36

151

QUALITY ASSURANCE PROJECT PLAN

MONITORING ORGANOPHOSPHOROUS PESTICIDES IN THE LOWER SAN JOAQUIN BASIN

Revision 0

Prepared by: Regional Water Quality Control Board
Central Valley
3443 Routier Road, Suite A
Sacramento, California 95827-3003

February 2000

QUALITY ASSURANCE PROJECT PLAN

MONITORING ORGANOPHOSPHOROUS PESTICIDES IN THE LOWER SAN JOAQUIN BASIN

Revision 0

Prepared by: Regional Water Quality Control Board
Central Valley
3443 Routier Road, Suite A
Sacramento, California 95827-3003

February 2000

QUALITY ASSURANCE PROJECT PLAN

MONITORING ORGANOPHOSPHOROUS PESTICIDES IN THE LOWER SAN JOAQUIN BASIN

Revision 0

Prepared by: Regional Water Quality Control Board
Central Valley
3443 Routier Road, Suite A
Sacramento, California 95827-3003

February 2000

1.0 TITLE PAGE AND APPROVAL

Quality Assurance Project Plan for Monitoring Organophosphorous pesticides in the lower San Joaquin Basin

Project Manager: _____

Shakoora Azimi-Gaylon, Quality Assurance, CVRWQCB

Project Manager: _____

Leslie F. Grober, Project Manager, CVRWQCB

Project Manager: _____

Chales R. Kratzer, Field Project Manager, USGS

1.0 TITLE PAGE AND APPROVAL

Quality Assurance Project Plan for Monitoring Organophosphorous pesticides in the lower San Joaquin Basin

Project Manager: _____
Shakoora Azimi-Gaylon, Quality Assurance, CVRWQCB

Project Manager: _____
Leslie F. Grober, Project Manager, CVRWQCB

Project Manager: _____
Chales R. Kratzer, Field Project Manager, USGS

TABLE OF CONTENTS

2.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) presents the organization, functions, procedures, and specific quality assurance (QA) and quality control (QC) activities for organphosphorous (OP) pesticides monitoring of thirteen sites in the Lower San Joaquin Basin during January and February 2000.

Data produced as a result of this study will be used as part of the development and implementation of an OP pesticide load reduction program for the San Joaquin River.

Primary users of this QAPP are the staff performing laboratory analyses and fieldwork for this study. Guidelines used to develop the specifications and procedures in this plan are presented in:

- *U.S. EPA Guidance on Quality Assurance Project Plans Final (*U.S. EPA QA/G-5)(February 1998)
- *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)
- *Field Guide For Collecting and Processing Stream-Water Sample for the National Water Quality Assessment Program* (U.S. Geological Survey) (1994)
- *Monitoring Organophosphorous Pesticides in Lower San Joaquin Basin during January and February 2000 (*Central Valley RWQCB- December 1999)

2.1 QAPP Objective and use

The goal of the procedures and specifications established in this QAPP is to provide standardized references, procedures and quality specifications for the sampling, analysis and data review procedures required for OP Pesticide Monitoring in the Lower San Joaquin River. This QAPP also establishes QA procedures for reviewing and documenting compliance with field and analytical procedures.

2.2 Project Planning Documents

This QAPP and the '*Field Guide For Collecting and Processing Stream-Water Sample for the National Water Quality Assessment Program* (U.S. Geological Survey) (1994)" are the two primary planning documents needed to conduct this study; the QAPP details the specific activities for this study, and the '*Field Guide For Collecting and Processing Stream-Water Sample for the National Water Quality Assessment Program* (U.S. Geological Survey) (1994)" is a reference for standard field procedures and specifications. The QAPP presents the site-specific data quality objectives (DQOs) and sampling plans that identify sampling locations, number of samples, field procedures and analytical methods to be used.

A health and safety plan (HASP) has also been prepared for this sampling event to establish the safety procedures and the level of personal protective equipment (PPE) required. This ensures that field activities are conducted in a manner that protects personnel performing the work and others in the vicinity.

3.0 SITE DESCRIPTION AND HISTORY

Storm water sampling and weekly sampling activities in the San Joaquin River Basin are undertaken to monitor organophosphate pesticides in the lower San Joaquin River Basin during the dormant spray season during January and February 2000.

Agricultural drainage and urban runoff enter the San Joaquin River and its tributaries from over 100 sites. Previous monitoring has demonstrated that agricultural drainage is the major source of pesticides entering the river. The focus of this monitoring effort is to collect data during the dormant spray season for additional monitoring of OP pesticides.

3.1 Site(s) Description

The study area includes thirteen sites in the lower San Joaquin River Basin from the San Joaquin River at Lander Avenue (near Stevenson) to the San Joaquin River near Vernalis. These sites includes:

Newman Wasteway located in the county of Merced. It discharges into San Joaquin River immediately south of Stanislaus-Merced County line. Access to the Wasteway is at the Highway 33 over-crossing.

Orestimba Creek located in the county of Stanislaus. It discharges into the San Joaquin River 0.9 miles due south of the Crows landing Bridge. The discharge is by gravity flow. The best access point is at River Road approximately 1.0 mile upstream of its discharge point. Orestimba Creek at River Road gives good access to the Creek and represent runoff water quality just prior to its entrance to the San Joaquin River at mile 109.

Turlock Irrigation District lateral No. 5 is located in Stanislaus County. Access to the site is via project levee off of Carpenter Road.

Tuolumne River at Toulumne City at Shiloh Road is on the left bank of the Tuolumne River, under the Shiloh Road Bride, approximately seven miles upstream of the confluence with San Joaquin River.

Stanislaus River at Caswell Park is on the right bank of the Stanislaus River approximately seven miles upstream of the confluence with San Joaquin River. Access is at campsite 24.

Merced River at River Road is at the abandoned bridge upstream of River Road, approximately one mile upstream of the confluence with the San Joaquin River.

San Joaquin River near Stevinson is located in Merced County approximately 16.5 miles north of Los Banos on Lander Avenue bridge (Highway 165).

San Joaquin River near Vernalis is located on the Airport Way bridge.

Del Puerto Creek at Vineyard Road is located in Stanislaus County on the Vineyard Road bridge.

Dry Creek at Claus Road is located on the right bank, about 50 feet upstream of the Claus Road bridge in Modesto.

Dry Creek at Gallo Bridge is located on a bridge to a Gallo facility about 2.0 miles downstream of the Highway 132 (Yosemite Blvd.) bridge in Modesto.

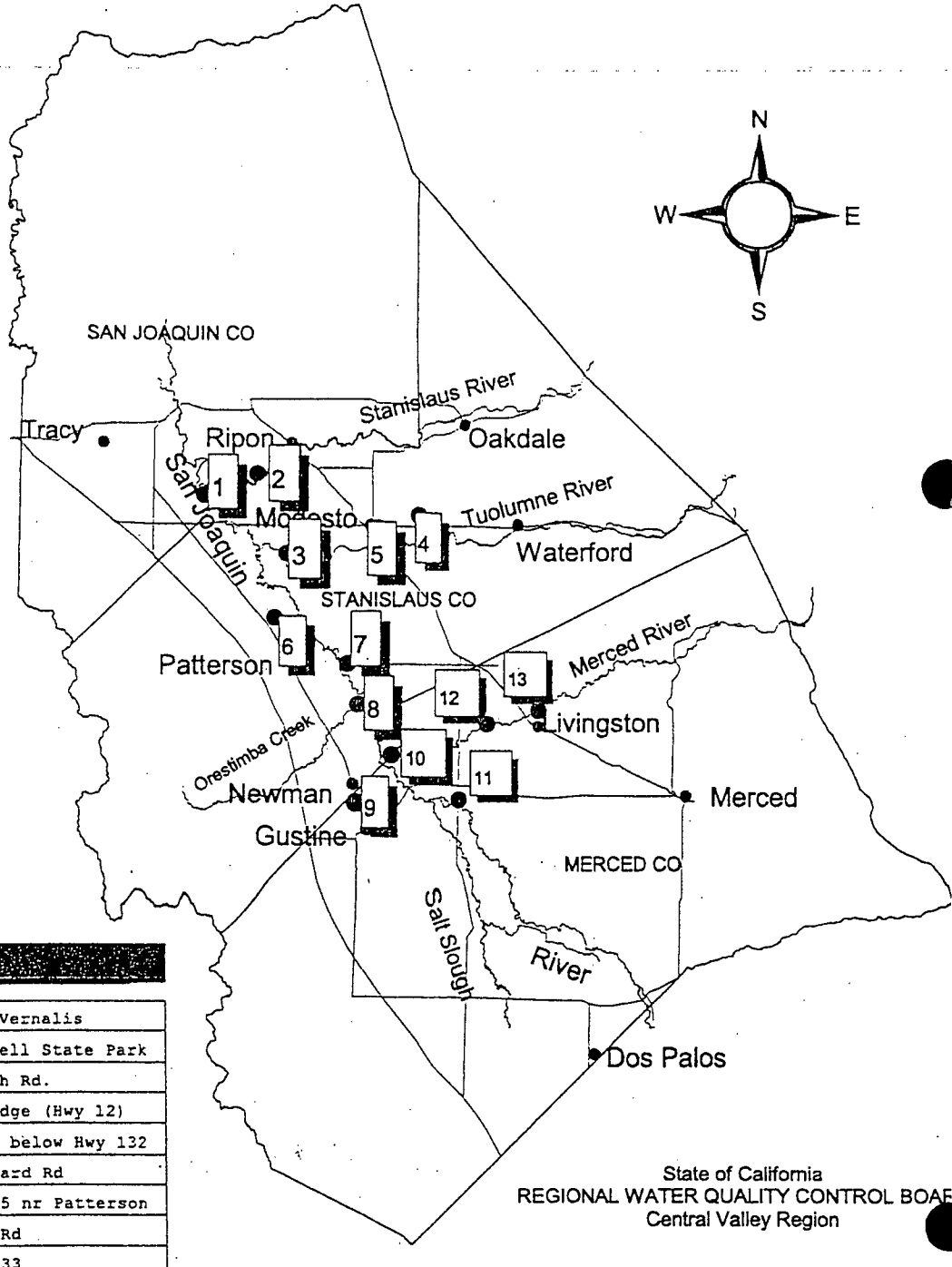
Highline Canal Spill is located along a Turlock Irrigation District levee along the right bank of the Merced River.

Livingston Canal Spill is located at a weir/gage on Merced Irrigation District's Livingston Canal at the entrance to Livingston STP.

Figure 3-1 shows the study area and the sampling sites.

FIGURE 3-1. The study area and the sampling sites

Sample Sites
Lower San Joaquin River



1	San Joaquin River near Vernalis
2	Stanislaus Riv. at Caswell State Park
3	Tuolumne River at Shiloh Rd.
4	Dry Crk at Claus Rd bridge (Hwy 12)
5	Dry Crk at Gallo bridge below Hwy 132
6	Del Puerto Crk at Vineyard Rd
7	Turlock ID lateral No. 5 nr Patterson
8	Orestimba Crk at River Rd
9	Newman Wasteway at Hwy 33
10	Merced Riv. at River Rd bridge
11	San Joaquin Riv. near Stevinson
12	Highline Canal Spill near Hilmar
13	Livingston Canal at Livingston STP

3.2 Type of Contaminants Reported

Several studies of the San Joaquin River and its tributaries have identified OP pesticides in suspended sediment samples, dissolved samples, surface water, groundwater, and fish species. Contaminants include organochlorine (OC) pesticides, organophosphorous (OP) pesticides, polynuclear aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and nitrate. Contaminants identified are reported in the following publications:

Occurrence of Nitrate and Pesticides in Groundwater Beneath Three Agricultural Land-Use Settings in the Eastern San Joaquin Valley, California 1993-1995 (U.S. Geological Survey Open File Report 97-4284).

Pesticides in Storm Runoff from Agricultural and Urban Areas in the Tuolumne River Basin in the Vicinity of Modesto, California (U.S. Geological Survey Open File Report 98-4017).

Pesticides in Surface and Ground Water of the San Joaquin-Tulare Basin, California: Analysis of Available data, 1966-1992 (U.S. Geological Survey Water-Supply Paper 2468).

Occurrence and Distribution of Dissolved Pesticides in San Joaquin River Basin, California (U.S. Geological Survey Open File Report 98-4032).

An Ecological Risk Assessment of Diazinon in the San Joaquin And Sacramento River Basins (Novartis Corp Protection, Inc. Report 11/97).

4.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

Two States and one Federal agency are involved in this study. The United States Geological Survey (USGS) and the California Regional Water Quality Control Board (CRWQCB) Central Valley Region cooperatively direct this study. Direction includes all decisions related to field sampling, analytical and field procedures and site safety. Department of Pesticide Regulations funds implementation of this study.
A copy of the project documentations is presented in Attachment A of this QAPP.

5.0 DATA QUALITY OBJECTIVES AND QUALITY ASSURANCE OBJECTIVES

Data Quality Objectives (DQOs) and Quality Assurance Objectives (QAOs) are related data quality planning and evaluation tools for all sampling and analysis activities. A consistent approach for developing and using these tools is necessary to ensure that enough data are produced and are of sufficient quality to make decisions for this study.

5.1 DQOs and Data Use Planning

DQOs specify the underlying reason for collection of data, data type, quality, quantity, and uses of data collection.

For this study, storm water sampling is needed to document the magnitude of OP pesticide loading in the lower San Joaquin River during the dormant spray period.

5.1.1 Data Quality Category

For this study, definitive data using standard US Environmental Protection Agency (EPA) or other reference methods is performed by USGS laboratory. Data are analyte-specific and both identification and quantitation are confirmed by GC/MS. These methods have standardized QC and documentation requirements, providing information necessary to verify all reported results. Definitive data are not restricted to use unless quality problems are documented and result in specific limitations and data qualifications.

5.2 Quality Assurance Objectives (QAOs)

Quality assurance objectives are the detailed QC specifications for precision, accuracy, representativeness, comparability and completeness (PARCC). The QAOs presented in this QAPP represent the minimum acceptable specifications for field and analysis that should be considered routinely for field and analytical procedures. The QAOs are then used as comparison criteria during data quality review (by USGS) to determine if the minimum requirements have been met and the data may be used as planned.

5.2.1 Development of Precision and Accuracy Objectives

Laboratory control spikes (LCSs) are used to determine the precision and accuracy objectives. LCSs are fortified with pesticides to monitor the laboratory precision and accuracy. The LCSs presented in this QAPP were developed by analyzing several reagent spikes at different concentration levels. These data were compiled over a defined time period. Control charts were developed for all target compounds.

Field duplicates measure sampling precision and variability for comparison of project data. Acceptable relative percent difference (RPD) is less than 50 for field duplicate analyses. If field duplicate sample results vary beyond these objectives, the results are further evaluated to identify the cause of the variability.

5.2.2 PARC Definitions

Precision measures the reproducibility of repetitive measurements. Precision is evaluated by calculating the RPD between duplicate spikes, duplicate sample analyses or field duplicate samples and comparing it with appropriate precision objectives established in this QAPP. Analytical precision is developed using repeated analyses of identically prepared control samples. Field duplicate samples analyses results are used to measure the field QA and matrix precision. Interpretation of precision data must include all possible sources of variability.

Accuracy measures correctness, or how close a measurement is to the true or expected value. Accuracy is measured by determining the percent recovery of known concentrations of analytes spiked into field sample or reagent water before extraction. The stated accuracy objectives for Laboratory control spike or matrix spike should reflect the anticipated concentrations and/ or middle of the calibration range.

Representativeness is obtained by using standard sampling and analytical procedures in this QAPP to generate data that is representative of the sites.

Completeness is calculated for each method and matrix for an assigned group of samples. Completeness for a data set is defined as the percentage of unqualified and estimated results divided by the total number of the data points. This represents the usable data for data interpretation and decision-making. Completeness does not use results that are qualified as rejected or unusable, or that were not reported as sample loss or breakage. The overall objective for completeness is 95% for this project.

Table 5-1 presents the quality control acceptance limits for this project.

Table 5-1. Quality Control Acceptance Criteria for the Pesticides in Water by Selective Ion Monitoring (SIM) Gas Chromatography/ Mass Spectrometry (GC/MS).

Analyte	Laboratory control spike (% Recovery)	Matrix Spike/ Duplicate (% Recovery)	Field Duplicate (% Recovery)	Surrogate (% Recovery)
Diazinon	50-131	a	a	68-113
Chlorpyrifos	53-120	a	a	56-137

(a) No Limits have been established for these sites.

6.0 FIELD PROCEDURES

This section includes brief descriptions of field procedures used for this study. Detailed equipment and procedure descriptions are included in Attachment B of this QAPP. Field coordinators ensure that field personnel have adequate training and a copy of the QAPP. All field activities are conducted following the health and safety procedures included in Attachment C of this QAPP.

6.1 Site Selection

Proper site selection is critical to producing representative data. Locations selected for sampling must represent site, zone and matrix under study. Selection of sample locations and the number of samples is a cooperative effort between the USGS and RWQCB staff.

6.1.1 Sampling Locations

Sampling locations for surface water and drinking water are selected using a judgmental sampling approach.
The criteria used to select sampling locations are:

- Land Use
- Pesticide Application (historical use areas)
- Known contaminants
- A designated number of samples to be collected per location

6.2 General Field Sampling Requirements

The standard elements for field and sampling activities are addressed in this section.

6.2.1 Decontamination Procedures

All field and sampling equipment that may contact samples must be decontaminated after each use in a designated area. A detail description of

cleaning of equipment for water sampling is included in the *National Field Manual*- (U.S.Geological Survey Book 9, Chapter 3). A copy of the Surface-Water Sampler Cleaning Procedures from Chapter 3 is presented in Attachment B of this QAPP.

6.2.2 Sample Storage, Preservation and Holding Times

Sample containers are pre-cleaned according to United States Environmental Protection Agency (U.S. EPA) specification for the appropriate methods. Table 6-1 Sample Storage and Preservations Requirements.

Table 6-1. Sample Storage and Preservation Requirements.

Reference Parameters	Methods	Holding Time	Container(s)	Preservations	Storage
Pesticides	NWQL SOP # ODO250.P	7 days prior to extraction (a)	1-Liter amber glass bottle	None	4 degree C

(a) Holding times very for each analyte after extraction according to the study conducted by NWQL. See *Method 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* for details.

6.2.3 Documentation

All field activities must be adequately and consistently documented to support data interpretation and ensure defensibility of any data used for decision-making. Example of field data sheets and other documentations required for this field procedure are included in Attachment F of this QAPP. Field personnel must record the following information:

- Name(s) of field personnel;
- Site/ sampling location identification;
- Date of sample collection;
- Field calibration
- All field measurements such as pH, temperature, conductivity (when applicable);
- Observation of weather and condition that can influence sample results; and
- Any problems encountered during sampling.

6.2.4 Sample Identification Scheme

All samples must be uniquely identified to ensure that results are properly reported and interpreted. Samples must be identified such that the site, sampling location, matrix, sampling equipment and sample type (Normal field sample or QC sample) can be distinguished by a data reviewer or user.

6.2.5 Field and Laboratory Staff Training

All staff performing field or laboratory procedures shall receive training to ensure that the work is conducted correctly and safely. At a minimum, all staff shall be familiar with the field guidelines and procedures and the laboratory SOP included in this QAPP. All work shall be performed under the supervision of experienced staff, field managers, laboratory managers or other qualified individuals.

6.3 Sample Collection Methods

Proper sampling techniques must be used to ensure that a sample is representative of the flow in the cross section. Samples should be collected using a standard multivertical depth integrating method to obtain the most representative isokinetic sample possible. By using this method the water entering the sampler is hydrodynamically equivalent to the portion of the stream being sampled. Abbreviated sampling methods (that is, weighted-bottle or dip sample) can be used for collecting a sample representative of the stream chemistry.

For this study the Equal-Width-Increment (EWI) sampling method will be used as recommended by NAWQA. The EWI sampling method is described in the "Field Guide for Collecting and Processing Stream Water Samples for The National Water Quality Assessment Program" included in Attachment B of this QAPP.

6.3.1 QC Sample Collection

Field blanks and field duplicates are collected at a frequency of about 1 per 20 normal samples. Matrix spikes are collected at frequency of about 1 per 20 normal samples.

6.3.2 Field measurements

For all water bodies sampled, the specific conductance is measured prior to collecting samples for laboratory analyses. Calibration and operation of the instruments are presented in Attachment B of this QAPP.

6.3.3 Record keeping and Sample Handling Procedure

All data collected in the field are recorded on sample field sheets. Pertinent field information, including (as applicable), the width, depth, flow rate of the stream, the surface water condition and location of the tributaries are recorded on the field sheets. Sample control information is documented in a master sample log. Chain of custody record is completed subsequent to sample collection.

7.0 SAMPLE CUSTODY AND DOCUMENTATION

Sample possession during all sampling efforts must be traceable from the time of collection until results are reported and verified by the laboratory and samples are disposed. Sample custody procedures provide a mechanism for documenting information related to sample collection and handling.

7.1 Documentation Procedures

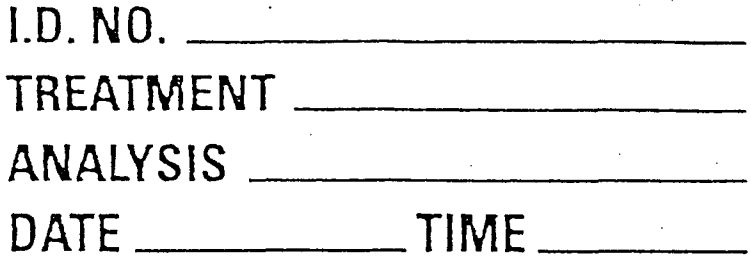
The USGS field activities coordinator is responsible for ensuring that the field sampling team adheres to proper custody and documentation procedures. A master sample logbook is maintained for all samples collected during each sampling activity.

