon or nitrogen before leaving for the field—consult with the laboratory.
2. Do not allow the bottle to overflow when filling with sample.
3. Leave a slight headspace in the bottle to allow for expansion of the sample.
4. Cap the bottle securely and tape the cap to prevent it from working loose during shipping.
5. Record the date and time of sampling on the bottle label and ASR form.

For tritium samples—Keep luminescent devices far from sample collection, handling, or storage areas.

5.6.3.1 Radon-222

Modify the sample collection setup to collect raw samples for radon analysis. Sample is collected in a glass vial containing liquid-scintillation solution (obtain radon kit from NWQL). Label radon-222 samples as "RUR-SV" and add the laboratory code.

Do not write on or put any labels on the side of the radon vial.

Precautions are needed when collecting samples for radon analyses to prevent introducing gas bubbles into the sample and to prevent the sample from degassing.

- Use insulated sample tubing to prevent warming of the sample.
- Inspect sample tubing to determine whether gas bubbles are forming inside the tubing or whether any air is being drawn into the sample at any connection.
- Dislodge bubbles in sample tubing by striking the tubing firmly with a blunt object.
- Tighten connections to help prevent entrainment of air.
- To reduce degassing during sample collection, create back pressure by partially closing the valve on the radon-collection unit.

1. Collect the radon sample into a syringe directly from the pump discharge or other sampling device.
2. Rinse the syringe as follows: Insert the glass syringe needle through the septum port with the collection-unit valve partially closed. Close the valve further until there is sufficient back pressure to create an almost effortless withdrawal of sample into the syringe. Fill the syringe partially, withdraw it from the septum and invert (needle up). Eject the water to waste. Repeat at least once.
3. With the syringe plunger completely depressed (no air or water in the syringe barrel) and after the final rinse, reinsert the needle through the septum. Withdraw about 15 mL of sample into the syringe barrel slowly; avoid suction and degassing.

4. Withdraw the needle, invert the syringe (needle up), and eject the sample slowly until 10 mL remain in the syringe.
5. Tip the syringe needle downward, and insert the needle tip into the mineral oil and down to the bottom of the radon sample vial.
6. Inject the entire sample slowly. Remove the syringe and cap the vial firmly. Record the date and the exact time of sample collection on the top of the cap (do not write on or put a label on the vial).
7. Shake the vial for 30 seconds after injecting the sample. Repack it in the shipping tube and cap the tube. Complete the ASR form, wrap it around the tube, secure with a rubber band, and place the tube into a sealable plastic bag. **Ship to the NWQL immediately by overnight delivery. Do not ship samples on a Friday. Do not ship radon-222 samples in coolers.**

Do not allow air to contact samples for radon analysis.

Tritium/Helium-3 ($^3H/^3He$) 5.6.3.J

Refer to NWQL Technical Memorandum 97.04S for detailed information and instructions.

Do not allow air to contact samples for $^3H/^3He$ analysis.

Water samples for the helium determination are collected, in duplicate, in special pinch-off copper tubes that hold approximately 40 mL of water. These tubes are supplied through the NWQL but are the property of the analyzing laboratory (Lamont-Doherty Earth Observatory). Unused tubes must be returned to Lamont-Doherty. Notify NWQL of the number of tubes returned.

1. Set up the sampling apparatus. Collect the sample in duplicate. These samples must also be accompanied by 500 mL of sample in a glass or high-density polyethylene bottle for tritium analysis. In addition, archive a duplicate 500-mL sample.
   a. Remove plastic caps covering the ends of the copper tube. **Handle the copper tube with care—damage to the ends from scratches and bends can prevent a good vacuum connection and thus compromise sample integrity.**
   b. Connect the copper tube to the submersible pump discharge tubing.
      - Do not exceed 5 ft between the pump discharge and the sampling apparatus.
      - The connector to the pump-discharge tubing can be plastic, rubber, or metal, but it must be airtight.
      - Clear plastic tubing is preferred to allow visual inspection for possible air bubbles.
      - Airtight connections must not come loose when back pressure is applied during closing of copper tubes. Secure the connections with stainless steel hose clamps, placing clamps approximately 1 in. from the end of the copper tube. (Do not damage ends of copper tube.)
      - Attach a small valve to the discharge end of the copper tube and insert clear plastic (Tygon™) tubing to allow the operators to check for air bubbles (NWQL Technical Memorandum 97.04S provides photographs and diagrams).
2. Begin flow of the sample to the copper tube, checking for bubbles.
   a. Hold the copper tube at a 45-degree angle, discharge up, while flushing bubbles from the system.
   b. Forcibly tap the entire sample tubing and aluminum track that holds the copper tube with a socket wrench or other blunt object to dislodge gas bubbles. This typically takes about 1 minute.
3. Any backpressure to prevent formation of gas bubbles. Close valve until flow is reduced, tap channel, then close completely.
4. Seal the sample container.
   a. Position the copper tube in approximate center of the pinch-off clamp.

b. Use a socket wrench to close the bolts on the pinch-off clamps, starting at the discharge end.

c. Turn the bolts in successive order (back and forth approximately four times until firmly closed) so that the blades of the pinch-off clamp close approximately evenly.

d. Center the copper tube between the blades again, and close the pinch-off clamp on the inflow end as described in step c above.

e. Double check to ensure that all bolts are tight.

5. Repeat procedure above (1–4) to collect a duplicate sample.

6. Disconnect the copper tube from the pump discharge tubing and remove the backpressure valve from the discharge end of the copper tube, taking care not to scratch or otherwise damage the ends.

   a. If the sample is saline, acidic, or otherwise corrosive, wash the ends of the copper tube with DIW.

   b. Take care not to bend the ends of the sealed copper tube.

   c. Do not replace the plastic caps on the ends of the copper tube.

   d. Place label onto the aluminum track of each sample—do not write on the tube. Include station identification, date, and time of sampling on the label.

7. Prepare the sample(s) for shipment. Fill out a form or submit a letter to the analyzing laboratory with the following information:

   - Unique site identification number(s).
   - Date and time of sample collection.
   - Ground-water temperature at time of collection and recharge temperature, if known.
   - Estimated or known tritium concentration.
   - Estimated or known elevation of the recharge area for the sample.
   - General description of the hydrogeologic environment, location, and well-construction information.
   - Information regarding possible tritium contamination of the sample.
   - Name, fax number, E-mail address, and phone number of the person responsible for the sample(s).

5.6.3.K Chlorofluorocarbons (CFC-11, CFC-12, CFC-113)

Chlorofluorocarbons (CFCs) can be analyzed in samples of ground water, surface water, or air. The information that follows is summarized from the Office of Water Quality/Office of Ground Water Technical Memorandum 95.02 and, while generally applicable to all media, is focused toward collection of ground water for CFC analysis. Before collecting CFC samples, review this memorandum for more detailed information on field sampling, site selection, analysis requests, and applications of CFC analyses in environmental investigations. Important information for collecting CFC samples is also provided in Busenberg and Plummer (1992) and Plummer and others (1993).

Do not allow air to contact samples for CFC analysis.

- **The collection, transport, and storage of water samples without contamination is critical in order to reliably age-date waters containing CFCs.**
- Contact the CFC laboratory (USGS, Reston, Va.) to arrange for training and to plan for CFC sampling. Remain in contact with the CFC laboratory throughout the planning, sampling, and analysis phases.

1. Schedule CFC sampling several months in advance, using the CFC request form (fig. 5-4), in order to
   - Reserve the sampling equipment. Special sampling apparatus is loaned to USGS study personnel who will collect water samples for CFC analyses and who have had the training required for CFC sampling.
   - Obtain the required number of borosilicate-glass ampoules (five ampoules per ground-water sample). The borosilicate-glass ampoules are supplied by the USGS CFC laboratory and are included in the price of analysis.
   - Obtain cylinders of compressed ultra-pure nitrogen gas and welding-grade oxygen.

2. Assemble additional tools, materials, and equipment needed (table 5-8; Office of Water Quality/Office of Ground Water Technical Memorandum 95.02).
    - Discuss the type and modification of pumping equipment with the CFC laboratory. USGS personnel should contact the laboratory in Reston, Va., by phone (703-648-5847), fax (703-648-5832), or E-mail (cfc@usgs.gov). The CFC laboratory will provide the guidance needed to prevent cross-contamination of samples collected contemporaneously for CFCs and trace elements.
    - Replace the sample discharge tubing with the appropriate tubing (table 5-8): refrigeration-grade copper or aluminum tubing are recommended; nylon tubing can be used but should be analyzed by the CFC laboratory before use; chromatographic-grade 304 stainless steel tubing also can be used. **Do not use fluorocarbon polymer tubing.**
3. Collect an equipment blank and submit for CFC analysis at least 1 week before collecting environmental samples.
    - For CFC sampling only, the matrix of the blank typically is water collected from a relatively deep well tapping an aquifer recharged only with pre-1940 water.
    - Ship the sample by overnight delivery to the USGS CFC Laboratory in Reston, Va.
    - Review QC-data results and make equipment changes accordingly. Proceed with sampling only if the equipment blanks are clean.
4. Collect preliminary samples for radiochemicals and VOC analyses at the well(s) selected (steps 5a through c below) and review the results before collecting or submitting the samples for CFC analyses. Select wells that are open hole or have metal or threaded (not glued) PVC casing. **Do not submit samples for CFC analyses that contain the following**:
    - Hazardous radioactive substances.
    - More than 0.5 mg/L of any CFC or other halocarbon (vinyl chloride, methyl chloride, methyl chloroform, methyl bromide, methylene chloride, chloroform, trichloroethylene, carbon trichloride, and tetrachloroethylene).

5. Sample collection.
   a. Review sampling plans.
   b. Measure the water level and prepare to purge the well.
   c. Purge the well, recording field measurements for specific electrical conductance, pH, temperature, and dissolved oxygen at approximately 5-minute intervals (NFM 4.2; NFM 6).
      - **The measurement of dissolved-oxygen concentrations is particularly important.**
      - **Record on field forms whether or not a hydrogen sulfide odor is detected.** Collect the samples needed for other organic and inorganic analyses. **Collection of samples for analysis of VOCs and tritium is strongly recommended when collecting samples for CFC analysis.**
   d. Set up the CFC sampling equipment. Replace the sample tubing, if necessary, or make adjustments to direct the sample flow through copper lines or other appropriate tubing.
      - **CFC samples must not come in contact with air.** Use only the CFC apparatus specifically designed for this purpose that is supplied by the CFC Laboratory.
      - Review the precautions listed for radon sampling (section 5.6.3.I) to prevent sample degassing and air contact.
   e. **Collect ground water into a borosilicate-glass ampoule—you will need five ampoules per well.** Flame-seal the ampoule. Repeat for each of the remaining ampoules. (It takes about 5 minutes to collect sample into an ampoule.)
      - Follow the instructions given in training for site evaluation and use of the CFC sampling apparatus.
      - After the last ampoule is filled and sealed, measure specific electrical conductance, pH, temperature, and dissolved oxygen and record the measurements on the field form.

6. Determine, if feasible, concentrations of hydrogen sulfide and methane, tritium/helium-3, and dissolved nitrogen and argon gases.
   a. Measure hydrogen sulfide concentrations (Baedecker and Cozzarelli, 1992) if there is a hydrogen sulfide odor.
   b. Collect sample for tritium/helium-3 age dating.
   c. Collect sample for analysis of dissolved nitrogen and argon gases (to determine temperature of recharge water) and arrange for dissolved gas analyses. USGS personnel should contact the Northeastern Region Common Use Laboratory at (703) 648-6234.
7. Label the sample ampoules as directed by the CFC Laboratory. Pack the ampoules in the boxes supplied by the CFC Laboratory (place padding on top of the ampoules). Be sure to pack the field form (fig. 5-4) in the box with the ampoules.
8. **Ship the CFC samples to arrive the next day,** from Monday through Thursday. Do not ship on a Friday; there must be no weekend overlay of samples.

USGS Chlorofluorocarbon Laboratory 1 of 2

Reston, VA 20192

REQUEST FOR CFC SAMPLING EQUIPMENT AND ANALYSIS

Today's date: _____ Name of contact: _____

Phone: _____ E-Mail: _____

FAX:_____

Description of job (where? project? purpose of CFC dating?):

_____

_____

_____

Shipping Address: _____

_____

_____

_____

_____

Account number for billing:_____

Dates of sampling:_____

When to ship equipment:_____

Date equipment and ampules will be returned to CFC lab:_____

Number of wells: _____

Well/Source: ___monitor; ___domestic; ___municipal; ___spring; ___other

Well diameters: ___2 in.; ___4 in.; ___6 in.; ___other: _____

Range of well depths: _____feet

Materials of well construction: ___PVC; ___metal; ___other

Pump to be used: _____

Figure 5–4. Request form for equipment, instructions, and analysis of chlorofluorocarbon samples.

REQUEST FOR CFC SAMPLING EQUIPMENT AND ANALYSIS, *Continued* 2 of 2

Material of discharge tubing of pump:_____

Equipment normally provided by laboratory includes CFC sampler, spare parts, CFC trap, ampoules, ampoule holder.

Do you also need:

Garden-hose connector to well? ____

Other? _____

Are dissolved gases to be sampled? ____ Contact 703-648-6234 or E-mail cfc@usgs.gov).

Which gases? _____

How many?_____

Will surface water be collected for CFC analysis? ____

How many samples and (or) stations? _____

Will air samples be collected for CFC analysis? ____

How many samples and (or) stations? _____

Do you need training on CFC sampling procedures? ___yes; ___no

Do you need the CFC laboratory to send personnel to help with training or sampling? ___yes; ___ no

Contacts and address for Reston CFC laboratory:

U.S. Geological Survey
432 National Center
12201 Sunrise Valley Drive
Reston, VA 20192

E-Mail: cfc@usgs.gov
Phone: 703-648-5838
FAX: 703-648-5832

Figure 5–4. Request form for equipment, instructions, and analysis of chlorofluorocarbon samples—*Continued.*

Table 5-8. Equipment and supplies used for collection of samples for chlorofluorocarbon analysis

[CFC, chlorofluorocarbon; %, percent; MAPP, methyl acetylene-propadiene + petroleum gas (liquefied); QW Tech Memo, Office of Water Quality Technical Memorandum 95.02]

Item	Description	Source
CFC sample apparatus and ampoules	Refer to Busenberg and Plummer (1992). Return unused ampoules to the laboratory. Check with CFC laboratory for pump type, fittings, and special connectors needed.	CFC Laboratory, USGS, MS 432, Reston, VA 20192 or E-mail cfc@usgs.gov
Field gases		Hardware or plumbing supplies
Ultra-pure nitrogen	*Two C-size tanks. Carrier grade 99.999% pure or better; one tank is used for backup.*	
Welding-grade oxygen	One C-size or two D-size tanks; or, cannisters for welding kit.	
MAPP gas or propane	Fuel gas, provided in a fully gaseous state.	
Sample tubing, fittings[1]		Plumbing supplies. For aluminum tubing, refer to QW Tech Memo 95.02
Copper, aluminum, or stainless steel	1/4-inch, refrigeration grade. Stainless steel: use chromatographic 304 grade.	
Compression fittings (such as Swagelok)	1/4-inch, preclean to remove lubricating oils or special order without lubricating oils.	Hardware supplies, or special order
Nylon[1] (copper or aluminum are preferred)	1/4-inch tubing; preclean as described for inorganic constituent samples in NFM 3.	Scientific suppliers
Torch and regulator equipment		Hardware suppliers
Welding kit (refer to description in QW Tech Memo 95.02	Example: Bernzomatic™ Model OX2500 or equivalent (contains torch, hoses, valves for canisters of oxygen and fuel gases, spark igniter).	If kit will not be used, have welding supplies assembled by a welding equipment store.
Oxygen regulator	Recommended for oxygen line.	
Field tools		Hardware suppliers
Wrenches, adjustable	12 inch (for attaching regulators to gas cylinders). 6-inch (for attaching gas and water lines). Allen wrench set (for sampler repairs).	
Pliers	Needle-nose and standard.	
Screwdrivers	Phillips and standard.	
Tubecutter	For 1/8-inch and 1/4-inch tubing.	
Tape	Fluorocarbon polymer (PTFE) and electrical.	
Spark igniter	To light torch.	
Wash bottle	250 milliliter (for water to clean off sampler).	
Metal file	To smooth the cut edges of metal tubing.	

[1]**Materials not suitable for tubing:** Tygon, silicone rubber, most plastics (including fluorocarbon polymers), rubbers. Use only refrigeration-grade copper or aluminum tubing, as other grades have oil coatings inside. If using nylon tubing, send it to the CFC laboratory for analysis to confirm that it does not contain substances that might affect CFC analysis.

CONVERSION FACTORS, SELECTED TERMS, ABBREVIATIONS, AND CHEMICAL FORMULAS

CONVERSION FACTORS

Multiply	By	To obtain
micrometer (µm)	0.00003937	inch
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
microliter (µL)	0.0000338	ounce, fluid
milliliter (mL)	0.0338	ounce, fluid
	0.000264	gallon
liter (L)	0.2642	gallon
nanogram (ng)	3.53×10^{-11}	ounce
microgram (µg)	3.53×10^{-8}	ounce
milligram (mg)	0.0000353	ounce
gram (g)	0.03527	ounce, avoirdupois
kilopascal	0.1450	pound per square inch
picocurie (pCi)	0.037	Becquerle (Bq)

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$

Selected Terms

Editors and authors of the *National Field Manual* have attempted to use terms common in the water-quality community. Some of the terms used have restricted meanings within the context of this report. The following terms either are used in a context familiar primarily to USGS personnel, or in a format that is more succinct, or that is considered to be more specific than a common usage:

Accuracy: The degree of agreement of a measured value with the true or expected value (from Taylor, 1987).

Analyte (target analyte): "Substances being determined in an analysis" (from Bennett, 1986). The term target analyte is used in this report to refer to any chemical or biological substance for which concentrations in a sample will be determined. The definition for target analyte does not include field-measured parameters such as temperature, specific electrical conductance, pH, dissolved oxygen, Eh, alkalinity, color, or turbidity.

Bias: Systematic error inherent in a method or caused by some artifact or idiosyncrasy of the sample measurement, collection, or processing system. The error can be positive (indicating contamination) or negative (indicating loss of analyte concentration) (from Taylor, 1987).

Contaminant: Biological or chemical substances added to the medium of concern, commonly through human activity.

Contamination (of water): Change of ambient water composition by the addition of biological or chemical substances as a result of human activity or natural processes. Addition of such substances can be detrimental to the quality of the water resource.

Data-quality requirements: The subset of data-quality objectives pertaining specifically to the analytical detection level for concentrations of target analytes and the variability allowable to fulfill the scientific objectives of the study.

Quality Assurance (QA): The systematic management of data-collection systems by using prescribed guidelines and criteria for implementing technically approved methods and policies. Quality assurance incorporates a comprehensive plan that outlines the overall process for providing a product or service that will satisfy the given requirements for quality.

Quality Control (QC): The specific operational techniques and activities used to obtain the required quality of data. Quality control consists of the application of technical procedures to achieve prescribed standards of performance and to document the quality of collected data. Quality-control data are used to identify and evaluate any corrective actions necessary to improve performance or data interpretation to acceptable levels.

Trace element(s): For the purpose of this report and to maintain consistency with common usage, the term trace element(s) is used to refer to metal and nonmetal inorganic elements such as arsenic, antimony, selenium, and tellurium that usually are present in natural surface-water and ground-water systems in concentrations less than 1 mg/L (modified from Hem, 1985). Common usage of this term, as defined above, is inexact and not rigorous with respect to aqueous chemistry.

Abbreviations

cc	cubic centimeter
lb/in^2	pounds per square inch
min	minute
mg/L	milligram per liter

µg/L	microgram per liter (equivalent to parts per billion (ppb))
mL/min	milliliters per minute
ng/L	nanogram per liter
ng/µL	nanogram per microliter
pCi	picocuries
ppb	parts per billion (see µg/L)
ANC	*acid neutralizing capacity*
ASR	Analytical Services Request
BNA	base-neutral acids
CFC	chlorofluorocarbon
CH	Clean Hands
DH	Dirty Hands
DIC	dissolved inorganic carbon
DIW	distilled/deionized water
DOC	dissolved organic carbon
FA	filtered, acidified sample
FAM	filtered, acidified sample for analysis of mercury
FAR	filtered, acidified sample for analyses of selected radiochemicals
FCA	filtered, chilled, acidified sample
FCC	filtered, chilled sample
FEP	fluorinated ethylene-propylene
FU	filtered, untreated sample
GCC	glass, chilled sample for analysis of nonvolatile organic compounds
GC/MS	gas chromatograph/mass spectrophotometer
IBW	inorganic-grade blank water (water with certified analysis of trace elements and other inorganic constituents and used for blank QC samples for analysis of inorganic constituents)
MBAS	methylene blue active substances
NAWQA	National Water-Quality Assessment Program
NFM	*National Field Manual for the Collection of Water-Quality Data*
NPDES	National Pollutant Discharge Elimination System
NWQL	National Water Quality Laboratory of the U.S. Geological Survey (Denver, Colo.)
OWQ	*Office of Water Quality of the U.S. Geological Survey* (Reston, Va.)
PBW	pesticide-grade blank water (water certified free of pesticide compounds)
PCB	polychlorinated biphenyl
QA	quality assurance
QC	quality control

QW	quality of water
QWSU	Quality of Water Service Unit of the U.S. Geological Survey (Ocala, Fla.)
RA	raw, acidified sample
RAH	raw, acidified sample for analysis of antimony, arsenic, and (or) selenium
RAM	raw, acidified sample for analysis of mercury
RCB	raw, chilled sample
RU	raw, untreated sample
RUR	raw, untreated sample for analysis of selected radiochemicals
RUS	raw, untreated sample for analysis of stable isotopes
SOC	suspended organic carbon
SPE	solid-phase extraction
TOC	total organic carbon
URL	Uniform Resource Locator
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VBW	volatile-organic-compounds-grade blank water (water certified free of VOCs)
VOC	volatile organic compounds
WCA	raw, chilled, acidified nutrient sample

Chemical Formulas

Ag_2S	silver sulfide
$AgNO_3$	silver nitrate
$BaSO_4$	barium sulfate
$^{13}C/^{12}C$	carbon-13/carbon-12 isotope ratio
^{14}C	carbon-14
$CuSO_4$	copper sulfate
$^{2}H/^{1}H$	deuterium/protium isotope ratio
$^{3}H/^{3}He$	tritium/helium-3 isotope ratio
HCl	hydrochloric acid

H_2O	water
H_2S	hydrogen sulfide
H_2SO_4	sulfuric acid
H_3PO_4	phosphoric acid
HNO_3	nitric acid
$HNO_3/K_2Cr_2O_7$	nitric acid/potassium dichromate
NaCl	sodium chloride
NaOH	sodium hydroxide
$^{15}N/^{14}N$	nitrogen-15/nitrogen-14 isotope ratio
$^{18}O/^{16}O$	oxygen-18/oxygen-16 isotope ratio
$^{34}S/^{32}S$	sulfur-34/sulfur-32 isotope ratio
$SrCl_2$	strontium chloride

SELECTED REFERENCES AND INTERNAL DOCUMENTS

SELECTED REFERENCES FOR PROCESSING OF WATER SAMPLES

American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Standard methods for the examination of water and wastewater (18th ed.): Washington, D.C., American Public Health Association, variously paged.

Baedecker, M.J., and Cozzarelli, I.M., 1992, The determination and fate of unstable constituents of contaminated groundwater, *in* Lesage, Suzanne, and Jackson, R.E., eds., 1992, Groundwater contamination and analysis at hazardous waste sites: New York, Marcel Dekker, p. 425-461.

Bennett, H., ed., 1986, Concise chemical and technical dictionary (4th ed.): New York, *Chemical Publishing Co., p. 99.*

Burkhardt, M.R., Kammer, J.A., Jha, V.K, Omara-Lopez, P.G., and Woodworth, M.T., 1997, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of nonpurgeable suspended organic carbon by wet-chemical oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 97-380, 33 p.

Busenberg, Eurybiades, and Plummer, L.N., 1992, Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age-dating tools—Example, The alluvium and terrace system of central Oklahoma: Water Resources Research, v. 28, no. 9, p. 2257-2283.

Capel, P.D., and Larson, S.J., 1996, Evaluation of selected information on splitting devices for water samples: U.S. Geological Survey Water-Resources Investigations Report 95-4141, 103 p.

Capel, P.D., Nacionales, F.C., and Larson, S.J., 1995, Precision of a splitting device for water samples: U.S. Geological Survey Open-File Report 95-293, 6 p.

Carmody, R.W., Plummer, L.N., Busenberg, Eurybiades, and Coplen, T.B., 1998, Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotopic composition: U.S. Geological Survey Open-File Report 97-234, 91 p.

Edwards, T.K., and Glysson, G.D., 1998, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 80 p.

Gibs, Jacob, and Imbrigiotta, T.E., 1990, Well-purging criteria for sampling purgeable organic compounds: Ground Water, v. 28, no. 1, p 68-78.

Horowitz, A.J., Demas, C.R., Fitzgerald, K.K., Miller, T.L., and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.

Horowitz, A.J., Elrick, K.A., and Colberg, M.R., 1992, The effect of membrane filtration artifacts on dissolved trace element concentrations: Water Resources, v. 26, no. 6, p. 753-763.

Keith, L.H., ed., 1988, Principles of environmental sampling: Washington, D.C., American Chemical Society, 458 p.

Keith, L.H., ed., 1991, Compilation of EPA's sampling and analysis methods: Chelsea, Mich., Lewis Publishers, 803 p.

Keith, L.H., Crummett, W., Deegan, J., Libby, R.A., Taylor, J.K., and Wentler, G., 1983, Principles of environmental analysis: Analytical Chemistry, v. 55, p. 2210-2218.

Kennedy, V.C., Jenne, E.A., and Burchard, J.M., 1976, Backflushing filters for field processing of water samples prior to trace-element analyses: U.S. Geological Survey Water-Resources Investigations Report 76-126, 12 p.

Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1997, Guidelines and standard procedures for studies of ground-water quality—selection and installation of wells, and supporting documentation: U.S. Geological Survey Water-Resources Investigations Report 96-4233, 110 p.

Lindley, C.E., Stewart, J.T., and Sandstrom, M.W., 1996, Determination of low concentrations of acetochlor in water by automated solid-phase extraction and gas chromatography with mass-selective detection: Journal of AOAC International, v. 79, no. 4, p. 962-966.

Manning, T.K., Smith, K.E., Wood, C.D., and Williams, J.B., 1994, Pesticide-sampling equipment, sample-collection and processing procedures, and water-quality data at Chicod Creek, North Carolina, 1992: U.S. Geological Survey Open-File Report 94-50, 35 p.

McCarthy, J.F., 1988, Mobility of colloidal particles in the subsurface—chemistry and hydrology of colloid-aquifer interactions: Oak Ridge, Tenn., Oak Ridge National Laboratory, 111 p.

McCarthy, J.F., and Zachara, J.M., 1989, Subsurface transport of contaminants: Environmental Science and Technology, v. 5, no. 23, p. 496-502.

Norris, J., 1988, Techniques for sampling surface and industrial waters—special considerations and choices, *in* Keith, L.H., ed., Principles of environmental sampling: Washington, D.C., American Chemical Society, p. 247-253.

Plummer, L.N., Michel, R.L., Thurman, E.M., and Glynn, P.D., 1993, Environmental tracers for age dating young ground water, *in* Alley, W.M., ed., Regional ground-water quality, chap. 11: New York, Van Nostrand Reinhold, p. 255-294.

Puls, R.W., and Barcelona, M.J., 1989, Ground water sampling for metals analyses: Washington, D.C., U.S. Environmental Protection Agency, Office of Research and Development, EPA Ground Water Issue, EPA/540/4-89/001, 6 p.

Robards, Kevin, McKelvie, I.D., Benson, R.L., Worsfold, P.J., Blundell, N.J., and Casey, Harry, 1994, Determination of carbon, phosphorus, nitrogen and silicon species in waters: Analytica Chemica Acta, v. 287, p. 147-190.

Salonen, Kalevi, 1979, Comparison of different glass fibre and silver metal filters for the determination of particulate organic carbon: Hydrobiologia, v. 67, p. 29-32.

Sandstrom, M.W., 1990, Sampling requirements for organic contaminants, *in* American Water Works Association Annual Conference: Cincinnati, Ohio, Management Challenges of New Monitoring Requirements for Organic Chemicals, American Water Works Association Seminar Proceedings, p. 71-85.

Sandstrom, M.W., 1995, Filtration of water-sediment samples for the determination of organic compounds: U.S. Geological Survey Water-Resources Investigations Report 95-4105, 13 p.

Sandstrom, M.W., Wyodoski, D.S., Schroeder, M.P., Zamboni, J.L., and Foreman, W.T., 1992 [1994], Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of organonitrogen herbicides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 91-519, 26 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.

Taylor, J.K., 1987, Quality assurance of chemical measurements: Chelsea, Mich., Lewis Publishers, 328 p.

Timme, P.J., 1995, National Water Quality Laboratory 1995 services catalog: U.S. Geological Survey Open-File Report 95-352, 120 p.

U.S. Environmental Protection Agency, 1980, Samplers and sampling procedures for hazardous waste stream: EPA 600/2-80-018, 70 p.

_____1982a, Sampling protocols for collecting surface water, bed sediment, bivalves, and fish for priority pollutant analysis: Washington, D.C., Final Draft Report, Office of Water Regulations and Standards Monitoring and Data Support Division, EPA 68-01-6195, variously paged.

_____1982b, Handbook for sampling and sample preservation of water and wastewater: Cincinnati, Ohio, Environment Monitoring and Support Laboratory, EPA 600/4-82-029, 402 p.

_____1983, Addendum to Handbook for sampling and sample preservation of water and wastewater: Environment Monitoring and Support Laboratory, Cincinnati, Ohio, EPA 600/4-82-029, 28 p.

_____1987, A compendium of Superfund field operations methods: Washington, D.C., Office of Emergency and Remedial Response, EPA/540-P-87/001, 508 p.

U.S. Geological Survey, 1984, Chemical and physical quality of water and sediment, chap. 5 *in* U.S. Geological Survey, National handbook of recommended methods for water-data acquisition: p. 5-1 to 5-194.

Ward, J.R., and Harr, C.A., eds., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90-140, 71 p.

Wells, F.C., Gibbons, W.J., and Dorsey, M.E., 1990, Guidelines for collection and field analysis of water-quality samples from streams in Texas: U.S. Geological Survey Open-File Report 90-127, 79 p.

Werner, S.L., Burkhardt, M.R., and DeRusseau, S.N., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open-File Report 96-216, 42 p.

Williams, P.M., Bauer, J.E., Robertson, K.J., Wolgast, D.M., and Occelli, M.L., 1993, Report on DOC and DON measurements made at Scripps Institution of Oceanography, 1988-1991: Marine Chemistry, v. 41, p. 271-281.

Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181, 49 p.

Internal Documents

Office of Water Quality and National Water Quality Laboratory technical memorandums are available through the USGS Home Page on the World Wide Web. The site address (URL) is http://water.usgs.gov/lookup/get?techmemo.

Memo No.	Title	Date
	Water Quality	

qw92.01	Distilled/Deionized Water for District Operations	December 20, 1991
qw92.02	FIELD TECHNIQUES--Field Preparation of Containers for Aqueous Samples	December 20, 1991
qw92.06	Report of Committee on Sample Shipping Integrity and Cost	March 20, 1992
qw92.11	FIELD TECHNIQUES--Return of Spent Mercury and Dichromate Ampoules to the National Water Quality Laboratory	July 16, 1992
qw94.09	Revision of New Division Protocol for *Collecting and Processing Surface-Water* Samples for Low-Level Inorganic Analyses	January 28, 1994
qw94.16	New Preservation Techniques for Nutrient Samples	August 5, 1994
qw95.02*	Establishment of U.S. Geological Survey (USGS) Laboratory for Determination of Chlorofluorocarbons (CFCs) in Air and Water Samples	December 29, 1994
qw97.03	Protocols for Cleaning a Teflon Cone Splitter to Produce Contaminant-Free Subsamples for Subsequent Determinations of Trace Elements	February 7, 1997
qw97.06	Comparison of the Suspended-Sediment Splitting Capabilities of the Churn and Cone Splitters	May 5, 1997
qw99.04	Changes in Field Treatment Protocols and Bottle Types for Whole-Water Samples Collected for Total Ammonium Plus Organic Nitrogen and Total Phosphorus Determinations	November 25, 1998

*95.02 was prepared jointly by the Office of Water Quality and the Office of Ground Water.

Memo No.	Title	Date
	National Water Quality Laboratory	
92.01	Technology Transfer. Availability of Equipment Blank Water for Inorganic & Organic Analyses	March 25, 1992
92.04	Bottles for Tritium Analyses	August 12, 1992
93.01	Identification of Low Levels of Sodium Contamination in Nitric Acid Samples	October 5, 1992
93.09	Radon—Discontinuance of Duplicate Samples for Radon-In-Water	August 24, 1993
95.04	Shipping Samples to the National Water Quality Laboratory	December 2, 1994
95.05	Nitrogen Isotope Sample Preservation for Water Samples	March 8, 1995
96.05	Collection, Processing, and Analysis of Carbon Isotope Samples	April 5, 1996
97.01 97.01S	Use of Syringes to Add Volatile Organic Compounds to Water Samples for Use as Matrix Spike Samples (97.01S is supplementary)	November 5, 1996
97.04S	Collection, Processing, and Analysis of Ground-Water Samples for Tritium/Helium-3 Dating	April 7, 1997
97.05	Using the National Water Quality Laboratory for the Analysis of Drinking Water Samples	February 28, 1997

PUBLICATIONS ON TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The material is grouped under major subject headings called books and is further divided into sections and chapters. For example, Section A of Book 9 (Handbooks for Water-Resources Investigations) pertains to collection of water-quality data. The chapter, which is the unit of publication, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises.

The Techniques of Water-Resources Investigations (TWRI) reports listed below are for sale by the U.S. Geological Survey, Branch of Information Services, Box 25286, Federal Center, Denver, CO 80225 (authorized agent of the Superintendent of Documents, Government Printing Office). Prepayment is required. Remittance should be sent by check or money order payable to the U.S. Geological Survey. Prices are not included because they are subject to change. Current prices can be obtained by writing to the above address. When ordering or inquiring about prices for any of these publications, please give the title, book number, chapter number, and "U.S. Geological Survey Techniques of Water-Resources Investigations." An updated list of TWRI reports can be found by accessing the World Wide Web url: http://water.usgs.gov/lookup/get?TWRI.

Book 1. Collection of Water Data by Direct Measurement

Section D. Water Quality

1–D1. Water temperature—influential factors, field measurement, and data presentation, by H.H. Stevens, Jr., J.F. Ficke, and G.F. Smoot: USGS—TWRI Book 1, Chapter D1. 1975. 65 pages.

1–D2. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents, by W.W. Wood: USGS—TWRI Book 1, Chapter D2. 1976. 24 pages.

Book 2. Collection of Environmental Data

Section D. Surface Geophysical Methods

2–D1. Application of surface geophysics to ground-water investigations, by A.A.R. Zohdy, G.P. Eaton, and D.R. Mabey: USGS—TWRI Book 2, Chapter D1. 1974. 116 pages.

2–D2. Application of seismic-refraction techniques to hydrologic studies, by F.P. Haeni: USGS—TWRI Book 2, Chapter D2. 1988. 86 pages.

Section E. Subsurface Geophysical Methods

2–E1. Application of borehole geophysics to water-resources investigations, by W.S. Keys and L.M. MacCary: USGS—TWRI Book 2, Chapter E1. 1971. 126 pages.

2–E2. Borehole geophysics applied to ground-water investigations, by W.S. Keys: USGS—TWRI Book 2, Chapter E2. 1990. 150 pages.

Section F. Drilling and Sampling Methods

2–F1.Application of drilling, coring, and sampling techniques to test holes and wells, by Eugene Shuter and W.E. Teasdale: USGS—TWRI Book 2, Chapter F1. 1989. 97 pages.

Book 3. Applications of Hydraulics

Section A. Surface-Water Techniques

3–A1.General field and office procedures for indirect discharge measurements, by M.A. Benson and Tate Dalrymple: USGS—TWRI Book 3, Chapter A1. 1967. 30 pages.

3–A2.Measurement of peak discharge by the slope-area method, by Tate Dalrymple and M.A. Benson: USGS—TWRI Book 3, Chapter A2. 1967. 12 pages.

3–A3.Measurement of peak discharge at culverts by indirect methods, by G.L. Bodhaine: USGS—TWRI Book 3, Chapter A3. 1968. 60 pages.

3–A4.Measurement of peak discharge at width contractions by indirect methods, by H.F. Matthai: USGS—TWRI Book 3, Chapter A4. 1967. 44 pages.

3–A5.Measurement of peak discharge at dams by indirect methods, by Harry Hulsing: USGS—TWRI Book 3, Chapter A5. 1967. 29 pages.

3–A6.General procedure for gaging streams, by R.W. Carter and Jacob Davidian: USGS—TWRI Book 3, Chapter A6. 1968. 13 pages.

3–A7.Stage measurement at gaging stations, by T.J. Buchanan and W.P. Somers: USGS—TWRI Book 3, Chapter A7. 1968. 28 pages.

3–A8.Discharge measurements at gaging stations, by T.J. Buchanan and W.P. Somers: USGS—TWRI Book 3, Chapter A8. 1969. 65 pages.

3–A9.Measurement of time of travel in streams by dye tracing, by F.A. Kilpatrick and J.F. Wilson, Jr.: USGS—TWRI Book 3, Chapter A9. 1989. 27 pages.

3–A10.Discharge ratings at gaging stations, by E.J. Kennedy: USGS—TWRI Book 3, Chapter A10. 1984. 59 pages.

3–A11.Measurement of discharge by the moving-boat method, by G.F. Smoot and C.E. Novak: USGS—TWRI Book 3, Chapter A11. 1969. 22 pages.

3–A12.Fluorometric procedures for dye tracing, Revised, by J.F. Wilson, Jr., E.D. Cobb, and F.A. Kilpatrick: USGS—TWRI Book 3, Chapter A12. 1986. 34 pages.

3–A13.Computation of continuous records of streamflow, by E.J. Kennedy: USGS—TWRI Book 3, Chapter A13. 1983. 53 pages.

3–A14.Use of flumes in measuring discharge, by F.A. Kilpatrick and V.R. Schneider: USGS—TWRI Book 3, Chapter A14. 1983. 46 pages.

3–A15.Computation of water-surface profiles in open channels, by Jacob Davidian: USGS—TWRI Book 3, Chapter A15. 1984. 48 pages.

3–A16.Measurement of discharge using tracers, by F.A. Kilpatrick and E.D. Cobb: USGS—TWRI Book 3, Chapter A16. 1985. 52 pages.

3–A17.Acoustic velocity meter systems, by Antonius Laenen: USGS—TWRI Book 3, Chapter A17. 1985. 38 pages.

3–A18.Determination of stream reaeration coefficients by use of tracers, by F.A. Kilpatrick, R.E.þRathbun, Nobuhiro Yotsukura, G.W.þParker, and L.L. DeLong: USGS—TWRI Book 3, Chapter A18. 1989. 52 pages.

3–A19.Levels at streamflow gaging stations, by E.J. Kennedy: USGS—TWRI Book 3, Chapter A19. 1990. 31 pages.

3–A20.Simulation of soluble waste transport and buildup in surface waters using tracers, by F.A. Kilpatrick: USGS—TWRI Book 3, Chapter A20. 1993. 38 pages.

3–A21.Stream-gaging cableways, by C. Russell Wagner: USGS—TWRI Book 3, Chapter A21. 1995. 56 pages.

Section B. Ground-Water Techniques

3–B1. Aquifer-test design, observation, and data analysis, by R.W. Stallman: USGS—TWRI Book 3, Chapter B1. 1971. 26 pages.

3–B2.Introduction to ground-water hydraulics, a programed text for self-instruction, by G.D. Bennett: USGS—TWRI Book 3, Chapter B2. 1976. 172 pages.

3–B3.Type curves for selected problems of flow to wells in confined aquifers, by J.E. Reed: USGS—TWRI Book 3, Chapter B3. 1980. 106 pages.

3–B4.Regression modeling of ground-water flow, by R.L. Cooley and R.L. Naff: USGS—TWRI Book 3, Chapter B4. 1990. 232 pages.

3–B4.Supplement 1. Regression modeling of ground-water flow—Modifications to the computer code for nonlinear regression solution of steady-state ground-water flow problems, by R.L. Cooley: USGS—TWRI Book 3, Chapter B4. 1993. 8 pages.

3–B5.Definition of boundary and initial conditions in the analysis of saturated ground-water flow systems—An introduction, by O.þL.þFranke, T.E. Reilly, and G.D. Bennett: USGS—TWRI Book 3, Chapter B5. 1987. 15 pages.

3–B6.The principle of superposition and its application in ground-water hydraulics, by T.E. Reilly, O.L.þFranke, and G.D.þBennett: USGS—TWRI Book 3, Chapter B6. 1987. 28 pages.

3–B7.Analytical solutions for one-, two-, and three-dimensional solute transport in ground-water systems with uniform flow, by E.J. Wexler: USGS—TWRI Book 3, Chapter B7. 1992. 190 pages.

Section C. Sedimentation and Erosion Techniques

3–C1.Fluvial sediment concepts, by H. P. Guy: USGS—TWRI Book 3, Chapter C1. 1970. 55 pages.

3–C2.Field methods for measurement of fluvial sediment, by T.K. Edwards and G.D. Glysson: USGS—TWRI Book 3, Chapter C2. 1998. 80 pages.

3–C3.Computation of fluvial-sediment discharge, by George Porterfield: USGS—TWRI Book 3, ChapterþC3. 1972. 66 pages.

Book 4. Hydrologic Analysis and Interpretation

Section A. Statistical Analysis

4–A1.Some statistical tools in hydrology, by H.C. Riggs: USGS—TWRI Book 4, Chapter A1. 1968. 39þpages.

4–A2.Frequency curves, by H.C. Riggs: USGS—TWRI Book 4, Chapter A2. 1968. 15 pages.

Section B. Surface Water

4–B1.Low-flow investigations, by H.C. Riggs: USGS—TWRI Book 4, Chapter B1. 1972. 18 pages.

4–B2.Storage analyses for water supply, by H.C. Riggs and C.H. Hardison: USGS—TWRI Book 4, Chapter B2. 1973. 20 pages.

4–B3.Regional analyses of streamflow characteristics, by H.C. Riggs: USGS—TWRI Book 4, ChapterþB3. 1973. 15 pages.

Section D. Interrelated Phases of the Hydrologic Cycle

4–D1.Computation of rate and volume of stream depletion by wells, by C.T. Jenkins: USGS—TWRI Bookþ4, Chapter D1. 1970. 17 pages.

Book 5. Laboratory Analysis

Section A. Water Analysis

5–A1.Methods for determination of inorganic substances in water and fluvial sediments, by M.J.þFishman and L.C. Friedman, editors: USGS—TWRI Book 5, Chapter A1. 1989. 545 pages.

5–A2.Determination of minor elements in water by emission spectroscopy, by P.R. Barnett and E.C.þMallory, Jr.: USGS—TWRI Book 5, Chapter A2. 1971. 31 pages.

5–A3.Methods for the determination of organic substances in water and fluvial sediments, edited by R.L. Wershaw, M.J.þFishman, R.R. Grabbe, and L.E. Lowe: USGS—TWRI Book 5, Chapter A3. 1987. 80 pages.

5–A4.Methods for collection and analysis of aquatic biological and microbiological samples, by L.J.þBritton and P.E. Greeson, editors: USGS—TWRI Book 5, Chapter A4. 1989. 363 pages.

5–A5.Methods for determination of radioactive substances in water and fluvial sediments, by L.L.þThatcher, V.J. Janzer, and K.W.þEdwards: USGS—TWRI Book 5, Chapter A5. 1977. 95þpages.

5–A6.Quality assurance practices for the chemical and biological analyses of water and fluvial sediments, by L.C. Friedman and D.E. Erdmann: USGS—TWRI Book 5, Chapter A6. 1982. 181þpages.

Section C. Sediment Analysis

5–C1.Laboratory theory and methods for sediment analysis, by H. P. Guy: USGS—TWRI Book 5, ChapterþC1. 1969. 58 pages.

Book 6. Modeling Techniques

Section A. Ground Water

6–A1.A modular three-dimensional finite-difference ground-water flow model, by M.G. McDonald and A.W. Harbaugh: USGS—TWRI Book 6, Chapter A1. 1988. 586 pages.

6–A2.Documentation of a computer program to simulate aquifer-system compaction using the modular finite-difference ground-water flow model, by S.A. Leake and D.E. Prudic: USGS—TWRI Book 6, Chapter A2. 1991. 68 pages.

6–A3.A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 1: Model Description and User's Manual, by L.J. Torak: USGS—TWRI Book 6, Chapter A3. 1993. 136 pages.

6–A4.A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 2: Derivation of finite-element equations and comparisons with analytical solutions, by R.L. Cooley: USGS—TWRI Book 6, Chapter A4. 1992. 108 pages.

6–A5.A modular finite-element model (MODFE) for areal and axisymmetric ground-water-flow problems, Part 3: Design philosophy and programming details, by L.J. Torak: USGS—TWRI Book 6, Chapter A5, 1993. 243 pages.

6–A6.A coupled surface-water and ground-water flow model (MODBRANCH) for simulation of stream-aquifer interaction by E.D. Swain and Eliezer J. Wexler: USGS—TWRI Book 6, Chapter A6, 1996. 125 pages.

Book 7. Automated Data Processing and Computations

Section C. Computer Programs

7–C1.Finite difference model for aquifer simulation in two dimensions with results of numerical experiments, by P.C. Trescott, G.F.þPinder, and S.P. Larson: USGS—TWRI Book 7, Chapter C1. 1976. 116 pages.

7–C2.Computer model of two-dimensional solute transport and dispersion in ground water, by L.F.þKonikow and J.D.þBredehoeft: USGS—TWRI Book 7, Chapter C2. 1978. 90 pages.

7–C3.A model for simulation of flow in singular and interconnected channels, by R.W. Schaffranek, R.A.þBaltzer, and D.E.þGoldberg: USGS—TWRI Book 7, Chapter C3. 1981. 110 pages.

Book 8. Instrumentation

Section A. Instruments for Measurement of Water Level

8–A1.Methods of measuring water levels in deep wells, by M.S. Garber and F.C. Koopman: USGS—TWRI Book 8, Chapter A1. 1968. 23 pages.

8–A2.Installation and service manual for U.S. Geological Survey manometers, by J.D. Craig: USGS—TWRI Book 8, Chapter A2. 1983. 57 pages.

Section B. Instruments for Measurement of Discharge

8–B2.Calibration and maintenance of vertical-axis type current meters, by G.F. Smoot and C.E. Novak: USGS—TWRI Book 8, Chapter B2. 1968. 15 pages.

Book 9. Handbooks for Water-Resources Investigations

Section A. National Field Manual for the Collection of Water-Quality Data

9–A1.Preparations for water sampling, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo: USGS—TWRI Book 9, Chapter A1. 1998. Variously paged.

9–A2.Selection of equipment for water sampling, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A2. 1998. Variously paged.

9–A3. Cleaning of equipment for water sampling, by F.D. Wilde, D.B., Radke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A3. 1998. Variously paged.

9–A4.Collection of water samples, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A4. 1999. Variously paged.

9–A5.Processing of water samples, by F.D. Wilde, D.B. Radtke, Jacob Gibs, and R.T. Iwatsubo, editors: USGS—TWRI Book 9, Chapter A5. 1999. Variously paged.

9–A6.Field measurements, by F.D. Wilde and D.B. Radtke, editors: USGS—TWRI Book 9, Chapter A6. 1998. Variously paged.

9–A7.Biological indicators, by D.N. Myers and F.D. Wilde, editors: USGS—TWRI Book 9, Chapter A7. 1997. Variously paged.

9–A8.Bottom-material samples, by D.B. Radtke: USGS—TWRI Book 9, Chapter A8. 1998. Variously paged.

9–A9.Safety in field activities, by S.L. Lane and R.G. Fay: USGS—TWRI Book 9, Chapter A9. 1998. Variously paged.

Appendix A5-A. Sample-designation codes and a summary of field-processing requirements for analyses of organic compounds in water

[NWQL, National Water Quality Laboratory of the U.S. Geological Survey; mL, milliliters; °C, degrees Celsius; HCl, hydrochloric acid; mg, milligram; L, liter; LC, laboratory code; %, percent; H_3PO_4, phosphoric acid; $CuSO_4$, copper sulfate; g/L, grams per liter; µm, micrometer; GF/F, baked glass fiber filter media; SH, schedule number; mm, millimeter; SPE, solid-phase extraction; <, less than; oz, ounce; in, inch]

Organic compound[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation[3]
Volatile or purgeable organic compounds (VOCs or POCs)	40-mL baked glass septum vial. Replicates are required and numbered in the order filled. Fill 3 vials for ground water, 4 vials for surface water. **No field rinse.**	VOC	Raw sample. Do not let sample degas. Chill/maintain at 4°C. • For treated sample[4]: Add two drops of 1:1 HCl from Teflon™ dropper bottle • If residual chlorine is present, add 25 mL ascorbic acid to vial before filling.
Methylene-chloride-extractable compounds (BNAs)	500-mL baked glass bottle. **No field rinse.**	GCC	Fill bottle to shoulder. Add 1 mL concentrated sulfuric acid to adjust to pH <2. If chlorine is suspected in the sample, add 100 mg ferrous sulfate. Mix, chill, and maintain at 4°C.
Phenols	1-L baked amber glass bottle. **No field rinse.**	LC0052	Raw sample. Add 2 mL of 8.5% H_3PO_4 to 1 L sample to pH 4. Add 10 mL $CuSO_4$ (100 g/L). Fill to shoulder. Chill/maintain at 4°C.
Polychlorinated biphenyls (PCBs)	1-L baked glass bottle. **No field rinse.**	GCC	Raw, untreated sample. Chill/maintain at 4°C.
Pesticides (raw)	1-L baked amber glass bottle. **No field rinse.**	GCC	Raw, untreated sample. Chill/maintain at 4°C.
• Organo-nitrogen herbicides	1-L baked amber glass bottle. **No field rinse.**	GCC	Raw sample, untreated. Chill/maintain at 4°C.
Pesticides (filtered)	1-L baked amber glass bottle. **No field rinse.**	GCC	Filtered sample (0.7-µm GF/F). Chill/maintain at 4°C.
• Organo-nitrogen herbicides	125-mL baked amber glass bottle. **No field rinse.**	GCC (SH1379)	Filtered sample, untreated. Optional: use 25-mm nylon filter capsule. Chill/maintain at 4°C.

Appendix A5-A. Sample-designation codes and a summary of field-processing requirements for analyses of organic compounds in water—*Continued*

Organic compound[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation[3]
• Broad spectrum pesticides by C-18 SPE	C-18 SPE column.	SH2010	Filtered sample (0.7-µm GF/F), pass through SPE column and treat as described in text. Chill/maintain at 4°C.
• Broad spectrum pesticides by Carbopak-B™ SPE	Carbopak-B™ SPE column.	SH2051	Filtered sample (0.7-µm GF/F), pass through SPE column and treat as described in text. Chill/maintain at 4°C
Total particulate carbon (TPC)[5]	6-oz and 18-oz Whirl-Pak bags	TPC (LC2606)	Retain particulate material on 25-mm baked glass microfiber filters (GF/F). Fold filters into 6-in x 6-in aluminum foil squares, as described in the text, label, and place into 6-oz bag and then into 18-oz bag. Chill/maintain at 4°C.
Total organic carbon (TOC)	125-mL baked glass bottle. **No field rinse.**	TOC (LC0114)	Raw sample, untreated. Fill to shoulder. Chill/maintain at 4°C.
Dissolved (filtered) organic carbon (DOC)	125-mL baked glass bottle. **No field rinse.**	DOC (LC0113)	Filtered sample (silver filter media), untreated. Fill to shoulder. Chill/maintain at 4°C.
Suspended organic carbon (SOC)	Petri dish, plastic. No field rinse.	SOC (LC0305)	Retain suspended materials on silver filter, untreated. Chill/maintain at 4°C.
Methylene blue active substances (MBAS)	250-mL polyethylene bottle. **Field rinse.**	RCB	Raw sample, untreated. Fill to shoulder. Chill/maintain at 4°C.
Oil and grease	1-L baked glass bottle. **No field rinse.**	GCC (LC2125)	Raw sample. Leave small headspace. Add about 2 mL H_2SO_4 to lower pH to <2. Chill/maintain at 4°C.

Appendix A5-A. Sample-designation codes and a summary of field-processing requirements for analyses of organic compounds in water—*Continued*

Explosives	1-L baked amber glass bottle. **No field rinse.**	GCC (SH 1377)	Filtered sample (0.7 µm GF/F), untreated. Chill/maintain at 4°C.
Total petroleum hydrocarbons	1-L baked glass bottle. **No field rinse.**	GCC (LC2126)	Raw sample. Leave small headspace. Add about 2 mL H_2SO_4 to lower pH to <2. Chill/maintain at 4°C.
Ultraviolet-absorbing substances			

[1]This table is not complete or comprehensive. Check with NWQL for the most current information on analytical schedules, laboratory codes, parameter codes, sample requirements, prices, and associated information.

[2]Container size is subject to sample-volume and analytical-method requirements. Glass bottles must be received from the laboratory baked, capped, and ready for use. **Do not use glass bottles that arrive uncapped.**

[3]Procedures for sample treatment and preservation are also described in Shelton and others (1994), Koterba and others (1995), Timme (1995), Sandstrom (1995), Zaugg and others (1995), and Werner and others (1996).

[4]Acidification of VOC samples is mandatory for NPDES and NAWQA programs, but normally is optional (unless study objectives dictate acidified samples).

[5]The summary for particulate inorganic carbon (PIC), sample designation code LC2608, is identical for that of TPC.

Appendix A5-B. Sample-designation codes and a summary of field-processing requirements for analyses of inorganic constituents in water

[NWQL, National Water Quality Laboratory of the U.S. Geological Survey; mL, milliliters; °C, degrees Celsius; H_2SO_4, sulfuric acid; HNO_3, nitric acid; <, less than; $K_2Cr_2O_7$, potassium dichromate; NaOH, sodium hydroxide; >, greater than]

Inorganic constituent[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation
Nutrients: Nitrogen and phosphorus (raw)	125-mL translucent polyethylene bottle. **Field rinse.**	WCA	Raw sample, treated: Add 1 mL of H_2SO_4. Chill/maintain at 4°C.
Nitrogen and phosphorus (filtered)	125-mL brown polyethylene bottle. **Field rinse.**	FCC	Filtered sample, untreated. Chill/maintain at 4°C.
		FCA	Filtered sample: Add 1 mL of H_2SO_4. Chill/maintain at 4°C.
Anions	250-mL polyethylene bottle. **Field rinse.**	RU	Raw sample, untreated.
		FU	Filtered sample, untreated.
Cations (major cations, trace elements)	250-mL polyethylene bottle, acid rinsed. **Field rinse.**	RA	Raw sample. Acidify with HNO_3 to pH<2.
		FA	Filtered sample. Acidify with HNO_3 to pH<2
Mercury	250-mL glass bottle, (clear), acid rinsed. **Field rinse.**	RAM	Raw sample. Acidify with $HNO_3/K_2Cr_2O_7$.
		FAM	Filtered sample. Acidify with $HNO_3/K_2Cr_2O_7$.
Antimony Arsenic Selenium	250-mL polyethylene bottle, acid rinsed. **Field rinse.**	RAH	Raw sample. Acidify with HNO_3 to pH<2.
Cyanide	250-mL polyethylene bottle. **Field rinse.**	LC0023	Raw sample. Add NaOH to pH >12. Chill/maintain at 4°C.
		LC0880	Filtered sample. Add NaOH to pH >12. Chill/maintain at 4°C.

[1]List of constituents and sample-designation codes is not complete or comprehensive. Some notable omissions include chemical oxygen demand and sulfide. Check with NWQL for a comprehensive list of analyses and sample designations and instructions. Check National Water Quality Technical Memorandum 97.05 for requirements of the USEPA Drinking Water Program.

[2]Container size is subject to sample-volume and analytical-method requirements. Acid-rinsed bottles must be received from the laboratory capped. Do not use acid-rinsed bottles that arrive uncapped.

Appendix A5-C. Sample-designation codes and a summary of field-processing requirements for analyses of stable isotopes and radiochemicals in water

[NWQL, National Water Quality Laboratory of the U.S. Geological Survey; L, liter; LC, laboratory code; DIC, dissolved inorganic carbon; mL, milliliters; $HgCl_2$, mercuric chloride; °C, degrees Celsius; HNO_3, nitric acid; <, less than; TDS, total dissolved solids]

Stable isotopes and radio-chemicals[1]	Size and type of sample container[2]	Sample-desig-nation codes of NWQL[1]	Treatment and preservation[3]
$^{13}C/^{12}C$	1-L glass bottle, narrow neck, with Teflon™/silicon septum. **Field rinse.**	RUS LC440	Raw sample, untreated. Contact laboratory for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ combined sample (LC1243). Fill bottle to overflowing.
^{14}C	Safety-coated or glass bottles with Teflon™/silicon septum. **Field rinse.** Secure cap with electrical tape. Bottle size depends on sample pH and concentration of DIC per volume of sample.	RUS/RUR	Raw or filtered sample—Filter samples with visible particulates; untreated. Fill bottle to overflowing. Exclude air and (or) flush headspace with nitrogen gas. Store chilled and in the dark. Contact NWQL.
$^{2}H/^{1}H$	60 mL clear glass bottle. Leave small headspace. Option: 250 mL polyethylene, no headspace. Use caps with polyseal conical inserts. Do not use plastic bottles if sample will be held or archived. **No field rinse.**	RUS, LC1574 or SH1142 if analyzing together with $^{18}O/^{16}O$.	Raw or filtered sample, untreated. Fill bottle to overflowing; then decant to leave a slight headspace. (Can be collected with $^{18}O/^{16}O$.)
$^{18}O/^{16}O$	Same as $^{2}H/^{1}H$ (LC1574) No field rinse.	RUS, LC0489 or SH1142 if analyzing together with $^{2}H/^{1}H$.	Filtered or unfiltered sample, untreated. Fill bottle to overflowing.

Appendix A5-C. Sample-designation codes and a summary of field-processing requirements for analyses of stable isotopes and radiochemicals in water —*Continued*

Stable isotopes and radio-chemicals[1]	Size and type of sample container[2]	Sample-designation codes of NWQL[1]	Treatment and preservation[3]
$^{15}N/^{14}N$	1-L amber glass bottle or high-density polyethylene (HDP) bottle. Use caps with polyseal conical inserts. **No field rinse.**	RUS, LC1717 (ammonia), LC1718 (as nitrate), or LC1921 (as nitrate plus ammonia)	Filtered sample, untreated. Fill bottle to shoulder. Wrap HDP bottle in aluminum foil. (Do not add $HgCl_2$.) Chill/maintain at 4 °C. **Send overnight to NWQL.**
$^{34}S/^{32}S$	[Refer to Carmody and others (1998) or E-mail **isotopes@usgs.gov.**]	RUS, Add appropriate laboratory code.	[Refer to Carmody and others (1998) or E-mail isotopes@usgs.gov.]
Radium 226	2-L polyethylene bottle, acid rinsed. (Check with laboratory.) **No field rinse.**	FAR, LC794	Filtered sample. Fill bottle to shoulder. Add HNO_3 to pH <2.
Radium 228	2-L or 7-L polyethylene bottle (check laboratory requirements), acid rinsed. **No field rinse.**	FAR, LC1364	Filtered sample. Fill bottle to shoulder. Add HNO_3 to pH <2.
Uranium U-234 U-235 U-238	Two 1-L polyethylene bottles, acid rinsed. **No field rinse.**	FAR, SH1130	Filtered sample. Fill bottle to shoulder. Add HNO_3 to pH <2.
Gross radio-activity (Gross alpha and gross beta)	1-L polyethylene bottle(s), acid rinsed. **No field rinse.**	FAR, SH456 or SH458, depending on TDS	Filtered sample. Fill bottle to shoulder. Add HNO_3 to pH <2.

Appendix A5-C. Sample-designation codes and a summary of field-processing requirements for analyses of stable isotopes and radiochemicals in water —*Continued*

Stable isotopes and radio-chemicals[1]	Size and type of sample container[2]	Sample-desig-nation codes of NWQL[1]	Treatment and preservation[3]
Tritium[1]	High-density, nonbreakable, polyethylene (HDPE) or 1-L glass GCC bottle. **No field rinse.**	RUR	Raw sample, untreated. Leave slight headspace. Do not store sample near radium (for example, glowing clocks, watches, signs)
Radon-222	Glass vial containing liquid-scintillation solution. **No field rinse.**	RUR-SV	Raw sample. Inject 10 mL of sample below liquid-scintillation solution.

[1]This table is not complete or comprehensive. Check with NWQL for the most current information on analytical schedules, laboratory codes, parameter codes, sample requirements, prices, and associated information. "G" indicates glass container; "CC" indicates chilled sample; "LC", laboratory code; "SH," laboratory schedule; "R" designates a raw or wholewater sample. For tritium/helium-3 and chlorofluorocarbon sampling requirements, see sections 5.6.3.J and 5.6.3.K, respectively.

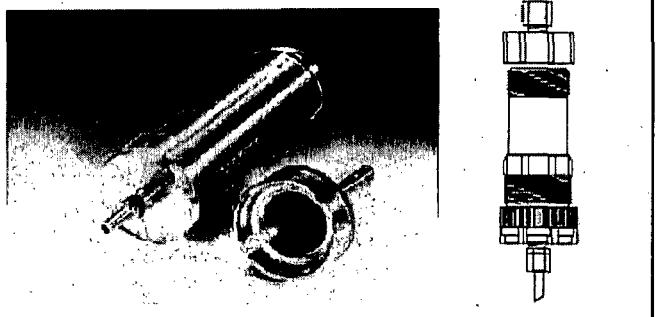
[2]If glass bottles are used, leave enough air space in bottles to accommodate expansion of chilled samples unless instructed otherwise. Seal cap with wax or plastic tape, or as directed by laboratory. Send electronic mail requests to isotopes@usgs.gov. Container size is subject to sample-volume and analytical-method requirements. Acid-rinsed bottles must be received from the laboratory capped. Do not use acid-rinsed bottles that arrive uncapped.

[3]Procedures for collection and processing of isotope and radiochemical samples are also described in Shelton and others (1994), Koterba and others (1995), and Timme (1995).

Appendix A5-D. Procedures for Processing Samples for Analysis of Dissolved and Suspended Organic Carbon Using a Silver Filter and Gas-Pressurized Filtration Apparatus.

This appendix describes the original procedure ("Gas-Pressurized Filter Procedures for Processing Samples for Analysis of Dissolved and Suspended Organic Carbon," NFM 5.2.2.C, Version 5/99) for processing samples for analysis of dissolved organic carbon (DOC) and suspended organic carbon (SOC).[1] This procedure may be used as an alternative to those described in section 5.2.2.C. The laboratory analysis of SOC samples requires a different method from that of POC or TPC samples. The field team needs to ensure that the correct method code has been entered onto the laboratory analytical request form.

SOC and DOC can be processed through a 47-mm-diameter, 0.45-µm pore-size, silver-metal filter medium. A gas-pressurized filter assembly (SOC/DOC filter apparatus) constructed of either stainless steel or fluorocarbon polymer is required for this procedure (fig. A5-D.1). In addition, either a peristaltic pump, a manual air pump, or compressed gas (usually organic-free nitrogen gas) is used to pressurize the filtration apparatus and force the sample through the silver filter. Filtration procedures are identical for ground-water and surface-water samples.



A. Stainless steel filter assembly

B. Fluorocarbon polymer filter assembly

Figure A5-D.1. Apparatus for filtering samples for analysis of dissolved/suspended organic carbon: (A) stainless steel pressure-filter assembly and (B) fluorocarbon polymer pressure-filter assembly. (Published with permission: A, Gelman Sciences; B, Savillex Corporation.)

[1]Refer to Office of Water Quality Technical Memorandums 2000.05, 2000.07, and 2000.08 for an explanation of changes to the field procedures for collecting and processing samples for organic carbon analysis.

A different set of procedures and separate silver filters are used to process the SOC and the DOC samples, unless suspended-material concentrations are low (up to about 30 mg/L). This section describes methods for (1) filtration of SOC samples only, (2) combined SOC and DOC sample filtration, and (3) filtration of DOC samples only.

- **If sample contains a large amount of suspended materials, at least two filtrations must be performed: one for SOC and one for DOC.**
- If sample contains low concentrations of suspended materials, filtration procedures can be combined using the same silver filter.
- Unless the study plan dictates an additional sample for quality control, only one silver filter should be needed for the SOC filtration.
  - The SOC filtration requires a minimum of 0.5 mg of suspended material in the 125-mL sample.
  - If filter clogging is a problem, or if it is difficult to obtain the 125-mL volume of sample needed for the SOC analysis, 64 mL of sample or multiple 64-mL samples can be substituted.
- Immediately after each use, rinse the filter apparatus several times with organic-grade DIW.
  - Field clean the filter apparatus while still wet if it is to be used at the next site. Otherwise, rinse, bag, and return the apparatus to the office laboratory for cleaning.
  - Thoroughly rinse the white (fluorocarbon polymer) O-ring and any other fluorocarbon polymer parts.
  - After cleaning, double-wrap all apertures and the filter apparatus with aluminum foil and place filter apparatus inside a sealable plastic bag.
- Blank water (VBW or PBW) from a freshly opened bottle should be used for quality-control samples for the DOC analysis. This blank water can also be used for prerinsing the filter media, if necessary. Once the bottle has been opened, the VBW or PBW must not be used for collection of future quality-control samples.
- Document on field forms and in field notes the filtration procedures used.

Do not use methanol or any other solvent to clean SOC, DOC, or TOC equipment (NFM 3).

TECHNICAL NOTE: Use of 64 mL or 125 mL baked glass bottles (available from OWQRL) is recommended instead of a graduated cylinder to measure sample volume for the DOC or combined SOC/DOC analysis. The advantage of using the baked glass bottles to measure volume is that they are certified as clean, whereas graduated cylinders can be difficult to clean adequately, especially under field conditions (Burkhardt and others, 1997), and cannot be baked because calibration will be lost.

- Bottles for DOC samples must have been baked at 400°C and meet a detection limit criterion for organic carbon of <0.1 mg/L.
- Volumetric accuracy of the 125-mL and 64-mL baked glass bottles is about ±1 mL.

SOC sample processing:

SOC analysis of the suspended material left on the silver filter requires that the volume of sample passed through the silver filter be measured and recorded. Determination of the volume of sample to be filtered for SOC analysis can depend on the concentrations of suspended materials; however, the concentration of humic and other substances that cause colored water, such as organic and inorganic colloids, will affect the volume that can pass through the silver filter. The sample volume that can pass through the silver filter decreases as the concentration of suspended materials increases. A graph of the historical stream stage compared to a graph of the suspended-material concentration will aid in estimating suspended-material concentrations at a given surface-water site. Guidelines for selecting the volume of sample to be filtered for SOC analysis, based on suspended-material concentrations, are shown in table 5-6d.

1. Collect the SOC sample(s) in a baked glass bottle, either at the centroid of the streamflow (NFM 4) or as a subsample from the churn or cone splitter. The data-quality requirements of the study and site characteristics determine where to withdraw the sample. If collecting sample at the centroid of flow with a weighted-bottle sampler, fill the bottle to the top; this is not necessary if subsampling from the churn or cone splitter. Cap the bottle securely.

   - Use a 125-mL baked glass bottle for water with relatively small concentrations of suspended materials (concentrations approximately less than 250 to 300 mg/L) (table 5-6d).
   - 64-mL baked glass bottles are recommended for samples that are colored or particulate laden.
   - A clean, graduated cylinder may be used when the volume of sample to be filtered is less than 64 mL.

Table 5-6d. Guidelines for selecting the volume needed for filtration of samples for analysis of suspended and particulate organic carbon
[Guidelines are based on sand-sized materials; other physical property factors and chemical composition were not taken into account; mg/L, milligrams per liter; mL, milliliters; >, greater than]

Approximate concentration of suspended materials (mg/L)	Volume of sample to be filtered (mL)
1 - 30	250
> 30 - 300	100
> 300 - 1,000	30
> 1,000	10

2. Cover the bench or table with a sheet of aluminum foil to make a clean work surface. Put on appropriate disposable, powderless gloves. Assemble necessary equipment on the clean work surface.
   a. To remove airborne particulates, attach an in-line, 0.2-µm pore-size filter (Acrodisc 50™) to the inlet side of a dry pump hose that goes to the filter apparatus when using peristaltic or hand pumps to pressurize the apparatus.
   b. Change gloves.
   c. Remove the aluminum foil wrapping from equipment.
3. Disassemble the clean filter apparatus.
4. Using metal forceps, place a silver filter on the base of the filter apparatus between the support screen and the fluorocarbon polymer gasket, and screw the barrel onto the filter base. (There is no gasket in the fluorocarbon polymer apparatus.)
5. Pour a minimum of 100 mL of ASTM Type II reagent water (Burkhardt and others, 1997) or VBW or PBW into the barrel. Analysis of the water used must indicate less than 0.1 mg/L of organic carbon.
6. Screw the top part of the filter apparatus onto the barrel and attach a clean, dry hose, either from a peristaltic pump, hand pump, or compressed gas cylinder (use a clean metal hose clamp to secure the discharge hose to the inlet connector). Set the filter apparatus into a stand.

7. Apply pressure to start the flow of rinse water through the filter apparatus, using either a peristaltic pump or hand pump, or by regulating the flow of compressed gas (usually nitrogen).

   a. The pump pressure must be regulated to less than 15 lb/in^2.

   b. If compressed gas (for example, organic-free nitrogen) is used, ensure that the gas is clean by way of gas-purveyor certification or by attaching an in-line 0.2-mm Gelman Acro™ 50 hydrophobic membrane filter disk. **Do not use any other type of filter**. Proceed as follows:

      i. **Make sure that the pressure regulator valve is closed.** Turn the handle on the pressure regulator counterclockwise for several turns until the pressure-regulator valve is closed.

      ii. Open the valve to the nitrogen cylinder.

      iii. Open the pressure-regulator valve by turning the handle clockwise until up to 15 lb/in^2 registers on the pressure gage. Do not exceed 15 lb/in^2 of pressure.

   c. Discard rinse water.

8. Depressurize the filter apparatus. **Always point the apparatus away from your body, face, and other people.** When using compressed gas,

   a. Close the valve to the pressure regulator after the pressure gage shows no pressure.

   b. Close the valve to the gas cylinder.

   c. Change gloves.

Wear safety glasses when pressurizing or depressurizing the filter apparatus.

9. Remove the top of the filter apparatus carefully.

10. Shake the sample vigorously (swirl if using a graduated cylinder) to suspend all particulate matter. (This is possible even if the bottle is filled to the top.)

11. Pour an aliquot of the sample immediately into the barrel of the filter apparatus, keeping particulates suspended.

12. Screw the top part of the filter apparatus onto the barrel and pressurize to filter the sample. Follow the instructions in step 7 (above) for pressurizing the filter apparatus.

13. After an aliquot of sample has been filtered or filtrate is being collected at less than one drop per minute:

    a. Depressurize apparatus (step 8).

    b. Remove the top of the filter apparatus.

    c. Check if there is water on the silver filter and if it is covered with particulates.

    - If the silver filter is dry but not covered with particulates, add another aliquot of sample by repeating steps 10–12.
    - After the silver filter is dry and covered with particulates, continue to step 14.

TECHNICAL NOTES:

It is important that all the water in the barrel be passed through the silver filter, leaving the filter "dry." To accomplish this, it might be necessary to filter the sample as separate aliquots, repeating steps 10–13 until the filter is loaded to capacity.

Shake the sample to resuspend particulates before pouring each aliquot into the barrel.

If using a 125-mL or 64-mL bottle, it is not necessary to empty the entire sample volume. Use of a clean, graduated cylinder also is acceptable.

It is recommended (but not required) that the sides of the barrel of the filter apparatus be rinsed with organic-grade DIW.

14. Collect the filtrate in a 50-mL or other appropriately sized graduated cylinder.

    - If additional aliquots will be filtered through the same silver filter, collect all the filtrate in the graduated cylinder.
    - When the entire filtration is complete, record the total volume of filtrate on field forms and on the Analytical Services Request (ASR) form.
    - Discard filtrate in the graduated cylinder—**Do not send to laboratory for analysis.**

15. Depressurize (step 8) and disassemble the bottom of the filter apparatus.
    a. Use a pair of metal forceps to remove the silver filter.
    b. Fold the silver filter in half with suspended material on the inside, taking care not to lose any suspended material. **Do not wrap the silver filter in aluminum foil.**
    c. Place the folded silver filter into a petri dish for SOC analysis.
    d. Close the petri dish and label it with site identification, date and time, total filtered volume of sample, and laboratory sample designation code. (The total volume of filtered sample includes the volume used to precondition the silver filter(s).)
    e. Maintain SOC sample at or below 4°C during storage and shipment to the laboratory.

Combined SOC/DOC sample processing:

Procedures for a combined filtering of samples for SOC and DOC analysis are listed below. Additional information can be found in Burkhardt and others (1997).

1. Collect the sample for SOC/DOC analysis as instructed in NFM 4.
2. Cover the bench or table with a sheet of aluminum foil to make a clean work surface. Put on appropriate disposable, powderless gloves. Assemble necessary equipment on the clean work surface.
    a. To remove airborne particulates, attach an in-line, 0.2-µm pore-size filter (Acrodisc 50™) to the inlet side of a dry pump hose that goes to the filter apparatus when using peristaltic or hand pumps to pressurize the apparatus.
    b. Change gloves.
    c. Remove the aluminum foil wrapping from equipment.
3. Disassemble the clean filter apparatus.
4. Using metal forceps, place a silver filter on the base of the filter apparatus between the support screen and the fluorocarbon polymer gasket, and screw the barrel onto the filter base. (There is no gasket in the fluorocarbon polymer pressure-filter apparatus.)
5. Pour a minimum of 100 mL of ASTM Type II reagent water (Burkhardt and others, 1997) or VBW or PBW into the barrel. Analysis of the water used must indicate less than 0.1 mg/L of organic carbon.
6. Screw the top part of the filter apparatus onto the barrel and attach a clean, dry hose, either from a peristaltic pump, hand pump, or compressed gas cylinder (use a clean metal hose clamp to secure the discharge hose to the inlet connector). Set the filter apparatus into a stand.

7. Apply pressure to start the flow of rinse water through the filter apparatus, using either a peristaltic pump or hand pump, or by regulating the flow of compressed gas (usually nitrogen).

Wear safety glasses when pressurizing or depressurizing the filter apparatus.

   a. The pump pressure must be regulated to less than 15 lb/in^2.
   b. If compressed gas (for example, organic-free nitrogen) is used, proceed as follows:
      i. **Make sure that the pressure regulator valve is closed.** Turn the handle on the pressure regulator counterclockwise for several turns until the pressure-regulator valve is closed.
      ii. Open the valve to the nitrogen cylinder.
      iii. To pressurize the filter apparatus, open the pressure-regulator valve by turning the handle clockwise until up to 15 lb/in^2 registers on the pressure gage.
   c. Discard rinse water.

Do not exceed 15 lb/in^2 of pressure.

8. Depressurize the filter apparatus. **Always point the apparatus away from your body, face, and other people.** When using compressed gas,
   a. Close the valve to the pressure regulator after the pressure gage shows no pressure.
   b. Close the valve to the gas cylinder.
   c. Change gloves.
9. Remove the top of the filter apparatus carefully.
10. Condition the silver filter for the SOC/DOC sample:
   a. Select the volume of wholewater (either 64 mL or 125 mL) to be filtered based on the estimated suspended-materials concentration of the sample, and record the volume on the ASR and the field forms. The volume to be filtered can be based on the table 5-6 guidelines and on previous experience of filtering samples from the site.

b. Shake the sample vigorously to resuspend settled particles and measure the sample volume using a clean, baked 64-mL or 125-mL bottle filled to the very top. **Do not field rinse baked glass bottles.** Immediately transfer the entire volume of the sample container to the barrel of the filter apparatus.

c. Screw the top part of the filter apparatus onto the barrel and pressurize to filter the sample. Follow the instructions in step 7 (above) for pressurizing the filter apparatus.

d. Condition the silver filter by passing 15 to 25 mL of sample water through the filter to waste. (Pass 15 mL of sample water through the silver filter if using a 64-mL volume of sample; 15 mL is the minimum volume of sample that should be used.) Record the total volume of water that was passed through the silver filter.

Do not field rinse DOC bottle.

11. Place a 125-mL baked glass bottle under the discharge tube of the filter apparatus and collect the sample filtrate for the DOC analysis (100 mL is recommended; a minimum of 50 mL is required). If the silver filter clogs before sufficient volume for the SOC analysis can be filtered, start the process over and filter a smaller volume of water; the 64-mL bottles are useful for such conditions. **If the silver filter clogs before the entire volume of the 64-mL bottle can be filtered, this combined SOC/DOC method cannot be used. Start over and filter SOC and DOC samples separately.**

    - If the volume needed for the SOC analysis is insufficient for a DOC analysis (less than 50 mL), two or more filtrations through separate silver filters can be combined into one DOC bottle. (Retain two of the filters if a duplicate SOC analysis is planned and record the total volume of sample that passed through each of the retained filters.)
    - Each time a new silver filter is used, repeat steps 3–10, rinsing and conditioning the silver filter as described. Discard the first 15 or 25 mL of sample filtrate to waste. Reposition the DOC bottle under the discharge tube and collect the sample filtrate. Record the total volume of sample that was passed through each silver filter.
    - If the volume needed for SOC analysis is greater than the 100 mL of sample to be used for DOC analysis, remove DOC bottle after filling with 100 mL of filtrate, but continue filtering until the entire volume needed for SOC analysis has been filtered. (Record total volume filtered and discard extra filtrate.)

12. After the DOC sample has been collected and the volume for SOC analysis has been filtered, cap the DOC bottle securely and check that the bottle is labeled correctly and completely. Place the bottle in a foam sleeve before placing in an ice-filled shipping container.

13. Depressurize the filter apparatus (step 8), then disconnect the hose from the filter apparatus cylinder and remove the top. When depressurizing the compressed-gas-operated apparatus:

    a. Close the valve to the pressure regulator only after the gage indicates no pressure.

    b. Close the valve to the nitrogen cylinder.

14. Using no more than a total of 20 mL of organic grade DIW:

    - Rinse residual suspended matter from the bottle that was used to measure sample volume and pour into the filter barrel.
    - Rinse any residual suspended matter from the sides of the filter barrel.

15. Reconnect the top of the filter apparatus. Attach the pressure hose and pressurize (step 7), passing the organic-grade DIW rinse water through the silver filter. Discard rinse water to waste. Depressurize the filter apparatus (step 8).

16. Disassemble the bottom of the filter apparatus and remove the silver filter.

    a. Use a pair of metal forceps when removing the silver filter.

    b. Fold the filter in half with suspended material on the inside, taking care not to lose any suspended material. **Do not wrap the silver filter in aluminum foil.**

    c. Place the folded filter in a petri dish for SOC analysis.

    d. Close the petri dish and label dish with site identification, date and time, total filtered volume of sample, and the laboratory sample designation code. (Include the volume used to precondition the silver filter(s) in the total volume of filtrate.)

    e. Place the labeled petri dish in a sealable plastic bag.

    f. Chill DOC and SOC samples and maintain at or below 4°C without freezing (section 5.5). For SOC samples submitted to NWQL, record the total volume of filtrate on the comment line of the ASR form.

g. If more than one silver filter was needed for the SOC sample, place each silver filter into a separate petri dish that is labeled as described in step 16d. Place all the petri dishes for a single sample into one sealable plastic bag labeled with the site identification and the date and time of sample collection. This is submitted as a single sample.

- Package the silver filter(s) for duplicate SOC analysis separately.
- Ship samples for SOC analysis to the laboratory with a note on the ASR form stating the number of silver filters used.

For SOC analysis, record TOTAL VOLUME of sample that passed through each silver filter.

DOC sample processing:

Procedures for filtering a DOC-only sample are listed below. Additional information can be found in Burkhardt and others (1997).

1. Collect the sample for DOC analysis (NFM 4).
2. Cover a bench or table with a sheet of aluminum foil to make a clean work surface. Put on appropriate disposable, powderless gloves. Assemble necessary equipment on the clean work surface.
   a. To remove airborne particles, attach an in-line filter, 0.2-µm pore size, (Acrodisc 50™) to a dry pump hose in front of the filter apparatus when using peristaltic or hand pumps to pressurize the apparatus.
   b. Change gloves.
   c. Remove the aluminum foil wrapping from equipment.
3. Disassemble the clean filter apparatus.
4. Using metal forceps, place a silver filter on the base of the filter apparatus between the support screen and the fluorocarbon polymer gasket, and screw the barrel onto the filter base. (There is no gasket in the fluorocarbon polymer pressure-filter apparatus.)
5. Pour a minimum of 100 mL of ASTM Type II reagent water (Burkhardt and others, 1997) or VBW or PBW into the barrel. Analysis of the water used must indicate less than 0.1 mg/L of organic carbon.
6. Screw the top part of the filter apparatus onto the barrel and attach a clean, dry hose, either from a peristaltic pump, hand pump, or compressed gas cylinder (use a clean metal hose clamp to secure the discharge hose to the inlet connector). Set the filter apparatus into a stand.

7. Apply pressure to start the flow of rinse water through the filter apparatus, using either a peristaltic pump or hand pump, or by regulating the flow of compressed gas (usually nitrogen).

Wear safety glasses when pressurizing or depressurizing the filter apparatus.

   a. The pump pressure must be regulated to less than 15 lb/in^2.
   b. If compressed gas (for example, organic-free nitrogen) is used, proceed as follows:
      i. **Make sure that the pressure regulator valve is closed.** Turn the handle on the pressure regulator counterclockwise for several turns until the pressure-regulator valve is closed.
      ii. Open the valve to the nitrogen cylinder.
      iii. Open the pressure-regulator valve by turning the handle clockwise until up to 15 lb/in^2 registers on the pressure gage. Do not exceed 15 lb/in^2 of pressure.
   c. Discard rinse water.

8. Depressurize the filter apparatus. **Always point the apparatus away from your body, face, and other people.** When using compressed gas,
   a. Close the valve to the pressure regulator after the pressure gage shows no pressure.
   b. Close the valve to the gas cylinder.
   c. Change gloves.
9. Remove the top of the filter apparatus carefully.
10. Condition the prerinsed silver filter:
   a. Open the barrel of the filter apparatus and pour about 125 mL of wholewater sample into the barrel (or about 64 mL if silver filter media is expected to clog). For water with large concentrations of suspended materials, collect the sample first into a baked glass bottle, allow suspended materials to settle, and pour 125 mL of the clear supernatant into the filter barrel.
   b. Screw the top part of the filter apparatus onto the barrel.
11. Apply pressure to start the flow of sample through the filter apparatus (step 7).
   - **Do not exceed 15 lbs/in^2.**
   - If using compressed gas, open the pressure-regulator valve first, then the valve to release gas from the cylinder (tank).

12. Condition the silver filter media by passing about 25 mL of sample through the silver filter to waste.

13. Filter the sample:

    a. Place a 125-mL organic-free amber glass bottle under the discharge tube of the filter apparatus. **Do not prerinse the DOC bottle.**

    b. If the silver filter media clogs, depressurize the filter apparatus and replace the silver filter.

        i. Rinse the new filter with blank water as described in steps 5–9.

        ii. Fill a clean DOC bottle with the water to be sampled and let the suspended materials settle before decanting the sample into the barrel of the filter apparatus.

        iii. Condition the new silver filter by passing about 25 mL of sample through the filter to waste.

        iv. Reposition the DOC bottle under the discharge tube and continue to collect the filtrate.

    c. Fill the bottle until sufficient volume for DOC analysis has been collected (50 mL is the minimum requirement; 100 mL is recommended). Cap the bottle securely and check that the bottle is labeled correctly. Place the bottle in a foam sleeve before placing in an ice-filled shipping container.

14. Depressurize the filter apparatus (step 8).

15. Chill and maintain the DOC sample at or below 4°C without freezing (section 5.5).

16. Disassemble the bottom of the filter apparatus. Remove the silver filter with metal forceps and place the filter in a plastic bag for disposal or recycling. **Do not reuse silver filters.**

Never increase the pressure in a filter apparatus to greater than 15 lb/in^2 in order to increase the rate of filtration.

5.6.1.C Phenols

Label 1-L baked amber glass phenol bottle as "LC0052."

1. Fill the bottle with raw sample directly from the sampling or splitting device.
2. Leave a small headspace in the bottle.
3. Add 2 mL of 8.5 percent H_3PO_4 to a 1-L sample to achieve pH 4, and 10 mL of $CuSO_4$ to a 1-L sample (100 g/L).
4. Chill and maintain at or below 4°C without freezing.

WASTEWATER, PHARMACEUTICAL, AND ANTIBIOTIC COMPOUNDS 5.6.1.F

The USGS differentiates between samples collected for analysis of wastewater compounds and those collected for analysis of pharmaceutical and antibiotic compounds, based on the analytical schedule for the laboratory method.[1] Currently, only the wastewater laboratory method for field-filtered samples (SH1433) is an approved, routine (production) method. (The unfiltered wastewater method LC 8033 also is available but requires a proposal for custom analysis.) At this time, analysis of samples for pharmaceutical and antibiotic compounds is confined to research studies and is available only on a custom basis.

To collect and process surface-water and ground-water samples that will be analyzed for concentrations of wastewater, pharmaceutical, and antibiotic compounds, the standard USGS procedures for collecting and filtering organic compounds are used (see NFM 4, 5.1, 5.2.2). However, special considerations related to personal safety and to sample contamination are required.

Samples collected for analysis of these compounds may be collected directly from sources of raw or treated wastewater. Sources of wastewater include treated and untreated domestic sewage, leaking septic systems or sewer lines, sanitary sewer overflows, and runoff from animal feeding operations. **Handling of such samples can expose personnel to pathogenic microorganisms, and therefore requires strict adherence to safety protocols.**

[1]The compounds included in a given laboratory schedule are subject to change and should be checked when planning a sampling activity that involves collecting data on wastewater, pharmaceutical, or antibiotic compounds.

Samples collected for analysis of wastewater, pharmaceutical, and antibiotic compounds are susceptible to contamination because they are ubiquitous in daily use. **To ensure sample integrity, field personnel should avoid contact with or consumption of products that contain the compounds targeted for analysis, and must adhere scrupulously to equipment-cleaning, equipment-handling, sample-processing, and sample-handling protocols.**

CAUTION: Raw or treated wastewater samples can contain microorganisms harmful to human health—use safe handling protocols.

- **Adhere to safety protocols.** The following precautions must be followed by field personnel when collecting, processing, or handling raw or treated wastewater samples for analysis of wastewater, pharmaceutical, or antibiotic compounds:
  - — Be familiar with the basic procedures to minimize exposure to and effects from contaminated water, as described in NFM 9.7.
  - — Receive proper immunizations before engaging in field activities and consult with your safety officer on this issue.
  - — Avoid direct contact with sewage and other types of wastewater and with equipment still contaminated through contact with the sample or source water.
  - — Avoid breathing in sewage and wastewater fumes or mist.
  - — Do not use workspace surfaces or equipment that have come into contact with polluted water until they have been decontaminated. Use only those decontamination procedures that are described below under "Prevent sample contamination."

► **Prevent sample contamination:**

— On the day of sampling activities, avoid contact with or consumption of the products listed below. Where contact with or consumption of these products is unavoidable, the collection of field blanks is strongly recommended.

Wastewater compounds

- Soaps and detergents, including antibacterial cleansers
- DEET (active ingredient in most insect repellents)
- Fragrances (cologne, aftershave, perfume)
- Sunscreen
- Animal or human urine or excrement
- Caffeine (coffee, tea, colas)
- Tobacco

Pharmaceutical compounds

- Prescription drugs, medications, and hormonal substances
- Over-the-counter medications
- Selected human antibiotics

Antibiotics

- Human antibiotics
- Veterinary antibiotics

— Wear powderless nitrile laboratory gloves during sampling and processing. Change to clean gloves with each change in activity or potential glove contamination.

— Avoid breathing directly over open samples/equipment.

— Avoid direct contact between yourself (including clothing) and the sample, sampling device, and processing equipment. Clothing is a source of detergents, fragrances, and fire retardants.