Field personnel have the following responsibilities:

- Keep an accurate written record of sample collection activities on the field form and logbook
- Ensure that all entries are legible, written in waterproof ink and contain accurate and inclusive documentation of the field activities
- Date and initial daily entries
- Note errors or changes using a single line to cross out the entry and date and initial the change
- Complete the chain of custody forms accurately and legibly

A sample label is affixed to each sample collected. Sample labels uniquely identify samples with an identification number, analytical method requested; and date and time of sample collection. Figure 7-1 shows an example sample label.

FIGURE 7-1. Sample Label



7.2 Chain-of-Custody Form

A chain-of-custody form (U.S. Geological Survey- National Laboratory Analytical Services Request Form) is completed after sample collection, and prior to sample shipment or release. The chain-of-custody form, sample labels, and field documentation are crossed checked to verify sample identification, type of analyses, and number of containers, sample volume, preservatives and type of containers.

Information to be included in the chain of custody forms includes:

- Sample identification;
- Date and time of collection;
- Sample(s) initials;
- Analytical method(s) requested;
- Sample volume;
- Sample matrix;
- Preservatives;
- QC sample identification;
- Signature blocks for release and acceptance of samples; and
- Any comments to identify special conditions or requests.

Sample transfer between field staff and, courier, laboratory is documented by signing and dating "relinquished by" and "received by" blocks whenever sample possession changes. If samples are not shipped on the collection day, they are refrigerated in a sample control area.
An example of chain-of-custody form is shown in Figure 7-2.

STATE OF CALIFORNIA — ENVIRONMENTAL PROTECTION AGENCY
REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION
3443 ROUTIER ROAD, SUITE A • SACRAMENTO, CA 95827-3098
PHONE: (916) 255-3000 • FAX: (916) 255-3015

CHAIN OF CUSTODY

PROGRAM	PCA	PROJECT NAME

SAMPLER (Signature)	PRINT NAME

SAMPLE				CONTAINER		MATRIX			COMPOSITE	GRAB	PRESERVATIVES	ANALYSIS REQUIRED									FIELD CONDITIONS (TEMP., WIND, ETC.)
IDENTIFICATION	LOCATION	DATE	TIME	TYPE	NO.	WATER	WASTE-WATER	SOIL / SLUDGE													LAB NO.

SPECIAL INSTRUCTIONS / SUSPECTED CONSTITUENTS

RELINQUISHED BY (Signature)	DATE / TIME	RECEIVED BY (Signature)	RELINQUISHED BY (Signature)	DATE / TIME	RECEIVED BY (Signature)

FIGURE 7-2. Example of a chain-of-custody (U.S. Geological Survey- National Water Laboratory Analytical Services Request Form) form.

7.3 Sample Shipments and Handling

All sample shipments are accompanied by the chain-of-custody form, which identifies the content. The original accompanies the shipment and a copy is retained in the project file.

All shipping containers are secured with chain-of-custody seals for transportation to the laboratory. Samples are shipped to the USGS National laboratory according to Department of Transportation standard. Ice is packed with the samples; the ice must contact each sample and be approximately 2 inches deep at the top and bottom of the cooler. The ice may be contained in recloseable bags, but must contact the samples to maintain temperature. The method(s) of shipments, courier name, and other pertinent information is entered in the "Received By" or "Remark" section of the chain of custody form.

The following procedures are used to prevent bottle breakage and cross-contamination:

- Bubble wrap or other cushioning material is used to keep bottles from contacting one another to prevent breakage.
- Sample bottles are individually sealed in plastic recloseable bags.
- All samples are transported inside hard plastic coolers.
- The coolers are taped shut and sealed with chain-of-custody seals to prevent accidental opening.
- Prior to shipment of the samples field staff must notify laboratory sample control.

7.4 Laboratory Custody Procedures

The following sample control activities must be conducted in the laboratory:

- Initial sample log-in and verification of samples received with the chain of custody form;
- Document any discrepancies noted during log-in on the chain of custody;
- Initiate internal laboratory custody procedure;
- Verify sample preservation such as temperature;
- Notify the project coordinator if any problems or discrepancies are identified;

- Proper sample storage, including daily refrigerator temperature monitoring and sample security;
- Distribute samples or notify the laboratory of sample arrival; and
- Return shipment of coolers

8.0 FIELD INSTRUMENT CALIBRATION PROCEDURES

A conductivity meter is used in this study to monitor and evaluate physical parameters in water.

Routine calibration must be performed prior to and during use to ensure instruments are operating properly and produce accurate and reliable data. Calibration should be performed at a frequency recommended by the manufacturer. Field calibration should be performed at least once per day, prior to instrument use. If field calibration reveals that the instrument is outside established accuracy limits, the instrument should be serviced in the field. Back-up instruments must be available for each of the critical real-time instruments used in the field.

8.1 Water Sampling Instrument Calibration

The conductivity meter is used to measure salinity when collecting groundwater and surface water samples. The meter is calibrated prior to collecting samples. Conductivity is calibrated with at least two standard calibration solutions that bracket the expected range of measurements. The field instrument calibration is described in detail in "*Field Guide for Collecting and Processing Stream-Water Samples for the National Water-Quality Assessment Program*" presented in Attachment B of this QAPP.

9.0 ANALYTICAL PROCEDURES AND CALIBRATION

This section describes the analytical methods and calibration procedures for the water samples that will be collected during this study.

The analytical methods included in this QAPP included the following two methods: *Method of Analysis by The U.S. Geological Survey National Water Quality laboratory- Determination of Pesticides in Water by C-18 Solid-Phase Extraction (SPE) and Capillary-Column Gas Chromatography/ Mass Spectrometry With Selected Ion Monitoring- US Geological Survey Open report 95-181* that is used as sample preparation procedure, *and the National Water Quality Laboratory Standard Operating Procedure for analysis of pesticides in Water by SIM GC/MS, SOP number ODO250.P*, which is used for sample analysis. Attachment D of this QAPP includes a copy of both reports;

they provide a detailed description of all aspect of the methods, including equipment, reagents, instrument calibration, and the SPE procedure required for sample analysis.

9.1 Detection and Quantitation Limits

The method detection limit (MDL) is the minimum analyte concentration that can be measured and reported with a 99% confidence that the concentration is greater than zero. The quantitation limit (QL) represents the concentration of an analyte that can be routinely measured in the sample matrix within stated limits and confidence in both identification and quantitation. Table 9 of the *Open File Report 95-181* (Attachment D) presents the method detection limit study conducted by NWQL. These detection limits will be used as project quantitation limits.

10.0 DATA REDUCTION, VERIFICATION, AND REPORTING

The laboratory data reduction, verification, and reporting procedures ensures that complete documentation is maintained, transcription and reporting errors are minimized, and data received from laboratory are properly reviewed.

10.1 Laboratory Data reduction and Verification

The laboratory analyst performing the analyses is responsible for the reduction of the raw data generated at the laboratory bench to calculate the concentrations. The analytical process includes verification or a quality assurance review of the data. This includes:

- Verifying the calibration samples for compliance with the laboratory and project criteria;
- Verifying that the batch QC were analyzed at a proper frequency and the results were within specifications;
- Comparing the raw data (e.g. chromatogram) with reported concentration for accuracy and consistency;
- Verifying that the holding times were met and that the reporting units and quantitation limits are correct;
- Determining whether corrective action was performed and control was re-established and documented prior to reanalysis of QC or project samples;
- Verifying that all project and QC sample results were properly reported and flagged; and
- Preparing batch narratives that adequately identify and discuss any problems encountered.

The QC check is conducted at several levels by the laboratory analyst, supervisors, and laboratory quality assurance staff. The specific procedures are documented in the laboratory quality assurance manual. After the data have been reviewed and verified, the laboratory reports are signed for release and distributions. Raw data and supporting documentation is stored in confidential

files by laboratory document control. The laboratory will provide the electronic copy of these results.

11.0 INTERNAL QUALITY CONTROL (QC)

Internal quality control (QC) is achieved by collecting and/ or analyzing a series of duplicate, blank, spike and spike duplicate samples to ensure that analytical results are within the specified QC objectives. The QC sample results are used to quantify precision and accuracy and identify any problem or limitation in the associated sample results. The internal QC components of a sampling and analyses program will ensure that the data of known quality are produced and documented. The internal QC checks, frequency, acceptance criteria and corrective action required to meet project objectives are presented in the U.S. Geological Survey National Water Quality Laboratory (NWQL) Organic Chemistry Program QA/QC Guidance Manual included in Attachment E of this QAPP.

11.1 Analytical Laboratory QC Samples

Laboratory QC is necessary to control the analytical process within method and project specifications, and to assess the accuracy and precision of analytical results.

The laboratory will perform the following QC checks:

- Calibration standards
- Laboratory control samples
- Method blanks
- Matrix spike and Matrix spike duplicates
- Surrogate spikes
- Laboratory duplicates

The procedures for analysis and review of these QC checks samples are described in the Laboratory QA/QC Guidance Manual presented in Attachment E of this QAPP.

11.2 Field QC Samples

Field QC samples are used to assess the influence of sampling procedures and equipment used in sampling. They are also used to characterize matrix heterogeneity.

The following field QC samples will be collected for this study:

- Field duplicate samples
- Equipment blanks, and
- Field Spikes

A summary of calibration and internal Quality Control Procedures for Pesticides by SIM GC/MS is presented in NWQL Standard Operating procedure for Analysis of Pesticides in Water by SIM GC/MS. This document is included in Attachment D of this QAPP.

12.0 AUDIT AND DATA VALIDATION

The laboratory is audited by the U.S. Geological Survey quality assurance group on a yearly basis. U.S. Geological Survey field audit team conducts the field audit on a 20 % of the projects conducted by U.S. Geological Survey. These audits are independent of sample collection and analysis procedures.

12.1 Technical System Audit:

A technical system audit is a quantitative review of a sampling or analytical system. Qualified technical staff members who have the authority to act independently of the laboratory, field and project management perform audits.

The laboratory system audit results are used to review operations and ensure that the technical and documentation procedures provide valid and defensible data

Critical items for a laboratory system audit include:

- Sample storage procedures;
- Availability of and compliance with calibration procedures and documentation requirements;
- Standard operating procedures;
- Source and handling of standards;
- Completeness of data forms, notebooks and other records of analysis and QC activities;
- Data review and verification procedures;
- Data storage, filing and record keeping procedures;
- Sample custody procedures;
- Establishments and use of quality control procedures, control limits and corrective actions that comply with specification in this QAPP;
- Operating conditions of the facilities and the equipment;
- Documentation of the instruments maintenance activities; and
- Laboratory staff training and documentation.

Critical items for sampling system audits includes:

- Calibration procedures and documentation for field meter;
- Field activity documentation in logbooks and sampling data sheets;
- Minimization of potential sample contamination in the field by using proper equipment decontamination procedures;
- Availability of SOPs and compliance to ensure proper sample collection, storage and transportation procedures;
- Compliance with established chain of custody procedures for sample documentation and transfer to the laboratory; and
- Field staff training and implementation of project-specific-requirements.

The checklist for each audit contains detailed questions regarding the critical items, requesting yes/no answers and comments. The laboratory manager and the field coordinator must prepare a corrective action plan to address any findings or negative observations noted in the project audit report. The corrective action plan must address the immediate corrective actions and procedures that will be implemented to prevent recurrence of the problems noted.

12.2 Performance Evaluation Audits

Performance evaluation audits quantitatively assess the data produced by a measurement system. Performing an evaluation audit involves submitting certified samples for each analytical method. The matrix standards are selected to reflect the concentration range expected for the sampling program. The performance evaluation audit evaluates whether the measurement system is operating within the project control limit specified in this QAPP and the data produced meet the project and analytical quality control specifications.

The performance evaluation (PE) samples are prepared and submitted to the laboratory by U.S. Geological Survey quality assurance group. Critical items for the performance evaluation audits are:

- Accurate identification of the analytes included in the PE samples
- Quantitation within acceptance limits
- Accurate reporting of results and any problems identified
- Acceptable analytical batch QC sample results

These items are used to identify when a system is outside acceptable control limits. Any problem associated with PE samples must be evaluated to determine the influence on field samples analyzed during the same time period. The laboratory must provide a written response to any PE sample result deficiencies.

12.3 Data Validation

Data validation (data quality audit) is conducted to verify whether an analytical method has been performed according to the method and project specifications, and the results have been correctly calculated and reported. The U.S. Geological Survey will conduct the data validation prior to submitting the data to RWQCB. Specific items that are reviewed during data validation are:

- Chain of custody records
- Documentation of the laboratory procedures (e.g., standard preparation records, run logs, data reduction and verification)
- Accuracy of data reduction, transcription, and reporting
- Adherence to method-specific calibration procedures and quality control parameters
- Precision and accuracy of recorded results

12.4 Field Technical Audits

U.S. Geological Survey field project managers routinely observe field operations to ensure consistency and compliance with sampling specifications presented in the QAPP. Audit checklists document field observations and activities.
A copy of the field audit checklist is included in Attachment F of this QAPP.

13.0 PREVENTIVE MAINTENANCE

A preventive maintenance program's primary objective is to assure the timely and effective completion of a measurement effort by minimizing the downtime of crucial sampling and/or analytical equipment from unexpected component failure. The program's efforts are focused in the three principal areas: maintenance responsibilities, maintenance schedule and inventory of critical spare parts and equipment.

Maintenance performed on the analytical instruments used for this project are described in Section 8.0 of NWQL Standard Operating Procedure for analysis of pesticides in Water by SIM GC/MS. A copy of this SOP is presented in Attachment D of this QAPP.

14.0 DATA ASSESSMENT PROCEDURES

Measurement data must be consistently assessed and documented to determine whether project quality assurance objectives (QAOs) have been met, quantitavely assess data quality and identify potential limitations on data use.

The laboratory is responsible for following the procedures and operating the analytical systems within the statistical control limits. These procedures include proper instrument maintenance, calibration of the instruments, and the laboratory QC sample analyses at the required frequency (i.e., method blanks, laboratory control samples, etc.). Associated QC

sample results are reported with all sample results so the project staff can evaluate the analytical process performance.

All project data must be reviewed as part of the data assessment. Review is conducted on a preparation batch basis by assessing QC samples and all associated field sample results. Project data review established for this project includes the following steps:

- Initial review of analytical and field data for complete and accurate documentation, chain of custody procedures, analytical holding times compliance, and require frequency of field and laboratory QC samples;
- Evaluation of analytical and field blank results to identify random and systematic contamination;
- Comparison of all spike and duplicate results with project objectives for precision and accuracy;
- Assigning data qualifiers flags to the data as necessary to reflect limitations identified by the process; and
- Calculating completeness by matrix and analyte.

U.S. Geological Survey staff conducting the data assessment is responsible for ensuring that data qualifier flags are assigned, as needed, based on the established QC criteria. Staff is also responsible for communalizing any limitations to data users.

15.0 CORRECTIVE ACTION

During the course of sample collection and analysis in this study, the laboratory supervisors and analysts, and field supervisors and team members will make sure that all measurements and procedures are followed as specified in this QAPP, and measurements meet the prescribed and acceptance criteria. If a problem arises, prompt action to correct the immediate problem and identify its root causes is imperative. Any related systematic problems must also be identified.

Problems about analytical data quality that may require corrective action are documented in the U.S. Geological Survey, NWQL Organic Chemistry program; QA/QC Guidance Manual is presented in Attachment E of this QAPP. Problems about field data quality that may require corrective action are documented in the field data sheets.

16.0 ANALYTICAL DATA AND QUALITY ASSURANCE REPORT

The U.S. Geological Survey will prepare a report after conducting a data validation.

The elements described below will be addressed and included in the report:

- Description of the project including the number of samples, analyses, completeness and any significant problems or occurrences that influence data use.
- The QA/QC activities performed during this project.

- QC sample results, type and number of samples including the results that did not meet the projective objectives, and the impact on usability.
- Tables of analytical results for usable and unusable data.

17.0 SITE MANAGEMENT

The U.S. Geological Survey field manager will observe field activities to ensure tasks are conducted according to the project specifications. The field coordinator is equipped with a cellular telephone for improved communication among the team members. Decontamination of field equipments will occur at a designated area assigned by the field manager. Access for sites is coordinated through the RWQCB and U.S. Geological Survey. This includes obtaining any necessary permits and coordinating with facilities and units where site activities will take place.

ATTACHMENT A

PROJECT DOCUMENTATIONS

Monitoring Organophosphate Pesticides in the Lower San Joaquin River Basin during January and February 2000

Executive Summary / Scope of Work

This is a proposal to monitor organophosphate pesticides in the lower San Joaquin River Basin during the dormant spray season in January and February 2000. Sampling will commence in the first week of January with weekly sampling 14 sites. In addition to the weekly sampling, two storm events will be sampled beginning in mid-January. The frequency and number of samples collected at each site will depend upon the duration of the flood wave at each site, with more samples collected over a longer time period at the larger river sites. The weekly sampling will put the storm transport in context with overall transport during the dormant spray application period.

Study Area

The study area includes fourteen sites in the lower San Joaquin River Basin from the San Joaquin River (SJR) at Lander Avenue (near Stevinson) to the SJR near Vernalis. A summary of these sites is presented in table 1.

San Joaquin River Sites

The fourteen SJR sites include two sites along the main stem of the SJR: Lander Avenue near Stevinson and Airport Way near Vernalis. Both sites have real time flow and Electrical Conductivity (EC) data. Three major east side tributary sites will be sampled: Stanislaus River at Caswell Park, Tuolumne River at Shiloh, and the Merced River at River Road. Although flow data is not available at these sites, both flow and EC data is available nearby at three USGS gage stations. Five small tributaries and drains will be sampled on the east side of the SJR: Dry Creek at Gallo Bridge, Dry Creek at Claus Road, Turlock Irrigation District Lateral 5, Highline Canal Spill, and the Livingston Canal. Of these sites, only Dry creek at Claus Road, Highline Canal Spill, and the Livingston Canal have continuous flow measurements. Four small tributaries and drains will be sampled on the west side of the SJR: Del Puerto Creek at Vineyard Road, Spanish Grant Drain, Orestimba Creek at River Road, and the Newman Wasteway.

Sampling Program

Samples will be collected at 14 sites (table 1) during the dormant spray season starting with the first storm event after the application of dormant sprays in mid-January 2000. Instantaneous streamflow measurements will be made for each sample collected at ungaged sites.

Storm Sampling

Sampling for the dormant spray season will commence in mid-January with sampling of the first storm following the application of dormant sprays. One additional storm will then be sampled. Sampling will occur at 14 sites for the two storm events. The frequency and number of samples collected at each site will depend upon the duration of the flood wave at each site, with more samples collected over a longer time period at the larger river sites. Six samples will be collected per storm event at the SJR near Vernalis. Five samples per storm event will be collected for the Stanislaus, Tuolumne, and the Merced Rivers, and four samples each at the SJR near Lander Avenue, Orestimba Creek at River Road, and Highline Canal Spill. Three samples per storm event will be collected at the seven remaining storm sampling sites.

Weekly Sampling

Weekly samples will be collected at the same 14 sites commencing with the first week in January. These samples will be collected weekly during January and February when storm samples are not being collected. These samples will help put the storm transport in context of transport before, between, and after storms. These will provide non-storm background loads in the system from which to calculate storm transport and will also provide total transport for the dormant spray application period. These samples also provide a "safety net" for storm sampling in case the storms sampled were prior to the main application period, or if there are more than two major storms during January and February, or if storm hydrographs are drawn out for days due to overlapping storms.

Analytical Methods

To provide the most reliable information for both diazinon and chlorpyrifos, as well as additional information for 45 other pesticides, Gas Chromatography-Mass Spectrometry (GC-MS) will be used for all sample analyses. All samples will be analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. USGS schedule 2001 (table 2), which includes solid phase extractions by the NWQL, will be used for all samples collected during the dormant spray season because field staff will not have sufficient time to perform the extractions. Cost of this analysis is approximately $430 per sample. The method detection level for diazinon is 0.002 µg/L and for chlorpyrifos is 0.004 µg/L.

Deliverables

Pesticide and flow data will be made available electronically to the DPR and CRWQCB within four months of the sample collection. A draft interpretive USGS Water Resources Investigations Report will be available for review by late September, assuming the pesticide application data for the study area is available from DPR by May. This report will include a calculation of loads for diazinon and chlorpyrifos for the January and February sampling period. Major sources will be prioritized in terms of overall loads and yields. The loads will be related to application, runoff, and land use in each subbasin

using GIS coverages of drainage basin boundaries, daily pesticide applications, land use, and precipitation data. The analysis will be similar to that done in Kratzer, 1999 ("Transport of diazinon in the San Joaquin River Basin, California", Journal of the American Water Resources Association, vol. 35, no.2, pp. 379-395).

Costs

Full cost of the proposed monitoring is $229,300 for Federal Fiscal Year 2000. This includes collection and analysis of 221 samples, per diem (field sampling), support (storm tracking, sample tracking, data processing, and reporting), data interpretation/report writing, report editing/printing, equipment and supplies, and miscellaneous expenses. A detailed breakdown of the costs is shown in table 3.

Table 1. Proposed Monitoring for Organophosphate Pesticides in San Joaquin River Basin

(dormant spray period only; January 2000 - February 2000)

Map No.	Site Name	Agency	Station ID	Continuous Data	Frequency	No. of Storm Samples	No. of Annual Samples
	SJR sites						
	SJR nr Vernalis	USGS	11303500	Flow, EC, Temp	W,ST	12	6
	Stanislaus R at Caswell	RWQCB	STC514		W,ST	10	6
	Stanislaus R at Ripon	USGS	11303000	Flow, Temp			
	Tuolumne R at Shiloh	RWQCB	STC513		W,ST	10	6
	Tuolumne R at Modesto	USGS	11290000	Flow, EC, Temp			
	Dry Creek at Gallo Bridge				W,ST	6	6
	Dry Creek at Claus Road	DWR		Flow	W,ST	6	6
	Del Puerto Cr at Vineyard Rd				W,ST	6	6
	Spanish Grant Drain				W,ST	6	6
	Turlock ID lateral 5				W,ST	6	6
	Orestimba Cr at River Road	USGS	11274500	Flow, EC, Temp	W,ST	8	6
	Merced R at River Road	USGS	11273500		W,ST	10	6
	Merced R nr Stevinson	DWR		Flow, EC, Temp			
	Highline Canal Spill	TID		Flow	W,ST	8	6
	Livingston Canal			Flow	W,ST	6	6
	Newman Wasteway				W,ST	6	6
	SJR at Lander Ave	RWQCB	MER522	Flow, EC, Temp	W,ST	8	6
	Total Samples					108	84

ST= storm sampling, W = weekly sampling (Jan, Feb, May, Jun, Jul, Aug),

Table 3. Costs for dormant period sampling only

Task Description	Labor cost	Sample cost	Quantity	Analytical cost	Other costs	Total cost
Analytical costs						
Dormant spray season (storm)		$430	108	$46,440		$46,440
Dormant spray season QC *1		$430	16	$6,966		$6,966
Dormant spray season (weekly)		$430	84	$36,120		$36,120
Dormant spray season QC *1		$430	13	$5,418		$5,418
Sampling costs (storm)	15,000					$15,000
Sampling costs (weekly)	14,400					$14,400
per diem					$15,000	$15,000
Sampling support *2					$35,000	$35,000
Data interpretation/report writing					$20,000	$20,000
Report editing/printing					$15,000	$15,000
Equipment and supplies					$10,000	$10,000
Miscellaneous					$10,000	$10,000
Total	$29,400			$94,944	$105,000	$229,344

*1 Quality Control (QC) adds 15 percent more samples to sampling program
*2 storm tracking, sample tracking, data processing, data reports

California Regional Water Quality Control Board

Central Valley Region

Steven T. Butler, Chair

Winston H. Hickox
Secretary for Environmental Protection

Gray Davis
Governor

Sacramento Main Office
Internet Address: http://www.swrcb.ca.gov/~rwqcb5
3443 Routier Road, Suite A, Sacramento, California 95827-3003
Phone (916) 255-3000 • FAX (916) 255-3015

TO: Marshall Lee
Department of Pesticide Regulation

FROM: Jerry Bruns
Environmental Program Manager

SIGNATURE: _____

DATE: 15 October 1999

SUBJECT: MONITORING NEEDS FOR COMPLETION OF TMDLS FOR OP PESTICIDES

This memorandum is in response to recent discussions between the Department of Pesticide Regulation, State Board and Regional Boards regarding monitoring that is needed to facilitate development of TMDLs for OP pesticides. The Regional Board must complete TMDLs within the next few years for diazinon and chlorpyrifos in the San Joaquin River, the Delta and urban creeks in Stockton and Sacramento. In addition, a TMDL for diazinon in the Sacramento and Feather Rivers must be completed within the same time frame. To accomplish this, some key elements that must be addressed are the development of numeric targets (water quality objectives), identification of principal sources, determinations of loads and load reductions necessary to meet water quality objectives, identification of practices or conditions that result in elevated pesticide levels in surface waters, development of new and/or modified practices to reduce pesticide levels in surface waters, analysis of the costs and environmental consequences of implementing such practices (as compared to existing practices), development of a program to assure that appropriate practices are implemented, and follow-up evaluations to confirm the success of programs.

The Regional Board is responsible for determining what pesticide concentrations are unacceptable in surface waters. As the Department is responsible for regulating pesticide use, it seems appropriate that the Department determine what practices cause pesticide loading to the rivers, determine the amount of loading and concentrations attributable to the practices identified, assure that practices are developed and implemented to reduce the loads, and conduct follow-up evaluations to confirm that loadings have been reduced to appropriate and specified levels. Because of the short time schedules that we have for development of the OP pesticide TMDLs and the high level of stakeholder interest, it will be necessary to complete most of the data collection to characterize and define sources within the next 18 months. The following is a brief description of the monitoring and special studies that would be the most critical in assisting with the development of the TMDLs.

San Joaquin River Watershed

- Agricultural drainage and urban runoff enter the San Joaquin River and its tributaries at over 100 sites. Monitoring has demonstrated that the agricultural drainage is the major source of pesticides entering the river. Monitoring should focus initially on the agricultural drainage and the problems associated with diazinon and chlorpyrifos. Monitoring should be initiated this winter and include approximately 20 representative sites that could also serve as sites for longer-term monitoring (several years) to document the success of programs to control pesticide runoff.

The monitoring efforts should focus on two critical periods; winter application of dormant sprays and irrigation season use of these two chemicals.

The irrigation season monitoring should be designed to document the type of use or application practices that results in runoff with the irrigation water. Under this program, the goal should be to define whether the application practice or the use of irrigation water is the cause of the pesticide entering surface waters.

The dormant spray program should focus on characterizing concentrations and loads entering the river in runoff, the agricultural use practices responsible for this load and how the material finds its way into the surface waters.

Sacramento River Watershed

- Limited monitoring is proposed for this year to characterize concentrations and loads of pesticides entering the Sacramento and Feather Rivers during the winter. More sources need to be evaluated.

Delta

- More data is needed on OP pesticide loadings to Delta sloughs to determine the significance of problems and to define sources.

Applicable to all watersheds

- Studies are needed to document the specific activities, practices or conditions associated with dormant spray applications and in-season use that result in elevated OP pesticide levels in the rivers and Delta (i.e., crop type, slope, soil characteristics, drift, tailwater and stormwater runoff, pesticide formulations, application rates, modes of application, etc.). Studies have been conducted in Orestimba Creek to identify practices, use patterns and pesticide transport processes, but results are inconclusive. Information is needed to determine which practices need to be modified or eliminated and to develop alternative practices.

  Work is in progress to evaluate management practices that can be implemented to reduce OP pesticide levels in the rivers (UC Cooperative Extension, DPR and others). We would like the Department to take the lead in evaluating and guiding these efforts to assure that all of the options are fully evaluated (i.e., reduced use alternatives, changes in application patterns, using different pesticides) and that they address all significant activities or actions that contribute to the problem. We would like a report prepared by the Department that includes a description of all the practices that are under evaluation, including an analysis of what additional practices should be considered. Economics and associated environmental impacts should be a part of this evaluation. We recommend that this evaluation be completed this winter and evaluation of additional practices be initiated soon after. Adequate monitoring should be associated with these efforts to allow us to determine the expected load reductions for each practice, along with the costs and any associated environmental impacts.

- Volatilization of OP pesticides during and after application and subsequent deposition in rainfall may be a significant source of pesticides to surface waters, and appears to exacerbate problems in urban creeks. More information is needed to characterize the origins and loads attributable to

this source and strategies need to be developed (i.e., different formulations, etc.) to reduce the loads.

- Baseline monitoring is needed in the Sacramento River, Feather River, San Joaquin River, Merced River, Tuolumne River, Stanislaus River and the Delta to document the efficacy of control efforts.

Urban Runoff

- Urban sources of pesticides need to be better defined to determine the urban uses that result in elevated concentrations in urban creeks (i.e., use on lawns, structure or in gardens) and whether they result from legal or illegal uses. Exhaustive studies do not need to be completed in every urban area. We recommend that the Regional Board and Department work through the Urban Pesticide Committee to develop generic studies that will be applicable in most urban areas. More monitoring is not needed in this Region's urban areas to document that OP pesticides are often detected at toxic concentrations.

We are anxious to start working with you to develop the details of monitoring efforts. We want to discuss what studies and monitoring the Department is willing to undertake in order to determine how other resources will be spent. In this memorandum, we have suggested monitoring and special studies that would facilitate the development and implementation of load reduction programs.

Please call me at (916) 255-3093 if you have any questions or wish to discuss any of the topics in this memorandum.

ATTACHMENT B

FIELD GUIDE FOR COLLECTING AND PROCESSING STREAM WATER SAMPLERS FOR THE NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

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.

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

National Water-Quality Assessment Program
Study Units

FIELD GUIDE FOR COLLECTING AND PROCESSING STREAM-WATER SAMPLES FOR THE NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

By Larry R. Shelton

U.S. GEOLOGICAL SURVEY
Open-File Report 94-455

8056-22

Sacramento, California
1994

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

U.S. GEOLOGICAL SURVEY
GORDON P. EATON, Director

For sale by the
U.S. Geological Survey
Earth Science Information Center
Open-File Reports Section
Box 25286, MS 517
Denver Federal Center
Denver, CO 80225

For additional information write to:
Chief, Pesticides National Synthesis Project, NAWQA
U.S. Geological Survey
Federal Building, Room W-2233
2800 Cottage Way
Sacramento, CA 95825

CONTENTS

FIGURES

TABLES

CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATIONS, AND ACRONYMS

Conversion Factors

Multiply	By	To obtain
foot (ft)	0.3048	meter
foot per second (ft/s)	0.3048	meter per second
gallon (gal)	3.785	liter
inch (in.)	25.4	millimeter
inch per second (in/s)	25.4	millimeter per second
pound, avoirdupois (lb)	4.536	kilogram
pound per square inch (lb/in^2)	6.895	kilopascal
square mile (mi^2)	2.590	square kilometer

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F=1.8(°C)+32$$

Vertical Datum

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviations

cm, centimeter
g/L, gram per liter
L, liter
µL, microliter
µm, micrometer
µS/cm, microsiemens per centimeter at 25 degrees Celsius
mg/L, milligram per liter
mg/µL, milligram per microliter
mL, milliliter
mL/min, milliliter per minute
mm, millimeter

DIW	deionized water
DOC	dissolved organic carbon
EDI	equal-discharge increment
EWI	equal-width increment
FA	filtered acidified
FC	filtered chilled
FU	filtered untreated
GCMS	gas chromatography/mass spectrometer
HPLC	high-pressure liquid chromatography
N	normal
OCALA	Quality Water Service Unit, USGS, Ocala, Florida
PPB	parts per billion
PVC	polyvinyl chloride
RC	raw (unfiltered) chilled
RU	raw (unfiltered) untreated
SOC	suspended-organic carbon
SPE	solid-phase extraction
TOC	toxic organic compounds
VOC	volatile organic compound

Acronyms

ASTM	American Society for Testing and Materials
HIF	Hydrologic Instrumentation Facility, USGS, Mississippi
NAWQA	National Water-Quality Assessment
NWQL	National Water Quality Laboratory
OSW	Office of Surface Water
OWQ	Office of Water Quality
TWRI	Techniques of Water-Resources Investigations
USGS	U.S. Geological Survey
WRD	Water Resources Division
YSI	Yellow Springs Instrument

GLOSSARY

Basic Fixed Sites—Sites on streams at which streamflow is measured and samples are collected for temperature, salinity, suspended sediment, major ions and metals, nutrients, and organic carbon to assess the broad-scale spatial and temporal character and transport of inorganic constituents of stream water in relation to hydrologic conditions and environmental settings.

Bed-Sediment and Tissue Studies—Assessment of concentrations and distributions of trace elements and hydrophobic organic contaminants in stream bed sediment and tissues of aquatic organisms to identify potential sources and assess spatial distribution.

Depth-integrating sampler—A sampler that will integrate and represent the area of a stream section.

Discharge-weighted samplers—A sampler that will isokinetically represent the stream flow.

Ecological Studies—Studies of biological communities habitat characteristics to evaluate the effects of physical and chemical characteristics of water and hydrologic conditions on aquatic biota and to determine how biological and habitat characteristics differ among environmental settings in Study Units.

Equal-width increment (EWI) sampling—A composite sample across a section of stream with equal spacing between verticals and equal transit rates within each vertical that yields a representative sample of stream conditions.

Gaging station—A fixed site on a stream or river where hydrologic and environmental data are collected.

Indicator Sites—Stream sampling sites located at outlets of drainage basins with relatively homogeneous land use and physiographic conditions. Basins are as large and representative as possible, but still encompassing primarily one Environmental Setting (typically, 50 to 500 km^2).

Integrator Site—Stream sampling sites located downstream of drainage basins that are large and complex and often contain multiple Environmental Settings. Most Integrator Sites are on major streams with drainage basins that include a substantial portion of the Study Unit area (typically, 10 to 100 percent).

Intensive Fixed Sites—Basic Fixed Sites with increased sampling frequency during selected seasonal periods and analysis of dissolved pesticides for 1 year. Most Study Units have one or two integrator Intensive Fixed Sites and one to four indicator Intensive Fixed Sites.

Isokinetic sampling—The water entering the sampler is hydrodynamically equivalent (velocity, area, and direction) to the portion of the stream being sampled.

Occurrence and Distribution Assessment—Assessment of the broad-scale geographic and seasonal distributions of water-quality conditions for surface and ground water of a Study Unit in relation to major contaminant sources and background conditions.

Solid-phase extraction (SPE)—A procedure to isolate specific organic compounds onto a bonded silica extraction column.

Study Unit—A major hydrologic system of the United States in which NAWQA studies are focused. NAWQA Study Units are geographically defined by a combination of ground- and surface-water features and usually encompass more than 10,000 km^2 of land area. The NAWQA design is based on assessment of 60 Study Units, which collectively cover a large part of the Nation, encompass the majority of population and water use, and include diverse hydrologic systems that differ widely in natural and human factors that affect water quality.

Water-Column Studies—Assessment of physical and chemical characteristics of stream water, including suspended sediment, dissolved solids, major ions and metals, nutrients, organic carbon, and dissolved pesticides, in relation to hydrologic conditions, sources, and transport.

FIELD GUIDE FOR COLLECTING AND PROCESSING STREAM-WATER SAMPLES FOR THE NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

By Larry R. Shelton

Abstract

The U.S. Geological Survey's National Water-Quality Assessment program includes extensive data-collection efforts to assess the quality of the Nation's streams. These studies require analyses of stream samples for major ions, nutrients, sediments, and organic contaminants. For the information to be comparable among studies in different parts of the Nation, consistent procedures specifically designed to produce uncontaminated samples for trace analysis in the laboratory are critical. This field guide describes the standard procedures for collecting and processing samples for major ions, nutrients, organic contaminants, sediment, and field analyses of conductivity, pH, alkalinity, and dissolved oxygen. Samples are collected and processed using modified and newly designed equipment made of Teflon to avoid contamination, including nonmetallic samplers (D-77 and DH-81) and a Teflon sample splitter. Field solid-phase extraction procedures developed to process samples for organic constituent analyses produce an extracted sample with stabilized compounds for more accurate results. Improvements to standard operational procedures include the use of processing chambers and capsule filtering systems. A modified collecting and processing procedure for organic carbon is designed to avoid contamination from equipment cleaned with methanol. Quality assurance is maintained by strict collecting and processing procedures, replicate sampling, equipment blank samples, and a rigid cleaning procedure using detergent, hydrochloric acid, and methanol.

INTRODUCTION

The National Water-Quality Assessment (NAWQA) program of the U.S. Geological Survey (USGS) is designed to assess the status and trends in the quality of the Nation's ground- and surface-water resources and to develop an understanding of the major factors that affect water-quality conditions (Hirsch and others, 1988; Leahy and others, 1990; Gilliom and others, 1994). The design is based on balancing the unique assessment requirements of individual hydrologic systems with a nationally consistent design structure that incorporates a multiscale, interdisciplinary approach. Investigations of water quality in 60 major hydrologic basins and aquifer systems, referred to as NAWQA Study Units, form the building blocks of the program.

The Occurrence and Distribution Assessment, described in Gilliom and others (1994), is the largest and most important component of the first intensive study phase in each Study Unit. The goal of the Occurrence and Distribution Assessment is to characterize, in a nationally consistent manner, the broad-scale geographic and seasonal distribution of water-quality conditions in relation to major contaminant sources and background conditions. The national study design for streams has three interrelated components. Water-Column Studies assess the occurrence and distribution of major ions, nutrients, and dissolved pesticides and their relation to hydrologic conditions, sources, and transport. Bed-Sediment and Tissue Studies assess the occurrence and spatial distribution of trace elements and hydrophobic organic

contaminants. Ecological Studies evaluate the physical, chemical, and biological characteristics of streams relative to environmental settings. Sampling designs for these components coordinate sampling of varying intensity and scope at common sites. The glossary at the front of this report includes brief definitions of the NAWQA study components, indicated throughout the report with capital first letters, and other key terms.

This report describes standard methods for collecting and processing water-column samples from streams as part of the Occurrence and Distribution Assessment component of the NAWQA program. Complimentary methods and procedures are described for collecting and processing biological tissues (Crawford and Luoma, 1992; Meador and others, 1993) and bed sediments (Shelton and Capel, 1994). The methods and techniques described in this report are intended to enable investigators to meet the specific goals of the NAWQA program and are oriented to specific USGS equipment, practices, and support facilities. However, they also can be adapted for use by other Federal and state agencies, as well as by other programs of the USGS.

The procedures described conform to methods presented in the USGS Techniques of Water-Resources Investigations (TWRI) series and in the technical memorandums of the Office of Water Quality (OWQ) and the Office of Surface Water (OSW) of the USGS (see appendix A). The procedures are based, in part, on guidelines released by the OWQ and on a field manual prepared by M.A. Sylvester and others of the U.S. Geological Survey (see appendix B). New material has been added for selected procedures, and some guidelines have been modified to conform with the NAWQA Study-Unit design guidelines. The development of new and improved field techniques is a continuing process; therefore, this field guide will require periodic updating. If these updates outline a different or improved procedure, investigators in each Study Unit will evaluate the effect on the resulting data. Compatibility with previously collected data is essential for the duration of each project.

Trade names used in connection with equipment or supplies do not constitute an endorsement of the product. References are made throughout this document to the U.S. Geological Suvey's National Water Quality Laboratory (NWQL); Quality Water Service Unit at Ocala, Florida (OCALA); and the Hydrologic Instrumentation Facility (HIF).

OVERVIEW OF WATER-COLUMN STUDY DESIGN

Water-Column Studies in NAWQA focus on assessing physical and chemical characteristics of stream water, including suspended sediment, dissolved solids, major ions and metals, nutrients, organic carbon, and dissolved pesticides, and on relating these characteristics to hydrologic conditions, sources, and transport. The sampling designs for Water-Column Studies rely on coordinated sampling of varying intensity and scope at two general types of sites, Integrator Sites and Indicator Sites. Integrator Sites are chosen to represent water-quality conditions of streams and rivers in heterogeneous large basins that often are affected by complex combinations of land-use settings, point sources, and natural influences. Indicator Sites, in contrast, are chosen to represent water-quality conditions of streams in relatively homogeneous and usually smaller basins associated with specific individual environmental settings (for example, a particular combination of land-use and geological setting).

Water-column conditions are assessed by three primary sampling strategies employed at the selected Integrator and Indicator Sites:

1. Basic Fixed-Site assessments characterize the spatial and temporal distribution of general water-quality and constituent transport in relation to hydrologic conditions and contaminant sources;

2. Intensive Fixed-Site assessments characterize seasonal and short-term temporal variability of general water quality and constituent transport and determine the occurrence and seasonal patterns in concentrations and transport of dissolved pesticides; and

3. Synoptic studies are investigations of the geographic distribution of selected water-quality characteristics in greater detail during specific seasons and in relation to sources.

Site choices and sampling strategies for Basic Fixed Sites and Intensive Fixed Sites are particularly important to the success of the stream-water design for national water-quality assessment because in this part of the study design all components are integrated by a nationally consistent strategy in all Study Units. The focus of this report is on field procedures for collecting and processing samples from Basic Fixed Sites and Intensive Fixed Sites.

Each Study Unit typically has three to five integrator Basic Fixed Sites and four to eight indicator Basic Fixed Sites. Intensive Fixed Sites usually are composed of one or two Integrator Sites and one to four Indicator Sites. Samples are collected from each site at fixed intervals and at extreme flows. The analytical strategy for samples collected at Basic Fixed Sites is summarized in table 1; the strategy for samples collected at Intensive Fixed Sites is the same, but with the addition of laboratory analyses of dissolved pesticides (table 2).