- Thoroughly field rinse and seal in a plastic bag all reusable equipment that comes in contact with sewage until the equipment can be properly decontaminated and disinfected (NFM 3.2.2).
- Clean scrupulously all workspace surfaces that come into contact with sewage—use a non-antibacterial soap[2] and water, followed by wiping all potentially contaminated sufaces with a clean, disposable isopropyl alcohol (70-90 percent) pad.
- Avoid any actions at the field site that result in the disposal or release of wastewater and pharmaceutical substances.

▶ **Implement quality control.** Quality-control samples are a required, integral part of water-quality investigations. As previously noted, samples for analysis of wastewater, pharmaceutical, and antibiotic compounds are vulnerable to contamination.

- Check your quality-control plan for instructions on the collection of field blanks and replicates for these sample types. Although the specific type, number, and distribution of quality-control samples are determined by the design and data-quality requirements of the study (NFM 4.3), field blanks are processed more frequently for these samples than for most other sample types.
- When using a a custom analysis, consult with the laboratory analysts for quality-control recommendations.
- Process an initial field blank to evaluate the potential for contamination associated with the field methods, materials used, and sampling environment. Distribute subsequent field blanks areally and temporally to meet data-quality requirements of the project.
- Use either pesticide- or VOC-grade blank water as the source solution for the field blanks.

[2]The laboratory analysis of wastewater includes triclosan, an active ingredient in most antibacterial soaps. Triclosan is also commonly found in some deodorants, toothpastes, mouthwashes, skin creams, lotions, laundry detergents, and dish soaps.

- The analytical methods used for pharmaceuticals and antibiotics are currently unapproved and are available only on a cutsom basis for research projects. It is reasonable to assume that blank water tested and certified contaminant free for approved organic constituent methods is an appropirate source solution for field blanks for these unapproved methods; however, a more rigorous approach would be to include a source solution blank as an integral part of the project quality-control plan.
- Process the field blanks in the same manner and under the same environmental conditions as the environmental sample (NFM 4.3.1.B).

Wastewater, pharmaceutical, and antibiotic samples are vulnerable to contamination and thus require rigorous quality control, usually by processing field and source-solution blanks.

- **When planning sampling activities that will result in a request for a custom analysis:**
  - Contact the NWQL in Lakewood, Colorado, (http://nwql.usgs.gov/) before collecting any samples for unfiltered wastewater-compound analysis or pharmaceutical-compound analysis.
  - Contact the OWQRL in Ocala, Florida, (http://owqrl.er.usgs.gov/) before collecting any samples for antibiotics that will be analyzed using this laboratory's methods.
  - Contact the Organic Geochemistry Laboratory in Lawrence, Kansas, (http://ks.water.usgs.gov/Kansas/reslab/) before collecting any samples for antibiotics that will be analyzed using this laboratory's methods.

To collect and process samples:

1. Order and assemble all equipment. Select sampling and processing equipment made of fluorocarbon polymers, glass, aluminum, or stainless steel. Avoid equipment made of Tygon®, polyethylene, or other plastics.

2. Clean equipment thoroughly before use, following the general protocols for organic-compound samples described in NFM 3.2.2, but with the following caveats:

   - Use non-antibacterial detergents.
   - Take extra care to ensure that equipment is copiously rinsed with deionized water (DIW) after the detergent wash—detergents are a source of interference in the analysis of pharmaceutical compounds and may include a target analyte (triclosan) of the wastewater analytical method.
   - Follow the DIW rinse with a methanol rinse. Collect the used methanol solution into an appropriate container for disposal.
   - Do not clean or field-rinse the baked-glass sample bottles obtained from OWQRL or another laboratory.

3. Collect and process the samples using methods appropriate for organic compounds, as described in NFM 4 and 5.2.2. Use laboratory-baked, brown (amber) glass sample bottles.

   - For wastewater and pharmaceuticals being shipped to the NWQL for analysis, use 1-L GCC bottles.
   - For antibiotic samples being shipped to the OWQRL for analysis, use 1-L GCC bottles.
   - For antibiotic samples being shipped to the Lawrence Organic Geochemistry Laboratory for analysis, use two 125-mL baked-glass bottles with Teflon® caps per sample.

4. Label bottles with site ID (identifier), date, time, sample type ("filtered" or "unfiltered"), and laboratory code or schedule number.

   a. For samples being shipped to the NWQL:

      - Wastewater, field-filtered – Label sample bottle "GCC—SH 1433"
      - Wastewater, raw – Label sample bottle "GCC–LC 8033" (add this laboratory code to the Analytical Services Request (ASR) form: **currently this is a custom analysis**)
      - Pharmaceuticals – Label sample bottle "LC9003"

   b. For antibiotic-analysis samples being shipped to the OWQRL – Label sample bottle "Antibiotics"

   c. For antibiotic-analysis samples being shipped to Lawrence, Kansas – Label sample bottles "LC-AN"

5. If collecting wholewater samples for custom wastewater analysis – Fill the 1-L GCC bottle to the shoulder.

6. When collecting filtered samples for wastewater, pharmaceutical, or antibiotic analyses – Filter the samples at the field site.

   - Pass samples through a 0.7-µm nominal pore-size glass microfiber plate filter (GF/F grade), following the procedures for organic compounds described in NFM 5.2.2.A.
   - Fill the 1-L GCC or two 125-mL baked-glass bottles to the shoulder.

7. For samples collected from polluted water, decontaminate the exterior of bottles:

   a. Rinse bottles with copious amounts of water.

   b. Wipe each bottle with a clean, disposable isopropyl alcohol (70-90 percent) pad.

   c. Rinse off each bottle with water.

8. Keep the samples chilled to 4°C or less until they are prepared for shipping.

9. After sample collection and processing, use a non-antibacterial soap and water to thoroughly clean any workspace surfaces that have come into contact with polluted water. Follow the cleaning by decontaminating the workspace with isopropyl alcohol. **Do not use a bleach solution for decontamination of surfaces that come in contact with samples, since any bleach residue will degrade target analytes.**

To ship the sample(s):

1. For raw or treated wastewater, use the following precautions when packing and shipping, as these samples can pose a health hazard to field and laboratory personnel.

   a. Decontaminate any sample bottles containing raw or treated wastewater as described in step 7 above.

   b. Check bottle cap to ensure a tight closure.

   c. Place each bottle inside a foam sleeve and then place bottles into a ziplock bag along with four 3M high-capacity chemical sorbent pads (pads are available from Lab Safety and Supply at www.labsafety.com). Seal the bag.

   d. Place the sealed bag inside two additional ziplock bags (a total of three bags) and seal each bag.

   e. Clearly note in the "Login Comments" section of the ASR form "SAMPLE CONTAINS RAW OR TREATED SEWAGE. HANDLE WITH CARE." Sampling staff or shipping staff should notify the laboratory login staff by telephone or e-mail of the expected delivery of these samples, in advance of their arrival at the lab.

2. For all other samples,
   a. Check that sample bottles are securely capped.
   b. Check that sample bottles are correctly labeled and match the information shown on the ASR form.
   c. Pack all samples in ice to maintain a temperature of or below 4°C without freezing, using standard procedures (NFM 5.5.3 - 5.5.4). Check that the ASR form has been properly sealed in doubled plastic bags and included with the samples.
3. Ship all samples to the laboratory via overnight delivery.

CONSTITUENT SPECIES 5.6.4

ARSENIC SPECIATION 5.6.4.A

Two sample-processing methods (field speciation and laboratory speciation) used at the USGS National Water Quality Laboratory (NWQL) are specific to sample analysis by inductively coupled plasma-mass spectrometry (ICP-MS) for determining the concentration of inorganic and organic arsenic species in a water sample. The field-speciation method requires NWQL Schedule 1729. The laboratory-speciation method requires use either of NWQL Schedule 1730, 1731, or 1732, as appropriate for study objectives. For either the field- or laboratory-speciation method, prior knowledge is needed of sample matrix-composition characteristics (that is, major-ion concentrations in filtered samples). Major-ion data are necessary to determine (1) the volume of ethylenediaminetetraacetic acid (EDTA) that will be required for sample preservation, and (2) if sample dilution is required.[1]

TECHNICAL NOTE:

- The field-speciation method (Schedule 1729) uses an SPE cartridge to separate inorganic arsenic species (arsenite and arsenate) in a filtered water sample. The eluate (containing arsenite) and the cartridge (containing arsenate) are sent to NWQL and analyzed by ICP–MS.
- The laboratory-speciation methods (Schedule 1730 or 1731) use a strong anion exchange column and high-performance liquid chromatography to separate inorganic (arsenite and arsenate) and organic arsenic species (monomethylarsonate, dimethylarsinate, and others) in a filtered water sample. As the species elute from the column, the corresponding arsenic concentration is determined using ICP–MS.

[1]The necessity for major-ion data is related to the sample preservative (EDTA) that is needed when ICP-MS analytical methods are used. For a discussion of other methods for As(III)/AS(V) species analysis, see McCleskey and others (in press).

Regardless of the speciation method used, all samples must be collected and filtered using standard USGS procedures, as described in NFM 4. For most applications, a laboratory speciation method (for example, Schedule 1730) should be selected unless the field method offers distinct advantages for a particular water-quality study. The field-speciation method involves relatively complex sample-processing steps, is applicable only for determination of inorganic arsenic species (arsenite and arsenate), is subject to interferences from other unknown charged arsenic species, and may require sample dilution due to the limited ion-exchange capacity of the SPE cartridge (see footnote below).

- **Field-speciation (separation) method** (NWQL Schedule 1729)
  - This method is used to determine concentrations of arsenite (As (III)) and arsenate (As (V)) by separation of the species using a solid-phase-extraction (SPE) cartridge in the field. The eluate and cartridge are submitted to NWQL for analysis.
  - Sample matrix composition can exceed the ion capacity of the SPE cartridge used to separate the arsenic species; therefore, the major-anion concentration must be known or closely estimated in advance to determine if sample dilution is required. Sample matrix information also is needed to determine the volume of EDTA to be added to preserve the sample.
  - As(V) results will be biased positively when monomethylarsonate (MMA), dimethylarsinate (DMA), or other anionic species is present in a sample. If the presence of MMA and DMA is unknown, use the Schedule 1730 laboratory-speciation method.

- **Laboratory-speciation methods** (NWQL Schedules 1730, 1731, and 1732)
  - Select Schedule 1730 to determine concentrations of arsenite (As (III)), arsenate (As (V)), monomethylarsonate (MMA), dimethylarsinate (DMA), and other organoarsenic species.
  - Select Schedule 1731 for a custom analysis; for example, for determination of organoarsenic species in addition to As(III), As (V), MMA, and DMA .
  - Schedules 1730 and(or) 1731 should be requested whenever there are questions about which inorganic and organic arsenic species are present in a sample and whenever the sample matrix composition (major-ion concentration) is unknown.
  - Sample matrix information (major-ion concentrations) is needed to determine the volume of EDTA to be added to preserve the sample. Samples must be collected in an opaque sample bottle.
  - Schedule 1732 is the laboratory-preparation analog of the field-speciation method and provides speciation only of As(III) and As(V). If the presence of MMA and DMA is unknown, Schedule 1730 should be requested.

Both field and laboratory arsenic speciation methods can be affected by the precipitation of metal oxides. Many suboxic or anoxic ground-water samples having arsenic concentrations greater than the drinking-water standard of 10 µg/L also can contain substantial concentrations of reduced aluminum, iron, or manganese. Oxidation of these metal species during sample collection and processing produces metal-oxide precipitates that can sorb arsenic, resulting in negatively biased data. Furthermore, arsenite can be oxidized to arsenate by photolytically produced free radicals; therefore, the exposure of the sample to light also should be minimized.

- Exposure of the sample to air and sunlight should be minimized to prevent metal-oxide precipitation.
- EDTA must be added immediately after sample filtration.

Quality Control

Collection and analysis of quality-control samples are required as an integral part of all water-quality investigations, and is the same whether using the field-separation or laboratory-speciation method. The final types, number, and distribution of quality-control samples generally are determined according to the design and data-quality requirements of the study (NFM 4.3).

The rule of thumb for studies collecting arsenic speciation data is to collect a set of blank, replicate, and spike QC samples with every 20 environmental samples, at a minimum, as follows:

1. Process an initial field blank to evaluate the potential for contamination associated with the field methods, materials used, and sampling environment. Distribute subsequent field blanks to address field-site concerns, the sampling timeframe, and data-quality requirements.
   - — Use either inorganic- (IBW), pesticide- (PBW), or volatile/pesticide- (VPBW) grade blank water as the source solution for field blanks (table 5-9 or 5-10).
   - — Process field blanks in the same manner and under the same environmental conditions as environmental samples (NFM 4.3.1.B). Take precautions to limit exposure of samples to air (NFM 4.0.3).
2. Collect and process replicate environmental samples to evaluate variability of the analytical results.
   - — Duplicate or triplicate samples are collected and processed one after the other and in the same manner as the other environmental samples.
   - — An additional replicate sample is collected and processed for use as a field spike.

3. Process an initial field-spike sample for an evaluation of matrix effects. Distribute subsequent field-spike samples to address field-site concerns, the sampling timeframe, and data-quality requirements. Use one of the replicate samples that has been processed as the spike sample. Always submit the spike sample for analysis along with an unspiked (duplicate) sample.

   a. Using a 100-µL micropipet and a clean micropipet glass bore or disposable plastic tip, dispense the spike solution into the replicate sample (table 5-9 or 5-10).

   b. Record spiking information on the worksheet (fig. 5-5 or 5-6 for the field- or laboratory-speciation methods, respectively) so that the percentage recovery can be calculated.

Calculation of diluent and EDTA volumes

Anions in the sample represent a potential source of method interference because they compete with arsenic for exchange sites on the strong anion exchange packing in the SPE cartridge. When using the field-speciation method, field personnel may need to dilute the samples with blank water (diluent) to alleviate this interference; diluent volume depends on the estimated anion concentration of the sample. The volume of EDTA preservative added to the sample (for either the field or laboratory method) depends on the estimated cation concentration of the sample filtrate.

Before beginning to process the sample using the field speciation method, calculate the volume of diluent as follows:

1. Estimate the concentration of anions in the sample using historical data for the sampling site or a representative site, if available. If prior knowledge of the sample matrix composition is unavailable, a laboratory method such as Schedule 1730 should be requested.

2. To calculate the anion concentration of the sample:

$C_a = [HCO_3^- \times 1.6(10^{-4})] + [Cl^- \times 2.8(10^{-4})] + [NO_3^- \times 7.1(10^{-4})] + [HPO_4^{-2} \times 2.1(10^{-4})] + [SO_4^{-2} \times 2.1(10^{-4})]$

where:

C_a = anion concentration in milliequivalents (meq) in 10-mL sample

HCO_3^- = bicarbonate concentration in mg/L as HCO_3^-

Cl^- = chloride concentration in mg/L as Cl^-

NO_3^- = nitrate concentration in mg/L as N

HPO_4^{-2} = phosphate concentration in mg/L as HPO_4^{-2}

SO_4^{-2} = sulfate concentration in mg/L as SO_4^{-2}

a. If the milliequivalents (meq) of total anions calculated for the sample exceeds the LC-SAX™ SPE cartridge capacity of 0.1 meq, the sample must be diluted with blank water to obtain a sample with 0.1 meq or less total anions.

b. **Do not excessively dilute samples because this results in diluting the arsenic species concentrations.**

c. Record the diluent volume on the worksheet (fig. 5-5) so that a dilution factor can be applied to the sample results. If the diluent volume is not provided, it will be assumed that the sample was not diluted.

For the field-speciation method: Estimate the total anion concentration of the sample to determine the diluent volume needed to prevent exceeding the ion-exchange capacity of the SPE cartridge.

To determine the volume of EDTA needed to preserve samples (NWQL Schedules 1729, 1730, 1731, and 1732), estimate the cumulative concentration of major cations in the sample, as follows:

1. Estimate the concentration of cations in the sample using historical data for the same site or a representative site, if available.
2. To calculate the volume of 250 mM (millimolar) EDTA required for a 10-mL sample:

$$V_{EDTA} = 4.0(10^{6}) \times ([Al \times 3.7(10^{-10})] + [Fe \times 1.8(10^{-10})] + [Mn \times 1.8(10^{-10})] + [Ca \times 2.5(10^{-7})] + [Mg \times 4.1(10^{-7})] + [Sr \times 1.1(10^{-10})])$$

where:

V_{EDTA}	= microliters of 250-mM EDTA required for a 10-mL sample
Al	= dissolved aluminum concentration, in µg/L as Al
Fe	= dissolved iron concentration, in µg/L as Fe
Mn	= dissolved manganese concentration, in µg/L as Mn
Ca	= dissolved calcium concentration, in mg/L as Ca
Mg	= dissolved magnesium concentration, in mg/L as Mg
Sr	= dissolved strontium concentration, in µg/L as Sr

3. If V_{EDTA} is less than 100 µL, add 100 µL of EDTA to the sample.
4. **If a sample is diluted for the field-speciation method, use the estimated cation concentration in the diluted sample in the equation above.**
5. Record the volume of EDTA added to the sample on the worksheet (fig. 5-5 or 5-6). If the EDTA volume is not provided, it will be assumed that 100 µL was added.

Sample processing

Sample-collection and -processing equipment should be cleaned according to USGS protocols for inorganic-constituent sampling (NFM 3.2.1). If an acid rinse is used, be sure to follow it with a thorough deionized-water rinse rinse. Do not acid rinse a filter membrane through which samples for arsenic analysis will be passed.

The field-speciation method of sample processing (NWQL Schedule 1729) is as follows:

1. Before leaving for the field:

   a. Fill out the header information on the worksheet for NWQL Schedule 1729 (fig. 5-5). Record the estimated anion and cation concentrations, diluent volume, and EDTA volume (see instructions in the section above). Referring to table 5-9, assemble the equipment needed.

   b. The strong anion exchange cartridge must be pre-conditioned before collecting samples. Prepare the cartridge-conditioning solutions as follows:

      ii. **pH ≥ 4** (Chloride-form LC-SAX cartridge): use methanol (CH_3OH, CAS 67-56-1) as received from the supplier. This is the most commonly used form for surface-water and ground-water matrices with pH ≥ 4.

      ii. **pH < 4** (Acetate-form LC-SAX cartridge): prepare a 1.7 M acetic acid solution by diluting trace-metals-grade acetic acid (CH_3COOH, CAS 64-19-7) by 1:10. This form works best to buffer samples with pH < 4. The 1.7 M acetic acid solution is stable for up to 30 days.

Always add acid to water, not water to acid.

2. At the field site, continue to fill out the sample worksheet for NWQL Schedule 1729 (fig. 5-5).
3. Assemble and organize on a clean work surface the necessary processing equipment and supplies (table 5-9).
4. Wear appropriate disposable, powder-free gloves. Before proceeding, prepare the 0.45-µm capsule filter (NFM 5.2.1.A, making sure that the capsule filter has been pre-

cleaned with DIW and is ready to be used. Study objectives may dictate use of a filter membrane with a smaller pore size (McCleskey and others, in press); these also should be precleaned (NFM 5, table 5-3). **Do not rinse the filter with acid.**

5. Collect environmental (surface-water and ground-water) samples and quality-control samples using the "clean-sampling procedures prescribed for trace-element samples at low part-per-billion concentrations (NFM 4.0.1). Prevent exposure of samples to the atmosphere and light to prevent oxidation.

   - **Surface-water samples should be collected from a single vertical or a point and should not be composited.** If stream mixing conditions are a concern, multiple samples from different points in the cross section should be individually collected and processed, or a sample should be collected from a different cross section where mixing is not a concern. Collection of a multiple vertical, EWI, or EDI composite surface-water sample can result in substantial aeration of the sample, causing the distribution of arsenic species to change.
   - Ground-water samples are particularly susceptible to changes in arsenic species distribution when sampling waters with low dissolved-oxygen concentration and redox potential (Eh). Appropriate precautions should be taken to avoid the aeration or light exposure of ground-water samples (NFM table 4.4).

Minimize the amount of time the sample is exposed to air and light.

The remaining steps in the field-speciation method are time dependent; therefore, it is important to complete the previous steps before continuing.

6. Rinse centrifuge tubes **A** and **B** and syringe twice with blank water. Cap the tubes and set aside.

7. Remove the LC-SAX™ SPE cartridge from the shipping container. Noting the sample pH, condition the cartridge as follows:

   - **Sample pH ≥ 4:** Using the syringe, push about 2 mL of methanol followed by about 10 mL blank water through the chloride-form cartridge at a rate of 1 to 2 drops per second. Collect the methanol for proper disposal. Use the syringe to blow out excess water. **Use cartridge immediately after conditioning.**
   - **Sample pH < 4:** Using the syringe, push about 5 mL of 1.7 M acetic acid followed by about 10 mL of blank water through the acetate-form cartridge at a rate of 1 to 2 drops per second. Collect the acetic acid for proper disposal. Use the syringe to blow out excess water. **Use cartridge immediately after conditioning.**

8. If a sample dilution is required (see *"Calculation of diluent and EDTA volumes"*), add the appropriate volume of blank water (diluent) to centrifuge **tube A** (the centrifuge tube is graduated).

9. Using the micropipet and disposable glass bores or an adjustable micropipet and a clean tip, add the appropriate volume of EDTA solution to centrifuge **tube A** (see *"Calculation of diluent and EDTA volumes"*). If processing a spike sample, next add the field spike solution using a 100-µL micropipet and clean, disposable glass bore or plastic tip.

   a. If more than 100 µL of EDTA is needed, use either an adjustable volume micropipet that is capable of delivering the calculated volume of EDTA, or use a 100-µL micropipet and round the calculated volume of EDTA up to the nearest 100-µL increment.

   b. Be careful not to add excessive EDTA to the field speciation sample. An excess of EDTA will compete with arsenic species for ion-exchange sites in the SPE cartridge, thus causing positive bias in the As(III) results.

10. Filter 10.0±0.2 mL (or 10.0 mL minus the diluent volume) of sample directly into the centrifuge tube. Cap **tube A** tightly, and mix well. **The EDTA and the filtered sample must be combined in tube A immediately after filtration.**
    - Filter the environmental samples using in-line procedures as described in NFM 5.2.
    - Take precautions to prevent oxidation of chemical species when filtering ground water; the risk of oxidation is of lesser concern for aerated surface water.
11. Remove the plunger from the syringe barrel. Connect the barrel to the SPE cartridge using the red cartridge adapter.
12. Pour the contents of **tube A** into the syringe barrel attached to the cartridge. Carefully insert the plunger into the syringe barrel.
    a. Slowly push the plunger to elute the sample through the cartridge at a rate of 1 to 2 drops per second, collecting the eluate in the centrifuge tube labeled **B**.
    b. Pass the entire sample volume through the cartridge. Use the syringe to blow out any remaining sample from the cartridge.
    c. Tightly cap **tube B**. Label **tube B** with station ID, date, and time. Discard **tube A** and the syringe.
13. Label the cartridge and the container into which the cartridge will be placed with station ID, date, and time. Place the cartridge into its original container, and cap tightly.
14. Complete the NWQL Schedule 1729 worksheet (fig. 5-5). Retain the original copy of the worksheet in station folder.
15. Place **tube B**, the SPE cartridge, and a copy of the completed worksheet (fig. 5-5) into the original kit bag. Label the bag with the station ID, date, and time. **Chill and maintain at 4°C. The cartridge and eluate are stable for up to 7 weeks; however, both should be shipped to NWQL to arrive within 14 days of sample collection.**

Laboratory-speciation methods of sample processing (NWQL Schedules 1730, 1731, and 1732):

1. Before processing samples, begin to fill out the sample worksheet (fig. 5-6), indicating the NWQL Schedule being requested (Schedule 1730, 1731, or 1732).
2. Assemble and organize on a clean work surface the necessary processing equipment and supplies (table 5-10).
3. Wear appropriate disposable, powder-free gloves. Before proceeding, prepare the 0.45-µm capsule filter (NFM 5.2.1.A), making sure that the capsule filter has been pre-cleaned with DIW and is ready to be used. Study objectives may dictate use of a filter membrane with a smaller pore size (McCleskey and others, in press); these also should be precleaned (NFM 5, table 5-3). **Do not rinse the filter with acid.**
4. Collect environmental (surface-water and (or) ground-water) samples and quality-control samples, using the prescribed procedures for samples with trace-element concentrations at the part-per-billion level. (NFM 4). Prevent exposure of samples to the atmosphere and light to prevent oxidation.
   - **Surface-water samples should be collected from a single vertical or a point and should not be composited.** If stream mixing conditions are a concern, multiple samples from different points in the cross section should be individually collected and processed or a sample should be collected from a different cross section where mixing is not a concern. Collection of a multiple vertical, EWI, or EDI composite surface-water sample can result in substantial aeration of the sample, causing the distribution of arsenic species to change.

- Ground-water samples are particularly susceptible to changes in arsenic species distribution when sampling waters with low dissolved-oxygen concentration and redox potential (Eh). Appropriate precautions should be taken to avoid the aeration or light exposure of ground-water samples (NFM table 4-4).

5. Rinse an opaque polyethylene sample bottle twice with blank water.

6. Using the micropipet and disposable glass bores or plastic tips or an adjustable micropipet and a clean tip, add at least 100 µL of EDTA solution to the sample bottle (see *"Calculation of diluent and EDTA volumes"*). If more than 100 µL of EDTA is needed, use either an adjustable volume micropipet that is capable of delivering the calculated volume of EDTA, or use a 100-µL micropipet and round the calculated volume of EDTA up to the nearest 100-µL increment.

7. If processing a spike sample, add the field spike solution (N1613) using a 100-µL micropipet and clean, disposable glass bore or plastic tip.

8. Record the volumes of EDTA solution and spike solution used on the laboratory-speciation methods worksheet (fig. 5-6). If the EDTA volume is not provided, it will be assumed that 100 µL was added.

9. Filter the sample, filling the opaque sample bottle to the top. Do not fill to overflowing. The opaque sample bottle holds about 11.5± 0.1 mL when completely full. The bottle must be filled completely to the brim so that the dilution factor and spike recovery can be accurately calculated. Cap bottle tightly.

   - Filter the environmental samples using in-line procedures as described in NFM 5.2.
   - Take precautions to prevent oxidation of chemical species when filtering ground water; the risk of oxidation is of lesser concern for aerated surface water.

10. Label bottle with station ID, date, and time.

11. Complete the worksheet (fig. 5-6). Retain the original copy of the worksheet in the station folder and place a copy in a sealed bag with the sample bottle.

12. Chill and maintain the sample at 4°C. The sample is stable for up to 3 months; however, the sample should be shipped to the NWQL to arrive within 14 days of sample collection.

Selected References

Bednar, A.J., Garbarino, J.R., Ranville, J.F., Wildeman, T.R., 2002, Preserving the distribution of inorganic arsenic species in groundwater and acid mine drainage samples: Environmental Science and Technology, v. 36, p. 2213-2218.

Garbarino, J.R., Bednar, A.J., and Burkhardt, M.R., 2002, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Arsenic speciation in natural-water samples using laboratory and field methods: U.S. Geological Survey Water-Resources Investigations Report 02-4144, 40 p.

McCleskey, R.B., Nordstrom, D.K., and Maest, A.S., 2003, Preservation of water samples for arsenic(III/V) determinations: an evaluation of the literature and new analytical results: Accepted for publication in Applied Geochemistry (special volume).

Nordstrom, D.K., 2002, Worldwide occurrence of arsenic in ground water: Science, v. 296, no. 5576, p. 2143-2145.

Nordstrom, D.K., and Archer, D.G., 2002, Arsenic thermodynamic data and environmental geochemistry, *in* Welch, A.H., and Stollenwerk, K.G., eds., Arsenic in Ground Water: Geochemistry and Occurrence, Boston, Kluwer Academic Publishers, p. 1-26.

Table 5-9. Checklist of supplies and equipment required for arsenic speciation using the field-separation method (NWQL Schedule 1729)

[mL, milliliter; mg, milligram; µg-As/L, micrograms-arsenic per liter; <, less than; SPE, solid-phase extraction cartridge; mM, millimoles per liter; M, moles per liter; EDTA, ethylenediaminetetraacetic acid; L, microliter; As(III), arsenite; As(V), arsenate]

√	Supplies	Description	Number required	Supplier and One Stop Shopping item number for USGS studies
	Blank water	• Inorganic-grade (IBW), or • Pesticide-grade (PBW), or • Volatile-organic/pesticide-grade (VPBW)	As needed	Q378FLD, N1580, N1590
	Field speciation kit (arsenic)	• Tube A, graduated, 15 mL for sample filtrate • Tube B, graduated, 15 mL for cartridge eluate • LC-SAX™ SPE cartridge • Syringe, 10 mL	1 per sample	N1610
	EDTA solution (store at room temperature)	25 mL of 250 mM EDTA for sample preservation. EDTA shelf life is one year from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed	N1611
	Schedule 1729 spike solution (store at room temperature)	10 mL of 2,500 µg-As/L of As(III) and As(V). Spike solution shelf life is 90 days from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed for Schedule 1729	N1612
	Methanol *or* acetic acid	Methanol (high purity grade, CAS 67-56-1), certified with <1 µg-As/L contamination; Acetic acid (CAS 64-19-7), certified with <1 µg-As/L contamination (trace-element grade). See footnote below for proper disposal.	As needed	Open market
	Micropipet	100-µL fixed volume or adjustable-volume, for EDTA and spikes	1	N1370 (fixed volume) or Open market
	Glass bores or plastic micropipet tips	Disposable glass bores, for 100-µL fixed-volume micropipet or disposable 100-µL fixed-volume or larger volume plastic tips for adjustable-volume micropipets	Ample supply	N1300 (glass bores) or Open market (plastic tips)
	Pipet	1- to 10-mL variable volume with tips, for sample dilution	1	Open market
	SPE tube adapter	For 3-mL SPE cartridge (field speciation only)	1	N1614
	Wash bottles: • Teflon® • Polyethylene	• 500 mL, for methanol or 1.7 M acetic acid for SPE cartridge conditioning • 250 mL or 500 mL, for blank water	1	Q377FLD, Q357FLD or Q335FLD

TECHNICAL NOTE: Material Safety Data Sheets are supplied with the EDTA and arsenic field spike solutions. Persons using these materials should become familiar with the associated warnings and safety guidelines prior to using the materials in the field. Expired EDTA and spike solutions, methanol, and acetic acid must be disposed of according to Federal, State, and local regulations. The District safety officer and water-quality specialists can be consulted for proper disposal methods.

Table 5-10. Checklist of supplies and equipment required for arsenic speciation using the laboratory-speciation methods (NWQL Schedules 1730, 1731, or 1732)

[mL, milliliter; µg-As/L, micrograms-arsenic per liter; mM, millimoles per liter; EDTA, ethylenediaminetetraacetic acid; µL, microliter; As(III), arsenite; As(V), arsenate; DMA, dimethylarsinate; MMA, monomethylarsonate]

√	Supplies	Description	Number required	*Supplier and One Stop* Shopping item number for USGS studies
	Blank water	• Inorganic-grade (IBW), or • Pesticide-grade (PBW), or • Volatile-organic/pesticide-grade (VPBW)	As needed	Q378FLD, N1580, N1590
	Schedules 1730 and 1731 spike solution (store at room temperature)	10 mL of 2,500 µg-As/L of As(III), As(V), DMA, and MMA. Spike solution shelf life is 90 days from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed for Schedules 1730 or 1731	N1613
	Schedule 1732 spike solution (store at room temperature)	10 mL of 2,500 µg-As/L of As(III) and As(V). Spike solution shelf life is 90 days from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed for Schedule 1732	N1612
	EDTA solution (store at room temperature)	25 mL of 250 mM EDTA for sample preservation. EDTA shelf life is one year from date of preparation and is printed on each bottle. See footnote below for proper disposal.	As needed	N1611
	Micropipet	100-µL fixed volume or adjustable-volume, for EDTA and spikes.	1	N1370 (fixed volume) or Open market
	Glass bores or plastic micropipet tips	Disposable glass bores, for 100-µL fixed-volume micropipet or disposable 100-µL fixed-volume or larger volume plastic tips for adjustable-volume micropipets.	Ample supply	N1300 (glass bores) or Open market (plastic tips)
	Sample bottles	Opaque (brown) "8-mL", polyethylene (holds 11.5 mL of sample when full).	1 per sample	N1615

TECHNICAL NOTE: Material Safety Data Sheets are supplied with the EDTA and arsenic field spike solutions. Persons using these materials should become familiar with the associated warnings and safety guidelines prior to using the materials in the field. Expired EDTA and spike solutions must be disposed of according to Federal, State, and local regulations. The District safety officer and water-quality specialists can be consulted for proper disposal methods.

Arsenic Field-Speciation Method Checklist and Worksheet
(Schedule 1729)

Site ID: _____ *Date/Time:* _____
Site Name: _____ *Collector:* _____

_ Filter sample using 0.45-µm capsule filter; do not clean media with acid
_ SPE Cartridge Conditioning: 2 mL methanol and 10 mL deionized water – pH ____

or

_ SPE Cartridge Conditioning: 5 mL 1.7 M acetic acid and 10 mL deionized water – pH ____
_ Estimated anion milliequivalents in 10 ml sample:_____ meq

$C_a = [HCO_3^- \times 1.6(10^{-4})] + [Cl^- \times 2.8(10^{-4})] + [NO_3^- \times 7.1(10^{-4})] + [HPO_4^{-2} \times 2.1(10^{-4})] + [SO_4^{-2} \times 2.1(10^{-4})]$

where: C_a = anion concentration in milliequivalents in 10-mL sample
HCO_3^- = bicarbonate concentration in mg/L as HCO_3^-
Cl^- = chloride concentration in mg/L as Cl^-
NO_3^- = nitrate concentration in mg/L as N
HPO_4^{-2} = phosphate concentration in mg/L as HPO_4^{-2}
SO_4^{-2} = sulfate concentration in mg/L as SO_4^{-2}

_ Diluent (blank water) volume added to tube A to give <0.1 anion milliequivalents in 10-mL sample _____ mL
_ EDTA preservative added to tube A _____µL
(100 µL or the volume calculated below, whichever is greater)

(Note: if sample is diluted, account for dilution factor when using the following equation):

$V_{EDTA} = 4.0(10^6) \times ([Al \times 3.7(10^{-10})] + [Fe \times 1.8(10^{-10})] + [Mn \times 1.8(10^{-10})] + [Ca \times 2.5(10^{-7})] + [Mg \times 4.1(10^{-7})] + [Sr \times 1.1(10^{-10})])$

where: V_{EDTA} = microliters of 250-mM EDTA required per sample
Al = dissolved aluminum concentration, in µg/L as Al
Fe = dissolved iron concentration, in µg/L as Fe
Mn = dissolved manganese concentration, in µg/L as Mn
Ca = dissolved Ca concentration, in mg/L as Ca
Mg = dissolved magnesium concentration, in mg/L as Mg
Sr = dissolved strontium concentration, in µg/L as Sr

_ Sample volume added to tube A
(10.0±0.2 or 10.0 mL minus diluent volume)_____ mL
_ Spike Solution lot number_____**F**
Solution concentration_____ µg/L
Volume added_____ µL
_ Push all the sample through cartridge at 1 to 2 drops per second.
_ Collect eluate in tube B; cap tightly.
_ Write Station ID, date, and time on the cartridge, tube B, and shipping container.
_ Place tube B, cartridge (inside its shipping container), and copy of worksheet inside the kit bag. Label bag with station ID, date, and time.
_ Maintain at 4 °C. Ship chilled sample and a copy of the worksheet to the NWQL within 14 days of collection.

COMMENTS:

Figure 5-5. Worksheet for field-speciation method to determine arsenic species in water samples.

Arsenic Laboratory-Speciation Methods Checklist and Worksheet
(Schedule 1730, 1731, or 1732)

Site ID: _____ *Date/Time:* _____
Site Name: _____ *Collector:* _____
Lab schedule requested: _____

Laboratory-speciation methods Schedules 1730, 1731, or 1732

_ Filter sample using 0.45-µm disposable capsule filter;
do not clean media with acid
_ EDTA preservative added to opaque bottle_____µL
(100 µL or the volume calculated below, whichever is greater)

$$V_{EDTA} = 4.0(10^{-6}) \times ([Al \times 3.7(10^{-10})] + [Fe \times 1.8(10^{-10})] + [Mn \times 1.8(10^{-10})] + [Ca \times 2.5(10^{-7})] + [Mg \times 4.1(10^{-7})] + [Sr \times 1.1(10^{-10})])$$

where: V_{EDTA} = microliters of 250-mM EDTA required per sample
Al = dissolved aluminum concentration, in µg/L as Al
Fe = dissolved iron concentration, in µg/L as Fe
Mn = dissolved manganese concentration, in µg/L as Mn
Ca = dissolved Ca concentration, in mg/L as Ca
Mg = dissolved magnesium concentration, in mg/L as Mg
Sr = dissolved strontium concentration, in µg/L as Sr

_ Spike Solution lot number_____**L or F**
(circle one)
Solution concentration_____ µg/L
Volume added _____ µL

Spiked or unspiked sample volume completely fill bottle, but do not overflow.

Note "8-mL" opaque bottle contains 11.5 ± 0.1 mL when completely full: 11.5 mL

_ Write Station ID, date, and time on bottle.
_ Maintain at 4 °C. Ship chilled sample and a copy of the worksheet to the NWQL within 14 days of collection.

COMMENTS:

Figure 5-6. Worksheet for laboratory-speciation methods to determine arsenic species in water samples.



Water Resources--Office of Water Quality



CHAPTER A6. FIELD MEASUREMENTS

Cover/Title Page
Back of Title Page

Abstract
Introduction

Purpose and scope
Field manual review and revision
Acknowledgments

- **Comments/Errata Sheet for Chapter A6**
- **Citation Information**

6.0 General information and guidelines
F.D. Wilde and D.B. Radtke

6.1 Temperature
D.B. Radtke, J.K. Kurklin, and F.D. Wilde

6.2 Dissolved oxygen
D.B. Radtke, A.F. White, J.V. Davis, and F.D. Wilde

6.3 Specific electrical conductance
D.B. Radtke, J.V. Davis, and F.D. Wilde

6.4 pH
D.B. Radtke, Eurybiades Busenberg, F.D. Wilde, and J.K. Kurklin

6.5 Reduction-oxidation potential (electrode method)
D.K. Nordstrom and F.D. Wilde

6.6 Alkalinity and acid neutralizing capacity *(second edition)*
Revised and edited by S.A. Rounds and F.D. Wilde

6.7 Turbidity
F.D. Wilde and Jacob Gibs

Conversion factors, selected terms and symbols, chemical symbols and formulas, and other abbreviations

Selected references and internal documents and publications on Techniques of Water- Resources Investigations

---

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

⇨ *Abstract*
⇧ *Return to Field Manual Complete Contents*
⇧ *Return to Water Quality Information Pages*

Submit a question or comment related to this National Field Manual.
Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: Feb. 19, 2004 imc
Privacy Statement || Disclaimer || Accessibility
URL: http://water.usgs.gov/owq/FieldManual/Chapter6/Ch6_contents.html

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data



Chapter A6. FIELD MEASUREMENTS

Edited by
F.D. Wilde and D.B. Radtke

⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages
Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 24Apr00 imc

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, *Secretary*

U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, *Acting Director*

Any use of trade, product, or firm names is for descriptive purposes only *and does not imply endorsement by the U.S. Government.*

For additional information write to:

Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

Copies of this report can be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Federal Center
Denver, CO 80225

⇧Return to Chapter A6 Contents Page
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages
Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort

Last Modified: 24JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

National Field Manual
CHAPTER A6. FIELD MEASUREMENTS

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* provides guidelines and standard procedures for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. Chapter A6 presents procedures and guidelines for the collection of data on air and water temperature, and on dissolved-oxygen concentrations, specific electrical conductance, pH, reduction-oxidation potential, alkalinity, and turbidity in water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Public Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. A high degree of reliability and standardization of these data are paramount to fulfilling this mission. Documentation of nationally accepted methods used by USGS personnel serves to maintain consistency and technical quality in data-collection activities. The USGS publishes Techniques of Water-Resources Investigations (TWRI) reports that document scientific methods used by USGS personnel. TWRI publications are listed at the end of this report.

TWRIs are grouped under major subject headings called books. The Book 9 series, Handbooks for Water-Resources Investigations, is designed for field use and was developed to summarize, from other TWRIs and other references, techniques for planning and conducting specialized work in water-resources investigations. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* is Section A of Book 9. The *National Field Manual* is comprised of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*.

Chapter A6 on field measurements includes procedures, techniques, and guidelines for planning and conducting specialized work in water-resources investigations. Sections and other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the chapter and (or) section number. For example, general information on temperature measurements is covered in section 6.1 of Chapter A6 "Field Measurements" and is cited here as NFM 6.1.

Purpose and Scope

The *National Field Manual* provides guidelines and standard procedures to be used by USGS personnel for field activities related to water-quality data collection and analysis. This manual is targeted specifically toward data collectors in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (3) provide methods that minimize biasing the data and, when properly applied, that result in data that are reproducible within defined limits of variability.

Data collectors must have formal training and field apprenticeship in order to correctly implement the procedures described in this report. The information provided in Chapter A6 is to be used in conjunction with *Water Temperature--Influential Factors, Field Measurement, and Data Presentation* by H.H. Stevens, Jr., J.F. Ficke, and G.F. Smoot (Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1, 1975), and *Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents* by W.W. Wood (Techniques of Water-Resources Investigations, Book 1, Chapter D2, 1981).

It is impractical to provide guidance that would encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. The fundamental responsibility of field personnel is to select methods that are compatible with the scientific objective for the field work and to use procedures that are consistent with USGS standard procedures to the extent possible. Under some circumstances, data collectors may have to modify standard procedures. Whenever a standard procedure is modified or an alternative procedure is used, a description of the procedure used and supporting quality-assurance information are to be reported with the data.

Field Manual Review and Revision

Chapters of the National Field Manual will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Please send comments or corrections to: NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to: nfm-owq@usgs.gov). Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

Acknowledgments

The information included in the *National Field Manual* is based on existing manuals, a variety of reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials included unpublished USGS training and field manuals and technical memorandums. The authors wish to acknowledge those individuals in the USGS who developed the field and training manuals that provided the foundation for this *National Field Manual*: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Iwatsubo, R.T. Kirkland, J.R. Knapton, C.E. Lamb, L.R. Lister, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The editors and authors are indebted to Chester Zenone, for his insightful suggestions and guidance; I.M. Collies, who provided editorial assistance; C.M. Eberle and B.B. Palcsak for a thorough editorial review of the first draft; and E.A. Ciganovich and G.J. Allord for their expertise, talent, and innovation in book design and publication. Appreciation is extended to the scientists consulted from the U.S. Environmental Protection Agency and from private industry, including Hach Company, Hydrolab

Corporation, and Yellow Springs Instrument Company.

The following colleague reviewers provided valuable contributions that improved the quality of this document: R.T. Iwatsubo and K.A. Pearsall, who reviewed this document in its entirety for technical soundness, and

H.D. Ardourel	J.M. Neil	L.R. Shelton
O.P. Bricker	V.W. Norman	D.A. Sherwood
M.E. Brigham	C.E. Oberst	R.L. Snyder
R.E. Broshears	G.B. Ozuna	D.L. Stanley
I.M. Cozzarelli	C.J. Patton	D.Y. Tai
J.V. Davis	L.N. Plummer	D.C. Thorstenson
M.E. Dorsey	T.J. Popowski	R.J. Wagner
D.J. Gellenbeck	K.C. Rice	W.E. Webb
C.M. Harris	R.L. Rickman	A.H. Welch
R.J. Hoffman	F.A. Rinella	F.C. Wells
M.M. Kennedy	G.F. Ritz	J.S. Zogorski
R.J. LaCamera	I.J. Roberts	
J.D. Martin	H.W. Sanger	

Many thanks go to T.L. Miller, whose encouragement and faith in this project have been instrumental to its achievement; and to D.A. Rickert for providing the support needed to produce a national field manual for water-quality studies.

⇨Section 6.0 Contents
⇧Return to Chapter A6 Contents
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages
Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 11SEP03 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

National Field Manual
CHAPTER A6. FIELD MEASUREMENTS

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* provides guidelines and standard procedures for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. Chapter A6 presents procedures and guidelines for the collection of data on air and water temperature, and on dissolved-oxygen concentrations, specific electrical conductance, pH, reduction-oxidation potential, alkalinity, and turbidity in water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Public Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. A high degree of reliability and standardization of these data are paramount to fulfilling this mission. Documentation of nationally accepted methods used by USGS personnel serves to maintain consistency and technical quality in data-collection activities. The USGS publishes Techniques of Water-Resources Investigations (TWRI) reports that document scientific methods used by USGS personnel. TWRI publications are listed at the end of this report.

TWRIs are grouped under major subject headings called books. The Book 9 series, Handbooks for Water-Resources Investigations, is designed for field use and was developed to summarize, from other TWRIs and other references, techniques for planning and conducting specialized work in water-resources investigations. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* is Section A of Book 9. The *National Field Manual* is comprised of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual.*

Chapter A6 on field measurements includes procedures, techniques, and guidelines for planning and conducting specialized work in water-resources investigations. Sections and other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the chapter and (or) section number. For example, general information on temperature measurements is covered in section 6.1 of Chapter A6 "Field Measurements" and is cited here as NFM 6.1.

Purpose and Scope

The *National Field Manual* provides guidelines and standard procedures to be used by USGS personnel for field activities related to water-quality data collection and analysis. This manual is targeted specifically toward data collectors in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (3) provide methods that minimize biasing the data and, when properly applied, that result in data that are reproducible within defined limits of variability.

Data collectors must have formal training and field apprenticeship in order to correctly implement the procedures described in this report. The information provided in Chapter A6 is to be used in conjunction with *Water Temperature--Influential Factors, Field Measurement, and Data Presentation* by H.H. Stevens, Jr., J.F. Ficke, and G.F. Smoot (Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1, 1975), and *Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents* by W.W. Wood (Techniques of Water-Resources Investigations, Book 1, Chapter D2, 1981).

It is impractical to provide guidance that would encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. The fundamental responsibility of field personnel is to select methods that are compatible with the scientific objective for the field work and to use procedures that are consistent with USGS standard procedures to the extent possible. Under some circumstances, data collectors may have to modify standard procedures. Whenever a standard procedure is modified or an alternative procedure is used, a description of the procedure used and supporting quality-assurance information are to be reported with the data.

Field Manual Review and Revision

Chapters of the National Field Manual will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Please send comments or corrections to: NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to: nfm-owq@usgs.gov). Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

Acknowledgments

The information included in the *National Field Manual* is based on existing manuals, a variety of reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials included unpublished USGS training and field manuals and technical memorandums. The authors wish to acknowledge those individuals in the USGS who developed the field and training manuals that provided the foundation for this *National Field Manual*: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Iwatsubo, R.T. Kirkland, J.R. Knapton, C.E. Lamb, L.R. Lister, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The editors and authors are indebted to Chester Zenone, for his insightful suggestions and guidance; I.M. Collies, who provided editorial assistance; C.M. Eberle and B.B. Palcsak for a thorough editorial review of the first draft; and E.A. Ciganovich and G.J. Allord for their expertise, talent, and innovation in book design and publication. Appreciation is extended to the scientists consulted from the U.S. Environmental Protection Agency and from private industry, including Hach Company, Hydrolab

Corporation, and Yellow Springs Instrument Company.

The following colleague reviewers provided valuable contributions that improved the quality of this document: R.T. Iwatsubo and K.A. Pearsall, who reviewed this document in its entirety for technical soundness, and

H.D. Ardourel	J.M. Neil	L.R. Shelton
O.P. Bricker	V.W. Norman	D.A. Sherwood
M.E. Brigham	C.E. Oberst	R.L. Snyder
R.E. Broshears	G.B. Ozuna	D.L. Stanley
I.M. Cozzarelli	C.J. Patton	D.Y. Tai
J.V. Davis	L.N. Plummer	D.C. Thorstenson
M.E. Dorsey	T.J. Popowski	R.J. Wagner
D.J. Gellenbeck	K.C. Rice	W.E. Webb
C.M. Harris	R.L. Rickman	A.H. Welch
R.J. Hoffman	F.A. Rinella	F.C. Wells
M.M. Kennedy	G.F. Ritz	J.S. Zogorski
R.J. LaCamera	I.J. Roberts	
J.D. Martin	H.W. Sanger	

Many thanks go to T.L. Miller, whose encouragement and faith in this project have been instrumental to its achievement; and to D.A. Rickert for providing the support needed to produce a national field manual for water-quality studies.

⇨Section 6.0 Contents
⇧Return to Chapter A6 Contents
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages
Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 11SEP03 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

National Field Manual
CHAPTER A6. FIELD MEASUREMENTS

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* provides guidelines and standard procedures for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. Chapter A6 presents procedures and guidelines for the collection of data on air and water temperature, and on dissolved-oxygen concentrations, specific electrical conductance, pH, reduction-oxidation potential, alkalinity, and turbidity in water.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters will be announced on the USGS Public Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects data needed to assess the quality of our Nation's water resources. A high degree of reliability and standardization of these data are paramount to fulfilling this mission. Documentation of nationally accepted methods used by USGS personnel serves to maintain consistency and technical quality in data-collection activities. The USGS publishes Techniques of Water-Resources Investigations (TWRI) reports that document scientific methods used by USGS personnel. TWRI publications are listed at the end of this report.

TWRIs are grouped under major subject headings called books. The Book 9 series, Handbooks for Water-Resources Investigations, is designed for field use and was developed to summarize, from other TWRIs and other references, techniques for planning and conducting specialized work in water-resources investigations. The *National Field Manual for the Collection of Water-Quality Data (National Field Manual)* is Section A of Book 9. The *National Field Manual* is comprised of individually published chapters. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual*.

Chapter A6 on field measurements includes procedures, techniques, and guidelines for planning and conducting specialized work in water-resources investigations. Sections and other chapters of the *National Field Manual* are referred to in this report by the abbreviation "NFM" and the chapter and (or) section number. For example, general information on temperature measurements is covered in section 6.1 of Chapter A6 "Field Measurements" and is cited here as NFM 6.1.

Purpose and Scope

The *National Field Manual* provides guidelines and standard procedures to be used by USGS personnel for field activities related to water-quality data collection and analysis. This manual is targeted specifically toward data collectors in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistent use of field methods for the purpose of producing nationally comparable data, and (3) provide methods that minimize biasing the data and, when properly applied, that result in data that are reproducible within defined limits of variability.

Data collectors must have formal training and field apprenticeship in order to correctly implement the procedures described in this report. The information provided in Chapter A6 is to be used in conjunction with *Water Temperature--Influential Factors, Field Measurement, and Data Presentation* by H.H. Stevens, Jr., J.F. Ficke, and G.F. Smoot (Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1, 1975), and *Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents* by W.W. Wood (Techniques of Water-Resources Investigations, Book 1, Chapter D2, 1981).

It is impractical to provide guidance that would encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. The fundamental responsibility of field personnel is to select methods that are compatible with the scientific objective for the field work and to use procedures that are consistent with USGS standard procedures to the extent possible. Under some circumstances, data collectors may have to modify standard procedures. Whenever a standard procedure is modified or an alternative procedure is used, a description of the procedure used and supporting quality-assurance information are to be reported with the data.

Field Manual Review and Revision

Chapters of the National Field Manual will be reviewed, revised, and reissued periodically to correct any errors, incorporate technical advances, and address additional topics. Please send comments or corrections to: NFM-QW, USGS, 412 National Center, Reston, VA 20192 (or send electronic mail to: nfm-owq@usgs.gov). Newly published and revised chapters will be announced on the USGS Home Page on the World Wide Web under "New Publications of the U.S. Geological Survey." The URL for this page is http://water.usgs.gov/lookup/get?newpubs.

Acknowledgments

The information included in the *National Field Manual* is based on existing manuals, a variety of reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials included unpublished USGS training and field manuals and technical memorandums. The authors wish to acknowledge those individuals in the USGS who developed the field and training manuals that provided the foundation for this *National Field Manual*: M.E. Dorsey, T.K. Edwards, W.B. Garrett, W.J. Gibbons, R.T. Iwatsubo, R.T. Kirkland, J.R. Knapton, C.E. Lamb, L.R. Lister, R.F. Middelburg, Jr., J. Rawson, L.R. Shelton, M.A. Sylvester, and F.C. Wells.

The editors and authors are indebted to Chester Zenone, for his insightful suggestions and guidance; I.M. Collies, who provided editorial assistance; C.M. Eberle and B.B. Palcsak for a thorough editorial review of the first draft; and E.A. Ciganovich and G.J. Allord for their expertise, talent, and innovation in book design and publication. Appreciation is extended to the scientists consulted from the U.S. Environmental Protection Agency and from private industry, including Hach Company, Hydrolab

Corporation, and Yellow Springs Instrument Company.

The following colleague reviewers provided valuable contributions that improved the quality of this document: R.T. Iwatsubo and K.A. Pearsall, who reviewed this document in its entirety for technical soundness, and

H.D. Ardourel	J.M. Neil	L.R. Shelton
O.P. Bricker	V.W. Norman	D.A. Sherwood
M.E. Brigham	C.E. Oberst	R.L. Snyder
R.E. Broshears	G.B. Ozuna	D.L. Stanley
I.M. Cozzarelli	C.J. Patton	D.Y. Tai
J.V. Davis	L.N. Plummer	D.C. Thorstenson
M.E. Dorsey	T.J. Popowski	R.J. Wagner
D.J. Gellenbeck	K.C. Rice	W.E. Webb
C.M. Harris	R.L. Rickman	A.H. Welch
R.J. Hoffman	F.A. Rinella	F.C. Wells
M.M. Kennedy	G.F. Ritz	J.S. Zogorski
R.J. LaCamera	I.J. Roberts	
J.D. Martin	H.W. Sanger	

Many thanks go to T.L. Miller, whose encouragement and faith in this project have been instrumental to its achievement; and to D.A. Rickert for providing the support needed to produce a national field manual for water-quality studies.

⇨Section 6.0 Contents
⇧Return to Chapter A6 Contents
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages
Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 11SEP03 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Complete pdf for Section 6.0 (Version 1.1, 7/2003, with revisions to 6.0.2.A)
Archive pdf available for Section 6.0, 4/98

National Field Manual

6.0 GENERAL INFORMATION AND GUIDELINES

By F.D. Wilde and D.B. Radtke

6.0 General Information and Guidelines

6.0.1 Records, field instruments, and quality assurance
6.0.2 Sample collection, preservation, and storage

6.0.2.A Locating point(s) of measurement in still and flowing water
6.0.2.B In situ and subsample measurement procedures

6.0.3 Ground water

6.0.3.A Well purging: standard procedure and exceptions
6.0.3.B Downhole, flowthrough-chamber, and subsample measurement procedures

---

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Illustrations

6.0-1 Flow chart showing in situ field-measurement procedures for surface water

6.0-2 Flow chart showing subsample field-measurement procedures for conductivity, pH, and alkalinity of surface water

6.0-3 Example of a field form to record well purging

6.0- Flow chart showing field-measurement procedures using downhole and flowthrough-chamber

6.0-4 systems for ground water

6.0-5 Flow chart showing subsample field-measurement procedures for conductivity, pH, and alkalinity of ground water

Tables

6.0-1 Stabilization criteria for recording field measurements

6.0-2 Example of field notes for a discharge-weighted conductivity measurement

6.0-3 Example of field notes for an area-weighted conductivity measurement

---

⇨Section 6.0
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 15Aug03 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.0.pdf

6.0
GENERAL INFORMATION AND GUIDELINES

Field measurements: determinations of physical or chemical properties that are measured onsite, as close as possible in time and space to the media being sampled.

This section summarizes information, guidelines, and minimum requirements that generally apply to field measurements for all studies of water quality and the collection of basic data. Another term commonly used for field measurements is field parameters. Guidelines applicable to the individual field measurements are described in detail in the respective sections of this chapter (NFM 6.1 through 6.7). Before proceeding with field work, check each field-measurement section for recommended methods and equipment, detailed descriptions of measurement and quality-control procedures, and guidelines for troubleshooting and data reporting.

⇨Section 6.0.1
⇧Return to Contents for 6.0--General Information and Guidelines
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 12AUG98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.0.1.pdf

6.0.1
RECORDS, FIELD INSTRUMENTS, AND QUALITY ASSURANCE

Field-measurement data and other field information must be recorded, either on paper or electronically, while in the field. "Reported" field measurements are defined as those data that are entered into the National Water Information System (NWIS) data base of the USGS (Maddy and others, 1989) as well as data that are to be published but cannot be stored in NWIS. The conventions used for reporting field-measurement data are described at the end of each field-measurement section.

- Record field-measurement data, methods and equipment selected, and calibration information on field forms and in instrument log books.
  - -- Field forms include national or study-customized field forms and analytical services request forms; other forms and records (for example, chain-of-custody records) may be required for the study.
  - -- Instrument log books for each field instrument are required to document calibrations and maintenance.
- Records are maintained for each uniquely identified sampling location.

Field personnel must be familiar with the instructions provided by equipment manufacturers. This manual provides only generic guidelines for equipment use and maintenance or focuses on a particular instrument or instruments that currently are in common use in the USGS; there is a large variety of available field instruments and field instruments are being continuously updated or replaced using newer technology. Field personnel are encouraged to contact equipment manufacturers for answers to technical questions. Refer questions regarding equipment and supplies obtained from the USGS-WRD Quality of Water Service Unit (QWSU) in Ocala, Fla., the National Water Quality Laboratory (NWQL) in Arvada, Colo., or the Hydrologic Instrumentation Facility (HIF) at Stennis Space Center, Miss., to the respective facility. Information on instrument systems that have been tested and compared for accuracy and precision by HIF is found in the following issues of *Instrument News*, a publication of the HIF: 1991, for Hydrolab H2O™; 1992 and 1993, for pH; 1992, for conductivity; 1993, for dissolved oxygen; and 1994, for temperature, turbidity, and the YSI 3800™.

Field measurements should represent, as closely as possible, the natural condition of the surface-water or ground-water system at the time of sampling. Field teams must determine if the instruments and method to be used will produce data of the type and quality required to fulfill study needs as well as USGS requirements. Experience and knowledge of field conditions often are indispensable for determining the most accurate field-measurement value. To ensure the quality of the data collected:

- Calibration is required at the field site for most instruments. **Make field measurements only with calibrated instruments.**
- Each field instrument must have a permanent log book for recording calibrations and repairs. Review the log book before leaving for the field.
- Test each instrument (meters and sensors) before leaving for the field. Practice your measurement technique if the instrument or measurement is new to you.
- Have backup instruments readily available and in good working condition.

Quality-assurance protocols are mandatory for every data-collection effort of the USGS, and include practicing good field procedures and implementing quality-control checks. Make field measurements in a manner that minimizes artifacts that can bias the result. Check field-measurement precision and accuracy (variability and bias).

- **Rule of thumb:** For measurements made on subsamples, such as alkalinity, check precision in the field every tenth sample by repeating the measurement three times using separate sample aliquots from the same sample volume.
- **Requirement:** By using reference samples, document your ability to make an accurate measurement. **Field personnel, including non-USGS employees that collect field-measurement data entered into the NWIS, are required to participate in the National Field Quality Assurance (NFQA) Program (Stanley and others, 1992).** Field teams also are encouraged to verify accuracy of their measurements at least quarterly against reference samples obtained from QWSU.

Before making field measurements, sensors must be allowed to equilibrate to the temperature of the water being monitored. Sensors have equilibrated adequately when instrument readings have "stabilized," that is, when the variability among measurements does not exceed an established criterion. **The criteria for stabilized field readings are defined operationally in table 6.0-1, for a set of three or more sequential measurements.** The natural variability inherent in surface water or ground water at the time of sampling generally falls within these stability criteria and reflects the accuracy that should be attainable with a calibrated instrument.

Table 6.0–1. Stabilization criteria for recording field measurements

[±, plus or minus value shown; °C, degrees Celsius; ≤, less than or equal to value shown; µS/cm, microsiemens per centimeter at 25°C; >, greater than value shown; unit, standard pH unit; mg/L, milligram per liter; NTU, nephelometric turbidity unit]

Standard direct field measurement[1]	Stabilization criteria for measurements (variability should be within the value shown)
Temperature:	
Thermistor thermometer	± 0.2°C
Liquid-in-glass thermometer	± 0.5°C
Conductivity:	
when ≤ 100 µS/cm	± 5 percent
when > 100 µS/cm	± 3 percent
pH:	
Meter displays to 0.01	± 0.1 unit
Dissolved oxygen:	
Amperometric method	± 0.3 mg/L
Turbidity:	
Turbidimetric method, in NTU	± 10 percent

[1]Eh is not considered to be a routine or direct field measurement (see NFM 6.5). Alkalinity and acid neutralizing capacity require a titration procedure and, thus, are not direct measurements.

- **For surface water:** Allow at least 60 seconds (or follow the manufacturer's guidelines) for sensors to equilibrate with sample water. Take instrument readings until the stabilization criteria in table 6.0-1 are met. Record the median of the final three or more readings as the value to be reported for that measurement point (see 6.0.2).
- **For ground water:** Start recording measurements after sensors have equilibrated with purge water. Take instrument readings until the stabilization criteria in table 6.0-1 are met and the required number of well volumes of ground water have been purged. Record the median of the final five or more readings as the value to be reported for that site (see 6.0.3).
- **For sites at which variability exceeds the criteria of table 6.0-1:** Allow the instrument a longer equilibration time and record more measurements. To determine the value to be reported for that measurement point or well, either use the median of the final five or more measurements recorded, or apply knowledge of the site and professional judgment to select the most representative of the final readings.

⇨Section 6.0.2
⇧Section 6.0
⇧Return to Contents for 6.0--General Information and Guidelines
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 12AUG98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

6.0.2 (Version 1.1) SURFACE WATER

Field measurements must accurately represent the body of surface water or that part of the water body being studied. Field teams need to select a method to locate the point(s) of measurement (6.0.2.A) and the method(s) to be used to make the field measurements (6.0.2.B).

Normally, the point(s) at which field measurements are made correspond to the location(s) at which samples are collected. Standard USGS procedures for locating points of sample collection for surface-water sampling are detailed in Chapter A4 (NFM 4) of this *National Field Manual* and in Edwards and Glysson (1998).

Properties such as temperature, dissolved-oxygen concentration, and Eh must be measured directly in the water body (in situ). Other properties such as pH, conductivity, and turbidity often are measured in situ, but also may be measured in a subsample of a composited sample collected using discharge-weighted methods. Because determinations of alkalinity or acid-neutralizing capacity (alkalinity/ANC) cannot be made in situ, a discrete sample must be collected or subsampled from a composite.

6.0.2.A LOCATING POINT(S) OF MEASUREMENT IN STILL AND FLOWING WATER

The method selected to locate the point(s) of measurement usually differs for still water and flowing water. If the water system is well-mixed and its chemistry is relatively uniform, a single sample could be sufficient to represent the water body. Often, however, multiple points of measurement are needed to determine a representative set of field-measurement values.

Still water

Still-water conditions are found in storage pools, lakes, and reservoirs. Field measurements usually are made in situ at multiple locations and depths. Alternatively, pH, conductivity, and turbidity can be measured in a discrete sample or subsample (see 6.0.2.B). Measurement of alkalinity/ANC must be in a discrete sample. The location, number, and distribution of measurement points are selected according to study objectives.

- Measurements made at discrete depths through the vertical water column must not be averaged or reported as a median value that represents the entire vertical.
- Report the value selected to represent each point measured in the vertical as individual stations or distinguish measurements in that vertical by assigning a unique time to each measurement.

Flowing water

Flowing water conditions are found in perennial and ephemeral streams. The location and the number of field measurements depend on study objectives (see Technical Note, below). Generally, a single set of field-measurement data is used to represent an entire stream cross section at a sampling site and can be useful when calculating chemical loads.

To obtain data representative of the section, the variability of discharge and field measurements across the stream must be known. This information is used to determine if the equal-discharge-increment (EDI) or equal-width-increment (EWI) method of locating field-measurement points should be used.

1. Check the cross-sectional profile data of the stream site to determine the variability of discharge per unit width of the stream and of field-measurement values across the section.

    - Make individual measurements at a number of equally-spaced verticals along the cross section and at multiple depths within each vertical; or, consult previous records for the site.

    - Make in situ (6.0.2.B) field measurements for the profile.

    - Field-measurement profiles of stream variability are needed for low- and high-flow conditions and should be verified at least every 2 years or as study objectives dictate.

2. Select the EDI or EWI method to locate points of measurement (refer to NFM 4 or Edwards and Glysson (1998) to select and execute the appropriate method).

    - If stream depth and velocities along the cross section are relatively uniform, use the EWI method.

    - If stream depth and velocities along the cross section are highly variable, use the EDI method.

    - In a small and well-mixed stream, a single point at the centroid of flow may be used to represent the cross section. The centroid of flow is defined as the point in the increment at which discharge in that increment is equal on both sides of the point.

TECHNICAL NOTE: Standard USGS procedure is to use either the equal-discharge increment or equal-width increment method for locating measurement points to ensure that chemical loads can be calculated. Different study objectives could dictate different methods for locating the measurement point(s). For example, field measurements designed to correlate water chemistry with benthic invertebrates may require measurements on one or more grab samples that represent populated sections of the stream channel.

Equal-Discharge Increments (EDI)

The stream cross section is divided into increments of equal discharge. Field measurements can be made in situ at the centroid of each increment or by collecting an isokinetic depth-integrated sample at the centroid of each increment and determining the value either of each sample or of a composite of the samples. These methods result in data that are discharge-weighted (Edwards and Glysson, 1998).

- Knowledge of streamflow distribution in the cross section is required to select verticals at which measurements will be made or subsamples collected. Streamflow distribution can be based on long-term discharge record for the site or on a discharge measurement made just prior to sample collection.

- **Rule of thumb:** divide the stream into a minimum of four increments. More increments could be needed for a stream site that is poorly mixed.
- If the stream is well-mixed with relatively uniform discharge, the EDI can consist of a single vertical at the centroid of flow.

To divide the cross section into increments of equal discharge:

1. Visually inspect the stream from bank to bank, observing velocity, width, depth distribution, and the apparent distribution of sediment and aquatic biota in the cross section. Note location of stagnant water, eddies, backwater, reverse flows, areas of faster than normal flow, and piers or other obstructions.

2. If the channel and the control governing the stage are stable, historical streamflow data can be used to determine the measurement locations. If the channel is unstable or if no historical data are available, make a discharge measurement and preliminary field measurements across the selected section of channel.

   a. From the available discharge data, either

      - construct a graph using cumulative discharge or cumulative percent of total discharge plotted against the cross-sectional width, or

      - determine EDI sections directly from the discharge measurement note sheet.

   b. If profile values of pH, conductivity, temperature, and DO differ by less than 5 percent and show that the stream is well mixed both across the section and from top to bottom, a single measurement point at the centroid of flow can be used to represent field-measurement values of the cross section.

3. From the graph or measurement notes, determine the number and locations of EDIs and the centroids of those increments.

   EXAMPLE: If 5 increments will be used, select points of measurement by dividing the total stream discharge by 5 to determine increment discharge: in this case, each EDI equals 20 percent of discharge. The first vertical is located at the centroid of the initial EDI, the point where cumulative discharge equals 10 percent of the total discharge. The remaining 4 centroids are found by adding increment discharge to the discharge at the initial EDI centroid. The EDI centroids will correspond to points along the stream cross section where 10, 30, 50, 70, and 90 percent of the total discharge occur.

When making field measurements:

1. Select either the in situ or subsample method and follow the instructions in 6.0.2.B.

   - In-situ method--Go to the centroid of the first equal-discharge increment. Using submersible sensors, measure at mid-depth (or multiple depths) in the vertical. Repeat at each vertical. The value recorded at each vertical represents the median of values observed within approximately 60 seconds after sensor(s) have equilibrated with stream water.

   - Subsample method--Collect an isokinetic depth-integrated sample at the centroid of each equal-discharge increment, emptying the increment sample into a compositing device.

Measure field parameters either in the sample collected at each increment or in a subsample taken from the composite of all the increment samples.

2. The final field-measurement value is the mean of the in situ or individual increment-sample value for all the EDI verticals in the section (the composite subsample yields a single value). (Note: for computation of mean pH, use the method described in section 6.4.3.A).

3. Enter data on field forms.

EXAMPLE: Table 6.0-2 is an example of how mean conductivity measured in situ is calculated using the equal-discharge-increment method.

Table 6.0–2. Example of field notes for a discharge-weighted conductivity measurement

[ft/sec, feet per second; ft, feet; ft^2, square feet; ft^3/sec, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; LEW, left edge of water; —, not available; REW, right edge of water]

Equal discharge increment	Percent of flow in increment	Mean velocity, in ft/sec	Width of increment, in ft	Depth of increment, in ft	Area of increment, in ft^2	Increment discharge, in ft^3/sec	Median conductivity, in µS/cm
LEW	0	—	—	—	—	—	—
1	20	2.0	22	5.7	125	250	185
2	20	2.2	11	10.4	114	250	170
3	20	2.3	9	12.0	109	250	155
4	20	3.9	5	12.8	64	250	155
5	20	3.4	10	7.4	74	250	150
REW	0	—	—	—	—	—	—

Calculation of conductivity: mean of median conductivity measurements (815 divided by 5)= 163 µS/cm.

- In the example, the correct value for the discharge-weighted mean conductivity is 163 µS/cm, calculated from 815 divided by 5 (the sum of the recorded median values divided by the number of median measurements).

- Note that at the midpoint of the center centroid of flow (increment 3) the median conductivity would have been reported as 155 µS/cm; if conductivity had been measured near the left edge of the water (increment 1), the conductivity would have been reported as 185 µS/cm.

Equal-width increment (EWI)

The stream cross section is divided into increments of equal width. Knowledge of the streamflow distribution in the cross section is not required.

- In situ field measurements are made at the midpoints of each increment. Area-weighted concentrations can be computed from these measurements (table 6.0-3).

- Subsample field measurements are made in discrete samples that usually are withdrawn from a composite sample collected using an isokinetic sample and isokinetic depth-

integrating method. The volume of the isokinetic sample must be proportional to the amount of discharge in each increment and measurements in subsamples taken from the compositing device result in discharge-weighted values.

Table 6.0-3. Example of field notes for an area-weighted conductivity measurement

[ft, feet; LEW, left edge of water; ft^2, square feet; µS/cm, microsiemens per centimeter at 25 degrees Celsius; —, not available; REW, right edge of water]

Section number	Cumulative percent of flow in section	Vertical location, in ft from LEW	Width of section, in ft	Depth of vertical, in ft	Area of section, in ft^2	Median conductivity, µS/cm	Product of median conductivity and area
LEW	0	0	—	—	—	—	—
1	2	2	4	1.0	4.0	150	600
2	4	6	4	2.0	8.0	145	1,160
3	6	10	4	2.6	10.4	145	1,508
4	10	14	4	3.2	12.8	140	1,792
5	16	18	4	3.5	14.0	135	1,890
6	22	22	4	4.0	16.0	130	2,080
7	28	26	4	4.5	18.0	130	2,340
8	34	30	4	5.4	21.6	125	2,700
9	42	34	4	6.0	24.0	125	3,000
10	50	38	4	5.7	22.8	125	2,850
11	62	42	4	5.1	20.4	125	2,550
12	76	46	4	4.6	18.4	125	2,300
13	88	50	4	3.5	14.0	125	1,750
14	96	54	4	1.4	5.6	135	756
15	99	58	4	1.0	4.0	140	560
REW	100	60	—	—	—	—	—

Calculation of conductivity: sum of values in last column divided by the total cross-sectional area $\left(\frac{27,830}{214} = 130\ \mu S/cm\right)$

To divide the cross section into increments of equal width:

1. Visually inspect the stream from bank to bank, observing velocity, width, depth distribution, and the apparent distribution of sediment and aquatic biota in the cross section. Note location of stagnant water, eddies, backwater, areas of faster than normal flow, and piers or other obstructions.

2. Determine stream width using a tagline or from station markings on bridge railings or cableways.

3. Divide the section into equal-width increments based on flow and stream-channel characteristics along the cross section, field-measurement variability from the cross-section profile, and data objectives for the study. This interval width will govern the number of verticals used, and applies also to streams in which flow is divided (for instance, in a braided channel).

Rule of thumb:

- In streams 5-ft wide or greater, use a minimum of 10 equal-width increments.

- In streams less than 5-ft wide, use as many increments as practical, but equally spaced a minimum of 3 inches apart.

4. Locate the midpoint of the first vertical at a distance of one-half of the selected increment width from edge of water. Locate other measurement verticals at the centers of the remaining increments.

   EXAMPLE: In a stream 60-ft wide that has been divided into 15 increments of 4 ft each, the first measurement vertical would be 2 ft from water's edge and subsequent verticals would be at 6, 10, 14 ft, and so forth, from the starting point at water's edge.

When making field measurements:

1. Select either the in situ or subsample method and follow the instructions in 6.0.2.B.

   - In situ method--Measure at the midpoint of each equal-width increment. Using submersible sensors, measure at mid-depth in the vertical.

   - Subsample method--Collect an isokinetic depth-integrated sample at the midpoint of each equal-width increment, emptying each sample into a compositing device. **Use of the correct sampling equipment is critical to execute this method successfully: standard samplers cannot meet isokinetic requirements when stream velocity is less than 1.5 ft/sec.**

2. Record a value for each field measurement for each vertical. The value recorded represents the stabilized values observed within approximately 60 seconds after the sensor(s) have equilibrated with the stream or subsample water.

   EXAMPLE: Table 6.0-3 provides an example of an area-weighted median measurement for conductivity measured in situ.

   - In the example, the area-weighted median conductivity equals 130µS/cm.

   - To calculate an area-weighted median, multiply the area of each increment by its corresponding field measurement, sum the products of all the increments, and divide by total cross-sectional area.

   - Note that if the conductivity reported was selected at mid-depth of the vertical of centroid of flow (section 10), it would have been reported as 125µS/cm; if the conductivity reported was near the left edge of water, it would have been reported as 150µS/cm.

- ► The final field-measurement value normally is calculated as the mean of the values recorded at all EWI increments, resulting in an area-weighted mean. (Note: for pH, calculate the mean using the method described in section 6.4.3.A).
- ► Alternatively for EWI, if the area-weighted median best represents integrated stream chemistry, you can report the median instead of the mean--but, be sure to document this on the field form and in the final data report (a parameter code currently is not available for median values).

6.0.2.B

IN SITU AND SUBSAMPLE MEASUREMENT PROCEDURES

In situ and subsample procedures used for making field measurements are summarized in figures 6.0-1 and 6.0-2, respectively. For guidance, specific instructions, and potential interferences to the measurement method, consult the individual field measurement sections of this chapter (NFM 6.1 through 6.7).

In situ measurement

In situ measurement (fig. 6.0-1), made by immersing a field-measurement sensor directly in the water body, is used to determine a profile of variability across a stream section. In situ measurement can be repeated if stream discharge is highly variable and measurement points need to be located at increments of equal discharge. However, in situ measurements are point samples, and, thus, are not depth integrated.

Measurements made directly (in situ) in the surface-water body are preferable in order to avoid changes that result from removing a water sample from its source. **In situ measurement is necessary to avoid changes in chemical properties of anoxic water.**

- **In situ measurement is mandatory for determination of temperature, dissolved-oxygen concentration, and Eh.**
- In situ measurement also can be used for pH, conductivity, and turbidity, but not for alkalinity.

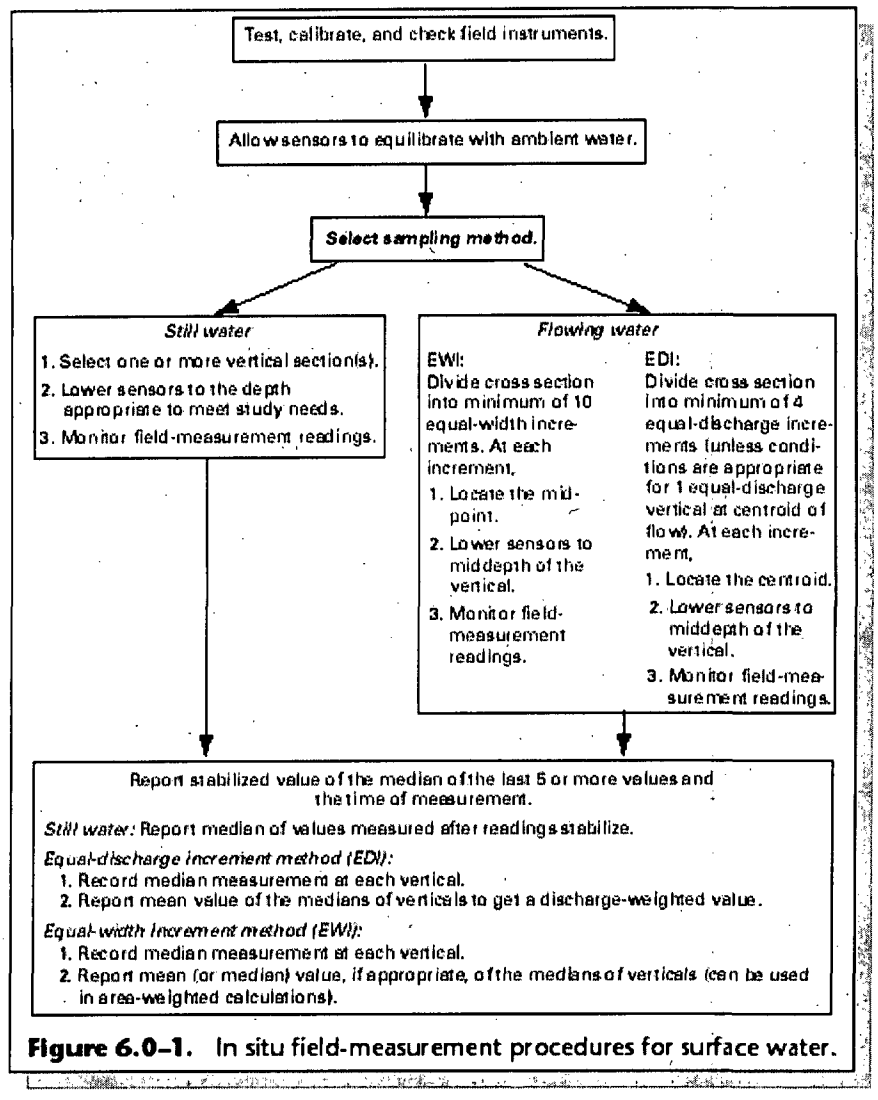


Figure 6.0–1. In situ field-measurement procedures for surface water.

Subsample measurement

Depth- and width-integrating sampling methods are used to collect and composite samples that can be subsampled for some field measurements. The same field measurements can be performed on discrete samples collected with thief, bailer, or grab samplers. Subsamples or discrete samples that have been withdrawn from a sample-compositing device or point sampler can yield good data for conductivity, pH, turbidity, and alkalinity as long as correct procedures are followed and the water is not anoxic (fig. 6.0-2).

- **Subsamples are necessary for alkalinity determinations.**
- Before using a sample-compositing/splitting device, preclean and field rinse the device in accordance with USGS-approved procedures (Horowitz and others, 1994).
- When compositing and splitting a sample, follow instructions for the clean hands/dirty hands technique detailed in Horowitz and others (1994), as required.

Do not measure temperature, dissolved oxygen, or Eh on subsamples.

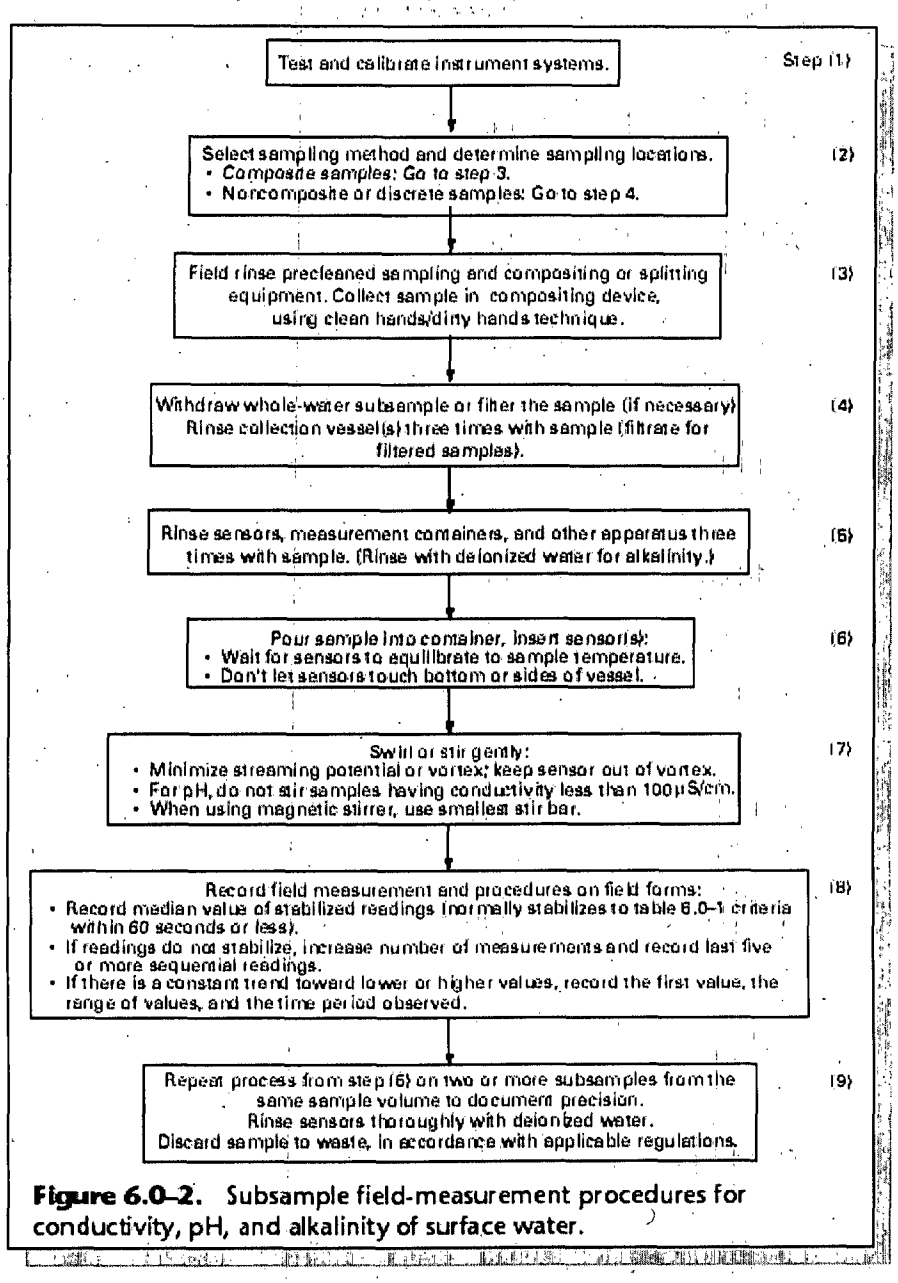


Figure 6.0–2. Subsample field-measurement procedures for conductivity, pH, and alkalinity of surface water.

⇨Section 6.0.3
⇧Section 6.0.1
⇧Return to Contents for 6.0--General Information and Guidelines
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 15Aug03 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.0.3.pdf

6.0.3
GROUND WATER

Field measurements in ground water must accurately represent the properties of the aquifer. This generally requires purging the well of standing water before making measurements (6.0.3.A), and involves setting up either a flowthrough-chamber or downhole field-measurement system (6.0.3.B). Standard USGS procedures for purging and the use of measurement systems are described below. However, the purging protocol followed and the measurement system to be used also depend on the type of well to be sampled and study objectives (detailed information can be found in Koterba and others, 1995; and Lapham and others, 1997).

Ground water for alkalinity is collected as a discrete sample: use a point-source sampler (for example, a Kemmerer sampler or double-check-valve bailer) or a pump with the intake positioned at the interval corresponding to the depth at which other measurements are made and at which samples will be collected.

Measurements at a monitoring well

- The standard purging procedure usually is necessary (6.0.3.A).
- Either a downhole or a flowthrough-chamber system can be used for field measurements (6.0.3.B). If samples will be collected, however, use the flowthrough chamber instead of the downhole system in order to avoid bias of chemical analyses from sample contact with downhole instruments.

Measurements at a supply well (a domestic well or a municipal, industrial, commercial, irrigation, or other production well)

- The standard purging procedure may not be appropriate (see "Exceptions to the standard USGS three-well-volume purging procedure" in 6.0.3.A).
- Identify well-construction materials and any equipment permanently installed in the well (such as a pump) that can affect the logistics and quality of the field measurement.
- Use a flowthrough-chamber type of system (6.0.3.B).
- Connect the field-measurement system to the wellhead at a point before the sample would pass through holding tanks, backflow pressure tanks, flow meters, or chemical treatment systems.

6.0.3.A
WELL PURGING: STANDARD PROCEDURE AND EXCEPTIONS

Well purging removes standing water from a well. Purging reduces chemical and biochemical artifacts caused by well installation, inadequate well development, well-construction materials, or infrequent pumping (American Society for Testing and Materials, 1992). Purging also serves to rinse and condition sampling equipment with well water.

When selecting purging equipment for monitoring wells, a portable, submersible nonaerating pump that also will be used for sampling is recommended.

- When the water table is deeper than 250 ft and (or) a large volume of water must be purged, a dual-pump system often is used: position a submersible pump downhole and a centrifugal pump at the surface. Water from the slow-pumping submersible pump is used for field measurements and to collect the sample, while the centrifugal pump operates at a higher rate to evacuate the required purge volume.
- When the water table is less than 25 to 30 ft from land surface, a peristaltic pump sometimes is used to purge small-diameter wells; a peristaltic pump or other comparable suction-lift device should not be used if dissolved-oxygen concentrations or Eh are being monitored during purging.
- To reduce the volume and time required for purging, especially in deep wells or in wells for which purge water must be contained, an inflatable packer sometimes is set above the pump and above the screened or open interval. Packers can fail to form a complete seal between aquifer intervals, and should be used with pressure transducers to indicate water leakage.
- **A bailer is not recommended for purging.** The plunging action of the bailer can release or stir up particulates that are not ambient in ground-water flow, resulting in biased measurements and analyses. (Refer to "Subsample measurement" in 6.0.3.B for information about using a bailer.)

Steel tapes and electric tapes or acoustic sensors are used to measure water level. An electric tape or other water-level sensor is recommended for continuous monitoring of drawdown during purging--repeated lowering of a weighted steel tape can release or stir up particulate materials and affect turbidity readings.

Standard USGS procedure for purging

Purge a minimum of three well volumes while monitoring temperature, pH, conductivity, dissolved-oxygen concentration, and turbidity.

- Sequential measurements of these parameters are used as criteria to help determine when water withdrawn from the well is representative of water flowing through the aquifer and when purging should end and sampling begin (table 6.0-1).
- The criteria normally are met within three well volumes, but well characteristics and study objectives could require removal of additional well volumes.
- The same pump should be used for purging and sampling, if possible, without stopping or removing the pump (see Koterba and others, 1995), unless the dual-pump system is used.

Exceptions to the standard USGS three-well-volume purging procedure

The number of well volumes removed and the parameters used as purge criteria can be subject to data-collection objectives, well characteristics, and equipment.

- Study objectives could require a different purge volume or require sequential sampling of additional chemical constituents.
- A lesser purge volume and modified procedures are needed, for example, for wells

  -- that are being pumped continuously or regularly every few hours (such as in-service public-supply wells).

  -- that are pumped dry or that have a water column of less than 4 ft plus the length of the submersible pump.

  -- in which sampling zones are isolated by packers.

  -- in which the pump intake is installed permanently within the screened or open interval.

Before purging begins:

1. Check the well-identification number. Check the well's record of water levels, drawdown, and field-measurement variability (if available).
2. Prepare the necessary field forms, such as the well-purge record, national or study field form, and chain-of-custody record. Record the type of equipment being used.
3. Lay plastic sheeting around the well to prevent contaminating the equipment. Unlock the well housing or top of the protective casing and remove the well cap.

To purge the well:

1. Measure and record the depth to static water level (fig. 6.0-3).

RECORD OF WELL PURGING

Date:_____ By:_____

SITE ID_____ STATION NAME_____ OTHER ID_____

WELL PURGING METHOD AND PUMP TYPE (describe) _____

TIME	WATER LEVEL below MP or LS	DRAW-DOWN	WELL YIELD	TEMPER-ATURE	CON-DUC-TIVITY	pH	DIS-SOLVED OXYGEN	TURBID-ITY	APPROX. PUMPING RATE
HR:MIN	ft or m	ft or m	gpm or cfs	°C	µS/cm	units	mg/L	NTU (or FTU)	gal/min or L/min

Well volume = V = 0.0408 HD² = ____ gallons Purge volume = (n)(V) = ____ gallons

V = volume of water in well, in gallons; D = inside well diameter, in inches; H = height of water column, in feet; n = number of well volumes to purge. If casing diameter = 2 in., well volume is 0.16 gallons per foot of casing.

FIELD MEASUREMENTS NTU, Nephelometric Turbidity Units; FTU, Formazin Turbidity Units	STABILITY CRITERIA Allowable difference in sequential parameter values
pH	± 0.1 standard units
Temperature, in degrees Celsius (°C)	± 0.2°C (thermistor)
Specific electrical conductance (SC), in microsiemens per centimeter at 25°C (µS/cm)	± 5%, for SC ≤ 100 µS/cm ± 3%, for SC > 100 µS/cm
Dissolved-oxygen concentration, in milligrams per liter (mg/L)	± 0.3 mg/L
Turbidity (TBY), in NTU (FTU ~ NTU)	± 10%, for TBY < 100 NTU; ambient TBY is <5 NTU for most ground-water systems (visible TBY > 5 NTU)

Figure 6.0–3. Example of a field form to record well purging.

2. Calculate and record the well volume as shown on fig. 6.0-3. Note that the depth to the screened or open interval and the inside casing diameter must be known to calculate well volume.

3. In a monitoring well, lower a submersible pump followed by a water-level sensor to the desired location of the pump intake. **The final pump intake position always is located at the point of sample collection.** Note that the pump position is fixed in supply wells and in monitoring wells with a permanently installed sampling system. **Lower the equipment slowly and smoothly to avoid stirring up particulates.**

    - Position the pump intake between 3 ft (~0.9 m) below static water surface and a minimum distance above the top of the open/screened interval of 10 times the well diameter (20 in. for a 2-in. well diameter), if the sample is to be integrated over the entire screened or open area

of the aquifer. The location of the intake may be different when the study objective requires collecting the sample from a point within the open/screened interval or from wells in which packers are installed.

- The water-level sensor should be a maximum of 1 ft (~0.3 m) below water surface.

4. Start the pump. Gradually increase and (or) adjust the pumping rate to limit drawdown to between 0.5 and 1.0 ft (~0.15 to ~0.3 m). Measure the water level as purging progresses.

   - If the final intake position is above the screened or open interval, the final pumping rate should be about 500 to 1,000 milliliters per minute. Do not exceed 1 ft of drawdown.

   - If the final intake position is within the screened or open interval, the final pumping rate should be about 200 to 500 milliliters per minute. Do not exceed 0.5 ft of drawdown.

   - If the pump and intake position are fixed, as in a supply well, control the rate of flow for field measurements through flow-splitting valve(s).

5. **Do not move the pump during purging or sample collection after the intake has been set at the final location.**

6. Purge a minimum of three well volumes or the purge volume dictated by study objectives (note "Exceptions to the standard USGS three-well-volume purging procedure"). Throughout purging, monitor and record field-measurement readings (fig. 6.0-3).

   - Check for special instructions regarding field-measurement or field-analysis requirements dictated by the study objectives.

   - Contain purge water as required by Federal, State, or local regulations.

7. **As the third or last well volume is purged, when the final field measurements are recorded, adjust the purge rate to the pumping rate to be used during sampling.**

   - Record field measurements at regular time intervals--about 3 to 5 minutes apart. For deep wells, the time intervals could be 15 minutes or longer. The time intervals selected will depend on the well characteristics and hydraulic properties of the aquifer, but the intervals must be sufficiently spaced to yield results representative of aquifer properties.

   - Consult criteria for field-measurement stabilization (table 6.0-1). Field experience, understanding of the effects of hydrologic and geochemical conditions, and knowledge of data-collection and data-quality requirements often are necessary to determine the most accurate field value.

     If criteria are being met--record at least five sequential measurements and report the median value.

     If criteria are not being met--consult the study requirements and objectives. Extend the purge time if readings still do not stabilize; report the median value of the last five or more sequential measurements.

Complete field forms and report the data

Report the median of the recorded field-measurement readings as the final well volume is purged.

- Record anomalies, difficulties, and adjustments on the field form.
- Record the purge volume, rate of pumping, initial and final intake locations, and time and respective reading of sequential field measurements (fig. 6.0-3).

Containment and disposal of purge water must conform to Federal, State, or local regulations.

6.0.3.B DOWNHOLE, FLOWTHROUGH-CHAMBER, AND SUBSAMPLE MEASUREMENT PROCEDURES

A flowthrough-chamber system is recommended for direct field measurements (fig. 6.0-4), if samples also will be collected for chemical analysis. A downhole system is recommended if field measurements will be monitored without sampling. If samples must be bailed from the well, measure only pH and conductivity in subsamples of the bailed volume (fig. 6.0-5).

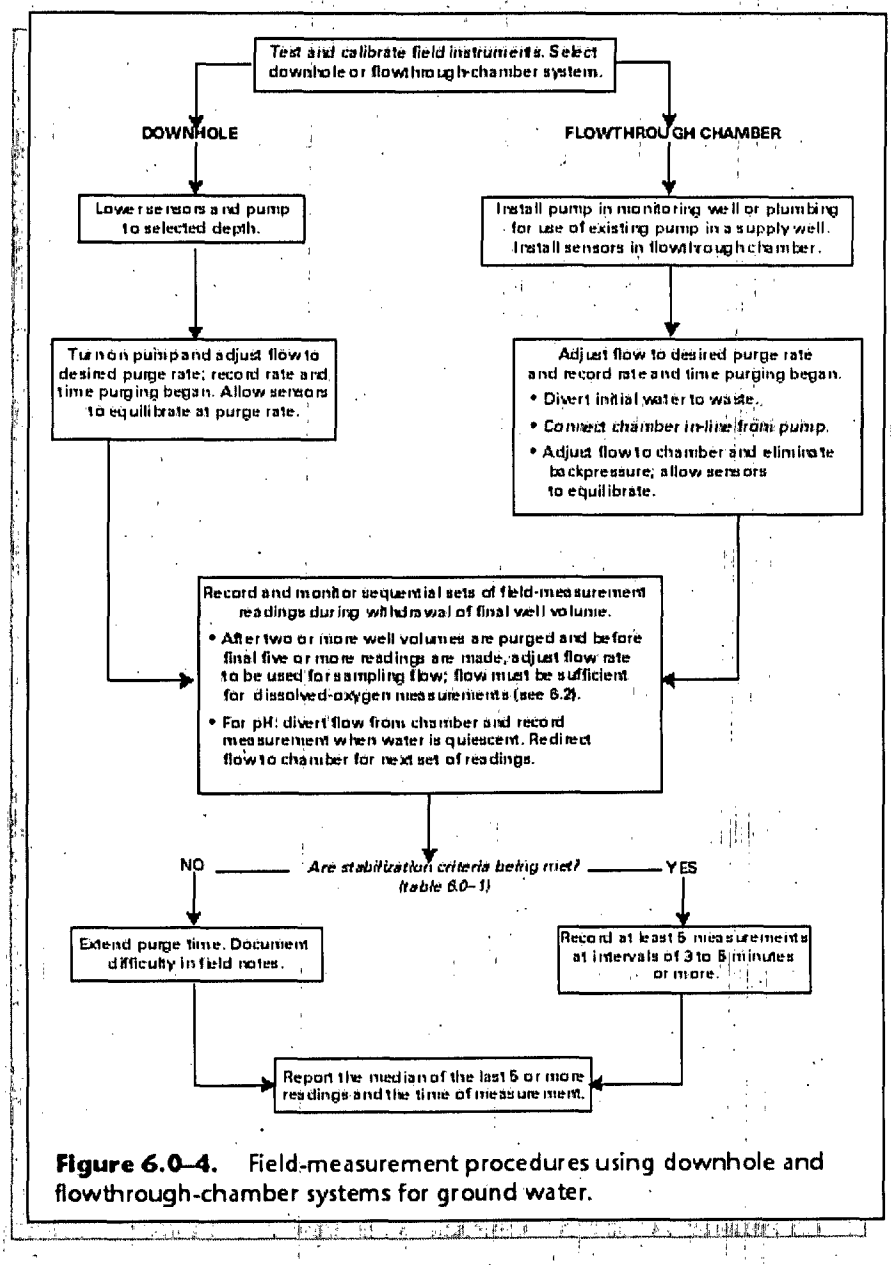


Figure 6.0–4. Field-measurement procedures using downhole and flowthrough-chamber systems for ground water.

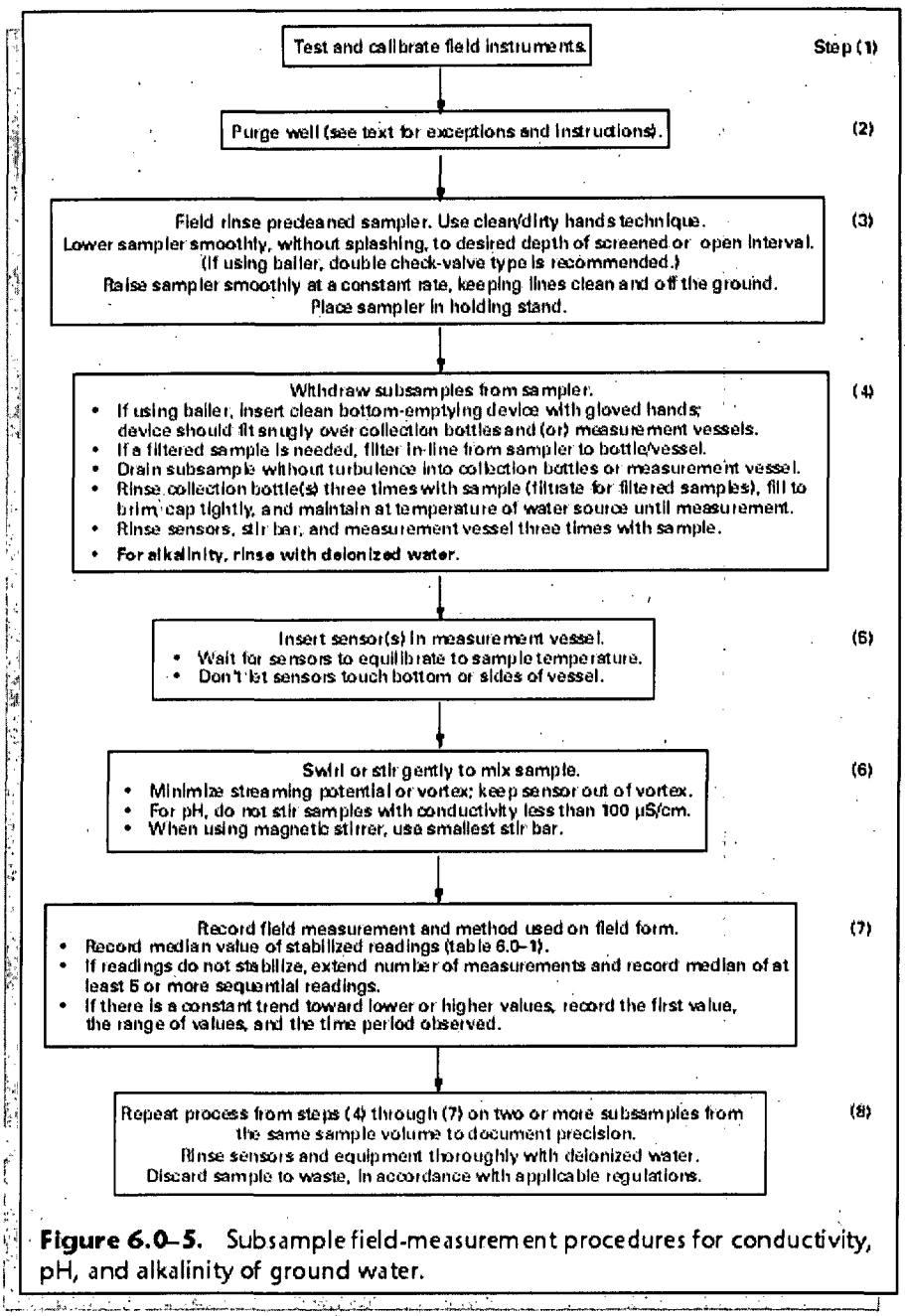


Figure 6.0–5. Subsample field-measurement procedures for conductivity, pH, and alkalinity of ground water.

- **Downhole or flowthrough-chamber systems are required for reported values of temperature, dissolved oxygen (DO), and Eh**--do not make these measurements in a bailed subsample or other discrete sample.
- Downhole or flowthrough-chamber systems are preferred for reported values of pH and conductivity.

A positive-displacement submersible pump is recommended for downhole and flowthrough-chamber systems. Lower a length of pipe to check that the well is free from obstructions before lowering a pump or downhole instrument in a well--this practice will prevent loss of costly equipment.

Downhole system

A downhole system is used for in situ field measurements. Ground water should flow upward past downhole sensors in order to obtain values representative of the depth interval being sampled; therefore, a submersible pump follows the downhole instrument. Because of this constraint, the downhole method may not be practical at wells with dedicated pumps or when using multiple equipment in small-diameter wells. Figure 6.0-4 shows the steps for downhole measurement of field parameters.

- The depth at which sensors are located depends on study objectives. If a sample is to represent ground water that is integrated over the screened interval, locate sensors approximately 1 ft above the screened interval in a 2-in. diameter well and just below the pump intake.
- Remove downhole sensors from the well before collecting samples for chemical analysis in order to prevent these instruments from affecting sample chemistry. Note that the process of removing these instruments and putting the pump back in the well causes disturbances that can affect the quality of samples subsequently collected for chemical analyses (Puls and others, 1991; Kearl and others, 1992; Puls and Powell, 1992).

Flowthrough-chamber system

A flowthrough chamber is an airtight, transparent vessel with a pressure-relief valve and either (1) grommeted ports to accommodate individual sensors or (2) a multiparameter instrument. Several types of flowthrough-chamber systems are available and can be designed for a specific measurement (for example, see NFM 6.2.2 for the description of a flowthrough cell for the spectrophotometric determination of dissolved-oxygen concentration).

When setting up a flowthrough chamber:

1. Install the chamber in-line from the pump and as close to the wellhead as possible.
    - Keep the chamber, field-measurement instruments, and tubing off the ground, shaded from direct sunlight, and shielded from wind.
    - Keep the tubing as short as possible.
2. Install the dissolved-oxygen sensor immediately downstream from the chamber inflow, and install the pH sensor downstream from the conductivity sensor.
3. Turn on the pump; direct initial flow to waste to avoid introducing sediment into the chamber.
    - Adjust the flow into the chamber so that a constant stream of water is maintained at the rate required for dissolved-oxygen measurements (see NFM 6.2).
    - Correct any backpressure conditions; tilt the chamber to expel trapped air.

Subsample measurement

Subsamples or discrete samples are aliquots of sample collected from a nonpumping sampling device such as a bailer, a thief sampler, or a syringe sampler. Measurements of field parameters made in discrete or nonpumped samples are more vulnerable to bias from changes in temperature, pressure,

turbidity, and concentrations of dissolved gases than measurements using a downhole or flowthrough-chamber system.

- Subsamples can be used for conductivity, pH, and alkalinity.
- Subsamples must not be used for reported measurements of temperature, dissolved oxygen, Eh, or turbidity.
- Subsample procedures must not be used in reducing (anoxic) waters.

Figure 6.0-5 shows the steps for measurement of field parameters on a bailed sample. If collecting a sample with a bailer, use one with a double check valve. Field rinse the sampler with sample water before using. To shield the sample from atmospheric contamination, make measurements in a collection chamber or in a glove box filled with inert gas. Indicate on field forms the sampling and measurement procedures used.

⇨Section 6.1--Temperature
⇧Section 6.0.2
⇧Return to Contents for 6.0--General Information and Guidelines
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 26MAY98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document (version 1.2) is also available in pdf format:

Section 6.1--Temperature

National Field Manual

6.1 TEMPERATURE (Version 1.2, April 2004)

By D.B. Radtke, J.K. Kurklin, and F.D. Wilde

6.1 Temperature

6.1.1 Equipment and supplies
6.1.1.A Maintenance, cleaning, and storage

6.1.2 Calibration

6.1.3 Measurement
6.1.3.A Air
6.1.3.B Surface water
6.1.3.C Ground water

6.1.4 Troubleshooting
6.1.5 Reporting

Tables

6.1-1. Equipment and supplies used for measuring temperature

6.1-2. Troubleshooting guide for temperature measurement

⇨Section 6.1
⇧Section 6.0.3
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 9APR04 imc

Archive of Version 1.1, Sept. 2002 and April 1998 pdf

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.1.pdf

6.1 TEMPERATURE

Temperature: a measure of warmth or coldness of a substance with reference to a standard value.

Measurements of water and air temperatures at the field site are essential for water-data collection. Determinations of dissolved-oxygen concentrations, conductivity, pH, rate and equilibria of chemical reactions, biological activity, and fluid properties rely on accurate temperature measurements.

Accurate water- and air-temperature data are essential to document thermal alterations to the environment caused by natural phenomena and by human activities. Water temperature is subject to environmental monitoring by State and local agencies.

The USGS has adopted the Celsius (C) scale for measuring temperature. This section describes methods for measuring temperature in air, surface water, and ground water. The methods are appropriate for fresh to saline waters.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances--follow the manufacturer's instructions.

⇨Section 6.1.1.
⇧Return to Contents for 6.1--Temperature
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 28OCT98 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

6.1.1
EQUIPMENT AND SUPPLIES

Temperature instruments must be tested before each field trip and cleaned soon after use (table 6.1-1). Each instrument must have a log book in which all calibrations and repairs are recorded, along with the manufacturer make and model description and serial or property number.

A thermometer is any device used to measure temperature, consisting of a temperature sensor and some type of calibrated scale or readout device. Liquid-in-glass thermometers and thermistor thermometers are most commonly used to measure air and water temperature.

- Extreme field conditions (for example, frigid climates or thermal waters) may require thermometers capable of measuring a broader temperature range.

CAUTION: Do not use mercury-filled thermometers in the field.

The operating instructions for thermometers are provided by the manufacturer.

- **Liquid-in-glass thermometer**--Recommended liquid-in-glass thermometers are total-immersion thermometers filled with alcohol. Thermometers for field use must not be mercury-filled. Before measuring temperature, check the type of liquid-filled thermometer being used. (Partial-immersion thermometers are not recommended: these have a ring or other mark to indicate the immersion depth required.)
- **Thermistor thermometer**--A thermistor thermometer is an electrical device made of a solid semiconductor with a large temperature coefficient of resistivity. An electrical signal processor (meter) converts changes in resistance to a readout calibrated in temperature units. Thermistors commonly are incorporated in instruments used for surface-water and ground-water measurements.

6.1.1.A
MAINTENANCE, CLEANING, AND STORAGE

Thermometers can easily become damaged or out of calibration. Take care to:

- Keep thermometers clean (follow manufacturer's recommendations).
- Carry thermometers in protective cases; thermometers and cases must be free of sand and debris.
- Store liquid-filled thermometers in a bulb-down position and in a cool place away from direct sunlight.

As an additional precaution on field trips, carry extra calibrated thermometers as spares, and a supply of batteries for instrument systems.

⇨Section 6.1.2
⇧Section 6.1
⇧Return to Contents for 6.1--Temperature
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 9APR04 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

6.1.2 CALIBRATION

To calibrate a thermometer, instrument readings are checked across a range of temperatures against those of a thermometer of certified accuracy.

Calibrate liquid-in-glass and thermistor thermometers in the office at regularly scheduled intervals. Tag acceptable thermometers with date of calibration.

Minimum calibration requirements

- **Liquid-in-glass thermometer:**

  -- **Every 3 to 6 months,** using a 2-point calibration, and

  -- **Annually,** using a 3-point calibration.
- **Thermistor thermometer:**

  -- **Every 3 to 4 months,** check calibration

  -- **Annually,** using a 5-point calibration.
- The standard thermometer against which all other thermometers are calibrated must be either NIST certified or NIST traceable, and carry a certificate of NIST certification or traceability from the manufacturer. The calibration thermometer may only be used within the period for which it was certified as NIST traceable; once certification has expired, the calibration thermometer either must be replaced or sent to an accredited laboratory for recertification. These protocols apply to electronic thermistor thermometers as well as to liquid-in-glass thermometers. The calibration must be accurate to at least 0.1°C.

Check the certificate of calibration for the NIST thermometer before calibrating field thermometers. **NIST-certified thermometers are not for field use.**

Thermometers being calibrated must meet NIST specifications to a minimum of three temperatures at approximately 0°, 25°, and 40°C. Thermistors must be calibrated at 5 points within this range. If environmental water or air temperatures will fall below 0°C or rise above 40°C, add additional calibration points to bracket the temperatures to be measured.

Field checking thermometer calibration by comparing readings with another field thermometer does not substitute for required laboratory calibration procedures. When measuring water temperature in the laboratory:

- Submerge the bulb and liquid column of the total-immersion thermometer.
- Keep the NIST-certified thermometer and the thermistor sensor submerged in the container throughout calibration.
- Read the NIST-certified thermometer and record the thermistor readings throughout warming and cooling periods.
- Check the meter batteries periodically for proper voltage.
- Record the calibration data in the instrument log book for each thermistor thermometer, noting if a sensor has been replaced.

If using a commercial refrigerated water bath:

1. Precool the sensor of the thermometer being tested (test thermometer) to 0°C by immersing it in a separate ice/water bath.

2. Immerse the test and NIST-certified thermometer sensors in the refrigerated bath with a water temperature of approximately 0°C.

3. Position the thermometer sensor(s) so that they are properly immersed and so that the scales can be read. Stir the water bath and allow at least 2 minutes for the thermometer readings to stabilize.

4. Without removing the thermometer sensor from the refrigerated water bath, read the test thermometer(s) to the nearest graduation (0.1 to 0.5°C) and the NIST-certified thermometer to the nearest 0.1°C.

    - Take three readings within a 5-minute span for each thermometer.
    - Calculate the mean of the three temperature readings for each thermometer and compare its mean value with the NIST-certified thermometer.
    - If the liquid-filled test thermometer is found to be within ±1 percent of full scale or ±0.5°C of the NIST-certified thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
    - If the test thermistor is found to be within ±0.2°C of the NIST-certified thermometer, set it aside for calibration checks at higher temperatures.

5. Repeat steps 1-3 in 25°C and 40°C water. Keep the bath temperature constant. Check the thermistors at two or more additional intermediate temperatures (for example, 15°C and 30°C).

6. Tag acceptable thermometers as "District certified" with calibration date and certifier's initials.

If a commercial refrigerated water bath is not available:

1. Freeze several ice cube trays filled with deionized water.

2. Fill a 1,000-mL plastic beaker or Dewar flask three-fourths full of crushed, deionized ice. Add chilled, deionized water to the beaker. Place the beaker of ice/water mixture in a larger, insulated container or Dewar flask. Place the NIST-certified thermometer into the ice/water mixture and make sure that the temperature is uniform at 0°C by stirring and checking at several locations.

3. Precool the test thermometer sensor to 0°C by immersing it in a separate ice/water bath.

4. Add the test thermometer sensor(s) to the ice/water mixture. Position the sensor(s) so that they are properly immersed and so that the scales can be read. Periodically stir the ice/water mixture and allow at least 2 minutes for the thermometer readings to stabilize.

5. When the readings stabilize, compare the temperature of one test thermometer at a time with that of the NIST-certified thermometer. Without removing the temperature sensor(s) from the test bath, read the test thermometer(s) to the nearest graduation (0.1 to 0.5°C) and the NIST-certified thermometer to the nearest 0.1°C.

    - Take three readings for each thermometer within a 5-minute span.
    - Calculate the mean of the three temperature readings for each thermometer and compare its mean value with the NIST thermometer.
    - If the test liquid-filled thermometer is found to be within ±1 percent of full scale or ±0.5°C of the NIST-certified thermometer, whichever is less, set it aside for calibration checks at higher temperatures.
    - If the test thermistor is found to be within ±0.2°C of the NIST-certified thermometer, set it aside for calibration checks at higher temperatures.

6. For "room temperature" calibration (about 25°C), place a Dewar flask or container filled with about 1 gallon of water in a box filled with packing insulation. (A partially filled insulated ice chest can be used for multiparameter instruments.) Place the calibration container in an area of the room where the temperature is fairly constant (areas away from drafts, vents, windows, and harsh lights).

7. Properly immerse the NIST-certified and test thermometer sensor(s) in the water. Cover the container and allow the water bath and thermometers to equilibrate. Stir the water and check every couple of hours for temperature uniformity using the NIST-certified thermometer--it may be necessary to let the bath equilibrate overnight.

8. Compare one test thermometer at a time with the NIST-certified thermometer. Calibrate as described in step 5 above.

    - For greater than 25°C temperature calibration, place a beaker (1,000 mL or more) of warm water (about 40°C) on a magnetic stirrer plate and repeat procedure as described in step 5 above.
    - Tag acceptable thermometers as "District certified" with calibration date and certifier's initials.

Corrections can be applied to measurements made with a thermometer that is within +/- 1 percent of full scale or +/- 0.5°C of the calibration thermometer. Corrections should be applied by using a calibration curve or table, which is plotted in the log book for the instrument. **Thermistors found to be out of calibration by more than 0.2°C must be recalibrated per manufacturer's instructions or returned to the manufacturer for proper calibration and (or) repairs.**

Thermistors included in other field-measurement instruments must be calibrated routinely. Accurate determination of other field measurements depends on accurate temperature measurements. This must be underscored for thermistors incorporated in specific electrical conductance, dissolved-oxygen, and pH instruments, because these thermistors are used for automatic temperature compensation of the measurement being made.

Tag and date acceptable thermometers.

⇨ Section 6.1.3
⇧ Section 6.1.1
⇧ Return to Contents for 6.1--Temperature
⇧ Return to Chapter A6 Contents Page
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 28OCT98 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.1.3.pdf

6.1.3 MEASUREMENT

Water-quality sampling should include an air-temperature measurement and a water-temperature measurement. Before measuring temperature:

- Inspect liquid-in-glass thermometers to be certain liquid columns have not separated.
- Inspect bulbs to be sure they are clean.
- Inspect protective cases to be sure they are free of sand or debris.

6.1.3.A AIR

Read air temperature with a dry, calibrated thermometer.

- Place the thermometer about 5 ft above the ground in a shaded area protected from strong winds but open to air circulation. Avoid areas of possible radiant heat effects, such as metal walls, rock exposures, or sides of vehicles.
- Allow 3 to 5 minutes for the thermometer to equilibrate, then record the temperature and time of day.
- Measure the air temperature as close as possible to the time when the water temperature is measured.
- Report routine air temperature measurements to the nearest 0.5°C. If greater accuracy is required, use a thermistor thermometer that has been calibrated to the accuracy needed.

6.1.3.B SURFACE WATER

The reported surface-water temperature must be measured in situ--**do not measure temperature on subsamples** from a sample compositing device. Measure temperature in such a manner that the mean or median temperature at the time of observation is represented (consult NFM 6.0 and fig. 6.0-1). Record any deviation from this convention in the data base and report it with the published data.

To measure the temperature of surface water:

- Make a cross-sectional temperature profile to determine temperature variability--A thermistor thermometer works best for this purpose.
- Determine from the cross-sectional profile and from study objectives which sampling method to use (see NFM 6.0).
- Measure temperature in those sections of the stream that represent most of the water flowing in a reach. Do not make temperature measurements in or directly below stream sections with turbulent flow or from the stream bank (unless this represents the condition to be monitored).

1. Use either a liquid-in-glass thermometer tagged as "District certified" within the past 12 months, or a thermistor thermometer tagged "District certified" within the past 4 months.

2. Record on field forms the temperature variation from the cross-sectional profile, and the sampling method selected.

   - **Flowing, shallow stream**--wade to the location(s) where temperature is to be measured. To prevent erroneous readings caused by direct solar radiation, stand so that a shadow is cast on the site for temperature measurement.

   - **Stream too deep or swift to wade**--measure temperature by lowering from a bridge, cableway, or boat a thermistor thermometer attached to a weighted cable. Do not attach a weight to the sensor or sensor cable.

   - **Still-water conditions**--measure temperature at multiple depths at several points in the cross section.

3. Immerse the sensor in the water to the correct depth and hold it there for no less than 60 seconds until the sensor equilibrates thermally. The sensor must be immersed properly while reading the temperature; this might require attaching the thermistor to a weighted cable.

   TECHNICAL NOTE: For in situ measurement with liquid-filled thermometers--the water depth must be no greater than twice the length of the liquid column of the thermometer in order to make an accurate measurement.

4. Read the temperature to the nearest 0.5°C (0.2°C for thermistor readings)--**do not remove the sensor from the water.**

   - Using a liquid-in-glass thermometer, check the reading three times and record on field forms the median of these values.

   - Using a thermistor thermometer, wait until the readings stabilize to within 0.2°C, then record the median of approximately the last 5 values.

5. Remove the temperature sensor from the water, rinse it thoroughly with deionized water, and store it.

6. Record the stream temperature on field forms:

   - **In still water--median** of three or more sequential values.

- **EDI--mean** value of subsections measured (use median if measuring one vertical at the centroid of flow).

- **EWI--mean or median** value of subsections measured.

6.1.3.C
GROUND WATER

Measurements of ground-water temperature must be made downhole at the end of purging for temperature to represent aquifer conditions (consult NFM 6.0 for guidance).

To measure the temperature of ground water:

- Select either the downhole or flowthrough-chamber sampling system of measurement (see NFM 6.0, fig. 6.0-4) and record on field forms. **Do not report a temperature value measured from a bailed sample.**
- Measure temperature with a thermometer that has been District certified and is calibrated within the temperature range to be encountered.

1. Prepare the instruments for either the downhole or the flowthrough-chamber system.

    - **Downhole system**--lower the sensor in the well to just below the pump intake (the intake location depends on the sampling objectives).

    - **Flowthrough-chamber system**--properly immerse the thermistor or liquid-in-glass thermometer in the chamber. Keep the tubing from the well to the chamber as short as possible, out of direct sunlight, and off the ground.

2. Begin water withdrawal from the well.

3. Allow the thermometer sensor to equilibrate with the well water for 5 minutes; record the readings and time intervals throughout the period of purging.

4. Toward the end of purging, record five measurements, spaced at increments of 3 to 5 minutes or more.

    - If the thermistor temperature is stable within the 0.2°C criterion (for a liquid-in-glass thermometer, there should be only slight fluctuation within the 0.5°C interval), report the median of the final five measurements (table 6.0-1).

    - If the stability criterion has not been met, extend the purge time and consult the well-purging objectives of the study. Report the median of the last five (or more) sequential measurements and record any instability on field forms.

5. Remove and clean the temperature sensors.

⇨ Section 6.1.4

⇧Section 6.1.2
⇧Return to Contents for 6.1--Temperature
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 15AUG00 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.1.4.pdf

6.1.4 TROUBLESHOOTING

Contact the instrument manufacturer if the suggestions on table 6.1-2 fail to resolve the problem.

When using thermistor thermometers:

- Check the voltage of the batteries.
- Start with good batteries in instruments and carry spares.

Table 6.1-2. Troubleshooting guide for temperature measurement

Symptom	Possible cause and corrective action
Liquid-in-glass thermometer doesn't read accurately	• Check thermometer to see that the liquid is not separated—if separated, take back to the office to reunite column.
Thermistor thermometer doesn't read accurately	• Dirty sensor—remove dirt and oil film. • Weak batteries—replace with new batteries.
Erratic thermistor thermometer readings	• Bad or dirty connection at meter or sensor—tighten or clean connections. • Break in the cables—replace cables. • Weak batteries—replace with new batteries.
Thermistor thermometer slow to stabilize	• Dirty sensor—clean sensor to remove dirt and oily film.

⇨Section 6.1.5
⇧Section 6.1.3
⇧Return to Contents for 6.1--Temperature
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Patsy Campbell
Last Modified: 27MAY98 pac

Table 6.1–2. Troubleshooting guide for temperature measurement

Symptom	Possible cause and corrective action
Liquid-in-glass thermometer doesn't read accurately	• Check thermometer to see that the liquid is not separated—if separated, take back to the office to reunite column.
Thermistor thermometer doesn't read accurately	• Dirty sensor—remove dirt and oil film. • Weak batteries—replace with new batteries.
Erratic thermistor thermometer readings	• Bad or dirty connection at meter or sensor—tighten or clean connections. • Break in the cables—replace cables. • Weak batteries—replace with new batteries.
Thermistor thermometer slow to stabilize	• Dirty sensor—clean sensor to remove dirt and oily film.

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.1.5.pdf

6.1.5 REPORTING

Report temperature measurements in the data base to the nearest 0.5°C.

- For studies for which greater accuracy is desired, temperatures can be reported to the accuracy requested, provided the thermometer has been calibrated to that accuracy.
- Enter field measurements of air and water temperature on NWQL Analytical Services Request forms, and in the data base under the correct parameter code.
- Record the accuracy range of the instrument in the data base, if possible. Report accuracy range with the published values.

Report only those water temperature values that were measured in situ.

⇨Section 6.2 Contents
⇧Section 6.1.4
⇧Return to Contents for 6.1--Temperature
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Patsy Campbell
Last Modified: 27MAY98 pac

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Complete pdf for Section 6.2--Dissolved Oxygen

National Field Manual

6.2 DISSOLVED OXYGEN

By D.B. Radtke, A.F. White, J.V. Davis, and F.D. Wilde

6.2 Dissolved oxygen

6.2.1 Amperometric method
- 6.2.1.A Equipment and supplies
  - Maintenance and storage
- 6.2.1.B Calibration
  - Atmospheric pressure correction
  - Calibration procedures
    1. Air-calibration chamber in water
    2. Air-saturated water
    3. Air-calibration chamber in air
    4. Iodometric (Winkler) titration
- 6.2.1.C Measurement
  - Surface water
  - Ground water
- 6.2.1.D Troubleshooting (amperometric method)

6.2.2 Spectrophotometric method
- 6.2.2.A Equipment and supplies
- 6.2.2.B Calibration and interferences
- 6.2.2.C Measurement

6.2.3 Reporting

6.2.4 Correction factors for oxygen solubility and salinity

Illustrations

6.2-1. Graph showing factors used to correct atmospheric pressures adjusted to sea level

Tables

6.2-1. Equipment and supplies used for amperometric method of dissolved-oxygen determination
6.2-2. Factors used to correct atmospheric pressures adjusted to sea level
6.2-3. Equipment and supplies used for the iodometric dissolved-oxygen determination
6.2-4. Troubleshooting guide for amperometric determination of dissolved-oxygen concentration
6.2-5. Equipment and supplies (Rhodazine-D[a] technique)
6.2-6. Solubility of oxygen in water at various temperatures and pressures
6.2-7. Salinity correction factors for dissolved oxygen in water (based on conductivity)

⇨Section 6.2
⇧Section 6.1.5
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 26MAY98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.2.pdf

6.2
DISSOLVED OXYGEN

Dissolved oxygen: molecular oxygen (oxygen gas) dissolved in water.

Accurate data on concentrations of dissolved oxygen (DO) in water are essential for documenting changes to the environment caused by natural phenomena and human activities. Sources of DO in water include atmospheric reaeration and photosynthetic activities of aquatic plants. Many chemical and biological reactions in ground water and surface water depend directly or indirectly on the amount of oxygen present. Dissolved oxygen is necessary in aquatic systems for the survival and growth of many aquatic organisms.

Two field methods for determining concentrations of dissolved oxygen in surface and ground waters are the amperometric method and the spectrophotometric method.

- The amperometric method is the standard procedure for determination of DO concentrations.
- The spectrophotometric method described in this report (the Rhodazine-D™, technique) is recommended for determining concentrations of DO less than 1.0 mg/L.
- Except where noted, these methods are applicable to unfiltered surface and ground waters, from fresh to saline.
- The iodometric (Winkler) method generally is not recommended for field determination of dissolved oxygen because the accuracy and reproducibility achieved depend largely on the experience and technique of the data collector. The iodometric method is described under amperometric calibration procedures (6.2.1.B).

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.

[1]Rhodazine-D™, a colorless, reduced phenzone dye, is a proprietary product of CHEMetrics, Incorporated, and constitutes approximately 0.01 volume percent of solution in the ampoule. Remaining constituents in the ampoule are water, diethylene glycol, hydroxymethyl aminomethane, and potassium hydroxide.

⇨Section 6.2.1
⇧Return to Contents for 6.2--Dissolved Oxygen
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 28MAY98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.2.1.pdf

6.2.1
AMPEROMETRIC METHOD

The most commonly used field method for measuring DO in water is the amperometric method, in which DO concentration is determined with a temperature-compensating instrument or meter that works with a polarographic membrane-type sensor.

6.2.1.A EQUIPMENT AND SUPPLIES

The instrument system used to measure DO must be tested before each field trip and cleaned soon after each use. Battery-powered instruments are recommended. A variety of DO meters and sensors are available--**read thoroughly the instructions provided by the manufacturer.** Every DO instrument and the barometer must have a log book in which repairs and calibrations are recorded, along with the manufacturer make and model description, and the serial or property number.

- The term "dissolved-oxygen sensor" refers to the entire sensor assembly, including the electrodes, electrolyte solutions, membranes, and thermistor thermometers.
- Dissolved-oxygen sensors must be temperature compensating: the permeability of the membrane and solubility of oxygen in water change as a function of temperature.
- The type of membrane selected for the sensor depends on the anticipated rate of flow. **For ground water, "low-flow" membranes should be used.**
- All built-in thermistor thermometers must be calibrated and field checked before use (see section 6.1, "Temperature").

Yellow Springs Instrument Company (YSI) DO instruments are used as an example in this chapter because they are in common use by USGS field personnel. The YSI 5700 series sensors have two separate thermistors. The temperature of the solution is measured by the temperature-display thermistor, mounted in a stainless steel tube on the side of the sensor. Next to the temperature-display thermistor is the temperature-compensation thermistor that compensates for temperature-caused changes in membrane-oxygen permeability. **The permeability of the Teflon™ membrane changes about 3 percent for each 1°C change in temperature.**

Table 6.2–1. Equipment and supplies used for amperometric method of dissolved-oxygen determination[1]

[DO, dissolved oxygen; YSI, Yellow Springs Instrument Company; mm, millimeter; g, gram; mL, milliliter; L, liter; DIW, deionized water]

- ✓ DO instrument and DO sensor or multiparameter instrument with DO capability
  - Temperature readout display, analog or digital
  - Temperature and pressure compensated
  - Operating range at least -5°C to +45°C
  - Measure concentrations ≥1 to 20 mg/L
  - Minimum scale readability, preferably 0.05 mg/L DO
  - Calibrated accuracy within 5 percent or ±0.3 mg/L DO, whichever is less
- ✓ DO sensor membrane replacement kit: membranes, O-rings, filling solution
- ✓ Stirrer attachment for DO sensor
- ✓ Calibration chamber: YSI model 5075A sensor, or equivalent
- ✓ Pocket altimeter-barometer, calibrated; measures to nearest 2 mm, Thommen model 2000
- ✓ Thermometer, calibrated (see section 6.1 for selection and calibration criteria)
- ✓ Zero DO calibration solution[2]: dissolve 1 g sodium sulfite and a few crystals of cobalt chloride in 1 L DIW
- ✓ Flowthrough chamber for determining DO in ground water
- ✓ Oxygen solubility table (table 6.2–6)
- ✓ Waste disposal container or equivalent
- ✓ Spare batteries, filing solution, and membranes
- ✓ Log books for DO instrument and barometer for recording all calibrations, maintenance, and repairs

[1] Modify this list to meet specific needs of the field effort. See table 6.2–3 for equipment list for iodometric DO determination and Table 6.2–5 for equipment list for Rhodazine-D™ DO determination.

[2] Prepare fresh zero DO solution before each field trip.

Analog YSI instruments have two thermistors that compensate for the effects of temperature. Digital YSI instruments do not contain instrument-compensating thermistors, but rely on the temperature-display thermistor in the sensor to calculate membrane permeability.

CAUTION: Before handling any chemicals, refer to the Material Safety Data Sheet (MSDS) for safety precautions.

Maintenance and storage

Dissolved-oxygen instruments and sensors are sophisticated electronic equipment that require care in handling and operation.

- Follow the manufacturer's recommendations for short-term (field) and long-term (office) storage of sensors and for performance checks.
- Protect instruments and sensors from being jostled during transportation, from sudden impacts, sudden temperature changes, and extremes of heat and cold.

Before each field trip:

1. Check the temperature-display thermistor in the DO sensor against a certified thermometer over

the normal operating range of the instrument. If a thermistor reading is incorrect, apply a correction or return the instrument to the manufacturer for adjustment.

2. Recondition the DO sensor if it fails a performance check.

3. Check the instrument batteries and all electrical connections.

4. Test the instrument to ensure that it will read zero in a DO-free solution.

   - If the instrument reading exceeds 0.2 mg/L, then the sensor membrane and electrolyte (if present) need to be replaced or the sensor needs to be repaired.

   - Before repairing or replacing the sensor, check zero DO again with a freshly prepared zero DO solution.

5. On analog instruments:

   - Check mechanical zero (if applicable) before turning the instrument on; adjust it if necessary.

   - Check redline and zero readings (if applicable) and adjust as needed.

   - If the instrument cannot be adjusted, recharge or replace the batteries.

6. Calibrate the pocket altimeter-barometer.

6.2.1.B CALIBRATION

Calibration and operation procedures for the amperometric method differ among instrument types and makes--refer to manufacturer's instructions. Record all calibration information in instrument log books and copy calibration data onto field forms at the time of calibration.

Atmospheric pressure, temperature of the water or water vapor, and conductivity (or salinity) of the water must be known to determine the theoretical amount of oxygen that can be dissolved in water. Although the salinity correction can be made either during calibration or after measurement, **the preferred USGS method is to apply salinity correction factors after calibration and measurement** (recalibration is necessary for each field variation in salinity and temperature if the correction is made during calibration). For salinity-correction procedures, see section 6.2.4.

Atmospheric pressure correction

Ambient atmospheric pressure is true atmospheric pressure at the measurement site, not that which has been adjusted to sea level. Atmospheric pressure reported by the National Weather Service generally is not the true (ambient) value. Weather Service atmospheric readings usually are adjusted to sea level and must be adjusted back to the elevation of the weather station. Upon request, a weather station sometimes provides unadjusted atmospheric pressure.

▶ Use a calibrated pocket altimeter-barometer to determine ambient atmospheric pressure

to the nearest 1 mm of mercury.

- Check the accuracy of all field barometers before each field trip, and record readings and adjustments in the log book. If possible, check barometer accuracy with information from an official weather station.
- Use table 6.2-2 and figure 6.2-1 if the value used for atmospheric pressure has been adjusted to sea level.
- To correct weather station readings adjusted to sea level to ambient atmospheric pressure: subtract appropriate values shown (table 6.2-2, fig. 6.2-1) from atmospheric readings adjusted to sea level (shown in millimeters of mercury).

Although atmospheric pressure does not decrease linearly with increases in elevation, linear interpolation is acceptable within the elevation ranges given in table 6.2-2. Alternatively, plot the values from table 6.2-2 and extrapolate subtraction factors directly from the graph. Section 6.2.4 contains the table of oxygen solubilities at various temperatures and pressures.

Table 6.2–2. Factors used to correct atmospheric pressures adjusted to sea level

Elevation of weather station (feet above sea level)	Value to subtract (millimeters of mercury)
0	0
1,000	27
2,000	53
3,000	79
4,000	104
5,000	128
6,000	151

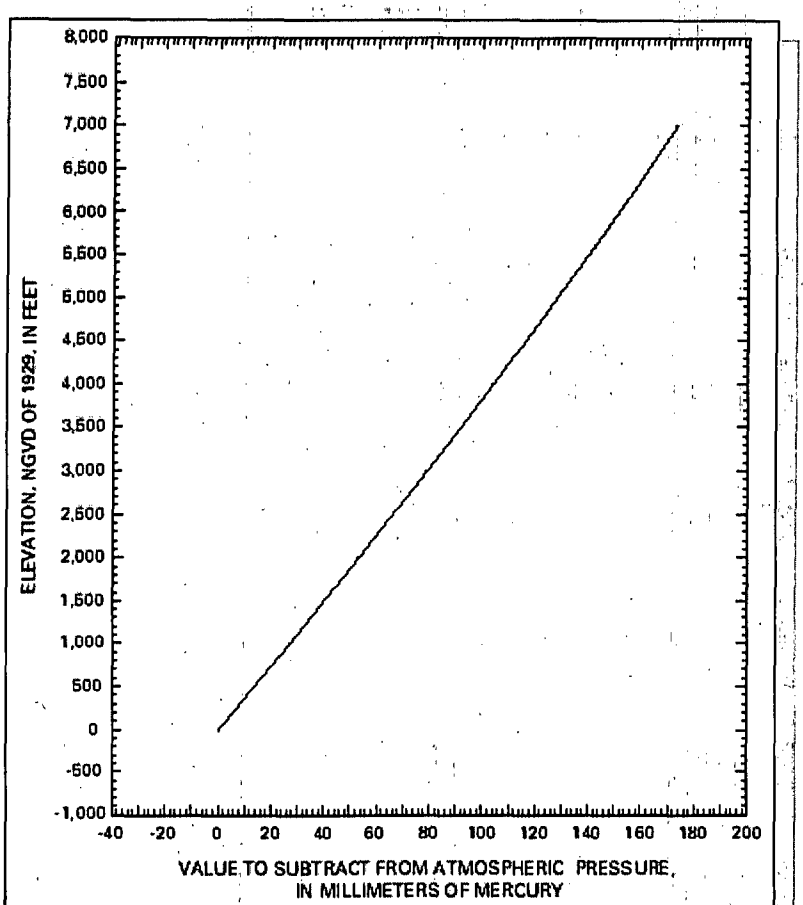


Figure 6.2–1. Factors used to correct atmospheric pressures adjusted to sea level.

Calibration procedures

Four procedures are described below for calibrating a DO system: (1) air-calibration chamber in water, (2) calibration with air-saturated water, (3) air-calibration chamber in air, and (4) iodometric (Winkler) titration.

When using an analog instrument:

- Do not change scales without either recalibrating or verifying that identical readings are obtained on both scales.
- Place an analog instrument in its operating position-- either vertical, tilted, or on its back--before calibration. More readjustments may be necessary if the operating position is changed, so do not change the position of the meter until DO measurement is complete.

Procedure 1--Air-calibration chamber in water

An air-calibration chamber permits calibration of the DO sensor at the temperature of the water in which DO concentration is to be measured. This calibration procedure minimizes errors caused by temperature differences. Keep the interior of the chamber just moist during the calibration procedure, not filled with

water.

1. Dip the calibration chamber into the surface or ground water to be measured; pour out the excess water (leave a few drops).

    - Insert the DO sensor into the wet chamber (this ensures 100-percent humidity).
    - If a YSI model 5739 sensor is used, the pressure-compensating diaphragm on the side of the sensor must be enclosed within the calibration chamber during calibration.

2. Immerse the calibration chamber into the water to be measured. Allow 10 to 15 minutes for the air temperature inside the chamber to equilibrate with the water (see technical note at end of Procedure 1).

    - For streams, choose an area of the stream that closely approximates mean stream temperature. In shallow streams, try to place the chamber in an area that represents the stream but that is shaded from direct sunlight.

    Use of an air calibration chamber in water is the preferred field procedure.

    - For ground water, use temperature-stabilized purge water.
    - Check that no water can leak into the calibration chamber and that the membrane does not have droplets of water adhering to it. The water droplets reduce the rate of oxygen diffusion through a membrane, producing erroneous results. If water has entered the chamber, repeat the procedure from step 1.

3. Determine the ambient atmospheric pressure with a calibrated pocket altimeter-barometer to the nearest 1 mm of mercury.

4. Read the temperature within the chamber to the nearest 0.5°C.

    - The temperature inside the chamber should approximate the water temperature, measured with a calibrated thermometer.
    - If the two temperatures do not match, allow additional time for equilibration of the chamber with the water temperature.
    - If the temperature in the chamber still does not approximate the water temperature, the thermistor in the DO sensor might be malfunctioning. Measure the water temperature with a calibrated field thermometer.

5. Use the tables in section 6.2.4 to determine the DO saturation value at the measured water temperature and atmospheric pressure (table 6.2-6). If a salinity correction will be applied during calibration, consult the instructions in section 6.2.4.

6. Select a proper scale:

- Analog YSI instruments--0 to 10 or 0 to 20 mg/L.
- Digital YSI instruments--0.1 or 0.01 mg/L.

7. Adjust the calibration control until the instrument reads a DO saturation value determined from oxygen solubility (table 6.2-6).
   - The instrument is now calibrated and ready for use. Remove the sensor from the calibration chamber.
   - As long as no excess water is in the chamber, the sensor is ready to be placed in the environment to be measured.

   TECHNICAL NOTE: The YSI 5075A calibration chamber is designed to allow the membrane surface of a DO electrode (model 5739) to be at ambient atmospheric pressure while in the chamber. Because the pressure-compensating diaphragm must remain at atmospheric pressure, check the calibration chamber vent tube (from chamber through end of handle) to ensure that it is not plugged with debris or filled with water.

Do not let water leak from or droplets adhere to the dissolved-oxygen membrane.

Procedure 2--Air-saturated water

In this procedure, the DO sensor or instrument system is calibrated against water that is saturated with oxygen at a known temperature and ambient atmospheric pressure.

1. The temperature and conductivity of water used for calibration should be about the same as the temperature and conductivity of the water to be measured.
   - **At the field site**--obtain about 1 L of water from the water body to be measured.
   - **In the laboratory**--obtain about 1 L of deionized or tap water.
2. Place the DO sensor and calibration water in a large beaker or open-mouth container.
   - Allow the sensor to come to thermal equilibrium with the water temperature.
   - Shield the beaker or container from direct sunlight and wind to minimize temperature variations.
3. Aerate the water for 5 to 10 minutes. Using a battery-operated aquarium pump or minnow-bucket aerator and a short piece of tubing, attach a gas diffusion stone to the end of the tubing and place it at the bottom of the beaker of calibration water.
4. Determine if the water is 100 percent saturated with oxygen.
   - Switch the DO instrument to the 0- to 10-mg/L scale on an analog instrument or to the 0.1-mg/L scale on a digital instrument.

- Adjust the instrument reading to approximately 8 mg/L with the calibration control.
- Observe the instrument while aerating the calibration water. When no change in the DO reading is observed on the instrument for 4 to 5 minutes, assume that the water is saturated.

5. Read the ambient atmospheric pressure from the pocket altimeter-barometer to the nearest 1 mm of mercury.
6. Check mechanical zero. Adjust if necessary.
7. Read the temperature of the calibration water to the nearest 0.5 °C.

   Calibration must be completed with the temperature of calibration water at the value measured, to ensure that the actual DO saturation of calibration water is not less than 100 percent (undersaturated) or greater than 100 percent (oversaturated).

8. Using the oxygen solubility table 6.2-6, determine the DO saturation value at the measured temperature and atmospheric pressure of the calibration water. (Refer to section 6.2.4 and table 6.2-7 for salinity corrections.)
9. Select a proper scale:
   - Analog YSI instruments--0 to 10 or 0 to 20 mg/L.
   - Digital YSI instruments--0.1 or 0.01 mg/L.
10. Turn off the aerator and adjust the calibration control until the instrument reads a saturation value of DO as determined above. The instrument is now calibrated and ready for use.

For accurate calibration, be sure that the water is 100 percent saturated with oxygen (step 4 above).

Procedure 3--Air-calibration chamber in air

This procedure is similar to the procedure for air-calibration chamber in water, except that the calibration chamber is in air rather than in water.

- ► The air-calibration-chamber-in-air procedure requires sensors in which the temperature-sensing thermometer is adjacent to the membrane.
- ► The DO instrument used must be able to automatically compensate for temperature changes. The YSI analog and digital DO instruments are automatically temperature compensating for changes in the solubility of oxygen in water and in the permeability of the sensor membrane.

1. Wet the inside of the calibration chamber with water--pour out the excess water (leave a few drops) and insert the sensor into the chamber (this ensures 100-percent humidity).

2. Allow 10 to 15 minutes for the DO sensor and the air inside the calibration chamber to equilibrate.

3. Read the ambient atmospheric pressure (from the pocket altimeter-barometer) to the nearest 1 mm of mercury.

4. Check mechanical zero. Adjust if necessary.

5. Measure the temperature in the calibration chamber and observe the readings until the instrument stabilizes. Read the temperature to the nearest 0.5°C.

    - The temperature inside the chamber should approximate the water temperature, measured with a calibrated thermometer.

    - If the two temperatures do not match, allow additional time for the chamber and the water temperature to equilibrate.

    - If the temperature in the chamber still does not approximate the water temperature, the thermistor in the DO sensor might be malfunctioning. Measure the water temperature with a calibrated field thermometer.

6. Use the oxygen-solubility table 6.2-6 to determine the DO saturation at the measured temperature and atmospheric pressure. (Refer to section 6.2.4 and table 6.2-7 for salinity corrections.)

7. Select a proper scale:

    - Analog YSI instruments--0 to 10 or 0 to 20 mg/L.

    - Digital YSI instruments--0.1 or 0.01 mg/L.

8. Adjust the calibration control until the instrument reads the DO saturation value determined from the oxygen-solubility table. The instrument is now calibrated and ready for use.

Do not use the air-calibration-in-air procedure if the calibration chamber temperature differs from the temperature of the water to be measured.

Procedure 4--Iodometric (Winkler) titration

The iodometric (Winkler) procedure is excellent for calibrating DO instrument systems in a laboratory environment (see TECHNICAL NOTE).

The USGS currently uses the Alsterberg-Azide modification to the Winkler titration procedure for iodometric determination of DO. **The accuracy of measurements using this method should be within at least ±0.05 mg/L.**

Equipment and supplies needed for the iodometric titration are listed in table 6.2-3. The procedure involves the use of reagent packets that are available in premeasured pillow packets from QWSU and from commercial suppliers, or they can be prepared as described in Skougstad and others (1979) and American Public Health Association and others (1992). Clean all equipment before use.

Table 6.2–3. Equipment and supplies used for the iodometric dissolved-oxygen determination
[mL, milliliter; *N*, normal; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

✓ Beaker, 2,000 mL, glass or Teflon™
✓ Bottles for biological oxygen demand (BOD) analysis, glass stoppered, 300 mL
✓ Stirrer, magnetic
✓ Stirring bars, Teflon™ coated
✓ Cylinder, graduated, 250 mL
✓ Flask, Erlenmeyer, 250 mL
✓ Buret, 25-mL capacity with 0.05-mL graduations and Teflon™ stopcock
✓ Buret, support stand
✓ Buret, clamp, double
✓ Alkaline iodide-azide reagent
✓ Manganous sulfate reagent
✓ Sulfamic acid granules
✓ Phenylarsine oxide (PAO), 0.025 *N* titrant
✓ Starch indicator solution
✓ Clippers, for opening reagent pillows
✓ Appropriate safety gloves, glasses, and apron
✓ Waste disposal container
✓ White background sheet
✓ Deionized water (maximum conductivity of 1 µS/cm)
✓ Bottle, squeeze dispenser, for deionized water
✓ Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)
✓ Pocket altimeter-barometer, calibrated, Thommen model 2000™ or equivalent

TECHNICAL NOTE: The iodometric procedure might be appropriate under some circumstances for making field measurements of DO. It is not recommended for routine determination of DO in surface and ground water because (1) the accuracy achievable can be variable and is dependent on the experience and technique of the data collector, and (2) field conditions can make preventing exposure of the sample to atmospheric oxygen difficult.

- When calibrating instruments in the laboratory using the Winkler procedure, the DO instrument is calibrated against deionized water (or the pure saline solution equivalent to that of the ambient water to be measured) in which the DO concentration has been determined iodometrically.
- If a saline solution is used to approximate the environmental water, do not apply a salinity correction factor.

Measure DO on at least two subsamples, for quality control. Results of two iodometric titrations should agree within 1 mg/L. If they do not agree, repeat the titration on a third subsample.

1. Fill a 2,000-mL beaker with deionized water that is near DO saturation. The water temperature should be close to the ambient laboratory temperature.

2. Prepare the DO instrument system for operation per the manufacturer's instructions.

3. Place the DO sensor in a beaker of distilled water. With a magnetic stirrer, maintain a velocity of at least 1 ft/s past the DO sensor.

4. Monitor the DO concentrations of the deionized water with the DO instrument system. After the DO instrument reading has stabilized, fill two BOD bottles with deionized water from the beaker.

5. Determine the DO concentration of the water in each BOD bottle, as follows:

   a. Add one each of the following dry reagent pillow packets:

      - alkaline iodide-azide (white powder).
      - manganous sulfate (pinkish-colored powder).

   b. Recap the bottle. **Do not allow air bubbles to be trapped in the bottle.**

   c. Invert the bottle 25 times or more to completely dissolve the reagents.

      - A brown flocculent indicates the presence of DO.
      - Allow the brown flocculent to settle halfway down the bottle (approximately 5 minutes).
      - Invert the bottle 25 times again; let the flocculent settle again.

   d. Invert the bottle another 25 times; add one reagent pillow of sulfamic acid (grayish granules, the longest of the three pillows).

   e. Recap the bottle without introducing air or air bubbles. Invert the bottle 25 times, until all of the flocculent and granules are dissolved.

   f. Fill a clean 25-mL buret with 0.025 N phenylarsine oxide (PAO) titrant. Remove any air bubbles beneath the stopcock and zero the meniscus.

   g. Use a clean graduated cylinder to measure 200 mL of the sample and pour the sample into a clean, wide-mouth Erlenmeyer flask.

   h. Place the flask on a magnetic stirrer. Add a clean Teflon™ stirring bar and stir the sample at a moderate rate **without aerating the sample**.

   i. Add increments of PAO titrant until the color turns pale straw-yellow.

   j. Add 1 to 2 mL of starch solution (this causes the sample to turn blue).

   k. Very slowly add more PAO titrant until the sample just turns clear (a white background behind the bottle will help you see the color change).

   l. Record the volume of PAO titrant used, in milliliters.

- For a 200-mL sample, the volume of titrant added is directly proportional to the amount of DO in milligrams per liter.
- To calculate DO for a sample volume greater or less than 200 mL,

$$DO\ (mg/L) = \left(\frac{200}{sample\ \ volume} \right) \times titrant\ added\ (in\ mL)$$

m. Record the DO value. Rinse the equipment with deionized water.

n. **Quality control**--Repeat steps 1 through 5 on a second subsample. Both titration values should agree within 0.1 mg/L. If they do not, repeat titration on a third bottle.

o. Recheck the field instrument for proper functioning per the manufacturer's instructions: adjust the calibration control until the DO instrument system reads the DO concentration determined.

6.2.1.C MEASUREMENT

The solubility of oxygen in water depends on the partial pressure of oxygen in air, the temperature of the water, and the dissolved-solids content of the water.

- The higher the atmospheric pressure and the lower the temperature and conductivity, the more oxygen can be dissolved in the water.
- Degassing, mineral precipitation, and other chemical, physical, and biological reactions can cause the DO concentration of a water sample to change significantly within minutes after sample collection.
- The solubility of oxygen in water decreases as salinity increases. Correction factors for salinity normally are applied after measuring DO. Information about oxygen solubility and salinity and a salinity correction factors table are in 6.2.4.

Surface water

Standard DO determination for surface water represents the cross-sectional median or mean concentration of dissolved oxygen at the time of observation.

- Measuring DO concentration at one distinct spot in a cross section is valid only for flowing water with a cross-sectional DO variation of less than 0.5 mg/L.
- Determining DO in a single vertical at the centroid of flow at the midpoint of the vertical is only representative of the cross section under ideal mixing conditions.
- Do not measure DO in or directly below sections with turbulent flow, in still water, or from the bank, unless these conditions represent most of the reach or are required by the study objectives.
- Apply salinity correction, if needed, after measurement.

Dissolved oxygen must be measured in situ. Never measure DO in subsamples from a sample splitter.

Follow the 7 steps below to measure DO in surface water:

1. Calibrate the DO instrument system at the field site and check that the temperature thermistor has been District-certified within the past 4 months (within 12 months if a liquid-in-glass thermometer is used).

2. Record the DO variation from the cross-sectional profile and select the sampling method (NFM 6.0):

   - **Flowing, shallow stream--**Wade to the location(s) where DO is to be measured.
   - **Stream too deep or swift to wade--**Lower a weighted DO sensor with calibrated temperature sensor from a bridge, cableway, or boat. (Do not attach the weight to the sensors or sensor cables.)
   - **Still-water conditions--**Measure DO at multiple depths at several points in the cross section.

3. Immerse the DO and temperature sensors directly into the water body and allow the sensors to equilibrate to the water temperature (no less than 60 seconds).

   - If the water velocity at the point of measurement is less than about 1 ft/s, use a stirring device or stir by hand to increase the velocity (to hand stir, raise and lower the sensor at a rate of about 1 ft/s, but do not break the surface of the water).
   - Very high velocities can cause erroneous DO measurements.

4. Record the temperature without removing the sensors from the water. Turn the operation switch to the range that was used during instrument calibration.

5. After the instrument reading has stabilized (allow 1 to 2 minutes and ±0.3 mg/L), record the median DO concentration (see NFM 6.0).

6. For EWI or EDI measurements, proceed to the next station in the cross section and repeat steps 3 through 5. When measurements for the stream have been completed, remove the sensor from the water, rinse it with deionized water, and store it according to the manufacturer's instructions.

7. Record DO concentrations on the field forms:

   - **In still water--**median of three or more sequential values.
   - **EDI--mean** value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
   - **EWI--mean (or median)** of all subsections measured.

Ground water

To determine the concentration of DO in an aquifer, the water being measured must not contact air. Study objectives and site characteristics will dictate the specific procedures selected. **If the DO concentration is less than 1 mg/L, refer to the spectrophotometric method (section 6.2.2).**

- Throughout measurement, use equipment that avoids aeration, and operate equipment to mitigate losses or gains of dissolved gases (consult NFM 6.0 for proper downhole and flowthrough-chamber sampling procedures).
- Use a positive-displacement submersible pump and high-density plastic sample tubing that is relatively gas impermeable, if possible.
- Use optically clear materials for the tubing and chamber (to check that entrained bubbles are not present). Air bubbles that adhere to the sides of the tubing and flowthrough chamber will add significant error to low-level DO measurements (A.F. White, U.S. Geological Survey, written commun., 1993).

Never use a bailed or other discrete sample for DO determination.

Follow the 7 steps below to measure DO in ground water:

1. Calibrate the DO system on site. Check that the thermistor thermometer has been District certified within the past 4 months.

2. Install the DO equipment (see section 6.0.3, "Ground Water"):

   - **Downhole system**--Lower the DO and temperature sensors to the sampling point, followed by the pump, to monitor DO variation during purging. If a downhole system will be used only for final DO determination after the samples are collected and the pump is removed, attach a stirrer to the DO instrument before lowering it to the sampling point.

   - **Flowthrough-chamber system**--Refer to section 6.0.3 for installation guidelines. Be sure to:

     a. Install the DO sensor through an air-tight grommet, checking that the seal is intact. Check that the sensors are properly immersed.

     b. Flush air bubbles from the tubing walls and flowthrough chamber--Tap the tubing with the blunt end of a tool to dislodge entrained air bubbles (see technical note).

     c. Check for and eliminate backpressure in the chamber.

3. Keep flow passing the DO sensor laminar and constant.

4. Measure and record DO at regular intervals throughout purging. Allow the sensors to equilibrate with ground water for 5 minutes or more at the flow rate to be used for sampling.

5. Check the stability (variability) of DO toward the end of purging.

   - The stability criterion is met when five consecutive readings made at regularly spaced intervals of 3 to 5 minutes or more are within 0.3 mg/L. (For each reading, monitor fluctuations for 30 to 60 seconds and record the median value, if necessary.)

   - If the ±0.3 mg/L criterion is not met, lengthen the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals.

6. Report sample DO as the median of the final five DO readings recorded. Record any difficulty with stabilization on field forms.

7. Remove the sensor from water and rinse it with deionized water.

TECHNICAL NOTE: Anomalously high DO measurements commonly are caused by aeration of ground water during pumping. This can result from air leakage through loose fittings on production-well pumps (for example, turbine pumps) and also if drawdown in the aquifer introduces air into the cone of depression or through well-screen perforations. To avoid these problems, review information about the pump, well-construction and drawdown data, and previous data records (A.F. White, U.S. Geological Survey, written commun., 1993).

Air bubbles in the lines and flowthrough chamber can add significant error to low DO readings.

6.2.1.D TROUBLESHOOTING (AMPEROMETRIC METHOD)

The troubleshooting suggestions given in table 6.2-4 are not exhaustive; consult the instrument manufacturer for additional guidance. Faulty batteries can cause erratic readings.

- Check the voltage of the batteries.
- Start with good batteries in the instrument and carry spares.

Table 6.2–4. Troubleshooting guide for amperometric determination of dissolved-oxygen concentration

Symptom	Possible cause and corrective action
Instrument does not adjust to red line	• Weak batteries—replace. • Faulty meter compensation thermistor (analog instruments only)—repair.
Instrument drifts or takes excessive time to stabilize	• Thermal equilibrium of DO sensor with water has not been reached—wait longer. • Weak batteries—replace. • DO sensor needs maintenance—recondition.
Erratic instrument readings	• Break in cable—replace cable. • Faulty connection at instrument or sensor—clean contact and tighten connection. • Hole in membrane—replace membrane, recondition. • Air bubble in sensor—recondition sensor. • Weak batteries—replace with new batteries.
Instrument is slow to react	• Gold cathode tarnished—buff with pencil eraser and recondition sensor. • Fouled membrane—recondition sensor and replace membrane.
Instrument will not read zero in sodium sulfite solution.	• Solution contains oxygen—add additional sodium sulfite. • Instrument still does not read zero—recondition sensor. • Faulty oxygen or polarizing thermistors (analog instruments only)—replace or repair.
Instrument cannot be calibrated to read standards	• Unable to adjust upward—check if more than one membrane is on the sensor. • Unable to adjust downward (membrane is probably too tight or too thin)—replace membrane. • Faulty polarizing voltage thermistor (analog instruments only)—repair. • Faulty meter compensation thermistor (analog instruments only)—repair. • Faulty oxygen thermistor (analog instruments only)—repair.
Instrument shows inaccurate temperature	• Faulty or uncalibrated temperature thermistor—calibrate, repair, or replace.

⇨Section 6.2.2
⇧Section 6.2.
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 15AUG00 imc

To print this table click here for a pdf file Table 6.2-6

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures

[From R.F. Weiss (1970). Temp °C, temperature in degrees Celsius; atmospheric pressures from 695 to 600 millimeters mercury begin after 40°C]

Temp	Atmospheric pressure, in millimeters of mercury																			
°C	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	
0.0	15.3	15.2	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	1
0.5	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	1
1.0	14.8	14.7	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2	1
1.5	14.6	14.5	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2	13.1	13.0	1
2.0	14.4	14.3	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	1
2.5	14.2	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	1
3.0	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.5	1
3.5	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3	1
4.0	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3	12.2	12.1	1
4.5	13.5	13.4	13.3	13.2	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.1	12.0	1
5.0	13.3	13.2	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	1
5.5	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.7	1
6.0	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	1
6.5	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.9	11.8	11.7	11.6	11.5	11.5	11.4	1
7.0	12.7	12.6	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2	1
7.5	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	1
8.0	12.4	12.3	12.2	12.1	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	1
8.5	12.2	12.1	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	1
9.0	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.8	10.7	1
9.5	11.9	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6	1
10.0	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	1
10.5	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	1
11.0	11.5	11.4	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.3	10.2	1
11.5	11.4	11.3	11.2	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	1
12.0	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0	
12.5	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9	
13.0	11.0	10.9	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.7	
13.5	10.9	10.8	10.7	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6	
14.0	10.8	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	
14.5	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp	Atmospheric pressure, in millimeters of mercury																			
°C	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	7
15.0	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9
15.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9
16.0	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9
16.5	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.4	9.3	9.2	9.2	9.1	9.0	9
17.0	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8
17.5	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8
18.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8
18.5	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8
19.0	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8
19.5	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8
20.0	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8
20.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8
21.0	9.3	9.2	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8
21.5	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8
22.0	9.1	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8
22.5	9.0	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7
23.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7
23.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7
24.0	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7
24.5	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7
25.0	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7
25.5	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7
26.0	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7
26.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7
27.0	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7
27.5	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7
28.0	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7
28.5	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7
29.0	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7
29.5	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp	Atmospheric pressure, in millimeters of mercury															
°C	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715
30.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1
30.5	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0
31.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9
31.5	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9
32.0	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8
32.5	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8
33.0	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7
33.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7
34.0	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7	6.6
34.5	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5
35.0	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5
35.5	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4
36.0	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4
36.5	7.1	7.0	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3
37.0	7.0	7.0	6.9	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
37.5	7.0	6.9	6.9	6.8	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2
38.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2
38.5	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1
39.0	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1
39.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0
40.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																	
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605
0.0	13.3	13.2	13.1	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6
0.5	13.1	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4
1.0	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3
1.5	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1
2.0	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0
2.5	12.4	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.0	10.9	10.8
3.0	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7
3.5	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5
4.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4
4.5	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.3	10.3
5.0	11.6	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1
5.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0
6.0	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	9.9	9.9
6.5	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7
7.0	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.3	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6
7.5	10.9	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7	9.7	9.6	9.5
8.0	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6	9.5	9.5	9.4
8.5	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.3	9.3
9.0	10.5	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2
9.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.0
10.0	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	8.9
10.5	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8
11.0	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7
11.5	9.9	9.9	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6
12.0	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7	8.7	8.6	8.5
12.5	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.6	8.6	8.5	8.4
13.0	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.5	8.5	8.4	8.3
13.5	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.2
14.0	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2
14.5	9.3	9.2	9.2	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continue

Temp °C	Atmospheric pressure, in millimeters of mercury																	
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610
15.0	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0
15.5	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0
16.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9
16.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8
17.0	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7
17.5	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.7	7.7	7.6
18.0	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.5
18.5	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5
19.0	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.4	7.4
19.5	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3
20.0	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2
20.5	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2
21.0	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1
21.5	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0
22.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0
22.5	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9
23.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8
23.5	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.7
24.0	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7
24.5	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6
25.0	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6
25.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5
26.0	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4
26.5	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.6	6.6	6.5	6.5	6.4	6.4
27.0	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3
27.5	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
28.0	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2
28.5	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1
29.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1	6.1
29.5	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																			
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
30.0	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9
30.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8
31.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8
31.5	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7
32.0	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7
32.5	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6
33.0	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6
33.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5
34.0	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5
34.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4
35.0	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4
35.5	6.2	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3
36.0	6.2	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3
36.5	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.2
37.0	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2
37.5	6.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2
38.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2	5.1
38.5	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1
39.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0
39.5	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0
40.0	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0	5.0

⇧Back to Section 6.2.4

⇧Return to Section 6.2 contents--Dissolved Oxygen

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 4 JULY98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.2.2.pdf

6.2.2 SPECTROPHOTOMETRIC METHOD

The spectrophotometric method described here is recommended for accurate determination of DO concentrations in suboxic waters (less than 1.0 mg/L DO concentration). The method is based on a Rhodazine-D™ colorimetric technique adapted by White and others (1990), which minimizes atmospheric interaction with the water sampled.

- This technique has a sensitivity to 0.2 µmoles/L (0.006 mg/L)–an order of magnitude lower than the amperometric method.
- The technique was developed for ground water but it can be adapted for work in anoxic zones of lakes and reservoirs.

6.2.2.A EQUIPMENT AND SUPPLIES

Two sampling systems can be used: an in situ (downhole) sampler (see White and others, 1990) or a closed-system flowthrough cell through which sample water is pumped. Either sampling system uses partially evacuated oxygen-free glass ampoules containing Rhodazine-D™, that are broken along a prescored capillary tip while they are submerged in the water to be analyzed. Equipment and supplies needed for this method are listed on table 6.2-5.

Table 6.2-5. Equipment and supplies (Rhodazine-D™ technique)
[mL, milliliters; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

✓ Portable spectrophotometer, Bausch and Lomb Minispect-10™ or equivalent
✓ Ampoules with reagents, 10-mL glass, CHEMetrics Inc., Model K7553™
✓ Downhole sampler, to meet criteria described in White and others (1990)
✓ Flowthrough cell, modified to a closed-system device (alternative to sampling tool)
✓ Safety gloves, glasses, and apron
✓ Waste disposal container
✓ White background sheet
✓ Deionized water (maximum conductivity of 1 µS/cm)
✓ Bottle, squeeze dispenser, for deionized water

Kits available from CHEMetrics Incorporated contain prepackaged glass ampoules filled with a

Rhodazine-D™ dye solution for two concentration ranges of dissolved oxygen: 0 to 1 mg/L (0 to 310 µmoles/L) or 0 to 40 mg/L (0 to 13 µmoles/L).

White and others (1990) used a portable Milton Roy Minispect-10™ battery-powered spectrophotometer. Any spectrophotometer of equal or better quality can be used.

> **TECHNICAL NOTE:** The closed-system cell is not the same as the flowthrough-chamber system used in routine ground-water field measurements. The cell consists of a three-way tee to which inflow, outflow, and discharge tubing sections are fitted tightly; outflow is fitted with a short length of 3/8-in. tubing.

6.2.2.B CALIBRATION AND INTERFERENCES

Dissolved oxygen is measured as percent absorbance by the spectrophotometer.

- A calibration chart is provided in the CHEMetrics kit, along with a regression formula to convert absorbance to micrograms per liter of DO for use with the Minispect-10™ spectrophotometer. No other standards are provided.
- The CHEMetrics kit contains a blank ampoule used to zero the spectrophotometer.
- Interferences from total salinity and major dissolved inorganic species are negligible.
- The method is affected significantly by the presence of reducible inorganic species such as ferric and cupric ions and hexavalent chromium, resulting in high-biased DO readings. The effect from reducible inorganic species can be corrected if the concentrations of the interfering species are known.
- Additional calibration is needed if the method will be used for heavily contaminated or acidic waters, by equilibrating a water sample with known partial pressures of atmospheric oxygen (White and others, 1990). Atmospheric oxygen standards are available from suppliers of gas chromatography equipment.

6.2.2.C MEASUREMENT

Rhodazine-D™ reagent reacts with DO to produce an oxidized complex characterized by a red-blue color. The color intensity is proportional to the concentration of the initial DO present.

Follow the 7 steps below to measure DO using the Rhodazine-D™ method:

1. Zero the spectrophotometer, using the blank provided in the kit (follow the manufacturer's instructions).

2. Set the spectrophotometer to the correct wavelength.

   - The Minispect-10™ spectrophotometer is set at a wavelength of 615 nm for calibrating and measuring.

   - Refer to the manufacturer's instructions for the correct wavelength when using a different spectrophotometer.

3. Collect the sample. Install either the downhole sampling tool (White and others, 1990) or use a

closed-system flowthrough cell with a suitable pump.

- **Downhole system—**

  a. Carefully lower a sampling tool attached to a wire line.

  b. At the collection point (in the well or surface water), break the scored tip of the ampoule using a sharp upward tug on the sampling tool. (This permits sample water to be drawn into the ampoule. During transit to the surface, progressively decreasing pressure in the ampoule prevents cross contamination from overlying water through the capillary tip.)

- **Closed-system flowthrough cell—**

  a. Fit inflow, outflow, and discharge tubing tightly into the three-way tee. Fit the outflow with a short length of 3/8-in. tubing. All fittings must be airtight to prevent aerating the sample.

  b. Insert the glass ampoule, tip first, into the outflow tubing. The seal must be airtight.

  c. Pinch the tubing so that the scored tip of the ampoule will break in the flow of water.

4. Insert the ampoule directly into the 1.27-cm spectrophotometer cell holder immediately after retrieval.

5. Read absorbance to the nearest 0.2 µmoles/L on the analog meter.

   - Allow the readings to stabilize first (usually within 2 minutes).
   - Read each DO value three times and record the median value.

6. Calculate the DO concentrations using regression equations (White and others, 1990).

   - To correct for appreciable concentrations of oxidized species of transition metals, use the stoichiometric relationships as described by White and others (1990).

7. **Quality control—**

   - Repeat steps 4 through 6 twice to document precision.
   - To document the variability of DO concentrations within the water system, repeat steps 3 through 6 on three sequentially collected samples.

Analyze samples in the field immediately.

⇨Section 6.2.3
⇧Section 6.2.1

⇧Return to Contents for 6.2--Dissolved Oxygen
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 22MAY98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.2.3.pdf

6.2.3 REPORTING

Dissolved-oxygen concentrations are determined to the nearest 0.1 mg/L for amperometric measurements.

- Values less than 0.1 mg/L can be stored in the current NWIS data base, but will print out as "0.0" unless the data are retrieved as a flat file.
- If the concentration exceeds 20 mg/L, report ">20 mg/L."
- Note that the percentage of saturation can be greater than 100.
- Record the accuracy range of the instrument system or the method used in the data base (if possible). Report the accuracy range with the published values.
- Enter the DO value on the NWQL Analytical Services Request form and on the field form under the correct parameter code for the method used.

⇨Section 6.2.4
⇧Section 6.2.2
⇧Return to Contents for 6.2--Dissolved Oxygen
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 22MAY98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.2.4.pdf

6.2.4
CORRECTION FACTORS FOR OXYGEN SOLUBILITY AND SALINITY

Correction factors for the solubility of oxygen at various temperatures and pressures and for salinity based on conductivity are given in tables 6.2-6 and 6.2-7, respectively. Tables 6.2-6 and 6.2-7 were generated from the equations of Weiss (1970) and can be customized to cover the range and decimal places needed (see OWQ Technical Memorandum 81.11).

You can convert oxygen-saturation values for salinity using correction factors based on chloride concentration or conductivity. Refer to the manufacturer's instructions for the DO instrument before applying a salinity correction.

- Correcting DO solubility for saline waters (salinities greater than 2,000 µS/cm or 1,000 mg/L chloride) varies with instrument type, calibration method, and the salts in solution.
- The correction based on conductivity (table 6.2-7) is more useful because accurate conductivity can be easily determined from a field measurement. Salinity correction factors based on chloride can be calculated using information provided in OWQ Technical Memorandum 79.10.
- Dissolved-oxygen instruments use either an automatic internal salinity correction, a manual salinity control knob for internal correction, or the calibration control knob for manual salinity correction.
- Check that instruments with automatic internal salinity correction use approved salinity correction factors.

Example of salinity correction:

$$8.2\ mg/L \times 0.951 = 7.8\ mg/L$$

where,

8.2 mg/L is 100 percent DO saturation from table 6.2–6,
0.951 is the correction factor from table 6.2–7, and
7.8 mg/L is the corrected value.

For this example, you would adjust the DO instrument to 7.8 mg/L from 8.2 mg/L.

To express results as percent saturation, use the following equation:

$$DO\ (percent\ saturation) = \frac{measured\ DO\ (mg/L)}{DO\ (mg/L\ at\ 100\ percent\ saturation)} \times 100$$

Click here to see Table 6.2-6.

Click here to see Table 6.2-7.

⇨ Contents for Section 6.3
⇧ Section 6.2.3
⇧ Return to Contents for 6.2--Dissolved Oxygen
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

Maintainer:
Webversion by: Genevieve Comfort
Last Modified: 22MAY98 ghc

To print this table click here for a pdf file Table 6.2-6

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures

[From R.F. Weiss (1970). Temp °C, temperature in degrees Celsius; atmospheric pressures from 695 to 600 millimeters mercury begin after 40°C]

Temp	Atmospheric pressure, in millimeters of mercury																		
°C	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705
0.0	15.3	15.2	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5
0.5	15.1	15.0	14.9	14.8	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3
1.0	14.8	14.7	14.7	14.6	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2
1.5	14.6	14.5	14.5	14.4	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.2	13.2	13.1	13.0
2.0	14.4	14.3	14.3	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8
2.5	14.2	14.2	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6
3.0	14.1	14.0	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.5
3.5	13.9	13.8	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3
4.0	13.7	13.6	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.6	12.6	12.5	12.4	12.3	12.2	12.1
4.5	13.5	13.4	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.1	12.0
5.0	13.3	13.3	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8
5.5	13.2	13.1	13.0	12.9	12.8	12.7	12.7	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.7
6.0	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5
6.5	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.3	12.2	12.1	12.0	11.9	11.9	11.8	11.7	11.6	11.5	11.5	11.4
7.0	12.7	12.6	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2
7.5	12.5	12.4	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1
8.0	12.4	12.3	12.2	12.1	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0
8.5	12.2	12.1	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8
9.0	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.8	10.7
9.5	11.9	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6
10.0	11.8	11.7	11.6	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4
10.5	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3
11.0	11.5	11.4	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.3	10.2
11.5	11.4	11.3	11.2	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1
12.0	11.3	11.2	11.1	11.0	11.0	10.9	10.8	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0
12.5	11.1	11.1	11.0	10.9	10.8	10.8	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9
13.0	11.0	10.9	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.7
13.5	10.9	10.8	10.7	10.7	10.6	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6
14.0	10.8	10.7	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5
14.5	10.6	10.6	10.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp	Atmospheric pressure, in millimeters of mercury																		
°C	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715	710	705	7
15.0	10.5	10.5	10.4	10.3	10.3	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9
15.5	10.4	10.4	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9
16.0	10.3	10.2	10.2	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9
16.5	10.2	10.1	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.4	9.3	9.2	9.2	9.1	9.0	9
17.0	10.1	10.0	10.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8
17.5	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8
18.0	9.9	9.8	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8
18.5	9.8	9.7	9.7	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8
19.0	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8
19.5	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8
20.0	9.5	9.4	9.4	9.3	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8
20.5	9.4	9.3	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8
21.0	9.3	9.2	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8
21.5	9.2	9.2	9.1	9.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8
22.0	9.1	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8
22.5	9.0	9.0	8.9	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7
23.0	9.0	8.9	8.8	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7
23.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7
24.0	8.8	8.7	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7
24.5	8.7	8.7	8.6	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7
25.0	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7
25.5	8.5	8.5	8.4	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7
26.0	8.5	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7
26.5	8.4	8.3	8.3	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7
27.0	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7
27.5	8.2	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7
28.0	8.2	8.1	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7
28.5	8.1	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7
29.0	8.0	8.0	7.9	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7
29.5	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7

Table 6.2–6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp	Atmospheric pressure, in millimeters of mercury																
°C	795	790	785	780	775	770	765	760	755	750	745	740	735	730	725	720	715
30.0	7.9	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1
30.5	7.8	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0
31.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9
31.5	7.7	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9
32.0	7.6	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8
32.5	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8
33.0	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7
33.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7
34.0	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7	6.6
34.5	7.3	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5
35.0	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5
35.5	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4
36.0	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4
36.5	7.1	7.0	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3
37.0	7.0	7.0	6.9	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
37.5	7.0	6.9	6.9	6.8	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2
38.0	6.9	6.9	6.8	6.8	6.7	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2
38.5	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1
39.0	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1
39.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0
40.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0

Table 6.2-6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																		
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605
0.0	13.3	13.2	13.1	13.0	12.9	12.8	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6
0.5	13.1	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4
1.0	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.6	11.5	11.4	11.3
1.5	12.8	12.7	12.6	12.5	12.4	12.3	12.2	12.1	12.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1
2.0	12.6	12.5	12.4	12.3	12.2	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0
2.5	12.4	12.4	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.4	11.3	11.2	11.1	11.0	10.9	10.8
3.0	12.3	12.2	12.1	12.0	11.9	11.8	11.7	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7
3.5	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5
4.0	12.0	11.9	11.8	11.7	11.6	11.5	11.4	11.3	11.3	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4
4.5	11.8	11.7	11.6	11.5	11.5	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.3	10.3
5.0	11.6	11.6	11.5	11.4	11.3	11.2	11.1	11.1	11.0	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1
5.5	11.5	11.4	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0
6.0	11.4	11.3	11.2	11.1	11.0	10.9	10.9	10.8	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	9.9	9.9
6.5	11.2	11.1	11.0	11.0	10.9	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7
7.0	11.1	11.0	10.9	10.8	10.7	10.7	10.6	10.5	10.4	10.3	10.3	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6
7.5	10.9	10.9	10.8	10.7	10.6	10.5	10.5	10.4	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.7	9.7	9.6	9.5
8.0	10.8	10.7	10.6	10.6	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.6	9.5	9.5	9.4
8.5	10.7	10.6	10.5	10.4	10.4	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.3	9.3
9.0	10.5	10.5	10.4	10.3	10.2	10.2	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2
9.5	10.4	10.3	10.3	10.2	10.1	10.0	10.0	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.0
10.0	10.3	10.2	10.1	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	8.9
10.5	10.2	10.1	10.0	9.9	9.9	9.8	9.7	9.7	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8
11.0	10.1	10.0	9.9	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7
11.5	9.9	9.9	9.8	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6
12.0	9.8	9.8	9.7	9.6	9.5	9.5	9.4	9.3	9.2	9.2	9.1	9.0	9.0	8.9	8.8	8.7	8.7	8.6	8.5
12.5	9.7	9.6	9.6	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.6	8.6	8.5	8.4
13.0	9.6	9.5	9.5	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.5	8.5	8.4	8.3
13.5	9.5	9.4	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.2
14.0	9.4	9.3	9.3	9.2	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2
14.5	9.3	9.2	9.2	9.1	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1

Table 6.2-6. Solubility of oxygen in water at various temperatures and pressures—Continue

Temp °C	Atmospheric pressure, in millimeters of mercury																	
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610
15.0	9.2	9.1	9.1	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0
15.5	9.1	9.0	9.0	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0
16.0	9.0	8.9	8.9	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9
16.5	8.9	8.8	8.8	8.7	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8
17.0	8.8	8.7	8.7	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7
17.5	8.7	8.6	8.6	8.5	8.5	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.7	7.7	7.6
18.0	8.6	8.6	8.5	8.4	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.5
18.5	8.5	8.5	8.4	8.3	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5
19.0	8.4	8.4	8.3	8.3	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.4	7.4
19.5	8.4	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3
20.0	8.3	8.2	8.2	8.1	8.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2
20.5	8.2	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2
21.0	8.1	8.1	8.0	7.9	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1
21.5	8.0	8.0	7.9	7.9	7.8	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0
22.0	8.0	7.9	7.8	7.8	7.7	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0
22.5	7.9	7.8	7.8	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9
23.0	7.8	7.7	7.7	7.6	7.6	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8
23.5	7.7	7.7	7.6	7.6	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.7
24.0	7.7	7.6	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7
24.5	7.6	7.5	7.5	7.4	7.4	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6
25.0	7.5	7.5	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6
25.5	7.4	7.4	7.3	7.3	7.2	7.2	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5
26.0	7.4	7.3	7.3	7.2	7.2	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4
26.5	7.3	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.6	6.6	6.5	6.5	6.4	6.4
27.0	7.2	7.2	7.1	7.1	7.0	7.0	6.9	6.9	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3
27.5	7.2	7.1	7.1	7.0	7.0	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
28.0	7.1	7.1	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2
28.5	7.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1
29.0	7.0	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.2	6.2	6.1	6.1
29.5	6.9	6.9	6.8	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0

Table 6.2-6. Solubility of oxygen in water at various temperatures and pressures—Continued

Temp °C	Atmospheric pressure, in millimeters of mercury																			
	695	690	685	680	675	670	665	660	655	650	645	640	635	630	625	620	615	610	605	600
30.0	6.9	6.8	6.8	6.7	6.7	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9
30.5	6.8	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8
31.0	6.7	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8
31.5	6.7	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7
32.0	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7
32.5	6.6	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6
33.0	6.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6
33.5	6.5	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5
34.0	6.4	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5
34.5	6.4	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4
35.0	6.3	6.3	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4
35.5	6.2	6.2	6.2	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3
36.0	6.2	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3
36.5	6.1	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.2
37.0	6.1	6.1	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2
37.5	6.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2
38.0	6.0	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.3	5.3	5.3	5.2	5.2	5.1
38.5	6.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1
39.0	5.9	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0
39.5	5.9	5.8	5.8	5.7	5.7	5.6	5.6	5.5	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0
40.0	5.8	5.8	5.7	5.7	5.6	5.6	5.6	5.5	5.4	5.4	5.4	5.3	5.3	5.2	5.2	5.1	5.1	5.0	5.0	5.0

⇧Back to Section 6.2.4

⇧Return to Section 6.2 contents--Dissolved Oxygen

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 4 JULY98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Complete pdf for Section 6.3--Specific Electrical Conductance

National Field Manual

6.3 SPECIFIC ELECTRICAL CONDUCTANCE

By D.B. Radtke, J.V. Davis, and F.D. Wilde

6.3 Specific electrical conductance

6.3.1 Equipment and supplies
6.3.1.A Maintenance, cleaning, and storage

6.3.2 Calibration

6.3.3 Measurement
6.3.3.A Surface water
In situ measurement
Subsample measurement
6.3.3.B Ground water]
Downhole and flowthrough-chamber measurement]
Subsample measurement

6.3.4 Troubleshooting

6.3.5 Reporting

Tables

6.3-1. Equipment and supplies used for measuring conductivity

6.3-2. Example of cell constants for contacting-type sensors with electrodes and corresponding conductivity ranges

6.3-3. Correction factors for converting non-temperature-compensated values to conductivity at 25 degrees Celsius, based on 1,000 microsiemens potassium chloride solution

6.3-4. Troubleshooting guide for conductivity measurement

⇨Section 6.3
⇧Section 6.2.4
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 09JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.3.pdf

6.3
SPECIFIC ELECTRICAL CONDUCTANCE

Specific electrical conductance (conductivity): a measure of the electrical conductance of a substance normalized to unit length and unit cross section at a specified temperature.