Table 1. Analytical strategy for Basic Fixed Sites

Field measurements
Dissolved oxygen
pH and Alkalinity
Specific conductance (hourly or daily if local conditions require)
Temperature (hourly for 1 year)
Laboratory analyses
Suspended sediment
Major constituents:
Dissolved solids
Major ions and metals:
Calcium
Chloride
Fluoride
Iron
Magnesium
Manganese
Potassium
Silica
Sodium
Sulfate
Nutrients
Nitrogen:
Total
Total dissolved
Ammonia
Nitrite
Nitrate
Phosphorus:
Total
Total dissolved
Ortho
Organic carbon:
Suspended
Dissolved

Table 2. Analytical strategy for Intensive Fixed Sites in addition to the Basic Fixed Site analyses

Field measurements			
Specific conductance (hourly or daily for 1 year)			
Laboratory analyses: dissolved pesticides			
Amides:			
Alachlor	Napropamide	Propachlor	
Metolachlor	Pronamide	Propanil	
Carbamates:			
Aldicarb	Carbofuran	Molinate	Thiobencarb
Aldicarb sulfone	Carbofuran, 3-Hydroxy	Oxamyl	Triallate
Aldicarb sulfoxide	EPTC	Pebulate	
Butylate	Methiocarb	Propham	
Carbaryl	Methomyl	Propoxure	
Chloropheoxy herbicides:			
2,4-D (acid)	2,4-DB	MCPB	2,4,5-T
Dichlorprop (2,4-DP)	MCPA	Silvex (2,4,5-TP)	Triclopyr
Dinitroanalins:			
Benfluralin	Oryzalin	Trifluralin	
Ethafluralin	Pendimethalin		
Organochlorines:			
Chlorothalonil	Decthal (mono acid)	Dichlobenil	alpha-HCH
Dacthal (DCPA)	*p,p'*-DDE	Dieldrin	gamma-HCH
Organophosphates:			
Azinphos-methyl	Dimethoate	Fonofos	Parathion
Chlorpyrifos	Disulfoton	Malathion	Phorate
Diazinon	Ethoprop	Methyl parathion	Terbufos
Pyrethroids:			
cis-Permethrin			
Triazine herbicides:			
Atrazine	Cyanazine	Prometon	
Atrazine, desethyl	Metribuzin	Simazine	
Uracils:			
Bromacil	Terbacil		
Ureas:			
Fenuron	Fluometuron	Neburon	
Diuron	Linuron	Tebuthiuron	
Miscellaneous:			
Actifluorfen	Clopyralid	DNOC	Picloram
Bentazon	Dicamba	Esfenvalerate	Propargite
Bromoxynil	2,6-Diethylanaline	1-Napthol	
Chloramben	Dinoseb	Norflurazon	

PREPARATION FOR SAMPLE COLLECTION

SITE SELECTION

All Basic Fixed Sites and Intensive Fixed Sites should be at or near streamflow gaging stations because stream discharges associated with chemical-constituent concentrations are needed to compute constituent transport and to evaluate relations between streamflow and water-quality characteristics (Gilliom and others, 1994). The sample collection site should not be more than a few hundred feet from the site of the gage, unless no appreciable inflow is between the sampling site and the gaging station.

Criteria for selecting a site for water-sample collection are different from those for selecting a site for measurement of streamflow. Greater accuracy in computing constituent transport may be attained by selecting a cross section based on sediment-transport and mixing characteristics rather than hydraulic measurements such as velocity. Collection sites should be located in relatively straight channel reaches where the flow is uniform. Collecting samples directly in a ripple or from ponded or sluggish water should be avoided. Sites upstream or downstream of confluences or point sources also should be avoided to minimize problems caused by backwater effects or poorly mixed flows. Samples collected directly downstream from a bridge can be contaminated from the bridge structure or runoff from the road surface.

SAMPLING EQUIPMENT

The standard samplers used in the NAWQA program for collecting water samples include the DH-81, D-77 TM, D-77 Bag, and weighted- and open-bottle samplers with Teflon or glass components. These samplers will collect representative water-chemistry samples in most stream environments; however, their limitations must be carefully considered when collecting isokinetic samples (see OSW technical memorandum 94.05, appendix A). For a more thorough discussion of the proper use of each sampler, see the "Collection Methods" section.

Knowledgeable, independent field judgement is essential for collecting a sample representative of the stream chemistry. The following information should be considered before making a decision on which sampler to use:

-Understand the sampling purpose and the desired results,
-Evaluate the stream conditions (depth, velocity, and distribution),
-Know the limits and consequences of the available samplers, and
-Decide which sampler and procedure will give the best results for the stream conditions.

Whichever sampler and procedure is used, document the stream conditions, sampler limitations, and method used. The equipment and supplies used in the collection procedures are listed in table 3.

Table 3. List of equipment and supplies for sampling and processing stream-water samples

[Sources for some items are listed to maintain quality standards or when volume discounts are available. HIF, Hydrologic Instrumentation Facility; OCALA, Quality Water Service Unit at Ocala, Florida; DIW, deionized water; NWQL, National Water Quality Laboratory; FMI, Fluid Metering Incorporated; OWQ, Office of Water Quality; ASTM, American Society for Testing and Materials; DO, dissolved oxygen; SPE, solid-phase extraction. ft, foot; gal, gallon; g/L, gram per liter; in. inch; L, liter; mL, milliliter; mm, millimeter; µm, micrometer; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Sampling equipment

- D-77 TM (HIF)
- DH-81 (HIF)
- D-77 Bag (plans from HIF)
- Krammerer sampler, Teflon
- Weighted-bottle sampler (plans from HIF)
- Support for D-77--bridgeboard, reels, cranes, and so forth (HIF)
- Wading rod, plastic, shrink wrapped (HIF)
- Cap, Teflon (for D-77 and DH-81) (HIF)
- Nozzles, Teflon (1/4 in., 5/16 in.) (HIF)
- Adaptor, Teflon (for 3-L bottle)
- Adaptor, Teflon (for 1-L bottle)
- Bottle, sampling, Teflon, 3 L
- Bottle, sampling, Teflon, 1 L

Cleaning equipment and supplies

- Gloves, vinyl, powderless (OCALA-130 HWS)
- Detergent, phosphate free, 0.2 percent by volume (OCALA-62 FLD)
- Acid, hydrochloric, trace element-free grade; 5 percent by volume
- Methanol, organic-free grade
- DIW (see OWQ technical memorandum 92.01, appendix A) (OCALA-378 FLD)
- DIW, organic-free (NWQL)
- Bottles, wash, plastic
- Bottles, wash, Teflon (OCALA-377 FLD)
- Basins, wash, plastic (three per site)
- Brush, scrub, nonmetallic
- Brush, small bottle, nonmetallic
- Bag, plastic, sealable, small (OCALA-24 FLD)
- Bag, plastic, sealable, medium (OCALA-23 FLD)
- Tape, Teflon, 2-in. wide
- Foil, aluminum, heavy duty
- Container, waste, acid, 5 gal
- Container, waste, solvent, 5 gal

Processing equipment and supplies

Splitting

- Cone splitter, Teflon (decaport) with fitting (Geotech-0901)
- Tubing, Teflon, 1/4 in. (for cone splitter)
- Chamber, processing (from plans)
- Bottles for splitting, amber glass, prebaked, 1 L (NWQL)
- Bottles, sediment, plastic, 1 L (NWQL)
- Bottles, subsample, (NWQL)
- Bags, plastic, large clear (for processing chamber)

Filtration-inorganic constituents

- Chamber, processing (plans from HIF)
- Pump, peristaltic, head (OCALA-20 FLD)
- Pump, peristaltic, motor assembly (OCALA-20 FLD)

Table 3. List of equipment and supplies for sampling and processing stream-water samples—*Continued*

Filtration-inorganic constituents--*Continued*

Tubing, pump, Tygon or silicon
Forceps, nonmetallic
Cartridges, capsule filter, 0.45 µm (OCALA-398 FLD)
Gloves, vinyl, powderless, (OCALA-130 HWS)
Bags, plastic, large clear (for processing chamber)
Battery, 12-volt hotshot, dry cell (OCALA-82 FLD)
Bottles, plastic, brown, 125 mL (NWQL)
Bottles, plastic, clear, 250 mL (NWQL)
Bottles, plastic, clear, 500 mL (NWQL)

Filtration-organic carbons

Filter assemble, pressure barrel, stainless steel, 500 mL
Hand vacuum/pressure pump (OCALA-361 FLD)
Tubing, Tygon, 1/4 in. by 5 ft
Forceps, stainless steel, (OCALA-347 BACT)
Filters, silver, 47 mm by 0.45 µm (OCALA-68 FLD)
Cylinder, graduated, glass, 100 mL
Cylinder, graduated, glass, 250 mL
Bottle, sample, amber glass, prebaked, 250 mL (NWQL)
Bottle, analyses, amber glass, prebaked, 125 mL (NWQL)
Petri dishes (OCALA-5 BACT)
DIW, organic-free (NWQL)
Bag, plastic, sealable (OCALA-24 FLD)
Gloves, vinyl, powderless (OCALA-130 HWS)

Filtration-organic compounds (kit available OCALA-386 FLD)

Balance, portable, 6,000 by 1.0 grams (Ohaus-CT6000)
Pump, metering, 1/8-in. adapters (FMI-QB-1-CSC)
Pump, metering, fitting (FMI-RHB-0-CKC)
Filter support, aluminum, 147 mm, fittings (Geotech-0860)
Tubing, Teflon, corrugated, 1/4 in. by 5 ft
Tubing, Teflon, 1/8 in. by 10 ft
Bottles, wash, Teflon, 250 mL (OCALA-377 FLD)
Dispenser, bottle top, bottle (1.0 by 10 mL)
Valves, Teflon, flow control, (NWQL)
Cylinder, graduated, glass, 25 mL
Cylinder, graduated, glass, 50 mL
Forceps, stainless steel (OCALA-347 BACT)
Syringe, disposable, 50 mL (OCALA-105 FLD)
Micropipette, fixed volume, 100 mL
Fitting, union, adaptor for SPE cartridge (NWQL)
Filters, glassfiber, prebaked, (147 mm by 0.7 µm) (OCALA-375 FLD)
Bottles, amber glass, prebaked, 1,000 mL (NWQL)
Methanol, organic-free grade
DIW, organic free (NWQL)
Spike mixture, vials, 4 mL (NWQL)
SPE cartridges, analytichen C-18 (NWQL)
SPE cartridges, carbopak-B (NWQL)
Bores, glass, disposable, for micropipette (NWQL)
Surrogate mixture, vials, 200 mL (NWQL)
Acid, ascorbic, 10 g/L
Beaker, plastic, 1,000 mL
Foil, aluminum, heavy duty
Gloves, vinyl, powderless (OCALA-130 HWS)
Battery, hotshot, 12 volt, dry cell (OCALA 82 FLD)

Table 3. List of equipment and supplies for sampling and processing stream-water samples–*Continued*

Preservation

Chamber, preservation (2) (from plans)
Gloves, vinyl, powderless (OCALA-130 HWS)
Nitric acid, ampules (NWQL)
Nitric acid/potassium dichromate, ampules (NWQL)
Sleeves, foam (OCALA-136 FLD, 358 FLD)
Ice

Field analyses equipment and supplies

Thermistor, electronic thermometer
Thermometer (ASTM)
Meter, specific conductance, electrode
Meter, pH
Electrode, pH, combination, liquid filled (OCALA-351 FLD)
Meter, dissolved oxygen
Probe, dissolved oxygen (OCALA-116 FLD)
Standards, specific conductance, 100 to 50,000 µS/cm (OCALA-42 FLD--54 FLD)
Buffers, pH 4 (OCALA-123 FLD)
Buffers, pH 7 (OCALA-125 FLD)
Buffers, pH 10 (OCALA-127 FLD)
Membrane repair kit, DO (OCALA-115 FLD)
Solution, zero, DO (OCALA-119 FLD)
Titrator, digital (OCALA-145 FLD)
Acid, sulphric, titrator cartridge (OCALA-142 FLD, 143 FLD)
Stirrer, magnetic, portable (OCALA-356 FLD)
Stirring bar, Teflon, magnetic
Beakers, glass, 100 mL
Beakers, glass, 250 mL
Beakers, glass, 500 mL
Barometer
Chamber, air-calibration (Wand)
Pipet, volumetric, 50 mL
Pipet, volumetric, 100 mL
Bottle, wide mouth, plastic, 1,000 mL
Meter logs
Tissues, laboratory
DIW (see OWQ technical memorandum 92.01, appendix A) (OCALA-378 FLD)

Miscellaneous equipment and supplies

Boots, hip
Waders, chest
Tools
Kit, first aid
Kit, highway emergency
Forms, field documentation (OWQ)
Forms, analytical request (NWQL)
Coolers, shipping, 1 gal
Coolers, shipping, 5 gal
Bottle tags (OCALA-84 FLD)
Ropes, nylon, 1/4 and 1/2 in. (OCALA-84 FLD)
Pens, marking, permanent, (OCALA-77 FLD)

HAND-HELD SAMPLERS

The DH-81 or an open-bottle sampler should be used when streamflow conditions permit the stream to be waded. The DH-81 sampler consists of a polypropylene collar screwed onto a plastic-coated wading rod. The collar is notched to accept the D-77-type Teflon cap and nozzle assembly, which is locked in the sampling position. A 1- or 3-L Teflon bottle can be used with the appropriate cap-bottle adaptor. The DH-81 can use a 1/4- or 5/16-in. Teflon nozzle. An open-bottle sampler is the simplest means of collecting a water sample. An uncapped glass or Teflon bottle is submerged in the stream by hand (see "Weighted Bottle" section).

SUSPENDED SAMPLERS

The following suspended samplers can collect depth-integrated samples when used within their recommended limits. These samplers are suspended from, and lowered into, the stream by a rope or cable and usually require the use of additional equipment because of their weight (see "Support Equipment" section).

D-77 TM

This 75-lb sampler (epoxy coated to prevent trace-element contamination) collects large-volume (nearly 3 L) samples. This sampler is approved for flow velocities from 2.0 to 8.0 ft/s, though some instability has been noted in turbulent flow velocities exceeding 6.0 ft/s. Depth limitations of the D-77 TM sampler are dependent on a combination of depth and velocity, preventing the sampler from overfilling when used with the recommended transit rate and the required nozzles. The recommended operating depth is between 3 and 15 ft. The Teflon cap has standard Mason-jar threads to make it compatible with a large glass sample bottle. The older Teflon caps require a Teflon cap-bottle adaptor when using the 3-L bottle. Caps purchased after July 1994 will not require the use of the cap-bottle adaptor. The recommended nozzle sizes for the D-77 TM sampler is 1/4- and 5/16-in. and must be made of Teflon. However, in extremely high flows or when sampling depths cause the 3-L sample bottle to overfill in a single vertical, a 3/16-in. nozzle can be used. This sampler was counterweighted during manufacturing for specific-sample bottle use. Always check the balance to ensure that the sampler is level when fitted with an empty bottle, cap, adapter, and nozzle.

D-77 Bag

This sampler is designed to collect large-volume (up to 8 L) samples. Counterweights suspended below this sampler allow for sample collection in streams where depths exceed the limits of the D-77 TM and where the combination of depth and velocity cause other samplers to overfill. The sampler uses the standard D-77 Teflon cap and nozzles. Teflon bags attached to the cap are held in place by a large rigid bottle, a frame, or both. The bag enables this sampler to collect larger volume samples. Prototypes currently are being tested. It is not known if the sampler collects samples isokinetically; the pressure inside the nozzle must be greater then the pressure outside the nozzle for the bag to fill. This sampler is difficult to use because of the collapsible bag and the sediment is hard to remove. Its use is not recommended when velocities are less than 2 ft/s and should be used only when the D-77 TM is inappropriate. Plans and operating instructions for this sampler are available from HIF. Document the use of this sampler.

Under Ice

Under-ice samplers that use the D-77 bottle, cap, and nozzle are currently being developed. The sampler is based on the DH-81 design and pivots into a vertical position, allowing it to go through an 8-in. ice hole. Contact the HIF for more information. Until this sampler is available, a DH-81 or a weighted bottle sampler should be used. A hand-held ice chisel should be used when making holes in the ice to avoid leaving residual contamination from the power equipment.

Weighted bottle

A weighted bottle is a simple way to collect a water sample in slow moving streams. Weights are added to an uncapped glass or Teflon bottle suspended from a rope for depth sampling. The sampler can be handmade (plans are available from HIF) and consists of a plastic basket or frame with a weight attached that holds a specific-size bottle. These samplers do not collect a depth-integrated, isokinetic sample; the sampling depth is mainly dependent on the capacity and inside diameter of the bottle opening. However, a representative sample usually can be collected from shallow streams when the suspended sediment is distributed uniformly in the vertical and the velocity is less than 2.0 ft/s. These samplers are most appropriate where differences in water-quality distribution within the cross section of the stream are insignificant.

A Teflon Kemmerer sampler can be used to composite depth-integrated samples from various depths. A Kemmerer sampler is a 4- by 18-in. tube with end caps that close by means of a messenger and entrap a 4.2-L water sample inside. This sampler collects a point sample from a specific depth. Composite several point samples from one vertical for a depth-integrated sample.

NOTE: When suspending a weighted-bottle sampler, use a single-filament line or rope (for example, a synthetic fiber such as nylon or Kevlar). Attach the line to the corner of the sampler to hold the bottle at a slight angle to avoid dripping river water from the line into the sample bottle.

SUPPORT EQUIPMENT

Some of the equipment used for streamflow monitoring also is used as support equipment for collecting water samples. A discussion of the various types of support equipment is presented in a report by Rantz and others (1982). Great care is needed when using multipurpose equipment for water-quality sampling and sample processing. The clean hands/dirty hands technique outlined in OWQ technical memorandum 94.09 (appendix A) should be followed when using metal support equipment. With this procedure one person (dirty hands) operates the support equipment and another person (clean hands) handles the cleaned collecting equipment.

Many field vehicles are used for more than one purpose (that is, streamflow measurements, gage maintenance, construction, stream sampling, and sample processing). Sample contamination is more likely to occur when multiuse vehicles are used to collect and process water samples. Therefore, it is strongly recommended that all water-quality sampling and processing be restricted to vehicles designed for that purpose. The processing area in the vehicle needs to be free of contaminants, metallic objects, dirt, and oil residue. Separate storage areas for the sampling equipment, acids, and solvents should be available, and the vehicle must be well ventilated. Several specially designed vehicles are currently in use. One example is a truck-mounted laboratory designed for use at the Rocky Mountain Arsenal by USGS personnel in Denver, Colorado.

PROCESSING EQUIPMENT

The equipment used to prepare and preserve the stream samples for laboratory analyses is specific to the desired results and includes processing chambers, splitters, filtering systems, and preservation chambers. A complete list of processing equipment and supplies is given in table 3.

PROCESSING AND PRESERVATION CHAMBERS

The use of processing chambers reduces the possibility of contamination and is required during the splitting and filtration processes (see OWQ technical memorandum 94.09, appendix A). Sample preservation must be done inside separate chambers to avoid cross contamination. These processing and preservation chambers are handmade (plans are available from HIF). Generally a 2- by 2- by 2-ft frame is constructed using 1/4-in. polyvinyl chloride (PVC) to support a clear plastic bag, which forms a protective tent to work inside when processing and preserving samples.

SAMPLE SPLITTERS

Two types of splitters are available for compositing and splitting, the cone (decaport) and the churn. The cone splitter is a positive pour-through device that composites and splits the sample in one step. A funnel-shaped reservoir receives the sample and directs it into a splitting chamber. The splitting chamber is a solid block with 10 outlet ports (placed at 36° intervals around the circumference and drilled at 45° angles) that meet in the center to form an inverted cone. The resulting configuration splits samples into 10 equal subsamples. Tests have shown that the cone splitter can split sample volumes as small as 250-mL into 10 equal subsamples, each subsample volume within an accuracy of 5 percent (see OWQ technical memorandum 80.17, appendix A). Tests of the distribution characteristics of the cone splitter (Capel and Nacionales, 1993) indicate that, even with a slight difference in the volume of the subsamples, the relative percent of sediment mass to sample volumes are within 3 percent at each port, and the particle-size distribution of the finer than coarse-sand fraction is within 5 percent.

Tests indicate that the churn splitter does not produce equivalent subsamples for sediments coarser than 63 mm. There is concern that a metal spring in the spigot may contaminate the samples for trace-element analyses (see OWQ technical memorandum 94.09, appendix A). The churn should be used only as a compositing vessel for dissolved inorganic samples withdrawn from the top (see OWQ technical memorandum 94.13, appendix A). The churn is limited in sample volume and currently is available only in a plastic version.

Based on all available information, the Telfon cone splitter is the best available equipment for compositing and splitting whole water samples for analyses of major ions, nutrients, trace elements, pesticides, and sediment. It is presently the only alternative for splitting pesticide and sediment samples. However, when methanol is used for cleaning the cone, it is not suitable for splitting samples for total organic compounds (TOC), dissolved organic compounds (DOC), and volatile organic compounds (VOC). Those samples must be collected separately, directly from the stream, to avoid contamination. The churn is suitable for compositing dissolved inorganic constituent samples, but NAWQA studies seldom sample for these constituents in isolation. Thus, for the multipurpose needs of NAWQA, the use of the Teflon cone splitter is required.

FILTER SYSTEMS

Some samples collected for inorganic constituents and most samples for organic constituents must be filtered in the field. Filtration equipment and procedures vary slightly depending on the type of constituents the filtration process is intended to isolate. The equipment basically consists of a variable-speed, battery-operated pump fitted with a peristaltic pump head or a metering pump that forces the sample through Tygon, silicon, or Teflon tubing into a filter assembly. A capsule filter system with an effective pore size of 0.45 µm is used for filtering inorganic constituents. The filter type used to process the dissolved organic-carbon samples has the same pore size, but uses a stainless-steel pressure filter unit to hold a 47-mm-diameter silver filter. The plate filter used for organic-compound analyses is 142 mm in diameter and is made of glass fiber with a pore size of 0.7 µm.

EQUIPMENT CLEANING

INORGANIC CONSTITUENTS AND ORGANIC COMPOUNDS

The collecting and processing equipment are soaked in dilute phosphate-free detergent solution, rinsed with tap water, soaked in 5.0 percent hydrochloric acid (HCl), rinsed with deionized water (DIW), rinsed with methanol, and then air dried prior to each field trip and between sites (see OWQ technical memorandum 94.09, appendix A). Detergents, methanol, and acids should be used with care to avoid possible contamination of the sample by their residue. A thorough native-water rinse is required at each field site before sampling to remove any remaining cleaning agents and equilibrate the equipment to the sampling conditions. A list of the supplies needed for equipment cleaning is given in table 3, and details on procedures are outlined below.