Electrical conductance is a measure of the capacity of water (or other media) to conduct an electrical current. Electrical conductance of water is a function of the types and quantities of dissolved substances in water, but there is no universal linear relation between total dissolved substances and conductivity.

The USGS reports conductivity in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C). The method described in this section for measuring conductivity is applicable to surface water and ground water, from fresh to saline.

⇨Section 6.3.1.
⇧Return to Contents for 6.3--Specific Electrical Conductance
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 09JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.3.1.pdf

6.3.1 EQUIPMENT AND SUPPLIES

The instrument system used to measure conductivity must be tested before each field trip and cleaned soon after use. Every conductivity instrument must have a log book in which repairs and calibrations are recorded, along with manufacturer make and model description and serial or property number.

Table 6.3–1. Equipment and supplies used for measuring conductivity[1]

[°C, degrees Celsius; L, liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

- ✓ Conductivity instrument and conductivity sensor
  - Battery powered Wheatstone bridge
  - Direct readout
  - Temperature range at least –5 to +45°C
  - Temperature compensating (25°C)
  - Accuracy: Conductivity ≤100 µS/cm, within 5 percent of full scale
    Conductivity >100 µS/cm, within 3 percent of full scale
- ✓ Thermistor thermometer sensor (for automatic temperature-compensating models)
- ✓ Thermometer, liquid-in-glass or thermistor
- ✓ Extra sensors (if possible) and batteries, or backup instrument
- ✓ Conductivity standards at conductivities that approximate and bracket field values
- ✓ Compositing and splitting device for surface-water samples
- ✓ Flowthrough chamber or downhole instrument for ground-water measurements
- ✓ Plastic beakers (assorted sizes)
- ✓ Soap solution, nonphosphate (1 L)
- ✓ Hydrochloric acid solution, 5 percent volume-to-volume (1 L)
- ✓ Deionized water, 1 L, maximum conductivity of 1 µS/cm
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Brush (small, soft)
- ✓ Waste disposal container
- ✓ Minnow bucket with tether (or equivalent) for equilibrating buffer solutions to sample temperature
- ✓ Instrument log book for recording calibrations, maintenance, and repairs

[1]Modify this list to meet the specific needs of the field effort.

- Many conductivity instruments are available; the specifications and instructions provided here are general. Users must be familiar with the instructions provided by the manufacturer.
- Conductivity sensors are either contacting-type sensors with electrodes or electrodeless-

type sensors.

-- **Contacting-type sensors with electrodes.** Three types of cells are available: (1) a dip cell that can be suspended in the sample, (2) a cup cell that contains the sample, or (3) a flow cell that is connected to a fluid line. Choose a cell constant on the basis of expected conductivity (table 6.3-2). The greater the cell constant, the greater the conductivity that can be measured. The cell constant is the distance between electrodes (in centimeters) divided by the effective cross-sectional area of the conducting path (in square centimeters).

-- **Electrodeless-type sensors.** These operate by inducing an alternating current in a closed loop of solution, and they measure the magnitude of the current. Electrodeless sensors avoid errors caused by electrode polarization or electrode fouling.

Quality-controlled conductivity standards ranging from 50 to 50,000 µS/cm at 25°C can be obtained from QWSU. Prepare standards outside this range or order them from suppliers of chemical reagents. Conductivity standards usually consist of potassium chloride dissolved in reagent-grade water.

Table 6.3–2. Example of cell constants for contacting-type sensors with electrodes and corresponding conductivity ranges

Conductivity range, in microsiemens per centimeter	Cell constant, in 1/centimeter
0.005–20	0.01
1–200	.1
10–2,000	1.0
100–20,000	10.0
1,000–200,000	50.0

6.3.1.A
MAINTENANCE, CLEANING, AND STORAGE

As soon as possible after delivery to the office, label conductivity standards with the date of expiration. Discard standards that have expired, been frozen, have begun to evaporate, or that were decanted from the storage container.

Maintenance

Maintenance of conductivity equipment includes periodic office checks of instrument operation. To help keep equipment in good operating condition:

- Protect the conductivity system from dust and excessive heat and cold.
- Keep all cable connectors dry and free of dirt and extraneous matter.
- Protect connector ends in a clean plastic bag when not in use.

Sensor cleaning

Conductivity sensors must be clean to produce accurate results; residues from previous samples can coat surfaces of sensors and cause erroneous readings.

- Clean sensors thoroughly with deionized water (DIW) before and after making a measurement (this is sufficient cleaning in most cases).
- Remove oily residue or other chemical residues (salts) with a detergent solution. Sensors can soak in detergent solution for many hours without damage.
- If oil or other residues persist, dip the sensor in a dilute hydrochloric acid solution. **Never leave the sensor in contact with acid solution for more than a few minutes.** Check the manufacturer's recommendations before using acid solution on sensors.
- Clean carbon and stainless steel sensors with a soft brush. Never use a brush on platinum-coated sensors.

Sensor storage

Refer to the manufacturer's recommendations.

- Sensors may be temporarily stored in deionized water between measurements and when the system is in daily use.
- For long-term storage, store sensors clean and dry.

CAUTION: Before handling conductivity standards or acids, refer to Material Safety Data Sheets (MSDS) for safety precautions.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.

⇨Section 6.3.2.
⇧Return to Section 6.3
⇧Return to Contents for 6.3--Specific Electrical Conductance
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 09JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.3.2.pdf

6.3.2 CALIBRATION

Conductivity systems must be calibrated before every water-quality field trip and again at each site before samples are measured. Calibration readings are recorded in the instrument log book and on field forms at the time the instrument is calibrated. Remember, the temperature sensor on the conductivity sensor must be calibrated and District certified within the past 4 months.

Calibration and operating procedures differ, depending on instrument and sensor type.

- Some conductivity sensors may need to be soaked overnight in deionized water before use--Check the manufacturer's instructions.
- Some analog instruments require an initial mechanical zero adjustment of the indicator needle.
- For a cup-type cell, calibration and measurement procedures described for the dip-type cell apply; the only difference is that standards are poured directly into the cup-type cell.
- When using a dip-type cell, do not let the cell rest on the bottom or sides of the measuring container.

Calibrate at your field site—bring standards to sample temperature.

Conductivity systems normally are calibrated with at least two standards. Calibrate sensors against a standard that approximates sample conductivity and use the second standard as a calibration check. The general procedures described in steps 1-15 below apply to most instruments used for field measurements-check the instrument manual for specific instructions.

1. Inspect the instrument and the conductivity sensor for damage. Check the battery voltage. Make sure that all cables are clean and connected properly.

2. Turn the instrument on and allow sufficient time for electronic stabilization.

3. Select the correct instrument calibration scale for expected conductivity.

4. Select the sensor type and the cell constant that will most accurately measure expected conductivity.

5. Select two conductivity standards that will bracket the expected sample conductivity. Verify that the date on the standards has not expired.

6. Equilibrate the standards and the conductivity sensor to the temperature of the sample.

   - Put bottles of standards in a minnow bucket, cooler, or large water bath that is being filled with ambient water.

   - Allow 15 to 30 minutes for thermal equilibration. Do not allow water to dilute the standard.

7. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.

   - **First**, rinse the sensor, the thermometer, and the container three times with deionized water.

   - **Next**, rinse the sensor, the thermometer, and the container three times with the standard to be used.

8. Put the sensor and the thermometer into the rinsed container and pour in fresh calibration standard.

9. Measure water temperature. **Accurate conductivity measurements depend on accurate temperature measurements or accurate temperature compensation.**

   - If the sensor contains a calibrated thermistor, use this thermistor to measure water temperature.

   - If using a manual instrument without a temperature display or temperature compensation, adjust the instrument to the temperature of the standard using a calibrated liquid-in-glass or a thermistor thermometer

10. Agitate a submersible-type conductivity sensor up and down under the solution surface to expel air trapped in the sensor. Read the instrument display. Agitate the sensor up and down under the solution surface again, and read the display. Repeat the procedure until consecutive readings are the same.

11. Record the instrument reading and adjust the instrument to the known standard value.

    - For nontemperature-compensating conductivity instruments, apply a temperature-correction factor to convert the instrument reading to conductivity at 25°C.

    - The correction factor depends to some degree on the specific instrument used-use the temperature-correction factor recommended by the manufacturer. If this is not available, use correction factors from table 6.3-3.

    - If an instrument cannot be adjusted to a known calibration standard value, develop a calibration curve. After temperature compensation, if the percentage difference from the standard exceeds 5 percent, refer to the troubleshooting guide (section 6.3.4).

Table 6.3–3. Correction factors for converting non-temperature-compensated values to conductivity at 25 degrees Celsius, based on 1,000 microsiemens potassium chloride solution

[Use of potassium-based constants on non-potassium-based waters generally does not introduce significant errors for general purpose instruments used to measure conductivity]

Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor
0.5	1.87	10.5	1.39	20.5	1.09
1.0	1.84	11.0	1.37	21.0	1.08
1.5	1.81	11.5	1.35	21.5	1.07
2.0	1.78	12.0	1.33	22.0	1.06
2.5	1.76	12.5	1.32	22.5	1.05
3.0	1.73	13.0	1.30	23.0	1.04
3.5	1.70	13.5	1.28	23.5	1.03
4.0	1.68	14.0	1.27	24.0	1.02
4.5	1.66	14.5	1.26	24.5	1.01
5.0	1.63	15.0	1.24	25.0	1.00
5.5	1.60	15.5	1.22	25.5	0.99
6.0	1.58	16.0	1.21	26.0	0.98
6.5	1.56	16.5	1.19	26.5	0.97
7.0	1.54	17.0	1.18	27.0	0.96
7.5	1.52	17.5	1.16	27.5	0.95
8.0	1.49	18.0	1.15	28.0	0.94
8.5	1.47	18.5	1.14	28.5	0.93
9.0	1.45	19.0	1.13	29.0	0.92
9.5	1.43	19.5	1.12	29.5	0.91
10.0	1.41	20.0	1.11	30.0	0.90

12. Record in the instrument log book and on field forms:
    - The temperature of the standard solution.
    - The known and the measured conductivity of the standard solution (including ± variation).
    - The temperature-correction factor (if necessary).
13. Discard the used standard into a waste container. Rinse the sensor, thermometer, and container thoroughly with deionized water.
14. Repeat steps 7 through 13 with the second conductivity standard.
    - The purpose for measuring a second standard is to check instrument calibration over the range of the two standards.
    - The difference from the standard value should not exceed 5 percent.
    - If the difference is greater than 5 percent, repeat the entire calibration procedure. If the second reading still does not come within 5 percent of standard value, refer to the troubleshooting guide in section 6.3.4 or calibrate a backup instrument.
    - **Switching instrument calibration scales could require recalibration.**

15. Record in the instrument log book and on field forms the calibration data for the second standard.

Do not use expired standards.
Never reuse standards.

To extend the temperature range shown in table 6.3-3, consult the manufacturer's guidelines. If these are unavailable, use the following equation:

$$C_{25} = \frac{C_m}{1 + 0.02\,(t_m - 25)}$$

where,

C_{25} = corrected conductivity value adjusted to 25°C;

C_m = actual conductivity measured before correction; and

t_m = water temperature at time of C_m measurement.

⇨Section 6.3.3.
⇧Return to Section 6.3.1
⇧Return to Contents for 6.3--Specific Electrical Conductance
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 10JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.3.3.pdf

6.3.3 MEASUREMENT

In situ measurement generally is preferred for determining the conductivity of surface water; downhole or flowthrough-chamber measurements are preferred for ground water. Be alert to the following problems if conductivity is measured in an isolated (discrete) sample or subsample:

- The conductivity of water can change over time as a result of chemical and physical processes such as precipitation, adsorption, ion exchange, oxidation, and reduction--Do not delay making conductivity measurements.
- Field conditions (rain, wind, cold, dust, direct sunlight) can cause measurement problems--Shield the instrument to the extent possible and perform measurements in a collection chamber in an enclosed vehicle or an on-site laboratory.
- For waters susceptible to significant gain and loss of dissolved gases, make the measurement within a gas-impermeable container (Berzelius flask) fitted with a stopper--Place the sensor through the stopper and work quickly to maintain the sample at ambient surface-water or ground-water temperature.
- Avoid contamination from the pH electrode filling solution--Measure conductivity on a separate discrete sample from the one used for measuring pH; in a flowthrough chamber, position conductivity sensor upstream of the pH electrode.

Conductivity must be measured in the field.

Document the precision of your measurements. Precision should be determined about every tenth sample or more frequently, depending on study objectives. Successive measurements should be repeated until they agree within 5 percent at conductivity $\leq$ 100 µS/cm or within 3 percent at conductivity >100 µS/cm.

The conductivity measurement reported must account for sample temperature. If using an instrument that does not automatically temperature compensate to 25°C, record the uncompensated measurement in your field notes, along with the corrected conductivity value. Use correction factors supplied by the instrument manufacturer if available; otherwise, refer to table 6.3-3.

6.3.3.A SURFACE WATER

Surface-water conductivity should be measured in situ, if possible; otherwise, determine conductivity in discrete samples collected from a sample splitter or compositing device. Filtered samples may be needed if the concentrations of suspended material interfere with obtaining a stable measurement.

In situ measurement

Conductivity measurements in flowing surface water should represent the cross-sectional mean or median conductivity at the time of observation (see step 7, below). Any deviation from this convention must be documented in the data base and with the published data.

First:

- Take a cross-sectional conductivity profile to determine the degree of system variability. A submersible sensor works best for this purpose.
- Refer to NFM 6.0 for criteria to help decide which sampling method to use.

Next, follow the 7 steps listed below:

1. Calibrate the conductivity instrument system at the field site after equilibrating the buffers with stream temperature.

2. Record the conductivity variation from a cross-sectional profile on a field form and select the sampling method.

    - **Flowing, shallow stream**--wade to the location(s) where conductivity is to be measured.

    - **Stream too deep or swift to wade**--lower a weighted conductivity sensor from a bridge, cableway, or boat. Do not attach weight to the sensor or the sensor cable.

    - **Still-water conditions**--measure conductivity at multiple depths at several points in the cross section.

3. Immerse the conductivity and temperature sensors in the water to the correct depth and hold there (no less than 60 seconds) until the sensors equilibrate to water conditions.

4. Record the conductivity and corresponding temperature readings without removing the sensors from water.

    - Values should stabilize quickly to within 5 percent at conductivity $\leq$ 100 µS/cm and within 3 percent at conductivity >100 µS/cm.

    - Record the median of the stabilized values on field forms.

    - If the readings do not meet the stability criterion after extending the measurement period, record this difficulty in the field notes along with the fluctuation range and the median value of the last five or more readings.

5. For EWI or EDI measurements, proceed to the next station in the cross section and repeat steps 3 and 4. Record on field forms the mean (or median, if appropriate) value for each subsection measured.

6. When the measurement is complete, remove the sensor from the water, rinse it with deionized water, and store it.

7. Record the stream conductivity on the field forms:

   - **In still water**--median of three or more sequential values.
   - **EDI**--mean value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
   - **EWI**--mean or median of all subsections measured (see NFM 6.0).

Subsample measurement

Representative samples are to be collected and split or composited according to approved USGS methods (Wells and others, 1990). Measure the conductivity of samples as soon as possible after collection. If the sample cannot be analyzed immediately, fill a bottle to the top, close it tightly, and maintain the sample at stream temperature until measurement.

Reported conductivity values normally are determined on an unfiltered sample. Large concentrations of suspended sediment can be a source of measurement error--record such conditions in the field notes.

- If sediment concentrations are heavy, measure conductivity on both unfiltered and filtered subsamples and record both values on the field form.
- If the conductivity value differs significantly between the filtered and unfiltered samples, report the filtered value as sample conductivity and identify it as a "filtered sample."

1. Calibrate the conductivity instrument system at the field site.

2. Select the sampling method (see NFM 6.0) and collect a representative sample.

3. Withdraw a homogenized subsample from a sample splitter or compositing device. Rinse the sample bottles three times with the sample--rinse them with sample filtrate, for filtered samples.

4. Rinse the conductivity sensor, the thermometer (liquid-in-glass or thermistor), and a container large enough to hold the dip-type sensor and the thermometer.

   a. First, rinse the sensor, the thermometer, and the container three times with deionized water.

   b. Next, rinse the sensor, the thermometer, and the container using sample water.

5. Allow the sensors to equilibrate to sample temperature, then discard the used sample water. Pour fresh sample water into a container holding the sensor and the thermometer. **When using a dip-type sensor, do not let the sensor touch the bottom or sides of the measuring container.**

6. Measure water temperature.

   - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
   - If the instrument is not temperature compensating, use a calibrated thermistor or a liquid-in-glass thermometer.
   - Adjust the instrument to the sample temperature (if necessary) and remove the thermometer.

7. Measure conductivity.

   a. Remove any air trapped in the sensor by agitating the sensor up and down under the water surface.

   b. Read the instrument display.

   c. Agitate the sensor up and down under the water surface, and read the display again.

   d. Repeat the procedure until consecutive readings are the same.

8. Record the conductivity and the sample temperature on field forms.

   - If the instrument is not temperature compensating, record the raw data and convert the values to conductivity at 25°C using temperature-correction factors provided by the manufacturer.
   - Report the median of the readings to three significant figures on the field forms.
   - Discard the sample into a waste container and dispose according to regulations.

9. **Quality control--**

   - Repeat steps 3 through 8 with at least two fresh subsamples, rinsing the instruments once only with sample water.
   - Subsample values should be within ±5 percent for conductivity $\leq$ 100 µS/cm, or ±3 percent for conductivity >100 µS/cm.
   - If criteria cannot be met: filter the samples, report the median of 3 or more samples, and record this difficulty in field notes.

10. Rinse the sensor, the thermometer, and the container with deionized water. If another measurement is to be made within the next day or two, store the sensor in deionized water. Otherwise, store the sensor dry.

6.3.3.B
GROUND WATER

Measurements of ground-water conductivity must represent aquifer conditions. Temperature changes resulting from transporting a well sample to land surface can affect conductivity.

- To minimize the effect from temperature changes, measure conductivity as close to the source as possible, using either a downhole or flowthrough-chamber sampling system (refer to NFM 6.0 for details).
- Bailed or other methods for collecting discrete samples isolated from the source are not recommended as standard practice, although such methods are sometimes called for owing to site characteristics or other study requirements.

Downhole and flowthrough-chamber measurement

1. Calibrate the conductivity instrument system on site.
    - Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.
        a. Check the temperature of the water flowing into the bucket against that of standards.
        b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.
    - After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.
2. Install the conductivity and temperature sensors.
    - **Downhole system**--Lower the conductivity and temperature sensors to sampling point, followed by pump.
        a. Remove any air from the system by agitating the conductivity sensor up and down under the water; read the instrument display.
        b. Repeat this procedure until rapid consecutive readings are approximately the same.
    - **Flowthrough-chamber system**--Install the chamber system as close to the well as possible and shield the system from direct sunlight.
        a. Position the conductivity sensor upstream from the pH electrode.
        b. Direct flow to the chamber after an initial discharge to waste to clear sediment from sample line.
        c. Release any air trapped in the chamber.
        d. Agitate the conductivity sensor up and down under the water to remove air from system. Rapid consecutive readings should be about the same.

3. During purging (table 6.0-1 in NFM 6.0):

   - Keep flow constant and laminar.
   - Allow the sensors to equilibrate with ground-water temperature for 5 minutes or more at the flow rate to be used for collecting all other samples.

4. Measure conductivity and associated temperature at regular intervals throughout purging; record the conductivity values and the associated temperature in the field notes.

   - If the conductivity sensor contains a calibrated thermistor, use this thermistor to measure water temperature.
   - If the instrument is not temperature compensating, install a calibrated thermometer in the flowthrough chamber, record raw data, and apply correction factors.

5. Check the variability of the conductivity values toward the end of purging.

   - The stability criterion is met when five readings taken at regularly spaced intervals of 3 to 5 minutes or more are within

     ±5 percent for conductivity $\leq$ 100 µS/cm
     ±3 percent for conductivity >100 µS/cm

   - When readings fluctuate rapidly, record the median of three or more readings within about 60 seconds as the value for a specific time interval.
   - If the criterion is not met, extend the purge period in accordance with study objectives and continue to record measurements at regularly spaced time intervals. Record this difficulty on the field forms.

6. Report conductivity.

   - Record the final five values on field forms.
   - Report the median value of the final five measurements as the sample conductivity.
   - If values exceed the stability criterion, report the range of values observed for the time interval, along with the median of the final five or more values.

Subsample measurement

Conductivity measurements reported from bailed or other discrete samples need to be identified in the data base, indicating the sampling method used. Refer to 6.0.3.B in NFM 6.0 for use of bailers and the subsample method.

1. Calibrate the conductivity instrument system onsite.

- Bring standard solutions to the temperature of the water to be sampled by suspending the standards in a bucket into which well water is flowing. Allow at least 15 minutes for temperature equilibration. Do not contaminate standards with sample water.

  a. Check the temperature of the water flowing into the bucket against that of standards.

  b. Check that the thermometer (usually a thermistor function in the conductivity meter) has been certified within the past 4 months for the temperature range to be measured.

- After calibration, rinse the conductivity and temperature sensors thoroughly with deionized water.

2. Draw off subsamples for measurement.

   - **Quality control--Collect three subsamples to check precision.**

   - If samples need to be stored for a short time, or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles--fill to the brim, cap tightly, and maintain at ambient ground-water temperature. Measure conductivity as soon as possible.

3. Follow procedures described in steps 4 through 10 for "Subsample measurement" of surface water (6.3.3.A).

TECHNICAL NOTE: If the sample is measured in an open container and readings do not stabilize within several minutes, the cause may be CO_2 degassing--use a closed system to measure the sample. Filter the conductivity sample if the settling of clay particles appears to interfere with the stability of the readings.

⇨Section 6.3.4.
⇧Return to Section 6.3.2
⇧Return to Contents for 6.3--Specific Electrical Conductance
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 10JUNE98 ghc

Table 6.3–3. Correction factors for converting non-temperature-compensated values to conductivity at 25 degrees Celsius, based on 1,000 microsiemens potassium chloride solution

[Use of potassium-based constants on non-potassium-based waters generally does not introduce significant errors for general purpose instruments used to measure conductivity]

Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor	Temperature (degrees Celsius)	Correction factor
0.5	1.87	10.5	1.39	20.5	1.09
1.0	1.84	11.0	1.37	21.0	1.08
1.5	1.81	11.5	1.35	21.5	1.07
2.0	1.78	12.0	1.33	22.0	1.06
2.5	1.76	12.5	1.32	22.5	1.05
3.0	1.73	13.0	1.30	23.0	1.04
3.5	1.70	13.5	1.28	23.5	1.03
4.0	1.68	14.0	1.27	24.0	1.02
4.5	1.66	14.5	1.26	24.5	1.01
5.0	1.63	15.0	1.24	25.0	1.00
5.5	1.60	15.5	1.22	25.5	0.99
6.0	1.58	16.0	1.21	26.0	0.98
6.5	1.56	16.5	1.19	26.5	0.97
7.0	1.54	17.0	1.18	27.0	0.96
7.5	1.52	17.5	1.16	27.5	0.95
8.0	1.49	18.0	1.15	28.0	0.94
8.5	1.47	18.5	1.14	28.5	0.93
9.0	1.45	19.0	1.13	29.0	0.92
9.5	1.43	19.5	1.12	29.5	0.91
10.0	1.41	20.0	1.11	30.0	0.90

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.3.4.pdf

6.3.4 TROUBLESHOOTING

Contact the instrument manufacturer if the actions suggested in table 6.3-4 fail to resolve the problem.

- If available, use a commercial, electronic calibrator to check the function of conductivity instruments.
- Check the voltage of batteries. Always have good batteries in instruments and carry spares.

Table 6.3-4. Troubleshooting guide for conductivity measurement
[HCl, hydrochloric acid; °C, degrees Celsius]

Symptom	Possible cause and corrective action
Will not calibrate to standards	• Standards may be old or contaminated—use fresh standards. • Electrodes dirty—clean with a detergent solution, then with 5 percent HCl. Before using any acid solution to remove resistant residues, check manufacturer's guidelines. • Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. • Weak batteries—replace. • Temperature compensation incorrect—ensure that thermometer is operating properly and is calibrated. • Sensor constant incorrect—replace sensor.
Erratic instrument readings	• Loose or defective connections—tighten or replace. • Broken cables—repair or replace. • Air trapped in conductivity sensor—agitate sensor up and down to expel trapped air. • Rapid changes in water temperature—measure in situ. • Outgassing of ground-water sample—use a downhole instrument; if unavailable, use a flowthrough chamber. • Broken sensor—replace.
Instrument requires frequent recalibration	• Temperature compensator not working—measure conductivity of a solution. Place solution in a water bath and raise solution temperature to about 20°C. Measure conductivity again, allowing sufficient time for temperature of conductivity sensor to equilibrate to temperature of sollution. If the two values differ by 5 percent or more, replace conductivity sensor.

⇨Section 6.3.5.
⇧Return to Section 6.3.3
⇧Return to Contents for 6.3--Specific Electrical Conductance

⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 10JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.3.5.pdf

6.3.5 REPORTING

Report routine conductivity measurements to three significant figures, whole numbers only, in microsiemens per centimeter at 25°C.

- Record the accuracy range of the instrument system in the data base, if possible, and always report it with published values.
- Enter field-determined conductivity measurements on NWQL Analytical Services Request form using the correct parameter code.

⇨Contents for 6.4--pH.
⇧Return to Section 6.3.4
⇧Return to Contents for 6.3--Specific Electrical Conductance
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 10JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

PDF for Section 6.4 (Version 1.2, 7/2003)
Archive pdf available for Section 6.4, 4/98

National Field Manual

6.4 pH

By D.B. Radtke, Eurybiades Busenberg, F.D. Wilde, and J.K. Kurklin

6.4 pH

6.4.1 Equipment and supplies
6.4.1.A pH buffer solutions
6.4.1.B pH electrodes: maintenance, reconditioning, cleaning, and storage

6.4.2 Calibration

6.4.3 Measurement
6.4.3.A Surface water
In situ measurement
Subsample measurement

6.4.3.B Ground water
Downhole and flowthrough-chamber measurements
Subsample measurement

6.4.4 Troubleshooting

6.4.5 Reporting

Tables

6.4-1. Equipment and supplies used for measuring pH

6.4-2. Troubleshooting guide for pH measurement

⇨Section 6.4
⇧Section 6.3.5

⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 18AUG03 imc (Version 1.2, 7/03)

USGS
science for a changing world

Water Resources--Office of Water Quality

6.4
pH

pH: a measure representing the negative base-ten logarithm of hydrogen-ion activity of a solution, in moles per liter.

pH is a symbol that represents the negative base-10 logarithm of the effective concentration (activity)of the hydrogen ion (H^+) in moles per liter (the theoretical basis of H^+ activity and measurement are described and referenced in greater detail in Hem, 1989, and in Pankow, 1991). By definition,

$$pH = -\log_{10}[H], \text{ and}$$

$$H^+ = 10\text{-}pH.$$

- Logarithmic units are used to express H^+ activity, because the activity of H^+ in most environmental waters is too low to be conveniently expressed in the same milligram-, microgram-, or mole-per-liter units as are most other chemical species (Hem, 1989).
- pH is reported on a scale that most commonly ranges from 0 to 14 and that is related directly to the ratio of H^+ and hydroxyl (OH^-) ion activities at a given temperature. However, a highly acidic solution (mine drainage, for example) can have a pH of less than 0; pH greater than 14 can be attained in concentrated base solutions (Nordstrom and Alpers, 1999; Hem, 1989).
- A solution is considered acidic if H^+ activity is greater than OH^- activity (pH less than 7 at 25°C); a solution is considered basic, or alkaline, when OH^- activity is greater than H^+ activity.
- Carbon dioxide-free water at 25°C is considered neutral because activities of H^+ and OH^- are equal.

Temperature has a strong effect on hydrogen-ion activity and must be taken into account when determining and recording pH measurements; for example, for pure water at 30°C, neutral pH is 6.92, while at 0°C neutral is 7.48. The pH of pure water at 25°C is considered to be 7.0.

⇨Section 6.4.1
⇧Return to Contents for 6.4--pH
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer:
Webversion by: Genevieve Comfort
Last Modified: 18AUG03 imc (Version 1.2, 7/03)

USGS
science for a changing world

Water Resources--Office of Water Quality

6.4.1
EQUIPMENT AND SUPPLIES

The instrument system that is used to measure pH must be tested before each field trip, and it must be cleaned soon after use. Because of the variety of pH meters and electrodes available, read thoroughly the instruction manual provided by the manufacturer. Every pH instrument must have a log book in which its manufacturer make and model, serial or property number, and all repairs and calibrations are recorded.

- **The electrometric measurement method uses a hydrogen ion electrode and is the only technique which is approved for measuring pH values that are to be reported or entered into the USGS data base.**
- The colorimetric method uses pH "litmus" indicators that change color with a change in pH. The colorimetric method is suitable only when rough estimates of pH are needed; for example, when assessing the volume of acid or base needed to preserve samples; or, when checking that equipment-cleaning solutions have been adequately neutralized prior to disposal.

pH electrodes and meters are sophisticated electronic instruments that require care in handling and operation. Instruments for pH measurement (including those that are part of multiparameter instruments) and pH buffers must be protected from dirt, extreme heat or freezing conditions, and from jostling or sudden impacts, either while in the field or in storage. Keep instrument systems clean and dry when they are not in use.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.

Table 6.4–1. Equipment and supplies used for measuring pH[1]

[Except for the multiparameter instrument, this equipment is required also for ANC or alkalinity determinations (see NFM 6.6); mL, milliliters; °C, degrees Celsius; mV, millivolt; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

- ✓ pH meter and pH electrodes
  - Battery powered, solid state, with automatic temperature and slope compensation, or multiparameter instrument (possible alternative to separate pH meter and electrode)
  - Range of at least 2 to 12 pH, preferably 0 to 14 pH
  - Accuracy of at least ±0.1 units
  - Temperature range of at least 0 to +45°C
  - Millivolt readout with accuracy of ±1.0 mV or better for instrument resolution of 0.1 mV
  - Bayonet nut connector (BNC) is recommended
- ✓ pH electrodes, gel-filled or liquid-filled, as appropriate for study objectives and site conditions
- ✓ pH electrode filling solution of appropriate composition and molarity (for liquid-filled electrode)
- ✓ Thermometer, calibrated
- ✓ Buffer solutions, 500 mL each of pH 4, 7, and 10; temperature correction chart(s) for buffers
- ✓ Stand for holding pH electrode (or stand for holding multiparameter instrument system)
- ✓ Bottle, delivery (squeeze), for deionized water
- ✓ Deionized water, maximum conductivity of 1 µS/cm
- ✓ Beakers or measurement vessels, polyethylene or Teflon™ preferable, assorted, 50 to 150 mL, clean but not acid rinsed
- ✓ Paper tissues, disposable, soft, and lint free
- ✓ Flowthrough chamber for ground-water measurements (used with meter and electrode equipment)
- ✓ Minnow bucket with tether or equivalent, used for temperature equilibration of buffer solutions
- ✓ Antistatic spray or polish
- ✓ Waste disposal container
- ✓ Stirrer, magnetic with thin insulating pad; or stirrer, mechanical with Teflon™ coated impeller
- ✓ Stirrer bar, magnetic, Teflon™ coated
- ✓ Instrument log book for recording calibrations, maintenance, and repairs

[1]Modify this list to meet the specific needs of the field effort.

CAUTION: Before handling pH buffers or other chemicals, refer to Material Safety Data Sheets (MSDS) for safety precautions. Wear eye guards and protective clothing.

6.4.1.A
pH BUFFER SOLUTIONS

pH measurements are only as accurate as the buffers used for calibration. Use buffers that have been certified traceable to the NIST Standard Reference Material; buffers with a pH of 4, 7, and 10 are available from QWSU.

- ► Note that the routine buffers obtained for measurement of pH from 4 to 10 have a high ionic strength. For pH measurements of dilute waters, obtain low ionic-strength buffers.

- Label buffer and reagent containers with the date when they are received.
- Label every buffer with its expiration date. Copy this date onto any container into which the buffer is transferred.
- **Discard buffers on their expiration dates.** The pH of the buffers may have changed substantially because of carbon dioxide absorption, mold growth, or evaporation.

Take the following precautions to maximize the accuracy of pH measurement (modified from Busenberg and Plummer, 1987):

1. Always cap buffer bottles to prevent evaporation and contamination from atmospheric carbon dioxide. (In order of greatest to least sensitivity to CO_2 contamination, pH buffer 10 > 7 > 4. Buffers are stable for the short exposure time during electrode calibration.)

2. Never pour used buffer back into stock solution bottles. Never insert an electrode or other material into stock solution bottles containing buffers--always pour the buffer into a separate container.

3. Be very careful not to contaminate the buffer with another buffer or with other fluids (pH 4 buffer is least resistant to contamination).

4. Do not dilute buffer--for example, with water dripping from sensors (more important for pH 7 buffer).

5. Before using buffers, bring them to the temperature of the sample solution, and check with the buffer manufacturer for temperature-correction factors. (In order of greatest to least pH variation with temperature, buffer of pH 10 > 7 > 4.)

6.4.1.B
pH ELECTRODES: MAINTENANCE, RECONDITIONING, CLEANING, AND STORAGE

The slope and the measured potential of a new electrode should be monitored daily for about 1 week before use (Busenberg and Plummer, 1987). The latest instruments have microprocessors that automatically calculate and display the slope. Some older instruments have a percent-slope readout or (and) millivolt readout. For instruments with a millivolt readout, the measured electrode potential is calculated as the difference between millivolts measured at the known pH of two buffers. Because the theoretical Nernst response is known, slope can be calculated from measured potentials as follows:

$$E=E^{o}-S(pH)$$

where
S = slope, and
E = electrode pair potential in mV.

Using two buffers of known pH (1, 2),

$$E_1=E^{o}-S(pH_1)$$

and

$$E_2=E^{o}-S(pH_2)$$

or

$$S=\frac{E_2-E_1}{pH_1-pH_2}$$

and

$$E^{o}=E_2+S(pH_2).$$

The theoretical slope is temperature dependent; the slope in mV can be calculated as follows:

$$S_t = 0.19841(273.15 + t)$$

where
t = temperature in degrees Celsius, and
S_t = slope at a given temperature.

Normally, electrodes drift from day to day and E° typically varies by ±2 mV; the slope remains fairly constant to within ±0.2 percent Nernst slope after the new electrode has been conditioned. Follow the procedures recommended by the manufacturer. Properly working electrodes commonly drift from about 0.1 to 0.2 mV per hour.

Electrode maintenance

Electrodes with gel-filled references require less maintenance than electrodes with liquid-filled references. Follow manufacturer's instructions.

Deterioration of the electrode is normal, and proper maintenance requires that electrode performance be monitored before every water-quality field trip and again at each site. Electrodes can give years of reliable service if maintained by following steps 1-8:

1. Do not handle the glass bulb with fingers. Oily film or scratches on the bulb will interfere with pH measurement. Fingers leave a protein film on the glass that decreases electrode sensitivity.

2. Inspect the electrode and electrode cable for physical damage; for example, check for

   - Scratched or broken bulb.
   - Cut, frayed, or broken cable.
   - Bent or broken connector.

3. **Rinse electrode thoroughly with deionized water before use. Do not wipe electrodes with paper towels or wipes--these scratch the glass bulb.** Gently blot droplets from a wet glass

electrode bulb with lens paper or soft tissue by contacting only the droplets to soak up excess solution.

> **TECHNICAL NOTE:** Wiping glass with paper causes a static charge (polarization) that results in drifting, sluggish, and erratic pH readings. It can take many minutes for the electrode to return to normal operation. Clothing also can produce a static charge that affects electrode response.

Gel-filled electrodes do not require filling, but should not be left in dilute water for long periods of time. (Salt can leach from the gel into the dilute water and produce a large junction potential, resulting in errors in pH measurement.)

For liquid-filled electrodes:

a. Remove salt crystal deposits from the electrode, membranes, and junctions. Check that the reference junction is not blocked.

- Rinse off salt buildup with deionized water.
- Check that you can observe seepage of the filling solution through the junction.

b. Always unplug the fill hole before making pH measurements, and replug it after use. If using an electrode after it has been in a storage solution, uncap the fill hole and suspend the electrode in air for about 15 minutes. This will allow the filling solution to flush residual storage solution through the porous reference junction and thoroughly wet it.

c. Check the filling solution level and replenish it if necessary--it should reach the bottom of the fill hole. Filling solutions differ in molarity and composition--always check that you are using the correct filling solution required by the manufacturer for a particular electrode.

d. Drain and flush the reference chamber of refillable electrodes, and routinely refill them with the correct filling solution (see manufacturer's recommendations).

4. **Monitor electrode response.** Keep a record of electrode operation in the pH meter log book. Record the Nernst slope reading and the millivolt readings at pH 7 and pH 4 after calibration.

- Properly working glass electrodes should give approximately 98.0 to 99.5 percent response of that expected from the theoretical Nernst relation (Busenberg and Plummer, 1987). The theoretical Nernst response is 59.16 mV/pH unit at 25°C.
- A slope of less than 94 percent signals possible electrode deterioration and the need to monitor closely any further decline in slope percent. If possible, replace or recondition the electrode at this point.
- **Do not use an electrode with a slope of 90 percent or less.**

5. Keep the electrode bulb moist and capped when not in use. Keep a moist piece of cotton or lint-free tissue in the cap to prevent the bulb from drying out.

Reconditioning liquid-filled electrodes

Before beginning a field trip, if you are unsure of an electrode's condition or have persistent problems during calibration, use the following procedures to recondition the electrode.

1. Remove the old filling solution from the electrode--

    a. Place the needle of a 1- or 3-mL syringe into the electrode filling hole (or use other methods of removing the filling solution, such as vacuum extraction or draining).

    b. Tilt the pH electrode until the filling solution is near the filling hole and the needle tip is covered with the filling solution.

    c. Pull back on the syringe plunger until the syringe is full.

    d. Discharge the solution from the syringe into a waste container and repeat steps 1(a) through (d) until all of the filling solution has been removed from the pH electrode chamber.

2. Flush the pH electrode chamber with deionized water--

    a. Use a syringe or squeeze bottle to partially fill the pH electrode chamber with deionized water.

    b. With a syringe, remove the deionized water from the pH electrode chamber.

    c. As a result of changes in pressure, temperature, and evaporation, crystals may form in the pH electrode chamber. If they form, repeat steps 2(a) and (b) until all crystals have been dissolved and removed from the pH electrode chamber.

3. Fill the electrode chamber with new filling solution--

    a. Flush the electrode chamber with fresh filling solution using a syringe or a plastic squeeze bottle.

        - Partially fill the pH electrode chamber with filling solution.
        - Tilt the pH electrode so that the filling solution will contact all of the internal electrode surfaces.
        - Remove and discard the filling solution to a waste container.

    b. Fill the electrode chamber with fresh filling solution until the filling-solution level is just below the fill hole. Be sure to use the correct molarity filling solution.

    c. Rinse any excess filling solution from the outside of the electrode with deionized water.

Filling solutions might not be interchangeable for different electrodes— check manufacturer's instructions.

Electrode cleaning

Electrodes must be kept clean and the liquid junction free flowing in order to produce accurate pH values. Because of the variety of electrodes available, check the manufacturer's cleaning instructions.

- Rinse the outside of the electrode thoroughly with deionized water after each use. In general, this should be the only routine cleaning needed.
- Rejuvenation procedures described by the manufacturer should be used if an electrode becomes clogged or extremely dirty.

  - After completing rejuvenation procedures on a liquid-filled electrode, drain, clean and refill the reference electrode chamber with fresh filling solution. Replace the fill-hole plug, and soak the electrode in storage solution overnight. Retest the electrode. If the procedures fail to remedy the problem, discard the electrode. Document electrode reconditioning or replacement in the instrument log book.
  - Gel-filled electrodes can be rejuvenated in some instances by placing the electrode in warm water (approximately 60°C) for about one minute or less. This procedure rejuvenates the junction by liquifying the salt gel.

Electrode storage

Electrodes must be clean before they are stored for any length of time.

Short-term storage. Short-term storage methods are appropriate only for in-service electrodes (those used daily or weekly). Storage solutions for short-term storage of electrodes differ with the type of electrode; follow the manufacturer's recommendations. Storage solutions can have a limited shelf life. Unless otherwise instructed by the manufacturer, avoid storing glass hydrogen-ion electrodes in deionized water or concentrated KCl solutions. In the latter case, absorbed potassium reduces the glass sensitivity to hydrogen ions.

- Store liquid-filled pH electrodes upright.
- Keep liquid-filled electrodes wet to maximize their accuracy and response time. Store them so that the bulb is fully immersed in proper electrode storage solution between uses at a field site. Before moving to the next field site, replace the plug on the fill hole, fill the protective cap with storage solution, and cover the electrode bulb with the cap.
- Gel-filled electrodes must only soak in a solution for short periods during measurements. Follow the manufacturer's instructions for storage of gel-filled electrodes.
- Clean the connector ends and store them in a plastic bag.

Long-term storage. pH measuring systems must be stored in an area that is clean, dry, and protected from extremely hot or cold temperatures. For long-term storage of liquid-filled electrodes, drain the filling solution from the electrode, rinse the outside of the electrode with deionized water, and store the electrode dry with a protective cap covering the bulb (put either storage or filling solution in the cap before placing the cap on the bulb if the manufacturer recommends that the bulb be kept moist). Clean the electrode connector ends (with alcohol, if necessary), and store them dry in a sealed plastic bag.

⇨ Section 6.4.2
⇧ Return to Section 6.4
⇧ Return to Contents for 6.4--pH
⇧ Return to Chapter A6 Contents Page
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 28AUG03 imc (Version 1.2, 7/03)

USGS
science for a changing world

Water Resources--Office of Water Quality

6.4.3 MEASUREMENT

The pH of a water sample can change significantly within hours or even minutes after sample collection as a result of degassing (such as loss of carbon dioxide, hydrogen sulfide, and ammonia); mineral precipitation (such as formation of calcium carbonate); temperature change; and other chemical, physical, and biological reactions. The electrometric method of pH measurement described below applies to filtered or unfiltered surface water and ground water, from fresh to saline.

The pH of a water sample must be measured immediately in the field; laboratory-measured pH should not be relied on in place of field-measured pH.

Field conditions, including rain, wind, cold, dust, and direct sunlight can cause measurement problems. To the extent possible, shield the instrument and measurement process from the effects of harsh weather.

- In dry, windy climates, a static charge can build up on the face of a pH meter and cause erratic readings on the display.
- Polish the face of the display with a soft, absorbent tissue treated with several drops of antistatic solution (such as plastic polish) to minimize this interference.

TECHNICAL NOTE: Temperature has two effects on pH measurement of a sample: it can affect electrode potential (Nernstian slope effect), and it can change hydrogen-ion activity (chemical effect). The electrode-potential problem can be solved by using an automatic or manual temperature compensator. The change in hydrogen-ion activity resulting from temperature changes in the sample can be minimized if the electrodes, buffers, and container are allowed to equilibrate to the same temperature.

6.4.3.A SURFACE WATER

It is generally preferable to measure pH in situ rather than on a sample taken from a splitter or compositing device. If stream conditions are such that water would pass the in situ pH sensor at a very high rate of flow, however, streaming-potential effects could affect the accuracy of the measurement. For such conditions, it is preferable to withdraw a discrete sample directly from the stream or compositing device and use the subsample measurement procedures described below. The pH instrument system should be set up on board the boat so that pH is measured at the time of sample collection.

Standard pH measurement in flowing surface water represents the cross-sectional mean hydrogen ion activity or median pH at the time of observation.

To compute a mean pH for the stream:

1. Convert each pH value to hydrogen-ion activity, using the equation, Activity = $10^{-1(pH)}$.
2. Calculate the mean of the activity values by adding the values and dividing the sum by the total number of values.
3. Convert the calculated mean activity back to pH units, using the equation, pH = (-) ($\log_{10}$)(mean H^+ activity).

In situ measurement

Follow the 7 steps listed below for in situ pH measurement:

1. Calibrate a pH system on site (after equilibrating the buffers with the stream temperature, if necessary). Check the electrode performance (see "Electrode Maintenance," in 6.4.1) and the calibration date of the thermometer being used.

2. Record the pH variation from a cross-sectional profile, if possible, to determine if pH is uniform at any given discharge, and select the sampling method (NFM 6.0.2) appropriate for study objectives.

    - **Flowing, shallow stream**--Wade to the location(s) where pH is to be measured.

    - **Stream too deep to wade**--Lower a weighted pH sensor with a calibrated temperature sensor from a bridge, cableway, or boat. Do not attach the weight to sensor or sensor cables.

    - **Still-water conditions**--Measure pH at multiple depths at several points in the cross section.

3. Immerse the pH electrode and temperature sensor in the water to the correct depth and hold them there for at least 60 seconds to equilibrate them to water temperature.

4. Measure the temperature.

    - If the pH instrument system contains an automatic temperature compensator (ATC), use the ATC to measure water temperature.

    - If the instrument system does not contain an ATC, use a separate calibrated thermometer, adjust the meter to the sample temperature (if necessary), and remove the thermometer.

5. Record the pH and temperature values without removing the sensor from the water.

    - Values generally stabilize quickly within ±0.05 to 0.1 standard pH unit, depending on the instrument system.

    - Record the median of the observed values.

    - If readings do not stabilize after extending the measurement period, note this difficulty on the field forms along with the pH readings, and record the median value of the last five or more readings.

6. EWI or EDI measurements--Proceed to the next station in the cross section. Repeat steps 3 through 5. After all stations in the cross section have been measured, rinse the sensors with deionized water and store them.

7. Record the mean or median stream pH on the field forms (note that pH values first must be converted to the negative antilogarithm, then the mean is calculated using the negative antilog values, and finally the mean value is converted back to pH units, as described earlier in section 6.4.3.A):

   - **In still water--median** of three or more sequential values.
   - **EDI--mean** value of all subsections measured (use the median if measuring one vertical at the centroid of flow).
   - **EWI--mean or median** of all subsections measured.

Subsample measurement

When streams are fast-flowing or the water contains much sediment or algae, pH measurement of a discretely collected subsample might be preferable to in situ measurement. Representative samples are to be collected and split or composited according to approved USGS methods (Wells and others, 1990). pH measurement in fast-flowing streams should be made at the time of collection from a boat that has been set up for such measurements.

- Measure pH as soon as possible after compositing the EDI or EWI sample.
- Filter the sample if the pH continues to drift: measure pH in the field on both unfiltered and filtered subsamples and record both values on the field form.
- If the filtered sample provides the only stable pH value, report this value as sample pH.

TECHNICAL NOTE: Reported pH values are normally determined on an unfiltered sample. However, large concentrations of suspended sediment or algae can be a source of measurement error; slow settling of clay particles or algal respiration can cause "drift" of an observed pH value.

Throughout collection and processing, avoid excess aeration to prevent losses and gains of dissolved gases (especially CO_2) from solution.

1. Calibrate the pH system on site (after equilibrating buffer temperature with stream temperature, if necessary). Check the electrode performance (see 6.4.1).

2. Select the appropriate sampling method (see NFM 6.0) and collect a representative sample.

3. Withdraw properly homogenized sample(s) from the compositing device.

   - Rinse the collection bottles three times with the sample (use filtrate, if a filtered sample is used).

- If the samples need to be stored for a short time or if several subsamples will be measured, collect sample aliquots in separate field-rinsed bottles, fill them to the brim, cap them tightly, maintain them at ambient stream temperature, and measure pH in the field as soon as possible.

4. Rinse thoroughly with deionized water--the pH electrode, thermometer or ATC sensor, stir bar, and a measurement container.

   - For pH, follow the deionized water rinse of equipment with a rinse using sample water.

   - For ANC or alkalinity, rinse with deionized water only; do not rinse with the sample when using this equipment (see NFM 6.6).

5. Immerse electrode and temperature sensor in sample water for at least 60 seconds to equilibrate to sample temperature.

6. Pour fresh aliquot of the sample water into a container holding the electrode and thermometer. **Do not let the electrode touch the bottom or sides of container during measurement.**

7. Measure and record the initial temperature. Use the ATC, if it is available and calibrated, or use a separate calibrated thermometer and adjust the meter manually to the sample temperature (if necessary).

8. Establish equilibrium between the electrode(s) and sample by stirring **slowly** (no vortex) or by manual swirling.

   - Do not stir if a vortex is formed that affects the electrode performance.

   - Do not use a magnetic stirrer for samples with low conductivity (less than 100 µS/cm).

   - Before recording a pH value, allow the sample to reach quiescence.

9. Record the pH and temperature measurements on the field forms, along with the sampling, processing, and measurement methods used and any observed anomalies.

10. **Quality control**--Repeat steps 6 through 9 with at least two fresh subsamples to check measurement precision. Subsample values should agree within ±0.1 pH unit (or study-determined criterion). Report the median of the values measured.

11. Rinse the electrode and temperature sensor thoroughly with deionized water. Replace the plug on the fill hole of refillable electrodes and follow the recommended storage procedure.

12. Discard the used sample into a waste container and dispose of it according to regulations.

6.4.3.B GROUND WATER

Measurements reported as ground-water pH must represent aquifer conditions (consult NFM 6.0 for guidance). Measure pH as close to the source as possible, either downhole or within a flowthrough chamber.

- Use equipment that minimizes aeration and operate equipment in a manner to help mitigate losses and gains of dissolved gases in solution (for example, carbon dioxide).
- Although downhole measurements are likely to be most representative of ground-water pH, proper use of pH instruments with flowthrough chambers can yield comparable values.
- The downhole system is not practical if samples will be collected after field measurements, because the instrument should not be left in the well during sampling and the pump should not be turned off between purging and sample collection--use a flowthrough-chamber system.
- Streaming potentials in the flowthrough chamber can result in biased pH values. Make the final (the reported sample pH) measurement in quiescent water.

Bailed or other methods for collecting discrete samples isolated from their source are not recommended for the determination of pH, although such methods are sometimes used owing to site characteristics or study requirements. Record the method used to obtain the sample for pH measurements on the field forms and in the data base.

Downhole and flowthrough-chamber measurements

1. Calibrate the pH instrument system on site.

    a. If necessary, bring the buffer solutions to the temperature of the water to be measured (discharge the well water into a bucket while suspending the standards in a net bag; allow at least 15 minutes for temperature equilibration; check temperature of the water flowing into the bucket against that of the buffers).

        - Check that the thermometer has been District certified within at least the past 4 months.
        - Check electrode performance (see 6.4.1 and 6.4.2).

    b. After calibration, rinse the pH electrode thoroughly with deionized water and blot it to remove excess water. Do not wipe the electrode.

2. Install the pH monitoring system for sample measurement (see 6.0.3 in NFM 6.0).

    - **Downhole system**--Lower sensors to the measuring point, followed by the pump, to monitor pH variation during purging.
    - **Flowthrough system**--Install the chamber system as close to the well as possible and shield the chamber and tubing from direct sunlight. Check that the electrode fill hole is open to the atmosphere and that the reference junction is entirely submerged. Check for and eliminate a backpressure condition.

3. During purging (see table 6.0-1 and fig.6.0-3 in NFM 6.0):

    - Keep the flow constant and laminar.
    - Allow the sensors to equilibrate with the ground water for 5 minutes or more at the flow

rate to be used for collecting all of the other samples.

4. Record pH values at regularly spaced time intervals throughout purging. Compare the variability of the pH values toward the end of purging with the stability criterion:

   - The stability criterion is met when five readings made at regularly spaced intervals of 3 to 5 minutes or more are within 0.1 standard pH unit or less (depending on the equipment). Routine measurement must fall within the ±0.1 unit criterion. When readings fluctuate rapidly, select the median of three or more readings within about 60 seconds as the value recorded for the specific time interval.

   - If the criterion is not met, extend the purge period in accordance with study objectives, and continue to record measurements at regularly spaced time intervals. Record any difficulty on the field forms.

5. Measure and report the pH:

   - If using a flowthrough system, divert the flow from passing into the flowthrough chamber after recording the other field measurements. Measure the sample pH in the chamber as soon as the water is still. Take several readings to be sure that the system has stabilized.

   - If using a downhole method, measure the sample pH after pumping has ceased. This entails installing the downhole sensors in the well after sample collection. If field measurements only are being monitored, stop the pump (after recording the other field-measurement values) and allow the pH to stabilize before recording the pH value.

   - Report the final value measured on a quiescent (no-flow) sample, if the values are stable. If the stability criterion is not met, record the range of values observed for the time interval monitored, and report the median of the final five or more values observed.

Subsample measurement

pH measurements reported from bailed or other discrete samples need to be identified in the data base by a description of the sampling method used. Refer to 6.0.3.B in NFM 6.0 for use of bailers and the subsample method.

Do not use a subsample method if waters are reducing.

1. Calibrate the pH system on site (after equilibrating the buffers with the ground-water temperature, if necessary). Check the electrode performance (see sections 6.4.1 and 6.4.2).

2. Draw off a subsample through a bottom-emptying device that fits tightly over the bottle opening.

   - **Quality control**--Collect three subsamples to check precision.

   - Rinse the sample bottles three times with sample; use filtrate if filtered sample is used. Cap the bottles until they are ready for use.

- If the samples need to be stored for a short time or if several subsamples will be measured, collect the sample aliquots in separate field-rinsed bottles, fill them to the brim, cap them tightly, maintain them at ambient ground-water temperature, and measure the pH as soon as possible.

3. Follow the procedures described in steps 4 through 12 for subsample measurement of surface water (6.4.3.A).

TECHNICAL NOTE: An alternative method is to pour the sample into an open container instead of measuring it in a closed system. If this method is used and readings do not stabilize within several minutes, the cause may be outgassing of carbon dioxide--measure the sample in a closed system. Filter the sample if settling of charged clay particles interferes with the stability of readings.

⇨Section 6.4.4
⇧Return to Section 6.4.2
⇧Return to Contents for 6.4--pH
⇧Return to Chapter A6 Contents Page
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 18AUG03 imc (Version 1.2, 7/03)

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.4.5.pdf

6.4.5 REPORTING

Report pH measurements in the data base to the nearest 0.1 standard pH unit.

- pH values to the nearest 0.05 unit can be published provided the instrument system has been calibrated at the required precision and accuracy.
- Report the instrument accuracy range with the published values and record the accuracy range in the data base, if possible.
- Enter the field-determined pH under the correct parameter code on the NWQL analytical services request form and on field forms.

⇨Section 6.5 Contents Page
⇧Return to Section 6.4.4
⇧Return to Contents for 6.4--pH
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 10JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Complete pdf for Section 6.5--Specific Electrical Conductance

National Field Manual

6.5 REDUCTION-OXIDATION POTENTIAL (ELECTRODE METHOD)

By D.K. Nordstrom and F.D. Wilde

6.5 Reduction-oxidation potential (electrode method)

6.5.1 Equipment and supplies
6.5.1.A Maintenance, cleaning, and storage

6.5.2 Equipment test procedure

6.5.3 Measurement
6.5.3.A Interferences and limitations
6.5.3.B Interpretation

6.5.4 Troubleshooting

6.5.5 Reporting

Illustrations

6.5-1. Form showing Eh data record: equipment test procedure

6.5-2. Form showing Eh data record: field measurements

Tables

6.5-1. Equipment and supplies used for Eh measurements

6.5- Standard half-cell potentials of selected reference electrodes as a function of temperature and

2. potassium chloride reference-solution concentration, in volts

6.5-3. 6.5-3. Eh of ZoBell's solution as a function of temperature

6.5-4. Troubleshooting guide for Eh measurement

⇨ Section 6.5
⇧ Section 6.4.5
⇧ Return to Chapter A6 Contents Page
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 09JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.5.pdf

6.5
REDUCTION-OXIDATION POTENTIAL (ELECTRODE METHOD)

Reduction-oxidation potential (as Eh): a measure of the equilibrium potential, relative to the standard hydrogen electrode, developed at the interface between a noble metal electrode and an aqueous solution containing electroactive redox species.

In contrast to other field measurements, the determination of the reduction-oxidation potential of water (referred to as redox) should not be considered a routine determination. Measurement of redox potential, described here as Eh measurement, is not recommended in general because of the difficulties inherent in its theoretical concept and its practical measurement (see "Interferences and Limitations," section 6.5.3.A).

- Eh measurement may show qualitative trends but generally cannot be interpreted as equilibrium values.
- Determinations of redox using the platinum (or other noble metal) electrode method (Eh) are valid only when redox species are (a) electroactive, and (b) present in the solution at concentrations of about 10^{-5} molal and higher. Redox species in natural waters generally do not reach equilibrium with metal electrodes.

Procedures for equipment calibration (test procedures) and Eh measurement are described in this section for the platinum electrode only. Although the general guidance given here applies to other types of redox electrodes (such as gold and glassy carbon electrodes), it is necessary to consult the manufacturer's instructions for correct use of the specific electrode selected. Concentrations of redox species can be determined by direct chemical analysis instead of using the electrode method (Baedecker and Cozzarelli, 1992).

⇨Section 6.5.1
⇧Return to Contents for 6.5--Reduction Oxidation Potential (Electrode Method)
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort

Last Modified: 16JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.5.1.pdf

6.5.1
EQUIPMENT AND SUPPLIES

The equipment and supplies needed for making Eh measurements using the platinum electrode method are listed in table 6.5-1. Eh equipment must be tested before each field trip and cleaned soon after use. Every instrument system used for Eh measurement must have a log book in which all the equipment repairs and calibrations or equipment tests are recorded, along with the manufacturer make and model numbers and serial or property number.

Electrodes. Select either a redox-sensing combination electrode or an electrode pair (a platinum and reference electrode). **Use of the correct electrolyte filling solution is essential to proper measurement and is specified by the electrode manufacturer.** Orion Company, for example, recommends selection of a filling solution to best match the ionic strength of the sample solution, in order to minimize junction potentials.

Table 6.5–1. Equipment and supplies used for Eh measurements[1]

[mV, millivolt; ±, plus or minus; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

- ✓ Millivolt meter or pH meter with millivolt reading capability, preferably with automatic temperature compensator; 0.1-mV sensitivity; scale to at least ±1,400 mV; BNC connector (see instrument specifications for pH meters, 6.4.1 in NFM 6.4)
- ✓ Redox electrodes, either (a) platinum and reference electrode (calomel or silver:silver-chloride) or (b) combination electrode
- ✓ Electrode filling solutions (refer to manufacturer's specifications)
- ✓ Thermometer (liquid-in-glass or thermistor type), calibrated (see NFM 6.1 for selection and calibration criteria)—for use with millivolt meters without temperature compensator
- ✓ Flowthrough cell with valves, tubing, and accessories impermeable to air (for use with pump system)
- ✓ Sampling system: (1) in situ (downhole) measurement instrument, or (2) submersible pump (used with closed-system flowthrough cell). Pump tubing must be "impermeable" to oxygen.
- ✓ ZoBell's solution
- ✓ Aqua regia or manufacturer's recommended electrode-cleaning solution
- ✓ Liquid nonphosphate laboratory-grade detergent
- ✓ Mild abrasive: crocus cloth or 400- to 600-grit wet/dry Carborundum™ paper
- ✓ Deionized water (maximum conductivity of 1.0 µS/cm)
- ✓ Bottle, squeeze dispenser for deionized water
- ✓ Safety equipment: gloves, glasses, apron, chemical spill kit
- ✓ Paper tissues, disposable, lint free
- ✓ Waste-disposal container

[1]Modify this list to meet specific needs of the field effort.

CAUTION: The standard hydrogen reference electrode (SHE) can be dangerous and is not recommended for field use.

- ► Silver:silver-chloride or calomel reference electrodes are the redox electrodes in common use.
- ► The Orion™ combination electrodes are platinum redox and silver: silver-chloride reference electrodes in one body (the Orion™ brand is used for purposes of illustration only).

ZoBell's solution. ZoBell's is the standard solution for testing redox instruments. ZoBell's solution can be obtained from the QWSU in Ocala, Fla., or it can be prepared fresh (see below). Quinhydrone solution is sometimes used but is not recommended because it is significantly less stable above 30°C and its temperature dependence is not as well defined as that of ZoBell's.

ZoBell's solution consists of a 0.1 molal KCl solution containing equimolal amounts of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. ZoBell's is reported stable for at least 90 days if kept chilled at 4°C. To prepare ZoBell's solution:

1. Weigh the chemicals (dry chemicals should be stored overnight in a desiccator before use).

   1.4080 g $K_4Fe(CN)_6\ 3H_20$ (Potassium ferrocyanide)

1.0975 g $K_3Fe(CN)_6$ (Potassium ferricyanide)

7.4557 g KCl (Potassium chloride)

2. Dissolve these chemicals in deionized water and dilute solution to 1,000 mL.

3. Store the solution in a dark bottle, clearly labeled with its chemical contents, preparation date, and expiration date. Keep the solution chilled.

CAUTION: ZoBell's solution is toxic—handle with care.

Aqua regia. Aqua regia can be used for cleaning the Eh electrode (check the electrode manufacturer's recommendations). Prepare the aqua regia at the time of use--do not store it. To prepare the aqua regia, mix 1 volume concentrated nitric acid with 3 volumes of concentrated hydrochloric acid.

6.5.1.A
MAINTENANCE, CLEANING, AND STORAGE

Refer to 6.4.1 of NFM 6.4 on pH for general guidelines on meter and electrode maintenance, cleaning, and storage. Follow the manufacturer's guidelines on the operation and maintenance of the meters and electrodes, and keep a copy of the instruction manual with each instrument system. Keep the meters and electrodes clean of dust and chemical spills, and handle them with care.

Maintenance

Keep the surface of noble electrodes clean of coatings or mineral deposits. A brightly polished metal surface prevents deterioration of electrode response. The billet tip is more easily cleaned than the wire tip on the platinum electrode. Condition and maintain the Eh electrodes as recommended by the manufacturer.

Cleaning

Keep the O-ring on electrodes moist during cleaning procedures.

- To remove precipitate that forms on the outside wall or tip of the reference or combination electrode, rinse the outside of the electrode with deionized water.
- If particulates or precipitates lodge in the space between the electrode sleeve and the inner cone of sleeve-type electrode junctions, clean the chamber by flushing out the filling solution (the precise procedure to be followed must come from the electrode manufacturer).
- To remove oily residues, use a liquid nonphosphate detergent solution and polish the surface with mild abrasive such as coarse cloth, a hard eraser, or 400- to 600-grit wet/dry Carborundum™ paper (Bricker, 1982).
- To recondition the Eh electrode, immerse the electrode in warm aqua regia (70°C) for about 1 minute. **Do not immerse the electrode for longer than 1 minute** because aqua

regia dissolves the noble metal as well as foreign matter and leads to an erratic electrode response (Bricker, 1982). Soak the electrode several hours in tap water before use.

TECHNICAL NOTE: Disassembly of the electrode is not recommended for routine cleaning and should only be used when absolutely needed. Additional cleaning and reconditioning procedures are discussed in NFM 6.4 and in American Public Health Association and others (1992), American Society for Testing and Materials (1990), Edmunds (1973), Adams (1969), and Callame (1968).

Storage

For short-term storage, immerse the electrode in deionized water to above the electrode junction and keep the fill hole plugged to reduce evaporation of the filling solution. The recommended procedures for long-term storage of electrodes vary with the type of electrode and by manufacturer. The Orion™ combination electrodes are stored dry after rinsing precipitates from outside of the electrode, draining the filling solution from the chamber, and flushing it with water (consult the manufacturer's cleaning instructions). The electrode connector ends must be kept clean. Clean them with alcohol, if necessary. Store the connector ends in a plastic bag when not in use.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances—follow the manufacturer's instructions.

⇨Section 6.5.2
⇧Return to Section 6.5
⇧Return to Contents for 6.5--Reduction Oxidation Potential (Electrode Method)
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 16JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.5.2.pdf

6.5.2 EQUIPMENT TEST PROCEDURE

Eh measuring systems can be tested for accuracy but they cannot be adjusted. Eh equipment must be tested, either in the laboratory or in the field, against a ZoBell's standard solution before making field measurements. In general, field testing with ZoBell's is not required, but the protocol used will depend on study needs.

- Before using, check that the ZoBell's solution has not exceeded its shelf life.
- Test the Eh equipment using the ZoBell's solution **before and after** field use.
- Be aware that:
  - -- ZoBell's is toxic and needs to be handled with care.
  - -- ZoBell's reacts readily with minute particles of iron, dust, and other substances, making field use potentially difficult and messy.

The Eh measurements are made by inserting a platinum electrode coupled with a reference electrode into the solution to be measured. The resulting potential, read directly in millivolts from a potentiometer (such as a pH meter), is corrected for the difference between the standard potential of the reference electrode being used at the solution temperature and the potential of the standard hydrogen electrode table 6.5-2).

TECHNICAL NOTE: E_{ref} is the whole-cell potential of the reference electrode in ZoBell's solution.

E_{ref} = 238 mV (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the silver:silver-chloride (Ag:AgCl) electrode;

E_{ref} = 185.5 mV (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the calomel ($Hg:HgCl_2$) electrode;

E° = 430 mV is the standard electrode potential of ZoBell's solution measured against the hydrogen electrode at 25°C.

Half-cell potentials for the calomel, silver:silver chloride, and combination electrodes are shown in table 6.5-2. Table 6.5-3 provides the theoretical Eh of ZoBell's solution as a function of temperature. For those temperatures not shown on tables 6.5-2 and 6.5-3, interpolate the values. Add the value corresponding to the solution temperature to the measured potential electromotive force (emf measurement).

Table 6.5–2. Standard half-cell potentials of selected reference electrodes as a function of temperature and potassium chloride reference-solution concentration, in volts

[Liquid-junction potential included—multiply volts by 1,000 to convert to millivolts; KCl, potassium chloride; Temp °C, temperature in degrees Celsius; *M*, molar; —, value not provided in reference]

Temp °C	Silver:silver chloride			Calomel[1]				Orion™ 96-78 combination electrode[3,4]
	3M KCl[1]	3.5M KCl[2]	Saturated KCl[2]	3M KCl[2]	3.5M KCl[2]	4M KCl[2]	KCl saturated[2]	
10	0.220	0.215	0.214	0.260	0.256	—	0.254	0.256
15	0.216	0.212	0.209	—	—	—	0.251	0.253
20	0.213	0.208	0.204	0.257	0.252	—	0.248	0.249
25	0.209	0.205	0.199	0.255	0.250	0.246	0.244	0.246
30	0.205	0.201	0.194	0.253	0.248	0.244	0.241	0.242
35	0.202	0.197	0.189	—	—	—	0.238	0.238
40	0.198	0.193	0.184	0.249	0.244	0.239	0.234	0.234

[1]Modified from Langmuir (1971).
[2]Modified from Bates (1973).
[3]Nordstrom (1977) and D.K. Nordstrom, U.S. Geological Survey, written commun., 1996; the half-cell potentials calculated from Nordstrom (1977) are recommended rather than the values from Ciskeau (1964) cited in the instrument manual provided by the Orion Company because Nordstrom's values were developed specifically for the Orion™ 96-78 redox electrode and provide greater accuracy and precision.
[4]Orion™ manufacturer recommends that for sample solutions with total ionic strength exceeding 0.2 molar (for example, seawater), use a 4M KCl-saturated filling solution (usually supplied with the Orion™ model 97-78 electrode) and the half-cell potentials shown above for the silver:silver chloride saturated KCl reference electrode.

Table 6.5–3. Eh of ZoBell's solution as a function of temperature

[From Nordstrom (1977); °C, degrees Celsius; mV, millivolts]

Temperature °C	Eh (mV)	Temperature °C, (continued)	Eh (mV), (continued)
10	467	26	428
12	462	28	423
14	457	30	418
16	453	32	416
18	448	34	407
20	443	36	402
22	438	38	397
24	433	40	393
25	430		

To test Eh equipment, complete the following 7 steps and record results on the Eh data record form for the equipment test procedure (fig. 6.5-1):

1. Follow the manufacturers' recommendations for instrument warm up and operation.
   - Set the scale to the desired millivolt range.
   - Record the type of reference electrode being used.
2. Unplug the fill hole. Shake the electrode gently to remove air bubbles from the sensing tip of the electrode. Check the level of the filling solution and replenish to the bottom of the fill hole.
   - The filling solution level must be at least 1 in. above the level of solution being measured.

- Use only the filling solution specified by the manufacturer.

3. Rinse the electrode, thermometer, and measurement beaker with deionized water. **Blot (do not wipe) excess moisture from the electrode.**

4. Pour ZoBell's solution into a measurement beaker containing the electrode and temperature sensor.

   - The Eh electrode must not touch the bottom or side of the container.
   - Add enough solution to cover the reference junction.
   - Allow 15 to 30 minutes for the solution and sensors to equilibrate to ambient temperature.

5. Stir slowly with a magnetic stirrer (or swirl manually) to establish equilibrium between the electrode(s) and solution. Switch the meter to the millivolt function, allow the reading to stabilize (±5 mV), and record the temperature and millivolt value.

6. Look up the half-cell reference potential for the electrode being used (table 6.5-2). Add this value to the measured potential to obtain the Eh of ZoBell's at ambient temperature.

   - If the value is within 5 mV of the ZoBell Eh given on table 6.5-3, the equipment is ready for field use. (See the example below.)
   - Refer to section 6.5.4 if the value is not within 5 mV of the ZoBell Eh.

7. Rinse off the electrodes and the thermometer thoroughly with deionized water. Store the test solution temporarily for possible verification.

EXAMPLE:

Example of the equipment test procedure using a silver:silver chloride-saturated KCl (Ag:AgCl) electrode.

$$Eh = emf + E_{ref}$$

where:

Eh is the potential (in millivolts) of the sample solution relative to the standard hydrogen electrode,

emf or $E_{measured}$ is the electromotive force or potential (in millivolts) of the water measured at the sample temperature,

E_{ref} is the reference electrode potential of the ZoBell's solution corrected for the sample temperature (table 6.5-2).

a. Follow steps 1-5 (above). For this example,

- Measured temperature = 22°C
- *emf = 238 mV.*

b. Check table 6.5-2. The interpolated reference potential = 202 mV for Ag:AgCl-saturated KCl at 22°C.

c. From $Eh = emf + E_{ref}$

$$Eh\ (ZoBell's) = 238\ mV + 202\ mV = 440\ mV.$$

d. Check table 6.5-3. The test value of 440 mV is within ±5 mV of 438 mV from table 6.5-3. Thus, the equipment is functioning well and ready for field use.

Check the date on Zobell's solution—do not use solution past its expiration date.

Eh Data Record

Equipment Test Procedure

Equipment description and identification (model and serial and/or W number):

Meter _____

Eh electrode _____ Reference electrode _____

ZoBell's solution: Lot # _____ Date: prepared _____ expired _____

		Before sample Eh:	After sample Eh:
1. *Temperature of ZoBell's solution:* (after equilibration to ambient temperature)	T =	_____	_____
2. Observed potential (in millivolts) of ZoBell's relative to measuring electrode, at ambient temperature ($E_{measured}$ or *emf*):	*emf* =	_____	_____
3. Reference electrode potential (in millivolts) at ambient temperature from table 6.5–2 (E_{ref}):	E_{ref} =	_____	_____
4. Calculate Eh of ZoBell's: Eh = *emf*+E_{ref}	Eh =	_____	_____
5. Theoretical potential (in millivolts) of ZoBell's at ambient temperature from table 6.5–3:	Eh (theoretical) =	_____	_____
6. Subtract calculated Eh from Eh theoretical (Zobell's)(step 4 minus step 5)	ΔEh =	_____	_____
7. Check: is ΔEh within ± 5 mV?	Observations:	_____	

Figure 6.5–1. Eh data record: equipment test procedure..

⇨Section 6.5.3
⇧Return to Section 6.5.1
⇧Return to Contents for 6.5--Reduction Oxidation Potential (Electrode Method)
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 16JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.5.3.pdf

6.5.3 MEASUREMENT

To obtain accurate results, it is necessary to prevent losses and gains of dissolved gases in solution. Consult NFM 6.0 for information on precautions and general procedures used in sample collection and NFM 6.2 for a description of the flowthrough cell used in dissolved-oxygen determination (the spectrophotometric method).

- Chemical, physical, and biological reactions can cause the Eh of water to change significantly within minutes or even seconds after the collection of a sample.
- Water samples cannot be preserved and stored for the Eh measurement.
- Use equipment that eliminates sample aeration and operate the equipment to meet this goal. If using a flowthrough chamber or cell:
  - -- Use tubing that is impermeable (relatively) to oxygen.
  - -- Channel the sample flow through an airtight cell (closed system) constructed specifically to accommodate redox or ion-specific electrodes, temperature, and other sensors.
  - -- Connections and fittings must be airtight.
  - -- Purge atmospheric oxygen from the sample tubing and associated flow channels before measuring Eh.

Do not use pumping systems in which inert gas contacts and lifts the sample to the surface: the gas could strip gaseous redox species from the water.

Measure Eh in situ with a submersible instrument or use an airtight flowthrough system.

First:

1. Record the type of reference-electrode system being used (fig. 6.5-1).
2. Check for the correct electrode filling solution. If working in very hot or boiling waters, change the reference electrode filling solution daily.

3. Keep the electrode surface brightly polished.

TECHNICAL NOTE: Temperature determines the Eh reference potential for a particular solution and electrode pair, and may affect the reversibility of the redox reactions, the magnitude of the exchange current, and the stability of the apparent redox potential reading. The observed potential of the system will drift until thermal equilibrium is established. **Thermal equilibrium can take longer than 30 minutes but it is essential before beginning the measurements.**

Next, measure the Eh and complete the field form (fig.6.5-2):

1. Select an in situ or closed-system sampling method. Immerse the electrodes and temperature sensors in the sample water.

   - **In situ (or downhole)**--Lower the sensors to the depth desired and follow the manufacturer's recommendations.

   - **Closed-system flow cell**--Check that the connections and sensor grommets do not leak, and that the water being pumped fills the flowthrough cell.

2. Allow the sensors to reach thermal equilibrium with the aqueous system being measured and record the time lapsed.

   - It is essential that platinum electrodes be flushed with large volumes of sample water to obtain reproducible values.

   - Record the pH and temperature of the sample water.

3. Switch the meter to the millivolt function.

   - Allow the reading to stabilize (±5 mV).

   - Record the value and temperature (see the technical note that follows step 7, below).

   - **Stabilization should occur within 30 minutes.**

4. Take readings of the sample temperature and potential (in millivolts) every few minutes for the first 15 to 20 minutes.

   - It is best to stop the flow of the sample while the reading is being taken to prevent streaming-potential effects.

   - After 15 to 20 minutes, begin to record the time, temperature, and potential in plus or minus millivolts about every 10 minutes. Continue until 30 minutes have passed from the initial measurement and until the measurements indicate a constant potential.

5. After the measurements have been completed for the day, rinse the electrode(s) thoroughly with deionized water.

If field calibration is required for a study,

a. Place the electrode(s) and other sensors in ZoBell's solution that has been equilibrated to the temperature of the aqueous system to be measured. The electrode(s) must not touch the container, and the solution must cover the reference junction.

b. Allow the electrode to reach thermal equilibrium (15 to 30 minutes).

c. Record the potential reading.

d. Follow steps 5-7 of the equipment test procedure in section 6.5.2.

6. Record all data and calculate Eh (see EXAMPLE, (section 6.5.2).

Fill out the Eh data record form for field measurements fig. 6.5-2).

Eh Data Record

Field Measurements

		Field Eh	Field Eh[1]
1. Temperature and pH of system measured:	T =		
	pH =		
2. Time to thermal equilibration:			
	Measurement began at		
	Measurement ended at		
3. Measured potential of water system (mV): *emf* =			
4. Reference electrode potential mV of ZoBell's at sample temperature:	E_{ref} =		
5. Calculate sample Eh: *emf* + E_{ref} (add step 3 + step 4):	Eh =		

6. Field measurements should agree within about 10 mV.
Observations: _____

[1]The second measurement is necessary for quality control.

Figure 6.5-2. Eh data record: field measurements.

7. **Quality control**--Repeat the measurement.

TECHNICAL NOTE: The response of the Eh measurement system may be considerably slower than that of the pH system and that response also may be asymmetrical: the time required for stabilization may be longer when moving from an oxidizing to reducing environment or vice versa. If the readings do not stabilize within about 30 minutes, record the potential and its drift; assume a single quantitative value is not possible. If an estimate of an asymptotic final (hypothetical) potential in such a drifting measurement is desired, refer to the method used by Whitfield (1974) and Thorstenson and others (1979).

6.5.3.A
INTERFERENCES AND LIMITATIONS

Measurements should not be carried out without an awareness of the interferences and limitations inherent in the method.

- Organic matter and sulfide may cause contamination of the electrode surface, salt bridge, or internal electrolyte, which can cause drift or erratic performance when reference electrodes are used (American Public Health Association and others, 1992).
- Hydrogen sulfide can produce a coating on the platinum electrode that interferes with the measurement if the electrode is left in sulfide-rich water for several hours (Whitfield, 1974; Sato, 1960).
- The platinum single and combination redox electrodes may yield unstable readings in solutions containing chromium, uranium, vanadium, or titanium ions and other ions that are stronger reducing agents than hydrogen or platinum (Orion Research Instruction Manual, written commun., 1991).
- Do not insert redox electrodes into iron-rich waters directly after electrode(s) contact with ZoBell's. An insoluble blue precipitate coats the electrode surface because of an immediate reaction between ferro- and ferricyanide ions in ZoBell's with ferrous and ferric ions in the sample water, causing erratic readings.

Many elements with more than one oxidation state do not exhibit reversible behavior at the platinum electrode surface and some systems will give mixed potentials, depending on the presence of several different couples (Barcelona and others, 1989; Bricker, 1982, p. 59-65; Stumm and Morgan, 1981, p. 490-495; Bricker, 1965, p. 65). Methane, bicarbonate, nitrogen gas, sulfate, and dissolved oxygen generally are not in equilibrium with platinum electrodes (Berner, 1981).

TECHNICAL NOTE: Misconceptions regarding the analogy between Eh (pe) and pH as master variables and limitations on the interpretation of Eh measurements are explained in Hostettler (1984), Lindberg and Runnells (1984), Thorstenson (1984), and Berner (1981). To summarize:

(1) Hydrated electrons do not exist in meaningful concentrations in most aqueous systems--in contrast, pH represents real activities of hydrated protons. Eh may be expressed as pe, the negative logarithm of the electron activity, but conversion to pe offers no advantage when dealing with measured potentials.

(2) Do not assume that redox species coexist in equilibrium. Many situations have been documented in which dissolved oxygen coexists with hydrogen sulfide, methane, and ferrous iron.

- The practicality of Eh measurements is limited to iron in acidic mine waters and sulfide in waters under- going sulfate reduction.
- Other redox species are not sufficiently electroactive to establish an equilibrium potential at the surface of the conducting electrode.

(3) A single redox potential cannot be assigned to a disequilibrium system, nor can it be assigned to a water sample without specifying the particular redox species to which it refers. Different redox elements (iron, manganese, sulfur, selenium, arsenic) tend not to reach overall equilibrium in most natural water systems; therefore, a single Eh measurement generally does not represent the system.

6.5.3.B

INTERPRETATION

A rigorous quantitative interpretation of a measurement of Eh requires interactive access to an aqueous speciation code. Exercise caution when interpreting a measured Eh using the Nernst equation. The Nernst equation for the simple half-cell reaction ($M^{I}_{(aq)} = M^{II}_{(aq)} + e$-) is

$$Eh = E^{o} + 2.303RT/nF \log (a^{II}_{M(aq)} / a^{I}_{M(aq)})$$

where:

R = gas constant;
T = temperature, in degrees kelvin;
n = number of electrons in the half-cell reaction;
F = Faraday constant; and
$a^{I}_{M(aq)}$ and $a^{II}_{M(aq)}$ = thermodynamic activities of the free ions $M^{I}_{(aq)}$ and $M^{II}_{(aq)}$ and not simply the analytical concentrations of total M in oxidation states I and II, respectively.

Measurements of Eh are used to test and evaluate geochemical speciation models, particularly for suboxic and anoxic ground-water systems. Eh data can be useful for gaining insights on the evolution of water chemistry and for estimating the equilibrium behavior of multivalent elements relative to pH for an aqueous system. Eh can delineate qualitatively strong redox gradients; for example, those found in stratified lakes and rivers with an anaerobic zone, in an oxidized surface flow that becomes anaerobic after passing through stagnant organic-rich systems, and in mine-drainage discharges.

⇨Section 6.5.4
⇧Return to Section 6.5.2
⇧Return to Contents for 6.5--Reduction Oxidation Potential (Electrode Method)
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 15AUG00 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.5.5.pdf

6.5.5
REPORTING

Report the calculated Eh in mV to two significant figures.

Potentials are reported to the nearest 10 mV, along with the temperature at which the measurement was made, the electrode system employed, and the pH at time of measurement.

⇨Section 6.6 Contents
⇧Return to Section 6.5.4
⇧Return to Contents for 6.5--Reduction Oxidation Potential (Electrode Method
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 01.29.02 imc

USGS science for a changing world

National Field Manual

6.6 Alkalinity and Acid Neutralizing Capacity (2nd Edition, 9/2001)

U.S. Geological Survey, Techniques of Water-Resources Investigations
Book 9, Chapter 6.6
Revised and edited by S.A. Rounds and F.D. Wilde

This report is available as a pdf below.
(The original report, dated 4/98, has been archived.)

CONTENTS

Alkalinity and acid neutralizing capacity
- 6.6.1 Equipment and supplies
  - 6.6.1.A Maintenance, cleaning, and storage
- 6.6.2 Calibration and standardization
- 6.6.3 Collection and processing
  - Surface water
  - Ground water
- 6.6.4 Measurement
  - 6.6.4.A Titration systems and procedures
    - Digital titrator
    - Buret titrator
  - 6.6.4.B Inflection point titration method
  - 6.6.4.C Gran-function plot method
- 6.6.5 Calculations
  - 6.6.5.A Alkalinity or ANC
  - 6.6.5.B Carbonate-speciation equations for samples with pH ≤ 9.2
  - 6.6.5.C Computer-program analysis of titration data
    - PCFF Program
    - Alkalinity Calculator Program
- 6.6.6 Troubleshooting
- 6.6.7 Reporting

Click here for pdf file (380KB)

If you have Adobe Acrobat Reader installed on your computer, you may view and/or print the PDF version of this report. If you do not have Acrobat Reader, you may download it here.

Users with visual disabilities can visit this site for conversion tools and information to help make PDF files accessible.

Next | Field Manual Contents | Table of Contents Chapter 6 | Back

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 14:29:14 Fri 27 Feb 2004
Privacy Statement || Disclaimer || Accessibility
URL: http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6 ALKALINITY AND ACID NEUTRALIZING CAPACITY

TWRI Book 9
(REVISED 9/2001)

Alkalinity and acid neutralizing capacity (ANC) are measures of the ability of a sample to neutralize strong acid. They are determined using identical electrometric procedures involving the acidimetric titration of a sample; the only difference is that the alkalinity sample is filtered, whereas the ANC sample is not filtered (raw, or unfiltered). The terms alkalinity, ANC, and carbonate alkalinity are used in this manual as follows:

- **Alkalinity** is the acid neutralizing capacity of solutes in a water sample, reported in equivalents per liter (or milliequivalents or microequivalents per liter). Alkalinity consists of the sum of titratable carbonate and noncarbonate chemical species in a **filtered water sample** (filter membrane of 0.45-µm pore size or smaller).
- **ANC** is the acid-neutralizing capacity of solutes plus particulates in an **unfiltered water sample**, reported in equivalents per liter (or milliequivalents or microequivalents per liter). ANC is equivalent to alkalinity for samples without titratable particulate matter.
- **Carbonate alkalinity** is the acid-neutralizing capacity attributable to carbonate solutes (bicarbonate and carbonate), reported either in equivalents per liter (or milliequivalents or microequivalents per liter) or in milligrams per liter as a carbonate species, and titrated on a **filtered water sample**. In many aqueous systems, alkalinity is controlled by carbonate chemistry and most commonly is attributable to bicarbonate (HCO_3^-) and less frequently to carbonate (CO_3^{2-}).

Alkalinity: the capacity of solutes in an aqueous system to neutralize acid.

Acid Neutralizing Capacity (ANC): the capacity of solutes plus particulates in an aqueous system to neutralize acid.

Alkalinity is used routinely to check the charge balance of a solution and to gain insights on the evolution of aqueous systems. Alkalinity and ANC provide information on the suitability of water for uses such as irrigation, determining the efficiency of wastewater processes, determining the presence of contamination by anthropogenic wastes, and maintaining ecosystem health.

Any substance in the water sample that reacts with strong acid titrant can contribute to the acid

neutralizing capacity.

- Important noncarbonate contributors may include organic ligands (especially acetate and propionate) as well as hydroxide, silicate, borate, and less commonly ammonia and sulfide (Hem, 1985). When found in unusually high concentrations, phosphate and arsenate also may contribute to the acid neutralizing capacity of the sample (Stumm and Morgan, 1981).
- Except for unusual natural waters and waters substantially affected by human activity, noncarbonate ionized contributors generally are not present in large enough quantities to affect alkalinity or ANC determinations.
- Particulate matter can be an important contributor, and must be removed by filtration before titrating the sample for the alkalinity determination.

Alkalinity is determined on a filtered sample. ANC is determined on an unfiltered sample.

TECHNICAL NOTE: Alkalinity and ANC are measured relative to a solution of carbon dioxide in water; therefore, they are independent of any exchange of carbon dioxide or other common gases between the sample and the atmosphere. However, atmospheric gas exchange can alter the concentrations of individual species, such as bicarbonate. Also, aeration of a sample during filtration can cause mineral precipitation on the filter—this may alter the alkalinity, especially in water systems closed to the atmosphere under ambient conditions.

Section 6.6.1	Field Manual Contents	Table of Contents Chapter 6	Table of Contents Section 6.6

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:39:51 Wed 20 Feb 2002
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6.1 EQUIPMENT AND SUPPLIES

TWRI Book 9
(REVISED 9/2001)

Equipment and supplies for the electrometric method for determining alkalinity and ANC are listed in table 6.6–1. The equipment must be tested before each field trip and cleaned immediately after each use.

Buret, micrometer buret, and digital titrator

The buret provides good accuracy and precision when used by a trained operator.

- Micrometer burets provide better accuracy and precision than burets—they can deliver acid increments to 0.0001 mL and are available commercially (for example, Gilmont® micrometer burets).
- The digital titrator is not as accurate as a buret, but is popular because it is more convenient and less fragile than a buret and keeps the acid in a virtually closed system. Empty titrant cartridges also are available. (The Hach® brand is used as an example in this document.) **Delivery tubes of clear (instead of red) plastic should be used.**

Volumetric pipet, graduated cylinder, and digital balance

The volumetric pipet is used only for dispensing the correct volume of filtered sample. Selection depends on whether the determination is on an alkalinity (filtered) sample or an ANC (unfiltered) sample.

- Use only class A "TD" pipets. TD is a calibration designation meaning "To Deliver" (TD is distinguished from "TC" or "To Contain" pipets).
- Class A pipets should not be used to aspirate or dispense solutions containing suspended particles—the small bore of this pipet tends to reject particles during aspiration and retain them during delivery (C.J. Patton, U.S. Geological Survey, written commun., 1995).

The graduated cylinder and digital balance are used only for measuring the correct volume of unfiltered (ANC) sample. The digital balance yields higher precision than the graduated cylinder.

Table 6.6–1. Equipment and supplies used for alkalinity or ANC titrations[1]
[mL, milliliters; ANC, acid neutralizing capacity; g, gram; µS/cm, microsiemens per centimeter at 25°Celsius; *N*, normal]

Equipment and supplies needed when using either a digital titrator or a buret
✓ pH meter, preferably with automatic temperature compensator (see NFM 6.4 for selection and associated supplies)

- ✓ pH electrode, calibrated, combination or equivalent, and appropriate filling solution, if required
- ✓ *Thermometer, calibrated (see NFM 6.1 for selection and calibration criteria)*
- ✓ Stirrer, magnetic (battery operated)
- ✓ Stirring bars, Teflon® coated, smallest size (always carry spare bars)
- ✓ Volumetric pipets, class A "TD" (for alkalinity)—25 mL, 50 mL, and 100 mL
- ✓ Graduated cylinder (for ANC). For higher precision, use a digital balance, 0.1- g accuracy, 200-g capacity, pocket-sized (available from Acculab, Inc.)
- ✓ Pipet squeeze bulb or pipet pump
- ✓ Sample bottles, 250 mL, acid rinsed or deionized-water rinsed
- ✓ Beakers, glass—50 mL, 100 mL, and 150 mL
- ✓ Beaker, Berzelius, 300 mL, tall form, spoutless, with two- or three-hole stopper
- ✓ Deionized water (DIW) (maximum conductivity of 1 µS/cm)
- ✓ Dispenser bottle, squeeze, for deionized water
- ✓ Filtration unit, in-line capsule or pressure unit with inert gas (for alkalinity)
- ✓ Sodium carbonate (Na_2CO_3) standard solution
- ✓ Safety gloves, glasses, acid spill kit, and apron
- ✓ Paper tissues, disposable, soft and lint free

Additional equipment and supplies needed when using a digital titrator

- ✓ Digital titrator and mounting assembly
- ✓ Delivery tubes, bent-stem, colorless, transparent
- ✓ Titrant solution: sulfuric acid (H_2SO_4) solution, 0.1600*N* and 1.600*N* (empty or prefilled cartridges are available for use with the Hach® system)

Additional equipment and supplies needed when using a buret

- ✓ Calibrated buret, 25-mL capacity with 0.05-mL graduations and Teflon® stop-cock
- ✓ Calibrated buret, 10-mL capacity with 0.02-mL graduations and Teflon® stop-cock
- ✓ Micrometer buret (alternative to standard burets, for greater accuracy)
- ✓ Titrant solution: sulfuric acid solution, 0.01639*N*
- ✓ Buret stand and clamp
- ✓ Wire pen cleaner (for cleaning buret tip)
- ✓ Buret cap
- ✓ Buret meniscus reader
- ✓ Acid bottle, pump (for filling buret)

---

[1]Modify this list to meet the specific needs of the field effort.

Sulfuric acid titrant

Sulfuric acid is the titrant used routinely by the USGS. The normality of sulfuric acid titrant is subject to change with time; proper storage and standardization of the acid titrant is essential.

- 0.1600*N* or 1.600*N* sulfuric acid solutions in prefilled cartridges for the Hach® digital titrator should be obtained by USGS personnel from the USGS Ocala Water Quality & Research Laboratory (OWQRL). The normality of sulfuric acid in these cartridges is tested by the OWQRL prior to distribution. OWQRL calculates and reports any correction factors necessary to compensate for cartridge manufacturing anomalies and/or variations in the reported acid normality. Hach Company, as of January 2001, reports a shelf life of 18 months for these cartridges. Expiration dates are printed on each cartridge.
- 0.01639*N* sulfuric acid solution for the buret system is available from the OWQRL. Alternatively, a sulfuric acid solution of similar normality may be prepared by following the procedure described in section 6.6.2. **Check the normality of this titrant solution each month.**
- Acid solutions of other normality may be needed, depending on the sample chemistry or ionic strength. Prepare the solution under a fume hood. Check the normality monthly.

TECHNICAL NOTE: For samples vulnerable to precipitation reactions, a Berzelius beaker can help minimize gas exchange. Select a size of Berzelius beaker that fits the sample volume and associated titrating equipment and yet minimizes headspace above the sample. Fit the Berzelius beaker with a two- or three-hole stopper to accommodate the electrode(s), the thermometer, and the digital or buret titrator. Another option is to work in a glove box filled with an inert gas atmosphere. Oceanographers use a closed cell with an expanding plunger to avoid gas exchange (Almgren and others, 1977).

CAUTION: Use the safety precautions outlined on the Material Safety Data Sheets (MSDS) when handling chemicals—wear safety glasses, gloves, and protective clothing.

6.6.1.A MAINTENANCE, CLEANING, AND STORAGE

Proper maintenance, cleaning, and storage of the pH instrument are critical for ensuring the accuracy of alkalinity or ANC determinations; guidance is provided in NFM 6.4.

Clean the volumetric pipets, beakers, bottles, burets, and stirring bars with hot water and nonphosphate detergent. Rinse them copiously with tap water followed by deionized water. If oily or chemical residues are difficult to remove, soak the glassware and nonmetal equipment in a mild (5 percent by volume) hydrochloric acid solution (see Horowitz and others, 1994), and repeat the detergent wash. Store cleaned equipment wrapped or bagged in plastic until ready for use.

Reagents must not exceed their shelf life. Store reagents, as appropriate, in a dust-free cabinet, desiccator, or refrigerator. When chemicals to be used for preparation of reagents are received, mark the dates of receipt and expiration on the container. When a reagent is prepared, label the container with the contents, date of preparation, expiration date, and preparer's initials. Store the 0.01639*N* standard sulfuric acid solution and filled Hach® titrant cartridges in a cool, dark place (a

storage cabinet or frost-free refrigerator). Seal the filled cartridges in plastic bags to avoid moisture loss or gain.

Some of the recommended procedures for equipment operation may be out of date if the equipment being used is different from that described or if the equipment incorporates more recent technological advances—follow the manufacturer's instructions.

Next: Section 6.6.2	Field Manual Contents	Table of Contents Chapter 6	Table of Contents Section 6.6	Back to Section 6.6

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:42:10 Wed 20 Feb 2002
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.1.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6.2 CALIBRATION AND STANDARDIZATION

TWRI Book 9
(REVISED 9/2001)

Calibration is required for the pH instrument—follow instructions in NFM 6.4.

Alkalinity and ANC determinations require the use of an acid titrant with a known concentration. **Accurate standardization of the acid titrant is essential.**

- The normality of locally prepared titrant or 0.01639*N* solution obtained from the OWQRL must be tested once per month. The acid is checked against a fresh standard solution of sodium carbonate, as described below.
- Record on field notes any correction factors necessary to compensate for cartridge manufacturing anomalies and/or variations in the stated acid normality for the lot of prefilled cartridges to be used. This information is available from OWQRL for USGS personnel.

CAUTION: When diluting concentrated acids, always add the acid to the water.

Prepare a sulfuric acid titrant solution:

To prepare your own acid titrant for the buret system, follow the procedure below (adapted from Fishman and Friedman, 1989).

1. Cautiously add 0.5 mL concentrated H_2SO_4 (specific gravity 1.84 g/mL) to approximately 950 mL of fresh deionized water (DIW).
2. Mix thoroughly; dilute with DIW to the 1-L mark.

This recipe results in an acid concentration of roughly 0.018*N*. To determine the actual acid concentration, the solution must be standardized—follow the procedure on the next page. If a concentration of exactly 0.01639*N* is desired, the standardized solution may be diluted with DIW and restandardized.

Prepare the standard solution:

To prepare a fresh standard solution of 0.01639*N* sodium carbonate (Na_2CO_3):

1. Dry 1.0 g primary standard Na_2CO_3 at 150 to 160°C for 2 hours.
2. Cool in a desiccator; weigh out 0.8686 g Na_2CO_3; add to a 1-L volumetric flask.
3. Dilute with DIW to the 1-L mark.

Standardize the sulfuric acid:

1. Calibrate the pH system following instructions in NFM 6.4.
2. Pipet 25 mL of sodium carbonate standard solution into a 100-mL beaker, and titrate with the sulfuric acid solution. Record the pH and volume of titrant added, following the procedure in section 6.6.4.A.
3. Determine the equivalence point of the titration using the inflection point method (section 6.6.4.B). The equivalence point is the point at which the change in pH per volume of titrant added is maximized, and generally will be found near pH 4.5.
4. Determine the normality of the acid as follows:

$$C_a = \frac{(25\ mL)\left(\frac{0.8686\ g\ Na_2CO_3}{1.0\ L}\right)\left(\frac{1\ mole\ Na_2CO_3}{105.989\ g\ Na_2CO_3}\right)\left(\frac{2\ eq}{1\ mole\ Na_2CO_3}\right)}{V_a}$$

$$= \frac{(25mL)\left(0.01639\frac{eq}{L}\right)}{V_a},$$

where

C_a is acid normality, in equivalents *(eq)* per liter, and

V_a is volume of sulfuric acid added to reach the equivalence point, in milliliters.

5. Store the solution in a tightly sealed 1-L glass bottle.

Next: Section 6.6.3	Field Manual Contents	Table of Contents Chapter 6	Table of Contents Section 6.6	Back to Section 6.6.1

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:43:39 Wed 20 Feb 2002
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.2.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6.3 COLLECTION AND PROCESSING

TWRI Book 9
(REVISED 9/2001)

Collect and process the samples in a manner that ensures that they represent environmental concentrations at the time of collection. Minimize the effects of wind, rain, cold, dust, and sun on the samples. Collect and (or) process the samples in a chamber to protect them from airborne particulates.

Before collecting or processing the sample, clean the samplers, compositing and splitting devices, sample bottles, measurement vessels, and other equipment that contacts the sample (for detailed procedures refer to NFM Chapters 3 and 4).

- Prerinse the sample bottles with deionized water and store in sealable plastic bags until ready for field sampling (acid-rinsed sample bottles are recommended, especially for samples with low alkalinity or ANC). Field rinse the bottle(s) three times with sample (sample filtrate for alkalinity).
- Do not field rinse the measurement vessels. Volumetric pipets and graduated cylinders should be clean and dry before use.

To collect and process the sample:

1. Filter the samples along with other anion samples, if determining alkalinity. The 0.45-µm flowthrough disposable filter capsule is the standard unit used by the USGS. Record on field forms if a different unit or membrane is used, as this can affect the determination.
2. Fill and securely cap two 250-mL sample bottles (instead of one 500-mL bottle) with the sample (filtrate for alkalinity) to ensure that there is sufficient volume to (a) repeat the titration, (b) preserve the integrity of the second aliquot after the first has been opened, and (c) accommodate any losses from spillage.
3. Prevent agitation of the sample or prolonged exposure to air in order to avoid oxidation of hydrogen sulfide, ferrous iron, and manganous manganese, and to prevent precipitation of mineral phases.

    - Loss of carbon dioxide (CO_2) from the sample will not change the alkalinity or ANC determination, but chemical or physical reactions can cause concentrations of bicarbonate and carbonate to change within minutes.
    - Begin the titration as soon as possible, as there is less chance of chemical precipitation once acidification begins. If the titration is delayed, maintain the samples at the temperature of their ambient environment.
    - If there is a tendency for mineral precipitation, collect and process the sample in an inert gas atmosphere.

Surface water

Collect and process a representative sample according to USGS-approved methods (see NFM 4.1, 5.0, and 5.1).

- The USGS NASQAN and BENCHMARK programs require filtration of alkalinity samples through a 0.45-µm membrane.
- To collect and process samples from anoxic lake or reservoir depth intervals, adapt procedures described for ground water.

Ground water

Collect the sample as close to the source as possible, minimize aeration of the sample, and take the precautions described in step 3 above. See NFM 4.2, 5.0, 5.1, and 5.2 for ground-water sample collection and filtration methods.

- Purge the well (NFM 4.2 and 6.0) and connect the filter unit in-line with the pump.
- Flush and fill the sample lines and filter unit with sample water so as to exclude air.

Next: Section 6.6.4	Field Manual Contents	Table of Contents Chapter 6	Table of Contents Section 6.6	Back to Section 6.6.2

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:44:47 Wed 20 Feb 2002
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.3.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6.3 COLLECTION AND PROCESSING

TWRI Book 9
(REVISED 9/2001)

Collect and process the samples in a manner that ensures that they represent environmental concentrations at the time of collection. Minimize the effects of wind, rain, cold, dust, and sun on the samples. Collect and (or) process the samples in a chamber to protect them from airborne particulates.

Before collecting or processing the sample, clean the samplers, compositing and splitting devices, sample bottles, measurement vessels, and other equipment that contacts the sample (for detailed procedures refer to NFM Chapters 3 and 4).

- Prerinse the sample bottles with deionized water and store in sealable plastic bags until ready for field sampling (acid-rinsed sample bottles are recommended, especially for samples with low alkalinity or ANC). Field rinse the bottle(s) three times with sample (sample filtrate for alkalinity).
- Do not field rinse the measurement vessels. Volumetric pipets and graduated cylinders should be clean and dry before use.

To collect and process the sample:

1. Filter the samples along with other anion samples, if determining alkalinity. The 0.45-µm flowthrough disposable filter capsule is the standard unit used by the USGS. Record on field forms if a different unit or membrane is used, as this can affect the determination.
2. Fill and securely cap two 250-mL sample bottles (instead of one 500-mL bottle) with the sample (filtrate for alkalinity) to ensure that there is sufficient volume to (a) repeat the titration, (b) preserve the integrity of the second aliquot after the first has been opened, and (c) accommodate any losses from spillage.
3. Prevent agitation of the sample or prolonged exposure to air in order to avoid oxidation of hydrogen sulfide, ferrous iron, and manganous manganese, and to prevent precipitation of mineral phases.

    - Loss of carbon dioxide (CO_2) from the sample will not change the alkalinity or ANC determination, but chemical or physical reactions can cause concentrations of bicarbonate and carbonate to change within minutes.
    - Begin the titration as soon as possible, as there is less chance of chemical precipitation once acidification begins. If the titration is delayed, maintain the samples at the temperature of their ambient environment.
    - If there is a tendency for mineral precipitation, collect and process the sample in an inert gas atmosphere.

Surface water

Collect and process a representative sample according to USGS-approved methods (see NFM 4.1, 5.0, and 5.1).

- The USGS NASQAN and BENCHMARK programs require filtration of alkalinity samples through a 0.45-µm membrane.
- To collect and process samples from anoxic lake or reservoir depth intervals, adapt procedures described for ground water.

Ground water

Collect the sample as close to the source as possible, minimize aeration of the sample, and take the precautions described in step 3 above. See NFM 4.2, 5.0, 5.1, and 5.2 for ground-water sample collection and filtration methods.

- Purge the well (NFM 4.2 and 6.0) and connect the filter unit in-line with the pump.
- Flush and fill the sample lines and filter unit with sample water so as to exclude air.

Next: Section 6.6.4	Field Manual Contents	Table of Contents Chapter 6	Table of Contents Section 6.6	Back to Section 6.6.2

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:44:47 Wed 20 Feb 2002
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.3.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6.3 COLLECTION AND PROCESSING

TWRI Book 9
(REVISED 9/2001)

Collect and process the samples in a manner that ensures that they represent environmental concentrations at the time of collection. Minimize the effects of wind, rain, cold, dust, and sun on the samples. Collect and (or) process the samples in a chamber to protect them from airborne particulates.

Before collecting or processing the sample, clean the samplers, compositing and splitting devices, sample bottles, measurement vessels, and other equipment that contacts the sample (for detailed procedures refer to NFM Chapters 3 and 4).

- Prerinse the sample bottles with deionized water and store in sealable plastic bags until ready for field sampling (acid-rinsed sample bottles are recommended, especially for samples with low alkalinity or ANC). Field rinse the bottle(s) three times with sample (sample filtrate for alkalinity).
- Do not field rinse the measurement vessels. Volumetric pipets and graduated cylinders should be clean and dry before use.

To collect and process the sample:

1. Filter the samples along with other anion samples, if determining alkalinity. The 0.45-µm flowthrough disposable filter capsule is the standard unit used by the USGS. Record on field forms if a different unit or membrane is used, as this can affect the determination.
2. Fill and securely cap two 250-mL sample bottles (instead of one 500-mL bottle) with the sample (filtrate for alkalinity) to ensure that there is sufficient volume to (a) repeat the titration, (b) preserve the integrity of the second aliquot after the first has been opened, and (c) accommodate any losses from spillage.
3. Prevent agitation of the sample or prolonged exposure to air in order to avoid oxidation of hydrogen sulfide, ferrous iron, and manganous manganese, and to prevent precipitation of mineral phases.

    - Loss of carbon dioxide (CO_2) from the sample will not change the alkalinity or ANC determination, but chemical or physical reactions can cause concentrations of bicarbonate and carbonate to change within minutes.
    - Begin the titration as soon as possible, as there is less chance of chemical precipitation once acidification begins. If the titration is delayed, maintain the samples at the temperature of their ambient environment.
    - If there is a tendency for mineral precipitation, collect and process the sample in an inert gas atmosphere.

Surface water

Collect and process a representative sample according to USGS-approved methods (see NFM 4.1, 5.0, and 5.1).

- The USGS NASQAN and BENCHMARK programs require filtration of alkalinity samples through a 0.45-µm membrane.
- To collect and process samples from anoxic lake or reservoir depth intervals, adapt procedures described for ground water.

Ground water

Collect the sample as close to the source as possible, minimize aeration of the sample, and take the precautions described in step 3 above. See NFM 4.2, 5.0, 5.1, and 5.2 for ground-water sample collection and filtration methods.

- Purge the well (NFM 4.2 and 6.0) and connect the filter unit in-line with the pump.
- Flush and fill the sample lines and filter unit with sample water so as to exclude air.

Next: Section 6.6.4	Field Manual Contents	Table of Contents Chapter 6	Table of Contents Section 6.6	Back to Section 6.6.2

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:44:47 Wed 20 Feb 2002
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.3.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6.4 MEASUREMENT

TWRI Book 9
(REVISED 9/2001)

Alkalinity, ANC, and concentrations of bicarbonate, carbonate, and hydroxide species are most commonly determined by analyzing acidimetric-titration data with either the inflection point titration method (section 6.6.4.B) or the Gran function plot method (section 6.6.4.C).

- **The Inflection Point Titration (IPT) method** is adequate for most waters and study needs. Difficulty in identifying the inflection points using the IPT method increases as the ratio of organic acids to carbonate species increases, or as the alkalinity decreases.
- **The Gran function plot (Gran) method** is recommended for water in which the alkalinity or ANC is expected to be less than about 0.4 meq/L (20 mg/L as $CaCO_3$), or in which conductivity is less than 100 µS/cm, or if there are appreciable noncarbonate contributors or measurable concentrations of organic acids

The Fixed Endpoint method (titration to pH 4.5) rarely is used and is no longer recommended by the USGS for determining alkalinity values because it is less accurate than the IPT and Gran methods. This decrease in accuracy is evident particularly for low concentrations of total carbonate species and for water with significant organic and other noncarbonate contributors to alkalinity or ANC.

> Titrate a filtered sample if checking the charge balance or if reporting results as carbonate alkalinity.

6.6.4.A TITRATION SYSTEMS AND PROCEDURES

Titration procedures are identical for surface-water and ground-water determinations on filtered or unfiltered aliquots of fresh to saline water samples. Become familiar with the information and detailed instructions for the buret and digital titration systems and the IPT and Gran methods before proceeding with the titration.

Titration System

Select the titration system to be used.

- The digital titration system is convenient but tends to be less precise and less accurate than the buret system because of mechanical inadequacies. Good technique is necessary to produce acceptable results.

- The buret system can be cumbersome and fragile in the field, and requires experience to execute with precision and accuracy.
- A micrometer buret can achieve accuracy to 0.1 mg/L (routine determinations are reported to whole numbers).

The buret system yields better accuracy than the digital titrator.

Sample volume and acid normality

The methods as presented in this manual require electrometric titration of a sample with incremental additions of a strong acid (commonly H_2SO_4) of known normality. Suggested combinations of titrant normality and sample volume for various ranges of alkalinity or ANC values are given in table 6.6–2. These ranges can overlap at the thresholds indicated and should not be interpreted as absolute. Generally, 1.600*N* acid is too strong for most samples and only is used when alkalinity or ANC is greater than 4.0 meq/L (200 mg/L as $CaCO_3$). A more dilute acid (0.01639*N*) commonly is used with the buret system.

Select the size of the delivery and measurement vessels according to the volume of sample needed. Use a volumetric pipet for an alkalinity sample and a graduated cylinder or digital balance for an ANC sample. When selecting the measurement vessel:

- 50 mL of sample in a 100-mL beaker is typical for most routine work.
- Use 100 mL (or more) of sample in a 150-mL (or larger) beaker for samples with low alkalinity or ANC.
- Use 25 mL or less of a sample in a 50-mL beaker for samples with high alkalinity or ANC. Larger volumes of sample may be used in combination with higher normality titrant.

Table 6.6—2. Suggested sample volume and titrant normality for approximate ranges of alkalinity or ANC

[ANC, acid neutralizing capacity as determined on an unfiltered sample; meq/L, milliequivalents per liter; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; mL, milliliter; >, greater than]

ANC or alkalinity (meq/L)	ANC or alkalinity (mg/L as $CaCO_3$)	Sample volume (mL)	Titrant normality
0-1.0	0–50	100 (or larger)	0.1600 (or lower)
1.0-4.0	50-200	50	.1600
4.0-20	200-1,000	100	1.600
>20	>1,000	50	1.600

To achieve greater accuracy, use lower normality titrant, decrease the volume of acid increments, or use a larger sample volume.

To pipet the sample for alkalinity determination:

A small volume of sample will remain in the tip of class A "TD" volumetric pipets—do not blow it out.

1. Suspend the pipet tip vertically in a beaker, touching neither the walls nor the contents of the receiving vessel.
2. Allow the sample to drain freely until the liquid it contains reaches the bottom of the pipet.
3. Touch the pipet tip to the beaker wall until the flow from the pipet stops—leave the tip in contact with the beaker wall for an additional 10 seconds after the flow stops.

Stirring method

When titrating, stirring helps to establish a uniform mixture of sample and titrant, and an equilibrium between sensors and sample. Select a stirring method and use a consistent technique.

- **If using a magnetic stirrer, stir the sample slowly and continuously**, using a small stir bar; avoid creating a vortex and large streaming potentials. If using a digital titrator, keep the delivery tube immersed throughout the procedure but keep the aperture of the tube away from the stir bar to avoid bleeding acid from the tube to the sample between titrant additions.
- If swirling the sample to mix, make the pH measurement as the sample becomes quiescent, after each addition of titrant.
- Avoid splashing the sample out of the beaker or onto the beaker walls. Droplets on the beaker walls can be rinsed down with deionized water. If you splash the sample out of the beaker, you must start over.
- Avoid splashing the sample out of the beaker or onto the beaker walls. Droplets on the beaker walls can be rinsed down with deionized water. If you splash the sample out of the beaker, you must start over.
- Allow sufficient time between titrant additions for the pH value displayed on the instrument to equilibrate. Emphasis should be placed on maintaining a consistent technique (titrant additions every 15 - 30 seconds) rather than waiting for the instrument to "lock on" to a particular pH value.

Titration methods

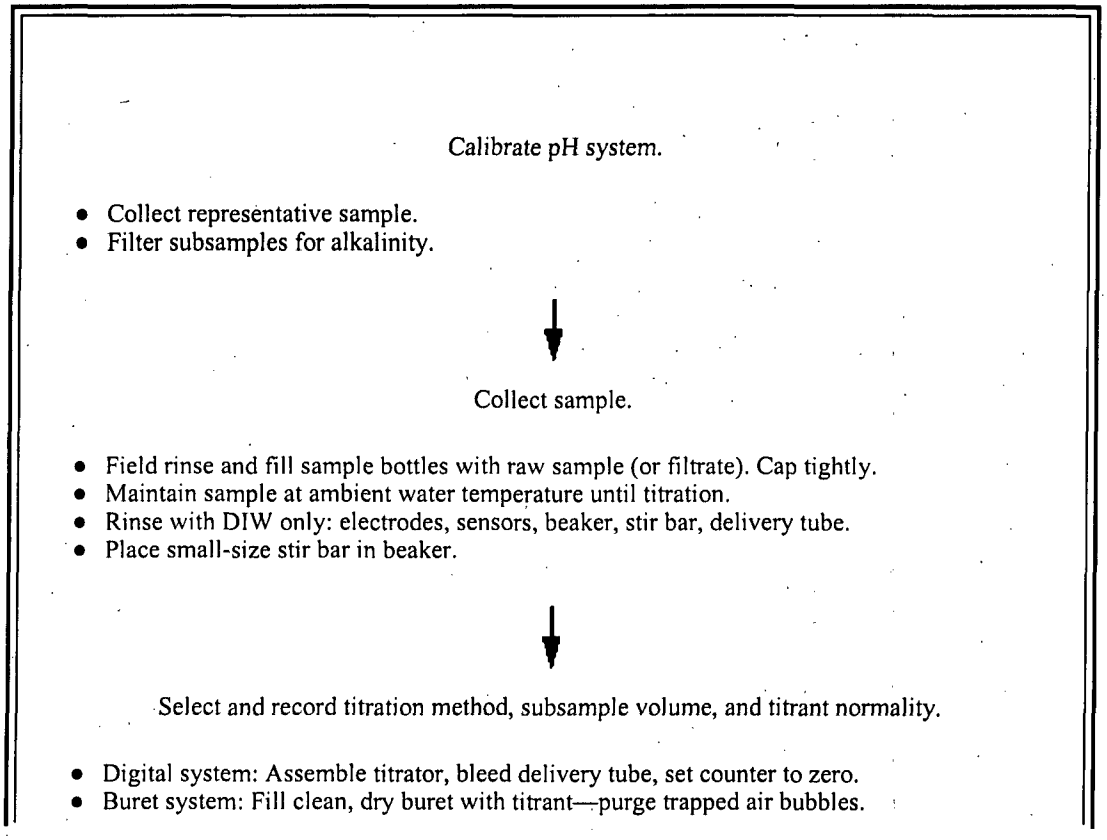
Select and plan your method of titration.

- **IPT method**. Titrate cautiously on both sides of the expected equivalence points (fig. 6.6-1).
  - **If concentrations of contributing carbonate species will be determined and the initial pH is greater than 8.1:** titrate to a pH of about 8.0, carefully using small increments of acid. These data are important in determining the carbonate equivalence point.

- **If concentrations of contributing carbonate species will not be determined:** titrate rapidly at first, adding relatively large acid increments to bring the pH to about 5.5. Do not skip the pH range above 5.5 completely, or you may pass the equivalence point.
- **If a pH is below 5.5:** titrate slowly, using small increments of acid. This region is important in determining the bicarbonate equivalence point. Titrate to a pH of 4.0 or lower (3.5 if the sample alkalinity or ANC range is unknown or if the sample contains high concentrations of noncarbonate contributors, such as organic acids).

Gran method. Collect data between and beyond the expected equivalence points (fig. 6.6-1).

- **If concentrations of contributing carbonate species will be determined:** record titration points throughout the entire pH range of the titration. A good rule of thumb is to collect data along the titration curve roughly every 0.2 to 0.3 pH units. The points on the titration curve that are somewhat removed from the carbonate and bicarbonate equivalence points are used by the Gran method (Pankow, 1991).
- **If concentrations of contributing carbonate species will not be determined:** it is not necessary to develop incremental titration points above a pH of about 5.5.
- **Titrate to a pH of 3.5 or lower** (3.0 or less if the sample alkalinity or ANC range is unknown). A sufficient number of titration points beyond the equivalence point are needed to ensure accuracy.



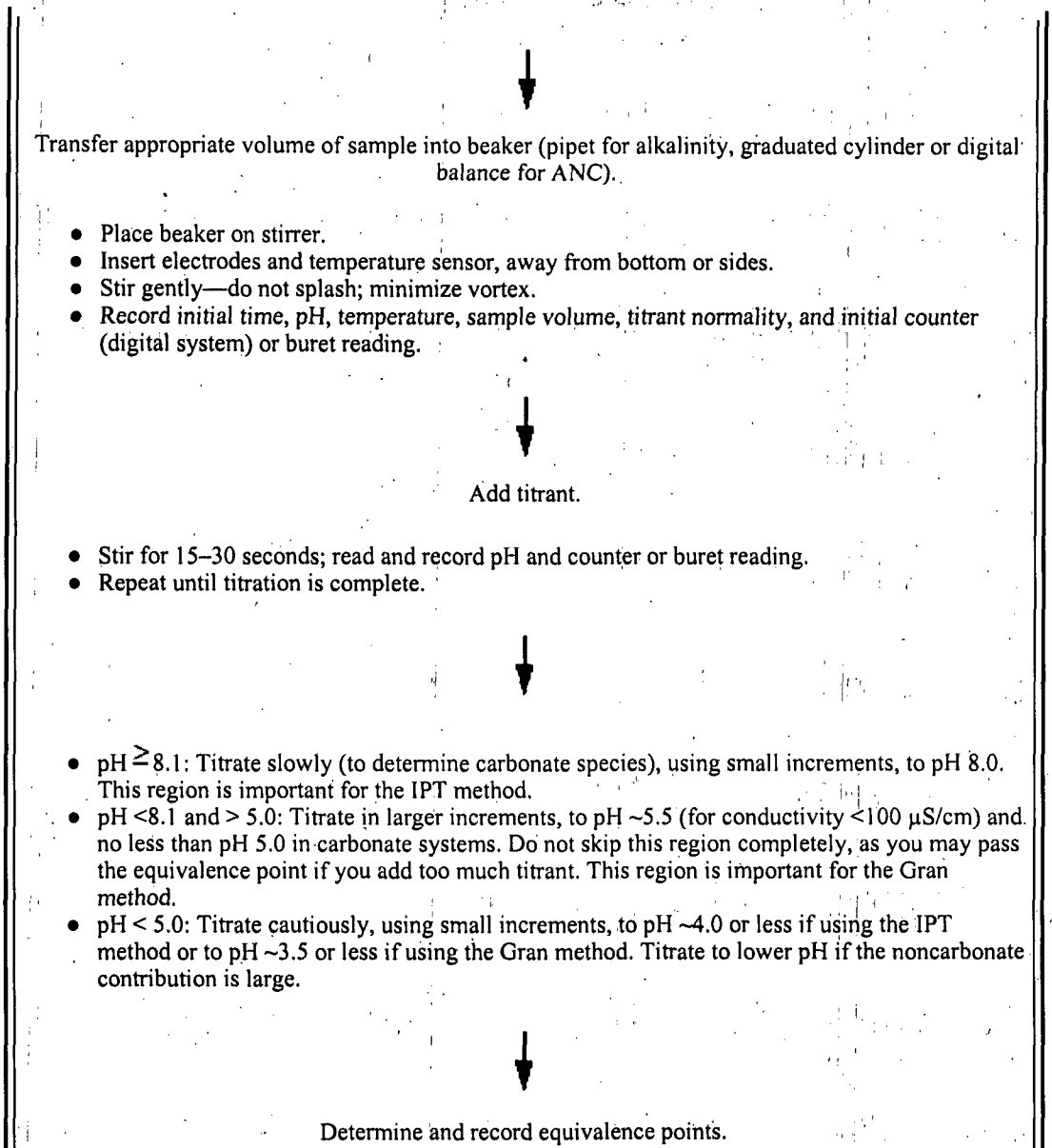


Figure 6.6–1. Summary of alkalinity or ANC titration procedures.

Quality-control (QC) procedures

- Verify your accuracy and ability to reproduce the alkalinity or ANC determinations by using reference samples and repeating the titration periodically on duplicate or triplicate samples. The frequency and distribution of QC determinations are established by study requirements.

Rule of thumb—QC samples should be collected and titrated no less than every tenth sample. The determination on a filtered sample should be reproducible within ±5 percent when titrating a duplicate aliquot from the same batch of sample filtrate.

- For filtered samples with alkalinity less than 0.4 meq/L (20 mg/L as $CaCO_3$), reproducibility should be between 5 and 10 percent.
- If the alkalinity is about 0.02 meq/L or less, differences between duplicate samples are likely to

exceed 10 percent because of rounding errors alone. Such rounding errors may be reduced by using a larger sample volume or a lower normality of titrant.

- **Compare ANC with alkalinity values**—When interferences are absent, titration on an unfiltered sample often results in a determination identical to or within 5 percent of the filtered sample and can be used as the QC check.
  - If filtered and unfiltered values fail the ±5-percent criterion, perform the QC check on the filtered sample.
  - Reproducibility of the ANC determination to within 5 percent on duplicate unfiltered samples can be problematical when the sample has large amounts of particulate matter—extend the quality-assurance criterion to ±10 percent.

To obtain the most accurate results for carbonate species, titrate at the field site without delay.

Digital titrator

Be thoroughly familiar with the operation of the digital titrator before field use. The procedures in this section describe use of the Hach® digital titrator, for which the Hach Company has provided accuracy and precision data. A plunger in the digital titrator forces acid in the titrant cartridge into the delivery tube. The plunger is controlled by a main-drive screw, which in turn is controlled by rotation of the delivery knob. The delivery knob controls the volume of titrant delivered through the delivery tube, as indicated by a digital counter. To minimize errors caused by uncertainty in the volume of titrant dispensed to the sample, titration procedures must account for the accuracy and precision of the titrant-delivery system.

To use the digital titrator:

1. Equilibrate titrant temperature to sample temperature.
2. Assemble the digital titrator.
   - Depress the plunger-release button and retract the plunger.
   - Insert the titrant cartridge into the titrator and twist the cartridge one-quarter turn to lock it into position.
   - Carefully depress the plunger-release button and push the plunger forward until it makes contact with the Teflon® seal inside the cartridge.
3. Remove the vinyl cap from the cartridge (save the cap) and insert the straight end of the delivery tube into the cartridge.
   - Do not push the delivery tube beyond the cartridge tip. Do not alter the delivery tube.
   - Use of a new delivery tube is recommended for each assembly of the titrator. Discard a tube that shows wear.

- If tubes are reused, store them in separate, clean plastic bags after rinsing with DIW. Do not reuse a tube for a different titrant normality.

4. To ensure that no air bubbles or water are in the delivery tube, hold the titrator with the cartridge tip up and turn the delivery knob to force a few drops of titrant through the end of the delivery tube. Rinse tube exterior with DIW and blot acid or water droplets from the tube before inserting it into the sample.
5. Set the digital counter to zero using the counter-reset knob (taking care not to turn the delivery knob).
6. Transfer the selected volume of the sample (pipet for alkalinity, graduated cylinder or digital balance for ANC) to a clean beaker. If a magnetic stirrer is used, place a clean, dry, small stir bar into the beaker before transferring the sample to the beaker. Do not use a magnetic stirrer for sample conductivity <100 µS/cm. Place beaker on stirrer.
7. Rinse the pH and temperature sensors with DIW. Gently blot with lint-free paper any water droplets adhering to the sensors.
8. Insert the sensors into the beaker.
   - Do not let sensors touch the bottom or wall of the beaker.
   - The amount of sample in the beaker must be sufficient to cover the junction of the reference electrode, the electrode bulb, and the temperature sensor.
9. Measure the initial pH and temperature while gently stirring or after gently swirling the sample.
   - Do not splash sample onto the beaker wall or out of the beaker.
   - Minimize the vortex caused by magnetic stirring, and ensure that the stir bar does not hit the pH electrodes.
   - Record on the field form the pH and temperature values, the initial counter reading (it should read "0000"), the titrant normality, the time, and the sample volume.
10. Immerse the end of the titrant delivery tube in the sample. To prevent bleeding of the titrant from the delivery tube, keep the aperture of the delivery tube away from the stir bar.
11. **Begin titration.** If using a magnetic stirrer, stir the sample slowly and continuously. Measure pH after each addition of titrant, and after the acid and sample are mixed homogeneously. If a magnetic stirrer is not used, swirl to mix the sample and acid after each addition of titrant. Allow 15 to 30 seconds after each addition for equilibration, then record the pH and counter readings.
    - **>pH ≥ 8.1**—To determine the carbonate equivalence point using the IPT method, slowly add the titrant in small (but no less than three digital-count) increments until the pH of the sample is less than 8.0. Larger increments can be used for samples containing high carbonate concentrations.
    - **pH < 8.1 and ≥5.0**—If using the IPT method, titrate with larger increments to pH ~5.0 (5.5 for sample alkalinity or ANC <0.4 meq/L (<20 mg/L as $CaCO_3$) or sample conductivity <100 µS/cm). Do not skip this pH region entirely; the equivalence point might be passed if too much acid is added. If using the Gran

method, collect data points every 0.2 to 0.3 pH units in this region.

- **pH < 5.0**—To determine the bicarbonate equivalence point with the IPT method, cautiously add the titrant in small (but no less than three digital-count) increments from pH 5.0 to ≤ 4.0. (The most sensitive part of the titration curve is between pH 4.8 and 4.3 for many natural waters.) If using the Gran method, extend the titration to pH ≤ 3.5 (≤ 3.0 for samples high in organic acids or other noncarbonate contributors, or when the alkalinity or ANC range is unknown). The Gran method relies on these low pH points beyond the equivalence point.

To reduce errors in the delivery of acid titrant, add the acid in minimum increments of three digital counts.

12. After completing the titration, remove the digital titrator from the sample; depress the plunger release, retract the plunger, and remove the titrant cartridge. Immediately replace the vinyl cap on the cartridge tip. Rinse the delivery tube with DIW or discard.
13. Analyze the titration data to determine the carbonate and bicarbonate equivalence points using the IPT method (section 6.6.4.B) and/or the Gran method (section 6.6.4.C).
14. Calculate the sample alkalinity or ANC and the concentrations of the carbonate species from the equivalence points, as described in section 6.6.5.

Buret titrator

When using a buret, exercise caution to ensure that the acid does not evaporate or become contaminated with extrinsic matter or moisture. The titrant temperature should be equilibrated to the sample temperature before use. Always empty the buret after each use. Never reuse the titrant solution; dispose of the solution properly.

To titrate with a buret:

1. Fill a clean, dry buret with sulfuric acid titrant (0.01639*N* or other known concentration).
   - Use a 10-mL semimicroburet with 0.05-mL graduations and a Teflon® stopcock for samples with alkalinity or ANC less than 4 meq/L (200 mg/L as $CaCO_3$).
   - Use a 25-mL buret with 0.1-mL graduations and a Teflon® stopcock for samples with alkalinity or ANC of 4 meq/L (200 mg/L as $CaCO_3$) or greater and when the sample pH exceeds 8.1.
   - If greater accuracy is desired, use a Gilmont®-type micrometer buret.
2. Make sure no air bubbles are trapped in the buret or the buret stopcock. Record on field forms the sulfuric acid normality and initial buret reading.
3. Transfer the selected volume of sample (pipet for alkalinity, graduated cylinder or digital balance for ANC) to a clean beaker. **Do not pipet by mouth.**
   - If a magnetic stirrer is used, place a clean, dry, small stir bar into the beaker before

transferring the sample to the beaker. Place the beaker on a magnetic stirrer.

- Do not use a magnetic stirrer if sample conductivity is <100 µS/cm.

4. Rinse the pH and temperature sensors with DIW. Gently blot water droplets adhering to the sensors with lint-free paper (residual DIW will not affect the determination).
5. Insert the sensors into the beaker.
   - Do not let sensors touch the bottom or wall of the beaker.
   - Sample depth in the beaker must be sufficient to cover the junction of the reference electrode, the electrode bulb, and the temperature sensor.
6. Measure the initial pH and temperature while gently stirring or after gently swirling the sample.
   - Do not splash the sample onto the beaker wall or out of the beaker.
   - Minimize the vortex caused by magnetic stirring, and ensure that the stir bar does not hit the pH electrodes.
   - Record on the field form the pH and temperature values, the initial buret reading, the titrant normality, the time, and the sample volume.
7. **Begin titration.** If using a magnetic stirrer, stir the sample slowly and continuously. Measure pH after each addition of titrant, and after the acid and sample are mixed homogeneously. If a magnetic stirrer is not used, swirl to mix the sample and acid after each addition of titrant. Allow 15 to 30 seconds after each addition for equilibration, then record the pH and buret readings.
   - **>pH ≥8.1**—To determine the carbonate equivalence point using the IPT method, add the titrant drop by drop in 0.01-mL increments until the pH is less than 8.0. Larger increments can be used for samples containing high carbonate concentrations.
   - **>pH < 8.1 and ≥5.0**—If using the IPT method, titrate with larger increments to pH ~5.0 (5.5 for sample with alkalinity or ANC <0.4 meq/L (<20 mg/L as $CaCO_3$) or with sample conductivity <100 µS/cm). Do not skip this pH region entirely; the equivalence point might be passed if too much acid is added. If using the Gran method, collect data points every 0.2 to 0.3 pH units in this region.
   - **>pH < 5.0**—To determine the bicarbonate equivalence point with the IPT method, cautiously add the titrant drop by drop in 0.0 1-mL increments from pH 5.0 to 4.0 or less (the most sensitive part of the titration curve is between pH 4.8 and 4.3 for many natural waters). If using the Gran method, extend the titration to pH 3.5 or less (3.0 or less for samples high in organic acids and other noncarbonate contributors, or when the alkalinity or ANC range is unknown). The Gran method relies on these low pH points beyond the equivalence point.

     TECHNICAL NOTE: 0.01 mL of a standard 0.05-mL drop of titrant tends to remain on the buret tip. To dispense a 0.01-mL titrant drop, quickly rotate the stopcock through 180 degrees (one-half turn) and then rinse the titrant from the buret tip into the beaker with a small quantity of DIW.
8. Analyze the titration data to determine the carbonate and bicarbonate equivalence points using the IPT method (section 6.6.4.B) and/or the Gran method (section 6.6.4.C).

9. Calculate the sample alkalinity or ANC and the concentrations of the carbonate species from the equivalence points, as described in section 6.6.5.

6.6.4.B INFLECTION POINT TITRATION METHOD

The inflection point titration (IPT) method uses the inflection points of the titration curve to determine equivalence points. Whereas for many natural water samples these points are near pH 8.3 and 4.5, it is more accurate to calculate their values from the titration data.

Inflection points are the points of maximum rate of change in pH per volume of titrant added. **Near equivalence points, rapid pH changes occur with small additions of titrant. For this reason, the titration must be performed slowly and cautiously near the expected equivalence points, using small incremental additions of titrant.** The relative error of the determinations can be within ±4 percent if the equivalence point is recognizable within ±0.3 pH unit of the true equivalence point.

To determine the inflection point(s), you can either construct a titration curve by plotting the change in pH divided by the change in titrant volume against the volume of titrant added to the sample, or calculate such values in a table or spreadsheet.

- Graphing the titration curve always is advisable. Such plots are helpful in uncovering typographical errors and spurious maxima that might confuse the detection of the inflection point(s).
- More than one inflection point in close proximity indicates that the true inflection point has been missed. If this occurs, titrate a duplicate sample using smaller acid increments near the inflection point or use a Gran plot. Note that if the acid increments are too small, the location of the inflection points may become masked by noise in the data.
- If the maximum rate of change in pH per volume of titrant occurs at two or more points near an equivalence point (two or more points are "tied" for the maximum value), then determine the location of the equivalence point as the middle of the range where ties were produced. For example, if the maximum rate occurs at digital counts 120, 122, and 126, then the calculated location of the equivalence point is at digital count 123.
- If no clear inflection point(s) can be determined easily, interferences from weak organic acids are likely—use the Gran method.

Example IPT–1A shows the results of an IPT analysis of a typical titration using a digital titrator. Example IPT–1B shows similar results from a buret titration. Both of these titrations have inflection points at both the carbonate and bicarbonate equivalence points. Example IPT–2 uses the IPT method on a sample with low alkalinity; that sample has only one inflection point.

Example IPT–1A: IPT method using the digital titrator

A titration was performed on a natural water sample from the South Diamond Canal inflow to the Donner und Blitzen River, Oregon. The data are plotted in figure 6.6–2 and listed in table 6.6–3. Using the IPT method, the maximum rates of change of pH per volume of titrant added occur at pH 8.27 and 4.50 (at counts 186 and 1014). Because these slopes represent changes between two

points, the actual inflection points are located between counts 183 and 186 for the carbonate equivalence point and between 1011 and 1014 for the bicarbonate equivalence point. Thus, the calculated digital-counter values for the inflection points are 184.5 (185) and 1012.5 (1013). The error in using 1014 rather than 1013 typically is insignificant but the larger the increments used, the greater the error. Calculation of the correct inflection point (Section 6.6.5) results in reduced errors; alkalinity for this ample is calculated at 101.3 mg/L as $CaCo_3$.

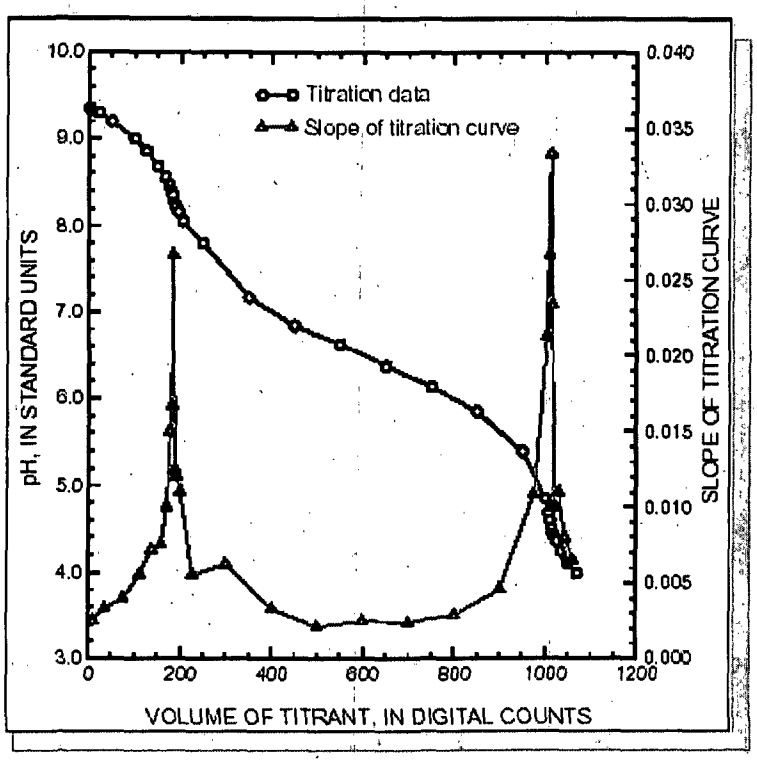


Figure 6.6-2. Plot of data for an inflection point titration using a digital titrator (Example 1PT-1A).

Table 6.6–3. Typical inflection point titration data using a digital titrator (Example IPT–1A)
[—, no data. The shaded rows indicate where the maximum rates of change of pH per digital count occur (at pH 8.27 and 4.50 in this sample)]

pH (standard units)	Change in pH (standard units)	Counter reading (counts)	Change in counter (counts)	Change in pH per change in counter
9.35	—	0	—	—
9.30	0.05	20	20	0.0025
9.20	.10	50	30	.0033
9.00	.20	100	50	.0040
8.86	.14	125	25	.0056
8.68	.18	150	25	.0072
8.56	.12	166	16	.0075
8.46	.10	176	10	.0100
8.40	.06	180	4	.0150
8.35	.05	183	3	.0167
8.27	.08	186	3	.0267

8.22	.05	190	4	.0125
8.16	.06	195	5	.0120
8.05	.11	205	10	.0110
7.80	.25	250	45	.0056
7.17	.63	350	100	.0063
6.84	.33	450	100	.0033
6.63	.21	550	100	.0021
6.38	.25	650	100	.0025
6.14	.24	750	100	.0024
5.85	.29	850	100	.0029
5.39	.46	950	100	.0046
4.85	.54	1000	50	.0108
4.68	.17	1008	8	.0213
4.60	.08	1011	3	.0267
4.50	.10	1014	3	.0333
4.43	.07	1017	3	.0233
4.40	.03	1020	3	.0100
4.35	.05	1025	5	.0100
4.24	.11	1035	10	.0110
4.12	.12	1050	15	.0080
3.99	.13	1070	20	.0065

Example IPT–1B: IPT method using the buret system

If the sample in Example IPT–1A had been titrated with the buret system, the titration data would be similar to that plotted in figure 6.6–3 and given in table 6.6–4. Using the IPT method, the maximum rates of change of pH per volume of titrant added occur at pH 8.27 and 4.50 (at 1.86 and 10.14 mL of acid added). Because these slopes are changes between two points, the actual inflection points are located between 1.83 and 1.86 mL for the carbonate equivalence point, and between 10.11 and 10.14 mL for the bicarbonate equivalence point. The calculated titrant volumes for the inflection points, therefore, are 1.85 and 10.13 mL. The calculated aklalinity (Section 6.6.5) that results is 101.3 mg/L as $CaCo_3$.

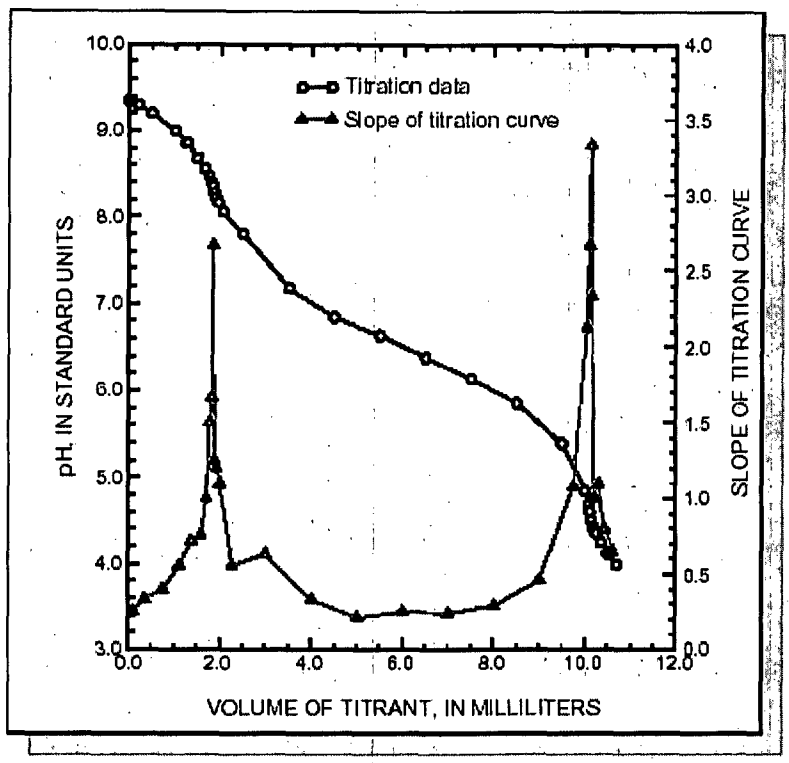


Figure 6.6-3. Plot of data for an inflection point titration using a buret (Example IPT-1B).

Table 6.6-4. Typical inflection point titration data using a buret (Example IPT-1B)
[—, no data. The shaded rows indicate where the maximum rates of change of pH per volume of titrant occur (at pH 8.27 and 4.50 in this sample); mL, milliliter]

pH (standard units)	Change in pH (standard units)	Buret reading (mL)	Titrant volume (mL)	Change in volume (mL)	Change in pH per change in volume
9.35	—	1.20	0.00	—	—
9.30	0.05	1.40	.20	0.20	0.250
9.20	.10	1.70	.50	.30	.333
9.00	.20	2.20	1.00	.50	.400
8.86	.14	2.45	1.25	.25	.560
8.68	.18	2.70	1.50	.25	.720
8.56	.12	2.86	1.66	.16	.750
8.46	.10	2.96	1.76	.10	1.000
8.40	.06	3.00	1.80	.04	1.500
8.35	.05	3.03	1.83	.03	1.667
8.27	.08	3.06	1.86	.03	2.667
8.22	.05	3.10	1.90	.04	1.250
8.16	.06	3.15	1.95	.05	1.200
8.05	.11	3.25	2.05	.10	1.100
7.80	.25	3.70	2.50	.45	.556
7.17	.63	4.70	3.50	1.00	.630
6.84	.33	5.70	4.50	1.00	.330

6.63	.21	6.70	5.50	1.00	.210
6.38	.25	7.70	6.50	1.00	.250
6.14	.24	8.70	7.50	1.00	.240
5.85	.29	9.70	8.50	1.00	.290
5.39	.46	10.70	9.50	1.00	.460
4.85	.54	11.20	10.00	.50	1.080
4.68	.17	11.28	10.08	.08	2.125
4.60	.08	11.31	10.11	.03	2.667
4.50	.10	11.34	10.14	.03	3.333
4.43	.07	11.37	10.17	.03	2.333
4.40	.03	11.40	10.20	.03	1.000
4.35	.05	11.45	10.25	.05	1.000
4.24	.11	11.55	10.35	.10	1.100
4.12	.12	11.70	10.50	.15	.800
3.99	.13	11.90	10.70	.20	.650

Example IPT–2: IPT method for a low alkalinity sample

A water sample collected from Little Abiqua Creek near Scotts Mills, Oregon, provides a good example for a low-alkalinity titration. In this titration, 200 mL of filtered sample were titrated with 0.16*N* titrant and analyzed by the IPT method. The results are shown in figure 6.6–4 and table 6.6–5. The bicarbonate equivalence point was found near a pH of 5.25, between digital counts 134 and 137. The correct digital-counter value at the inflection point, therefore, is 136 (135.5) counts. This results in a calculated alkalinity of 6.8 mg/L as $CaCO_3$.

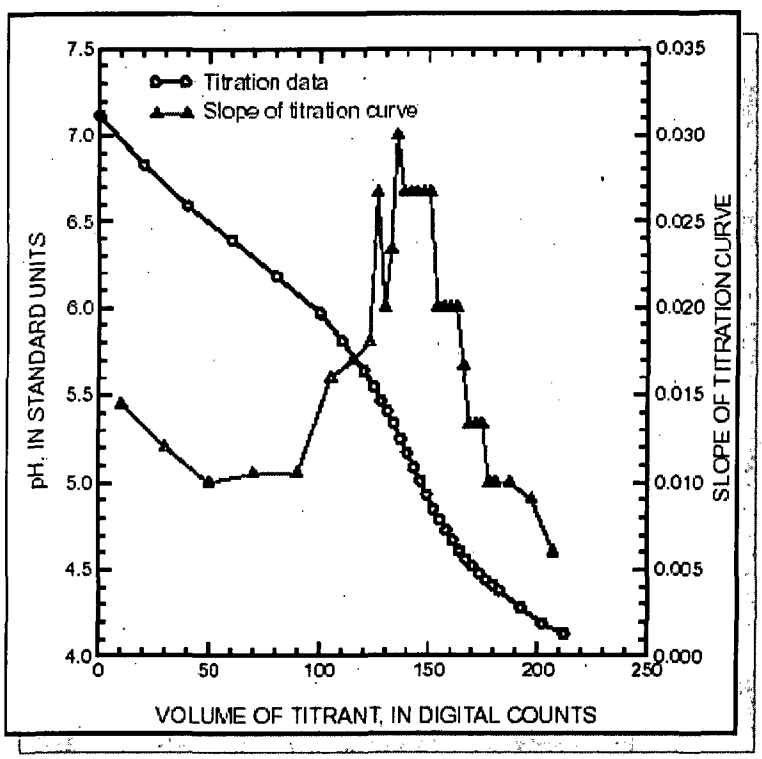


Figure 6.6–4. Plot of data for an inflection point titration of a low-alkalinity sample (Example IPT–2).

Table 6.6-5. Inflection pointanalysis for a low-alkalinity sample (Example IPT-2)
[—, no data. The shaded rows indicate where the maximum rates of change of pH per digital count occurs (at pH5.25 in this sample)]

pH (standard units)	Change in pH (standard units)	Counter reading (counts)	Change in counter (counts)	Change in pH per change in counter
7.12	—	0	—	—
6.83	0.29	20	20	0.0145
6.59	.24	40	20	.0120
6.39	.20	60	20	.0100
6.18	.21	80	20	.0105
5.97	.21	100	20	.0105
5.81	.16	110	10	.0160
5.64	.17	120	10	.0170
5.55	.09	125	5	.0180
5.47	.08	128	3	.0267
5.41	.06	131	3	.0200
5.34	.07	134	3	.0233
5.25	.09	137	3	.0300
5.17	.08	140	3	.0267
5.09	.08	143	3	.0267
5.01	.08	146	3	.0267
4.93	.08	149	3	.0267
4.85	.08	152	3	.0267
4.79	.06	155	3	.0200
4.73	.06	158	3	.0200
4.67	.06	161	3	.0200
4.61	.06	164	3	.0200
4.56	.05	167	3	.0167
4.52	.04	170	3	.0133
4.48	.04	173	3	.0133
4.44	.04	176	3	.0133
4.41	.03	179	3	.0100
4.38	.03	182	3	.0100
4.28	.10	192	10	.0100
4.19	.09	202	10	.0090
4.13	.06	212	10	.0060

6.6.4.C GRAN FUNCTION PLOT METHOD

Gran function plots commonly are used to determine alkalinity and ANC in sea water, low ionic-strength water, water with low carbonate concentrations, and water with measurable concentrations of organic compounds. Gran's method does not rely on the presence of inflection points in the titration curve; therefore, it particularly is useful for waters with low alkalinity.

Using the known chemistry of carbonic acid and some simplifying assumptions, Gran's method

linearizes a set of functions that describe parts of the titration curve (Gran, 1952). The linearizing assumptions used by Gran's method are valid only for data that are some distance away from the equivalence points (Pankow, 1991).

- Collect titration points throughout the entire pH range of the titration. A good rule of thumb is to collect data along the titration curve roughly every 0.2 to 0.3 pH unit.
- Titrate to a pH of 3.5 or lower (3.0 or less if the alkalinity or ANC range is unknown for the waters sampled). A sufficient number of titration points beyond the bicarbonate equivalence point are needed to ensure the accuracy of the calculation.

In contrast to the IPT method, the Gran function plot method uses data that are somewhat removed from the equivalence points.

Gran Functions

During an alkalinity titration (carbonate system), the hydrogen ions added convert carbonate to bicarbonate and then bicarbonate to carbonic acid. The titration continues until no more species are reacting. When this process is complete, additional hydrogen ions will be in excess in the solution. **The F_1 Gran function plot identifies the point at which all alkalinity has been titrated and hydrogen ions begin to be in excess.** Beyond the bicarbonate equivalence point, the shape of the curve is determined by hydrogen ions in excess of all hydrogen ion acceptors in the sample. Similar relations are used with the Gran functions in other parts of the titration curve.

Two Gran functions can be calculated for each equivalence point in the titration. Including the equivalence points for hydroxide, carbonate, and bicarbonate, six Gran functions (F_1 through F_6) are useful for analyzing titration data from natural water samples. The functions for the hydroxide equivalence point, however, commonly are not used. Derivations of these Gran functions are available (Stumm and Morgan, 1981).

For an acidimetric titration, the six Gran functions are where

$$F_1 = (V_o + V_t)\,(10^{-pH}) / \gamma = (V_t - V_s)\,C_a$$

$$F_2 = (V_s - V_t)\,10^{-pH} = (V_t - V_w)K_1'$$

$$F_3 = (V_t - V_w)\,10^{pH} = (V_s - V_t) / K_1'$$

$$F_4 = (V_s - 2V_w + V_t\,10^{pH} = (V_w - V_t) / K_2$$

$$F_5 = (V_w - V_t)\,10^{-pH} = (V_t - V_x)\,K_2'$$

$$F_6 = (V_o + V_t)\,10^{pH} = (V_x - V_t)\,C_a / K_w',$$

where

V_o is initial volume of the sample;

V_t is volume of acid titrant added;

V_s is titrant volume at the bicarbonate equivalence point;

V_w is titrant volume at the carbonate equivalence point;

V_x is titrant volume at the hydroxide equivalence point;

C_a is normality of the acid titrant;

γ is activity coefficient for H^+;

K_1' is first acid dissociation constant for H_2CO_3, corrected for the activity of carbonate species;

K_2' is second acid dissociation constant for H_2CO_3, corrected for theactivity of carbonate species; and

K_w' is acid dissociation constant for water, corrected for the activity of hydroxide.

Note that if these functions are calculated in the correct sequence, the function value on the left side of each equation will consist of known values. By extrapolating these function values to zero, the right side of each equation can be set to zero and can be used to solve for a previously unknown equivalence point.

- The F_1 function, followed by F_2, is the most commonly used Gran function.
- The Gran functions F_1 and F_3 are useful in determining the bicarbonate equivalence point because F_1 and F_3 are zero when $V_t = V_s$. Similarly, F_2 and F_4 are used to determine the carbonate equivalence point ($V_t = V_w$), whereas F_5 and F_6 can be used to determine the hydroxide equivalence point ($V_t = V_x$).

Gran Function Plots

Gran function plots are made by plotting each of the Gran functions against titrant volume and fitting a line through the data points for each function in a particular pH region.

- The F_1 function is valid for the pH range just below the bicarbonate equivalence point. The F_1 data only become linear somewhat beyond the bicarbonate equivalence point; therefore, it is often necessary to titrate the sample down to a pH between 3.5 and 3.0. For systems with measurable concentrations of organic acids, titrate to pH 2.5 (Baedecker and Cozzarelli, 1992).
- Functions F_2 and F_3 are valid in the pH range between the carbonate and bicarbonate endpoints.
- Functions F_4 and F_5 are valid for pH values between the carbonate and hydroxide endpoints.
- Function F_6 is valid for pH values higher than the hydroxide endpoint.

Equivalence points are found by extrapolating each function to where it crosses the x-axis. An idealized Gran analysis would result in a plot such as that shown in figure 6.6–5. The F_1 and F_2 functions are the most commonly used Gran functions.

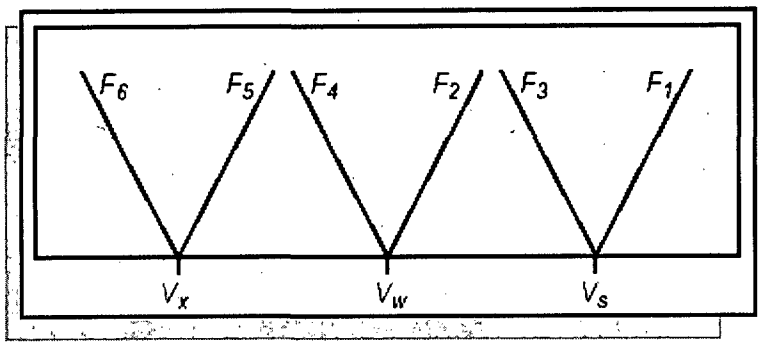


Figure 6.6–5. An idealized Gran function plot, showing six Gran functions.

The F_1 function must be calculated first. In order to calculate F_2, one needs to know the location of the bicarbonate equivalence point, V_s, which is obtained from the solution of F_1.

Similarly, the value of V_w from an analysis of F_2 is necessary to plot and analyze F_3. Function F_4 requires both V_s and V_w from the results of F_2 and either F_1 or F_3. Function F_5 requires a value for V_w from the results of either F_2 or F_4.

TECHNICAL NOTE: The Gran functions also can be used to extract useful information from their fitted slopes, such as the values of *Ca* and the various acid dissociation constants. Further explanation can be found in Stumm and Morgan (1981) and Pankow (1991).

Gran function plots are easy to prepare with a spreadsheet or computer program (see section 6.6.5).

To prepare a Gran function plot:

1. **Bicarbonate equivalence point (Gran function F_1).** Plot $(V_o + V_t)\ 10^{-pH}$ against the titrant volume, V_t. (This formulation ignores activity corrections, setting $\gamma = 1.0$.)
   - When developing this function, V_o and V_t must be in the same units (probably mL).
   - The value of V_t on the x-axis can be in either milliliter or digital counts.
2. Extrapolate a straight line through the data in the region beyond the bicarbonate equivalence point to where it meets the x-axis at $F_1 = (V_o + V_t)\ 10^{-pH} = 0$ or $V_t = V_s$. That point is the bicarbonate equivalence point. See **Example Gran–1** for an illustration of steps 1 and 2.
3. **Carbonate equivalence point (Gran function F_2).** Using the value of V_s from step 2, plot $(V_s - V_t)\ 10^{-pH}$ against the titrant volume, V_t, in the region between the carbonate and bicarbonate equivalence points. Make sure to use the same units for V_t and V_s in developing this function.
4. Extrapolate a straight line through the data in this region to where it meets the x-axis at $F_2 = (V_s - V_t)\ 10^{-pH} = 0$ or $V_t = V_w$. That point is the carbonate equivalence point.

Skip steps 5 and 6 (F_5 and F_6 Gran functions) if the initial sample pH is less than approximately 10.3.

5. **Hydroxide equivalence point (Gran function F_5).** Using the value of V_w from step 4, plot $(V_w - V_t)\ 10^{-pH}$ against the titrant volume, V_t, in the region above the carbonate equivalence point. Use the same units for V_t and V_w in developing this function.
6. Extrapolate a straight line through the data in the region between the carbonate and hydroxide equivalence points to where it meets the x-axis at $F_5 = (V_w - Vt)\ 10^{-pH} = 0$ or $V_t = V_x$. That point is the hydroxide equivalence point.

At this point, you can either stop, or try to verify your values of V_s, V_w and V_x by plotting additional Gran functions. To continue plotting, follow these optional steps:

7. In the region between the carbonate and bicarbonate equivalence points, plot $(V_t - V_w)\ 10^{pH}$ against the titrant volume, V_t. This is a plot of the Gran function F_3.
8. Extrapolate a straight line in this region to where it meets the x-axis at $F_3 = (V_t - V_w)\ 10^{pH} = 0$ or $V_t = V_s$ to get another estimate of the bicarbonate equivalence point.
9. In the region between the carbonate and hydroxide equivalence points, plot $(V_s - 2V_w + V_t)\ 10^{pH}$ against the titrant volume, V_t. This is a plot of the Gran function F_4.
10. Extrapolate a straight line in this region to where it meets the x-axis at $F_4 = (V_s - 2V_w + V_t)\ 10^{pH} = 0$ or $V_t = V_w$ to obtain another estimate of the carbonate equivalence point.
11. In the region above the hydroxide equivalence point, plot $(V_o + V_t)\ 10^{pH}$ against the titrant volume, V_t. This is a plot of the Gran function F_6.
12. Extrapolate a straight line in this region to where it meets the x-axis at $F_6 = (V_o + V_t)\ 10^{pH} = 0$ or $V_t = V_x$ to obtain another estimate of the hydroxide equivalence point.

Depending on the number of points used to develop each of the Gran functions, the equivalence points from each pair of functions (F_1 and F_3, F_2 and F_4, F_5 and F_6) may not be identical.

- If both functions appear to fit the data well and use a sufficient number of points, then average the estimates for that equivalence point.
- If one of the functions (F_3, for example) clearly has a poorer fit to the data or uses far fewer points than does its partner (F_1, in this case), then choose the equivalence point calculated from the other Gran function (F_1). Example Gran-1 illustrates the use of Gran function F_1 while Example Gran-2 illustrates use of Gran functions F_1 through F_4.

Example Gran–1: Gran function plot of F_1 only

Gran function plots are useful for samples with low alkalinity. Using the titration data obtained from a sample of Little Abiqua Creek near Scotts Mills, Oregon (from Example IPT–2), a Gran function plot is easily prepared. The necessary calculations are shown in table 6.6-6. The results are plotted in figure 6.6-6. In the region beyond the equivalence point in figure 6.6-6, a straight line results. Extrapolation of this straight line to $(V_o+V_t)10^{-pH} = 0$ locates the equivalence point. The extrapolated straight line intercept at $(V_o+V_t)\ 10^{-pH} = 0$ on figure 6.6-6 is at 139.5 digital counts of titrant added, corresponding to a bicarbonate equivalence point at a pH of approximately 5.18. The calculated alkalinity by this method is 7.0 mg/L as $CaCO_3$, in excellent agreement with the value of

6.8 mg/L as $CaCO_3$ calculated by the IPT method in Example IPT–2.

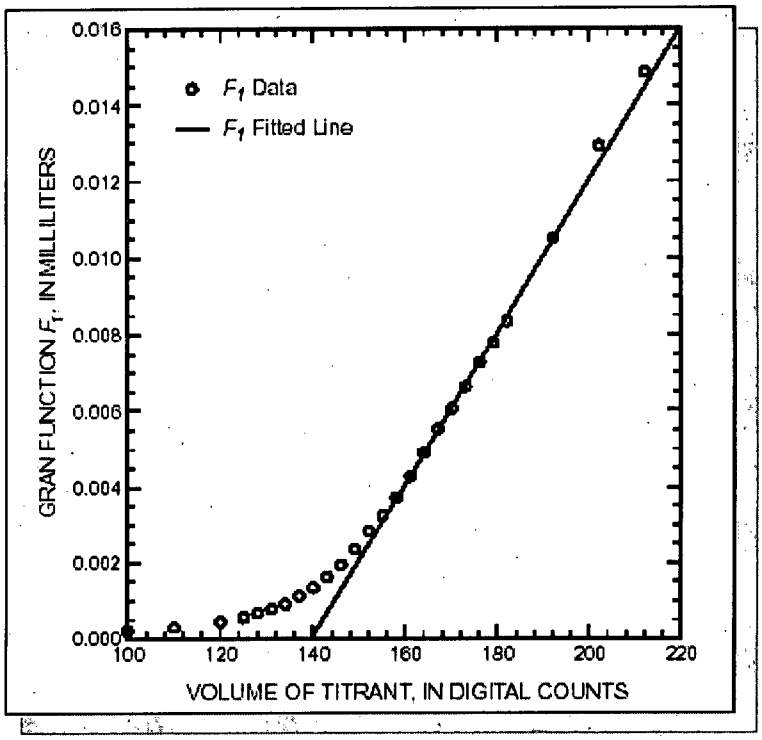


Figure 6.6–6. Example of a Gran function plot using F_1 to determine the bicarbonate equivalence point.

Table 6.6–6. Gran function plot analysis for a low-alkalinity sample—calculation of Gran function F_1 for Example Gran–1.

[V_o, volume of sample; V_t, volume of titrant; mL, milliliters]

pH (standard units)	Counter reading (counts)	Titrant volume, V_t (mL)	V_o+V_t(mL)	10^{-pH}	$(V_o+V_t)10^{-pH}$ (mL)
7.12	0	0.000	200.000	$7.586x10^{-08}$	$1.517x10^{-05}$
6.83	20	.025	200.025	$1.479x10^{-07}$	$2.959x10^{-05}$
6.59	40	.050	200.050	$2.570x10^{-07}$	$5.142x10^{-05}$
6.39	60	.075	200.075	$4.074x10^{-07}$	$8.151x10^{-05}$
6.18	80	.100	200.100	$6.607x10^{-07}$	$1.322x10^{-04}$
5.97	100	.125	200.125	$1.072x10^{-06}$	$2.144x10^{-04}$
5.81	110	.138	200.138	$1.549x10^{-06}$	$3.100x10^{-04}$
5.64	120	.150	200.150	$2.291x10^{-06}$	$4.585x10^{-04}$
5.55	125	.156	200.156	$2.818x10^{-06}$	$5.641x10^{-04}$
5.47	128	.160	200.160	$3.388x10^{-06}$	$6.782x10^{-04}$
5.41	131	.164	200.164	$3.890x10^{-06}$	$7.787x10^{-04}$
5.34	134	.168	200.168	$4.571x10^{-06}$	$9.149x10^{-04}$
5.25	137	.171	200.171	$5.623x10^{-06}$	$1.126x10^{-03}$
5.17	140	.175	200.175	$6.761x10^{-06}$	$1.353x10^{-03}$
5.09	143	.179	200.179	$8.128x10^{-06}$	$1.627x10^{-03}$
5.01	146	.183	200.183	$9.772x10^{-06}$	$1.956x10^{-03}$

4.93	149	.186	200.186	1.175×10^{-05}	2.352×10^{-03}
4.85	152	.190	200.190	1.413×10^{-05}	2.828×10^{-03}
4.79	155	.194	200.194	1.622×10^{-05}	3.247×10^{-03}
4.73	158	.198	200.198	1.862×10^{-05}	3.728×10^{-03}
4.67	161	.201	200.201	2.138×10^{-05}	4.280×10^{-03}
4.61	164	.205	200.205	2.455×10^{-05}	4.914×10^{-03}
4.56	167	.209	200.209	2.754×10^{-05}	5.514×10^{-03}
4.52	170	.213	200.213	3.020×10^{-05}	6.046×10^{-03}
4.48	173	.216	200.216	3.311×10^{-05}	6.630×10^{-03}
4.44	176	.220	200.220	3.631×10^{-05}	7.270×10^{-03}
4.41	179	.224	200.224	3.890×10^{-05}	7.790×10^{-03}
4.38	182	.228	200.228	4.169×10^{-05}	8.347×10^{-03}
4.28	192	.240	200.240	5.248×10^{-05}	1.051×10^{-02}
4.19	202	.253	200.253	6.457×10^{-05}	1.293×10^{-02}
4.13	212	.265	200.265	7.413×10^{-05}	1.485×10^{-02}

Example Gran–2: Gran function plot using F_1 through F_4

In this example, the same titration data that were used in Example IPT–1A in section 6.6.4.B are analyzed using the Gran method. The sample pH (9.35) was not high enough to justify the use of Gran functions F_5 and F_6, so only functions F_1 through F_4 are used.

The results are shown in figure 6.6–7, and indicate a bicarbonate equivalence point at 1005 counts (from F_3, only 2 data points could be used for F_1), and a carbonate equivalence point at about 209 counts (F_2 estimated the equivalence point at 214, F_4 at 204). Although this is not an ideal data set for Gran function analysis (the titration did not extend to pH values lower than about 4.0), the Gran method was able to provide reasonable estimates of the equivalence points.

Using a bicarbonate equivalence point of 1005 counts as determined by the Gran method, an acid titrant normality of 0.16*N*, and a sample volume of 100 mL, the calculated alkalinity of this sample is 100.5 mg/L as $CaCO_3$ (see section 6.6.5). Using an equivalence point of 1013 counts for this sample from the analysis in Example IPT–1A (inflection point method), the calculated alkalinity would be 101.3 mg/L as $CaCO_3$. The agreement between these two methods is very good, producing a discrepancy of less than 1 percent. Results from either method would be reported as 101 mg/L as $CaCO_3$.

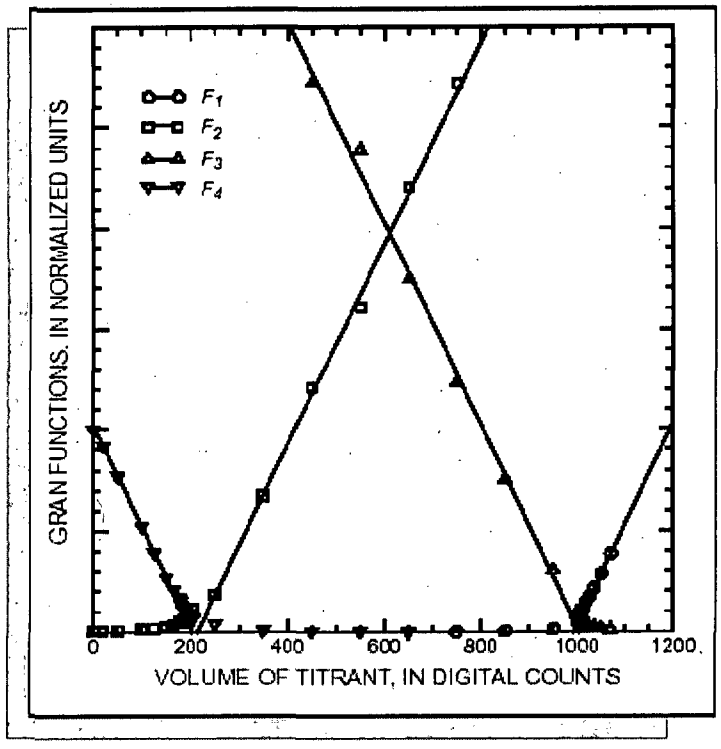


Figure 6.6–7. Example of a Gran function plot using F_1, F_2, F_3, and F_4 to determine carbonate and bicarbonate equivalence points.

Next: Section 6.6.5	Field Manual Contents	Table of Contents Chapter 6	Table of Contents Section 6.6	Back to Section 6.6.3

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:05:21 Fri 19 Apr 2002
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.4.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6.5 CALCULATIONS

TWRI Book 9
(REVISED 9/2001)

Concentrations of alkalinity or ANC and carbonate species can be calculated by hand (sections 6.6.5.A and 6.6.5.B), or by using a computer program (section 6.6.5.C). For hand calculations, first determine the equivalence points using the IPT (section 6.6.4.B) or Gran function (section 6.6.4.C) method. The equations below are valid for buret or digital titration equipment, and any acid concentration and sample volume.

6.6.5.A ALKALINITY OR ANC

Calculation of alkalinity or ANC is a simple accounting of the amount of acid used to neutralize the sample:

$$Alk\left(\frac{meq}{L}\right) = \left[\frac{B\,(mL) \times C_a\left(\frac{meq}{mL}\right) \times CF}{V_s\,(mL) \times \left(\frac{1\,L}{1000\,mL}\right)}\right] = 1000(B)(C_a)(CF)/V_s$$

and

$$Alk\left(\frac{mg}{L}\ as\ CaCO_3\right) = Alk\left(\frac{meq}{L}\right) \times \left(\frac{1\ mmol\ CaCO_3}{2\ meq}\right) \times \left(\frac{100.087\ mg\ CaCO_3}{1\ mmol\ CaCO_3}\right)$$
$$= 50044(B)(C_a)(CF)/V_s$$

where

Alk is alkalinity or ANC of the sample.

B is volume of acid titrant added from the initial pH to the bicarbonate equivalence point (near pH 4.5), in milliliters. To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts).

C_a is concentration of acid titrant, in milliequivalents (***meq***) per milliliter (same as equivalents per liter, or ***N***).

CF is correction factor (see below).

V_s is volume of the sample, in milliliters.

mmol is millimoles of calcium carbonate.

By default, the correction factor CF is equal to 1.0. Hach Company has determined that some digital titrator cartridges cause slightly larger volumes of acid to be delivered than are indicated. USGS personnel can contact the Ocala Water Quality & Research Laboratory (OWQRL) for

correction factors that compensate for this problem for specific cartridge lot numbers.

6.6.5.B CARBONATE-SPECIATION EQUATIONS FOR SAMPLES WITH pH ≤ 9.2

- **To calculate bicarbonate and carbonate species using the equations below, the following assumptions must apply:**
  - Bicarbonate and carbonate are the only species providing significant contributions to alkalinity or ANC. (If the sample contains other titratable species in significant amounts, the calculated bicarbonate and carbonate concentrations will be in error.)
  - he sample pH is ≤ 9.2.
- If sample pH is > 9.2, calculations are more complex and use of the Alkalinity Calculator computer program (section 6.6.5.C) is recommended.
- If the sample contains other titratable species such as ammonia, borate, or silicic acid that contribute significantly to alkalinity or ANC, use of a full geochemical model such as PHREEQC (Parkhurst and Appelo, 1999) is recommended.[2]

TECHNICAL NOTE: The equations provided below for bicarbonate and carbonate only apply for samples with a pH of 9.2 or less because the effects of hydroxide were neglected. The equations remain useful, however, because they still apply to a wide range of natural water samples. The error in using these equations should be less than 10 percent and/or less than 1 mg/L. Speciation equations for samples with a pH greater than 9.2 that account for the presence of hydroxide and the equilibrium chemistry of carbonic acid can be found at http://oregon.usgs.gov/alk/methods.html (refer to the documentation for the Alkalinity Calculator Program, section 6.6.5.C).

[2]A description of such geochemical models is beyond the scope of this manual.

1. Calculate bicarbonate and carbonate species as follows:

Constituent	Formula
Bicarbonate (meq/L)	$1000(B\text{-}2A)(C_a)(CF) / V_s$
Bicarbonate (mg/L as HCO_3^-)	$61017(B\text{-}2A)(C_a)(CF) / V_s$
Carbonate (meq/L)	$2000(A)(C_a)(CF) / V_s$
Carbonate (mg/L as CO_3^{2-})	$60009(A)(C_a)(CF) / V_s$

where

A is volume of acid titrant added from the initial pH to the carbonate equivalence point (near pH 8.3), in milliliters. To convert from digital counts to milliliters, divide by 800 (1.00 mL = 800 counts).

B is volume of acid titrant added from the initial pH to the bicarbonate equivalence point (near pH 4.5), in milliliters. To convert from digital counts to milliliters, divide by 800 (1.00 mL

= 800 counts).

C_a is concentration of acid titrant, in milliequivalents (*meq*) per milliliter (same as equivalents per liter, or *N*).

CF is correction factor (see below).

V_s is volume of the sample, in milliliters.

2. Double-check your calculations.

6.6.5.C COMPUTER-PROGRAM ANALYSIS OF TITRATION DATA

Two USGS computer programs that are available to simplify alkalinity or ANC plotting and calculation tasks include the Personal Computer Field Form (**PCFF**) program and the Web-based **Alkalinity Calculator**. These cover the full range of pH measured in natural waters and are useful for performing the complex calculations needed for samples with pH > 9.2.

PCFF Program

The PCFF program is a Windows-based tool that allows users to enter field-derived sample collection data into standard USGS field forms electronically.

The PCFF can be accessed at the following FTP address: *ftp://hqwiftp.er.usgs.gov/pub/owq/pcff*

- PCFF minimizes the manual input of information, helps eliminate transcription errors, and saves the user time.
- PCFF can perform some common field calculations, such as the analysis of titration data to determine alkalinity or ANC.
- PCFF uses the inflection point titration method (section 6.6.4.B) to find equivalence points in the titration data.

PCFF uses the IPT method to find equivalence points

Alkalinity Calculator Program

The Alkalinity Calculator is a Web-based program that allows users to analyze titration data and determine alkalinity or ANC with several different methods. The current version of the Alkalinity Calculator provides a choice of the following recommended methods:

- The inflection point (IPT) method
- The Gran function plot method

- A theoretical carbonate titration curve method.

The IPT and Gran methods implemented by the Alkalinity Calculator are as described in this manual. The carbonate titration curve method attempts to fit the titration data with a theoretical titration curve derived solely from the chemistry of carbonic acid. This method shows the user whether the chemistry of carbonic acid alone can account for the shape of the entire titration curve. If the fit is poor, it is likely that more than just hydroxide, carbonate, and bicarbonate were titrated in the sample. An excellent fit with this method is evidence that the titration curve is dominated by carbonate and bicarbonate.

The Alkalinity Calculator can be found on the Internet from a link that can be accessed at the following URL: *http://water.usgs.gov/owq/methods.html* or can be accessed directly at the following URL: *http://oregon.usgs.gov/alk*

Methods used by the Alkalinity Calculator are documented at *http://oregon.usgs.gov/alk/methods.html*

The Alkalinity Calculator Program allows the user to choose among the IPT, Gran, and other methods of finding equivalence points.

Next: Section 6.6.6	Field Manual Contents	Table of Contents Chapter 6	Table of Contents Section 6.6	Back to Section 6.6.4

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:57:42 Mon 07 Jun 2004
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.5.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6.6 TROUBLESHOOTING

TWRI Book 9
(REVISED 9/2001)

The major difficulties with equipment used to measure for alkalinity or ANC are the same as for pH measurement—refer to NFM 6.4. Particulate materials, including algae or other biota, can interfere with the stability and reproducibility of pH readings. Such difficulties normally are eliminated by filtering the sample.

When the sample has low ionic strength, or when dissolved organic compounds or noncarbonate inorganic species are present that can interfere with the titration (note color, odor, or previous chemical analysis), the Gran function determination is recommended to avoid some of these problems.

Next: Section 6.6.7	Field Manual Contents	Table of Contents Chapter 6	Table of Contents Section 6.6	Back to Section 6.6.5

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:49:32 Wed 20 Feb 2002
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.6.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS

National Field Manual for the Collection of Water-Quality Data

6.6.7 REPORTING

TWRI Book 9
(REVISED 9/2001)

Report alkalinity and ANC to three significant figures. Only the value from filtered samples is to be published as alkalinity. Titration values from unfiltered samples are to be entered and published as ANC (the current NWIS parameter code dictionary uses the outdated term "alkalinity, unfiltered" instead of ANC).

Alkalinity and ANC should be reported in milliequivalents per liter (or microequivalents per liter), if possible. If this option is not available in the data base, calculate alkalinity and ANC in milligrams per liter, assigning all neutralizing capacity to the carbonate system.

If calculating ANC, alkalinity, bicarbonate, or carbonate in milligram units, then report:

- Less than 1,000 mg/L, to whole numbers;
- 1,000 mg/L and above, to three significant figures.
- Carbonate alkalinity usually is reported in the data base in milligrams per liter as calcium carbonate.

Conversion factors listed below are taken from Hem (1985).

Multiply	By	To obtain
Alkalinity (mg/L as HCO_3^-)	0.8202	Alkalinity (mg/L as $CaCO_3$)
Alkalinity (mg/L as HCO_3^-)	0.4917	Alkalinity (mg/L as CO_3^{2-})
Alkalinity (mg/L as $CaCO_3$)	0.01998	Alkalinity (meq/L)
Bicarbonate (mg/L as HCO_3^-)	0.01639	Bicarbonate (meq/L)
Bicarbonate (mg/L as HCO_3^-)	16.389	Bicarbonate (µeq/L)
Carbonate (mg/L as CO_3^{2-})	0.03333	Carbonate (meq/L)
Hydroxide (mg/L as OH^-)	0.05880	Hydroxide (meq/L)

Report the average value for duplicate samples or the median when more than two replicate samples are used for quality control and the value falls within the appropriate quality-assurance criterion for variability.

Use the correct parameter code to indicate (1) the method of titration or calculation and (2) a filtered or unfiltered sample.

Field Manual | Table of Contents | Table of Contents | Back to Section

Contents | Chapter 6 | Section 6.6 | 6.6.6

U.S. Department of the Interior, U.S. Geological Survey
Maintainer: Publications Team
Last update: 09:50:35 Wed 20 Feb 2002
Privacy Statement || Disclaimer || Accessibility
URL:
http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/html/section6.6.7.htm

FIRSTGOV
Your First Click to the U.S. Government

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Complete pdf for Section 6.7--Turbidity, version 1

National Field Manual

By F.D. Wilde and Jacob Gibs

6.7 TURBIDITY

6.7 Turbidity

6.7.1 Equipment and supplies
6.7.1.A Maintenance, cleaning, and storage

6.7.2 Calibration

6.7.2.A Turbidimeter calibration
6.7.2.B Submersible turbidity sensor calibration
6.7.2.C Spectrophotometer calibration

6.7.3 Measurement

6.7.3.A Turbidimetric determination
6.7.3.B Determination by submersible sensor
6.7.3.C Absorptometric determination

6.7.4 Troubleshooting

6.7.5 Reporting

Illustrations

6.7.1. Example of turbidity calibration graph

6.7-2. Example of parallel setup for turbidimeter with debubbler and flowthrough chamber

TABLES

6.7-1. Equipment and supplies used for measuring turbidity

6.7-2. Measurement range and laboratory test results of selected turbidity instruments

6.7-3. Troubleshooting guide for field turbidity measurement

6.7-4. Guidelines for reporting nephelometric turbidity measurements

---

⇨Section 6.7
⇧Section 6.6.5
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 22June04 imc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.7.pdf

6.7 TURBIDITY

Turbidity: a measure of the collective optical properties of a water sample that cause light to be scattered and absorbed rather than transmitted in straight lines.

Turbidity measures the scattering effect that suspended solids have on light: the higher the intensity of scattered light, the higher the turbidity.[1] Primary contributors to turbidity include clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, plankton, and microscopic organisms (American Public Health Association and others, 1992). The measurement is qualitative and cannot be correlated directly as micrograms per liter of suspended solids.

Determination of turbidity is a common component of water-quality assessments.

- In surface water, the clarity of a natural body of water is used routinely as an indicator of the condition and productivity of the aqueous system.
- In ground water, turbidity commonly is measured during well development and well purging to indicate the extent to which particulates occurring as a result of well installation and sampling activities have been removed.

Turbidity measurements reported for regulatory purposes require a true nephelometric measurement using turbidimeter instruments that meet U.S. Environmental Protection Agency (USEPA) specifications (see 6.7.1).

Turbidity is measured in nephelometric turbidity units (NTU) or Formazin turbidity units (FTU), depending on the method and equipment used. Turbidity measured in NTU uses nephelometric methods that depend on passing specific light of a specific wavelength through the sample. FTU is considered comparable in value to NTU and is the unit of measurement when using absorptometric methods (spectrophotometric equipment). Jackson turbidity unit (JTU) values also approximate NTU but the JTU is no longer in common use. Turbidity values are entered into the USGS National Water Information System (NWIS) database only if the measurement is made in NTU and with instruments that are operated using USEPA-approved methods--not all turbidimeters that display NTU values meet these criteria.

Visible turbidity is found at greater than 5 NTU (Strausberg, 1983). The legal limit of turbidity in drinking water is 0.5 NTU.

Some of the procedures recommended herein for equipment operation may be out of date if the equipment being used is different from that described or incorporates more recent technological advances–follow the manufacturer's instructions.

---

[1]Turbidity measurements have not been systematically researched, tested, compared, or quality assured within the U.S. Geological Survey (USGS). Recommendations in this section were compiled from the references cited, instrument handbooks, field experience, and a limited series of tests on available instruments conducted by the USGS Hydrologic Instrumentation Facility (HIF).