The sampler bottle, cap and nozzle, cone splitter, churn splitter, filter support, pumphead, tubing, and any other equipment (except the aluminum filter support used for organic-compound filtering) that will contact the sample are cleaned prior to each field trip and between sites as follows:

1. Disassemble (if necessary) wearing vinyl gloves.
2. Soak for 30 minutes in a 0.2-percent solution of phosphate-free detergent and scrub with a nonmetallic brush. Use a small bottle brush for the cone-splitter parts.
3. Change gloves and rinse throughly with warm tap water to remove all soap residue.

NOTE: FOR EQUIPMENT USED EXCLUSIVELY FOR ORGANIC-COMPOUND PROCESSING OMIT STEPS 4 AND 5.

4. Soak for 30 minutes in a solution of 5.0-percent hydrochloric acid. Swirling the equipment in the acid solution will adequately desorb any metals not removed during the washing process. The used acid/water solution should be placed in a waste container for proper disposal (see OWQ technical memorandum 94.06, appendix A).
5. Change gloves and rinse three times with DIW water.

NOTE: IF ORGANIC-COMPOUNDS SAMPLES ARE NOT COLLECTED, OMIT STEPS 6 AND 7.

6. Rinse the equipment used for the collection of samples for organic-compound analyses with a minimum amount of methanol. The used methanol should be placed in a waste container for proper disposal (see OWQ technical memorandum 94.07, appendix A).
7. Allow to air dry.
8. Protect areas of the equipment that will contact the sample with Teflon tape and place in a sealable plastic bag for storage and transport.
9. Rinse sampling and splitting equipment at the site with 2 to 3 L of native water before sampling.
10. Rinse sampling and splitting equipment with DIW immediately after each use.

ORGANIC CARBON

Equipment used for filtering the organic-carbon samples should be baked at 450°C for 2 hours or cleaned using organic-free DIW and aggressive scrubbing. USE NO DETERGENT OR METHANOL as routine cleaning agents. Protect and keep equipment away from any procedure using methanol (even the vapors could contaminate the equipment). If this equipment is contaminated and requires additional cleaning, scrub with a 0.1-percent solution of phosphate free detergent, then soak and rinse several times with large volumes of organic-free DIW.

COLLECTION METHODS

Proper sampling techniques must be used to ensure that a sample is representative of the flow in the cross section. A discussion of sampling techniques is presented in reports by Edwards and Glysson (1988) and Ward and Hair (1990). Some aspects of sampling also are included in other USGS TWRIs, OWQ technical memorandums (see list of references, appendix A), and in the recommended methods for water-data acquisition (U.S. Geological Survey, 1978). A discharge measurement should be made prior to sampling if a rated discharge is not available.

Collect samples at the same cross section throughout the period of record, if possible. This will eliminate many of the potential problems that might arise during the interpretation of water-quality data. For example, measuring streamflow in a pool and sampling in a nearby riffle might prevent use of the hydraulic information to compute constituent transport. Sand may move through the pool as bedload and through the riffle as suspended load. This does not mean that the same section used during the low-water wading stage must be used during higher stages that require the use of a bridge or cableway. However, the flow characteristics at the different cross sections can result in incomparable data if the cross sections are not located near each other or in the same flow regime.

The number of verticals sampled at a site should be based primarily on the requirement to collect a sample representative of cross-sectional chemistry and secondarily to obtain the volume of the sample required. Samples usually should be collected using a standard multivertical depth-integrating method to obtain the most representative isokinetic sample possible. However, abbreviated sampling methods (that is, weighted-bottle or dip sample) are sometimes the best procedures for collecting a sample representative of the stream chemistry. Single vertical, dip, or other point-sampling methods can be used when the cross-sectional transport characteristics of the site are documented adequately or extreme flow conditions exist that preclude the use of standard methods. The Telfon bag sample might not provide a sample representative of stream hydrodynamics; however, it can collect a representative noncontaminated sample in deep or fast moving streams. Considering the limits of the other samplers, the D-77 TM might be the most appropriate sampler under many conditions, even when used beyond its limits. All samples collected by nonstandard methods should be checked periodically against standard cross-sectional samples to develop correction coefficients for the data.

Prior to initial sampling at a site, and again 3 to 4 times per year, obtain a stream profile of field measurements (velocities, specific conductance, temperature, pH, and dissolved oxygen). Record observations from several verticals and depths in the cross section to determine the uniformity of these characteristics. These measurements should be used as guides in selecting an adequate number of verticals for obtaining a representative sample.

The vertical transit rate and operational depth of each sampler is a function of the stream velocity, sample-container volume, and nozzle size. The following chart gives the recommended vertical transit rates and the maximum depths for isokinetic sampling based on samplers and nozzles. Specific limitations of the samplers are in OSW technical memorandum 94.05 (see appendix A).

Sampler	Nozzle diameter (inches)	Ratio	Depth (feet)
DH-81	1/4	0.4	9
DH-81	5/16	0.4	6
D-77 TM	1/4	0.1	15
D-77 TM	5/16	0.2	15

Stream velocity × *ratio* = *maximum vertical transit rate*

Because of the limits of existing samplers to collect an isokinetic sample, considerable independent judgement is necessary to collect a sample representative of the stream chemistry. The entire stream cross section must be represented in the final sample to avoid the potential loss of pollutants that might be seeping from the streambanks or streambed. Therefore, it might be necessary to increase the vertical transit rate or use a smaller nozzle to avoid overfilling the sampler when representing the entire stream depth. A weighted-bottle or D-77 bag sampler also might be used. Figure 1 illustrates the recommended sampler options for the NAWQA program based on stream depth and velocity.

Intermittent streams require special consideration because little opportunity exists to study conditions or sample in detail prior to a flow event. Rapidly changing stage, discharge, and constituent concentrations dictate that abbreviated sampling schemes and techniques be planned carefully in advance to ensure that the most representative samples possible are obtained.

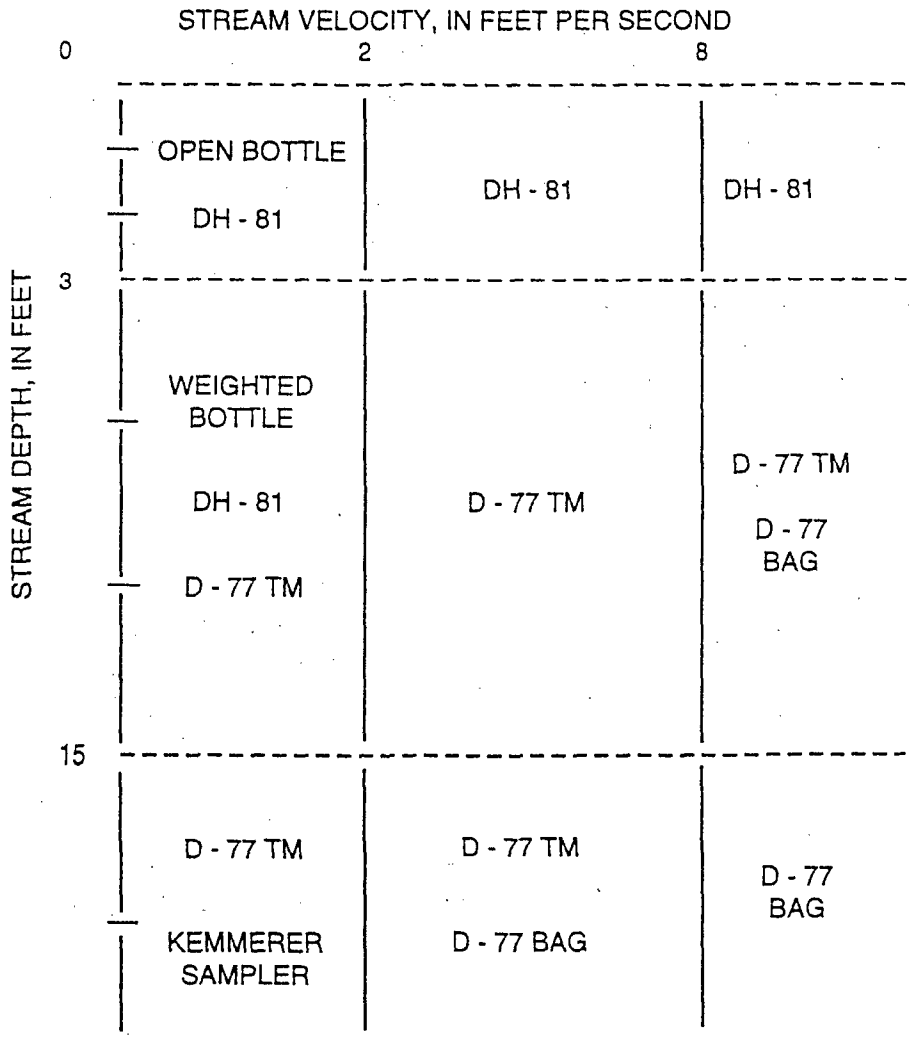


Figure 1. Schematic of suggested water-quality samplers for various stream regimes.

EQUAL-WIDTH-INCREMENT SAMPLING

The equal-width-increment (EWI) sampling method is the recommended procedure for NAWQA. The EWI method must be used during any sampling condition where a discharge measurement is not made before sampling; where the period of discharge record is insufficient to develop stage-discharge rating curves; where the streambed material is mobile, resulting in a poor stage-discharge relationship; or where inflow from a tributary is not well mixed in the sampling section. Detailed information on EWI sampling is presented in a report by Edwards and Glysson (1988).

The EWI method requires equal spacing of a number of verticals across the cross section and an equal transit rate, both upward and downward, in all verticals. The stream width is divided into a number of equal-width intervals; the number of intervals is dependent on results of water-quality profiles, uniformity of sediment distribution, channel width, and the depth and velocity distribution across the stream. Use 5 to 10 increments for cross sections less than 5 ft wide and a minimum of 10 increments in streams 5 ft wide or greater. A maximum of 20 increments should be used in extremely wide, shallow cross sections. The sample verticals should be spaced at least 6 in. apart.

Samples from several verticals can be accumulated in the same bottle. Do not allow the bottle to overfill because secondary circulation and enrichment of heavy particles can occur and bias the sample. Empty the bottle and resample the EWI stations if overfilling should occur.

The same transit rate must be used for all verticals. When additional verticals cannot be sampled without overfilling the bottle, empty the bottle directly into the cone splitter or use another bottle and continue sampling in the same manner until all of the verticals have been sampled. Transverse the EWI verticals as many times as necessary to ensure collection of the volume of sample required for analysis. When more than one traverse of each vertical is required, the composited cross-sectional sample will be proportional to the flow if each EWI vertical is transversed an equal number of times.

EQUAL-DISCHARGE-INCREMENT SAMPLING

The equal-discharge-increment (EDI) sampling method can be used on large streams only if the streamflow distribution within the cross section is known; that is, a discharge measurement is made prior to sampling. This method is not preferred, however, because it limits the number of verticals and could misrepresent a stream with stratified chemical characteristics. A discussion of this method is in a report by Edwards and Glysson (1988).

NONSTANDARD SAMPLING

Most samples collected for NAWQA are obtained by the depth-integrating samplers, DH-81 and D-77 TM. The quality of samples collected using nonstandard methods is likely to be inferior to those obtained with depth-integrating samplers (see the "Sampling Equipment" section). Identify all instances of nonstandard sampling in the field notes. Below are instances where other samplers or methods might be needed.

ORGANIC-CARBON SAMPLING

Special care must be taken when collecting samples for organic carbon analyses because the use of methanol as a cleaning agent will contaminate the DOC sample. Collect the sample directly into a baked 250-mL amber glass bottle using a weighted-bottle or open-bottle sampler at a single midstream vertical to avoid contamination from equipment or cleaning procedures. Because the sample probably will be more representative if the entire vertical is sampled, lower the sampler into the stream as quickly as possible. This compromised nonisokinetic collection procedure, designed to prevent equipment contamination, could affect the integrity of the suspended-organic-carbon (SOC) sample because the suspended sediments are not represented correctly.

LOW-FLOW SAMPLING

In very shallow or low-flow water where a depth-integrating sampler cannot be submerged, a representative sample usually can be obtained by immersing a hand-held open bottle (dip sample) in the centroid of flow or at multiple verticals with the mouth of the bottle directed toward the current. A dip sample should never be taken when it is possible to obtain depth-integrated samples. In natural streams when velocity is greater than 1.5 ft/s, suspended sediment normally has a higher concentration near the streambed than near the surface. The bias introduced by dip sampling can be considerable if the sample is analyzed for trace elements or other constituents that can sorb onto sediment particles.

HIGH-FLOW SAMPLING

If the velocity of the stream is so great that the sampler is pulled downstream and cannot be lowered in the vertical or the combination of depth and velocity cause the sampler to overfill, alternate sampling methods are necessary. Under these conditions, sample with a D-77 bag sampler or exceed the limit of D-77 TM sampler and document the procedure. The number of sampling verticals should be kept to a minimum during periods of storm runoff when the stage is rapidly changing and it is necessary to collect a large number of samples from several locations within a relatively short period of time. Under these conditions, collect the samples at a reduced number of verticals at each site and document the circumstances and number of verticals on the field notes.

SAMPLING FROZEN STREAMS

During periods of extreme cold when nozzles or air exhausts in samplers freeze up, use a sampler designed for collection under ice (such as described under section, "Sampling Equipment") or collect directly into an open bottle through a hole in the ice.

AUTOMATIC SAMPLERS

Automatic pumping samplers with a single-fixed intake are sometimes used to collect samples at remote sites or small streams with flashy hydrologic response. Pumped samples must be compared to EWI samples collected over the range of flow conditions at the site. EWI samples are used to develop coefficients for the point samples collected by the automatic pumping sampler. Analyze comparison samples for the same constituents as the pumped samples to determine the relation between the constituent concentrations at the single fixed-intake location and their respective mean concentrations in the cross section. Use this information to select the best location in the channel for the pump intake. Retrieve samples from the automatic sampler at the earliest possible time to reduce the chance of chemical or biological alteration of the sample. Refrigerated Teflon automatic samplers are available to help maintain sample integrity. Flow-composite samples can be obtained by withdrawing a small aliquot of sample from each bottle collected during an event and compositing into a single bottle for analyses.

SAMPLE PROCESSING

The EWI sampling method produces a composite sample that is representative of flow in a cross section. When sampling for multiple chemical constituents, the sample must be subdivided within a short time after collection into a number of subsamples, each equivalent in concentration of suspended and dissolved constituents. A complete list of the equipment and supplies used in processing water samples (splitting, filtration, and preservation) is given in table 3.

Precautions must be taken to avoid contamination from the atmosphere during the processing procedure. Sample processing equipment should be kept covered (when not dispensing sample), and subsample bottles should be covered or capped. All sample preparation and processing should be done in a field processing chamber or inside a clean field vehicle.

SPLITTING

The cone splitter is being used as the primary splitter to divide the collected sample into subsamples for inorganic-constituent, organic-constituent, and suspended-sediment analyses. Subsamples for filtered inorganic-constituent, organic-compound, suspended-sediment, and field analyses should be collected from the first set of split samples from the cone splitter. Subsequent splits should be used to collect subsamples for raw (unfiltered) inorganic-constituent analyses. If samples are collected only for dissolved inorganic-constituent analyses, the churn splitter may be used instead of the cone splitter (see OWQ technical memorandum 94.09, appendix A). The plastic churn splitter should not be used for compositing or splitting samples for the analysis of suspended sediment or organic compounds.

Individual samples collected in a D-77 TM sampler can be poured directly into the cone splitter from each vertical, or each time the D-77 bottle is full. Alternatively, the entire sample can be collected in several (three or four) D-77 sample bottles and later poured into the cone splitter. Either method allows the cone splitter to function as both a splitter and compositor. The sample should be well mixed in the D-77 sample bottle when dispensing the composited sample into the cone splitter. Agitate the bottle to resuspend adequately the sediment and pour rapidly into the splitter. Make sure all sediment is removed.

The splitting process is as follows:

1. Set up the cone splitter on a flat, open area. A level splitter is critical to performance. All Teflon tubes should be approximately the same length.
2. Field rinse all sample-collection and splitting equipment with native water. Collect the rinse water near the shore to avoid heavy suspended sediments. Pour rinse water from the D-77 sample bottle through the Teflon cap and nozzle and into the cone splitter. Three 1-L rinses are more effective then one 3-L rinse.
3. Place subsample containers under each outlet tube. The tubes need only extend into the receiving containers far enough to prevent spillage.
4. Cover the reservoir of the cone splitter and seal each port (with Teflon tape) as it enters the subsample bottle to prevent airborne contamination. A large plastic bag should be placed over the splitter and subsample bottles when not in use.
5. Agitate the sample (10 to 15 seconds) in the D-77 bottle to resuspend the sediments. Invert the bottle over the cone splitter reservoir. Sample transfer should be rapid. Maintain a head of water above the standpipe to prevent air from entering the splitting block.
6. Remove subsample containers from cone splitter and cap immediately.
7. An additional split is necessary to obtain the smaller volumes of some required subsamples. Reload splitter ports with the required bottles and pour a subsample from the first set of split samples.
8. Disassemble the cone splitter after completing the sample processing and clean before reuse or storing.

Below is an example of the splitting technique. Consider that an 8- to 9-L composite sample must be split to achieve a set of final subsamples as follows:

2,000 mL	-	FU, pesticide analyses
250 mL	-	RU, laboratory conductance, pH, and alkalinity
500 mL	-	FU, major anions and dissolved solids
250 mL	-	FA, major cations
125 mL	-	RC, total nutrients
125 mL	-	FC, dissolved nutrients
250 mL	-	FU, field alkalinity
500 mL	-	RU, field measurements (conductance and pH)
1,000 mL	-	RU, suspended-sediment analyses
5,000 mL		

where

F = filtered,
U = untreated,
A = acidified,
R = raw (unfiltered),
C = chilled

One 1-L bottle under each of the splitter ports will generate a set of subsamples with 800 to 900 mL in each bottle. If additional volume is desired in the 1-L subsamples, pore one of the subsamples back through the splitter to top off the volume in the remaining 9-L subsamples with an additional 80 to 90 mL. Set aside three of the 1-L bottles for filtering the pesticide samples and save one 1-L bottle for suspended-sediment analyses. Use one 1-L bottle for field measurements of conductance and pH. Two 1-L bottles can be used to filter samples for major ions, nutrients, and field alkalinity. Place a 125-mL bottle for the nutrient sample (RC) under one splitter port and combine two ports into a 250-mL bottle for the RU sample. Pour one of the 1-L subsamples from the first split through the splitter to fill the second set of subsamples with the approximate volumes. The remaining two 1-L bottles can be used for extra samples or for rinsing the equipment in the filtering process. An example of the first set of subsamples (approximately 850 mL each) follows:

3 - Pesticides (to be filtered),
2 - Major ions, nutrients, and field alkalinity (to be filtered),
1 - Sediment (RU),
1 - Field measurements, conductance, and pH (RU),
1 - Resplit for 250-mL RU and 125-mL RC samples, and
2 - Extra samples.

If a larger total-volume sample is required, use 2- or 3-L bottles under the ports of the cone splitter during the first split instead of the 1-L bottles. Additional cone splits may be necessary to achieve the proper volume of subsamples.

Three important issues to remember when using the cone splitter: never overfill a subsample bottle, always pour all of the sample into the splitter, and be careful not to spill any sample water when pouring.

D. Suspected suspended-sediment concentrations greater than 1,000 mg/L:

Follow procedure C when processing samples suspected of having a suspended-sediment concentration greater than 1,000 mg/L, except use a 10-mL sample volume at step 3 for the SOC analyses. Step 11 then will require an additional 90 mL for the DOC sample.

Clean all equipment immediately after use, wrap with aluminum foil, and store in a sealed container (sealable plastic bag). Avoid working and storing in areas where methanol vapors might contaminate the equipment. The filter assembly and any other equipment (tweezers, graduated cylinder, and so forth) should be routinely cleaned ONLY with organic-free DIW accompanied by an aggressive scrubbing with a nonmetallic brush. DO NOT USE METHANOL OR DETERGENT for routine cleaning.

Regular inspection of the filter assembly is important to determine if additional cleaning is necessary. A dirty filter unit or a suspected contaminated filter unit will require additional cleaning. Scrub filter unit with a solution of 0.1-percent Liquinox and rinse with GALLONS of tap water (you MUST remove the detergent). Scrub and rinse with organic-free DIW. Remember that three 1-L rinses are more effective than one 3-L rinse. Double wrap the equipment with aluminum foil for storage.

ORGANIC COMPOUNDS

Organic contaminants are manmade, synthetic compounds, many of which control insects (insecticides) and weeds (herbicides). The capillary-column gas chromatography/mass spectrometry (GCMS) method is used for pesticide analyses of organonitrogen herbicides (NWQL schedules 2001 and 2010). Samples collected for chorophenoxy-acid herbicides and carbamates (NWQL schedules 2050 and 2051) use the high-pressure liquid-chromatography (HPLC) method. These synthetic-organic compounds in stream water interact with sediment particles through sorptive processes; therefore, it is important to separate the solid phase from the sample as soon as possible after collection. Depth filters made from glass fibers with a 0.7-µm pore size are used to filter samples for analysis of organic compounds because they can be precleaned with organic solvents or baked at 450°C. Depth filters have a high-loading capacity, making them more suitable for filtering the larger sample volumes (1 to 3 L) are needed for organic analysis. More detailed information on filtering samples is found in OWQ technical memorandum 91.09 (see appendix A) or in a report by Sandstrom and others (1992).