⇨ Section 6.7.1
⇧ Return to Contents for 6.7--Turbidity
⇧ Return to Chapter A6 Contents Page
⇧ Return to Field Manual Complete Contents
⇧ Return to Water Quality Information Pages

Maintainer:
Webversion by: Genevieve Comfort
Last Modified: 22JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.7.1.pdf

6.7.1
EQUIPMENT AND SUPPLIES

Equipment and supplies commonly used for field measurement of turbidity are listed in table 6.7-1. Before field use of water-quality instruments, become familiar with the manufacturer's instructions for calibration, operation, and maintenance. **Test field instruments before use.**

Table 6.7–1. Equipment and supplies used for measuring turbidity[1]

[≤, equal to or less than; µm, micrometer; mL, milliliters; in., inch]

✓ Turbidimeter or spectrophotometer or submersible-sensor instrument (such as a multiparameter instrument with a turbidity sensor).[2]
✓ Turbidity stock solutions and standards:
• Formazin stock suspension, commercially obtained or prepared with hydrazine sulfate and hexamethylenetetramine chemicals.
• Manufacturer-provided secondary standards.
✓ Sample cells (cuvettes), clear colorless glass (supplied from instrument manufacturer).
✓ Debubbler (degassing apparatus, commercially available or self-made).
✓ Inert (dry) gas (for example, nitrogen) and gas delivery apparatus; tanks must be fitted with regulators and filter.
✓ Sample bottle (preferably a bottle that does not sorb suspended material; if the sample will be stored temporarily, use an amber bottle).
✓ Silicon oil, optical grade (with same index of refraction as sample cells; supplied by instrument manufacturer).
✓ Paper tissues, extra lint free.
✓ Turbidity-free water, deionized water filtered through a ≤0.2-µm filter membrane with precision-sized pores.
✓ Bottle to hold turbidity-free water, cleaned and rinsed three times with filtered water.
✓ Volumetric flask, Class A, 100 mL or 500 mL.
✓ Volumetric pipet, Class A, 5.0 mL and pipet filler.
✓ Filter flask, 500 mL; filter holder; filter pump, aspirator.
✓ Rubber stopper, one-hole, No. 7; tubing, 5/16-in. inside diameter.

[1] Modify this list to meet the specific needs of the field effort.
[2] See text for description of USEPA-approved instrumentation.

Turbidity instruments. Three basic types of instrumentation are used to measure turbidity: turbidimeters (nephelometers), spectrophotometers, and multiparameter instruments with submersible

sondes that can accommodate a turbidity sensor (commonly referred to as a turbidity probe). Choice of turbidity instrument depends on site characteristics and intended use of the data in addition to instrument specifications, performance, and reliability.[2]

- If measuring turbidity for regulatory or compliance purposes, the only method approved by the USEPA employs Method 180.1 (STORET NO. 00076) (USEPA, 1979).[3]
- For nonregulatory monitoring purposes, either a submersible sensor that measures turbidity using a near-infrared light source or a spectrophotometer in absorbance mode may be used.

  -- Turbidity probes (submersible sensors) are available for multiparameter instruments with pH, temperature, conductivity, and other sensors; this is convenient for monitoring turbidity along with other field measurements. For ground-water studies, multiparameter instruments are available with sondes that can be used in 2-in. diameter wells.

  -- Field spectrophotometers can be convenient for qualitative turbidity measurements if additional sample properties will be measured spectrophotometrically.

USEPA-approved specifications for turbidity instruments

- The light source should be a tungsten lamp operated at a color temperature between 2,200 to 3,000 Kelvin.
- The maximum distance traversed by incident and scattered light within the sample tube is 10 centimeters.
- The detector and any filter system are to have a spectral peak response between 400 and 600 nanometers.
- The detector should be centered at an angle of 90 degrees to the incident light path and must not exceed ± 30 from 90 degrees.
- Instrument sensitivity should permit detection of a turbidity difference of 0.02 NTU or less in water with less than 1 NTU.

Selected turbidity instruments were tested by the Hydrologic Instrumentation Facility. Referring to table 6.7-2, field tests of the Hach DR 2000™ indicated consistently higher FTU values compared with NTU values measured with the Analite 152™, Hach 2100P™, Hydrolab DataSonde 3™, and YSI 3800™. Not available at the time of testing were either the Hydrolab H20™ or YSI 6000™ multiparameter instruments with turbidity probe or the Analite 156™. Refer to Hydrologic Instrumentation Facility (1994) for test details.

Table 6.7–2. Measurement range and laboratory test results of selected turbidity instruments

[This table is meant to serve as a guide by which study criteria for turbidity instruments can be developed. Instruments listed were tested by the USGS Hydrologic Instrumentation Facility (HIF) unless otherwise noted. Turbidity instruments are being improved and new instruments are in development. NTU, nephelometric turbidity units; <, less than; ±, plus or minus; >, greater than; ~, approximately; %, percent; FTU, Formazin turbidity units; ≤, less than or equal to; YSI, Yellow Springs Instrument Company, Inc.; ISO, International Standards Organization]

Instrument	Measurement range	Percent difference from NTU standards
Hach 2100P™. (Handheld portable tubidimeter; 0.01 NTU resolution.)[1]	<10 to 1,000 NTU	~5%, 20 to 950 NTU
Hach Ratio/XR™. (Flowthrough cell, bench turbidimeter—can be adapted for field with a generator; 0.001 NTU resolution on 0–2 scale.)[1]	0 to 2,000 NTU	<5%, 20 to 950 NTU
Hydrolab DataSonde 3™ (DS-3)[2]. (Multiparameter, submersible instrument with internal logging and electronic communications capabilities.)	0 to 1,000 NTU	<2%, 40 to 950 NTU >10%, 20 NTU
YSI 3800™. (Multiparameter, submersible; 1 NTU resolution.)	0 to 1,000 NTU	≤3%, 40 to 950 NTU > 10%, 20 NTU
YSI 6000™. (Multiparameter, submersible instrument with internal logging and electronic communications capabilities; probe equipped with mechanical wiper.)[2]	0 to 1,000 NTU	Manufacturer specifications (not tested by HIF): ±5% of reading or 2 NTU (whichever is greater)
Analite 152™ and 156™. (Fiber optic portable nephelometer with wand-type sensor, 1-foot long.)[2]	<10 to >30,000 NTU	~5% or less, 400 to 950 NTU
Hach DR2000™. (Spectrophotometer; readings in FTU.)	0 to 450 NTU	5% or less, 20 to 400 NTU

[1]Meets USEPA regulatory specifications for turbidity measurements, has 90-degree hatchure and visible radiation.

[2]Hydrolab DataSonde3™, Analite 152™ and 156™, YSI 6000™ (not tested), and Hydrolab H20™ (not tested) use infrared technology. Instruments that conform to ISO 7027 criteria for backscatter angle of 90 degrees include the YSI 6000™, Hydrolab DS-3™, and Hydrolab H20™.

The method used for sample handling falls into three general categories, as dictated by instrument capabilities: (1) manual (discrete) sample, using a cuvette-based instrument, with sample decanted into a sample cell (cuvette); (2) pumped sample, in which a sample is pumped through a "flowthrough cell," which is a turbidity-sensor-containing cuvette that is an internal part of the instrument; and (3) direct determination, by positioning a turbidity probe either in situ or into a flowthrough chamber that receives pumped sample (see NFM 6.0).

Turbidity-free water. Turbidity-free water is used for preparation of turbidity standards and is prepared by filtering either sample water or deionized water (DIW) through a 0.2-mm or smaller pore-sized membrane. Turbidity-free water is recommended instead of unfiltered DIW for preparation of standards.

Turbidity standards. USEPA (1979) guidelines recommend monthly preparation of the stock turbidity suspension for the calibration standard, and daily preparation of the standard turbidity suspension at the dilutions needed (see Section 6.7.2). Formazin stock solution is available commercially.

Debubbler/degassing system. Bubbles in the sample will give false turbidity readings. A debubbler or degassing system is required if sample contains effervescing gases. The equipment plumbing must be set

up to maintain a constant head, resulting in constant velocity through the turbidimeter's flowthrough cell. When using a turbidity probe within a flowthrough chamber, it might be necessary to direct debubbled water through the chamber.

- Obtain a debubbler from the instrument manufacturer, or construct one as shown on figure 6.7-2 in section 6.7.3.
- Probe-based instruments are available with a wiper mechanism that clears bubbles from the optical surface of the submersible sensor (probe).

Instruments with gas-sweep capacity. Condensation must be removed or reduced throughout turbidity determination. Some flowthrough-cell instruments have the capacity to continuously sweep the sample compartment with dry gas, reducing condensation on the sample cell; otherwise, condensation is to be removed manually every few minutes.

6.7.1.A MAINTENANCE, CLEANING, AND STORAGE

Check manufacturer's instructions for instrument maintenance, cleaning, and storage. **Test equipment before each field trip and record all repairs in the instrument log book.** Manufacturer's instructions and the log book should accompany the instrument at all times.

Turbidity instruments. Protect instruments from extreme temperatures. Shield the instrument LED display panel from direct sunlight. If a bench-top turbidimeter gets wet, allow it to dry thoroughly before the next use (field turbidimeters are constructed to withstand moisture). Check and replace batteries routinely.

Sample cells (cuvettes). Handle and store sample cells in a manner to prevent dirt, scratches, or other damage. Follow instrument manufacturer instructions for the maintenance of sample cells. Keep sample cells scrupulously clean, inside and out. After each use, (1) wash with nonphosphate laboratory detergent, (2) rinse repeatedly with deionized water until all detergent residue is removed, and (3) allow cells to air dry in a dust-free environment.

Submersible turbidity probe. Exercise care that optical surfaces of probes are not scratched during cleaning, operation, or storage. Scratched or damaged probes must be replaced. Keep optical surfaces free of all foreign material by wiping with moist lens-cleaning paper or cloth.

Standard solutions. Discard turbidity standards with elapsed expiration dates. Protect turbidity standards from extreme temperatures. Never pour used standard or a portion of unused standard back into its original (stock) container.

Keep sample cells scrupulously clean and free of scratches.

---

[2]Turbidity instruments are being developed and improved by several companies; investigate instrument performance and reliability before making an equipment selection.

[3]The USEPA also approves the GLI-2 method turbidity instrument system (a microprocessor-based turbidity system using a pulsed-light, four-beam sensor); the GLI-2 provides stable and reproducible turbidity readings to 0.5 NTU but it is not a portable instrument.

⇨Section 6.7.2
⇧Return to Section 6.7
⇧Return to Contents for 6.7--Turbidity
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 22JUNE98 ghc

USGS
science for a changing world

Water Resources--Office of Water Quality

This document is also available in pdf format:

Chapter 6.7.3.pdf

6.7.3 MEASUREMENT

Three methods for field measurement of turbidity are described in this section: the nephelometric method or "turbidimetric determination," using a cuvette-based turbidimeter (6.7.3.A); "determination by submersible sensor" using a multiparameter water-quality instrument with a turbidity probe (6.7.3.B); and the absorptometric determination, using a spectrophotometer (6.7.3.C). Procedures are similar for use of turbidity instruments in surface water and ground water, although some applications may differ, as described below.

- **Turbidity is time sensitive--**Measure sample turbidity on site to avoid biased values that can result from (1) biodegradation, settling, or sorption of particulates in the sample; or (2) precipitation of humic acids and minerals (carbonates and hydroxides, for example) caused by changes in sample pH during transport and holding.
- **Biased or erroneous readings** can result from unmatched cell orientation, colored sample solutions, gas bubbles, condensation, and scratched or dirty sample cells (see Technical Note). Condensation on the sample cell commonly occurs on hot days when humidity is high.

TECHNICAL NOTE: Causes of low-biased readings include particulate settling or sorption on container surfaces, biodegradation, and sample solutions with true color (color from dissolved substances that absorb light--some instruments are designed with optics to eliminate bias from color). High-biased or false turbidity readings can be caused by the presence of condensation and finely-divided air or other gas bubbles in the sample or on the cell or probe surface, and scratches, fingerprints, or dirt on the surface of the sample cell or turbidity probe.

Be sure that sample cells are marked to indicate orientation—match orientation so that cells yield the same value when light passes through.

Surface Water

Collect samples for turbidity measurement or make in situ measurements using either discharge-weighted, pumped-sample, or grab-sample procedures, as appropriate for site characteristics and for study objectives (see NFM 6.0).

- If taking discrete samples from a churn splitter or other sample-compositing device, remove samples for turbidity measurement when the water volume in the compositor is

near maximum.

- Verify the turbidity determination by measuring turbidity on two or more samples, if samples are removed from a compositing device or collected as grab samples from the surface-water body. Collect turbidity sample directly into the cuvette for immediate measurement or into a clean amber glass bottle for short-term storage.
- If turbidity is measured in situ, take three or more sequential turbidity readings, until readings stabilize to within ±10 percent (see NFM 6.0).

Ground Water

Turbidity in ground water generally is less than 5 NTU. Natural ground-water turbidity of up to 19 NTU has been reported for some environmental settings (Nightingale and Bianchi, 1977; Strausberg, 1983; Puls and Powell, 1992). Contaminated ground-water systems, however, can have considerably higher turbidity (Wells and others, 1989; Gschwend and others, 1990; Puls and Powell, 1992; Backhus and others, 1993).

- **During well development**--Monitor turbidity caused by well installation, recording consecutive measurements to document decreases in turbidity as development proceeds.
- **During well purging**--Monitor changes in turbidity by taking sequential readings until purging criteria are met (NFM 6.0). The final stabilized turbidity value should be equal to or less than the value recorded at the end of well development. A decrease in turbidity values during purging indicates mitigation of subsurface disturbance caused by well installation and by deployment of data-collection equipment in the well.
- Report the median of the final five or more sequential measurements that meet the ±10-percent criterion for stability (NFM 6.0).

For discrete-sample measurement using a turbidimeter or spectrophotometer:

- **Pump the ground-water sample** directly from the sample discharge line into a precleaned glass or polyethylene sample-collection bottle.
- **Bailers are not recommended** for collecting turbidity samples, as bailer deployment can cause turbidity.
- Do not collect the discharge passing through the flowthrough chamber in which pH, conductivity, or other field-measurement sensors are installed.

For turbidimeter measurement using a flowthrough cell:

1. Split the sample flow from the well between the turbidimeter and the flowthrough chamber used for other field measurements, as illustrated in figure 6.7-2 (parallel lines are not needed if field measurements are made using a downhole or other in situ method, or when discrete samples are split from a composite). **The turbidimeter requires greater flow velocity than is appropriate for the flowthrough chamber.**
    a. Position the sample-line split to the turbidimeter/debubbler system in front of (closer to the well) the flowthrough chamber to avoid sediment in the flowthrough chamber. (The higher velocity flow required through the turbidimeter can result in mobilizing sediment--see Technical Note.)

b. Set up the debubbler plumbing to maintain a constant head and constant velocity through the turbidimeter's flowthrough cell.

2. To construct a debubbler, use a short length of rigid plastic tubing with one perpendicular tee through which sample enters, another tee at the top end (the atmospheric vent), and hose clamps to secure the tubing. The diameter of the tubing and fittings needed for the debubbler is proportional to the rate at which sample flows through the turbidimeter. Referring to figure 6.7-2:

   - Water entering debubbler at "A" must exit at both "B" and "C."
   - Flow exiting at the top ("C") must be greater than the flow exiting at the bottom ("B").
   - The tubing extending from the debubbler bottom ("B") to the turbidimeter will probably need a smaller diameter than the top tubing to ensure a minimum velocity of 0.46 to 0.61 meters per second (1 1/2 to 2 feet per second).
   - The atmospheric vent should be located at the highest point in the debubbler system to prevent siphoning.

TECHNICAL NOTE: Backpressure must not be allowed in a flowthrough chamber containing pH or dissolved-oxygen sensors, and the line to the flowthrough chamber must be disconnected or bypassed until any appreciable volume of sediment clears from the line. **Water should never discharge from the atmospheric vent.**

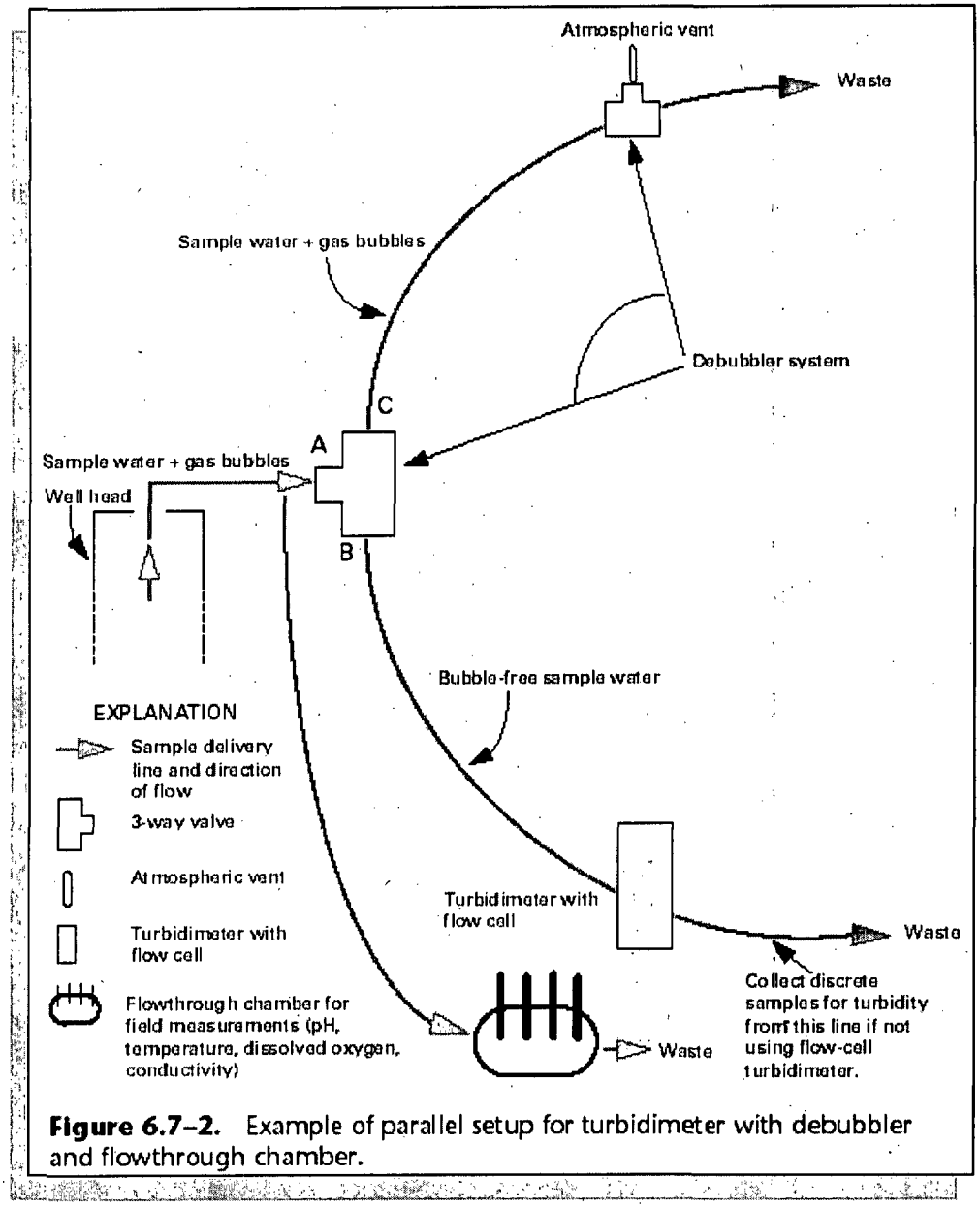


Figure 6.7–2. Example of parallel setup for turbidimeter with debubbler and flowthrough chamber.

6.7.3.A
TURBIDIMETRIC DETERMINATION

The nephelometric method for making turbidimetric determinations that is described in this section requires a photoelectric turbidimeter that meets USEPA specifications.[5] This method is applicable in the range of turbidity from 0 to 40 NTU without dilution, and from about 40 to 1,000 NTU with dilution. The method has been tested for drinking and process water and yields real values in NTU.

Check the turbidimeter against a standard before measuring sample turbidity:

1. Warm up the turbidimeter according to the manufacturer's instructions.

2. Rinse a clean, dry, scratch-free, index-marked cell with the turbidity standard selected at the NTU

within the range of interest.

3. Shake and pour standard into the sample cell to the fill mark and dry the cell exterior with a lint-free cloth.

4. Follow manufacturer's instructions for readout of turbidity value and record the NTU of the standard used and the turbidity value measured in the turbidimeter calibration log.

5. Determine the required reading for the turbidity standard from the calibration curve for the instrument's range and adjust the calibration to the required NTU reading.

6. Measure sample turbidity as soon as sample is collected (see Technical Note).

TECHNICAL NOTE: Turbidity should be measured immediately. However, if temporary storage of samples becomes necessary, collect samples in clean amber glass bottles, keep out of sunlight, and keep chilled at or below 4°C to prevent biodegradation of solids. The holding time must not exceed 24 hours (American Society for Testing and Materials, 1990).

Measurement of sample with turbidity less than 40 NTU:

1. After instrument standardization check, empty the cell of turbidity standard and field rinse a freshly cleaned cell with the sample to be tested. Change gloves.

2. **Measurement of discrete sample** (skip to step 3 for flowthrough cell measurement):

   a. Shake the sample vigorously to completely disperse the solids. Allow air bubbles to disappear before filling sample cell.

   b. Pour the sample into a sample cell to the line marked (to the neck if there is no line). Do not touch cell walls with fingers.

   c. Remove condensation from the cell with a clean, soft, lint-free cloth or tissue. If condensation continues, apply a thin coating of silicon oil on the outside of the cell about every third time the cell is wiped dry of moisture.

   d. Orient the cell with standard in the turbidimeter. Go to step 4.

3. **If using an instrument with an internal flowthrough cell:**

   a. Orient the cell in the cell chamber of the turbidity instrument.

   b. Pump a steady stream of sample in-line from the sample source.

      - Use a constant flow rate through the turbidity instrument.
      - Flow to the turbidimeter must be sufficient to keep particulates suspended (1 1/2 to 2 feet per second).

   c. Check periodically for condensation on flow cell--remove any moisture from cell using soft, lint-free wipe. If necessary, wipe cell walls with two drops of silicon oil and a lint-free

wipe. If available, try a gas sweep of the flowthrough cell compartment using dry nitrogen gas.

- **Make sure that the flow rate of the gas does not exceed the rate recommended by the manufacturer.**
- Filter the gas to remove particulates and moisture--use a filter that includes desiccant (particulates or moisture in the gas stream can cause additional variability in the turbidity readings).
- Eliminate air bubbles in sample before measurement using a debubbler device.

4. Determine the measured NTU value of the sample either by reading turbidity directly from the instrument scale or by using the instrument value and calibration curve, as is appropriate for the instrument being used (see Technical Note).

   a. Record three to five separate readings at regularly spaced intervals.

   b. Report the median of the last three or more sequential values that fall within ±10 percent.

   TECHNICAL NOTE: When using the 0.2-NTU scale only, you may need to subtract a correction factor from the reading to correct for stray light. The Hach Company reports the correction for the 0.2-NTU scale to be on the order of 0.04 NTU for the Hach 2100P™. The stray-light correction is determined by reading turbidity from an empty instrument (without cuvette).

5. **Quality control.**

   a. Repeat discrete sample measurement on two additional samples and check that they fall within the ± 10-percent criterion. Report the value of the first if two samples are measured, or report the median if three or more samples are measured.

   b. Using a clean sample cell, repeat the procedure, substituting turbidity-free water to run a blank. Run the blank either before or after the sample, following manufacturer's instructions.

For measurement of sample with turbidity exceeding 40 NTU:

1. Obtain discrete sample.

2. Dilute the sample with one or more equal volumes of turbidity-free water until turbidity is less than 40 NTU after mixing and degassing.

3. For 100- and 1,000-NTU ranges only--place the cell riser into the cell holder before the sample cell. This decreases the length of the light path in order to improve the linearity of measurements. **Do not use the cell riser for the lower NTU ranges.**

4. Follow procedures for samples with turbidity less than 40 NTU.

5. Based on the dilution factor and original sample volume, compute the turbidity of the original

sample (see 6.7.2, "Calibration for Turbidimeter," steps 11and 12):

a. Add volume of dilution water (in mL) to sample volume (in mL).

b. Multiply by NTU of diluted sample.

c. Divide by the volume of sample (in mL) that was diluted.

EXAMPLE: If 5 volumes of turbidity-free water were added to 1 volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample is computed as 180 units.

Don't forget to adjust the turbidity value of diluted samples using the dilution factor.

6.7.3.B DETERMINATION BY SUBMERSIBLE SENSOR

Determination of turbidity using a multiparameter instrument with submersible sensor-containing sonde is useful for water-quality studies in which the turbidity data will be used qualitatively and not for regulatory or compliance purposes. Turbidity sensors for these instruments utilize an LED with near infrared radiation as the light source and turbidity values normally are reported as NTU. Current instrumentation of this type is not approved by the USEPA.

Multiparameter instruments can be used with a flowthrough chamber, instead of being deployed in situ, for monitoring ground-water field measurements. If measurements will be made in a flowthrough chamber, the turbidity probe is part of the sonde bundle that includes other field-measurement sensors (for example, pH, conductivity, temperature, and dissolved oxygen) and a separate or parallel setup for turbidity measurement (fig. 6.7-2) is not needed.

Multiparameter instruments with internal batteries and memory can be used in surface-water studies that require long-term deployment. Guidelines for long-term instrument deployment falls under the topic of continuous monitors, and is beyond the scope of this chapter--refer to manufacturer's instructions and recommendations and to guidance documents for continuous monitors.

The following procedures apply to in situ determination and to determination of turbidity in a flowthrough chamber:

1. Calibrate the instrument in the laboratory or office before leaving for the field site (see 6.7.2).

2. At the field site, follow procedures for selection of surface-water and ground-water sampling locations and for in situ (Procedure A) or flowthrough-chamber (Procedure B) field measurements, as described in NFM 6.0.

   Procedure A: In situ measurement--Immerse the sonde with turbidity and other field-measurement sensors in the water body.

   Procedure B: Flowthrough chamber--Secure chamber cover over sonde/probe to form an air-tight and water-tight seal. Discharge first sample aliquot to waste, then open connection to

flowthrough chamber and pump sample from water source to flowthrough chamber according to instructions in NFM 6.0.3.

3. Activate instrument to display turbidity values in real time.

4. Agitate the turbidity-containing sonde to remove bubbles from the optical surface: move sonde up and down or in a circular pattern and (or) activate wiper mechanism if available.

5. Monitor turbidity readings as described for other field measurements in NFM 6.0.

   - Allow at least 2 minutes before recording the required number of sequential readings.
   - Stability is reached if values for three (for in situ procedure) to five (for flowthrough-chamber procedure) or more sequential readings, spaced at regular time increments, are within 10 percent.

6. Record turbidity readings on field form and in field notes. Log the reading into instrument memory, if applicable.

7. **Surface-water sites**--Repeat steps 2-5 for in situ measurements (Procedure A) at each vertical to be measured.

8. Before leaving the field site, clean the sonde with a thorough rinse of deionized water and replace sonde in the storage vessel.

9. **Quality control.** Check instrument performance periodically by placing a check standard in the instrument storage vessel and comparing standard value with the reading displayed.

6.7.3.C
ABSORPTOMETRIC DETERMINATION

The absorptometric method described below uses a field spectrophotometer to provide a relative measure of the sample turbidity. The spectrophotometer shoots a beam of light through the sample at a specific wavelength and measures the amount of transmitted light absorbed by solids present in the sample compared to how much of the transmitted light is absorbed by a Formazin standard.

- **This method is not approved by the USEPA.** It is a useful method, for example, if the purpose for the turbidity determination is as an indicator of ambient or "stabilized" conditions during well development or purging.
- Spectrophotometric measurement of turbidity yields readings in FTU. **Do not enter absorptometrically derived turbidity values into the data base.**
- **Turbidity values below 50 FTU--the range of most surface water and ground water--**are inaccurate using this method and the procedure is recommended only as a relative measure of sequential turbidity values.

The absorptometric method for a Hach DR/2000™ portable spectrophotometer is described below, because this is the instrument that currently is in use for most USGS field work. **Check operating instructions if using an instrument of different make, model, or manufacturer--the position on the dial for wavelength of turbidity may vary for different instruments.**

1. Enter the stored program number for turbidity and rotate the wavelength dial until the display indicates the wavelength value in nanometers (nm) for the instrument in use--450 nm for a Hach DR/2000TM, for example.

2. Put on gloves. Measure standards on the instrument that bracket the range anticipated in the sample solution. This step checks the accuracy of the calibration scales. **Change gloves with each change in standard and sample.**

3. Pour 25 mL of deionized water into a clean sample cell for the blank. Hold the cell by the rim--do not touch the cell wall.

4. Place blank sample into cell holder, close the light shield, and press zero. The display should show "wait" and then "0. FTU turbidity."

5. Shake environmental sample vigorously to suspend all solids and allow air bubbles to dissipate.

6. Pour 25 mL of sample into another clean sample cell, holding cell by the rim (top lip).

7. Carefully place sample into cell holder.

   a. Close the light shield. Press read/enter.

   b. The display first will show "wait" and then show the turbidity value in FTU.

   c. Record the FTU reading.

---

[5]The nephelometric method using a calibrated slit turbidimeter is not described--refer to American Society for Testing and Materials (1990).

⇨Section 6.7.4
⇧Return to Section 6.7.2
⇧Return to Contents for 6.7--Turbidity
⇧Return to Chapter A6 Contents Page
⇧Return to Field Manual Complete Contents
⇧Return to Water Quality Information Pages

Maintainer: Office of Water Quality
Webversion by: Genevieve Comfort
Last Modified: 22JUNE98 ghc

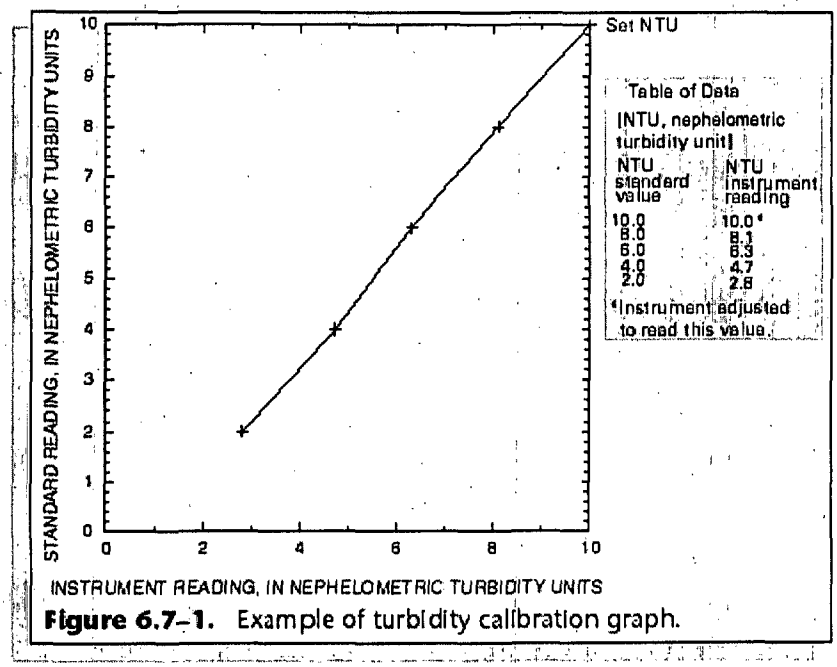


Figure 6.7–1. Example of turbidity calibration graph.

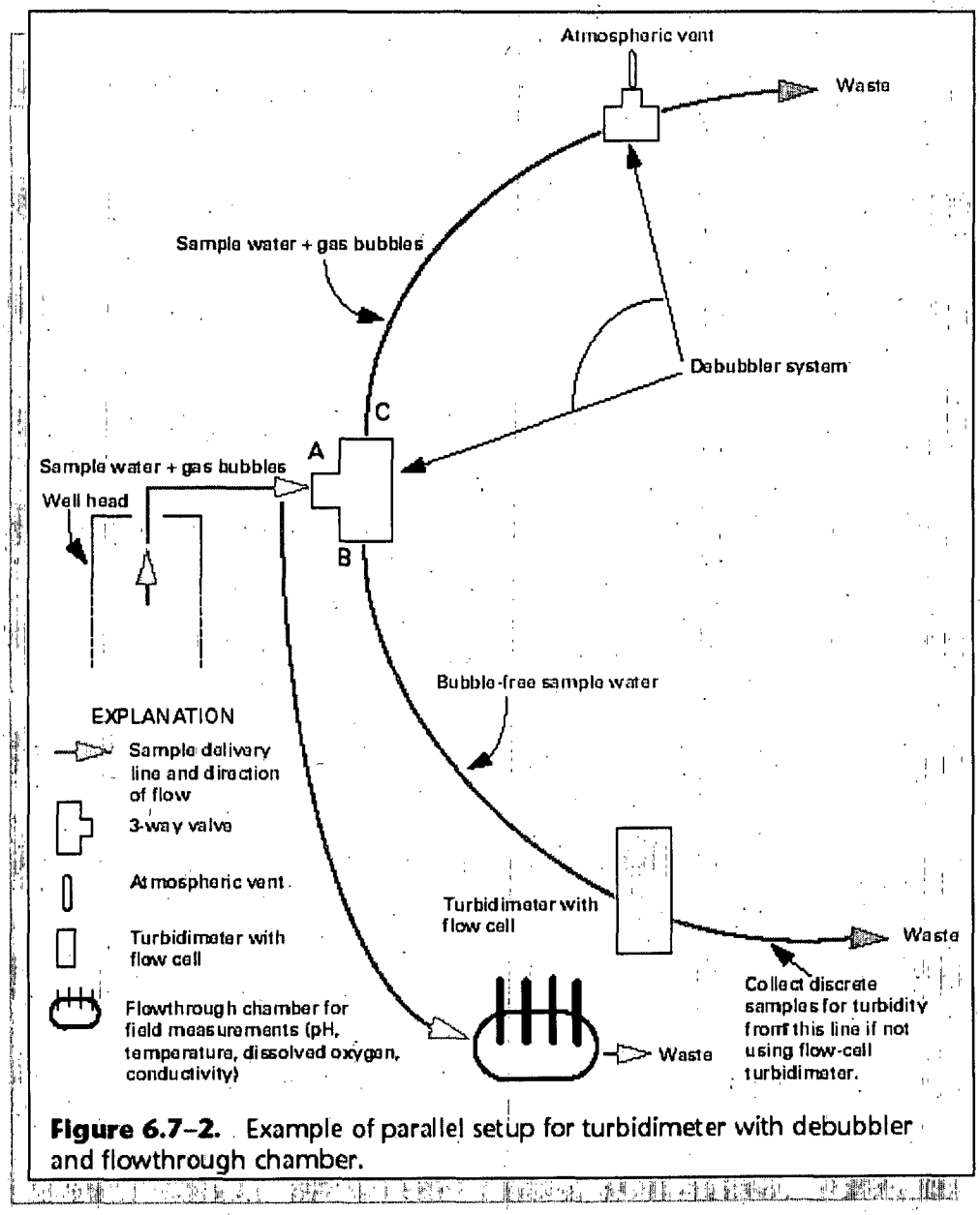


Figure 6.7–2. Example of parallel setup for turbidimeter with debubbler and flowthrough chamber.

Table 6.7–1. Equipment and supplies used for measuring turbidity[1]

[≤, equal to or less than; µm, micrometer; mL, milliliters; in., inch]

- ✓ Turbidimeter or spectrophotometer or submersible-sensor instrument (such as a multiparameter instrument with a turbidity sensor).[2]
- ✓ Turbidity stock solutions and standards:
  - Formazin stock suspension, commercially obtained or prepared with hydrazine sulfate and hexamethylenetetramine chemicals.
  - Manufacturer-provided secondary standards.
- ✓ Sample cells (cuvettes), clear colorless glass (supplied from instrument manufacturer).
- ✓ Debubbler (degassing apparatus, commercially available or self-made).
- ✓ Inert (dry) gas (for example, nitrogen) and gas delivery apparatus; tanks must be fitted with regulators and filter.
- ✓ Sample bottle (preferably a bottle that does not sorb suspended material; if the sample will be stored temporarily, use an amber bottle).
- ✓ Silicon oil, optical grade (with same index of refraction as sample cells; supplied by instrument manufacturer).
- ✓ Paper tissues, extra lint free.
- ✓ Turbidity-free water, deionized water filtered through a ≤ 0.2-µm filter membrane with precision-sized pores.
- ✓ Bottle to hold turbidity-free water, cleaned and rinsed three times with filtered water.
- ✓ Volumetric flask, Class A, 100 mL or 500 mL.
- ✓ Volumetric pipet, Class A, 5.0 mL and pipet filler.
- ✓ Filter flask, 500 mL; filter holder; filter pump, aspirator.
- ✓ Rubber stopper, one-hole, No. 7; tubing, 5/16-in. inside diameter.

[1] Modify this list to meet the specific needs of the field effort.
[2] See text for description of USEPA-approved instrumentation.

Table 6.7–2. Measurement range and laboratory test results of selected turbidity instruments

[This table is meant to serve as a guide by which study criteria for turbidity instruments can be developed. Instruments listed were tested by the USGS Hydrologic Instrumentation Facility (HIF) unless otherwise noted. Turbidity instruments are being improved and new instruments are in development. NTU, nephelometric turbidity units; <, less than; ±, plus or minus; >, greater than; ~, approximately; %, percent; FTU, Formazin turbidity units; ≤, less than or equal to; YSI, Yellow Springs Instrument Company, Inc.; ISO, International Standards Organization]

Instrument	Measurement range	Percent difference from NTU standards
Hach 2100P™. (Handheld portable tubidimeter; 0.01 NTU resolution.)[1]	<10 to 1,000 NTU	~5%, 20 to 950 NTU
Hach Ratio/XR™. (Flowthrough cell, bench turbidimeter—can be adapted for field with a generator; 0.001 NTU resolution on 0–2 scale.)[1]	0 to 2,000 NTU	<5%, 20 to 950 NTU
Hydrolab DataSonde 3™ (DS-3)[2]. (Multiparameter, submersible instrument with internal logging and electronic communications capabilities.)	0 to 1,000 NTU	<2%, 40 to 950 NTU >10%, 20 NTU
YSI 3900™. (Multiparameter, submersible; 1 NTU resolution.)	0 to 1,000 NTU	≤3%, 40 to 950 NTU > 10%, 20 NTU
YSI 6000™. (Multiparameter, submersible instrument with internal logging and electronic communications capabilities; probe equipped with mechanical wiper.)[2]	0 to 1,000 NTU	Manufacturer specifications (not tested by HIF): ±5% of reading or 2 NTU (whichever is greater)
Analite 152™ and 156™. (Fiber optic portable nephelometer with wand-type sensor, 1-foot long.)[2]	<10 to >30,000 NTU	~5% or less, 400 to 950 NTU
Hach DR2000™. (Spectrophotometer; readings in FTU.)	0 to 450 NTU	5% or less, 20 to 400 NTU

[1]Meets USEPA regulatory specifications for turbidity measurements, has 90-degree hatchure and visible radiation.

[2]Hydrolab DataSonde3™, Analite 152™ and 156™, YSI 6000™ (not tested), and Hydrolab H20™ (not tested) use infrared technology. Instruments that conform to ISO 7027 criteria for backscatter angle of 90 degrees include the YSI 6000™, Hydrolab DS-3™, and Hydrolab H20™.

Table 6.7–3. Troubleshooting guide for field turbidity measurement

Symptom	Possible cause and corrective action
Erratic readings	• Check voltage of the batteries: replace weak batteries with new batteries. • Condensation on cell wall: *see fourth symptom.* • Bubbles in sampling system or on optical surface of probe-based system: tap sample line to flowthrough cell or chamber systems to dislodge bubbles; adjust debubbler apparatus; remove bubbles on probe-based system by agitating the unit repeatedly or activating wiper mechanism.
Unusually high or low turbidity	• Bubbles in sampling system or on optical surface of probe-based system: see corrective action for erratic readings (first symptom).
Readings first appear stable, then begin to increase inexplicably	• Check for moisture on cell wall: see fourth symptom.
Moisture or condensation on wall of cell	• Wipe cell dry.[1] • Apply a thin veneer of silicon oil.[2] • Add gas sweep to system.
Blank samples or reference material standards do not read accurately	• Check that the cells are oriented as instructed. • Check accuracy against that of another instrument.

[1] Use soft, lint-free cloth.
[2] Check with instrument manufacturer before applying silicon oil.

Table 6.7–4. Guidelines for reporting nephelometric turbidity measurements (from USEPA, 1990)

NTU	Record to nearest
0–1	0.05
1–10	0.1
10–40	1
40–100	5
100–400	10
400–1,000	50
>1,000	100

U.S. Geological Survey
Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

National Field Manual for the Collection of Water-Quality Data



Chapter A7.

BIOLOGICAL INDICATORS

Third Edition

Edited by D.N. Myers and F.D. Wilde

USGS
science for a changing world

U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, *Secretary*

U.S. GEOLOGICAL SURVEY
Charles G. Groat, *Director*

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

For additional information
write to:
Chief, Office of Water Quality
U.S. Geological Survey
12201 Sunrise Valley Drive
Mail Stop 412
Reston, VA 20192

This report is accessible online at: http://pubs.water.usgs.gov/twri9A/

Foreword

The mission of the Water Resources Discipline of the U.S. Geological Survey (USGS) is to provide the information and understanding needed for wise management of the Nation's water resources. Inherent in this mission is the responsibility to collect data that accurately describe the physical, chemical, and biological attributes of water systems. These data are used for environmental and resource assessments by the USGS, other government agencies and scientific organizations, and the general public. Reliable and quality-assured data are essential to the credibility and impartiality of the water-resources appraisals carried out by the USGS.

The development and use of a *National Field Manual* is necessary to achieve consistency in the scientific methods and procedures used, to document those methods and procedures, and to maintain technical expertise. USGS field personnel use this manual to ensure that the data collected are of the quality required to fulfill our mission.

(signed)

Robert M. Hirsch
Associate Director for Water

Techniques of Water-Resources Investigations

Book 9
Handbooks for Water-Resources Investigations

Chapters of Section A, *National Field Manual for the Collection of Water-Quality Data*

A1. Preparations for Water Sampling

A2. Selection of Equipment for Water Sampling

A3. Cleaning of Equipment for Water Sampling

A4. Collection of Water Samples

A5. Processing of Water Samples

A6. Field Measurements

- 6.0 General Information and Guidelines
- 6.1 Temperature
- 6.2 Dissolved Oxygen
- 6.3 Specific Electrical Conductance
- 6.4 pH
- 6.5 Reduction-Oxidation Potential (Electrode Method)
- 6.6 Alkalinity and Acid Neutralizing Capacity
- 6.7 Turbidity

A7. Biological Indicators

- 7.0 Five-Day Biochemical Oxygen Demand
- 7.1 Fecal Indicator Bacteria
- 7.2 Fecal Indicator Viruses
- 7.3 Protozoan Pathogens

A8. Bottom-Material Samples

A9. Safety in Field Activities

National Field Manual for the Collection of Water-Quality Data



Chapter A7.

BIOLOGICAL INDICATORS

	Page
Abstract	7
Introduction	7
Purpose and scope	8
Requirements and recommendations	9
Field manual review and revision	10
Acknowledgments	11
7.0 Five-day biochemical oxygen demand G.C. Delzer and S.W. McKenzie	BOD-1
7.1 Fecal indicator bacteria D.N. Myers	FIB-1
7.2 Fecal indicator viruses R.N. Bushon	FIV-1
7.3 Protozoan pathogens R.N. Bushon and D.S. Francy	PP-1
Conversion factors, selected terms, symbols, chemical formulas, and abbreviations	CF-1
Selected references and documents	REF-1

Appendix A7-A. Parameter codes used in the National Water Information System (NWIS) of the U.S. Geological Survey..... APP-1

Table 1. Parameter code for 5-day biochemical oxygen demand..... 2
Table 2. Parameter codes for fecal indicator bacteria 2
Table 3. Parameter codes for somatic and F-specific coliphages 3
Table 4. Parameter codes for *Cryptosporidium* and *Giardia* 3

Notes:

The citation for this third edition of chapter A7 of the *National Field Manual* is as follows:

Myers, D.N., and Wilde, F.D., eds., November 2003, Biological indicators (3d ed.): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7, accessed ___ *date*___, from http://pubs.water.usgs.gov/twri9A/.

Citations for chapter sections are listed at the end of the table of contents for each section.



Chapter A7. BIOLOGICAL INDICATORS

Third Edition
Edited by **D.N. Myers and F.D. Wilde**

ABSTRACT

The *National Field Manual for the Collection of Water-Quality Data* (*National Field Manual*) provides guidelines and standard procedures for U.S. Geological Survey (USGS) personnel who collect data used to assess the quality of the Nation's surface-water and ground-water resources. This chapter of the manual includes procedures for the (1) determination of biochemical oxygen demand using a 5-day bioassay test; (2) collection, identification, and enumeration of fecal indicator bacteria; (3) collection of samples and information on two laboratory methods for fecal indicator viruses (coliphages); and (4) collection of samples for protozoan pathogens.

Each chapter of the *National Field Manual* is published separately and revised periodically. Newly published and revised chapters are posted on the World Wide Web on the USGS page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed November 25, 2003).

INTRODUCTION

As part of its mission, the U.S. Geological Survey (USGS) collects the data needed to determine the quality of our Nation's water resources. A high degree of reliability and standardization of these data are paramount to fulfilling this mission. Documentation of nationally accepted methods used by USGS personnel serves to maintain consistency and technical quality in data-collection activities. *The National Field Manual for the Collection of Water-Quality Data*

(National Field Manual) describes protocols (required and recommended procedures) and provides guidelines for USGS personnel who collect those data on surface-water and ground-water resources. Chapter A7 includes procedures for the (1) determination of biochemical oxygen demand using a 5-day bioassay test; (2) collection, identification, and enumeration of fecal indicator bacteria; (3) collection of samples and information on two laboratory methods for fecal indicator viruses (coliphages); and (4) collection of samples for protozoan pathogens. Many of the equipment-sterilization and sample-collection procedures are identical for fecal indicator bacteria, viruses, and protozoans; these nevertheless appear in each section for the convenience of the user.

The *National Field Manual* is Section A of Book 9 of the USGS publication series "Techniques of Water-Resources Investigations" (TWRI) and consists of individually published chapters designed to be used in conjunction with each other. Chapter numbers are preceded by an "A" to indicate that the report is part of the *National Field Manual.* Other chapters of the *National Field Manual* are referred to in the text by the abbreviation "NFM" and the specific chapter number (or chapter and section number). For example, NFM 6 refers to chapter A6 entitled *Field Measurements,* and NFM 6.4 refers to the section in Chapter A6 on field measurement of pH.

PURPOSE AND SCOPE

The *National Field Manual* is targeted specifically toward field personnel in order to (1) establish and communicate scientifically sound methods and procedures, (2) encourage consistency in the use of field methods for the purpose of producing nationally comparable data, (3) provide methods that minimize data bias and, when properly applied, result in data that are reproducible within acceptable limits of variability, and (4) provide citable documentation for USGS water-quality data-collection protocols.

Data collectors must have formal training and field apprenticeship in order to correctly implement the procedures described in this chapter. The *National Field Manual* is meant to complement such training. A description of the determination for ultimate carbonaceous biochemical oxygen demand is beyond the scope of Section 7.0 (Five-Day Biochemical Oxygen Demand), but is provided in Stamer and others (1979, 1983). The information

provided in Section 7.1 (Fecal Indicator Bacteria) and in Section 7.2 (Fecal Indicator Viruses) is to be used in conjunction with *Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples* edited by L.J. Britton and P.E. Greeson (TWRI, Book 5, Chapter A4, 1989), the 20th edition of Standard Methods for the Examination of Water and Wastewater, and with the other chapters of this *National Field Manual* series.

It is impractical to provide guidance that would encompass the entire spectrum of data-collection objectives, site characteristics, environmental conditions, and technological advances related to water-quality studies. The fundamental responsibility of data collectors is to select methods that are compatible with the scientific objective for the field work and to use procedures that are consistent with USGS standard procedures to the extent possible. Whenever a standard procedure is modified or not used, a description of the procedure used and supporting quality-assurance information are to be reported with the data.

REQUIREMENTS AND RECOMMENDATIONS

As used in the *National Field Manual,* the terms **required** and **recommended** have the following USGS-specific meanings.

Required (require, required, or requirements) pertains to USGS protocols and indicates that USGS Office of Water Quality policy has been established on the basis of research and (or) consensus of the technical staff and has been reviewed by water-quality specialists and selected District[1] or other professional personnel, as appropriate. Technical memorandums or other documents that define the policy pertinent to such requirements are referenced in this manual. Personnel are instructed to use required equipment or procedures as described herein. Departure from or modifications to the stipulated requirements that might be necessary to accomplishing specific data-quality requirements or study objectives must be based on referenced research and good field judgment, and be quality assured and documented in permanent and readily accessible records.

[1]"District" refers to an organizational unit of the USGS in any of the States or Territories of the United States.

Recommended (recommend, recommended, recommendation) pertains to USGS protocols and indicates that USGS Office of Water Quality policy recognizes that one or several alternatives to a given procedure or equipment selection are acceptable on the basis of research and (or) consensus. References to technical memorandums and selected publications pertinent to such recommendations are cited in this chapter to the extent that such documents are available. Specific data-quality requirements, study objectives, or other constraints affect the choice of recommended equipment or procedures. Selection from among the recommended alternatives should be based on referenced research and good field judgment, and reasons for the selection must be documented. Departure from or modifications to recommended procedures must be quality assured and documented in permanent and readily accessible records.

FIELD MANUAL REVIEW AND REVISION

This is the third edition of Chapter A7, "Biological Indicators," dated November 2003; this edition updates and expands upon the second edition dated March 2003. As chapters of the *National Field Manual* are reviewed and revised to correct any errors, incorporate technical advances, and address additional topics, dates of revisions appear in the footer of the report. Refer to "Comments and Errata" on the *National Field Manual's* Home page (http://pubs.water.usgs.gov/twri9A/) for each chapter's revision history.

Comments on the *National Field Manual*, and suggestions for updates or revisions, should be sent to nfm-owq@usgs.gov. Newly revised and reissued chapters or chapter sections will be posted on the World Wide Web on the USGS page "National Field Manual for the Collection of Water-Quality Data." The URL for this page is http://pubs.water.usgs.gov/twri9A/ (accessed November 25, 2003). This page also contains a link to the NFM "Comments and Errata" page that chronicles revisions to each chapter.

ACKNOWLEDGMENTS

The information included in this *National Field Manual* is based on existing manuals, a variety of reference documents, and a broad spectrum of colleague expertise. In addition to the references provided, important source materials included unpublished USGS training and field manuals and technical memorandums. The authors wish to acknowledge the work of M.A. Sylvester, who was instrumental in developing the original version of Section 7.1, Fecal Indicator Bacteria.

Technical critique and contributions that improved the section on *Five-Day Biochemical Oxygen Demand* were provided by C.R. Demas, D.N. Myers, G.B. Ozuna, F.A. Rinella, J.K. Stamer, W.E. Webb, and W.G. Wilber.

The authors wish to credit the following colleague reviewers, whose contributions improved the sections on Fecal Indicator Bacteria, Fecal Indicator Viruses, and Protozoan Pathogens: T.A. Abrahamsen, J.V. Davis, E.A. Frick, E.M. Godsy, J.J. Rote, F.W. Schaefer, D.M. Stoeckel, M.A. Sylvester, and M.W. Ware.

Editorial assistance was provided by I.M. Collies, C.M. Eberle, and L.N. Hout; production assistance was provided by G.H. Comfort, M.G. Cooke, and A.M. Weaver; and R.P. Frehs and C.T. Mendelsohn provided illustration assistance.

Special thanks go to T.L. Miller and S.K. Sorenson, whose support of this project continues to be instrumental to its achievement.

This page left blank intentionally.

FIVE-DAY BIOCHEMICAL OXYGEN DEMAND 7.0

by G.C. Delzer and S.W. McKenzie

	Page
7.0 Five-day biochemical oxygen demand	BOD-3
7.0.1 Equipment and supplies	6
7.0.2 Sample collection and storage	9
7.0.3 Five-day test for biochemical oxygen demand	11
7.0.3.A Sample preparation	11
7.0.3.B Interferences	13
7.0.3.C BOD_5 test procedure	14
7.0.4 Calculations	19
7.0.5 Troubleshooting	20
7.0.6 Reporting	21

Illustrations

7.0-1. Biochemical oxygen demand curves: (*A*) typical carbonaceous-demand curve showing the oxidation of organic matter, and (*B*) typical carbonaceous- plus nitrogeneous-demand curve showing the oxidation of ammonia and nitrite 4

7.0-2. Example of a 5-day biochemical oxygen demand worksheet 18

Tables

7.0-1. Equipment, supplies, chemical reagents, and preparation of dilution water and chemical solutions used in the procedure for determination of 5-day biochemical oxygen demand BOD-7

7.0-2. Recommended sample volumes for the 5-day biochemical oxygen demand test 13

7.0-3. Troubleshooting guide for the 5-day biochemical oxygen demand test 20

Notes:

References for section 7.0, Five-day biochemical oxygen demand, are located at the end of Chapter A7 in the "Selected References and Documents" section, which begins on page REF-1.

See Appendix A7-A, Table 1, for information on the parameter code for biochemical oxygen demand that is used in the National Water Information System (NWIS) of the U.S. Geological Survey.

The citation for this section (7.0) of NFM 7 is as follows:

Delzer, G.C., and McKenzie, S.W., November 2003, Five-day biochemical oxygen demand: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7 (3d ed.), section 7.0, accessed ___*date*___, from http://pubs.water.usgs.gov/twri9A/.

FIVE-DAY BIOCHEMICAL OXYGEN DEMAND 7.0

The presence of a sufficient concentration of dissolved oxygen is critical to maintaining the aquatic life and aesthetic quality of streams and lakes. Determining how organic matter affects the concentration of dissolved oxygen (DO) in a stream or lake is integral to water-quality management. The decay of organic matter in water is measured as biochemical or chemical oxygen demand. Oxygen demand is a measure of the amount of oxidizable substances in a water sample that can lower DO concentrations (Nemerow, 1974; Tchobanoglous and Schroeder, 1985).

Biochemical oxygen demand represents the amount of oxygen consumed by bacteria and other microorganisms while they decompose organic matter under aerobic conditions at a specified temperature.

The test for biochemical oxygen demand (BOD) is a bioassay procedure that measures the oxygen consumed by bacteria from the decomposition of organic matter (Sawyer and McCarty, 1978). The change in DO concentration is measured over a given period of time in water samples at a specified temperature. Procedures used to determine DO concentration are described in NFM 6.2. It is important to be familiar with the correct procedures for determining DO concentrations before making BOD measurements. BOD is measured in a laboratory environment, generally at a local or USGS laboratory.

Accurate measurement of BOD requires an accurate determination of DO.

There are two stages of decomposition in the BOD test: a carbonaceous stage and a nitrogenous stage (fig. 7.0-1).

- The carbonaceous stage, or first stage, represents that portion of oxygen demand involved in the conversion of organic carbon to carbon dioxide.
- The nitrogenous stage, or second stage, represents a combined carbonaceous plus nitrogeneous demand, when organic nitrogen, ammonia, and nitrite are converted to nitrate. Nitrogenous oxygen demand generally begins after about 6 days. For some sewage, especially discharge from wastewater treatment plants utilizing biological treatment processes, nitrification can occur in less than 5 days if ammonia, nitrite, and nitrifying bacteria are present. In this case, a chemical compound that prevents nitrification should be added to the sample if the intent is to measure only the carbonaceous demand. The results are reported as carbonaceous BOD (CBOD), or as $CBOD_5$ when a nitrification inhibitor is used.

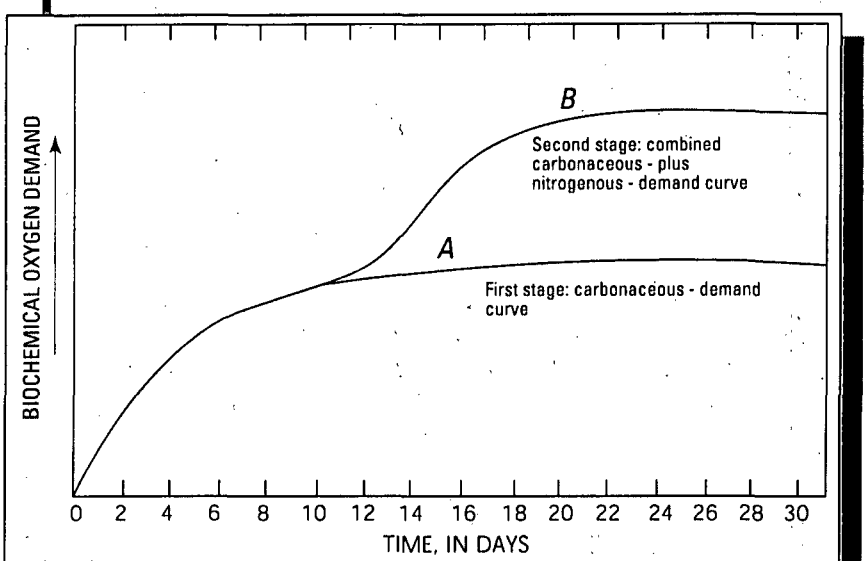


Figure 7.0-1. Biochemical oxygen demand curves: (*A*) typical carbonaceous-demand curve showing the oxidation of organic matter, and (*B*) typical carbonaceous- plus nitrogeneous-demand curve showing the oxidation of ammonia and nitrite. (Modified from Sawyer and McCarty, 1978.)

The standard oxidation (or incubation) test period for BOD is 5 days at 20 degrees Celsius (°C) (BOD_5). The BOD_5 value has been used and reported for many applications, most commonly to indicate the effects of sewage and other organic wastes on dissolved oxygen in surface waters (see TECHNICAL NOTE). The 5-day value, however, represents only a portion of the total biochemical oxygen demand. Twenty days is considered, by convention, adequate time for a complete biochemical oxidation of organic matter in a water sample, but a 20-day test often is impractical when data are needed to address an immediate concern.

- The BOD_5 and $CBOD_5$ tests have limited value by themselves in the assessment of stream pollution and do not provide all of the relevant information to satisfy every study objective (Nemerow, 1974; Stamer and others, 1983; Veltz, 1984). Additional analyses of water samples for chemical oxygen demand, fecal bacteria, and nutrients can aid in the interpretation of BOD_5.
- An ultimate carbonaceous BOD ($CBOD_u$) test is needed to obtain additional BOD information, and can be used for modeling DO regimes in rivers and estuaries (Hines and others, 1978; Stamer and others, 1983). Guidelines for the $CBOD_u$ determination are described in Stamer and others (1979, 1983).
- Note that BOD results represent approximate stream oxygen demands because the laboratory environment does not reproduce ambient stream conditions such as temperature, sunlight, biological populations, and water movement.

TECHNICAL NOTE: A 5-day duration for BOD determination has no theoretical grounding but is based on historical convention. Tchobanoglous and Schroeder (1985) provide the following background: "In a report prepared by the Royal Commission on Sewage Disposal in the United Kingdom at the beginning of the century, it was recommended that a 5-day, 18.3°C, BOD value be used as a reference in Great Britain. These values were selected because British rivers do not have a flow time to the open sea greater than 5 days and average long-term summer temperatures do not exceed 18.3°C. The temperature has been rounded upward to 20°C, but the 5-day time period has become the universal scientific and legal reference."

7.0.1 EQUIPMENT AND SUPPLIES

Table 7.0-1 lists equipment and supplies commonly used in the BOD_5 test using amperometric determination of DO. For more detailed guidance on equipment, supplies, maintenance, and calibration of the DO instrument, refer to NFM 6.2. If the iodometric (Winkler) method of DO determination is to be used, refer to table 6.2-3 in NFM 6.2 for a list of equipment and supplies. Equipment used for BOD sampling must be thoroughly cleaned with nonphosphate detergent and rinsed with tap water and deionized water, as described in NFM 3.

CAUTION: Before handling chemical reagents, refer to Material Safety Data Sheets. Wear safety glasses, gloves, and protective clothing.

Table 7.0-1. Equipment, supplies, chemical reagents, and preparation of dilution water and chemical solutions used in the procedure for determination of 5-day biochemical oxygen demand

[±, plus or minus; °C, degrees Celsius; BOD, biochemical oxygen demand; mL, milliliter; mm, millimeter; NFM, *National Field Manual for the Collection of Water-Quality Data*; L, liter; g, gram; KH_2PO_4, potassium dihydrogen phosphate; $KHPO_4$, potassium monohydrogen phosphate; Na_2HPO_4, sodium monohydrogen phosphate; NH_4Cl, ammonium chloride; *N*, normality; DO, dissolved oxygen; KCl, potassium chloride; $CoCl_3$, cobalt chloride]

Item	Description
Equipment and supplies	
Constant-temperature chamber or water bath	Thermostatically controlled to maintain 20 ± 1°C. During incubation, exclude all light to prevent the possibility of photosynthetic production of oxygen.
Aquarium pump, plastic air tubing, and air diffusion stones	Wash tubing and air diffusion stone thoroughly with a 0.2-percent nonphosphate detergent solution and rinse thoroughly 3 to 5 times with deionized or distilled water before use.
BOD bottles	300 mL, ground glass stoppered. Wash bottles thoroughly with a 0.2-percent nonphosphate detergent solution and rinse with deionized or distilled water before each test. Label bottles appropriately for sample identification.
Glass beads	Borosilicate, solid spherical; 5-mm diameter. Wash thoroughly with a 0.2-percent nonphosphate detergent solution and rinse with deionized or distilled water before use.
Graduated cylinder	Borosilicate, 50- to 250-mL capacity, depending on the volume of sample to be tested.
Overcap	Paper or plastic cup, or aluminum foil, to be placed over BOD stoppers to prevent evaporation of the water seal.
Pipet	Bacteriological, large bore, borosilicate, volume ranging from 1 to 50 mL, depending on the volume of sample to be tested.
Thermometer	Calibrated within temperature range of approximately 5 to 40°C with 0.5°C graduations (NFM 6.1).
Sample container(s)	Wide mouth, screwtop lid, polyethylene, polypropylene, or borosilicate glass. Containers of 1-L capacity are sufficient for most samples.
Waste disposal container(s)	Capped, and of appropriate material to contain specified sample and chemical wastes.
Chemical reagents[1] and preparation of dilution water	
Calcium chloride ($CaCl_2$) solution[2]	Dissolve 27.5 g of $CaCl_2$ in deionized water and dilute to 1 L.
Dilution water	Deionized water of high quality; must be free from toxic substances such as chlorine or toxic metals.
Ferric chloride ($FeCl_3$) solution[2]	Dissolve 0.25 g of $FeCl_3 \cdot 6H_2O$ in deionized water and dilute to 1 L.
Magnesium sulfate ($MgSO_4$) solution[2]	Dissolve 22.5 g of $MgSO_4 \cdot 7H_2O$ in deionized water and dilute to 1 L.
Phosphate buffer solution[2]	Dissolve 8.5 g of KH_2PO_4, 21.8 g of $KHPO_4$, 33.4 g of $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g of NH_4Cl in about 500 mL of deionized water. Dilute to 1 L.

(Table 7.0-1 continues on the next page.)

Table 7.0-1. Equipment, supplies, chemical reagents, and preparation of dilution water and chemical solutions used in the procedure for determination of 5-day biochemical oxygen demand—*Continued*

Item	Description
Chemical reagents for sample pretreatment and preparation of chemical solutions	
Sodium hydroxide (NaOH) for caustic acidity pretreatment	Add 40 g of NaOH to about 900 mL of deionized water. Mix and dilute to 1 L (1 *N* NaOH). Store in a plastic container.
Sodium sulfite (Na_2SO_3) or sodium thiosulfate ($Na_2S_2O_3$) for residual chlorine pretreatment solution	Dissolve 1.575 g of Na_2SO_3 or NaS_2O_3 in 1 L of deionized water. This solution is not stable and should be prepared daily to weekly, as needed. Store refrigerated in a dark bottle.
Sulfuric acid (H_2SO_4) for caustic alkalinity pretreatment	Slowly and while stirring add 28 mL of concentrated H_2SO_4 to about 900 mL of deionized water. Mix and dilute acid solution to 1 L (1 *N* H_2SO_4).
DO equipment and supplies (refer to NFM 6.2)	
Calibration chamber	Follow manufacturer's recommendations.
DO instrument system	Temperature and pressure compensated.
Stirrer attachment for DO sensor	Must fit in 300-mL BOD bottle.
Pocket altimeter-barometer	Calibrated, Thommen™ model 2000 or equivalent.
DO sensor membrane replacement kit	Membranes, O-rings, KCl filling solution.
Oxygen solubility table	Refer to table 6.2-6 in NFM 6.2.
Zero DO calibration solution	Dissolve 1 g Na_2SO_3 and a few crystals of $CoCl_3$ in 1 L water. Prepare fresh zero DO solution before each use.

[1] Properly discard chemical reagents if there is any sign of biological growth or if past the expiration date.
[2] Can be purchased from the HACH™ Instrument Company in the form of nutrient buffer pillows ready for immediate use.

SAMPLE COLLECTION AND STORAGE 7.0.2

Samples can degrade significantly during extended storage. To minimize sample degradation, and thus avoid negative bias in the measurement of BOD_5, analyze samples promptly or store chilled without freezing (maintain a temperature from 1 to 4°C). Chilling the sample is not necessary if the analysis begins within 2 hours of collection (American Public Health Association and others, 1995).

- If a sample is refrigerated prior to analysis, allow the sample to warm to 20°C before starting the test. A sample may be removed from an ice chest or refrigerator during transit to allow it to warm to 20°C before analysis begins.
- It is optimum to start the BOD_5 analysis immediately after sample collection to minimize changes in bacterial concentration.
- **The maximum holding time of a sample to be analyzed for BOD is 24 hours.**

Do not freeze samples.

Bacteria are commonly associated with suspended sediment, which can vary spatially and temporally along a stream cross section (Britton and Greeson, 1989). Like suspended sediment, the oxygen-demanding compounds may not be equally distributed along a cross section. Where possible, use the equal-width-increment or equal-discharge-increment procedures described in NFM 4 to collect a BOD sample representative of the stream cross section.

When using cross-sectional, depth-integrating, or discharge-weighted methods:

1. Use a DH-81 or D-77 sampler in most situations (NFM 2). If stream depths exceed 5m (meters) (16.4 feet), use the bag version of the D-77 sampler.
2. Clean all equipment thoroughly and rinse with sample water before use (NFM 3).
3. Collect samples using appropriate procedures and pour sample water into a compositing device (NFM 4; Edwards and Glysson, 1999).
4. Withdraw a composite sample from the sample-compositing device into a clean container of sufficient capacity to perform the desired BOD tests. The volume of sample depends on the number of BOD tests to be completed and any prior knowledge of BOD for the water of interest. Generally, a 1-liter (L) sample is sufficient.
5. Cap the container securely and protect the sample from light during transport to the laboratory for analysis.
6. Store the sample on ice if not processed and analyzed within 2 hours of collection.

If depth-width-integrated or discharge-weighted methods cannot be used, collect a grab sample by the hand-dip method. A grab sample can be collected directly from the stream using a clean container of sufficient capacity (American Public Health Association and others, 1995).

When collecting a hand-dipped sample:

1. Grasp the sample container near the base on the downstream side of the bottle.
2. Plunge the bottle opening downward below the water surface. **Avoid contact with the streambed during this process.**
3. Allow the sample container to fill with the opening pointed slightly upward into the current.
4. Cap the container securely and protect the sample from light during transport to the laboratory for analysis.

FIVE-DAY TEST FOR BIOCHEMICAL OXYGEN DEMAND 7.0.3

The BOD_5 test procedure is based on DO concentration and requires an accurate DO determination. Follow procedures described in NFM 6.2 to determine DO concentration. Iodometric titration or amperometric (DO meter) methods used to measure DO are used for the BOD_5 test procedure (American Public Health Association and others, 1995). The procedures presented below incorporate the amperometric method for determining DO concentration. Refer to section 6.2.1.B in NFM 6.2 if the iodometric method will be used to determine DO.

TECHNICAL NOTE: If using the iodometric titration method to measure DO concentration, double the sample volume, number of dilutions, and number of bottles to account for determining an initial DO and a final DO.

SAMPLE PREPARATION 7.0.3.A

Most relatively unpolluted streams have a BOD_5 that ranges from 1 to 8 mg/L (milligrams per liter) (Nemerow, 1974). If the BOD_5 value of a sample is less than 7 mg/L, sample dilution is not needed. A BOD_5 value greater than 7 mg/L requires sample dilution. Dilution is necessary when the amount of DO consumed by microorganisms is greater than the amount of DO available in the air-saturated BOD_5 sample (American Public Health Association and others, 1995). The BOD_5 analyst is responsible for determining the dilution(s) that will be needed. Table 7.0-2 provides general dilutions based on anticipated ranges of BOD_5 (Sawyer and McCarty, 1978).

BOD_5 values are acceptable only if the following criteria are met:

- The DO concentration after 5 days must be at least 1 mg/L and at least 2 mg/L lower in concentration than the initial DO (American Public Health Association and others, 1995).

- At least three different dilutions are set per sample to cover the anticipated range of BOD. The three sample volumes used are selected to provide an overlapping range in expected BOD concentrations. For example, if the BOD_5 is known to range from 3 to 28 mg/L for a particular stream, then the sample volumes used for the test would be 50 mL, 100 mL, and 300 mL (no dilution). If there is no prior knowledge of the BOD_5 of the stream water, use a minimum of four volumes to accommodate a range of BOD_5 from 0 to 210 mg/L.

When less than a 300-mL sample is to be analyzed, sample volumes are added to a standard solution of dilution water to bring the total sample volume to 300 mL. Because bacteria need nutrients and micronutrients to survive, these compounds are added to the dilution water. Similarly, the pH of the dilution water needs to be maintained in a range suitable for bacterial growth (6.5 to 7.5). Consequently, sulfuric acid or sodium hydroxide may need to be added to the dilution water to lower or raise the pH, respectively.

Some types of sewage, such as untreated industrial wastes, disinfected wastes, and wastes that have been heated to a high temperature contain too few bacteria to perform the test. Thus, the samples must be seeded with a population of microorganisms to produce an oxygen demand. Discussion of the seeding procedure is beyond the scope of this chapter. Most natural waters contain an adequate amount of microorganisms. For guidance on seeding procedures, including the BOD_5 equation when dilution water is seeded, refer to American Public Health Association and others (1995).

Table 7.0-2. Recommended sample volumes for the 5-day biochemical oxygen demand test

[Adapted from Sawyer and McCarty, 1978. BOD_5, 5-day biochemical oxygen demand]

Anticipated range of BOD_5 (in milligrams per liter)	Milliliters of sample	Milliliters of dilution water
0–7	300	0
6–21	100	200
12–42	50	250
30–105	20	280
60–210	10	290
120–420	5	295
300–1,050	2	298
600–2,100	1	299

INTERFERENCES 7.0.3.B

Certain constituents present in a water sample can inhibit biochemical oxidation and interfere with the BOD analysis. Interferences in the BOD analysis include caustic alkalinity or acidity; the presence of residual chlorine; or the presence of toxic elements, including trace elements such as copper, lead, chromium, mercury, and arsenic, or compounds such as cyanide. Procedures for pretreating samples for some common interferences are described in this chapter. Refer to American Public Health Association and others (1995) for further guidance on sample seeding and pretreatment.

The following preparations are needed before implementing the BOD_5 test procedure:

1. Prepare dilution water 3 to 5 days before initiating BOD_5 tests to ensure that the BOD of the dilution water is less than 0.2 mg/L. **Discard dilution water if there is any sign of biological growth.**
2. Determine sample pH. Adjust sample to a pH between 6.5 and 7.5, if necessary, using sulfuric acid (H_2SO_4) for samples with pH greater than 7.5 or sodium hydroxide (NaOH) for samples with pH less than 6.5 (American Public Health Association and others, 1995).
3. Add sodium sulfite (Na_2SO_3) to remove residual chlorine, if necessary. Samples containing toxic metals, arsenic, or cyanide often require special study and pretreatment (American Public Health Association and others, 1995). Samples must be seeded after pretreatment.

7.0.3.C BOD_5 TEST PROCEDURE

Use the following procedure for the BOD_5 test (troubleshooting suggestions are provided in section 7.0.5,* table 7.0-3*):

1. Determine the amount of sample to be analyzed; if available, use the historical results of a previous test of BOD_5 for a particular sampling site, and refer to table 7.0-2.
2. Place a clean, calibrated thermometer into the constant temperature chamber. (See NFM 6.1 for thermometer care and calibration.)
3. Turn on the constant temperature chamber to allow the controlled temperature to stabilize at 20°C ±1°C.
4. Turn on the DO instrument, but not the stirring attachment. Some DO instruments need to be turned on 30 to 60 minutes before calibration—check the manufacturer's instruction manual.
5. Aerate dilution water before adding nutrient solutions.

6. After aeration,

   a. Add to dilution water

      - 1 mL each of the potassium phosphate, magnesium sulfate, calcium chloride, and ferric chloride solutions per 1 L of dilution water, or
      - Hach Company nutrient buffer pillows to a selected volume of dilution water per the manufacturer's recommendation.

   b. Shake the container of dilution water for about 1 minute to dissolve the slurry and to saturate the water with oxygen.

   c. Place the dilution water in the constant temperature chamber to maintain a temperature of 20°C until sample dilutions and analyses begin.

   d. The initial and final (after 5 days ± 4 hours) DO tests of the dilution water is determined and recorded simultaneously with each batch of environmental samples.

7. Check the temperature of the air incubator or water bath using a laboratory thermometer to ensure that the temperature has been maintained at 20° ± 1°C. A minimum/maximum recording thermometer can be used to audit the temperature during times when checks cannot be made.

8. Place the sample container in the constant-temperature chamber or water bath to begin warming the sample to 20°C ± 1°C. While the sample is warming, insert the air diffusion stone into the container and aerate the sample for about 15 minutes. After removing the air diffusion stone, allow several minutes for excess air bubbles to dissipate. The initial DO of the BOD sample needs to be at or slightly below saturation.

9. **Prepare dilutions as required**—Measure the appropriate amounts of sample necessary for the analysis. BOD_5 dilutions should result in a DO residual of at least 1 mg/L and a DO depletion of at least 2 mg/L after a 5-day incubation to produce the most reliable results. Prepare the dilutions to obtain a DO uptake in this range using the dilution water prepared earlier.

   a. For each subsample, mix thoroughly by inverting 20 times.

      - Use a large-bore pipet for sample volumes less than 50 mL. Withdraw a subsample that is representative of all the particle sizes present.

- Use a graduated cylinder for sample volumes greater than or equal to 50 mL.

b. Dilute two additional samples to bracket the appropriate dilution by a factor of two to three. Prepare at least three samples diluted according to volumes specified in table 7.0-2.

c. Pour the sample from the pipet or graduated cylinder into a clean BOD bottle.

- Agitate the dilution water and fill the remaining portion of the BOD bottle with dilution water.
- Prepare three samples containing only dilution water. These samples serve as blanks for quality control. If two of the three samples meet the blank-water criterion, accept the data.

10. Calibrate the DO instrument in accordance with the procedures outlined in NFM 6.2.

11. After bringing the samples to saturation and preparing the dilutions (steps 8 and 9 above), measure the initial DO concentration (D_1) of each sample and each dilution blank.

    a. Carefully insert the self-stirring sensor into the BOD bottle, avoiding air entrapment.

    b. Turn on the stirrer and allow 1 to 2 minutes for the DO and temperature readings to stabilize.

12. Record the bottle number, date, time, and D_1 on a form similar to that shown in figure 7.0-2.

13. Turn off the stirrer and remove the sensor from the BOD bottle. Rinse the sensor and stirrer with deionized water from a wash bottle. Discard rinse water into a waste container.

14. Add glass beads to the BOD bottle, if necessary, to displace the sample up to the neck of the bottle so that inserting a glass stopper will displace all air, leaving no bubbles.

15. Carefully cap the BOD bottle with the ground-glass stopper. Tip the bottle to one side and check for an air bubble.
    - If an air bubble is present, add glass beads to the bottle until the bubble is removed. Cap the bottle and check again for an air bubble. Repeat if necessary.
    - If no bubble is present in the sample, create a water seal by adding distilled or deionized water to the top of the BOD bottle around the glass stopper. Then place the overcap over the stopper on the BOD bottle to minimize evaporation from the water seal.
16. Place the sealed BOD sample in the air incubator or water bath and incubate the sample at 20°C ± 1°C for 5 days.
17. At the end of 5 days ± 4 hours, remove the BOD bottles from the incubator, remove the overcap, pour off the water seal, remove the ground-glass stopper, and measure the final DO concentration (D_2).
    - The DO uptake ($DO_{0\ days}$ - $DO_{5\ days}$) in the dilution water should not be greater than 0.2 mg/L and preferably not more than 0.1 mg/L. **Exceeding the 0.2-mg/L criterion could be grounds for rejecting results of the BOD analysis of the environmental sample.**
    - Dilution water of poor quality will cause an oxygen demand and appear as sample BOD. Improve purification or get the dilution water from another source if DO uptake exceeds 0.2 mg/L (see section 7.0.5, Troubleshooting).
18. Complete the field form by recording the date, time, and D_2 for each respective sample bottle (fig. 7.0-2).

Quality control. The BOD_5 test can be quite variable. Collect sufficient field and split replicates (10 to 20 percent) to provide an estimate of method variability.

5-Day Biochemical Oxygen Demand (BOD_5) Worksheet

Site/station:_____ **Collection date and time:**_____
Project:_____ **Personnel:**_____

Dilution-water blanks

Bottle number	Initial DO reading (D_1)	Date/time of reading	Final DO reading (D_2)	Date/time of reading	BOD (D_1-D_2)	BOD average (<0.2 mg/L)

Environmental sample

Bottle number	Sample size (mL)	Initial DO reading (D_1)	Date/ time of reading	Final DO reading (D_2)	Date /time of reading	BOD $\frac{D_1 - D_2}{P}$	BOD average (mg/L)

If dilution-water demand is <0.2 milligrams per liter (mg/L), use

$$BOD_5\ (mg/L) = \frac{D_1 - D_2}{P}$$

where

D_1 = initial sample dissolved-oxygen (DO) concentration (in mg/L)
D_2 = sample DO (in mg/L) after 5 days
P = decimal volumetric fraction of sample used

Figure 7.0-2. Example of a 5-day biochemical oxygen demand worksheet.

CALCULATIONS 7.0.4

The general equation for the determination of a BOD_5 value is:

$$BOD_5\,(mg/L) = \frac{D_1 - D_2}{P}$$

where D_1 = initial DO of the sample,
D_2 = final DO of the sample after 5 days, and
P = decimal volumetric fraction of sample used.

If 100 mL of sample are diluted to 300 mL, then $P = \frac{100}{300} = 0.33$. Notice that if no dilution was necessary, $P = 1.0$ and the BOD_5 is determined by $D_1 - D_2$.

If more than one dilution of the sample results in residual DO of at least 1 mg/L and a DO depletion of at least 2 mg/L, and there is no evidence of toxicity at higher sample concentrations or the existence of an obvious anomaly, average the results that are in the acceptable range (American Public Health Association and others, 1995).

7.0.5 TROUBLESHOOTING

The troubleshooting suggestions in table 7.0-3 are not all-inclusive. Refer to the troubleshooting suggestions for DO instruments (table 6.2-4 in NFM 6.2). Remember that faulty batteries can cause erratic readings.

Table 7.0-3. Troubleshooting guide for the 5-day biochemical oxygen demand test

[DO, dissolved oxygen; BOD_5, 5-day biochemical oxygen demand; mg/L, milligrams per liter; HCl, hydrochloric acid]

Symptom	Possible cause and corrective action
DO readings drift downward	• Weak batteries for stirring unit result in inadequate flow across membrane—replace batteries.
BOD_5 demand in dilution water is greater than the acceptable 0.2 mg/L	• Deionized water contains ammonia or volatile organic compounds—increase purity of dilution water or obtain from another source. Age water for 5-10 days before use. • Deionized water contains semivolatile organic compounds leached from the resin bed—increase purity of dilution water or obtain from another source. Age water for 5-10 days before use. • Bacterial growth in reagents and poorly cleaned glassware—more vigorous cleaning of glassware, including washing followed by a 5- to 10-percent HCl rinse followed by 3-5 rinses with deionized water. Discard reagents properly.
Sample BOD values are unusually low in the diluted sample (BOD_5 dilution water is within the acceptable range)	• Dilution water contains interferences inhibiting the biochemical oxidation process—increase purity of dilution water or obtain from another source. • Use deionized water that has been passed through mixed-bed resin columns. **Never use copper-lined stills.** Distilled water may be contaminated by using copper-lined stills or copper fittings—obtain from another source.

REPORTING 7.0.6

When reporting results of a BOD_5 test, be sure to use the correct parameter code (Appendix A7-A, table 1).

- Report BOD_5 values less than 2 mg/L as <2 mg/L rather than as 2.0 mg/L.
- Report BOD_5 values less than 10 mg/L to the nearest 0.1 mg/L.
- Report BOD_5 values greater than or equal to 10 mg/L to two significant figures.
- Report the results of replicate samples and dilution blanks with the BOD_5 results.

This page left blank intentionally.

FECAL INDICATOR BACTERIA 7.1

By D.N. Myers

	Page
7.1 Fecal indicator bacteria	FIB–5
7.1.1 Sampling equipment and equipment sterilization procedures	9
7.1.1.A Autoclaving	14
7.1.1.B Flame sterilization of the Hydrosol® field filtration unit	15
7.1.2 Sample collection, preservation, storage, and holding times	17
7.1.2.A Surface-water sample collection	18
Depth-and-width-integrating methods	19
Hand-dip method	20
7.1.2.B Ground-water sample collection	22
Supply wells	22
Monitoring wells	24
7.1.2.C Sample preservation, storage, and holding times	29
7.1.3 Identification and enumeration methods	30
7.1.3.A Culture media and reagents	32
7.1.3.B Membrane-filtration method	34
7.1.4 Calculation and reporting of fecal indicator bacteria	49
7.1.5 Instructions for media preparation	53

Illustrations

7.1-1. Photograph showing procedure to flame sterilize the Millipore Hydrosol® field filtration unit FIB–16

7.1-2. Diagram showing preparation of sample volumes by dilution 37

7.1-3. Photograph showing steps in membrane-filtration procedure 38

7.1-4. Diagram showing a method for counting colonies on gridded membrane filters 43

7.1-5. Photographs of typical colonies of fecal indicator bacteria on culture media 46

Tables

7.1-1. Ranges of fecal indicator bacteria typically found in uncontaminated surface water and contaminated surface water 8

7.1-2. Equipment and supplies used for membrane-filtration analysis of samples for fecal indicator bacteria testing 11

7.1-3. Equipment cleaning and sterilization procedures 13

7.1-4. Summary of equipment for sample collection, procedures for sample preservation, and holding times for indicator bacteria 17

7.1-5. Fecal indicator test definitions, incubation times, and incubation temperatures 31

7.1-6. Recommended sample volumes for membrane-filtration analyses based on ideal colony count and concentration range 36

7.1-7. Membrane-filter pore sizes for fecal indicator bacteria tests 40

7.1-8. Preparation guidelines for dilution of samples to volumes less than 1.0 milliliter for fecal indicator bacteria analysis FIB-41

7.1-9. Test (medium type), ideal colony count, and typical colony color, size, and morphology for indicator bacteria colonies 48

Notes:

References for section 7.1, Fecal indicator bacteria, are located at the end of Chapter A7 in the "Selected References and Documents" section, which begins on page REF-1.

See Appendix A7-A, Table 2, for parameter codes for fecal indicator bacteria that are used in the National Water Information System (NWIS) of the U.S. Geological Survey.

The citation for this section (7.1) of NFM 7 is as follows:

Myers, D.N., November 2003, Fecal indicator bacteria: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7 (3d ed.), section 7.1, accessed ___*date*___, from http://pubs.water.usgs.gov/twri9A/.

Page left blank intentionally.

FECAL INDICATOR BACTERIA 7.1

Fecal indicator bacteria are used to assess the microbiological quality of water because although not typically disease causing, they are correlated with the presence of several waterborne disease-causing organisms. The concentration of indicator bacteria (the term indicator bacteria is used synonymously with fecal indicator bacteria in this section) is a measure of water safety for body-contact recreation or for consumption.

Fecal indicator bacteria: used to measure the sanitary quality of water.

- Wastes from warm-blooded animals contribute a variety of intestinal bacteria that are disease causing, or pathogenic, to humans.
- Body contact with and consumption of water that contains pathogens of the genera *Salmonella*, *Shigella*, and *Vibrio*, for example, can result in several types of disease in humans, including gastroenteritis and bacillary dysentery, typhoid fever, and cholera.

- The presence of *Escherichia coli (E. coli)* in water is direct evidence of fecal contamination from warm-blooded animals and indicates the possible presence of pathogens (Dufour, 1977). A few strains of *E. coli* are pathogenic, such as *E. coli* O157:H7, but most strains are not.
- The presence of *Clostridium perfringens (C. perfringens)* in water, as spores and (or) vegetative cells, indicates the contamination of water with treated or untreated sewage or similar wastes (Bisson and Cabelli, 1980; Fujioka and Shizumura, 1985).

Bacteriological tests are used to assess the sanitary quality of water and the potential public health risk from waterborne diseases. This section describes tests that can be completed in the field for identifying and enumerating five types of fecal indicator bacteria: total and fecal coliform bacteria, *E. coli*, fecal streptococci, and enterococci (Britton and Greeson, 1989; U.S. Environmental Protection Agency, 1985, 1991a, 1996, 1997, 2000a, 2000b). These are the most widely used indicator bacteria. Information for collecting samples for analysis of *C. perfringens* is included in this section, although membrane-filtration analysis of samples for *C. perfringens* is to be performed in a microbiological laboratory and not in the field.

CAUTION:
When sampling for fecal indicator bacteria, wear protective apparel to prevent nose, mouth, eye, and direct skin contact with polluted water.

Water-quality criteria have been developed by the U.S. Environmental Protection Agency (USEPA) for concentrations of indicator bacteria in recreational waters, shellfish-growing waters, and in ambient waters (U.S. Environmental Protection Agency, 1986). In 1986, *E. coli* and enterococci bacteria became the recommended indicator bacteria for recreational waters, replacing fecal coliform and fecal streptococci bacteria (U.S. Environmental Protection Agency, 1986, 2000b). Public Law 106-284 (Beaches Environmental Assessment and Coastal Health Act of 2000) requires the use of *E. coli* and (or) enterococci to assess beach-water quality in all bathing beach monitoring programs.

E. coli and enterococci are the preferred indicators to be used for primary-contact recreational waters because both are superior to total coliform, fecal coliform, and fecal streptococci bacteria as predictors of swimming-associated gastroenteritis in marine and fresh waters (Cabelli, 1977; Dufour and Cabelli, 1984). "Primary-contact recreational waters are waters where people engage in or are likely to engage in activities that could lead to ingestion or immersion in the water and are designated for use as such in state and tribal water-quality standards" (U.S. Environmental Protection Agency, 2002). Examples of primary-contact recreational activities are swimming, canoeing, and water skiing.

- Typical concentrations of indicator bacteria in contaminated and uncontaminated surface waters are shown in table 7.1-1.
- Ground water typically contains substantially lower concentrations of indicator bacteria than surface water.
- Although membrane-filtration procedures for total coliform and fecal coliform bacteria and *E. coli* are accepted for analysis of potable water, the Most Probable Number tests may provide superior results because they usually result in comparatively greater recoveries of microorganisms.
- USEPA regulations stipulate the methods to be used for monitoring and assessment of drinking water[2] and recreational water (U.S. Environmental Protection Agency, 1991b, 2002).

[2]The term "drinking water" is used when the information presented is within the context of U.S. Environmental Agency regulations; otherwise, the more general term "potable water" is used.

Table 7.1-1. Ranges of fecal indicator bacteria typically found in uncontaminated surface water and contaminated surface water

[Modified from Bordner and Winter, 1978, p. 127; American Public Health Association and others, 1998; U.S. Environmental Protection Agency, 1986, 1996, 1997, 2000a, and 2000b; Francy and others, 2000. <, less than; >, greater than]

Bacterial group	Uncontaminated surface water, colonies per 100 milliliters	Fecal-contaminated surface water, colonies per 100 milliliters
Total coliform	<1 to 80,000	1,200 to > 4,000,000
Fecal coliform	<1 to 5,000	200 to > 2,000,000
Escherichia coli	<1 to 576	126 to > 2,000,000
Fecal streptococcus	<1 to 1,000	400 to > 1,000,000
Enterococcus	<1 to 100	100 to > 1,000,000
Clostridium perfringens	<1 to 100	100 to > 10,000

SAMPLING EQUIPMENT AND EQUIPMENT STERILIZATION PROCEDURES 7.1.1

Sterile technique must be followed and documented when collecting and processing samples for fecal indicator bacteria. Specific equipment and supplies are needed for collection and membrane-filtration analysis of samples for indicator bacteria. The equipment and supplies listed in tables 7.1-2 and 7.1-3 should be sufficient to begin (a) membrane-filtration analysis of fecal indicator bacteria and (b) equipment cleaning and sterilization procedures, respectively. The equipment and procedures described in the following paragraphs may be used for fecal indicator bacteria and fecal indicator viruses.

- **Equipment for collection and analysis of bacterial samples must first be cleaned and then sterilized** (table 7.1-3). There are several sterilization methods, but autoclaving is preferred. Before autoclaving, wrap clean equipment in kraft paper, autoclavable bags, or aluminum foil. Sterilize and store the equipment in a clean area. Resterilize equipment if the foil, bag, or kraft paper is torn.
- **Quality assurance and quality control of sterilization procedures are mandatory.** Keep a logbook of autoclave operation or other sterilization procedure(s) used. In the log, include a brief description of the quality-assurance procedures used and quality-control tests run; note the date, the test results, and the name of the autoclave operator and (or) analyst. Record the autoclave temperature, pressure, date, and time of each autoclave run. If the autoclave does not reach the specified temperature and pressure or fails a quality-control test, service the autoclave and then resterilize all materials (American Public Health Association and others, 1998, p. 9-2 to 9-14).
- **Add sodium thiosulfate ($Na_2S_2O_3$) to sample bottles before sterilization if the water to be collected contains residual chlorine or other halogens.** Residual chlorine commonly is found in samples collected from sources such as treated drinking water (withdrawn from taps), wastewater effluents, and in the mixing zones directly downstream from wastewater-treatment plants.

To prepare a 10-percent solution of $Na_2S_2O_3$:

1. In a volumetric flask, dissolve 100 g (grams) of $Na_2S_2O_3$ into 500 mL of deionized or distilled water; stir until dissolved, and fill flask to 1,000 mL (Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19).
2. Using a pipet, dispense 0.5 mL of 10-percent $Na_2S_2O_3$ solution for every 1 L of sample.
3. Store the $Na_2S_2O_3$ solution in a dark bottle and keep it refrigerated; discard after 6 months and prepare a fresh solution. The $Na_2S_2O_3$ solution may be sterilized before storing, but will need to be autoclaved again if the bottle is left open and in contact with air.

Add ethylenediaminetetraacetic acid (EDTA) to sample bottles when water to be collected contains trace elements. Although references to toxic concentrations vary somewhat, concentrations of trace metals such as copper, nickel, or zinc that are present at concentrations greater than 10–1,000 µg/L (micrograms per liter) can be toxic to bacteria (Britton and Greeson, 1989, p. 56; Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19). When in doubt, add EDTA to sample bottles prior to collection. EDTA is prepared by dissolving 372 mg (milligrams) in 1,000 mL of deionized or distilled water (American Public Health Association and others, 1998, p. 9-19). Before sterilization, add 0.3 mL of the EDTA solution per 100 mL of sample to sample bottles. EDTA can be combined with the $Na_2S_2O_3$ solution in the sample bottle before sterilization. Keep bottles tightly capped between uses, and prepare a fresh stock solution every 6 months; discard any expired stock solution.

Sterilize the filtration apparatus and sampling equipment between sites or for each sample collected at the same site at different times. Table 7.1-3 shows specifications for sterilizing equipment and supplies using a variety of techniques, including autoclaving. Autoclaving is the preferred method.

Table 7.1-2. Equipment and supplies used for membrane-filtration analysis of samples for fecal indicator bacteria testing

[mENDO, total coliform medium; mTEC, *Escherichia coli* medium; mL, milliliters; °C, degrees Celsius; µm, micrometer; mm, millimeters; TD, to deliver; TTC, triphenyltetrazolium chloride; NIST, National Institute of Standards and Technology; NA-MUG, *Escherichia coli* medium; MI, total coliform and *Escherichia coli* medium; nm, nanometers; lb/in^2, pounds per square inch; cm, centimeters]

✓	Item	Description
	Absorbent pads	For use with total coliform test on mENDO medium and with *Escherichia coli* on mTEC medium for urease test
	Alcohol burner	Glass or metal, containing ethanol for flame sterilizing forceps
	Alcohol bottle	Wide mouth, 100 mL, containing ethanol for forceps sterilization
	Autoclave	For sterilization, capable of maintaining 121°C
	Bottles	Dilution bottles, 99 mL, with autoclavable screwcaps for sample dilution
	Buffered water	Specific to the test method and prepared in advance of field work
	Counter	Handheld, for counting bacterial colonies
	Filter disk	Sterile, disposable, 0.2-µm pore size for sterilizing reagents, to fit on 5-mL barrel syringe
	Filtration assembly	Filter funnel, filter base, and stainless steel, glass, or plastic filter holder; wrapped in aluminum foil, autoclavable bag, or kraft paper; sterile; autoclavable
	Flasks, stir bars	Narrow mouth, Erlenmeyer type flasks with stir bars for media preparation, 250 or 500 mL
	Forceps	Stainless steel, smooth tips
	Hot plate	With magnetic stirrer or boiling water bath for media preparation
	Graduated cylinders	Borosilicate glass or plastic, 25 and 100 mL, wrapped in sterile aluminum foil, autoclavable bag, or kraft paper
	Incubator	Aluminum heat sink (heater block) or water bath, capable of maintaining specified temperature ranges during incubation
	Membrane filters	47-mm, sterile, white, gridded, mixed cellulose ester, cellulose acetate, or cellulose nitrate composition, 0.45-µm (or 0.65-µm) pore size depending on the test

(Table 7.1-2 is continued on the next page.)

Table 7.1-2. Equipment and supplies used for membrane-filtration analysis of samples for fecal indicator bacteria testing—*Continued*

✓	Item	Description
	Media and reagents	Liquid or solid media and reagents specific to the test method, prepared in advance of field work
	Microscope	*Wide field type with 5 to 15 magnifications, dissecting* type with fluorescent lamp
	Pipets	Sterile, TD, bacteriological or Mohr, glass or plastic with cotton plugs; 1, 10, and 25 mL
	Pipettor or pipet bulb	For use with pipets **(do not pipet by mouth)**
	Petri dishes	Sterile, plastic, disposable top and bottom plates, 50 x 12 mm
	Syringe	5 mL, disposable, for delivering TTC
	Thermometer	Range of 40-110°C, glass mercury or dial, calibrated in 0.2°C increments, checked against a NIST-certified thermometer
	Ultraviolet lamp, long wave	For use with NA-MUG and MI tests, 366-nm, 6-watt bulb
	Vacuum source	Either a hand pump with gage or electric vacuum or peristaltic pump; vacuum pressure not to exceed 5 lb/in^2 or 25 cm of mercury
	Wrapping for equipment	Kraft paper, aluminum foil, autoclavable plastic bags

Table 7.1-3. Equipment cleaning and sterilization procedures

[DIW, distilled/deionized water; mL, milliliter; $Na_2S_2O_3$, sodium thiosulfate; µg/L, micrograms per liter; EDTA, ethylenediaminetetraacetic acid; °C, degrees Celsius; mg/L, milligrams per liter; >, greater than value shown]

Equipment	Procedures
	Cleaning
All equipment (this includes water-level tape measure, all sample-collection and sample-processing equipment used in the field and laboratory)	Wash equipment thoroughly with a dilute nonphosphate, laboratory-grade detergent. Rinse three times with hot tap water. Rinse again three to five times with deionized or distilled water. Wipe down the wetted portion of water-level tapes with disinfectant (0.005 percent bleach solution or methyl or ethyl alcohol) and rinse thoroughly with DIW.
	Sterilization
Autoclavable glass, stainless steel, plastic, and Teflon bottles and containers, volumetric flasks, and pipets and pipettors	If sample will contain residual chlorine or other halogens, add 0.5 mL of a 10-percent $Na_2S_2O_3$ solution per liter of sample to sample bottle before autoclaving. If sample will contain greater than 10 µg/L trace elements, add EDTA to sample bottle before autoclaving. Wrap equipment in kraft paper, aluminum foil, or place into autoclavable bags.[1] Autoclave at 121°C for 15 minutes.
Stainless steel field units	Flame sterilize with methanol (Millipore Hydrosol® units only), or autoclave at 121°C for 15 minutes.
Portable submersible pumps and pump tubing	**Autoclavable equipment** (preferred): Wrap components in kraft paper, aluminum foil, or place into autoclavable bags. Autoclave at 121°C for 15 minutes. **Non-autoclavable equipment:** (1) Submerge sampling system in a 50-mg/L (0.005 percent) sodium hypochlorite solution prepared from household laundry bleach. (2) Circulate solution through pump and tubing for 30 minutes. (3) Follow step 2 by thoroughly rinsing, inside and out, with 0.5 mL of a 10-percent sterile $Na_2S_2O_3$ solution per liter of water and circulate solution for 5 minutes. (4) Pump $Na_2S_2O_3$ to waste, then circulate sterile deionized or distilled water through pump, followed by sample water pumped from the well. **CAUTION:** Prolonged or repeated use of a hypochlorite solution on interior or exterior metallic surfaces of a pump can cause corrosion or other damage to the pump and compromise the quality of samples collected for a trace-element or organic-compound analysis.

[1]Equipment to be wrapped in kraft paper, aluminum foil, or placed into autoclavable bags includes, for example, bottles, tubing, flasks, bailers, pump components. The $Na_2S_2O_3$ solution is also autoclaved.

7.1.1.A AUTOCLAVING

Use only autoclaves that have temperature, pressure, and liquid- and dry-utensil-cycle controls (table 7.1-3). Steam sterilizers, vertical autoclaves, and pressure cookers without temperature controls are not recommended.

- Take care to ensure that materials to be autoclaved, such as tubing and containers, are thermally stable. Plastic polymers that can be autoclaved include polycarbonate, polypropylene, polyallomer, polymethylpentene, Teflon® and Tefzel® (such as perfluoroalkyoxy-polymers (PFA), ethylene tetrafluoroethylene (ETFE), fluorinated ethylene propylene (FEP), and polytetrafluoroethylene polymers (PTFE)). Note that each material type has different thermal characteristics and tolerances to repeated autoclaving.
- Consult the 20th edition of "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1998, p. 9-2 to 9-14) for specifications for the length of time, temperature, and pressure for autoclave sterilization of various media and materials.
- In addition to the guidance listed above, it is necessary to:
  - Use a sterilization indicator tape with each load.
  - Use commercially available biological indicators at least quarterly to test autoclave performance. Biological indicators are composed of endospores—living cells that are resistant to heat but are destroyed by autoclaving.
  - Wrap silicone tubing, in addition to other autoclavable equipment, in kraft paper, aluminum foil, or place in an autoclavable plastic bag.
  - Drain the autoclave at the end of each period of use. Clean with mild soap and water once per week during periods of daily use. Record cleaning procedures in the logbook.
  - Avoid overloading the autoclave with equipment or materials; overloading will result in incomplete sterilization.

Autoclaving is the preferred method for sterilizing equipment for fecal indicator bacteria.

FLAME STERILIZATION OF THE HYDROSOL® FIELD FILTRATION UNIT 7.1.1.B

The older style Millipore Hydrosol® field filtration units are designed to be flame sterilized with methanol. Formaldehyde gas, a byproduct of methanol combustion, kills all bacteria in the unit. The following sterilization procedure is acceptable for the Hydrosol® unit (fig. 7.1-1) in field situations where other sterilization techniques are not practicable (Millipore, 1973, p. 48–49).When following these procedures, work in a ventilated area and wear appropriate protective equipment such as safety glasses, face mask, and gloves. Avoid breathing noxious fumes.

To flame sterilize the Hydrosol® unit, carefully:

1. Remove the stainless steel flask from the base of the filter-holder assembly.
2. Saturate the asbestos ring (wick) around the base assembly with methanol dispensed from a Teflon squeeze bottle or with an eye dropper from a screw-top glass container.
3. Ignite the methanol on the asbestos wick and allow to burn for 30 seconds.
4. Invert the stainless steel flask over the funnel and the burning asbestos ring, and seat the flask on the base of the filter-holder assembly. Leave the flask in place for 15 minutes. Before filtering the next sample, rinse flask and funnel thoroughly with sterile buffered water to remove all residues of formaldehyde.
5. Repeat the sterilization procedure before processing the next sample.

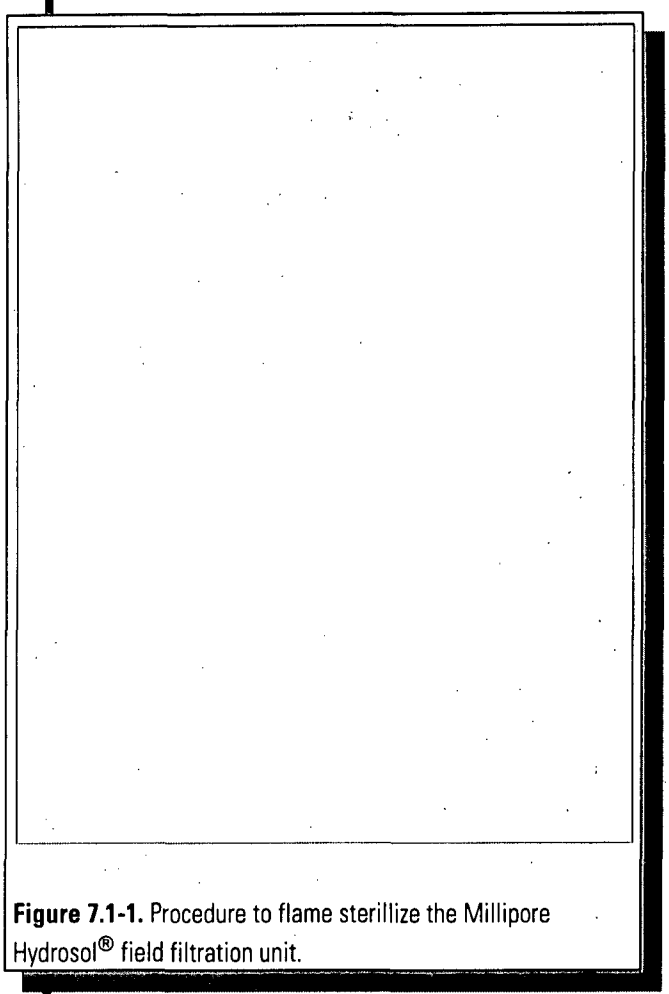


Figure 7.1-1. Procedure to flame sterillize the Millipore Hydrosol® field filtration unit.

CAUTION:
When flame sterilizing, have proper safety equipment such as a fire extinguisher on hand, and implement procedures carefully.

SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES 7.1.2

Sterile conditions must be maintained during collection, preservation, storage, and analysis of indicator bacteria samples. Specific procedures have been developed that must be strictly followed; these vary with types of equipment and sample source (surface water, ground water, treated water, or wastewater) (table 7.1-4).

Table 7.1-4. Summary of equipment for sample collection, procedures for sample preservation, and holding times for indicator bacteria

[EWI, equal-width increment; EDI, equal-discharge increment; L, liter; mL, milliliter; EDTA, ethylenediaminetetraacetic acid; °C, degrees Celsius; *E. coli, Escherichia coli*; *C. perfringens, Clostridium perfringens*]

Equipment for sample collection
To collect EWI or EDI surface-water samples: US D-95, US DH-95, or US DH-81 with sterile, 1-L wide-mouth bottle, with sterile caps and nozzles. US D-96 with sterile autoclavable bag.
To collect surface-water and ground-water samples using a pump, point samplers from a tap or by the hand-dipped method: a sterile, narrow-mouth container, 125-, 250-, 500-, or 1,000-mL capacity, depending on the number of tests and samples.
All containers must be composed of sterilizable materials such as borosilicate glass, polypropylene, stainless steel, or Teflon®.
Procedures for sample preservation
If necessary, add 0.5 mL of a 10-percent sodium thiosulfate solution per 1 L of sample for halogen neutralization.
If necessary, add 0.3 mL of a 15-percent EDTA solution per 100 mL of sample for chelation of trace elements.
Chill all samples at 1- 4°C before analysis.
Maximum holding times for samples obtained from surface water, ground water, or treated drinking water
Do not exceed the 6-hour maximum holding time period after sample collection and initiation of analysis for *E. coli*, fecal coliform bacteria, total coliform bacteria, enterococci, and fecal streptococci in **surface water and ground water** (Bordner and Winter, 1978, p. 30; U.S. Environmental Protection Agency, 2000b, 2002).
A 24-hour holding time for *C. perfringens* may be used. A 6-hour maximum holding time period after sample collection for *C. perfringens* (U.S.Environmental Protection Agency, 1996, p. XI-8) is recommended if comparisons between *C. perfringens* and other fecal indicator bacteria collected at the same time are planned (U.S. Environmental Protection Agency, 1996).
Do not exceed the 30-hour maximum holding time period after sample collection for total coliform bacteria, fecal coliform bacteria, and *E. coli* collected from treated **drinking-water sources** (Bordner and Winter, 1978 p. 30).

7.1.2.A SURFACE-WATER SAMPLE COLLECTION

The areal and temporal distribution of bacteria in surface water can be as variable as the distribution of suspended sediment because bacteria commonly are associated with solid particles. To obtain representative data for bacteria analysis, follow the same methods used to collect surface-water samples for suspended sediment analysis (Edwards and Glysson, 1999; NFM 4.1 and table 7.1-4).

- **Flowing water**—use depth-and-width-integrating sampling methods (NFM 4.1.1.A).[3]
- **Still water** (lakes or other surface-water conditions for which depth-and-width-integrating methods may not be applicable)—use the hand-dip method or a sterile point sampler (NFM 4.1.1.B).
- **Beach water**—use a hand-dip method in shallow wadable water and a sterile point sampler for deeper water. Collect samples by the hand-dip method at knee depth, a depth of approximately 6 to 12 inches (15 to 30 centimeters) below the water surface.
  - Sample near known or suspected pollution sources, in areas of concentrated activity (for example, near lifeguard chairs), or for every quarter mile (approximately every 500 meters) of beach length (U.S. Environmental Protection Agency, 2002) and record sampling location.
  - Position the sampler downstream from any water currents to collect the sample from the incoming flow (U.S. Environmental Protection Agency, 2002). Avoid contaminating the water sample with bottom material dislodged by disturbing the bottom while sampling.
  - A Chain-of-Custody record is recommended for beach sampling done in support of beach closures or posting of warnings to swimmers (U.S. Environmental Protection Agency, 2002, Appendix J).

[3]Sample-collection methods may be modified to ensure consistency with study objectives and as appropriate for site conditions.

Wear powderless laboratory gloves and avoid sample contact with eyes, nose, mouth, and skin when working in and with fecal-contaminated waters.

Depth-and-width-integrating methods

Depth-and-width-integrating sampling methods (the equal-discharge increment (EDI) method or the equal-width increment (EWI) method) are the standard methods to use when sampling flowing waters and generally are required unless study objectives or site characteristics dictate otherwise (NFM 4.1.1.A and table 7.1-4).

1. The EDI method is preferred to the EWI method for sites where the velocity distribution across a stream section is well established; for example, at a gaging station or at a section where the depth varies (Edwards and Glysson, 1999).
2. Select the appropriate sampler and equipment. **Sampling equipment must be sterile,** including the collection bottle, nozzle, and cap (or bag for the bag sampler) (table 7.1-3).
   - For streams with depths of 5 m or less, use a US D-95, US DH-95, or a US DH-81 sampler (NFM 2.1.1).
   - For stream sections where depths exceed 5 m, use the US D-96, with either autoclavable Teflon® bags or autoclavable cooking bags. Thermotolerant polymers are described in more detail in 7.1.1 under "Sampling Equipment and Equipment Sterilization Procedures."
   - To composite subsamples, use a sterile 3-L or larger bottle. For wide channels, several samples, each composed of subsamples composited into a sterile large-volume container, may be needed.
   - For narrow channels, collect subsamples at 5 to 10 or more vertical locations in the cross section without overfilling the bottle.
   - Use the proper nozzle size and transit rate for the velocity conditions in the section to ensure isokinetic collection of the sample.

Hand-dip method

If the stream depth and (or) velocity is not sufficient to use a depth-and-width-integrating method to collect a sample, then use the hand-dip method (table 7.1-4). Sampling still water or sampling at depth in lakes, reservoirs, estuaries, and oceans requires a sterile point sampler. Niskin, ZoBell, and Wheaton point samplers hold a sterilizable bottle or bag. Wearing laboratory gloves, collect a hand-dipped sample as follows:

1. Open a sterile, narrow-mouth borosilicate glass or plastic bottle; grasp the bottle near the base, with hand and arm on the downstream side of the bottle.
2. Without rinsing, plunge the bottle opening downward, below the water surface. Allow the bottle to fill with the opening pointed slightly upward into the current.
3. Remove the bottle with the opening pointed upward toward the water surface and tightly cap it, allowing about 2.5 to 5 cm of headspace (American Public Health Association and others, 1998, p. 9-19; Bordner and Winter, 1978, p. 8). This procedure minimizes collection of surface film and avoids contact with the streambed.

CAUTION:
Do not sample in or near a water body without wearing a correctly fitted personal floation device (PFD).

Quality control in surface-water sampling. Depending on the data-quality requirements of the study and site conditions, quality-control samples (field blanks, procedure and filter blanks, positive and negative controls, and field replicates) generally constitute from 5 to 20 percent or more of the total number of samples collected over a given period of time. Quality-control terms (shown below in bold type) are defined at the end of this chapter, beginning on page CF-2.

- **Field blank**—Collect and analyze field blanks at a frequency of 1 in every 10 to 20 samples to document that sampling and analysis equipment have not been contaminated. If sampling in a beach environment, collect a field blank at least once per sampling trip (U.S. Environmental Protection Agency, 2002, p. J-2). Process field blanks before collecting the water sample.
  1. Pass sterile buffered water through sterile sampling equipment and into a sterile sampling container.
  2. Analyze sterile buffered water for fecal indicator bacteria. If no growth is observed, then the sample was collected by use of sterile procedures.
- **Filter blank, procedure blank**—Collect and analyze filter blanks and procedure blanks during sample processing to document that filtration equipment and buffered water were sterile and not contaminated by the analyst. A filter blank is processed for each sample before the sample is filtered. A procedure blank is processed through the filtration apparatus after the sample has been filtered at a frequency of 1 in every 10 to 20 samples.
- **Positive and negative controls**—These types of quality-control samples are required if media are prepared from basic ingredients (not dehydrated media) by field or laboratory personnel. The analyses of positive and negative controls are performed in the laboratory, and not in the field.
- **Field replicate**—Collect and analyze 1 field replicate for every 10 to 20 samples. A split sequential replicate is recommended. Two samples are collected and each sample is analyzed in duplicate by membrane filtration.

7.1.2.B GROUND-WATER SAMPLE COLLECTION

As with surface water, most bacteria in ground water are associated with solid particles. Stable values of field measurements (turbidity, temperature, dissolved-oxygen concentration, pH, and specific conductance), especially turbidity and dissolved oxygen, are important criteria for judging whether a well has been sufficiently purged for collection of a representative ground-water sample for indicator bacteria analysis (NFM 4.2 and 6.0.3.A). Sampling equipment that has been subjected to chlorinating and dechlorinating agents can affect the chemistry of samples collected for non-microbial analysis; therefore, collect blank samples to be analyzed for chloride, sulfate, and other constituents, as appropriate, to document that sample quality has not been compromised.

- Collect samples for analysis of bacteria after all other water-quality sampling has been completed.
- If using the same equipment for chemical-analysis and bacteria-analysis samples, then clean the equipment by first using standard procedures (NFM 3), followed by the disinfecting and rinsing procedures described in section 7.1.1. Purge the well as described in NFM 4.2 before collecting samples.
- If different equipment will be deployed in a well for bacteria sampling, then first check for stable turbidity and dissolved-oxygen readings to ensure collection of a representative sample.

Supply wells

If samples are to be collected from a water-supply well (see definition in NFM 4.2), select a tap (spigot) that supplies water from a service pipe connected directly to the main: do not use a tap that leaks or one that is attached to a pipe served by a cistern or storage tank (American Public Health Association and others, 1998, p. 9-19 to 9-20; Britton

and Greeson, 1989, p. 5; Bordner and Winter, 1978, p. 5-16). Avoid sampling after downhole chlorination. Dechlorination with $Na_2S_2O_3$ is required if you cannot avoid collecting the sample before the water has passed through the treatment unit (refer to Section 7.1.1).

Do not sample from leaking taps.

To sample a supply well for indicator bacteria:

1. Before collecting the sample, remove screens, filters, or other devices from the tap.
2. Before sampling, swab the inside and outside rim of the tap with ethanol. Flame sterilize the tap and allow it to dry and cool. Rinse the tap with sterile deionized or distilled water.
3. Collect a sample directly from the tap into a sterile bottle without splashing or allowing the sample bottle to touch the tap.
   - Supply wells commonly are equipped with permanently installed pumps. If the well is pumped daily, then
     (a) purge the tap water for a minimum of 5 minutes, discarding the purged water appropriately;
     (b) monitor field measurements and record stabilized values (NFM 6); and
     (c) collect the sample directly from the tap into a sterile container (described in table 7.1-4).
   - If the well is used infrequently, then
     (a) purge the tap or well of water until a minimum of three borehole volumes are purged and stable field measurements are obtained in sequential measurements (NFM 4.2 and 6.0.3.A); and
     (b) collect the sample directly from the tap into a sterile container (table 7.1-4).

Monitoring wells

If a monitoring well does not have an in-place pump, then obtain samples by using a portable sampler, such as a submersible pump or a bailer (U.S. Environmental Protection Agency, 1982). The sampling devices, as well as the sample line, must be sterilized if possible or else disinfected (table 7.1-3). If disinfected, then the sampler and sample line must be dechlorinated and rinsed with sterile deionized or distilled water. In either case, finish by flushing the sampler and sample line with native ground water before samples are collected into sterile bottles.

- Use autoclavable samplers, if possible. After flushing the sterilized pump lines with sample water, collect the sample directly into the sterile sample bottles.
- Check data-collection objectives before using a disinfectant. Disinfectants are corrosive; they can damage the metal parts of a pump, and can render the pump inadequate for trace-element sampling and other constituent sampling.
- Some sampling equipment does not require chlorine disinfection. If the water level in a well is less than 7 to 10 m (roughly 20 to 30 ft) below land surface, then a sample can be collected without contamination and without chlorine disinfection by use of a peristaltic or vacuum pump, as long as the tubing is sterile.

To disinfect a pump:

1. Submerge the pump and pump tubing in a 0.005 percent (50 mg/L) sodium hypochlorite solution prepared from household laundry bleach. Most bleach is about 5 to 7 percent sodium hypochlorite (50,000 to 70,000 mg/L), but bleach in a container that has been opened for more than 60 days before use may not be full strength. Prepare solutions fresh with each use, because concentrations will diminish with time. Add 1 mL of household laundry bleach to 900 mL of water and bring to a volume of 1,000 mL for a 0.005 percent disinfectant solution (U.S. Environmental Protection Agency, 1982, p. 253 and 1996, p. VIII-41). This concentration is sufficient for waters with a range of pH between 6 and 8 and for temperatures greater than 20°C. Outside of these ranges, a more concentrated disinfectant solution, up to 0.02 percent (200 mg/L), should be used (U.S. Environmental Protection Agency, 1982, p. 253).
2. Circulate the disinfectant through the pump and tubing for 30 minutes.
3. Afterwards, rinse the pump thoroughly with a sterile $Na_2S_2O_3$ solution. The $Na_2S_2O_3$ solution is prepared by adding 0.5 mL of a 10-percent sterile solution to every 1 L of sterile deionized or distilled water. Recirculate this solution for 5 minutes.
4. Rinse the exterior of the pump and tubing thoroughly with sterile deionized or distilled water.
5. Lower the pump carefully into the well. Purge the residual chlorine and $Na_2S_2O_3$ from the system by pumping three tubing volumes of well water through the system; contain or appropriately discard this waste water. Take care not to contaminate samples for chemical analysis with residual disinfectant or $Na_2S_2O_3$. **The pump must have a backflow check valve (an antibacksiphon device) to prevent residual disinfectant from flowing back into the well.**

The type of well, its use, construction, composition, and condition could alter samples for fecal indicator bacteria analysis.

To use a pump that cannot be disinfected:

1. Handle the pump and tubing carefully to avoid contamination. If the pump is a downhole dedicated pump, skip to step 3.
2. Collect field blanks through the sampling equipment. Lower the pump in the well to the desired intake location.
3. Purge the well with the pump used for sampling to allow the pump and tubing to be thoroughly flushed with aquifer water before sampling (NFM 4.2 and 6.0.3.A).
4. An alternative to sampling with the pump is to remove the pump after purging the well, complete the collection of other samples, and then collect the bacteria sample using a sterile bailer (U.S. Environmental Protection Agency, 1982, p. 252–253). When using the bailer method, the potential for bias exists from stirring up particulates during pump removal and bailing that would not otherwise be included in the sample.

Sampling-preparation activities, such as purging, must be carried out in such a way as to avoid contaminating the well, the equipment, or the samples. Avoid collecting surface film from the well water in the sample, and ensure that the sampler intake is within the screened interval targeted for study. Select a point-source sampler, such as a bailer with a double-check valve. Do not use a bailer unless the bailer can be sterilized.

Be aware that the type of well, its use, construction, composition, and condition can lead to alteration or contamination of samples. For example, a poor surface seal around the well opening can allow contaminants to move quickly from the land surface into the well water.

Exercise the following precautions when collecting samples from monitoring wells:

1. Avoid collecting samples from wells with casings made of galvanized materials; such casings can contain bacteriocidal metals. If samples must be collected from these types of wells, add 0.3 mL of EDTA solution per 100 mL of sample to the sample bottle prior to autoclaving. Collect the sample directly into the bottle.

2. Purge the well (see NFM 4.2 and 6.0.3.A) while monitoring field measurements. Measurements of turbidity and dissolved oxygen are especially relevant. For wells in which field measurements do not stabilize after increasing the total number of measurements, record measurements and proceed with sampling.

Quality control for ground-water sample collection. Depending on the data-quality requirements of the study, quality-control samples (field blanks and field replicates) will constitute from a small to a large percentage of the total number of samples collected over a given time period. Quality-control terms (shown below in bold type) are defined at the end of this chapter, beginning on page CF-2.

- **Field blanks**—Collect field blanks with ground-water samples at a frequency of 1 in every 10 to 20 samples, if required by data-quality objectives. Process field blanks before collecting the water sample by passing sterile buffered water through sterile sampling equipment and into a sterile sampling container. Analyze sterile buffered water for fecal indicator bacteria and record results. If no growth is observed, the use of sterile procedures is confirmed and documented.

TECHNICAL NOTE: The field blank discussed herein is equivalent to the "pump blank" described in NFM 4.3.1. Refer to NFM 4.3.1 for more information on collecting a field blank for ground-water sampling. A standpipe may be used to collect a field blank, but first must be cleaned and then disinfected. **This type of blank should be collected a week or more ahead of sampling so that results can be evaluated before field sampling.**

- **Filter blank, procedure blank**—Collect and analyze a filter blank and procedure blank to document that filtration equipment and buffered water were sterile and not subsequently contaminated by the analyst. A filter blank is processed with each sample through the filtration apparatus before the sample is filtered. A procedure blank is processed through the filtration apparatus after the sample has been filtered at a frequency of 1 in every 10 to 20 samples.

- **Field sequential replicates**—Collect and analyze one set of sequential field replicates for every 10 to 20 samples. (Usually, a single 100-mL sample is collected from ground water.) Because few ground-water samples test positive for indicator bacteria, it may be necessary to collect field replicates at a higher frequency to determine variability.

SAMPLE PRESERVATION, STORAGE, AND HOLDING TIMES

7.1.2.C

After collection, immediately chill samples in an ice chest or refrigerator at 1 to 4°C. **Do not freeze samples.** Except for samples collected from drinking-water sources, **process samples as quickly as possible, preferably within 1 hour but not more than 6 hours after sample collection for initiation of analysis for the coliform and enterococci groups** (U.S. Environmental Protection Agency, 1985, 2000a, 2000b, and 2002). Adhering to holding times minimizes changes in the concentration of indicator bacteria. For treated drinking water, do not exceed 30 hours prior to initiation of analysis. *C. perfringens* spores can survive for extended periods of time, and a 24-hour holding time is acceptable if a relation between *C. perfringens* and other fecal indicator bacteria is not part of the planned study; otherwise, observe the same holding time as for the other indicators (U.S. Environmental Protection Agency, 1996). Holding times are summarized in table 7.1-4.

C. perfringens is analyzed at the laboratory, and not in the field. Ship samples for *C. perfringens* analysis to the laboratory in a double-bagged sample container separate from any bagged ice in the ice chest. Include a chain-of-custody form with sample identification and relevant information for use by the laboratory. Information on analysis of *C. perfringens* can be accessed at http://oh.water.usgs.gov/micro/clos.html (accessed November 25, 2003).

Strictly adhere to the maximum holding-time requirements for samples. Chill at 1°C to 4°C and store samples in the dark until analysis.

7.1.3 IDENTIFICATION AND ENUMERATION METHODS

Membrane-filtration (MF) and most probable number (MPN) methods are used for the presumptive identification, confirmation, and enumeration of indicator bacteria. Procedures to analyze water samples using the MF method are described in this section. For general use, the MF method is preferable to the MPN method, with a few exceptions. The MPN method is preferred if toxic substances are present in the sample or if, after filtration, a residue heavy enough to block the micropores of the membrane filter is visible. The MPN method also is preferable for the analysis of treated drinking water. The MPN method is not typically used in the field. Instructions for the MPN method are described in "Standard Methods for the Examination of Water and Wastewater" ("Standard Methods"), 20th edition (American Public Health Association and others, 1998, p. 9-47 to 9-56) and in Britton and Greeson (1989).

Fecal indicator bacteria are operationally defined by the method employed for identification and enumeration, as shown in table 7.1-5. Presumptive identification and enumeration are made from colonies that develop on selective media after filtration of one or more sample volumes onto gridded membrane filters. Detailed confirmation, identification, and enumeration of these bacteria require additional culturing and biochemical testing, the details of which are beyond the scope of this manual. Additional confirmation methods are needed under certain circumstances, such as use of the data in support of environmental regulation and enforcement. Although all of the methods described herein are suitable for analysis of water, methods should be selected that are appropriate for the source of water. For example, methods for analyzing total coliform and *E. coli* in ground water and drinking water are different from those recommended for surface water and recreational water (table 7.1-5).

Table 7.1-5. Fecal indicator test definitions, incubation times, and incubation temperatures

[mENDO, total coliform medium; ±, plus or minus; °C, degrees Celsius; MI, total coliform and *Escherichia coli* medium; $MgCl_2$, magnesium chloride; NA-MUG, *E. coli* medium; mTEC, *E. coli* medium; mFC, fecal coliform medium; KF, fecal streptococci medium; mE, enterococci medium; EIA, enterococci medium; mEI, enterococci medium; mCP, *Clostridium perfringens* medium

Test (medium)	Typical application	Incubation time and temperature	Buffered water type
Total coliform bacteria (mENDO)	Drinking water and ground water	24 ± 2 hours at 35.0 ± 0.5°C	Phosphate-buffered water with peptone
Total coliform bacteria (MI)	Drinking water and ground water	24 ± 2 hours at 35.0 ± 0.5°C	Phosphate-buffered water with $MgCl_2$
Escherichia coli (NA-MUG)	Drinking water and ground water	4 hours at 35 ± 0.5°C after primary culture on mENDO medium	Phosphate-buffered water with peptone
Escherichia coli (MI)	Drinking water and ground water	24 ± 2 hours at 35.0 ± 0.5°C	Phosphate-buffered water with $MgCl_2$
Escherichia coli (modified mTEC)	Recreational and surface water	First resuscitate for 2 hours at 35.0 ± 0.5°C, then incubate for 22 to 24 hours at 44.5 ± 0.2°C	Phosphate-buffered saline water or phosphate-buffered water with $MgCl_2$
Escherichia coli (on urea substrate broth after primary culture on mTEC)	Recreational and surface water	First resuscitate for 2 hours at 35.0 ± 0.5°C, and then incubate for 22 to 24 hours at 44.5 ± 0.2°C After 22 to 24 hours, transfer filter to urea substrate broth for 15 to 20 minutes before counting	Phosphate-buffered saline water or phosphate-buffered water with $MgCl_2$
Fecal coliform bacteria (mFC)	All waters	24 ± 2 hours at 44.5 ± 0.2°C	Phosphate-buffered water with peptone
Fecal streptococci (KF)	All waters	48 ± 2 hours at 35.0 ± 0.5°C	Phosphate-buffered water with peptone
Enterococci (mE and EIA)	All waters, but primarily recreational waters	48 to 50 hours at 41.0 ± 0.5°C on mE medium. Transfer filter to EIA medium for 20 minutes at 41.0°C before counting	Phosphate-buffered saline water or phosphate-buffered water with $MgCl_2$
Enterococci (mEI)	All waters, but primarily recreational waters	24 hours at 41.0°C ± 0.5°C	Phosphate-buffered saline water or phosphate-buffered water with $MgCl_2$
Clostridium perfringens (mCP)	All waters	24 ± 2 hours at 44.5 ± 0.2°C	Phosphate-buffered water with $MgCl_2$

7.1.3.A CULTURE MEDIA AND REAGENTS

MF analysis requires the use of several types of culture media and reagents, the types being dependent on the indicator bacteria and method. The necessary media and reagents include sterile buffered water, agar- or broth-based selective and differential growth media, and media and reagents for additional biochemical identification. **The preparation of selective and differential culture media for indicator bacteria is an important part of analysis. Adhering to proper preparation, storage, and holding-time requirements will help ensure the quality of the analysis.** Instructions for the preparation of 100 mL of primary culture media for MF tests and additional confirmation media or broth for three MF confirmation tests are described in section 7.1.5, "Instructions for Media Preparation."

Sterile buffered water (distilled or deionized water that has been buffered and autoclaved)[4] is used to dilute samples and to rinse the membrane-filter apparatus and utensils. USGS personnel can purchase sterile buffered water from the Ocala Water Quality and Research Laboratory in Ocala, Fla. (OWQRL or Ocala Laboratory). Sterile buffered water is provided in 250-mL bottles and in 99-mL dilution bottles. Three types of buffered water are available: (1) phosphate-buffered water with peptone, (2) phosphate-buffered saline water, and (3) phosphate-buffered dilution water with magnesium chloride ($MgCl_2$). Table 7.1-5 provides information on the types of buffered water to use with various types of media. **Buffered water that exceeds the expiration date indicated on the label should not be used.** Buffered water not obtained from the Ocala Laboratory should be prepared and autoclaved ahead of time. Instructions for preparing sterile buffered water are described in Britton and Greeson (1989, p. 18).

Culture media for enumeration of fecal indicator bacteria for USGS studies are provided in kits from the Ocala Laboratory. These kits include instructions for media preparation. Dehydrated media also can be purchased from scientific suppliers.

[4]Sterile buffered water is described in Britton and Greeson (1989, p. 18), "Standard Methods" (American Public Health Association and others, 1998, p. 9-18), and USEPA (1996, 1997, 2000a, 2000b),

To store media and reagents:

1. Store media kit (supplied by the Ocala Laboratory) or dehydrated, commercially prepared media in a desiccator. Store other reagents in a dust-free laboratory cabinet (not in a field vehicle).
2. Label all media with the date received, date opened, and analyst's initials. Discard media and reagents that have an expired shelf life.
3. Refrigerate reagents when necessary. When diluting a sample, use the sterile buffered water immediately after opening the bottle and discard any remainder.
4. Label all prepared petri dishes to identify the media type, the preparation date, and the analyst.
5. Store prepared petri dishes upside down in a plastic bag and refrigerate before use.

Quality control for culture media and reagents. Supplies of dehydrated media purchased either from the Ocala Laboratory or through established vendors of scientific supplies have been quality-control tested. Each batch of media that is prepared from basic ingredients by the analyst also must be quality-control tested. If sterile buffered water is prepared by the user, it should be prepared under laboratory conditions. In addition, quality-control procedures must be used to ensure that the sterile buffered water will produce a suitable medium for transfer of bacteria from samples to filters. To test the sterility of the buffered water, collect 100-mL blank samples and process them along with each set of environmental samples. Use the quality-control procedures applicable to microbiological testing found in the 20th edition of "Standard Methods" (American Public Health Association and others, 1998, p. 9-18).

If field work is conducted on a daily or weekly schedule, then analyze a **positive control** and **negative control** at least quarterly, when media are prepared from basic ingredients by field personnel. Analyze positive- and negative-control samples annually if sampling is performed intermittently. The positive-control sample tests the ability of the medium and reagents to support growth of the target microorganism. Negative-control samples are used to ensure that the test does not support the growth of nontarget organisms. Additional detailed information on positive and negative controls can be found in the 20th edition of "Standard Methods" (American Public Health Association and others, 1998, p. 9-10).

7.1.3.B MEMBRANE-FILTRATION METHOD

After collecting the sample and selecting the appropriate sample volumes, label the petri dish with the station number (or other site identifiers), the volume of sample filtered, and the date and time of sample collection. Select those sample volumes that are anticipated to yield one or two filters in the ideal colony count range.

> **TECHNICAL NOTE:** It is useful to review the historical data for each site to help determine the number of sample volumes to be filtered. Where past analyses of samples from a site have shown a small variation in the number of fecal indicator bacteria, the filtration of as few as three or four different sample volumes may suffice. However, where past analyses have shown the variation to be large or where the variation is not known, filtering five or more different sample volumes is recommended.

Always wear laboratory gloves when processing samples for fecal-indicator analysis.

To prepare to filter samples and make colony counts:

1. When collecting and processing samples, work inside the field vehicle, if possible, and out of direct sunlight and wind.
2. Prevent contamination of the work area. Before and after processing the samples, clean counter tops in field vehicles with an antibacterial cleaning solution, such as a 7-percent phenolic solution; 50- to 70-percent isopropyl or ethyl alcohol; 5-percent bleach; or a 7-percent ammonia solution.

3. Before beginning analysis, preheat incubators for at least 2 hours, according to specifications for each test (table 7.1-5). Portable heater-block incubators must not be left in closed, unventilated vehicles when the outside air temperature is less than 15°C (60°F) or greater than 37°C (98°F).

4. Using sterile equipment, collect field, filter, and procedure blank samples.

   - One or more colonies on the field or filter blank indicates inadequate sterilization of either the equipment or the sterile buffered water or contamination during the sampling and analysis process.
   - One or more colonies on the procedure blank indicates either inadequate rinsing or contamination of the equipment or the buffered water during sample processing.

To filter samples and make colony counts:

1. Select sample volumes (table 7.1-6, fig. 7.1-2) to provide at least one filter having colonies in the ideal counting range. The ideal range and number of sample volumes to filter depend on the test and the expected bacterial concentrations.

   - Record the site name, date, time of sample collection, and sample volume on the petri dish and on the record sheet or field form. Record the time of sample processing on the record sheet or field form.
   - Label replicates, blanks, filter blanks, and procedure blanks and other quality-control samples.

2. Assemble filtration equipment by inserting the base of the filter-holder assembly into a flask or manifold (fig. 7.1-3). Draw a vacuum by use of a hand-held pump, vacuum pump, or battery-operated peristaltic pump. If flame sterilization is used, rinse the inside of the filtration apparatus with sterile buffered water to remove any residue of formaldehyde.

Table 7.1-6. Recommended sample volumes for membrane-filter analyses based on ideal colony count and concentration range

[col/100 mL, colonies per 100 milliliters; mL, milliliters; <, less than value shown; >, greater than value shown]

Ideal colony-counting ranges for number of colonies per membrane filter within a range of concentrations from <1 to 2,000,000 col/100 mL

20–60 colonies

Sample volume (mL)[1]	Added as (mL)[2]	Concentration range
100	100	<1–60
30	30	60–200
10	10	200–600
3.0	3.0	600–2,000
1.0	1.0	2,000–6,000
.3	3.0 of a 1:10 dilution	6,000–20,000
.1	1.0 of a 1:10 dilution	20,000–60,000
.03	3.0 of a 1:100 dilution	60,000–200,000
.01	1.0 of a 1:100 dilution	200,000–600,000
.003	3.0 of a 1:1,000 dilution prepared by diluting 11 mL of a 1:100 in 99 mL[1]	600,000–2,000,000

20–80 colonies

Sample volume (mL)[1]	Added as (mL)[2]	Concentration range
100	100	<1–80
25	25	80–320
6.0	6.0	330–1,300
1.5	1.5	1,300–5,300
.4	4.0 of a 1:10 dilution	5,000–20,000
.1	1.0 of a 1:10 dilution	20,000–80,000
.025	2.5 of a 1:100 dilution	80,000–320,000
.006	6.0 of a 1:1,000 dilution prepared by diluting 11 mL of a 1:100 in 99 mL[1]	330,000–1,300,000

20–100 colonies

Sample volume (mL)[1]	Added as (mL)[2]	Concentration range
100	100	<1–100
20	20	100–500
5.0	5.0	400–2,500
1.0	1.0	2,000–10,000
.2	2.0 of a 1:10 dilution	10,000–50,000
.05	5.0 of a 1:100 dilution	50,000–200,000
.01	1.0 of a 1:100 dilution	200,000–1,000,000

[1] All sample volumes less than 1.0 mL require dilution in a 99-mL dilution bottle containing sterile buffered water.

[2] Sample volumes smaller than those indicated may be needed when bacterial concentrations are greater than those listed.

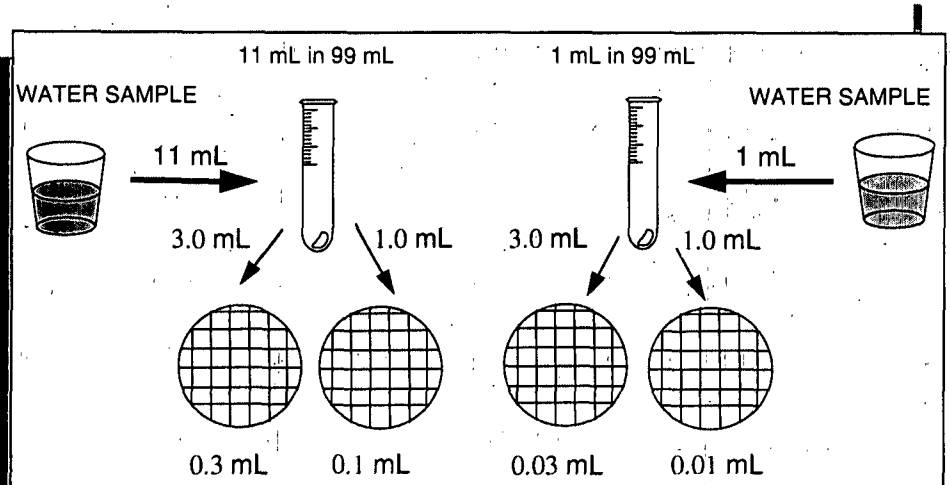
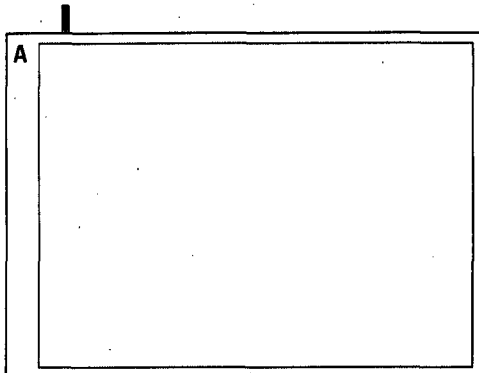
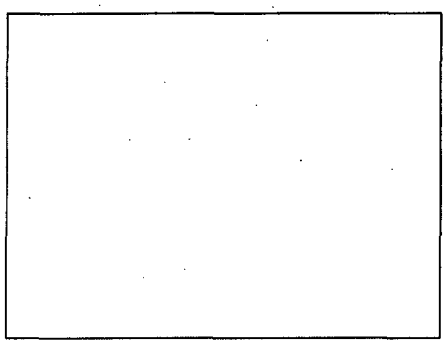
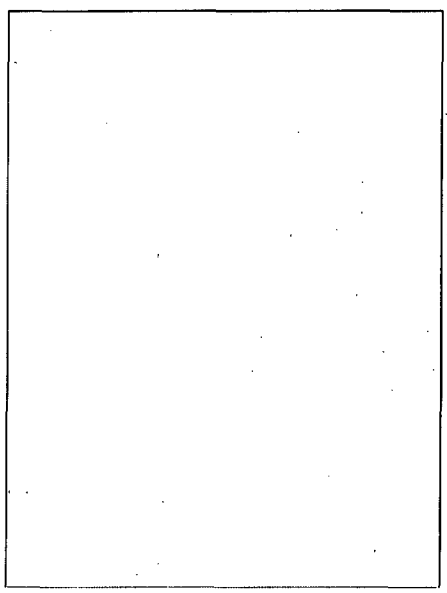


Figure 7.1-2. Preparation of sample volumes by dilution.

3. Sterilize stainless steel forceps:
   a. Immerse tips in a small bottle or flask containing 70- or 90-percent ethanol.
   b. Pass forceps through the open flame of an alcohol burner. Allow the alcohol to burn out and allow the forceps to cool for several seconds to prevent heat damage to the membrane filter.
   c. Resterilize forceps before each use. Return cooled forceps to alcohol container between transfers. **Do not set forceps on the countertop.**
4. Remove the sterilized funnel from the base. Always hold the funnel in one hand while placing or removing the membrane filter. (Placing the funnel on anything other than the filter apparatus might result in contamination of the funnel.) Using sterile forceps, place a sterile, gridded membrane filter (47 mm (millimeters)) on top of the filter base, gridded side up (fig. 7.1-3). Be sure to use the correct pore-size membrane filter for the test procedure (table 7.1-7).
5. Carefully replace and secure the filter funnel on the filter base. Avoid tearing or creasing the membrane filter.
   Quality control. Rinse the funnel with 100 mL of sterile buffered water before filtering sample volumes to obtain a filter blank.





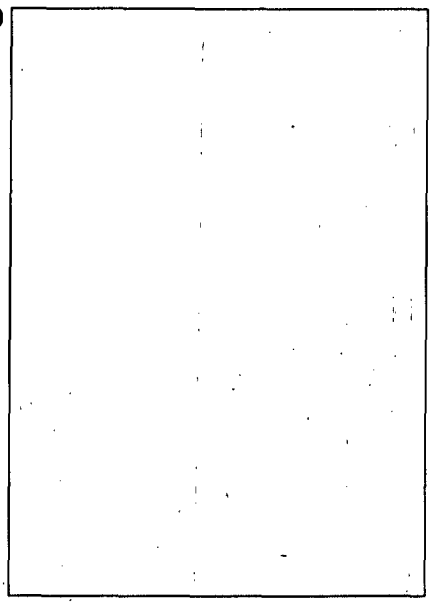


PROCEDURE

1. Preheat the incubator; prepare work areas.
2. Select sample volumes. If needed, prepare dilutions for filtration of sample volumes less than 1.0 mL (tables 7.1-6 and 7.1-8; and figure 7.1-2).
3. Label petri dishes.
4. Assemble sterile filtration apparatus.
5. Place sterile filter on filtration apparatus using sterile forceps (**A**).
6. Shake sample 25 times and deliver to filtration apparatus by use of graduated cylinder (**B**) or pipet (**C**). Add 20 mL sterile buffered water to filtration apparatus before filtering sample volumes less than 10 mL.
7. Apply vacuum; afterwards, rinse filtration apparatus and cylinder twice with sterile buffered water.

Figure 7.1-3. Steps in membrane-filtration procedure.

D



PROCEDURE

8. Sterilize forceps and remove filter (**D**). Replace funnel on filtration *apparatus.*

9. Roll filter onto media in petri dish (**E**). Place inverted petri dish in *incubator.*

10. Repeat steps 4-9 for each sample volume in order of the smallest to the largest volume. A filter blank is processed before each sample. Filter a procedure blank after every 10 to 20 samples or once per day at each site, according to study objectives.

11. Filter a replicate sample after every 10 to 20 samples or at each site, according to study objectives.

E

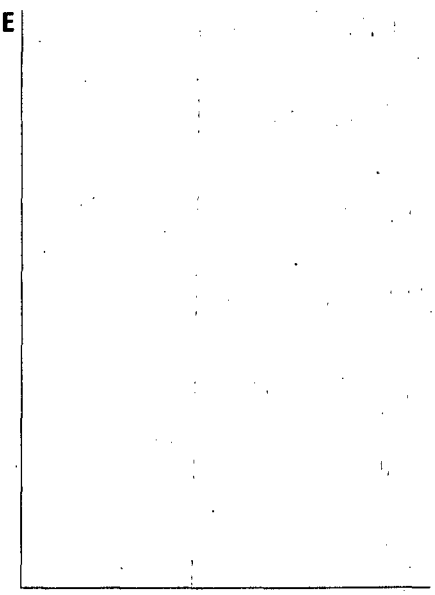


Figure 7.1-3. Steps in membrane-filtration procedure—*Continued.*

Table 7.1-7. Membrane-filter pore sizes for fecal indicator bacteria tests

Test	Pore size of membrane filter (in micrometers)
Total coliform	0.45
Fecal coliform	0.45 or 0.65
Escherichia coli	0.45
Fecal streptococci	0.45
Enterococci	0.45
Clostridium perfringens	0.45

6. Filter the sample in order of smallest to largest sample volume. If the sample volume is less than 1.0 mL, prepare dilutions with sterile buffered water in a 99-mL dilution bottle and transfer the appropriate volume of dilution to the membrane filter (fig. 7.1-2 and table 7.1-8).
   - When preparing dilutions, use a sterile pipet to measure each sample volume.
   - After each sample-volume transfer, close and shake the dilution bottle vigorously at least 25 times.
   - **Filter the diluted samples within 20 minutes after preparation.** Keep dilution bottles out of sunlight and do not transfer less concentrated sample volumes with pipets that were used to transfer concentrated sample volumes.
7. Shake the sample vigorously at least 25 times before each sample volume is withdrawn in order to break up particles and to ensure an even distribution of indicator bacteria in the sample container.
   a. Pour or pipet the shaken sample into the filter funnel within 5 seconds (fig. 7.1-3*B* or *C*). Pipet the sample from the center of the sample volume. You can use the upper and lower graduations (line-to-line) to measure the volume. Proceeding from smallest to largest sample volume, deliver the sample volume to the membrane filter by use of a pipettor or pipet bulb with a valve for volume control.

- **If the volume of sample to be filtered is from 1 to 10 mL,** pour about 20 mL of sterile buffered water into the funnel before pipetting the sample to facilitate distribution of bacteria on the membrane filter.
- **If the volume of sample to be filtered is more than 10 mL,** transfer the sample with a sterile pipet or graduated cylinder directly into the funnel.

b. Allow the pipet to drain, touching the pipet to the inside of the funnel to remove remaining sample (fig. 7.1-3*C*). However, if a serological pipet is used, a small amount of liquid will remain in the tip after the liquid is dispensed. Gently force out the remaining liquid using a pipettor or pipet bulb, taking care not to produce an aerosol by blowing out the pipet too forcefully.

CAUTION: Do not pipet by mouth.

Table 7.1-8. Preparation guidelines for dilution of samples to volumes less than 1.0 milliliter for fecal indicator bacteria analysis

[mL, milliliter]

Dilution factor	Volume (mL) of sample added to 99 mL sterile dilution water	To obtain this dilution, filter this volume
1:10	11.0 mL of original sample	for 0.3, use 3.0 mL of 1:10 for 0.1, use 1.0 mL of 1:10
1:100	1.0 mL of original sample	for 0.3, use 30 mL of 1:100 for 0.1, use 10 mL of 1:100 for 0.03, use 3.0 mL of 1:100 for 0.01, use 1.0 mL of 1:100
1:1,000	1.0 mL of 1:10 dilution	for 0.003, use 3.0 mL of 1:1,000 for 0.001, use 1.0 mL of 1:1,000

8. Apply a vacuum with a hand, peristaltic, or vacuum pump. **To avoid damage to bacteria, do not exceed a pressure of about 5 lb/in^2 (pounds per square inch) (25 cm of mercury).**

9. Rinse the inside of the funnel twice with 20 mL to 30 mL of sterile buffered water while applying a vacuum. If a graduated cylinder is used, rinse the cylinder with sterile buffered water and deliver rinse water to the filtration apparatus.

10. Remove the funnel and hold it in one hand—do not set the funnel on the counter top. Remove the membrane filter using sterile forceps (fig. 7.1-3*D*). Release the vacuum. (Releasing the vacuum after removing the filter prevents backflow of sample water onto the filter. Unnecessarily wet filters promote confluent growth of colonies and poor results.) Replace funnel on filter base.

11. Open a petri dish and place the membrane filter on the medium, grid side up, and starting at one edge by use of a rolling action (fig. 7.1-3*E*). Avoid trapping air bubbles under the membrane filter. If air is trapped, use sterile forceps to remove the membrane filter and roll it onto the medium again. **Do not expose prepared petri dishes to direct sunlight.**

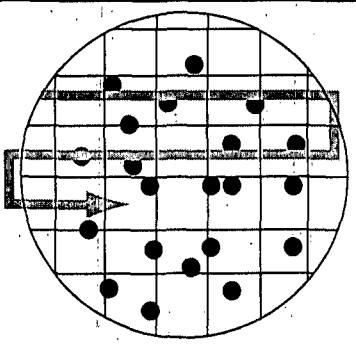
12. Close the petri dish by pressing the top firmly onto the bottom. Invert the petri dish. Incubate within 20 minutes to avoid growth of interfering microorganisms.

13. Continue to filter the other sample volumes in order, from smallest to largest volume. Record on the field forms the volumes filtered and the time of processing.
    Quality control. After filtrations are complete, place a sterile, gridded-membrane filter onto the funnel base and rinse the funnel with 100 mL of sterile buffered water to obtain a procedure blank. Procedure blanks are analyzed at a frequency of 1 in every 10 to 20 samples.

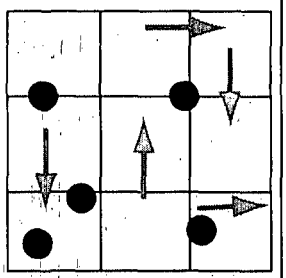
14. Place the inverted petri dishes into a preheated aluminum heater-block or into water-tight plastic bags and then into a water-bath incubator. Incubate at the prescribed times and temperatures (table 7.1-5). Wash, then flame sterilize or autoclave filter apparatus before the next use. Wash counter top between each sample with an antibacterial cleaning solution (see "To prepare to filter samples and make colony counts" in this section). Wash hands with bacteriocidal soap.

Quality control. Verify the incubator temperature on a regular schedule against a National Institute of Standards and Technology (NIST) thermometer or thermometer certified to a NIST thermometer. Record results in a logbook with the date and analyst's name. Do not use incubators that fail to meet temperature criteria until they are repaired or the problem is corrected.

15. After the prescribed length of incubation, remove the petri dishes from the incubator. For each sample volume filtered, count and record on the field forms the number of typical colonies (table 7.1-9). **Recount the colonies until results agree within 5 percent, and record the results.** Recounting is accomplished by turning the plate 90 degrees to obtain a slightly different angle. Count by use of a preset plan (a side-to-side pattern along grid lines is suggested; fig. 7.1-4). Count the colonies with the aid of 5 to 15 magnification and a fluorescent illuminator or other light source placed directly above the filter.



Count with a preset pattern along grid lines as indicated by the arrow (count top to bottom by rows)



Expanded view turned 90 degrees (count left to right by columns)

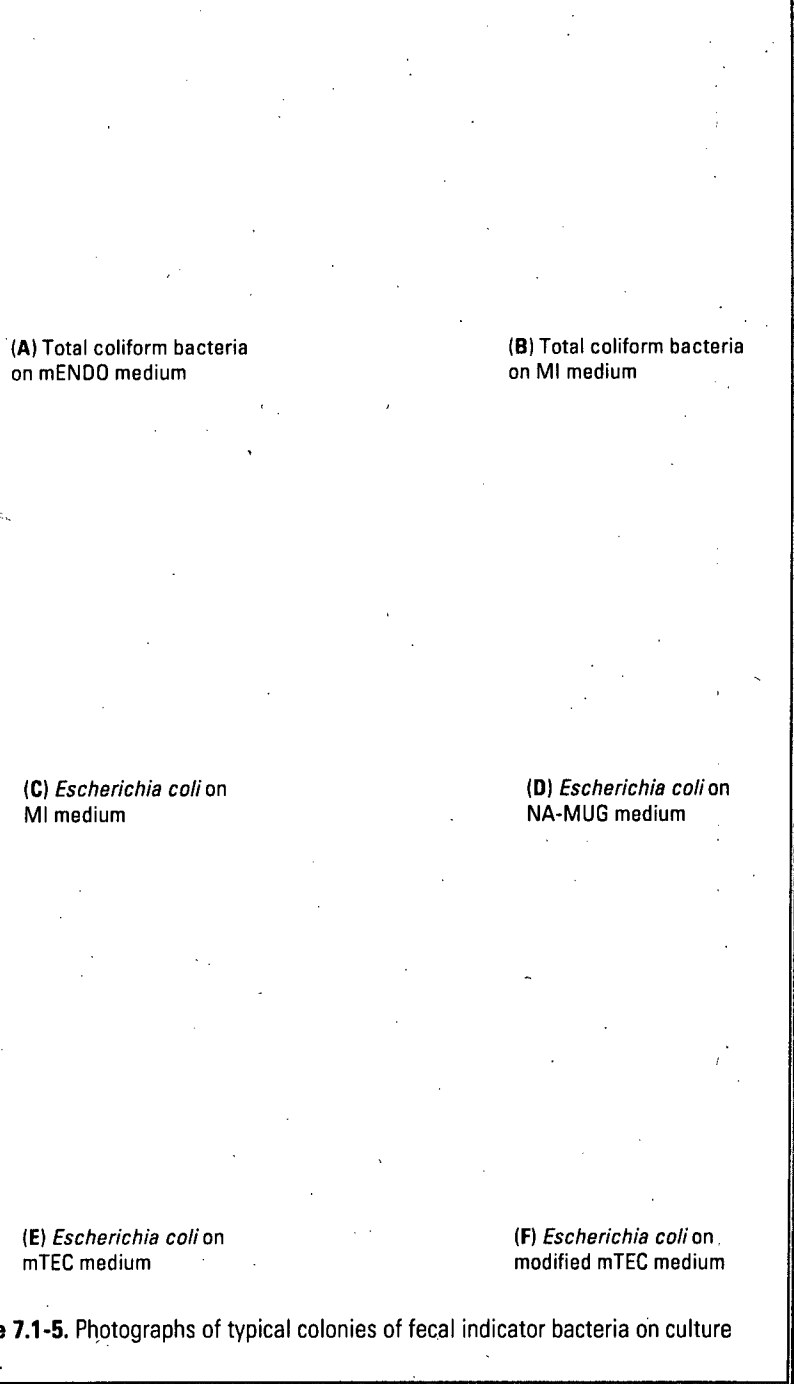
Figure 7.1-4. Method for counting colonies on gridded membrane filters.

- For total coliform colonies on mENDO medium, enhance sheen production by removing filters from media and placing them on absorbent pads to dry for at least 1 minute before counting (fig. 7.1-5*A*).
- For total coliform on MI medium, count under a long-wave ultraviolet light in a completely darkened room (U.S. Environmental Protection Agency, 2000a) or in a viewing box (fig. 7.1-5*B*).
- For *E. coli* on MI medium, count under natural light (with magnification) (fig. 7.1-5*C*).
- If the NA-MUG test is done for *E. coli*, transfer the total coliform filter onto NA-MUG petri dishes and incubate for 4 hours at 35°C. Afterwards, count under a long-wave ultraviolet light in a completely darkened room (U.S. Environmental Protection Agency, 1991b) or in a viewing box (fig. 7.1-5*D*).
- For *E. coli* on mTEC medium, transfer the filter to a filter pad saturated with urea-phenol reagent; count only yellow colonies after 15 to 20 minutes at room temperature (U.S. Environmental Protection Agency, 1985; fig. 7.1-5*E*).
- For *E. coli* on modified mTEC medium, count colonies directly from the petri dish under natural light (fig. 7.1-5*F*).
- For fecal coliform on mFC medium and fecal streptococci on KF medium, count colonies, using magnification, under fluorescent or incandescent light (fig. 7.1-5*G* and *H*, respectively).
- For enterococci on mE medium, transfer the filter to EIA medium after incubation for 20 minutes at 41°C; count colonies from the underside of the petri dish placed over a fluorescent illuminator (fig. 7.1-5*I*).
- For enterococci on mEI medium, count colonies directly from the petri dish under fluorescent or incandescent light (fig. 7.1-5*J*).
- For *C. perfringens* on mCP medium, count colonies directly from the petri dish under magnification, and under fluorescent or incandescent light (7.1-5*K*).

16. Check quality-control blanks for colony growth, and report results on the field forms. The presence of colonies on blanks indicates that results of the bacterial analyses are suspect and should not be reported or the results should be clearly qualified. It is not valid to subtract colony counts on blanks from results calculated for samples. Discard sample results bracketed by contaminated blanks.
Quality control. A second analyst should recount the colonies on the petri dishes and record the results for 1 in every 20 samples. Table 7.1-9 and figure 7.1-5 contain information on colony identification.

17. Calculate the number of colonies per 100 mL of sample as described in section 7.1.4, "Calculation and Reporting of Fecal Indicator Bacteria."

18. Put all petri dishes to be discarded into an autoclavable bag. Freeze or chill any petri dishes to be discarded until they can be autoclaved in the laboratory. **Autoclave all cultures at 121°C for a minimum of 30 minutes before discarding.**



(A) Total coliform bacteria on mENDO medium

(B) Total coliform bacteria on MI medium

(C) *Escherichia coli* on MI medium

(D) *Escherichia coli* on NA-MUG medium

(E) *Escherichia coli* on mTEC medium

(F) *Escherichia coli* on modified mTEC medium

Figure 7.1-5. Photographs of typical colonies of fecal indicator bacteria on culture media.

(G) Fecal coliform bacteria *on mFC medium*

(H) Fecal streptococci *bacteria on KF medium*

(I) Enterococci bacteria on EIA medium

(J) Enterococci bacteria on mEI medium

(K) *Clostridium perfringens* on mCP medium

Figure 7.1-5. Photographs of typical colonies of fecal indicator bacteria on culture media—*Continued.*

Table 7.1-9. Test (medium type), ideal colony count, and typical colony color, size, and morphology for indicator bacteria colonies

[m-ENDO, total coliform medium; mm, millimeters; MI, total coliform and *Escherichia coli* medium; nm, nanometer; NA-MUG, *Escherichia coli* medium; mTEC, *E. coli* medium; mFC, fecal coliform medium; KF, fecal streptococcus medium; mE, enterococcus medium; EIA, enterococcus confirmation medium; mEI, enterococci medium; mCP, *Clostridium perfringens* medium]

Test (medium type)	Ideal count range (colonies per filter)	Typical colony color, size, and morphology
Total coliform bacteria (mENDO)	20 to 80	Colonies are round, raised, and smooth; 1 to 4 mm in diameter, and red with a golden-green metallic sheen.
Total coliform bacteria (MI)	20 to 80	Colonies are blue white, blue green, or blue green with fluorescent halos under long-wave ultraviolet light (366 nm); 1 to 3 mm in diameter. Count under a long-wave ultraviolet lamp in a completely darkened room.
Escherichia coli After primary culture as total coliform colonies on mENDO (NA-MUG)	Much fewer in number than total coliforms on the same filter	Colonies are cultured on m-ENDO media as total coliform colonies. After incubation on NA-MUG, colonies have blue fluorescent halos with a dark center. Count under a long-wave ultraviolet lamp at 366 nm in a completely darkened room.
Escherichia coli (mTEC)	20 to 80	Colonies are round, raised, and smooth; 1 to 4 mm in diameter, remain yellow to yellow brown after urease test; may have darker raised centers.
Escherichia coli (modified mTEC)	20 to 80	Colonies are round, raised, and smooth; 1 to 4 mm in diameter, deep pink to magenta.
Escherichia coli (MI)	Much fewer in number than total coliforms on the same filter	Colonies are blue under ambient light, and blue green with or without fluorescent edges under long-wave ultraviolet light (366 nm); 1 to 3 mm in diameter.
Fecal coliform bacteria (mFC)	20 to 60	Colonies are round, raised, and smooth with even to lobate margins; 1 to 6 mm in diameter, and light to dark blue in whole or part. Some may have brown or cream-colored centers.
Fecal streptococci (KF)	20 to 100	Colonies are small, raised, and spherical; about 0.5 to 3 mm in diameter; glossy pink or red.
Enterococci (mE and EIA)	20 to 60	Colonies are round, smooth, and raised; 1 to 6 mm in diameter; pink to red with a black or red dish-brown precipitate on underside.
Enterococci (mEI)	20 to 60	Colonies have blue halos regardless of colony color; 1 to 6 mm in diameter. Count under a fluorescent lamp.
Clostridium perfringens (mCP)	20 to 80	Colonies are round and straw yellow before exposure to ammonium hydroxide, dark pink to magenta afterward; 1 to 4 mm in diameter.

CALCULATION AND REPORTING OF FECAL INDICATOR BACTERIA 7.1.4

The range of ideal colony counts depends on the fecal indicator group to be enumerated (table 7.1-9). Crowding and insufficient media to support full development of colonies can result if the bacterial concentration on the filter exceeds the upper limit of the ideal range. The lower limit of the ideal range is set as a number below which statistical validity becomes questionable (Britton and Greeson, 1989, p. 14). For potable waters, results are routinely reported from counts of less than 20 colonies per filter. Consult table 7.1-9 and figure 7.1-5 for information on typical colony color, size, and shape. The computation for concentration is the sum of the colony counts for each sample volume, multiplied by 100, and divided by the sum of the sample volumes.

- Enumeration results for the membrane-filtration method are expressed as a concentration in units of col/100 mL.
- Whole numbers are reported for results less than 10, and two significant figures are reported for results greater than or equal to 10.

Parameter codes for use in reporting fecal indicator bacteria in the USGS National Water Information System are listed in Appendix A7-A, table 2.

Examples of scenarios that are commonly experienced when counting colonies are presented in the following five cases:

Case 1. Ideal colony counts.

Case 2. Colony counts less than or greater than the ideal range but not zero or too numerous to count.

Case 3. No typical colonies on any of the filters.

Case 4. Less than the ideal range, including some zero counts but no filters with colonies that are too numerous to count.

Case 5. Colony counts on all filters are too numerous to count.

Case 1: Ideal colony counts.

Example 1: Ideal colony count on one filter

Sample volume	Colony count
6.0	7 (do not use)
25	21
100	101 (do not use)
Sum 25	21

col/100 mL = (21 x 100) / 25 = 84

Example 2: Ideal colony counts on two or more filters

Sample volume	Colony count
6.0	7 (do not use)
25	21
100	58
Sum 125	79

col/100 mL = (21 + 58) x 100 / (100 + 25) = 63

Example 3: If dilutions of the original sample were made before filtration (sample volumes less than 1 mL), calculate the volume (in mL) of original sample as follows: (TNTC, Too Numerous To Count)

Sample volume	Colony count
0.1 (1:10)	50
0.3 (3:10)	TNTC (do not use)
1.0	TNTC (do not use)
Sum 0.1	50

Colony count = 50

Volume of original sample = 0.1 mL

Volume of diluted sample = 1.0 mL

col/100 mL = 50 x 100 / 1 x 0.1 = 50,000

Case 2: Colony counts less than or greater than the ideal range but not zero or TNTC (Too Numerous To Count).

Results are reported with the statement,
"Estimated count based on non-ideal colony count."

Example 1: Less than the ideal range on all filters

Sample volume		Colony count
3.0		2
10		6
30		18
Sum	43	26

col/100 mL = (2 + 6 + 18) x 100 /(3 + 10 + 30) = 60

Example 2: Either greater than or less than the ideal range

Sample volume		Colony count
4		18
20		101
100		TNTC (do not use)
Sum	24	119

col/100 mL = (18 + 101) x 100 / (4 + 20) = 500

Case 3: No typical colonies on any of the filters.

Assume a colony count of one on the filter with the largest sample volume.

Result is reported as less than the calculated number per 100 mL. It is a maximum estimated number.

Sample volume		Colony count
3.0		0 (do not use)
10		0 (do not use)
30		assume 1
Sum	30	1

col/100 mL = (1 x 100) / 30 = < 3

Case 4: Less than the ideal range—including some zero counts—and no filters with colonies that are TNTC (Too Numerous To Count).

The result is reported as "Estimated count based on non-ideal colony count."

Sample volume	Colony count
3.0	0 (do not use)
10	0 (do not use)
30	5
Sum 30	5

col/100 mL = 5 x 100 / 30 = 17

Case 5: Colony counts on all filters are TNTC.

Assume maximum ideal count on filter with the smallest volume filtered.

Result is reported as greater than the calculated number per 100 mL. It is a minimum estimated number.

Sample volume	Colony count
3.0	TNTC (assume 60)
10	TNTC (do not use)
30	TNTC (do not use)
Sum 3	60

col/100 mL = 60 x 100 / 3 = >2,000

INSTRUCTIONS FOR MEDIA PREPARATION 7.1.5

1. mENDO medium for total coliform analysis.

   a. Empty the vial containing 4.8 g of dehydrated mENDO medium into a 250-mL flask and add 100 mL of a 2-percent ethanol solution.

   b. Stir the mixture well for several minutes to break up clumps and prevent agar from adhering to the flask.

   c. Place foil-covered flask in a heated water bath or on a hot plate and heat slowly to boiling. If using a hot plate, stir the mixture constantly or use a stir bar and magnetic stirring hot plate to prevent scorching. **Do not autoclave.**

   d. When medium reaches the boiling point, promptly remove from the heat. **Do not boil.**

   e. Cool the medium to a temperature of about 50°C and pour 6 to 7 mL into 50-mm petri-dish bottoms. Quickly place petri-dish tops loosely onto the bottoms to allow condensation to escape.

   f. When the medium has solidified (about 10 minutes), close the petri dishes by pressing firmly on the tops. The plates are suitable for use after the medium has solidified. About 15 to 20 plates can be prepared from 100 mL of medium. **Label and date the petri dishes.**

   g. Petri dishes that are not used immediately after preparation should be placed into small plastic bags to prevent drying and stored in darkness in a refrigerator for a **maximum of 5 days.**

2. NA-MUG medium for confirmation of *E. coli* after primary culturing of total coliform bacteria with mENDO medium.

   a. Add 2.3 g of NA-MUG medium to 100 mL of deionized or distilled reagent-grade water in a 250-mL flask.

   b. Stir the mixture well for several minutes to break up clumps and prevent medium from adhering to the flask.

   c. Place the flask into a heated water bath or on a hot plate and heat slowly to boiling. If using a hot plate, stir the mixture constantly or use a stir bar and magnetic stirring hot plate to prevent scorching.

   d. Autoclave at 121°C and 15 lb/in^2 for 15 minutes. Allow to cool to 44-46°C, or when the flask is cool enough to pick up barehanded.

   e. Pour 6 to 7 mL of medium into the bottom of a 50-mm petri dish. About 15 to 20 plates can be prepared from 100 mL NA-MUG medium. Quickly place petri-dish tops loosely onto the bottoms to allow condensation to escape.

   f. When the medium has solidified (about 10 minutes), close petri dishes by pressing firmly on the tops. The plates are suitable for use after the medium has solidified. Label and date the plates. Prepared petri dishes that are sealed in small plastic bags to prevent drying can be **stored in a refrigerator for up to 2 weeks**.

3. MI medium for total coliform bacteria and *E. coli* analysis.

   Commercial medium may be available; if so, prepare according to instructions. If not, prepare fresh medium in the laboratory prior to departing for the field site. Information on reagents and media preparation can be obtained from the U.S. Environmental Protection Agency (2000a).

   a. Prepare fresh agar according to U.S. Environmental Protection Agency (2000a) by weighing and adding 36.52 g of the combined reagents to 900 mL of reagent-grade deionized or distilled water. Mix to break up clumps. Adjust the volume to 1,000 mL. If dehydrated medium is used, add 36.52 g of dehydrated MI medium to 1 L of reagent-grade deionized or distilled water in a flask and heat to boiling until the ingredients dissolve. This volume will produce approximately 200 petri dishes. To prepare fewer, proportionately reduce the quantities of reagents and volume of deionized or distilled water.

   b. Prepare Cefsulodin (which is added to the MI medium after the medium is autoclaved and cooled). To prepare Cefsulodin solution, add 0.02 g of Cefsulodin to 20 mL of reagent-grade deionized or distilled water, sterilize the Cefsulodin solution by aseptically filtering through a disposable, sterile 0.22-µm-pore-size syringe filter. Store in a sterile tube in the refrigerator at about 5°C until needed. Prepare fresh solutions each time the test is used. Do not save any unused portion. Write the preparation date on the tube.

   c. Dispense MI medium into 100-mL dilution bottles. Autoclave the medium for 15 minutes at 121°C, then cool in a 50°C water bath.

   d. Allow the medium to cool to 45–50°C. Add 0.5 mL of freshly prepared Cefsulodin solution to each dilution bottle of tempered agar medium. The final pH should be 6.95 ± 0.2. Store medium in dilution bottles for up to 6 months in the refrigerator (about 5°C). Prepare petri dishes as needed from individual bottles of medium.

e. When ready to prepare petri dishes, melt the medium by autoclaving dilution bottles containing modified mTEC medium for 5 minutes at 121°C or by placing them in a boiling water bath. Cool the medium to 45–50°C. Pour 6 to 7 mL of the medium into each 50-mm petri dish. Be sure to loosen the screw tops on the bottles prior to heating to allow air to escape.

f. When the medium has solidified (about 10 minutes), close the petri dishes by pressing firmly on the tops. These dishes are suitable for use after the medium has solidified. About 15 to 20 plates can be prepared from 100 mL of medium.

g. Label and date the petri dishes. Prepared petri dishes, sealed in small plastic bags to prevent drying, can be **stored in a refrigerator for up to 2 weeks.**

h. All freshly prepared medium must be quality-control checked by the preparing laboratory through the use of positive and negative controls. Refer to "Standard Methods" (American Public Health Association and others, 1998, p. 9-1 to 9-78) for instructions.

4. mTEC medium for *E. coli* analysis.

a. Empty the vial containing 4.53 g of dehydrated mTEC medium into 100 mL of deionized or distilled water in a 250-mL flask.

b. Stir this mixture for several minutes to break up clumps. Make sure that none of the medium adheres to the bottom or side of the flask.

c. Place the flask containing the medium solution in a heated water bath or on a hot plate and begin heating slowly to boiling. If using a hot plate, stir the mixture constantly or use a stir bar and magnetic stirring hot plate to prevent scorching. After boiling begins, remove the flask from the hot plate or boiling water bath and autoclave at 121°C and 15 lb/in^2 for 15 minutes. Allow to cool to 45–50°C.

d. Pour 6 to 7 mL of the medium into 50-mm petri-dish bottoms. Quickly place the petri-dish tops loosely onto the bottoms to allow condensation to escape.

e. When the medium has solidified (about 10 minutes), close the petri dishes by pressing firmly on the tops. These plates are suitable for use after the medium has solidified. About 15 to 20 plates can be prepared from 100 mL of medium. Label and date.

f. Prepared petri dishes, sealed in small plastic bags to prevent drying, can be **stored in a refrigerator for up to 2 weeks.**

g. Begin preparation of urea-phenol broth for mTEC. Identification of *E. coli* using urea-phenol broth is required.

   i. After sample incubation, prepare the urea-phenol red broth by adding 100 mL of sterile deionized or distilled water to 2.0 g of urea and 0.01 g phenol red crystals in a 250-mL flask and mix thoroughly. Although all the phenol red crystals will not dissolve, the solution is nevertheless acceptable to use.

   ii. Adjust the pH of the urea-phenol solution to 5.0 with a few drops of 1 *N* HCl (hydrochloric acid). The substrate solution should be a straw-yellow color at this pH.

   iii. When preparing the filter pads for counting colonies, use a clean pipet or dropper and add 2.0 mL of the solution to each absorbent pad before placing the filter on the pad. Before transferring the filters from mTEC to urea-phenol broth, carefully drain excess solution from each pad by tilting the petri dish against a clean lab wipe.

   iv. Urea-phenol broth can be stored in the refrigerator for up to 2 weeks, as long as the solution remains straw-yellow in color.

5. Modified mTEC medium for *E. coli* analysis.

   Commercial dehydrated medium may be available; if so, prepare according to instructions. If not, prepare fresh medium in the laboratory prior to departing for the field site. Information on reagents and media preparation can be obtained from the U.S. Environmental Protection Agency (2000b).

   a. Prepare fresh agar by weighing and adding 45.6 g of combined reagents to 900 mL of reagent-grade deionized or distilled water. Stir the mixture to break up clumps. After the reagents are dissolved, adjust the volume to 1,000 mL. This volume will produce approximately 200 plates. To prepare fewer petri dishes, proportionately reduce the quantities of reagents and volume of deionized or distilled water.

   b. Autoclave the medium at 121°C for 15 minutes. Cool the medium. Store the medium in dilution bottles for up to 6 months in the refrigerator (at about 5°C). Prepare petri dishes as needed from individual bottles of medium. Write type of medium and date prepared on bottles.

   c. When ready to prepare petri dishes, melt the modified mTEC medium by autoclaving dilution bottles containing MI medium for 5 minutes at 121°C or by placing them in a boiling water bath. Be sure to loosen the screw tops on the bottles prior to heating to allow air to escape.

   d. Cool the medium to 45–50°C. Pour 6 to 7 mL of the medium into each 50-mm petri-dish bottom to a depth of about 1/8 inch (0.32 mm). Allow to cool 4 to 8 minutes and replace petri-dish tops tightly.

   e. When the medium has solidified (about 10 minutes), close the petri dishes by pressing firmly on the tops. The plates are suitable for use after the medium has solidified. About 15 to 20 plates can be prepared from 100 mL of medium. Label and date the plates. Prepared plates, sealed in small plastic bags to prevent drying, can be **stored in a refrigerator for up to 2 weeks**.

f. All freshly prepared medium must be quality-control checked by the preparing laboratory by means of positive and negative controls. Refer to American Public Health Association and others (1998, p. 9-1 to 9-78) for instructions.

g. Sterile agar petri dishes prepared ready for use can be purchased from commercial suppliers and do not need to be refrigerated during shipping. These plates can be stored in the refrigerator at about 5°C for up to 1 year. Write the date received on the plates.

6. mFC medium for fecal coliform bacteria analysis.

a. Prepare a rosolic acid solution by adding 10 mL of 0.2 *N* NaOH (sodium hydroxide) to 0.1 g of rosolic acid crystals. Shake the mixture to dissolve crystals. Do not heat. The crystals will dissolve in 15 minutes. Prepare a new solution for each analysis.

b. Empty the vial containing 5.2 g of dehydrated medium into 100 mL of deionized or distilled water in a 250-mL flask.

c. Stir the mixture well for several minutes to break up clumps and prevent medium from adhering to the flask.

d. Place the flask in a heated water bath or on a hot plate and heat slowly to 90°C. If using a hot plate, stir the mixture constantly or use a stir bar and magnetic stirring hot plate to prevent scorching. Do not autoclave.

e. With a clean pipet, add 1 mL of rosolic acid solution per 100 mL of medium when the medium reaches 90°C. Continue heating until boiling begins; then remove from the heat.

f. Cool the medium to a temperature of about 45–50°C and pour 6 to 7 mL in 50-mm petri-dish bottoms. Quickly place petri-dish tops loosely on petri-dish bottoms to allow condensation to escape.

g. When the medium has solidified (about 10 minutes), close petri dishes by pressing firmly on the tops. The plates are suitable for use after the medium has solidified. About 15 to 20 plates can be prepared from 100 mL of medium. Label and date the petri dishes. Prepared petri dishes, sealed in small plastic bags to prevent drying, can be **stored in a refrigerator for up to 72 hours.**

7. KF medium for fecal streptococci analysis.

   a. Empty the vial containing 7.64 g of dehydrated medium into 100 mL of deionized or distilled water in a 250-mL flask.

   b. Stir the mixture well for several minutes to break up clumps and prevent medium from adhering to the flask.

   c. In a separate small bottle, add 10 mL of deionized or distilled water to the 0.1 g of TTC (triphenyltetrazolium chloride crystals).

   d. Place the flask in a heated water bath or on a hot plate and heat slowly to boiling. If using a hot plate, stir the mixture constantly or use a stir bar and magnetic stirring hot plate to prevent scorching. After boiling begins, reduce to a simmer for 5 minutes.

   e. Remove the medium solution from the heat and cool to 50–60°C. Sterilize the TTC solution by aseptically filtering through a disposable sterile 0.22-mm pore-size membrane filter. Add 1 mL of sterile TTC solution to 100 mL of medium and stir. Prepare a fresh TCC solution each time the medium is prepared.

   f. Cool the medium to a temperature of about 50°C and pour 6 to 7 mL into 50-mm petri-dish bottoms. Quickly place the petri-dish tops loosely on the petri-dish bottoms to allow condensation to escape.

g. When the medium has solidified (about 10 minutes), close the petri dishes by pressing firmly on the tops. The plates are suitable for use after the medium has solidified. About 15 to 20 plates can be prepared from 100 mL of medium. Label and date the plates. Prepared plates, sealed in small plastic bags to prevent drying, can be stored in a refrigerator for up to 2 weeks if a sterile TTC solution is used. **If the TTC solution is not sterilized, use the medium within 24 hours.**

8. mE medium, followed by EIA medium, for enterococci bacteria analysis.

   a. Pour 5 to 10 mL of deionized or distilled water into a bottle containing 0.015 g of TTC crystals. Cap and shake the bottle to dissolve the crystals. If using a USGS kit, retain the remaining 90 mL of deionized or distilled water. Do not heat.

   b. Empty the vial containing 7.12 g of mE medium into the remainder of the deionized or distilled water (approximately 90 mL) in a 250-mL flask. Stir this mixture for several minutes to break up clumps. It is important that none of the medium adheres to the bottom or the sides of the flask.

   c. Prepare a nalidixic acid solution by adding 10 mL of 0.2 *N* NaOH solution to a bottle containing 0.25 g of nalidixic acid crystals. Shake the bottle to dissolve the crystals. Do not heat. Make sure all of the crystals dissolve.

   d. Place the flask containing the medium solution in a heated water bath or on a hot plate and stir the solution constantly, or use a stir bar and magnetic stirring hot plate to prevent scorching. After ingredients dissolve, autoclave at 121°C and 15 lb/in^2 for 15 minutes. Allow to cool long enough to pick up barehanded.

   e. Once cooled, the dissolved reagents can be added. Using a sterile pipet, add 1.3 mL of the nalidixic acid solution. If the medium is intended to be used within 24 hours, add all of the TTC solution directly from the bottle. If the prepared medium will be stored for a longer period before use, sterilize the TTC solution by passing it through a 0.22-mm membrane-filter syringe in an aseptic manner.

f. Pour 6 to 7 mL of the medium into 50-mm petri-dish bottoms. Quickly place the petri-dish tops loosely on the petri-dish bottoms to allow condensation to escape.

g. When the medium has solidified (about 10 minutes), close the petri dishes by pressing firmly on the tops. The petri dishes are suitable for use after the medium has solidified. About 15 to 20 petri dishes can be prepared from 100 mL of medium. Label and date the petri dishes. Prepared petri dishes, sealed in small plastic bags to prevent drying, can be stored in a refrigerator for up to 2 weeks, if sterile TTC is used. **If the TTC solution is not sterilized, use the medium within 24 hours.**

h. Begin preparation of EIA medium for enterococci bacteria. Use of the EIA medium is required.

   i. If using the USGS kit from the Ocala Laboratory, a second bottle of 100 mL deionized or distilled water is used to prepare the EIA medium.

   ii. Empty the vial containing 1.65 g of EIA medium into 133 mL of deionized or distilled water in a 250-mL flask.

   iii. Stir this mixture for several minutes to break up clumps. Make sure that none of the medium adheres to the bottom or the side of the flask.

   iv. Place the flask containing the medium solution in a heated water bath or on a hot plate and stir the solution constantly, or use a stir bar and magnetic stirring hot plate to prevent scorching.

   v. After ingredients dissolve, autoclave at 121°C and 15 lb/in^2 for 15 minutes. Allow the flask to cool long enough to pick up barehanded.

   vi. Pour 6 to 7 mL of EIA medium into the bottom of a 50-mm petri dish. Quickly place the petri-dish tops loosely on the petri-dish bottoms to allow condensation to escape.

vii. When the medium has solidified (about 10 minutes), close the petri dishes by pressing firmly on the tops. The plates are suitable for use after the medium has solidified. About 15 to 20 plates can be prepared from 100 mL of medium. Label and date the plates. Prepared plates, sealed in small plastic bags to prevent drying, can be stored in a refrigerator for up to 2 weeks.