The pumping system should be either a valveless metering pump with a ceramic piston (FMI-QB-1-CSC) or a Teflon diaphragm head mounted on a 12-volt electric pump drive. The filter support should be made of aluminum, Teflon, or stainless steel with a 142-mm diameter. The filter support is connected to the pump with 1/4-in. convoluted or corrugated Teflon tubing and Teflon or stainless-steel fittings.

All equipment and components should be made of materials that will not contaminate or sorb analytes and are suitable for use with organic solvents such as ceramics, glass, fluorinated polymers (Teflon), stainless steel, or aluminum. The equipment should be precleaned with a Liquinox/tap-water solution (approximately 0.2-percent Liquinox by volume), rinsed with tap water and then with high-purity methanol, and air dried. Do not use the hydrochloric-acid cleaning step for equipment used in this procedure. The following procedures should be done in a clean workplace, free from fumes and dust. The samples processed here should be subsamples directly from the cone splitter.

1. Rinse the filter, tubings, and the filter support by passing AT LEAST 100 mL of native water through the system; use a precleaned (oven baked at 450°C for 2 hours), glass-fiber, 0.7-µm pore-size filter (part OCALA-375FLD). Remove the air from the filter support and tubing by opening the vent located on the top of the filter support.
2. Tare weigh a precleaned 1-L amber glass bottle (from NWQL). Filter sample without rinsing the bottle. Collect approximately 1 L of the filtered sample for each schedule (do not completely fill the bottle; leave about a 2-cm headspace to add conditioner and surrogate).
3. Weigh and record the amount of sample filtered; that is, the total weight minus the tare weight of the bottle.
4. Refrigerate or store filtered sample on ice (approximately 4°C) for additional processing.

Changing Filter Paper

High sediment and colloid concentrations can slow the filtration rate by clogging the filter paper prior to achieving the volume necessary for analyses. Clogging might require changing the filter paper during the filtration procedure. To do this, remove the pump intake line from the stream-water sample bottle and pump dry the filter unit before disassembling. Remove the filtered sample from the filter unit. The unfiltered sample must not come in contact with the bottom half of filter unit while the filter paper is being changed. Fold the clogged filter in half with tweezers, carefully remove, and discard. Rinse the inside of the filter unit with organic-free DIW. Install a new filter paper and condition prior to continuing the filtration process.

Cartridge Processing

Samples collected for analysis of organic compounds must be processed through a solid-phase extraction (SPE) cartridge within 4 days of collection. Schedules 2001 and 2050 require laboratory-processed SPE, and schedules 2010 and 2051 require field processed SPE. The SPE method utilizes bonded silica, packed into an extraction column, which absorbs specific organic compounds. These compounds subsequently are removed from the extraction column using a solvent. This procedure produces a small sample that is analyzed for selected compounds. This extracted sample can be stored for extended periods before analyses.

1. Record the precleaned SPE cartridge type, lot number, and weight. Condition the SPE cartridge. Use approximately 2 mL of methanol for schedule 2010 and approximately 2 mL of ascorbic acid for schedule 2051. Follow with approximately 2 mL of organic-free DIW to remove excess conditioner. Allow the conditioner and water to flow by gravity through the cartridge. At no time should the cartridge go dry once conditioning has started. If it does, repeat the conditioning process. Maintain the water in the cartridge bed by replacing the water that drains through or by using an on-off valve to prevent the cartridge from draining completely.
2. Add to the filtered sample (from above) approximately 10 mL of methanol for schedule 2010 or approximately 10 mL of ascorbic acid for schedule 2051 using a bottle-top dispenser. Weigh and record the sample-plus-methanol weight.
3. Add the surrogate mixture (1.25 mg/μL) contained in the 2-mL amber vial. Use a different surrogate and micropipette for each schedule. Withdraw the solution into the glass bore using a 100-μL micropipette and a clean glass bore. Insert the tip into the sample bottle below the surface of the water and press the plunger to deliver the surrogate to the sample. Withdraw the micropipette, remove and discard the glass bore. Rinse the orange-colored Teflon tip with solvent. Cap and swirl the sample to mix.
4. Process the filtered sample through the SPE cartridge with a valveless, piston-type metering pump (FMI-RHB-0-CKC) fitted with 1/8-in. Teflon tubing. Insert the tubing from the inlet side of the pump into the sample bottle. Turn on the pump, allow the air to be rinsed from the tubing, then attach the outflow pump line to the SPE cartridge with a Luer-Lok fitting. For schedule 2010, use a female Luer-Lok fitting attached to the small end of the cartridge and invert the cartridge to discard any conditioning water remaining in the SPE reservoir. For schedule 2051, use a male Luer-Lok fitting and cartridge adapter attached to the large barrel end of the cartridge. Pump the sample through the cartridge at 20 to 25 mL/min. Collect the extracted water that passes through the cartridge in a plastic 1-L beaker. After the sample has been pumped through the cartridge, turn off the pump, and disconnect the SPE cartridge.
5. Remove excess water from the SPE cartridge using a syringe to blow out the water. Record the final weight of the sample. Write the sample identification number on the side of the cartridge and store in a 40-mL amber glass ampule. Store cartridges in a cool place (approximately 4°C).

Clean all equipment after use by rinsing with a phosphorus-free detergent (0.2 percent) and then several rinses with tap or distilled water to remove the detergent and approximately 30 mL of methanol. Wrap all openings with Teflon tape or aluminum foil.

PRESERVATION

Many of the ions normally present in natural waters change due to chemical and physical reactions, such as oxidation, reduction, precipitation, adsorption, and ion exchange, before analyses in a laboratory. Therefore, samples for many constituents must be stabilized by preservation. Some examples of preservative treatment are refrigeration to minimize chemical change caused by biologic activity and the addition of acid to prevent the precipitation of cations.

Below are some examples of bottles, caps, and treatments for various analyses.

Analyses	Bottle type	Bottle cap	Treatment
Anions	Clear plastic	Black	FU
Cations	Clear plastic	Clear	FA
Nutrients	Brown plastic	Black	RC,FC
Trace elements	Clear plastic	Clear	FA
Organic compounds	Brown glass	Teflon lined	FC

F = filtered
U = untreated
A = nitric acid (HNO_3)
R = raw (unfiltered)
C = chill and maintain to 4°C

Preservatives, such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid/potassium dichromate ($HNO_3/K_2Cr_2O_7$), sodium hydroxide (NaOH), and phosphoric acid (H_3PO_4), are available in ampules from OCALA supply. Every measure should be taken to reduce the possibility of contaminating samples and equipment during the preservation process. A preservation chamber will assist in this effort. Be sure the outside of the preservative ampules are clean. Bottles that require no preservation should be set aside in the shipping container. Do not add mercuric chloride ($HgCl_2$) to the samples that will be analyzed for nutrients (RC and FC). Samples collected for nutrient analyses should be chilled only (see OWQ technical memorandum 94.16, appendix A). The order in which the preservatives are added also should be considered. ALWAYS WEAR PERSONAL-PROTECTIVE EQUIPMENT (GOGGLES, GLOVES, AND APRON).

1. Preserve samples that require acids (nitric, sulfuric, hydrochloric, and phosphoric) inside a preservation chamber,.
2. Use the same chamber to add nitric-acid/potassium-dichromate solution to the samples that will be analyzed for total and dissolved mercury (RAM and FAM). Discard the gloves worn during these procedures along with the ampules. Wash hands thoroughly.
3. Change processing chambers and complete any other preservation techniques, such as the addition of sodium hydroxide, zinc acetate, or copper sulfate. If any of these bottles or remaining bottles require chilling, place them on ice. Discard the gloves worn during these procedures along with the acid ampules. Wash hands thoroughly.

By following this sequence for sample preservation, the risk of contaminating a sample with the residue of a preservative left in the air or on the gloves is reduced. Clearly, great care must be exercised in the field to prevent cross contamination. Acid and potassium-dichromate ampules should be stored and transported separately. Dispose of used ampules properly. If there are any questions concerning the correct preservation technique or the proper disposal of used ampules, consult your District Water-Quality Specialist or refer to OWQ technical memorandums 90.01, 92.11, 94.09, and 94.16 (see appendix A).

DISTRIBUTION

All bottles must be clearly labeled with a waterproof marker or preprinted labels so the NWQL can sort the bottles for the appropriate analyses. The minimum information required is the site identification number, date and time, sample designation (bottle type), and schedule number or lab code as shown below:

09498500
01-31-1993 @ 1200
RA
SCH-2001 (or LC00114)

A NWQL analytical services request form needs to be included with each sample. The forms and the instructions for completing the form are available from the NWQL. Be sure to retain the carbon copy of the form.

Place all glass containers in padded sleeves or pack in some other suitable manner to prevent breakage during shipment. Chilled samples need an adequate amount of ice. Good results have been obtained by packing the chilled bottles in a volume of ice equal to approximately twice the volume of the chilled sample. The amount of ice necessary varies depending on the length of time in transit from field to laboratory and the time of year. Insulated water coolers from 1 to 5 gal in volume make good shipping containers if the integrity of the container is ensured by removing the spigot assembly and sealing with a silicon or epoxy sealer. Larger volumes of chilled samples can be sent in ice chests as long as maximum weight restrictions of the carrier are not exceeded. Guidelines on shipping samples are discussed in OWQ technical memorandum 92.06 (see appendix A).

Samples should be sent to the NWQL on the day collected when possible. The NWQL also prefers to have all bottles for a single sample sent in one container. However, nutrient samples must be sent in a separate container. Unchilled samples can be sent separately from the chilled samples.

The NWQL has issued the following guidelines:

1. Inspect and replace any broken or leaking coolers. Spouts must be sealed. As part of a program to enhance relations with the post office, the laboratory will not return damaged and leaking coolers.
2. Line each shipping container with a plastic bag.
3. Make sure all bottle caps are screwed on tightly.
4. Place all 1-L glass containers in individual foam sleeves or in a foam box designed for shipping to prevent breakage when samples are sent in coolers.
5. Ice should be placed inside a double plastic bag in the shipping container.
6. During the summer, in particular, the cooler and samples should be prechilled. Pack the samples with fresh ice, at least a volume of ice equal to the volume occupied by the samples, but preferably twice the volume of ice to samples.
7. Protect the log-in forms and return labels from the ice by placing them in a plastic bag; the plastic bag should be sealed and fastened to the lid of the cooler with tape.
8. The plastic liner bag must be carefully sealed with a wire tie and the shipping container taped shut.

FIELD ANALYSES

Measurements of specific conductance, water temperature, dissolved oxygen, pH, and alkalinity could change dramatically within a few minutes or hours after sample collection. Immediate analysis in the field is required if results representative of in-stream conditions are to be obtained.

Water temperature and dissolved oxygen should be measured directly from the stream, and several readings are required in the cross section to obtain a stream average. Specific conductance, pH, and alkalinity should be measured from a cone-split subsample so that these results will be from the same water matrix as the other chemical analyses. A single field meter that measures specific conductance, water temperature, pH, and dissolved oxygen directly in the stream may be used if stream profiles are performed regularly. These profiles must confirm that the direct in-stream measurements are comparable to the values from a cone-split sample.

Field water-quality instruments, support equipment, and the reagents used for analyses are listed in table 3, in reports by Fishman and Friedman (1985) Ward and Hair (1990), and in selected OWQ technical memorandums (79.10, 81.08, 81.17, 82.05, and 89.01, see appendix A).

Maintain an instrument log and review it prior to each field trip. The operation and calibration of all field instruments (including back-up meters and electrodes) should be checked to ensure that all are in good working condition.

TEMPERATURE

The stream water temperature can affect density and gas solubility, and density affects the mixing of different water masses, especially seasonal stratification. Temperature also affects the rate of chemical reactions, biological activity, conductivity, dissolved oxygen, and pH.

Because of possible environmental contamination if broken, mercury-filled thermometers are not acceptable for field use (see OWQ technical memorandum 94.02, appendix A). The recommended procedure for determining field temperatures is a thermistor, an electrical device made of a solid semiconductor with a high temperature coefficient of resistivity. Thermistors can be constructed with a high sensitivity, but are subject to a variety of errors. Therefore, the calibration should be checked in the laboratory at several temperatures using an American Society for Testing and Materials (ASTM) thermometer to ensure the required accuracy. Never carry a mercury-filled ASTM thermometer in the field.

Field measurements of temperature should include both air-temperature and water-temperature readings. Air-temperature readings should be made by placing a dry thermistor in a shaded area protected from strong winds, but open to adequate air circulation. Avoid areas that may have radiant heat such as near metal walls or sides of vehicles. Allow the thermistor to equilibrate 3 to 5 minutes before recording the temperature.

Water temperatures should represent the mean temperature of the stream at the time of observation. A horizontal and vertical cross-section profile will determine the variability, if any, that exists. Streams with highly variable temperature profiles should have several readings averaged to use as the mean and those variations should be documented. Streams with a fairly uniform temperature (less than 2°C variance 95 percent of the time) generally will have one measurement that can be made and reported as the stream temperature. Make this measurement by suspending (from a weighted line) or placing a thermistor in midstream. Shade the thermistor probe to prevent erroneous readings caused by direct solar radiation. The thermistor should be immersed in the stream for a minimum of 1 minute prior to making measurements. Report all routine temperature measurements to the nearest 0.5°C. For special studies where more precision is required, verify the accuracy and report temperatures to the requested precision.

SPECIFIC CONDUCTANCE

Conductance is the reciprocal of resistance in ohms and is a measure of the capacity of water or other substance to conduct an electrical current. Specific conductance is the conductance measured at 25°C and is reported in microsiemens per centimeter at 25°C. The specific conductance of water is determined by the types and quantities of dissolved substances in the water. Thus, specific conductance indicates the concentration of dissolved solids in water.

The specific conductance of water may change significantly with time because of pollution, precipitation, adsorption, ion exchange, oxidation, and reduction. Therefore, specific conductance should be measured in the field with an accurate conductivity meter. Many commercial conductivity meters are available on the market. All meters come with operating instructions, and users should be totally familiar with these instructions. The following are some important features and characteristics of a specific-conductance meter:

1. Automatic temperature compensating (direct specific-conductance reading).
2. Multiple measurement ranges from 0 to 200,000 µS/cm at 25°C with 1-percent accuracy and three-number digital readout.
3. Platinum, carbon, stainless-steel, or gold electrode.
4. Dip-type electrode.

Conductivity electrodes must be clean to produce accurate results. Because of the wide variety of electrode material, the instructions provided by the manufacturer should be followed. Rinse the electrode thoroughly with DIW after cleaning.

CALIBRATION

Specific-conductance standards, 10 to 50,000 µS/cm at 25°C, are available from OCALA supply for meter calibration. Prior to every water-quality field trip and again onsite, standards should be used to calibrate the meter and to check meter calibration. Document calibration checks in the instrument log. Used standards should not be returned to the stock container.

Calibration and operating procedures vary with meter types and manufacturers. The procedures described below are generalized steps that should be followed and will apply to most meters used for field measurements:

1. Presoak electrode in DIW at least overnight.
2. Choose two specific-conductance standards that will bracket the expected value of the sample to be measured.
3. The standards should be approximately the same temperature as the sample to be measured.
4. Use the calibration standard closest to the expected value of the sample to be measured. Rinse the container and electrode with standard. Pour calibration standard into container holding the electrode. Allow a minute or two for equilibration and then discard the standard.
5. Calibration setting: Pour fresh calibration standard into the container holding the electrode. The electrode should not touch the sides or bottom of the container. Note the meter reading and ADJUST meter to the known standard value.
6. Discard calibration standard into a waste container.
7. Rinse electrode and container with the second standard. The second standard will bracket the range of expected stream conductance. Pour check standard into rinsed container holding the electrode. Allow to equilibrate, and then discard check standard into a waste container.
8. Calibration check: Pour second standard into the rinsed container holding the electrode. This check reading should be within 5 percent of the known standard value. If not, repeat entire calibration procedures. Electrode cleaning or replacement, a different meter, or both might be needed.

NOTE: Switching meter calibration range will require recalibrating.

9. Discard check standard into a waste container and then rinse electrode and container with DIW.
10. Record all calibration information in the instrument log and on the field notes.

MEASUREMENT

Measurements of specific conductance at stream sites should be made from an unfiltered subsample from the cone splitter. If a direct in-stream measurement is made, several readings are necessary (vertically and horizontally) in the cross section to determine a mean value.

1. Rinse electrode and container with sample water. Pour sample water into container holding the electrode. Allow to equilibrate for a minute and then discard the rinse sample into a waste container.
2. Sample measurement: Pour fresh sample into the rinsed container holding the electrode. Record the specific-conductance value on the field notes.
3. Discard sample into a waste container and then rinse electrode and container with DIW. It is advisable to store electrode in DIW.
4. Conductivity measurements are reported as specific conductance and are expressed as microsiemens per centimeter at 25°C. Results are reported to three significant figures, whole numbers only.

pH

The pH of a solution is a measure of the effective hydrogen-ion concentration (activity). In aqueous solutions, pH is controlled primarily by the hydrolysis of salts of strong bases and weak acids or vice versa. The pH is expressed in logarithmic units using a scale from 0 to 14. Solutions having a pH of less than 7 are described as acid; solutions with a pH of more than 7 are described as basic or alkaline. Dissolved gases, such as carbon dioxide, hydrogen sulfide, and ammonia, appreciably affect pH. Degasification (for example, loss of carbon dioxide), precipitation [for example, calcium carbonate ($CaCO_3$)], and other chemical, physical, and biological reactions may cause the pH of a water sample to change significantly within several hours or even minutes after sample collection. Immediate analysis of a pH in the field is REQUIRED if dependable results are to be obtained. A thorough discussion of pH is presented in a report by Wood (1981), and low ionic-strength water (less than 50 µS/cm conductance) is discussed in a report by Busenberg and Plummer (1987). Some important features of the meters and electrodes include the following:

1. Digital (LCD) meter readout with 0.02 pH unit accuracy.
2. Slope correction (preferably with percent of slope readout).
3. Standard BNC electrode connector.
4. Plastic or glass, liquid-filled, combination Ag/Cl electrode.

Because a large variety of pH meters and electrodes are available on the market, it is extremely important that operators are thoroughly familiar with the instruction manual provided by the manufacturer.

Electrodes must be clean and properly operating to produce accurate results. The liquid junction also must be free flowing, and the electrolyte solution in the electrode must be at the proper level. Because of the variety of electrodes available, follow the cleaning and storing instructions provided by the manufacturer. Never wipe the pH electrode membrane with anything or store it dry (check manufacturer's instructions).

CALIBRATION

Buffers used to calibrate and check pH meters are available from OCALA supply. The standard buffers have values of pH 4, 7, and 10 with a relatively high ionic strength. Two pH buffers are needed to calibrate the pH meter (4 and 7 or 7 and 10). Document calibration checks in the instrument log. Used standards should not be returned to the stock container.

Because calibration and operating procedures vary with meter types and manufacturers, the procedures described below are generalized steps that will apply to most meters used for field measurements:

1. Remove filling plug on refillable electrodes prior to use. Use only the solution recommended by the electrode manufacturer when filling solution must be added. The liquid-filled pH electrodes should always be stored upright.
2. Bring pH buffers to the temperature of the sample to be measured (within a few degrees). Apply temperature-correction factors when calibrating the pH meter.
3. Rinse electrode, thermistor, a small Teflon-coated magnetic stirring bar, and a glass beaker with pH-7 buffer. Pour buffer into rinsed container holding electrode, thermistor, and stirring bar. Allow temperature to equilibrate for a minute and then discard buffer into a waste container.
4. Calibration: Pour fresh pH-7 buffer in the same beaker holding the equipment. The pH electrode must not be resting on the bottom or touching the sides of the container. Place the beaker on a magnetic stirrer. Measure temperature, remove thermistor, and adjust meter to the temperature of the buffer. With the stirrer on low (do not create a vortex), adjust meter reading to the known buffer value at the specific temperature. Discard pH buffer into a waste container.

NOTE: Turn pH meter to "standby" (or "off" on meters without standby) position prior to removing electrode from a solution.

5. Select a second buffer to bracket the expected stream pH. Use a pH-10 buffer when expected pH is greater than 7 and a pH-4 buffer when the expected pH is less than 7. Always use a pH-4 buffer as the second buffer when titrating for alkalinity. Rinse electrode, thermistor, and stirring bar with DIW. Rinse another clean beaker, electrode, thermistor, and stirring bar with the second buffer (pH 4 or 10). Pour second buffer into that container. Allow temperature to equilibrate for a minute and then discard buffer into a waste container.
6. Slope adjustment: Pour fresh pH buffer in the same beaker holding the equipment. Measure temperature and remove thermistor. Set meter temperature to the buffer temperature and, with the stirrer on low, adjust slope to the value of pH buffer. (Some meters have separate slope-adjustment knobs, whereas others use the temperature knob. Always refer to instruction manual when uncertain.) Discard pH buffer into a waste container.
7. Rinse electrode, thermistor, and stirring bar with DIW. Repeat steps 3 and 4 to ensure that any slope adjustments did not change the calibration adjustment. This is a check so adjustment should not be needed. If adjustment is required, repeat the entire calibration procedure.
8. Record all calibration information in the instrument log and on the field notes.

MEASUREMENT

Measurements of pH at stream sites should be made from a raw (unfiltered) subsample from the cone splitter. If a direct in-stream measurement is made, several readings are necessary (vertically and horizontally) in the cross section to determine a mean value.

1. Rinse electrode, thermistor, stirring bar, and container with stream water. Pour stream water into container holding the electrode, thermistor, and stirring bar. Allow the temperature to equilibrate and the electrode to precondition itself to the sample. Discard sample in waste container.
2. Measurement: Pour fresh sample into the same container holding the equipment. Measure and set temperature and remove thermistor. Measure pH and record on field notes. Discard sample in waste container.
3. Rinse electrode, thermistor, and stirring bar with DIW, and store electrode as recommended by the manufacturer.
4. Measurements of pH are reported in pH units. Results are reported to the nearest 0.1 pH unit.