9. mEI medium for enterococci bacteria analysis.

   a. Prepare the nalidixic acid solution by adding a few drops of 0.1 *N* NaOH solution to a bottle containing 5 mL deionized or distilled water and 0.24 g of nalidixic acid. Shake the mixture thoroughly to dissolve. Do not heat.

   b. In another bottle, add 0.1 g of TTC to 10 mL of reagent-grade deionized or distilled water. Cap and shake for about 30 seconds to dissolve. Do not heat.

   c. Add 71.2 g of mE agar to 900 mL of reagent-grade deionized or distilled water in a 1,000-mL flask. Add 0.75 g of the indoxyl β-D-glucoside reagent (rinsing thoroughly), and adjust the volume to 1,000 mL.

   d. Stir this mixture for several minutes to break up clumps. It is important to make sure that none of the agar adheres to the bottom or sides of the flask.

   e. Place the flask containing the agar solution on a stove or burner and begin heating slowly. Stir the solution constantly to prevent scorching. After ingredients have dissolved, autoclave at 121°C and 15 lb/in^2 for 15 minutes. Allow the solution to cool to 44–46°C. The pH of the medium should be 7.1 ± 0.2.

f. The dissolved reagents may now be added. If the medium is to be used within 24 hours, add the nalidixic acid solution and mix thoroughly. Add 2 mL of the TTC solution per 1 L of medium using a clean pipet. **If, however, the prepared medium will be stored for a longer period prior to use, sterilize the nalidixic acid and TTC solutions by passing them through a 0.22-µm pore-size membrane filter aseptically, using a sterile syringe.** Mix thoroughly.

g. Pour 6 to 7 mL of mEI medium into 50-mm petri-dish bottoms. Quickly place the petri-dish tops loosely on the petri-dish bottoms to allow condensation to escape.

h. When the medium has solidified (about 10 minutes), close the petri dishes by pressing firmly on the tops. The plates are suitable for use after the medium has solidified. About 15 to 20 plates can be prepared from 100 mL of medium. Label and date the plates. Prepared plates, sealed in small plastic bags to prevent drying, can be stored in a refrigerator for up to 2 weeks.

10. mCP media for *C. perfringens* analysis.

The mCP medium for the analysis of *C. perfringens* is prepared by the analyzing laboratory, so preparation instructions are not included in this section. A culture of *C. perfringens* requires anaerobic conditions and a special incubator, as well as a fume hood in which to expose colonies to the ammonium-hydroxide reagent for identification.

FECAL INDICATOR VIRUSES 7.2

By R.N. Bushon

	Page
7.2 Fecal indicator viruses	FIV–3
7.2.1 Sampling equipment and equipment sterilization procedures	5
7.2.2 Sample collection, preservation, transport, and holding times	9
7.2.2.A Surface-water sample collection	10
Depth-and-width-integrating methods	11
Hand-dip method	12
7.2.2.B Ground-water sample collection	14
Supply wells	14
Monitoring wells	15
7.2.2.C Sample preservation, transport, and holding times	19
7.2.3 Laboratory methods	20
7.2.3.A Single-agar layer method	20
7.2.3.B Two-step enrichment method	21
7.2.4 Calculation and reporting of fecal indicator viruses	23

Tables

7.2-1. Equipment cleaning and sterilization procedures..... FIV–6

7.2-2. Summary of equipment for sample collection and procedures for sample preservation of fecal indicator viruses 10

Notes:

References for section 7.2, Fecal indicator viruses, are located at the end of Chapter A7 in the "Selected References and Documents" section, which begins on page REF-1.

See Appendix A7-A, Table 3, for parameter codes for somatic and F-specific coliphages that are used in the National Water Information System (NWIS) of the U.S. Geological Survey.

The citation for this section (7.2) of NFM 7 is as follows:

Bushon, R.N., November 2003, Fecal indicator viruses: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7 (3d ed.), section 7.2, accessed ___*date*___, from http://pubs.water.usgs.gov/twri9A/

FECAL INDICATOR VIRUSES 7.2

More than 100 types of human pathogenic viruses may be present in fecal-contaminated waters, but only a small number of them can be detected by currently available methods (Havelaar and others, 1993). Coliphages are used as indicators of fecal contamination and of the microbiological quality of the water.[5] Coliphages are viruses that infect and replicate in coliform bacteria and are not pathogenic to humans; coliphages have been suggested as potential indicators of enteric viruses because of their similar structure, transport, and persistence in the environment (Gerba, 1987).

Two main groups of coliphages are used as viral indicators:

Coliphages: Viruses that infect and replicate in coliform bacteria. Coliphages are used as indicators of fecal contamination in water.

- **Somatic coliphages** infect coliform bacteria by attaching to the outer cell membrane or cell wall. They are widely distributed in both fecal-contaminated and uncontaminated waters.
- **F-specific coliphages** attach only to hairlike projections (called F pili) of coliform bacteria that carry an extrachromosomal genetic element called the F plasmid; F pili are produced only by bacteria grown at higher temperatures. F-specific coliphages presumably come from warm-blooded animals or sewage (Handzel and others, 1993).

[5]The term "fecal indicator viruses" is used synonymously with coliphages in this report, as coliphage analysis currently is the only standard viral method used by the U.S. Geological Survey for indicating fecal contamination.

Somatic and F-specific coliphages are found in high numbers in sewage and are thought to be reliable indicators of sewage contamination of waters (International Association of Water Pollution Research and Control Study Group on Health Related Microbiology, 1991). Raw sewage typically contains somatic and F-specific coliphage concentrations of about 1,000 plaque-forming units per milliliter (Sobsey and others, 1995).

Two methods are commonly used to analyze samples for somatic and F-specific coliphages:

- The single-agar layer (SAL) method is recommended for use with surface-water samples. It is a quantitative, plaque assay method that can analyze sample volumes of 100 mL (milliliters).
- The two-step enrichment method is recommended for use with ground-water samples. It is a presence/absence method that can analyze sample volumes of either 100 mL, 1 L (liter), or 4 L.

Coliphage methods of analysis must be performed in the laboratory by a trained microbiologist.

The type of coliphage detected by these methods depends on the bacterial host strain used. Two host strains commonly used for the detection of somatic coliphages are *Escherichia coli* (*E. coli)* C and *E. coli* CN-13. Both hosts are equivalent in coliphage detection; however, *E. coli* CN-13 is resistant to nalidixic acid and is preferable for analyzing samples with a high background or unknown level of indigenous bacteria (Sobsey and others, 1995). Antibiotics such as nalidixic acid are used to minimize overgrowth of indigenous bacteria in environmental samples; this overgrowth may mask the detection of coliphage. Three host strains commonly used for the detection of F-specific coliphages are *E. coli* F-amp, *E. coli* C3000, and *Salmonella typhimurium* WG49. The *E. coli* F-amp strain appears to be the most reliable host for detecting only F-specific coliphages; the F-amp strain is resistant to ampicillin and streptomycin, so it is less susceptible to bacterial contamination in water samples (Sobsey and others, 1995).

SAMPLING EQUIPMENT AND EQUIPMENT STERILIZATION PROCEDURES 7.2.1

Sterile techniques must be followed and documented when collecting and processing samples for fecal indicator viruses. **The specific equipment and supplies that are needed to collect and analyze samples for fecal indicator viruses must be kept clean and sterile** (tables 7.2-1, 7.2-2). The equipment and procedures described in the following paragraphs are applicable to fecal indicator viruses and to fecal indicator bacteria (NFM 7.1). Equipment to be autoclaved must first be wrapped in aluminum foil, autoclavable bags, or kraft paper. Non-autoclavable equipment must be cleaned and, if possible, sterilized and then similarly wrapped for storage and transport.

- Sterilize and store the equipment in a clean area.
- Resterilize equipment if foil, bag, or kraft paper is torn.

Add sodium thiosulfate ($Na_2S_2O_3$) to sample bottles before sterilization if the water to be collected is suspected to contain residual chlorine or other halogens. $Na_2S_2O_3$ also may be added to the sample bottle immediately after sample collection. Residual chlorine commonly is found in treated (disinfected) potable water (for example, public water systems), and in sources such as wastewater effluents or mixing zones directly downstream from wastewater-treatment plants. Most taps or wells (for example, small private water systems) do not contain residual chlorine.

Autoclaving is the preferred method for sterilizing equipment.

Table 7.2-1. Equipment cleaning and sterilization procedures

[NFM, *National Field Manual for the Collection of Water-Quality Data*; DIW, distilled or deionized water; mL, milliliter; $Na_2S_2O_3$, sodium thiosulfate; °C, degrees Celsius; mg/L, milligrams per liter]

Equipment	Cleaning and sterilization procedures
All equipment (this includes water-level tape measure, all sample-collection and sample-processing equipment used in the field and laboratory)	Wash equipment thoroughly with a dilute nonphosphate, laboratory-grade detergent (NFM3). Rinse three times with hot tap water. Rinse again three to five times with DIW. Wipe down the wetted portion of water-level tapes with disinfectant (0.005-percent bleach solution or methyl or ethyl alcohol) and rinse thoroughly with DIW.
Autoclavable glass, plastic, and Teflon bottles	If sample will contain residual chlorine or other halogens, add 0.5 mL of a 10-percent $Na_2S_2O_3$ solution per liter of sample to the sample bottles. Wrap all autoclavable equipment in aluminum foil, kraft paper, or place into autoclavable bags.[1] Autoclave at 121°C for 15 minutes.
Portable submersible pumps and pump tubing	**Autoclavable equipment** (preferred): Wrap components in aluminum foil, kraft paper, or place into autoclavable bags. Autoclave at 121°C for 15 minutes. **Non-autoclavable equipment: (1)** Submerge sampling system into a 50-mg/L (0.005 percent) sodium hypochlorite solution prepared from household laundry bleach. **(2)** Circulate solution through pump and tubing for 30 minutes. **(3)** Follow step (2) by thoroughly rinsing, inside and out, with 0.5 mL of a 10-percent sterile $Na_2S_2O_3$ solution per liter of water and circulate solution for 5 minutes; **(4)** pump $Na_2S_2O_3$, discarding this waste appropriately; pump sterile DIW through the pump, followed by pumping three tubing volumes of well water to waste (discard appropriately) before collecting the sample. **CAUTION:** Prolonged or repeated use of a hypochlorite solution on interior or exterior surfaces of a pump can cause corrosion or other damage to the pump and compromise the quality of samples collected for trace-element or organic-compound analysis.

[1]Equipment to be wrapped in aluminum foil, kraft paper, or placed into autoclavable bags includes, for example, bottles, tubing, flasks, bailers, pump components. The $Na_2S_2O_3$ solution also is autoclaved.

To prepare for collecting a halogenated sample:

1. Prepare a 10-percent solution of $Na_2S_2O_3$ as follows:
   a. In a volumetric flask, dissolve 100 g of $Na_2S_2O_3$ into 500 mL of deionized or distilled water (DIW).
   b. Stir until dissolved.
   c. Fill the flask to 1,000 mL (Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19). Autoclave at 121°C for 30 minutes (U.S. Environmental Protection Agency, 1996, p. VIII–II).
   d. Store the $Na_2S_2O_3$ solution at room temperature or under refrigeration. After 6 months prepare a fresh solution.
2. Before collecting the sample, pipet into the sample bottle 0.5 mL of 10-percent $Na_2S_2O_3$ solution for every 1 L of sample. If the sterile $Na_2S_2O_3$ is used, be sure to use only sterile pipets and sterile sample bottles. If the $Na_2S_2O_3$ is not sterile, dispense the required volume of $Na_2S_2O_3$ into the sample bottle and autoclave at 121°C for 15 minutes.

$Na_2S_2O_3$ solution has a 6-month shelf life. Discard unused solution that has expired, prepare fresh solution, and label bottle with date of preparation.

Clean and sterilize sampling equipment (table 7.2-1). All equipment, including tubing and containers, must be cleaned and sterilized between sites or for each sample collected at the same site at different times. Autoclaving is the preferred method of sterilization.

- Use only autoclaves that have temperature, pressure, and liquid- and dry-utensil-cycle controls. Steam sterilizers, vertical autoclaves, and pressure cookers without temperature controls are not recommended.
- Take care to ensure that materials to be autoclaved are thermally stable. Plastics (such as polycarbonate, polypropylene, polyallomer, and polymethylpentene) and Teflons and Tefzel® (such as perfluoroalkyoxypolymers or PFA, ethylenetetrafluoroethylene or ETFE, fluorinated ethylene propylene or FEP, and polytetrafluoroethylene polymers or PTFE) can be autoclaved. **Note that each of these materials has different thermal characteristics and tolerances to repeated autoclaving.**
- When autoclaving, be sure to:
  - Use sterilization indicator tape with each load.
  - Use commercially available biological indicators at least quarterly to test autoclave performance. Biological indicators are composed of endospores—living cells that are resistant to heat, but are destroyed by autoclaving.
  - Drain the autoclave at the end of each period of use. Clean with mild soap and water once per week during periods of daily use. Record cleaning dates in the logbook.
  - Autoclave cultures of microorganisms and all media plates for at least 30 minutes before disposal.
  - Wrap silicone tubing in kraft paper or aluminum foil before autoclaving.
  - Avoid overloading the autoclave with equipment or materials; overloading will result in incomplete sterilization.

- The 20th edition of "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1998, p. 9-2 to 9-14) contains specifications for the length of time, temperature, and pressure for autoclave sterilization of various media and materials.

Quality control in sterilization procedures is mandatory. Keep a logbook of autoclave operation. Enter into the logbook the quality-assurance and quality-control procedures used, noting the date, the test results, and the name of the autoclave operator and (or) analyst. Record the autoclave temperature, pressure, date, and time of each autoclave run. If the autoclave does not reach the specified temperature and pressure or fails a quality-control test, then the autoclave should be serviced and all materials resterilized (American Public Health Association and others, 1998, p. 9-2 to 9-14).

SAMPLE COLLECTION, PRESERVATION, TRANSPORT, AND HOLDING TIMES 7.2.2

Sterile conditions must be maintained during collection, preservation, transport, and analysis of fecal indicator virus samples. Specific procedures have been developed that must be strictly followed. These procedures vary with types of sampling equipment and sources of sample (surface water, ground water, treated water, or wastewater).

A summary of requirements for sample-collection containers and procedures for sample preservation is given in table 7.2-2.

Table 7.2-2. Summary of equipment for sample collection and procedures for sample preservation of fecal indicator viruses

[EWI, equal-width-increment; EDI, equal-discharge increment; L, liter; NFM, *National Field Manual for the Collection of Water-Quality Data*; mL, milliliter; $Na_2S_2O_3$, sodium thiosulfate; °C, degrees Celsius]

Equipment for sample collection (All containers must be composed of sterilizable materials such as borosilicate glass, polypropylene, stainless steel, or Teflon®)
To collect EWI or EDI surface-water samples: US D-95, US DH-95, or US DH-81 with sterile 1-L wide-mouth bottle, caps, and nozzles. US D-96 with sterile autoclavable bag (NFM 2.1.1).
To collect surface-water and ground-water samples using point samplers from a tap, or hand-dipped method: a sterile, narrow-mouth container, 500 mL to 1 L capacity, or a sterile 3-L container if both types of coliphages are to be analyzed.
To collect pumped samples: Use sterile tubing, clean and sterile pump components (autoclaved, if possible; see text).
Procedures for sample preservation
Before sample collection, if halogen neutralization is necessary, add 0.5 mL of a 10-percent $Na_2S_2O_3$ solution per 1 L of sample. – If sterile $Na_2S_2O_3$ is used, dispense with sterile pipet into sterile bottle. – If $Na_2S_2O_3$ is not sterile, dispense with pipet into sample bottle and autoclave (table 7.2-1). **Chill all samples at 1-4°C before analysis.**

7.2.2.A SURFACE-WATER SAMPLE COLLECTION

The areal and temporal distribution of fecal indicator viruses in surface water can be as variable as the distribution of suspended sediment because viruses commonly are associated with solid particles. To obtain representative data for fecal indicator virus analysis, follow the same methods used to collect surface-water samples for suspended sediment analysis (Edwards and Glysson, 1999; NFM 4.1 and table 7.2-2).

- **Flowing water**—use depth-and-width-integrating sampling methods[6] (NFM 4.1.1.A).
- **Still water** (lakes or reservoirs, or other surface-water conditions for which depth-and-width-integrating methods are not applicable)—use the hand-dip method or a sterile point sampler (NFM 4.1.1.B).

[6]Sample-collection methods may be modified to ensure consistency with study objectives and as appropriate for site conditions. It is necessary to describe any methods modifications in a report of the results of the study.

- **Beach water**—use a hand-dip method in shallow wadable water and a sterile point sampler for deeper water. Collect samples by the hand-dip method at knee depth, a depth of approximately 15 to 30 cm (6 to 12 in.) below the water surface.
  - — Collect samples near known or suspected pollution sources, in areas of concentrated activity (for example, near lifeguard chairs), or for approximately every 500 m (every quarter mile) of beach length (U.S. Environmental Protection Agency, 2002).
  - — Position the sampler downstream from any water currents to collect the sample from the incoming flow (U.S. Environmental Protection Agency, 2002) and record sampling location. Avoid contaminating the water sample with bottom material dislodged by disturbing the bottom while sampling.
  - — A Chain of Custody record is recommended for beach sampling done in support of beach closures or posting of warnings to swimmers (U.S. Environmental Protection Agency, 2002, Appendix J).

Always wear laboratory gloves when handling sampling equipment and samples. Take care to prevent contaminated water from contacting skin, mouth, nose, or eye areas (NFM 9.7).

Depth-and-width-integrating methods

Depth-and-width-integrating sampling methods (the equal-discharge-increment (EDI) method or the equal-width-increment (EWI) method) are the standard USGS methods used when sampling flowing waters, and are recommended unless study objectives or site characteristics dictate otherwise (NFM 4.1.1.A and table 7.1-4).

Select the EDI or EWI method:

1. The EDI method is preferred to the EWI method for sites where the velocity distribution across a stream section is well established or at a section where the depth varies; for example, at a gaging station (Edwards and Glysson, 1999).

2. Select the appropriate sampler and equipment. **Sampling equipment must be sterile,** including the collection bottle, nozzle, and cap (or bags for the bag sampler) (table 7.2-1).
   - For streams with depths of 5 m (16.4 ft) or less, use a US D-95, US DH-95, or a US DH-81 sampler (NFM 2.1.1).
   - For stream sections where depths exceed 5 m (16.4 ft), use the US D-96, with either autoclavable Teflon® bags or autoclavable cooking bags. Thermotolerant polymers are described in more detail in section 7.2.1 under "Sampling Equipment and Equipment Sterilization Procedures."
   - For compositing subsamples, use a sterile 3-L or larger bottle.
     — For wide channels, several samples, each composed of subsamples composited into a sterile large-volume container, may be needed.
     — For narrow channels, collect subsamples at 5 to 10 or more vertical locations in the cross section without overfilling the bottle.
   - Use the proper nozzle size and transit rate for the velocity conditions in the section to ensure isokinetic collection of the sample.

Hand-dip method

If the stream depth and (or) velocity is not sufficient to use a depth-and-width-integrating method, collect a sample using a hand-dip method (table 7.1-4). Sampling still water or sampling at depth in lakes, reservoirs, estuaries, and oceans requires a sterile point sampler. Niskin, ZoBell, and Wheaton point samplers hold a sterilizable bottle or bag.

Wearing laboratory gloves, collect a hand-dipped sample as follows:

1. Open a sterile, narrow-mouth borosilicate glass or plastic bottle; grasp the bottle near the base, with hand and arm on the downstream side of the bottle.
2. Without rinsing, plunge the bottle opening downward, below the water surface. Allow the bottle to fill with the opening pointed slightly upward into the current.

3. Remove the bottle with the opening pointed upward from the water surface and tightly cap it, allowing about 2.5 to 5 cm of headspace (American Public Health Association and others, 1998, p. 9-19; Bordner and Winter, 1978, p. 8). This procedure minimizes collection of surface film and prevents contact with the streambed.

Do not sample in or near an open water body without wearing a correctly fitted personal flotation device (PFD).

Quality control in surface-water sampling. Depending on the data-quality requirements of the study and site conditions, quality-control (QC) samples (field blanks, field replicates, and matrix spikes) generally constitute from 5 to 20 percent or more of the total number of samples collected over a given period of time. See "Selected Terms and Symbols" in the Conversion Factors section at the end of this chapter, which contains definitions of the quality-control terms shown below in bold type.

- **Field blanks**—Collect field blanks at a frequency of 1 in every 10 to 20 samples to document that sampling equipment has not been contaminated.

  Process field blanks before collecting the water sample as follows:

  1. Pass sterile DIW through sterile sampling equipment and into a sterile sample container.
  2. Analyze sterile DIW for fecal indicator viruses. If no viruses are observed, then the sample was collected by use of sterile procedures.

- **Field replicates**—Collect one field replicate for every 10 to 20 samples.

- **Matrix spikes**—Collect a set of matrix spike samples for each coliphage type when samples are first received from a water source. Once received from a water source, collect a set of matrix spike samples after every 20th sample from that source. The matrix spike samples are spiked with known amounts of coliphage by the analyzing laboratory.

7.2.2.B GROUND-WATER SAMPLE COLLECTION

As with surface water, most viruses in ground water are associated with solid particles. Stable values of field measurements (turbidity, temperature, dissolved-oxygen concentration, pH, and specific conductance), especially turbidity and dissolved oxygen, are important criteria for judging whether a well has been sufficiently purged for the collection of a representative ground-water sample for fecal indicator virus analysis (NFM 4.2 and 6.0.3.A). Sampling equipment that has been subjected to chlorinating and dechlorinating agents can affect the chemistry of samples collected for non-microbial analysis; therefore, collect blank samples to be analyzed for chloride, sulfate, and other constituents, as appropriate, to document that chemical sample quality has not been compromised.

- If using the same equipment for chemical-analysis and virus-analysis samples, clean the equipment by first using standard procedures (NFM 3), followed by disinfecting and rinsing procedures described in section 7.2.1. Purge the well as described in NFM 4.2 before collecting samples.
- If different equipment will be deployed in a well for virus sampling, first check for stable turbidity and dissolved-oxygen readings to ensure collection of a representative sample.

Supply wells

If samples are to be collected from a water-supply well (see definition in NFM 4.2), select a tap (spigot) that supplies water from a service pipe connected directly to the main; do not use a tap on a pipe served by a cistern or storage tank (American Public Health Association and others, 1998, p. 9-19 to 9-20; Britton and Greeson, 1989, p. 5; Bordner and Winter, 1978, p. 5-16). Avoid sampling after downhole chlorination. Dechlorination with $Na_2S_2O_3$ is required if you cannot avoid collecting the sample before the water has passed through the treatment unit.

Do not sample from leaking taps.

To sample a supply well for fecal indicator viruses:

1. Before collecting the sample, remove screens, filters, or other devices from the tap.
2. Before sampling, swab the inside and outside rim of the tap with ethanol. Flame sterilize the tap and allow it to dry and cool. Rinse the tap with sterile DIW.
3. Collect a sample directly from the tap into a sterile bottle without splashing or allowing the sample bottle to touch the tap.
   - Supply wells commonly are equipped with permanently installed pumps. If the well is pumped daily, then (a) purge the tap water for a minimum of 5 minutes, discarding the purged water appropriately; (b) monitor field measurements and record stabilized values (NFM 6); and (c) collect the sample directly from the tap into a sterile container (described in table 7.2-2).
   - If the well is used infrequently, then purge the tap or well of water until a minimum of three borehole volumes are purged and stable field measurements are obtained in sequential measurements (NFM 4.2 and 6.0.3.A).

Monitoring wells

If a monitoring well does not have an in-place pump, then obtain samples by using a portable sampler, such as a submersible pump or a bailer (U.S. Environmental Protection Agency, 1982). Samplers and sample lines must be sterilized or disinfected (table 7.2-1). If disinfected, then the sampler and sample line must be dechlorinated and rinsed with sterile DIW. In either case, finish by flushing the sampler and sample line with native ground water before samples are collected into sterile bottles.

- Use autoclavable samplers, if possible. After flushing the sterilized pump lines with sample, collect the sample directly into the sterile sample bottles.
- Check data-collection objectives before using a disinfectant. Disinfectants are corrosive; repeated use can result in damage to the metal and plastic parts of a pump, thus rendering the pump inadequate for sampling trace elements and other constituents.

To disinfect a pump:

1. Submerge the pump and pump tubing in a 0.005 percent (50 mg/L) sodium hypochlorite solution prepared from household laundry bleach.
   - Most bleach is about 5 to 7 percent sodium hypochlorite (50,000 to 70,000 mg/L), but bleach in a container left open for more than 60 days may not be full strength.
   - Prepare solutions fresh with each use, because they will diminish in concentration with time. Add 1 mL of household laundry bleach to 900 mL of water and bring to a volume of 1,000 mL for a 0.005 percent disinfectant solution (U.S. Environmental Agency, 1982, p. 253 and 1996, p. VIII–41). This concentration is sufficient for waters with pH between 6 and 8 and temperatures greater than 20°C. Outside these ranges, a more concentrated disinfectant solution, up to 0.02 percent (200 mg/L), should be used (U.S. Environmental Protection Agency, 1982, p. 253).
2. Circulate the disinfectant through the pump and tubing for 30 minutes.
3. Next, rinse the pump thoroughly with a sterile $Na_2S_2O_3$ solution. The $Na_2S_2O_3$ solution is prepared by adding 0.5 mL of a 10-percent sterile solution to every 1 L of sterile DIW. Recirculate for 5 minutes and rinse with sterile DIW.
4. Lower the pump carefully into the well. Pump some well water to waste to remove any residual chlorine and $Na_2S_2O_3$. Take care not to contaminate samples for chemical analysis with residual disinfectant or $Na_2S_2O_3$. **The pump must have a backflow check valve (an antibacksiphon device) to prevent residual disinfectant from flowing back into the well.**

If the pump cannot be disinfected:

1. Handle the pump and tubing carefully to avoid contamination. If the pump is a downhole dedicated pump, proceed to step 3.
2. Collect field blanks through the sampling equipment. Lower the pump in the well to the desired intake location.
3. Purge the well with the pump used for sampling to allow the pump and tubing to be thoroughly flushed with aquifer water before sampling (NFM 4.2 and 6.0.3.A).
4. An alternative to sampling with the pump is to remove the pump after completion of purging and collection of other samples, and then to collect the coliphage sample using a sterile bailer (U.S. Environmental Protection Agency, 1982, p. 252–253). Evaluate the potential for bias from stirring up particulates during pump removal and bailing that otherwise would not be included in the sample.

Sample-preparation activities, such as purging, must be carried out in such a way as to avoid contaminating the well, the equipment, or the samples. Avoid collecting surface film from the well water in the sample and ensure that the sampler intake is within the screened interval targeted for study. Select a point-source sampler, such as a bailer with a double-check valve. Do not use a bailer unless the bailer can be sterilized.

The type of well, its use, construction, composition, and condition could lead to alteration or contamination of samples. For example, a poor surface seal around the well opening can allow contaminants to move quickly from the land surface into the well water.

- If the water level is less than 7 to 10 m (roughly 20 to 30 ft) below land surface, a sample can be collected without contamination and without chlorine disinfection by use of a surface peristaltic or vacuum pump, a sterile vacuum flask, and two lengths of sterile tubing (U.S. Environmental Protection Agency, 1982).

- Purge the well (see NFM 4.2 and 6.0.3.A) while monitoring field measurements, especially measures of turbidity and dissolved oxygen. For wells in which field measurements do not stabilize after increasing the total number of measurements, record the final measurements and proceed with sampling.

Be vigilant in avoiding contamination. The detection of even one coliphage in ground water is cause for concern because it indicates the possible presence of pathogens.

Quality control for ground-water sample collection. Depending on the data-quality requirements of the study, quality-control samples (field blanks and matrix spikes) generally constitute from 5 to 20 percent or more of the total number of samples collected over a given time period. See "Selected Terms and Symbols" in the Conversion Factors section at the end of this chapter, which contains definitions of the quality-control terms shown below in bold type.

- **Field blanks**—Collect field blanks at a frequency of 1 in every 10 to 20 samples if required by data-quality objectives. **Process field blanks before collecting the water sample.** Pass sterile DIW through the sampling equipment and into a sterile sample container. Analyze the field blank for fecal indicator viruses and record the results. If no viruses are observed, the use of sterile procedures is confirmed and documented.

  TECHNICAL NOTE: The field blank discussed herein is equivalent to the "pump blank" described in NFM 4.3.1. Refer to NFM 4.3.1 for more information on collecting a field blank for ground-water sampling. A standpipe may be used to collect a field blank, but first must be cleaned and then disinfected. **This type of blank should be collected a week or more ahead of time so that results can be evaluated before field sampling.**

- **Field replicates** (sequentially collected samples)—Field replicates for ground-water samples are optional and their use depends on study objectives and site conditions. Ground-water samples typically are negative for coliphage.
- **Matrix spikes**—Collect a set of matrix spike samples for each coliphage type when samples are first received from a water source or aquifer type. Once received from a water source or aquifer type, collect a set of matrix spike samples after every 20th sample from that source or type. The matrix spike samples are spiked with known amounts of coliphage by the analyzing laboratory.

SAMPLE PRESERVATION, TRANSPORT, AND HOLDING TIMES 7.2.2.C

After collection, immediately chill samples in an ice chest or refrigerator at 1 to 4°C. **Do not freeze samples.** To ship samples to the laboratory, double bag the sample containers before placing them into the bagged ice in the ice chest. Seal the analytical services request form and chain-of-custody form in double plastic bags and tape this to the inside lid of the ice chest being shipped to the laboratory. Check that the sample identification and relevant information for use by the laboratory have been recorded correctly. **The laboratory must begin the analysis of samples within 48 hours of sample collection.**

The holding time for fecal indicator virus samples is 48 hours from the time of sample collection.

7.2.3 LABORATORY METHODS

Two methods described in this manual for the detection of fecal indicator viruses are the single-agar layer (SAL) method and the two-step enrichment method. The host bacteria recommended for use by these methods are *E. coli* CN-13 for the detection of somatic coliphage and *E. coli* F-amp for the detection of F-specific coliphage. Analytical protocols are available in more detail from the USGS Ohio District Microbiology Laboratory (U.S. Geological Survey, website: http://oh.water.usgs.gov/micro/lab.html#am) (accessed November 25, 2003).

7.2.3.A SINGLE-AGAR LAYER METHOD

The SAL method detects and enumerates somatic and F-specific coliphages in water. It is a plaque assay method that is recommended for use with surface-water samples.

USEPA Method 1602 (U.S. Environmental Protection Agency, 2001b) is a SAL method that requires the addition of host bacteria, magnesium chloride, appropriate antibiotics, and double-strength molten agar to the sample, followed by pouring the total volume of the mixture into plates. After an overnight incubation, the plates from a sample are examined for plaque formation (zones of bacterial host lawn clearing). The plaques are counted and summed for all plates from a single sample. The quantity of coliphage in a sample is expressed as plaques per 100 milliliters. This method requires one overnight incubation; therefore, results are available 24 hours after the beginning of the analysis.

Quality Control. Each laboratory and analyst that uses USEPA Method 1602 must fulfill the following general quality-control requirements, as described in the method:

- **Initial Precision and Recovery (IPR)**—The laboratory and analyst must demonstrate the ability to generate acceptable results by performing an IPR test before analyzing any environmental samples.
- **Method Blanks**—The laboratory must analyze reagent water samples containing no coliphage to demonstrate freedom from contamination. Method blanks should be run with each batch of samples. A batch is defined as all samples analyzed during a single day, up to a maximum of 20 samples per coliphage type.
- **Ongoing Precision and Recovery (OPR)**—The laboratory must demonstrate that the method is in control on an ongoing basis through analysis of OPR samples. OPR samples are reagent-water samples spiked with known amounts of coliphage and analyzed exactly like environmental samples. The laboratory must analyze one OPR sample for each batch of samples. A batch is defined as all samples analyzed during a single day, up to a maximum of 20 samples per coliphage type. The OPR serves as the positive control for Method 1602.

TWO-STEP ENRICHMENT METHOD 7.2.3.B

The two-step enrichment method determines the presence or absence of somatic and F-specific coliphages in water. **This method is recommended for use with ground-water samples.**

USEPA Method 1601 (U.S. Environmental Protection Agency, 2001a) is a two-step enrichment method that requires the enrichment of coliphage in tryptic soy broth supplemented with magnesium chloride, appropriate antibiotics, and host bacteria. After an overnight incubation, samples are spotted onto a lawn of host bacteria specific for each type of coliphage. The spot plates are incubated and examined for lysis zone formation in the lawn. Lysis zone formation indicates the presence of coliphages in the sample. This method requires two overnight incubations; therefore, results are available 48 hours after the beginning of the analysis.

Quality control. Each laboratory and analyst that uses Method 1601 must fulfill the following general quality-control requirements as described in the method.

- **Initial Demonstration of Capability (IDC)**—The laboratory and analyst must demonstrate the ability to generate acceptable results by performing an IDC test before analyzing any environmental samples.
- **Method Blanks**—The laboratory must analyze reagent-water samples containing no coliphage to demonstrate freedom from contamination. The laboratory must analyze one method blank per spot plate.
- **Positive Controls**—The laboratory must analyze positive control samples (reagent water spiked with a known amount of coliphage) to demonstrate that method reagents are performing properly. The laboratory must analyze one positive control per spot plate.
- **Ongoing Demonstration of Capability (ODC)**—The laboratory must demonstrate that the method is in control on an ongoing basis through analysis of ODC samples. The laboratory must analyze one set of ODC samples after every 20 field and matrix spike samples. For each coliphage type, at a minimum, one out of three reagent-water samples spiked with a known amount of coliphage must be positive.

CALCULATION AND REPORTING OF FECAL INDICATOR VIRUSES 7.2.4

The calculation and reporting protocols differ, depending on the laboratory method used. A list of parameter codes for reporting coliphages in the USGS National Water Information System (NWIS) are given in Appendix A7-A, table 3.

- **SAL method**—Count the total number of plaques from all plates for a sample. If the plaques are not discrete, results should be recorded as "too numerous to count" (TNTC), and the remaining sample should be diluted and reanalyzed if possible within 48 hours of collection. Record the result as the total number of plaques per 100 milliliters (plaques/100 mL).
- **Two-step enrichment method**—Record results as presence (1) or absence (2) of coliphage.

For each sample analyzed, document:

- **the type of coliphage analyzed,**
- **the bacterial host strain used,**
- **the sample volume analyzed, and**
- **the corresponding QC results from the laboratory.**

This page left blank intentionally.

PROTOZOAN PATHOGENS 7.3

By R.N. Bushon and D.S. Francy

	Page
7.3 Protozoan pathogens	PP–3
7.3.1 Sterilization procedures for sampling equipment	6
7.3.1.A Sodium hypochlorite sterilization method	8
7.3.1.B Alternative sterilization method	9
Equipment washing	9
Autoclaving	10
7.3.2 Sample collection, preservation, transport, and holding times	12
7.3.2.A Sample collection	14
Quality control	16
Isokinetic sampling methods	17
Hand-dip sampling method	18
7.3.2.B Sample preservation, transport, and holding times	19
7.3.3 Laboratory method: USEPA Method 1623	22
7.3.4 Calculation and reporting of protozoan pathogens	24

Illustrations

7.3–1. Photograph showing samples for protozoan pathogens collected in a sterile 1-liter or 3-liter bottle and composited into a 10-liter sterile cubitainer PP-15

Tables

7.3–1. Summary of equipment cleaning and sterilization procedures 7

7.3–2. Summary of equipment and sample-preservation procedures used for surface-water sample collection for protozoan pathogen analysis 13

Notes:

References for section 7.3, Protozoan pathogens, are located at the end of Chapter A7 in the "Selected References and Documents" section, which begins on page REF-1.

See Appendix A7-A, Table 4, for parameter codes for protozoan pathogens that are used in the National Water Information System (NWIS) of the U.S. Geological Survey.

The citation for this section (7.3) of NFM 7 is as follows:

Bushon, R.N., and Francy, D.S., November 2003, Protozoan pathogens: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A7 (3d ed.), section 7.3, accessed ___*date*___, from http://pubs.water.usgs.gov/twri9A/.

PROTOZOAN PATHOGENS 7.3

Protozoan pathogens are widely distributed in the aquatic environment and have been implicated in several outbreaks of waterborne diseases (Lee and others, 2002; Rose and others, 1997). *Cryptosporidium* and *Giardia* are the principal protozoan pathogens that are known to affect the acceptability of water supplies for public use within the United States (U.S.). *Cryptosporidium* and *Giardia* produce environmentally resistant forms (oocysts for *Cryptosporidium* and cysts for *Giardia*) that allow for the extended survival of the organisms in natural and treated waters.

PROTOZOAN PATHOGENS, such as *Cryptosporidium* and *Giardia,* are unicellular microorganisms that cause disease in humans and other animals.

In comparison with fecal indicator bacteria, oocysts and cysts are more resistant to disinfection, survive longer in the environment, and are much larger and more complex. Fecal indicator bacteria are, therefore, inadequate as indicators for *Cryptosporidium* and *Giardia* in source waters. The presence of protozoan pathogens in water must be verified by identification of the pathogens themselves.

Fecal indicator bacteria cannot be used to indicate the presence of *Cryptosporidium* or *Giardia* in source water.

A sampling program for *Cryptosporidium* oocysts and *Giardia* cysts should be conducted over an extended period of time because of cyclical and seasonal variations in their environmental concentrations (LeChevallier and Norton, 1995). For example, seasonal differences in the volume and intensity of precipitation or in the shedding of parasites by animals can account for elevated occurrences of oocysts and cysts in water (Atherholt and others, 1998). The average percentages of *Cryptosporidium* and *Giardia* occurrence in U.S. waters vary considerably among published studies, ranging from 10 to 60 percent for *Cryptosporidium* and 16 to 90 percent for *Giardia* (Atherholt and others, 1998; LeChevallier and Norton, 1995; LeChevallier and others, 2003; Rose and others, 1988; Rose and others, 1991). In these studies, concentrations of protozoan pathogens in environmental waters were considerably lower than concentrations of fecal indicator bacteria; average concentrations of *Cryptosporidium* ranged from 0.7 to 10 oocysts per 10 liters (L) of water and of *Giardia* from 0.8 to 7 cysts per 10 L. Higher concentrations of *Cryptosporidium* and *Giardia* were found in waters receiving industrial and sewage effluents than were found in waters not receiving these wastes and (or) having more extensive watershed-protection practices (LeChevallier and others, 1991).

The U.S. Environmental Protection Agency (USEPA) Method 1623 (Method 1623—filtration/immunomagnetic separation (IMS)/fluorescent antibody (FA)) currently is the method of choice for detecting *Cryptosporidium* oocysts and *Giardia* cysts in water. This method does not identify the species of *Cryptosporidium* and *Giardia*, nor does it determine the viability or infectivity of the detected organisms. Method 1623 is a performance-based method, which means that alternative components not listed in the method may be used, provided that the results meet or exceed the acceptance criteria described in the method. Aspects of the method that may be modified can include, but are not limited to, the type of filter used, the manufacturer of the magnetic beads, and the protocol used to separate the oocysts and cysts from the magnetic beads. Because the method is complex, only experienced analysts should use it (U.S. Environmental Protection Agency, 2001a).

Recoveries of *Cryptosporidium* and *Giardia* are determined in the same manner as are recoveries of chemical constituents, such as pesticides. A suspension is prepared of *Cryptosporidium* oocysts and *Giardia* cysts and quantified by use of an accurate method, such as flow-cytometry, which uses a particle-sorting instrument capable of counting protozoa. The suspension with known concentrations of organisms then is used to spike an environmental water sample in the laboratory. Recoveries of oocysts and cysts from environmental water samples using Method 1623 can vary greatly, which is an important consideration for data interpretation.

TECHNICAL NOTE: Recoveries of *Cryptosporidium* ranged from 2 to 63 percent in 11 stream-water samples (Simmons and others, 2001), 20 to 60 percent in 430 samples from 87 source waters (U.S. Environmental Protection Agency, 2001b), and 9 to 88 percent in samples from 19 surface-water sites (Kuhn and Oshima, 2002). In one large study, average recoveries of *Giardia* were 47 percent, with a relative standard deviation of 32 percent (U.S. Environmental Protection Agency, 2001b).

7.3.1 STERILIZATION PROCEDURES FOR SAMPLING EQUIPMENT

Sterile technique must be implemented and documented when collecting and processing samples for protozoan pathogens. **In addition, the specific equipment and supplies that are needed to collect and analyze samples for protozoan pathogens must be kept clean and sterile** before sampling at each site and for each sample collected at the same site at different times (table 7.3-1, and table 7.3-2 in section 7.3.2).

- All equipment should be cleaned with nonphosphate, laboratory-grade detergent and rinsed thoroughly with deionized/distilled water (DIW) before being sterilized.
- Procedures to sterilize equipment involve either: (1) cleaning selected equipment with a 12-percent sodium hyplochlorite (bleach) solution (section 7.3.1.A), or (2) rigorous washing followed by autoclaving ("Alternative Sterilization Method," section 7.3.1.B).
- Equipment must be wrapped.
  - Wrap equipment that has been sterilized using the sodium hypochlorite method in sterile aluminum foil, sterile autoclavable bags, or sterile kraft paper. The equipment is then ready for storage or for transport.
  - If the sodium hypochlorite method is not used, then equipment first must be wrapped in aluminum foil, autoclavable bags, or kraft paper, and then autoclaved. After autoclaving, equipment must remain wrapped for storage or transport.
- Resterilize equipment if foil, bag, or kraft paper is torn.

Autoclaving kills oocysts and cysts and eliminates infectivity; however, epitopes (proteins on the surface of cells) are not inactivated by autoclaving. Epitopes attach to the fluorescent stain used in Method 1623 and are detected microscopically. To avoid false positives that are caused by residual epitopes from a previous sample, use a strong (12-percent) sodium hypochlorite solution (full-strength swimming-pool bleach) to sterilize the equipment (section 7.3.1.A).

Table 7.3-1. Summary of equipment cleaning and sterilization procedures

[L, liter; DIW, distilled or deionized water; g/L, grams per liter; °C, degrees Celsius]

Equipment and supplies
• Autoclavable 1-L bottle or 3-L bag, nozzle, and cap. • Collapsible low-density polyethylene cubitainer for collection of a 10-L bulk sample. • Regular and sterile DIW. • Nonphosphate, laboratory-grade detergent. • 12-percent sodium hypochlorite solution. • Aluminum foil, autoclavable bag, or kraft paper.
Cleaning and sterilization procedures
Sodium hypochlorite sterilization method: • Scrub equipment with a dilute (1-percent) nonphosphate, laboratory-grade detergent solution. • Rinse three to five times with tap water. • Submerge equipment in a 12-percent (120 g/L) sodium hypochlorite solution for 30 minutes. • Using sterile DIW, rinse thoroughly, inside and out, at least three times. • Wrap equipment in sterile aluminum foil or sterile kraft paper, or place into a sterile bag. **Do not use this method to disinfect equipment used to collect samples for subsequent determination of trace elements and organic substances – metallic and plastic equipment components can be damaged and subject to early deterioration after repeated sterilization with a strong sodium hypochlorite solution.**
Alternative sterilization method: (Use if equipment contact with sodium hypochlorite should be avoided). • Soak equipment in a dilute (1-percent) nonphosphate, laboratory-grade detergent solution for 30 minutes. • Scrub well and rinse three to five times with tap water. • Rinse again three to five times with DIW. • Wrap equipment in aluminum foil or kraft paper, or place into autoclavable bags. • Autoclave at 121°C for 20 minutes.

7.3.1.A SODIUM HYPOCHLORITE STERILIZATION METHOD

As noted previously, to avoid false positives that are caused by residual epitopes from a previous sample, it is necessary to immerse the equipment in a strong sodium hypochorite solution.

To sterilize sampling equipment using the bleach sterilization method:

1. Set up a clean area and assemble the needed equipment and supplies.
2. Scrub equipment with a dilute (1-percent) nonphosphate, laboratory-grade detergent (if equipment is being cleaned in the field, use a 0.1-percent detergent solution and rinse thoroughly with DIW).
3. Rinse three to five times with tap water.
4. Soak equipment for 30 minutes in a 12-percent (120 grams per liter) sodium hypochlorite (full-strength pool bleach) solution.
5. Rinse the equipment a minimum of three times with sterile DIW. Use only sterile DIW to rinse the equipment—**do not use a sodium thiosulfate solution to neutralize the sodium hypochlorite when rinsing the equipment.**
6. Wrap equipment in sterile aluminum foil or sterile kraft paper, or place into a sterile autoclavable bag.

The 12-percent sodium hypochlorite solution is very caustic and, over time, can damage sampling equipment.

ALTERNATIVE STERILIZATION METHOD 7.3.1.B

To avoid deterioration of equipment that also is used to collect samples for trace-element or organic-compound analyses, an alternative sterilization method should be used. As a result of repeated exposure to a strong sodium hypochlorite solution, metallic surfaces can corrode and plastic equipment components can become brittle, shortening the life of the equipment. The alternative sterilization method described below consists of two major steps: (1) rigorous equipment washing, and (2) autoclaving.

Equipment Washing

Rigorous washing of sample-collection and sample-processing equipment is essential before equipment is autoclaved.

To sterilize sampling equipment using the alternative sterilization method:

1. Soak equipment in 1-percent nonphosphate, laboratory-grade detergent for 30 minutes. Scrub the equipment well, using a soft brush.
2. Rinse all parts of the equipment thoroughly three to five times with tap water, followed by three to five rinses with DIW.
3. Wrap equipment in aluminum foil or kraft paper, or place into autoclavable bags.
4. Autoclave equipment, following the guidelines described below.
5. **Collect additional quality-control samples** (for example, equipment and field blanks) to determine whether the alternative sterilization method was effective. **Use sterile DIW as the blank solution.**

The alternative sterilization method avoids use of the strong sodium hypochlorite solution, but requires collection of an equipment blank for quality control of the method's efficacy.

Autoclaving

Sampling equipment must be autoclaved for 20 minutes at 121°C before use. (If the sodium hypochlorite sterilization method is used, autoclaving is not necessary.)

- Use only autoclaves that have temperature, pressure, and liquid- and dry-utensil-cycle controls. **Do not use** steam sterilizers, vertical autoclaves, and pressure cookers without temperature controls.
- Ensure that the materials to be autoclaved are thermally stable. Autoclavable materials include plastics (such as polycarbonate, polypropylene, polyallomer, and polymethylpentene) and Teflon® and Tefzel® (such as perfluoroalkyoxy-polymers (PFA), ethylenetetrafluoroethylene (ETFE), fluorinated ethylene propylene (FEP), and polytetrafluoroethylene polymers (PTFE)). **Note that each of these materials has different thermal characteristics and tolerances to repeated autoclaving.**
- Consult the 20th edition of "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1998, Section 9020 B, table 9020:III) for specifications regarding the length of time, temperature, and pressure for autoclave sterilization of various materials.

- When using the autoclave, it is necessary to:
  - Use sterilization indicator tape with each load.
  - Test the autoclave performance at least quarterly, using commercially available biological indicators. Biological indicators are composed of endospores—living cells that are resistant to heat but that can be destroyed by autoclaving.
  - Drain the autoclave at the end of each period of use.
  - Clean the autoclave with mild soap and water once a week during periods of daily use.
  - Avoid overloading the autoclave with equipment or materials; overloading will result in incomplete sterilization.
- Keep a logbook of the autoclave operation.
  - Record the temperature, pressure, date, and time of each autoclave run.
  - Record the date of each cleaning and the procedures used.
  - Enter into the logbook the results from the regularly scheduled quality-control (biological-indicator) checks, noting the date, the test results, and the name of the autoclave operator and (or) analyst.

Quality-control tests for autoclave operation are mandatory.

If the autoclave does not reach the specified temperature and pressure or fails the quality-control test, then service the autoclave, retest the autoclave, and resterilize all materials (American Public Health Association and others, 1998, p. 9-2 to 9-13).

7.3.2 SAMPLE COLLECTION, PRESERVATION, TRANSPORT, AND HOLDING TIMES

The specific procedures that have been developed for the collection, preservation, transport, and holding times of water samples before the samples are analyzed for protozoan pathogens must be followed strictly. These procedures can vary with types of sampling equipment and source of sample (surface water, ground water, treated water, or wastewater).

Maintain sterile conditions throughout sample collection, preservation, transport, and analysis.

Currently, samples for analysis of protozoan pathogens are collected primarily from surface water. Protozoan pathogens are not commonly found in ground water, although they have been known to occur in ground water that is in direct hydraulic connection with ("under the influence of") surface water. A summary of requirements for sample-collection equipment, procedures for sample preservation, and holding-time requirements is given in table 7.3-2.

Table 7.3-2. Summary of equipment and sample-preservation procedures used for surface-water sample collection for protozoan pathogen analysis

[EWI, equal-width increment; EDI, equal-discharge increment; L, liter; *NFM, National Field Manual for the Collection of Water-Quality Data*; mL, milliliter; $Na_2S_2O_3$, sodium thiosulfate; EDTA, ethylenediaminetetraacetic acid; °C, degrees Celsius]

Equipment for sample collection
For EWI or EDI surface-water samples: use US D-95, US DH-95, or US DH-81 samplers with a sterile 1-L wide-mouth bottle, and sterile caps and nozzles; or the US D-96 with a sterile 3-L autoclavable bag (NFM 2.1.1).
For surface-water samples using point samplers or the hand-dip method: use a sterile, narrow-mouth container, 1-L or 3-L capacity.
For preparing sample composites: use a collapsible, low-density polyethylene cubitainer for collection of the 10-L bulk sample (fig. 7.3-1)
Procedures for sample preservation
Before sample collection: if halogen neutralization is needed to preserve the sample, add 0.5 mL of a 10-percent $Na_2S_2O_3$ solution per 1 L of sample (NFM 7.3.2.B). -If sterile $Na_2S_2O_3$ is used, then dispense with sterile pipet into sterile bottle. -If $Na_2S_2O_3$ is not sterile, then dispense with pipet into sample bottle and autoclave.
Before sample collection: if chelation of trace elements is needed to preserve the sample, then add 0.3 mL of a 15-percent EDTA solution per 100 mL of sample (NFM 7.3.2.B).
After sample collection: Chill all samples at 0 to 8°C to preserve the sample until analysis.
Maximum holding time
Do not hold the sample for longer than 96 hours after sample collection and before sample analysis for protozoan pathogens.

7.3.2.A SAMPLE COLLECTION

The spatial and temporal distribution of microorganisms can be as variable as the distribution of suspended sediment in water because microorganisms generally associate with solid particles. **Collection of quality-control (QC) samples is an essential component of the sampling process.**

CAUTION: Always wear gloves when handling sampling equipment and samples. Take care to prevent contaminated water from contacting skin, mouth, nose, or eyes (NFM 9.7).

- **Ground Water:** Follow the guidelines described in NFM 7.1.1.B for the collection of fecal indicator bacteria in ground water, but collect a 10-L bulk sample. The use of the alternative sterilization method is recommended when using a pump with metallic components (see section 7.3.1).
- **Surface Water:** To obtain data that accurately represent the site at the time of sampling, use the same methods for collecting surface-water samples for protozoans as for suspended sediment (Edwards and Glysson, 1999; NFM 4.1).
  - For the isokinetic or hand-dip sample-collection methods described below, collect the water using 1-L bottles or 3-L bags and prepare a 10-L bulk composite sample by pouring the bottle or bag contents into a collapsible, low-density polyethylene cubitainer (fig. 7.3-1).
    - **Flowing water:** use isokinetic depth-and-width-integrating sampling methods[7] (NFM 4.1.1.A).

[7]Sample-collection methods may be modified to ensure consistency with study objectives and as appropriate for site conditions. It is necessary to describe any modifications to methods in a report of the results of the study.

- **Still water** (lakes or reservoirs, or other surface-water conditions for which depth-and-width-integrating methods are not applicable): use the hand-dip method or a sterile point sampler (NFM 4.1.1.B).

— Be sure to fill the cubitainer completely, to ensure collection of a full 10-L sample.

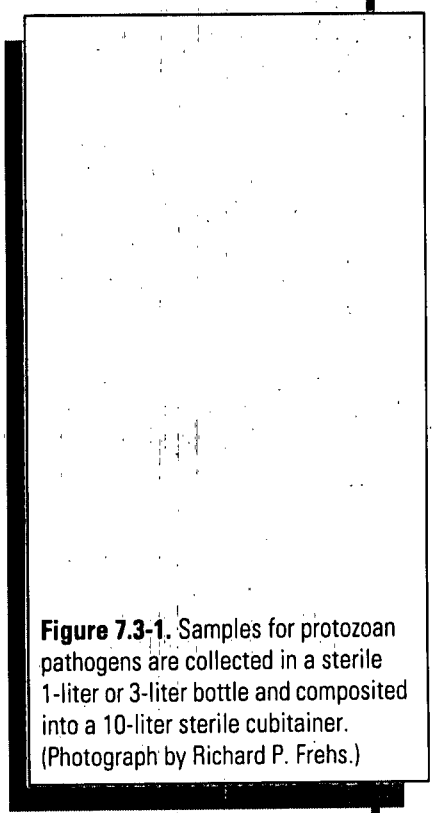


Figure 7.3-1. Samples for protozoan pathogens are collected in a sterile 1-liter or 3-liter bottle and composited into a 10-liter sterile cubitainer. (Photograph by Richard P. Frehs.)

Quality Control

Plan to collect quality-control samples. Although subject to the specific data-quality requirements and site conditions of the study, quality-control samples typically constitute at least 5 to 20 percent of the total number of samples collected over a given period of time at a given location. General requirements and recommendations for the common types of quality-control samples are described below ("Selected Terms" in the Conversion Factors section at the end of NFM 7 contains definitions of these quality-control terms as they apply to protozoan pathogens).

- **Equipment blanks**—An equipment blank is required when equipment is sterilized using the alternative sterilization method, or when study objectives require additional quality-control samples. Equipment blanks are optional for the sodium hypochlorite sterilization method.
- **Field blanks**—Field blanks generally are not required because of the low potential for contamination. Their use depends on study objectives and site conditions.
- **Field replicates**—Field replicates generally are optional because of the low numbers of protozoans in most waters. The use of replicate samples depends largely on site conditions and study objectives.
- **Matrix spikes**—Samples for matrix spikes are collected routinely for studies involving protozoan analyses. **A second 10-L sample must be collected for the matrix spike.** Matrix-spike samples are fortified (spiked) with known amounts of oocysts and cysts by the analyzing laboratory. As previously noted, the recovery of oocysts and cysts from environmental samples using Method 1623 has been found to be highly variable and affected by water chemistry, as well as by streamflow and other characteristics of the water body.

— Collection of a 10-L matrix-spike sample along with the first 10-L sample that is collected from a water source is required (U.S. Environmental Protection Agency, 2001a, Section 9.5).

— Although USEPA guidelines stipulate the collection of additional matrix-spike samples from the same source water after at least every 20th sample, **the USGS recommends collecting matrix-spike samples more frequently, as is appropriate for specific study objectives, streamflow conditions, and chemical characteristics.**

Isokinetic Sampling Methods

Isokinetic sampling methods, including the equal-discharge-increment (EDI) method, equal-width-increment (EWI) method, and single vertical at centroid-of-flow (VCF) method, are the standard USGS methods used for sampling flowing waters and are recommended unless study objectives or site characteristics dictate otherwise (NFM 4.1.1.A).

1. Select the appropriate isokinetic method (NFM 4.1). The EDI method is preferred at sites where the velocity distribution across a stream section is well established or at a section where the depth varies (for example, at a gaging station) (Edwards and Glysson, 1999).
2. Select the appropriate sampler and equipment and prepare the equipment for use (section 7.3.1). **Sampling equipment must be sterile,** including the collection bottle (or bags for the bag sampler), nozzle, and cap (table 7.3-1).
   - For streams with depths of 5 meters (m) (approximately 16.4 feet) or less, use a US D-95, US DH-95, or US DH-81 sampler (NFM 2.1.1).
   - For stream sections where depths exceed 5 m (16.4 feet), use the US D-96, with either autoclavable Teflon® bags or autoclavable cooking bags. Thermotolerant polymers are described in section 7.3.1.B under "Autoclaving."
   - Use the proper nozzle size and transit rate for the velocity conditions in the section to ensure isokinetic collection of the sample (NFM 4.1.1.A).

Hand-Dip Sampling Method

If the stream depth and (or) velocity are not sufficient to use an isokinetic sampling method, collect a sample using a hand-dip method. Sampling still water or sampling at depth in lakes, reservoirs, estuaries, and oceans requires a sterile point sampler. For example, Niskin, ZoBell, and Wheaton point samplers hold a sterilizable bottle or bag. Wearing nonpowdered nitrile or latex gloves (NFM 2), collect a hand-dip sample as follows:

1. Open a sterile, plastic bottle; grasp the bottle near the base, keeping hand and arm on the downstream side of the bottle.
2. Without rinsing it, plunge the bottle opening downward, below the water surface, with the opening pointed slightly upward into the current. Allow the bottle to fill.
3. Remove the bottle with the opening pointed upward from the water and tightly cap it. Composite several bottles into a 10-L cubitainer until it is full.

CAUTION:
Do not sample in or near an open water body without wearing a correctly fitted personal flotation device (PFD).

SAMPLE PRESERVATION, TRANSPORT, AND HOLDING TIMES 7.3.2.B

Halogens and trace metals that are present in the source water can compromise an accurate analysis of the sample for protozoan pathogens. Residual chlorine commonly is found in treated (disinfected) potable water (for example, public water systems), and in sources such as wastewater effluents or mixing zones directly downstream from wastewater-treatment plants. Most taps or wells (for example, small private water systems) do not contain residual chlorine. Trace metals such as copper, nickel, and zinc that are present at concentrations from 10 to greater than 1,000 micrograms per liter (µg/L) can be toxic to microorganisms; the concentration at which toxicity occurs varies in the literature (Britton and Greeson, 1989, p. 56; Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19). The sample must be treated at the time of collection to prevent halogen and trace-metal interferences.

- **Add sodium thiosulfate ($Na_2S_2O_3$)** to sample bottles, either before sterilization or immediately after sample collection, if the water to be collected is suspected to contain residual chlorine or other halogens.
- **Add ethylenediaminetetraacetic acid (EDTA)** to sample bottles before filling the bottles with sample, if trace-metal concentration is suspected at levels that could be toxic to protozoan pathogens.

To prepare for collecting a halogenated sample:

1. Prepare a 10-percent solution of $Na_2S_2O_3$ as follows:
   a. In a volumetric flask, dissolve 100 grams (g) $Na_2S_2O_3$ into 500 milliliters (mL) of DIW. Stir until dissolved. Fill flask to 1,000 mL with DIW (Bordner and Winter, 1978, p. 6; American Public Health Association and others, 1998, p. 9-19).
   b. Autoclave at 121°C for 30 minutes (U.S. Environmental Protection Agency, 1996, p. VIII–11).
   c. Store the $Na_2S_2O_3$ solution at room temperature or under refrigeration. **After 6 months, prepare a fresh solution** and label the bottle with the contents and date of preparation. **Discard unused solution that has expired, either through a certified laboratory or according to existing regulations for your locale.**
2. Before collecting the sample in the sample bottle, pipet into the sample bottle 0.5 mL of 10-percent $Na_2S_2O_3$ solution for every 1 L of sample. If the sterile $Na_2S_2O_3$ is used, then be sure to use only sterile pipets and sterile sample bottles. If the $Na_2S_2O_3$ is not sterile, then dispense the required volume of $Na_2S_2O_3$ into a sample bottle and autoclave at 121°C for 15 minutes.

To prepare for collecting samples with potential trace-metal toxicity:

1. Prepare the EDTA stock solution as follows:
   a. Dissolve 372 milligrams (mg) of EDTA in 1,000 mL of DIW (American Public Health Association and others, 1998, p. 9-19).
   b. Store the EDTA stock solution at room temperature.
   c. Keep the bottles tightly capped between uses. **After 6 months, prepare a fresh solution** and label the bottle with the contents and date of preparation. **Discard unused solution that has expired, either through a certified laboratory or according to existing regulations for your locale.**

2. Before sterilization, add 0.3 mL of the EDTA stock solution per 100 mL of sample to sample bottles. EDTA can be combined with the $Na_2S_2O_3$ solution in the sample bottle.
3. Autoclave the sample bottle containing EDTA stock solution at 121°C for 15 minutes.

$Na_2S_2O_3$ and EDTA solutions have a 6-month shelf life.

To prepare the samples for transport:

1. **Chill—do not freeze**—the 10-L sample cubitainer in an ice chest or refrigerator at 0 to 8°C **immediately after the samples have been collected and treated.**
2. Check that the sample identification and relevant information for use by the laboratory have been recorded correctly on the sample container and on the analytical services request (ASR) form and, if being used, on a chain-of-custody form.
   - Seal the ASR form and chain-of-custody form in plastic bags and tape the bags to the inside lid of the ice chest to be shipped to the laboratory.
   - Upon receipt, the laboratory should record the temperature of the samples and store them at 0 to 8°C until processed.
   - It is best for the laboratory to process the samples as soon as possible, but **sample analysis must be within 96 hours of sample collection.**

The holding time for samples to be analyzed using USEPA Method 1623 is 96 hours from sample collection.

7.3.3 LABORATORY METHOD: USEPA METHOD 1623

Project personnel should be aware of the analytical method to be used by a laboratory on samples to be analyzed for protozoan pathogens, and the requirements for quality control for the method. The field and laboratory procedures for protozoan samples that are described in this chapter are specific to analysis by USEPA Method 1623: *Cryptosporidium* and *Giardia* in water by filtration/IMS/FA (U.S. Environmental Protection Agency, 2001a). Method 1623 must be performed in a certified laboratory by a qualified analyst, and involves the following steps:

1. **Filtration**—*Cryptosporidium* oocysts and *Giardia* cysts from the water sample are concentrated on a filter, eluted from the filter with an elution buffer, and reconcentrated by centrifugation.
2. **Immunomagnetic separation (IMS)**—The oocysts and cysts are magnetized by attachment of magnetic beads conjugated to antibodies and then separated from extraneous materials in the sample with a magnet.
3. **Immunofluorescence assay (FA)**—Fluorescently labeled antibodies and vital dye are used to make the final microscopic identification of the oocysts and cysts. The organisms are identified when the size, shape, color, and morphology agree with specified criteria.

Quality Control. Laboratory performance is compared to established performance criteria to determine whether the results of the analyses meet the performance characteristics of the method, as described in U.S. Environmental Protection Agency, 2001a, Section 9.0. Any laboratory that uses USEPA Method 1623 must fulfill the following minimum quality-control requirements: Initial Precision and Recovery (IPR) tests, Ongoing Precision and Recovery (OPR) tests, and the use of method blanks.

- **Initial Precision and Recovery (IPR)**—Each analyst in the laboratory must establish the ability to demonstrate control over the analytical system and to generate acceptable precision and recovery. IPR tests consist of reagent-water samples that are spiked with known amounts of *Cryptosporidium* and *Giardia* and that are analyzed exactly like environmental samples. The IPR test must be completed before the analysis of any environmental samples (U.S. Environmental Protection Agency, 2001a, Section 9.4).

- **Ongoing Precision and Recovery (OPR)**—The laboratory must demonstrate that the method is under control by analyzing OPR samples. OPR samples consist of reagent-water samples that are spiked with known amounts of *Cryptosporidium* and *Giardia* and that are analyzed exactly like environmental samples. The laboratory must analyze one OPR sample for each week in which environmental samples are analyzed, or after every 20th environmental sample, whichever comes first (U.S. Environmental Protection Agency, 2001a, Section 9.7).

- **Method Blank**—The laboratory must analyze reagent-water samples containing no protozoans to demonstrate freedom from contamination. Method blanks should be analyzed immediately before conducting the IPR and OPR tests. The laboratory should analyze one method blank for each week in which environmental samples are analyzed, or after every 20th environmental sample, whichever comes first (U.S. Environmental Protection Agency, 2001a, Section 9.6).

7.3.4 CALCULATION AND REPORTING OF PROTOZOAN PATHOGENS

As prescribed by USEPA Method 1623, report the total number of *Cryptosporidium* oocysts and (or) *Giardia* cysts counted.

- Record the result as the total number of oocysts or cysts per 10 L.
- Record the percent recovery for matrix spikes analyzed.

Use the list of parameter codes shown in Appendix A7-A, table 4, when reporting protozoans in the USGS National Water Information System (NWIS).

CONVERSION FACTORS, SELECTED TERMS, SYMBOLS, CHEMICAL FORMULAS, AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	By	To obtain
micrometer (μm)	3.937×10^{-5}	inch (in.)
	3.3×10^{-6}	foot (ft)
millimeter (mm)	0.03937	inch
centimeter (cm)	0.3937	inch
square centimeter (cm^2)	0.155	square inch (in^2)
meter (m)	3.281	foot
nanometer (nm)	3.93×10^{-8}	inch
liter (L)	0.264	gallon (gal)
milliliter (mL)	0.0338	ounce, fluid (oz)
gram (g)	0.03527	ounce, avoirdupois
microgram (μg)	3.527×10^{-8}	ounce, avoirdupois
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois
kilopascal (kPa)	0.1450	pound per square inch (lb/in^2)

Temperature: Water and air temperature are given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$°F = 1.8(°C) + 32$$
$$°C = (°F/1.8) - 32$$

SELECTED TERMS

Distilled or deionized water: ASTM type 1 water or better.

Equipment blank: A quality control sample that consists of a blank solution processed sequentially through each component of the equipment system to be used in sample collection, processing, preservation, and handling in a controlled environment. The sample is prepared by passing sterile water or buffer through the sampling equipment (if applicable) and into a sterile sample container. Positive results for the equipment blank indicate sampling and analytical bias caused by contamination from equipment and supplies.

Field blank: A quality-control sample that consists of a laboratory-certified blank solution processed through all the equipment used in the various stages of sample collection, processing, preservation, and handling under field conditions. **For quality control of water samples for microbial analyses,** the blank sample is prepared by passing either sterile deionized or distilled water (DIW) or sterile buffered water through the sampling equipment (if applicable) into a sterile sample container. Positive growth on the field blank indicates sampling and analytical bias caused by contamination from equipment, supplies, and (or) ambient environmental conditions.

Field-generated sequential replicate and split replicate: Quality-control samples that measure the variability in all or part of the sampling and analysis system. Replicates—environmental samples collected in duplicate, triplicate, or higher multiples and collected close in time and space—are considered identical in composition and are analyzed for the same properties. **For quality control of water samples for microbial analyses,** two samples are collected sequentially in the field (sequential replicates) and each sample is analyzed twice (split replicate). The relative percent difference between the results is calculated as a measure of variability.

Filter blank (membrane-filtration): As applied to the quality control of water samples for microbial analyses, the filter blank measures the sterility of the equipment and supplies used during the membrane-filtration procedure for bacterial indicators. A 50- to 100-mL sample of sterile buffered water is passed through the filtration apparatus onto a sterile membrane filter before processing the sample. Positive growth on the filter after incubation on selective media indicates poor technique in analysis and positive bias (contamination) of results.

Matrix spike (laboratory matrix spike): A quality-control sample that determines the effect of the sample composition (matrix) on the recovery efficiency of the analytical method. For quality control of water samples for microbiological analyses, a sample is prepared in the laboratory by adding a known quantity of organisms to a specified amount of sample matrix for which an independent estimate of target analyte concentration is available.

Micrometer (μm): The millionth part of the meter. The pore diameter of filter media is expressed in micrometer units.

Negative control: A quality-control sample that measures the selectivity of the membrane-filtration medium for the test organism. A pure culture of nontarget organisms is passed through the filtration apparatus onto a membrane filter and cultured on a selective medium. The absence of growth on the filter after incubation on a selective medium indicates the selective medium is meeting its specifications for culture of the target organism.

Normality, *N* (equivalents per liter): The number of equivalents of acid, base, or redox-active species per liter of solution. Examples: a solution that is 0.01 *F* (formal) in HCl is 0.01 *N* in the hydronium ion (H^+). A solution that is 0.01 *F* in H_2SO_4 is 0.02 *N* in acidity.

Positive control: A quality-control sample that ensures the analytical method is correctly performed and that target organisms are correctly identified and detected. A pure culture of the target organism is passed through the filtration apparatus onto a membrane filter and cultured on a selective medium. Positive growth within a recommended range is considered indicative of the quality of the test medium and procedures to support growth under typical working conditions.

Procedure blank: A quality-control sample that measures the effectiveness of the analyst's rinsing technique during the membrane-filtration procedure for bacterial indicators. A 50- to 100-mL sample of sterile buffered water is passed through the filtration apparatus onto a sterile membrane filter after processing the sample. Positive growth on the filter after incubation on a selective medium indicates poor rinsing technique.

SELECTED SYMBOLS AND CHEMICAL FORMULAS

>	greater than
≥	equal to or greater than
<	less than
≤	equal to or less than
±	plus or minus
g/L	gram per liter
µm	micrometer
µg/L	microgram per liter (equivalent to parts per billion)
$CaCl_2$	calcium chloride
Cu	copper
$FeCl_3$	ferric chloride
H_2SO_4	sulfuric acid
K_2HPO_4	potassium hydrogen phosphate
KH_2PO_4	potassium dihydrogen phosphate
$MgSO_4$	magnesium sulfate
Na_2SO_3	sodium sulfite
$Na_2S_2O_3$	sodium thiosulfate
$NaHPO_4$	sodium phosphate
NaOH	sodium hydroxide
Ni	nickel
NH_4Cl	ammonium chloride
Zn	zinc

ABBREVIATIONS

BOD	biochemical oxygen demand
BOD_5	biochemical oxygen demand (5 day)
CBOD	carbonaceous biochemical oxygen demand
$CBOD_u$	ultimate carbonaceous biochemical oxygen demand
col/100mL	colonies per 100 milliliters
DIW	deionized or distilled water
DO	dissolved oxygen
E. coli	*Escherichia coli*
EDI	equal-discharge increment

	EDTA	ethylenediaminetetraacetic acid
	EIA	enterococcus confirmation medium (esculin substrate)
+	ETFE	ethylenetetraflouroethylene
	EWI	equal-width increment
	FEP	fluorinated ethylene propylene
	GWUDISW	ground water under the direct influence of surface water
	IPR	initial precision recovery
	KF	streptococcus medium
	mCP	*Clostridium perfringens* medium
	mE	membrane filter—Enterococci medium
	mEI	enterococcus medium
	mENDO	membrane filter—total coliform medium
	mF	membrance filter technique
	mFC	membrane filter—Fecal Coliform medium
	MI	total coliform and *Escherichia coli* medium
	MPN	most probable number
	mTEC	membrane filter—Thermotolerant *Escherichia coli* media
	N	normal
	NA–MUG	nutrient agar-4-methylumbelliferyl-b-D-glucuronide
+	NFM	National Field Manual (*National Field Manual for the Collection of Water-Quality Data*)
	NWIS	National Water Information System of the U.S. Geological Survey
	OPR	ongoing precision recovery
	OWQRL	USGS Ocala Water Quality & Research Laboratory, Ocala, Florida
	PDF	personal flotation device
	PFA	perflouroalkyoxy polymers
	PTFE	polytetraflouroethylene polymers ("Teflon")
	QC	quality control
	TCMP	2-chloro-6-(trichloro methyl) pyridine
	TD	to deliver
	TNTC	Too Numerous To Count
	TTC	triphenyltetrazolium chloride
	USEPA	U.S. Environmental Protection Agency
	USGS	U.S. Geological Survey

+

This page left blank intentionally.

SELECTED REFERENCES AND DOCUMENTS

7.0—SELECTED REFERENCES FOR FIVE-DAY BIOCHEMICAL OXYGEN DEMAND

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1995, Standard methods for the examination of water and wastewater (19th ed.): Washington, D.C., American Public Health Association, p. 5-1 to 5-6.

Britton, L.J., and Greeson, P.E., eds., 1989, Methods for collection and analysis of aquatic biological and microbiological samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A4, 363 p.

Edwards, T.K., and Glysson, G.D., 1998, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 80 p.

Hines, W.G., McKenzie, S.W., Rickert, D.A., and Rinella, F.A., 1978, Dissolved-oxygen regimen of the Willamette River, Oregon, under conditions of basinwide secondary treatment: U.S. Geological Survey Circular 715-I, 52 p.

Nemerow, N.L., 1974, Scientific stream pollution analysis: New York, McGraw-Hill, p. 69–116.

Sawyer, C.N., and McCarty, P.L., 1978, Chemistry for environmental engineering: New York, McGraw-Hill, p. 416–432.

Stamer, J.K., Bennett, J.P., and McKenzie. S.W., 1983, Determination of ultimate carbonaceous BOD and the specific rate constant (k_1): U.S. Geological Survey Open-File Report 82-645, 21 p.

Stamer, J.K., McKenzie, S.W., Cherry, R.N., Scott, C.T., and Stamer, S.L., 1979, Methods of ultimate carbonaceous BOD determination: Journal—Water Pollution Control Federation, v. 51, no. 5, p. 918–925.

Tchobanoglous, G., and Schroeder, E.D., 1985, Water quality—characteristics, modeling, modification: Menlo Park, Calif., Addison-Wesley Publishing Company, p. 107–121.

Veltz, C.J. 1984, Applied stream sanitation (2d ed.): New York, John Wiley and Sons, p. 149-280.

7.1 —SELECTED REFERENCES FOR FECAL INDICATOR BACTERIA

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1998, Standard methods for the examination of water and wastewater (20th ed.): Washington, D.C., American Public Health Association, p. 9-1 to 9-78.

Bisson, J.W., and Cabelli, V.J., 1980, *Clostridium perfringens* as a water pollution indictor: Journal—Water Pollution Control Federation, v. 52, no. 2, p. 241–248.

Bordner, Robert, and Winter, John, 1978, Microbiological methods for monitoring the environment, water, and wastes: U.S. Environmental Protection Agency, EPA 600/8–78–017, 338 p.

Britton, L.J., and Greeson, P.E., eds., 1989, Methods for collection and analysis of aquatic biological and microbiological samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A4, 363 p.

Cabelli, V. J., 1977, Indicators of recreational water quality, *in* Hoadley, A.W., and Dutka, B.J., eds., Bacterial indicators/health hazards associated with water, 1977: Philadelphia, American Society for Testing and Materials, ASTM STP 635, p. 222–238.

Dufour, A.P., 1977, *Escherichia coli*—the fecal coliform, *in* Hoadley, A.W., and Dutka, B.J., eds., Bacterial indicators/health hazards associated with water, 1977: Philadelphia, American Society for Testing and Materials, ASTM STP 635, p. 48–58.

Dufour, A.P., and Cabelli, V.J., 1984, Health effects criteria for fresh recreational waters: Cincinnati, Ohio, U.S. Environmental Protection Agency, EPA 600/1–84–004, 33 p.

Edwards, T.K., and Glysson, G.D., 1999, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 89 p.

Francy, D.S., Helsel, D.R., and Nally, R.A., 2000, Occurrence and distribution of microbiological indicators in groundwater and stream water: Water Environment Research, v. 72, no. 2, p. 152–161.

Fujioka, R.S., and Shizumura, L.K., 1985, *Clostridium perfringens*, a reliable indicator of stream water quality: Journal—Water Pollution Control Federation, v. 57, no. 10, p. 986–992.

Millipore Corporation, 1973, Biological analysis of water and wastewater: Bedford, Mass., Application Manual AM302, p. 48–51.

U.S. Environmental Protection Agency, 1982, Handbook for sampling and sample preservation of water and wastewater: Cincinnati, Ohio, Office of Research and Development, EPA 600/4–82–029, p. 251–254.

_____1985, Test method for *Escherichia coli* and enterococci in water by the membrane filter procedure: Cincinnati, Ohio, Environmental Monitoring and Support Laboratory, EPA 600/4–85/076, 24 p.

_____1986, Ambient water quality criteria for bacteria—1986: Washington, D.C., Office of Water Regulations and Standards Division, EPA 440/5–84–002, p. 15.

_____1991a, Test methods for *Escherichia coli* in drinking water, nutrient agar with MUG—membrane filter procedure: Cincinnati, Ohio, Office of Water (WH-550), EPA 600/4–91/016, 2 p.

_____1991b, Final rule, National primary drinking water regulations—filtration, disinfection, turbidity, *Giardia lamblia*, viruses, *Legionella*, and heterotrophic bacteria: U.S. Code of Federal Regulations, Title 40, Parts 141 and 142, Part II, p. 27.

_____1996, EPA Information Collection Rule microbial laboratory manual: Washington, D.C., EPA/600/R-95/178, p. XI-1 to XI-15.

_____1997, Method 1600—Membrane filter test method for enterococci in water: Washington, D.C., Office of Water, EPA-821-R-97-004, 9 p.

_____2000a, Membrane filter method for the simultaneous detection of total coliforms and *Escherichia coli* in drinking water: Cincinnati, Ohio, Office of Research and Development, EPA 600-R-00-013, 20 p.

_____2000b, Improved enumeration methods for the recreational water quality indicators: Enterococci and *Escherichia coli*: Washington, D.C., Office of Science and Technology, EPA/821/R-97/004, 49 p.

_____2002, National beach guidance and required performance criteria for grants: Washington, D.C., Office of Water, EPA-823-B-02-004, p. 4-1 to 4-12 and Appendix K.

U.S. Geological Survey, 2001, *Clostridium perfringens*, using the mCP agar method: accessed February 21, 2003 at http://oh.water.usgs.gov/micro/clos.html.

_____2002, Techniques of Water-Resources Investigations Reports, accessed December 31, 2002, at http://water.usgs.gov/pubs/twri/ [The U.S. Geological Survey publishes this series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The material is grouped under major subject headings called books and is further divided into sections and chapters. For example, Section A of Book 9 (Handbooks for Water-Resources Investigations) refers to this *National Field Manual*, this report being Chapter 7 of that publication.]

7.2 —SELECTED REFERENCES FOR FECAL INDICATOR VIRUSES

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1998, Standard methods for the analysis of water and wastewater (20th ed.): Washington, D.C., American Public Health Association, p. 9-1 to 9-73.

Bordner, Robert, and Winter, John, 1978, Microbiological methods for monitoring the environment, water, and wastes: U.S. Environmental Protection Agency, EPA 600/8-78-017, 338 p.

Britton, L.J., and Greeson, P.E., eds., 1989, Methods for collection and analysis of aquatic biological and microbiological samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A4, 160 p.

Edwards, T.K., and Glysson, G.D., 1999, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 89 p.

Gerba, C.P., 1987, Phage as indicators of fecal pollution, *in* Goyal, S.M. and others, eds., Phage ecology: New York, John Wiley and Sons, p. 197–209.

Handzel, T.R., Green, R.M., Sanchez, C., Chung, H., and Sobsey, M.D., 1993, Improved specificity in detecting F-specific coliphages in environmental samples by suppression of somatic phages: Water Science and Technology, v. 27, no. 3-4, p. 123–131.

Havelaar, A.H., van Olphen, Marja, and Drost, Y.C., 1993, F-specific bacteriophages are adequate model organisms for enteric viruses in fresh water: Applied and Environmental Microbiology, v. 59, no. 9, p. 2956–2962.

International Association of Water Pollution Research and Control Study Group on Health Related Water Microbiology, 1991, Bacteriophages as model viruses in water quality control: Water Research, v. 25, no. 5, p. 529–545.

Sobsey, M.D., Amanti, Adam, and Handzel, T.R., 1995, Detection and occurrence of coliphage indicator viruses in water, *in* Proceedings of the Water Quality Technology Conference, American Water Works Association, November 1995, New Orleans, La: p. 2087–2097.

U.S. Environmental Protection Agency, 1982, Handbook for sampling and sample preservation of water and wastewater: Cincinnati, Ohio, Office of Research and Development, EPA 600/4-82-029, p. 251–254.

_____1996, EPA Information Collection Rule microbial laboratory manual: Washington, D.C., EPA/600/R-95/178.

U.S. Environmental Protection Agency, 2001a, Method 1601: Male-specific (F+) and somatic coliphage in water by two-step enrichment procedure: Washington, D.C., EPA 821-R-01-030, 32 p.

_____2001b, Method 1602: Male-specific (F+) and somatic coliphage in water by single agar layer (SAL) procedure: Washington, D.C., EPA 821-R-01-029, 30 p.

_____2002, National beach guidance and required performance criteria for grants: Washington, D.C., Office of Water, EPA-823-B-02-004, p. 4-1 to 4-12 and Appendix K.

U.S. Geological Survey, 2001, Ohio District's Microbiology Program: U.S. Geological Survey data available online at URL http://oh.water.usgs.gov/microbiol.html, accessed January 10, 2003.

7.3—SELECTED REFERENCES FOR PROTOZOAN PATHOGENS

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1998, Standard methods for the analysis of water and wastewater (20th ed.): Washington, D.C., American Public Health Association [variously paged].

Atherholt, T.B., LeChevallier, M.W., Norton, W.D., and Rosen, J.S., 1998, Effect of rainfall on *Giardia* and *Crypto*, Journal of the American Water Works Association, v. 90, no. 9. p. 66–80.

Bordner, Robert, and Winter, John, 1978, Microbiological methods for monitoring the environment, water, and wastes: U.S. Environmental Protection Agency, EPA 600/8-78-017, 338 p.

Britton, L.J., and Greeson, P.E., eds., 1989, Methods for collection and analysis of aquatic biological and microbiological samples: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A4, 160 p.

Edwards, T.K., and Glysson, G.D., 1999, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 89 p.

Kuhn, R.C., and Oshima, K.H., 2002, Hollow-fiber ultrafiltration of *Cryptosporidium parvum* oocysts from a wide variety of 10-L surface water samples: Canadian Journal of Microbiology, v. 48, p. 542–549.

LeChevallier, M.W., Norton, W.D., and Lee, R.G., 1991, Occurrence of *Giardia* and *Cryptosporidium* species in surface water supplies: Applied and Environmental Microbiology, v. 57, no. 9, p. 2610–2616.

LeChevallier, M.W., and Norton, W.D., 1995, *Giardia* and *Cryptosporidium* in raw and finished water: Journal of the American Water Works Association, v. 87, no. 9, p. 54–68.

LeChevallier, M.W., Di Giovanni, G.D., Clancy, J.L., Bukhari, Z., Bukhari, S., Rosen, J.S., Sobrinho, J., and Frey, M.M., 2003, Comparison of Method 1623 and cell culture-PCR for detection of *Cryptosporidium* spp. in source waters: Applied and Environmental Microbiology, v. 69, no. 2. p. 971–979.

Lee, S.H., Levy, D.A., Craun, G.F., Beach, M.J., and Calderon, R.L., 2002, Surveillance for waterborne-disease outbreaks—United States, 1999–2000: Morbidity and Mortality Weekly Report—Surveillance Summaries, November 22, 2002, 51 (SS08), p. 1–28.

Rose, J.B., Darbin, H., and Gerba, C.P., 1988, Correlations of the protozoa, *Cryptosporidium* and *Giardia*, with water quality variables in a watershed: Water Science and Technology, v. 20, no. 11-12, p. 271–276.

Rose, J.B., Gerba, C.P., and Jakubowski, W., 1991, Survey of potable water supplies for *Cryptosporidium* and *Giardia*: Environmental Science & Technology, v. 25, no. 8, p. 1393–1400.

Rose, J.B., Lisle, J.T., and LeChevallier, M., 1997, Waterborne Cryptosporidiosis—Incidence, outbreaks, and treatment strategies, *in* Fayer, R. ed., *Cryptosporidium* and cryptosporidiosis: Boca Raton, Fla., CRC Press, p. 93–109.

Simmons, O.D., Sobsey, M.D., Schaefer, F.W., Francy, D.S., Nally, R.A., and Heany, C.D., 2001, Evaluation of USEPA Method 1622 for detection of *Cryptosporidium* oocysts in stream waters: Journal of American Water Works Association, v. 93, no. 1, p. 78–87.

U.S. Environmental Protection Agency, 1996, EPA Information Collection Rule microbial laboratory manual: Washington, D.C., EPA/600/R-95/178, p. VIII-11.

_____2001a, Method 1623—*Cryptosporidium* and *Giardia* in water by filtration, immunomagnetic separation, and fluorescent antibody: Washington, D.C., EPA 821-R-01-025, 52 p.

_____2001b, Implementation and results of the information collection rule supplemental surveys: Office of Water, Washington, D.C., EPA-815-R-01-003, 125 p.

SELECTED DOCUMENTS

The following memorandums are available on the Internet through the USGS Web page at http://water.usgs.gov/admin/memo/ (accessed March 31, 2003).

Quality of Water Branch Technical Memorandum No. 76.25-t, WATER QUALITY: Analytical Methods—Microbiological, September 1976, 28 p.

Office of Water Quality Technical Memorandum No. 93.10, PROGRAMS AND PLANS—(1) Disposal of petri dishes containing bacteria media, and (2) *Aspergillus*, April 1993, 2 p.

This page left blank intentionally.

APPENDIX A7-A.
Parameter Codes Used in the National Water Information System (NWIS) of the U.S. Geological Survey

Table 1. Parameter code for 5-day biochemical oxygen demand.

Table 2. Parameter codes for fecal indicator bacteria.

Table 3. Parameter codes for somatic and F-specific coliphages.

Table 4. Parameter codes for *Cryptosporidium* and *Giardia*.

Table 1. Parameter code for 5-day biochemical oxygen demand

Determination	Parameter code	Comments
Five-day biochemical oxygen demand (BOD)	00310	Parameter codes for methods other than the 5-day BOD can be found by accessing "Support Files" in the QWDATA database and searching for "Parameter Code Dictionary."

Table 2. Parameter codes for fecal indicator bacteria

[mENDO, total coliform medium; MI, total coliform and *Escherichia coli* medium; mFC, fecal coliform medium; µm, micrometer; mTEC, *Escherichia coli* medium; NA-MUG, *Escherichia coli* medium; mEI, enterococcus medium; EIA, enterococcus confirmation medium; mE, enterococcus medium; KF, fecal streptococcus medium; mCP, *Clostridium perfringens* medium]

Fecal indicator bacteria type[1]	Medium	Parameter code[2]
Total coliform bacteria	mENDO	31501
	MI	90900
Fecal coliform bacteria	mFC, 0.65-µm pore-size filter	31625
	mFC, 0.45-µm pore-size filter	31616
Escherichia coli	mTEC followed by urea phenol	31633
	Modified mTEC	90902
	MI	90901
	NA-MUG	50278
Enterococci bacteria	mEI followed by EIA	90909
	mE	31649
Fecal streptococci bacteria	KF	31673
Clostridium perfringens	mCP	90915

[1]Membrane-filtration method: all units are in colonies per 100 milliliters.
[2]The parameter codes listed are those that are in common (2003) use in the National Water Information System (NWIS) of the U.S. Geological Survey.

Table 3. Parameter codes for somatic and F-specific coliphages

[SAL, single-agar layer; *E. coli*, *Escherichia coli*; mL, milliliter; L, liter]

Type of coliphage	*E. coli* host strain[1]	Parameter code[2]	Unit of measurement[3]
SAL method			
Somatic	*E. coli* CN-13	90903	plaques/100 mL
F-specific	*E. coli* F-amp	90904	plaques/100 mL
Somatic	*E. coli* C	90905	plaques/100 mL
Two-step enrichment method			
Somatic	*E. coli* C	99328	Presence or absence/100 mL
Somatic	*E. coli* C	99329	Presence or absence/1 L
Somatic	*E. coli* C	99330	Presence or absence/4 L
Somatic	*E. coli* CN-13	99331	Presence or absence/100 mL
Somatic	*E. coli* CN-13	99332	Presence or absence/1 L
Somatic	*E. coli* CN-13	99333	Presence or absence/4 L
F-specific	*E. coli* F-amp	99334	Presence or absence/100 mL
F-specific	*E. coli* F-amp	99335	Presence or absence/1 L
F-specific	*E. coli* F-amp	99336	Presence or absence/4 L

[1]Bacterial host strain used to detect the specified coliphage type.
[2]The parameter codes listed are those that are in common use (2003) in the National Water Information System of the U.S. Geological Survey.
[3]Parameter codes vary by the sample volume associated with the unit of reporting.

Table 4. Parameter codes for *Cryptosporidium* and *Giardia*

[**Parameter code:** Analysis by U.S. Environmental Protection Agency Method 1623]

Parameter name	Parameter code	Unit of measurement
Cryptosporidium	99599	oocysts per 10 liters
Cryptosporidium—spike efficiency	99600	percent recovery
Giardia	99597	cysts per 10 liters
Giardia—spike efficiency	99598	percent recovery