QUALITY ASSURANCE AND QUALITY CONTROL

The sources of variability and bias introduced by sample collection and processing affect the interpretation of water-quality data. Establishment of quality-assurance plans ensure that the data collected are compatible and of sufficient quality to meet program objectives. This field guide and accompanying references, along with the study-unit design guidelines for NAWQA, should be used by the study units when preparing quality-assurance plans. Specific details for quality-assurance plans are described in a report by Shampine and others (1992).

Investigators in each study unit must document the quality of their data by collecting quality-control samples. A series of quality-control samples (field blanks, replicates, and field-matrix-spike samples) is obtained in water-quality investigations (Shampine and others, 1992) because the quality of the data collected and the validity of any interpretation cannot be evaluated without quality-control data. Quality-control samples should include the same sample set as the routinely scheduled samples. For the detailed procedures for preparing quality-control samples for organic compounds and the required percent of samples necessary, consult the NAWQA quality-assurance memorandums cited in appendix B. Quality-control requirements for inorganic constituent sampling and processing are discussed in OWQ technical memorandum 94.09 (see appendix A).

FIELD BLANKS

Field blanks are designed to demonstrate that (1) equipment-cleaning protocols adequately remove residual contamination from previous use, (2) sampling and sample-processing procedures do not result in contamination, and (3) equipment handling and transport between periods of sample collection do not introduce contamination.

Field blanks for pesticides are collected immediately before processing native water through the sample-processing sequence for field samples. Preparation of field blanks requires passing a volume of organic-free DIW through all sample equipment contacted by the actual sample.

Field blanks for major ions and nutrients should be collected by the same approach, but using inorganic-free DIW after preparation of the organic blank.

REPLICATES

Sample replicates are designed to provide information needed to (1) estimate the precision of concentration values determined from the combined sample-processing and analytical scheme and (2) evaluate the consistency of identifying target analytes for pesticides. Each replicate sample is an aliquot of native sample water from a splitter and is processed immediately after the primary cone-split sample using the same equipment; placed into the same type of bottle; prepared in the same way by SPE, if applicable; and stored and shipped in the same way.

FIELD-MATRIX SPIKES

Field-matrix spikes are designed to (1) assess recoveries from field matrices and (2) assist in evaluating the precision of results for the range of target analytes in different matrices.

A field-matrix spike is prepared by adding a standard spike solution provided by NWQL to a split of sample water processed in the same way as the regular pesticide analysis. A separate matrix-spike sample for each of the two pesticide schedules is prepared, stored, and shipped to NWQL. Matrix-spike kits with instructions are available from NWQL.

References Cited

Busenberg, Eurybiadas, and Plummer, L.N., 1987, pH measurement of low-conductivity waters: U.S. Geological Survey Water-Resources Investigations Report 87-4060, 22 p.

Capel, P.D., and Nacionales, F.C., 1993, Splitting device for water samples: U.S. Geological Survey Open-File Report CA491, 20 p.

Crawford, J.K., and Luoma, S.N., 1992, Guidelines for studies of contaminants in biological tissues for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 92-494, 69 p.

Edwards, T.K., and Glysson, D.G., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.

Fishman, M.J., and Friedman, L.C., eds., 1985, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1994, Design of the National Water-Quality Assessment program: Occurrence and distribution assessment: U.S. Geological Survey Circular 1112, 33 p.

Hem, J.D., 1985, Study and interpretation of chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 264 p.

Hirsch, R.M., Alley, W.M., and Wilber, W.G., 1988, Concepts for a National Water-Quality Assessment program: U.S. Geological Survey Circular 1021, 42 p.

Leahy, P.P., Rosenshein, J.S., and Knopman, D.S., 1990, Implementation plan for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 90-174, 10 p.

Meador, M.R., Cuffney, T.F, and Gurtz, M.E., 1993, Methods for sampling fish communities as part of the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 93-104, 40 p.

Rantz, S.E., and others, 1982, Measurement and computation of streamflow: Volume 1, Measurement of Stage. Volume 2, Computation of discharge: U.S. Geological Survey Water-Supply Paper 2175, v. 1, p. 1-284, v. 2, p. 285-631.

Sandstrom, M.W., Wydoski, D.S., Schroeder, M.P., Zamboni, J.L., and Foreman, W.T., 1992, 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, 19 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

Shampine, W.J., Pope, L.M., and Koterba, M.T., 1992, Integrating quality assurance in project work plans of the U.S. Geological Survey: U.S. Geological Survey Open-File Report 92-162, 12 p.

U.S. Geological Survey, 1978, Sediment, chapter 3 *in* U.S. Geological Survey, National handbook of recommended methods for water-data acquisition: p. 3-1 to 3-100.

Ward, J.R., and Hair, C.A., 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.

Weiss, R.F., 1970, The solubility of nitrogen, oxygen, and argon in water and seawater: Deep Sea Research, v. 17, no. 4, p. 721-735.

Wood, W.W., 1981, Guidelines for collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water-Resources Investigations, book 1, chap. D2, 24 p.

APPENDIX A--SELECTED TECHNICAL MEMORANDUMS

These Office of Water Quality (OWQ), Office of Surface Water (OSW) and Water Resources Division (WRD) memorandums are available in U.S. Geological Survey, Water Resources Division offices, nationwide.

OWQ 79.10 ANALYTICAL METHODS	Recommended procedures for calibrating dissolved oxygen meters
OWQ 80.17 EQUIPMENT AND SUPPLIES	New sample splitter for water-quality samples
OWQ 81.02 WATER QUALITY	Operation and availability - D-77 water-quality sampler
OWQ 81.08 WATER QUALITY	Electrodes for pH measurements in low-conductivity waters
OWQ 81.17 EQUIPMENT AND SUPPLIES	YSI model 32 conductance meters
OWQ 82.05 WATER QUALITY	Method for dissolved carbonate, dissolved bicarbonate, and carbonate alkalinity
OWQ 89.01 EQUIPMENT AND SUPPLIES	pH measurement in low conductivity waters
OWQ 90.01 WATER QUALITY	Sample preservation and ampule disposal
OWQ 91.02 PUBLICATIONS	Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses
OWQ 91.09 REPORTS	Filtration of water-sediment samples for the determination of organic compounds
OWQ 91.10 PROGRAMS AND PLANS	Dissolved trace element data (contamination)
OWQ 92.01 PROGRAMS AND PLANS	Dissolved/deionized water for district operations
OWQ 92.02 FIELD TECHNIQUES	Field preparation of containers for aqueous samples
OWQ 92.06 FIELD TECHNIQUES	Report of committee on sample shipping integrity and cost
OWQ 92.11 FIELD TECHNIQUES	Return of spent mercury and dichromate ampules to the national water quality laboratory
OWQ 92.12 PROGRAMS AND PLANS	Trace element concentrations in deionized water processed through selected surface-water samplers
OWQ 92.13 PROGRAMS AND PLANS	Trace element contamination: findings of studies on the cleaning of membrane filters and filtration systems
OWQ 93.05 PROGRAMS AND PLANS	Evaluation of capsule filters
OWQ 93.06 PROGRAMS AND PLANS	Trace element contamination--findings of study on the cleaning of sampler caps, nozzles, bottles, and bags
OWQ 93.11 PROGRAMS AND PLANS	Implementation of the protocol for collecting and processing surface-water samples for low-level inorganic analyses
OWQ 94.02 EQUIPMENT	Discontinuance of field use of mercury liquid-in-glass thermometers
OSW 94.05 EQUIPMENT	Maximum sampling depths and transit rates for suspended sediment and water-quality samplers

WRD 94.06 SAFETY	Storage, transport, handling, and disposal of hydrochloric acid
WRD 94.07 SAFETY	Storage, transport, handling and disposal of methyl alcohol
OWQ 94.09 PROGRAMS AND PLANS	Revision of new division protocol for collecting and processing surface-water samples for low-level inorganic analyses.
OWQ 94.13 EQUIPMENT	Evaluation of churn splitter for inclusion in the division protocol for collection and processing of surface-water samples for subsequent determination of trace elements, nutrients, and major ions in filtered water.
OWQ 94.16 PROGRAMS AND PLANS	New preservation techniques for nutrient samples.

APPENDIX B--SELECTED INTERNAL COMMUNICATIONS

These documents are available in U.S. Geological Survey, Water Resources Division offices where the National Water-Quality Assessment Program have active studies.

National Water-Quality Assessment program, U.S. Department of the Interior, written communication, U.S. Geological Survey memorandum dated July 15, 1993, on quality-assurance/quality-control plan for intensive-fixed sites.

National Water-Quality Assessment program, U.S. Department of the Interior, written communication, U.S. Geological Survey memorandum dated August 10, 1993, on quality-assurance/quality-control plan for basic-fixed sites.

Sylvester, M.A., Kister, L.R., and Garrett, W.B., eds, 1990, Guidelines for collection, treatment, and analyses of water samples--U.S. Geological Survey Western Region Field Manual: U.S. Geological Survey, Western Region, Internal Document, 144 p.

ATTACHMENT C

SAFTEY PLAN AND CHECKLIST

Appenix 6:
SAFETY PLAN AND CHECKLIST

APPENDIX 6

SAFETY PLAN AND CHECKLIST

It is Survey policy that each project leader provide a safety plan for their current project(s). This includes providing required equipment and training for all personnel working on the project, complying with all mandated safety programs, and eliminating employee identified hazards. The safety element of project planning has been established to ensure that safety is considered early in the project planning, that mandated safety programs are identified, and that adequate resources are included in the project budget.

There are three parts to safety planning: site evaluation; identification of mandated safety programs, equipment, and training; and resource allocation for safety. Site evaluation should identify unique hazards at the site, and the scope of work should determine any mandated safety training requirements. This information will help in determining the amount of time and money needed to ensure safety in the project.

The safety check list will be completed by the project team as part of the project planning package. The check list must be reviewed and signed by the District Safety Officer. It will also be included in the archive package for the project. The check list and documentation showing that the safety plan was implemented is the project leader's and the District's best defense in a liability suit by an employee or the public.

CHECK LIST

I. SITE EVALUATION

	Yes	No
1. Site Remoteness		
A. Phone Access:	____	____
1. Is there cellular phone access problem?	____	____
2. Has cellular phone access been tested?	____	____
3. Location of nearest accessible telephone?	____	____
4. Travel time to phone?	____	____
	____	____
B. Site Access:	____	____
1. Condition of access road.	____	____
2. Distance to main road.	____	____
3. Could road be blocked?	____	____
4. Are there alternate routes?	____	____
5. Could a helicopter land at the site?	____	____
6. Has coordination been established with the emergency responder?	____	____
7. Special conditions or problems (restricted access, locked gates, private land, etc):	____	____
	____	____
C. Working Conditions:	____	____
1. What is the distance between site/sites and office? _____		
2. What is the maximum length of an expected work day?		

3. Is lodging being budgeted? ____ ____
4. Minimum number of employees at site? _____
5. If single employee, what check-in procedure will be used? _____

APPENDIX 6—*Continued*

2. Environmental Hazards

A. Weather	Yes	No		Yes	No
Heat?	___	___	Cold?	___	___
Rain?	___	___	High water?	___	___
Cold water?	___	___	Bright sun?	___	___
High altitude?	___	___	Others?	___	___

B. Health hazards:					
Untreated sewage?	___	___	Poison oak?	___	___
Hantavirus?	___	___	Metal?	___	___
Rocky Mtn. spotted fever?	___	___	Insects?	___	___
Poisonous snakes?	___	___	Contaminated dust?	___	___
Hazardous materials?	___	___	Others?	___	___

C. Public Attitude:

Locals hostile to project?	___	___
Locals hostile to Government?	___	___
Project interferes with public use of site?	___	___
Project interferes with possible illegal activities in the area?	___	___

3. Site Assessment:

A. Are there hazards generic to site or type of investigation (boats, hazardous materials, confined space, etc.?) _____

B. Are there hazards specific to site (dangerous or potentially dangerous conditions unique to site?) ___ ___

C. Field Sanitation:

1. Is potable water available?	___	___
2. Is a wash facility available?	___	___
3. Are toilet facilities available?	___	___

D. Has site(s) been visited? ___ ___

E. Site Security:

1. Is vandalism likely due to location, publicity, or experience?	___	___
2. Is there a nearby residential area (inquisitive kids)?	___	___
3. List site security requirements to protect the public and Government property	___	___

4. Emergency Response

A. Who has jurisdiction for emergency response? _____

B. Estimated travel distance and response time? _____

C. Has contact been made with the emergency responder? ___ ___

D. Should contact be made with the emergency responder? ___ ___

E. Special equipment or training needed if response time is excessive? _____

APPENDIX 6—*Continued*

II. PROJECT SAFETY PROGRAM

1. Basic Safety Plan:

A. Principal hazards: _____

B. Employee awareness: _____

1. Safety meetings/reviews. _____

2. Frequency. _____

3 Documentation (when, who attended, and what was discussed) _____

_____

_____

C. Plan for resolving employee identified problems: _____

_____

D. Equipment:

1. Inspection program? _____

2. Maintenance schedule (to include vehicles)? _____

3. Documentation (when, by whom, what was found, and corrective actions): _____

_____

E. Integration with mandated programs: _____

2. Mandated Safety Programs (check all that apply):

A. Job Hazard Analysis ____

B. Respiratory Protection Program ____

C. Hazard Communication Program ____

D. Environment Safety ____

1 Transport of hazardous material ____

2. Disposal of hazardous waste ____

3. Storage of hazardous materials and waste ____

E. Hazardous Waste Sites ____

F. Lockout/tagout Program ____

G. Confined Space ____

H. Diving ____

I. Aircraft ____

J. Motor Vehicles ____

1. Standard vehicles ____

2. Special vehicles ____

3. Storage of hazardous materials and waste ____

APPENDIX 6—*Continued*

K. Watercraft ____

L. Hearing protection ____

M. Blasting safety ____

N. Ionizing radiation safety ____

O. Fire arms ____

P. Drilling ____

Q. Construction ____

3. Mandated Safety Plans and Certificates

A. Required safety plans: _____

B. Scheduled completion date: _____

C. Scheduled for acquisition: _____

4. Training

A. Required training: _____

B. Training deficits (by employee): _____

C. Training schedule to correct deficits: _____

5. Personnel Protective Equipment (PPE)

A. Required PPE _____

B. PPE shortages (by employee): _____

C. Purchase plan: _____

6. Safety Equipment

A. Required safety equipment: _____

B. Inventory: _____

C. Purchase plan: _____

	Yes	No
7. Laboratory Support		
A. Are new procedures or equipment needed?	____	____
1. New reagents/chemicals:	____	____
a. Are they hazardous?	____	____
b. Will disposal be a problem?	____	____
c. What volumes? _____		
d. Is there adequate storage:	____	____
e. Are there special handling requirements?	____	____
If yes, what are they? _____		
f. Training requirements? _____		
g. Safety equipment?	____	____
2. New equipment:		
a Is there room?	____	____
b Special requirements (electrical, compressed gasses, venting, cooling water)?	____	____
c. Potential safety hazards?	____	____
If yes, what are they? _____		
3. Have the written procedures been completed?	____	____
B Will established procedures and equipment be used?	____	____
1. Reagents/chemicals:		
a Will there be significant changes in the volumes used?	____	____
b. What impact on storage? _____		
c. Waste disposal? _____		
2. Equipment		
a. Will there be significant changes in the work load/lab?	____	____
If yes, what? _____		
b. Will disposal be a problem?	____	____
3. Have written procedures been reviewed and revised if needed? _____		
8. Safety Requirements for Contracted Work		
A. What safety requirements for contractors have been identified? _____		
_____		
B. Are requirements specified in contracts? _____		
C. How will contract compliance be monitored? _____		

APPENDIX 6—*Continued*

III. SAFETY BUDGET SUMMARY

1. Equipment Cost: _____

_____

2. Training Cost: _____

_____

3. Time (Work days/hours): _____

_____

_____ _____

Project Chief Date

_____ _____

Group Leader Date

_____ _____

District Safety Officer Date

Next appendix
Back to previous appendix
Project Planning & Management Guide

This page maintained by Tammy Shelton <tshelton@usgs.gov>

USGS

U.S. Geological Survey
California District Internal Page

Policies & Procedures

CA District Traffic Control Plan for Bridges and Roadways

June 1999

CONTENTS

Encroachment Permits

STATE HIGHWAYS

When traffic control is needed, employees should make encroachment permit applications to work on State highways. District Encroachment Permit offices are authorized to issue permits for maintenance and survey work for a two year period. The next page lis ts the address and telephone numbers for the CalTrans District Encroachment Permit offices. Employees should contact the office that handles the area wherer the traffic control is necessary and arrange for making an encroachment permit application.

COUNTY HIGHWAYS

If the bridge or roadway is owned by the county, the employees should contact the Department of Public Works in the county in which they intends to work to obtain encroachment permits.

State Encroachment Office

Traffic Control Equipment

Minimum required equipment for the following situations:

Type 1 Park on shoulder of road.

Rotating flashing light on cab

Type 2 Bridge measurement off bridge without lane markings (ie. small rural bridge).

A 36" Road work ahead sign 500 ft from each end of bridge.
Traffic cones starting 125 ft from the side of the bridge where work is in progress.
Retroreflective safety vest for each worker.

Type 3 Bridge measurement on two lane bridge where one lane is partially or completely blocked.

Quantity	Description
6	Telescoping sign stand
12	Ribs for flexible signs
2	48" flexible sign, Flagger 500 ft
2	One lane bridge 500 ft
2	One lane bridge 1000 ft
2	One lane bridge 1500 ft
2	Shoulder work
20	Traffic cones
2	Sign paddle
2	Radio, two way
1	Retroreflective safety vest for each worker

Type 4 Bridge measurement on four lane bridge where one lane is partially or completely blocked.

Quantity	Description
4	Telescoping sign stands
8	Ribs for flexible signs
1	48" flexible sign, Road work ahead
2	Right lane closed ahead
1	End road work
20	Traffic cones
1	Sign paddle
1	Retroreflective safety vest for each worker

Control of Traffic Through Work Zones 5-07

5-07.1 Function

The primary function of traffic control procedures is to move traffic safely and expeditiously through or around work zones. It is an essential part of highway construction and maintenance operations.

Maintaining good public relations is necessary. The cooperation of the various news media in publicizing the existence of and reasons for work sites, therefore, can be of great assistance in keeping the motoring public well informed.

5-07.2 Hand Signaling Device

A C28 sign paddle bearing the clear messages STOP and SLOW shall be used for hand signaling to control traffic through work zones.

The sign paddle shall conform to the requirements of Sections 5-02.1 and 5-02.2 of this Manual.

5-07.3 Flaggers

Flaggers are responsible for human safety and make the greatest number of public contacts of all construction personnel. It is important that qualified personnel be selected. Flaggers shall be trained in the proper fundamentals of flagging traffic before being assigned as flaggers.

Because of their extremely exposed position with a high accident potential, alternate effective means of control should be used wherever possible.

A critical examination should be made of each roadwork job to determine if flagging is necessary, and if so, what is the minimum level that can be used commensurate with job and safety needs. Flaggers are used basically at locations where it is necessary to change traffic controls frequently. Examples are the stopping of through traffic for equipment movement and alternate directional use of a single traffic lane. For these functions the flagger must, at all times, be clearly visible to approaching traffic for a distance sufficient to permit proper response by the motorist to flagging instructions, and to permit traffic to reduce speed before entering the work site. The distance between the flagger and the work area varies with the approach speed of traffic, roadway geometries and physical conditions.

This distance in urban areas where speeds are low and streets closely spaced will necessarily be shorter than for open highway conditions.

The flagger must be protected and the motorist forewarned of his or her presence by the use of advance warning signs, and, where appropriate, cones or other delineators.

The use of orange vests, jackets, or shirts shall be required for all flaggers. All flaggers performing operations during hours of darkness shall be outfitted with a reflectorized garment. The retroreflective material shall be either orange, white (including silver-colored reflecting coatings or elements that reflect white light), yellow, fluorescent red-orange, or fluorescent yellow-orange. The design of the retroreflective portions including stripe width, extent, design and type of material shall be determined by the contracting agency or purchaser of the vest.

During hours of darkness, flagger stations shall be illuminated such that the flagger will be clearly visible to approaching traffic. Lights for illuminating the station shall be approved by the Engineer of the public agency or authority having jurisdiction over the highway.

Flagging procedures (signaling) shall be the same as those prescribed for day work. Under emergency conditions the flagger may use a flashlight and hand signals to direct traffic, until proper illumination can be effected.

5-07.4 Flagging Procedures (Signaling)

The following methods of signaling with a C28 paddle should be used. The paddle may be either hand held or supported by a staff.

1. To Stop Traffic - The flagger shall face traffic and hold the STOP paddle in a vertical position at arms length. For greater emphasis, the free arm may be raised with the palm toward approaching traffic.
2. When It Is Safe for Traffic to Proceed - The flagger shall stand parallel to the traffic movement, and with the SLOW paddle held in a vertical position, motion traffic ahead with the free arm.
3. Where It Is Desired to Alert Or Slow Traffic - The flagger shall face traffic and hold the SLOW paddle in a vertical position at arm's length. For added emphasis, the flagger may slowly raise and lower the free hand with the palm down.

The use of the sign paddle is illustrated in Figure 5-4.

Whenever practicable, the flagger should advise the motorist of the reason for the delay and the approximate period that traffic will be halted. Flaggers and operators of construction machinery or trucks should be made to understand that every reasonable effort must be made to allow the driving public the right of way and prevent excessive delays.

5-07.5 Flagger Stations

Flagger stations shall be located far enough in advance of the work site so that approaching traffic will have sufficient distance to reduce speed before entering the work area. This distance is related to approach speed and physical conditions at the site. In urban areas when speeds are low and streets closely spaced, the distance necessarily must be less than on high-speed highways.

The flagger should stand either on the shoulder adjacent to the traffic being controlled or in the closed lane. At a "spot" obstruction, a position may have to be taken on the opposite shoulder to operate effectively. Under no circumstances should a flagger stand in the lane being used by moving traffic. The flagger should be clearly visible to approaching traffic at all times. For this reason the flagger should stand alone, never permitting a group of workers to congregate around the flagger station. The flagger should be stationed sufficiently in advance of the work force to warn them of approaching danger, such as out-of-control vehicles.

Flagger stations should be adequately protected and preceded by proper advance warning signs. At night, flagger stations shall be adequately illuminated. (See Section 5-07.3)

At short construction and maintenance lane closures where adequate sight distance is available for the safe handling of traffic, use of one flagger may be sufficient.

5-07.6 One-Way Traffic Control

Where traffic in both directions must, for a limited distance, use a single lane, provision should be made for alternate one-way movement to pass traffic through the constricted section. At a "spot" obstruction, such as an isolated pavement patch, the movement may be self-regulating. However, where the one-lane section is of any length, there should be some means of coordinating movements at each end so that vehicles are not simultaneously moving in opposite directions in the section and so that delays are not excessive at either end. Control points at each end of the route should be chosen so as to permit easy passing of opposing lines of vehicles.

Alternate one-way traffic control may be effected by the following means:

1. Flagger control.
2. Flag-carrying or official car.
3. Pilot car.
4. Traffic signals.

5-07.7 Flagger Control

Where the one-lane section is short enough so that each end is visible from the other end, traffic may be controlled by means of a flagger at each end of the section. One of the two should be designated as the chief flagger for purposes of coordinating movement. They should be able to communicate with each other verbally or by means of signals. These signals should not be such as to be mistaken for flagging signals.

Where the end of a one-lane section is not visible from the other end, the flaggers may maintain contact by means of radio or field telephones. So that a flagger may know when to allow traffic to proceed into the section, the last vehicle from the opposite direction can be identified by description or license. (See Figure 5-11).

5-07.8 Flag-Carrying or Official Car

Flag carrying is effective when the route is well defined and nonhazardous. It should be employed only when the one-way traffic is confined to a relatively short stretch of road, usually not more than 1 mile in length.

10341950 Little Truckee R blw Diversion Dam, one lane gravel road with minimal traffic. Use cones and vehicle flasher.

10346000 Truckee R at Farad, park in approved parking place on shoulder of I80. Use extreme caution entering and exiting vehicle and parking spot.

11402000 Spanish C ab Blackhawk C at Keddie, bridge has separated walkway, traffic minimal. Use cone by vehicle.

11421890 Bear River blw Dutch Flat Afterbay, wide county road bridge with no significant traffic, use cones.

Redding Bridges and Roadway Sites

11342000 Sacramento River at Delta, high flow measurements are made from a USFS bridge utilizing a truck mounted Texas Boom. (NST).

11345500 South Fork Pit River near Likely, roadside parking is safely accomplished by the deployment of several traffic safety cones leading up to and isolating vehicle from road.

11348500 Pit River near Canby, in winter when snow bank may obstruct turnout, roadside parking is safely accomplished by the deployment of traffic safety cones leading up to and isolating vehicle from state Hwy 299.

11370700 ACID Canal at Sharon Street at Redding, city bridge, traffic is slow and is limited primarily to residents. Safety cones are placed at each end of the bridge and around parked vehicle to alert residents of streamgaging activities.

11390000 Butte Creek near Chico, roadside parking is safely accomplished by the deployment of traffic safety cones leading up to and isolating vehicle from roadway.

11519500 Scott River near Fort Jones, roadside parking is safely accomplished by the deployment of traffic safety cones leading up to and isolating vehicle from roadway.

11521500 Indian Creek near Happy Camp, roadside parking may be safely accomplished by the deployment of traffic safety cones isolating the roadside turnout and vehicle from the roadway.

11525580 Little Grass Valley Creek near Lewiston, parking along state Hwy 299 W is safely accomplished by the deployment of several (at least six) traffic safety cones leading up to and isolating the vehicle from the roadway.

11525600 Grass Valley Creek at Fawn Lodge near Lewiston, one lane bridge with limited traffic, use truck mounted Texas Boom. Traffic is limited solely to California Dept. of Forestry emergency vehicles. Due to the seasonal operation of the fire station , winter time high flow measurements do not conflict with CDF use of the bridge.

11523000 Klamath River at Orleans, two lane suspension bridge on state Hwy 96 utilizing truck mounted Texas Boom. Trained flag persons, safety cones and signs are set up in accordance with CalTrans regulations.

Sacramento Bridges and Roadway Sites

11242400 NF Willow Creek nr Sugar Pine, One lane bridge, Forest Service road, traffic is minimal, requires traffic safety cones only.

11264500 Merced River at Happy Isles. One lane bridge with sidewalks, traffic is minimal.

11266500 Merced River at Pohono Bridge. Two lane, one way bridge with moderate traffic, requires traffic cones and road sign.

11274000 San Joaquin River near Newman. Two lane bridge with moderate-heavy traffic, requires traffic cones, road signs and

STATE OF CALIFORNIA
BUSINESS, TRANSPORTATION AND HOUSING AGENCY
DEPARTMENT OF TRANSPORTATION

MANUAL OF TRAFFIC CONTROLS

for
Construction and Maintenance Work Zones

1990

GEORGE DEUKMEJIAN
Governor

ROBERT K. BEST
Director
Department of Transportation

C.D. BARTELL
Chief
Division of Traffic Operations

J. F. MALONEY
Chief Deputy Director
Highway Maintenance and
Traffic Operations

FRED JAGER
Editor
Office of Signs & Delineation

→ 11273500 Merced R at River Rd: Samples can be taken from foot bridge without impeding traffic.

→ 11274538 Orestimba Cr nr Crows Landing: Two lane bridge with moderate traffic. Site requires cones and one person to control traffic.

→ 11303500 San Joaquin R nr Vernalis: Two lane bridge with moderate to heavy traffic. Site requires signs, cones, and one person to control traffic.

11255575 Panoche Cr at I-5: Two lane bridge with shoulders, extremely high traffic. Requires shoulder closure including signs, cones, and one person to control traffic.

Salinas Bridges and Roadway Sites

11143200 Carmel River at Robles del Rio, measuring bridge has a separated walkway on downstream side used for medium flow measurements. High flow measurements are made from upstream side of bridge (not separated or raised)-- has a 4 ft shoulder, separa ted from traffic by a white line. Traffic moves fairly slowly across the bridge and is usually light. Traffic cones are placed on white line during measurement.

11147500 Salinas River at Paso Robles, measuring bridge has a 5 ft wide separated walkway.

11148500 Estrella River nr Estrella, vehicle is parked on shoulder of road adjacent to gage (about 2 ft of vehicle is in active street area). Traffic cones are used to warn oncoming traffic of vehicle. Traffic is normally light.

11158600 San Benito River at Hwy 156, use 4 ft wide shoulder on upstream side of Cienega Road Bridge. Traffic cones are used. Traffic is normally light.

11159000 Pajaro River at Chittenden, 4 ft wide raised walkway on downstream side of Rogge Road Bridge, about 2.5 miles downstream. Traffic cones are used around vehicle, which is parked on shoulder of road, about 2 ft from traffic area.

11160000 Soquel Creek at Soquel, 4 ft wide, raised walkway on upstream side of Soquel Road Bridge.

11160430 Bean Creek near Scotts Valley, vehicle is parked along Mt. Hermon Road, about 2 ft within white line separating shoulder from road. Vehicle traffic is swift and heavy. Traffic cones are used.

11160500 San Lorenzo River at Big Trees, 4 ft wide raised walkway on downstream side of bridge at entrance to Henry Cowell State Park.

11161000 San Lorenzo River at Santa Cruz, 6 ft wide, raised walkway on the upstream side of the Water Street Bridge.

11161300 Carbonera Creek at Scotts Valley, 5 ft wide, raised walkway on Carbonero Road.

11162500 Pescadero Creek nr Pescadero, narrow, two lane bridge on Pescadero Road. Traffic is normally light but swift and could be hazardous during storm conditions. Traffic cones and vests are used. Use warning signs on approach.

11162630 Pilarcitos Creek at Half Moon Bay, vehicle is parked on shoulder of state Hwy 1, about 3 ft from white line (traffic cones used). Measurements are made from 4 ft wide, raised walkway on downstream side of Hwy 1 bridge.

11169500 Saratoga Creek at Saratoga, vehicle is parked on shoulder of Saratoga Road, about 4 ft from traffic (traffic cones used). Measurements are made from 5 wide shoulder at bridge at entrance to apartment complex. Traffic is light and traffic cones used.

11255575 Panoche Cr at I-5: Two lane bridge with shoulders, extremely high traffic. Requires shoulder closure including signs, cones, and one person to control traffic.

Santee Bridges and Roadway Sites

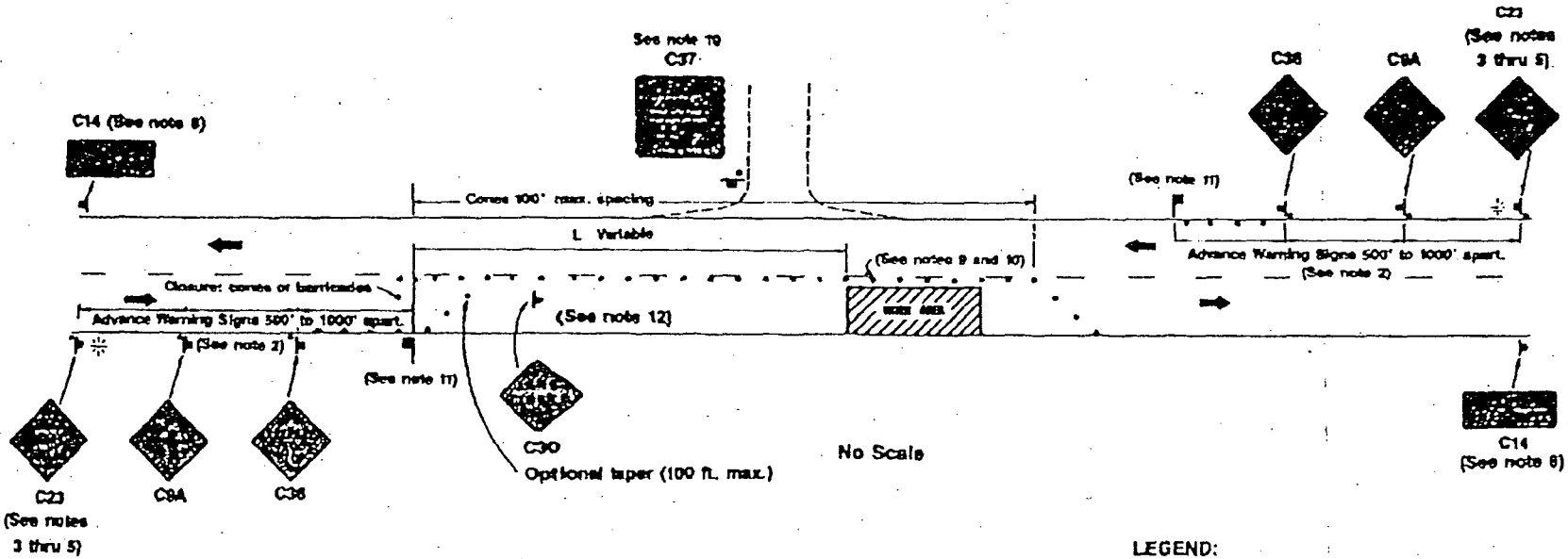


Figure 5-11
TYPICAL LANE CLOSURE WITH REVERSIBLE CONTROL (TRAFFIC CONTROL SYSTEM FOR MULTILANE CONVENTIONAL HIGHWAYS)

SPECIAL NOTE:

Field conditions could require deviations from these plans and accompanying notes.

NOTES:

1. This plan does not apply where there are emergency conditions. Under emergency conditions, equipment and personnel which are available should be utilized to implement a closure even though such closure does not meet the standards contained in this plan. As equipment or personnel become available an immediate effort should then be made to implement the standards shown on this plan.
2. Where approach speeds are low, signs may be placed at 300 feet spacings and even closer in urban areas.
3. All advance warning signs shall be 48"x 48" minimum on highways with approach speeds of 45 mph or more. When speeds are less than 45 mph the C23 sign shall be 30"x 30" minimum; other advance warning signs shall be 36"x 36" minimum.
4. All warning signs for night closures shall be illuminated or reflectorized.
5. A C18 "ROAD CONSTRUCTION AHEAD" or C15 "ONE LANE ROAD AHEAD" sign may be used in lieu of the C23. (See Note 3)
6. A C13 "END CONSTRUCTION " sign, as appropriate, may be used in lieu of the C14. The sign is optional if the end of work zone is obvious, or falls within a larger project limit.
7. Warning (W) series signs used in work zones shall be black on orange. Existing yellow warning signs already in place within these areas may remain in use.
8. All cones shall be internally illuminated or fitted with reflective white sleeves for night closures.
9. The spacing between cones along centerline should be approximately 100 feet throughout the length of the work zone. Centerline cones may be eliminated if a pilot car operation is used.
10. When a pilot car is used a "TRAFFIC CONTROL WAIT FOR PILOT CAR" sign (C37) should be posted at intersecting driveways and roads. Flaggers may be used in lieu of C37 signs.
11. An additional advance flagger should be considered upstream on high volume highways, to warn traffic where queues may develop. Flaggers' stations for work at night shall be illuminated as noted in Section 5-07.
12. Place C30 "LANE CLOSED" sign (30"x 30" minimum) at 500'-1000' intervals throughout extended work zones. They are optional if the work area is visible from the flagger station.

ATTACHMENT D

METHOD OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY (NWQL) DETERMINATION OF PESTICIDES IN WATER BY C-18 SOLID-PHASE EXTRACTION AND CAPILLARY-COLLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) WITH SELECTED ION MONITORING (SIM)

And

NWQL STANDARD OPERATING PROCEDURES
ANALYSIS OF PESTICIDES IN WATER BY SIM GC/MS

ATTACHMENT D

NWQL Standard Operating Procedure

Analysis of Pesticides in Water by SIM GC/MS

LS 2001/2010

By Chris Lindley, Jana Iverson, and Mike Schroeder

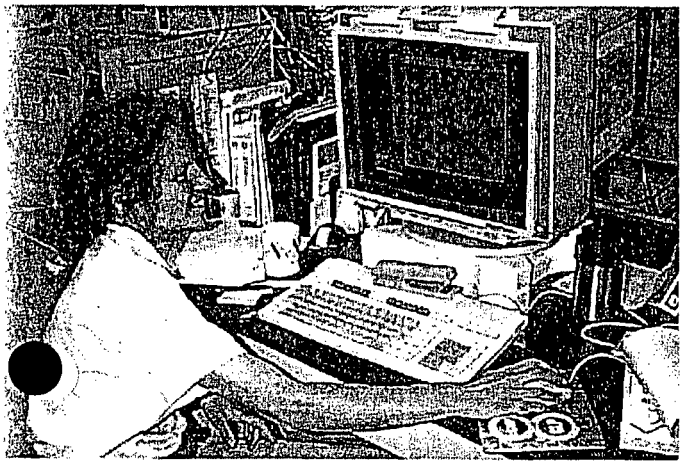
Table of Contents

1. Scope and Application

This SOP provides a description of the use of Hewlett-Packard (HP) 5971and 5972 GC/MS systems, with UNIX based Target© software, for the analysis of pesticides in water according to laboratory schedules (LS) 2001 and 2010. Specific information regarding the use of the HP and Target software for data acquisition can be found in SOP OX0098, "General Procedure for Data Acquisition and Analysis with HP GC/MS Systems". The SOP may be appropriate for the analysis of the same types of samples using other GC/MS systems, with proper consideration given to possible hardware and software differences.

1.1 **Method Reference** — Zaugg, et al, "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", USGS Open-File Report (OFR) 95-181, 1995.

1.2 **Analytes** — Method report limits and ions used for quantitation and verification are listed in Appendix A.



1.3 **Applicable matrices** — The method was developed for the analysis of filtered environmental water samples collected for the National Water Quality Assessment program (NAWQA). The method may be applicable to the data quality objectives of other projects. Application of the analytical portion may be made to other matrices on a custom or special analysis basis.

1.4 **Dynamic Range** — The dynamic range of the method is normally 0.001- 4.0 µg/L, with 1000 mL of sample in approximately 200 µL of undiluted sample extract. Dilution extends the range to 20.0 µg/L for all analytes. Matrix interferences may require the report level to be raised, or for other accepted data qualifiers, such as the "E" (estimated value) qualifier, to be used.

2. Summary of Procedure

Samples are usually field-filtered using 0.7 µm glass fiber filters. The filtered water samples are pumped through C-18 solid phase extraction columns either in the field (LS2010) or in the laboratory (LS2001). The C-18 column is dried, then eluted with solvent. Internal standard solution is added to the solvent extract, which is then concentrated to approximately 200 µL and analyzed by selected ion monitor (SIM) GC/MS. The physical location of sample extraction and the number of QC samples are the only distinctions between LS2001 and LS2010.

This SOP pertains only to the instrumental analysis portion of the method. For a more detailed explanation of the sample preparation procedure, refer to SOP OD0053, "Automated Preparation of Schedules 2001 and 2010".

3. **Revisions** — None

4. Safety Issues

Follow all standard safety practices for the use of solvents, compressed gases, and analytes. Exposure to electrical current at high voltages as well as thermally hot surfaces may occur during some maintenance procedures. Consult with your supervisor, safety personnel, or other experienced person if you are at all uncertain about what to do. Some of the reagents and analytes are, or are suspected to be human carcinogens, or may be teratogenic or mutagenic. Copies of Material Safety Data Sheets (MSDS) for the relevant reagents and analytes are available for reference in the NWQL Safety Office and should be reviewed prior to the use of the method. Disposal of materials must be carried out in strict accordance with current waste handling regulations. Disposal procedures are described as necessary in the method and in pertinent sections of this SOP. The NWQL Safety Office is the principal source for instructions regarding current waste handling procedures. Check with supervisory or Safety Office personnel if you have any doubt as to the proper disposal procedures, or if you have other safety concerns.

5. Sample Preservation, Containers, and Holding Times — Refer to OFR 95-181 for specifications.

6. Reagents and Standards

An example of the working standard solution preparation volumes and concentrations is shown in table 1; the solvent is toluene, and the concentration of the parent Supelco custom standard mixture is 50 ng/µL. The standards are prepared by dilution of the Supelco mixture. Note that the 100 and 200 ng/µL working standards have one-fifth of the material required to achieve their stated concentrations — this is compensated by an addition of one-fifth the amount of internal standard as would be required by calculation. These two standard concentrations are modified in this way to eliminate overloading the column; samples determined as having concentrations in this range are likewise diluted 1:5. Also note the absence of surrogate in the higher level standards; the relatively low surrogate responses are often overwhelmed by high concentrations of adjacent analyte peaks.

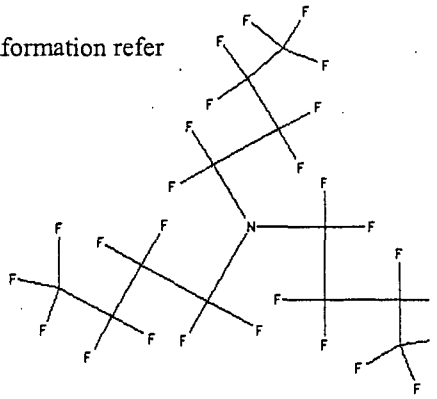
Table 1 — LS2001 Working Standards

	LS2001 Working Standards													
Desired Concentration (ng/µL)	0.01	0.02	0.04	0.1	0.2	0.4	1.0	2.0	4.0	10	20	40	100	20
Supelco Mix @ 50 ng/µL (µL)	1	2	4	10	20	40	100	200	400	200	400	800	400	800
Internal Standard (µL)	25	25	25	25	25	25	25	25	25	5	5	5	1	1
Surrogate (µL)	50	50	50	50	50	50	50	50	50	0	0	0	0	0
Final Volume (mL)	5	5	5	5	5	5	5	5	5	1	1	1	1	1

Refer to the LS2001/2010 standards logbook for current stock and working solution concentrations; these concentrations may change due to the nature of projects in progress and the vendor solutions used. Standards should be prepared every 6 months; typically every November and May, and brought into effect in December and June, respectively. Out-dated solutions must be disposed of properly. Check with safety staff for current requirements. Verification of solutions is done according to the SOP "Validation of Standard Solutions for GC/MS Analyses" (in development at this writing).

7. Sample Preparation

This SOP pertains to the GC/MS analysis portion of the method. For sample preparation information refer to OFR 95-181, and SOP OD0053, "Automated Preparation of Schedules 2001 & 2010".



8. Instrumental Analysis

8.1 Mass spectrometer tune

8.1.1 PFTBA abundance criteria — The PFTBA (perfluorotributylamine) abundance targets are listed in table 2 for use with **Target Tune**. The Target® program "Max Sensitivity Autotune" usually does an adequate job of tuning, sometimes requiring only minor manual adjustment of the mass axis and peak widths to achieve the table 2 tune criteria. If an acceptable tune is not accomplished, then source cleaning or other maintenance may be required. A graphic of a typical tune is shown in figure 1.

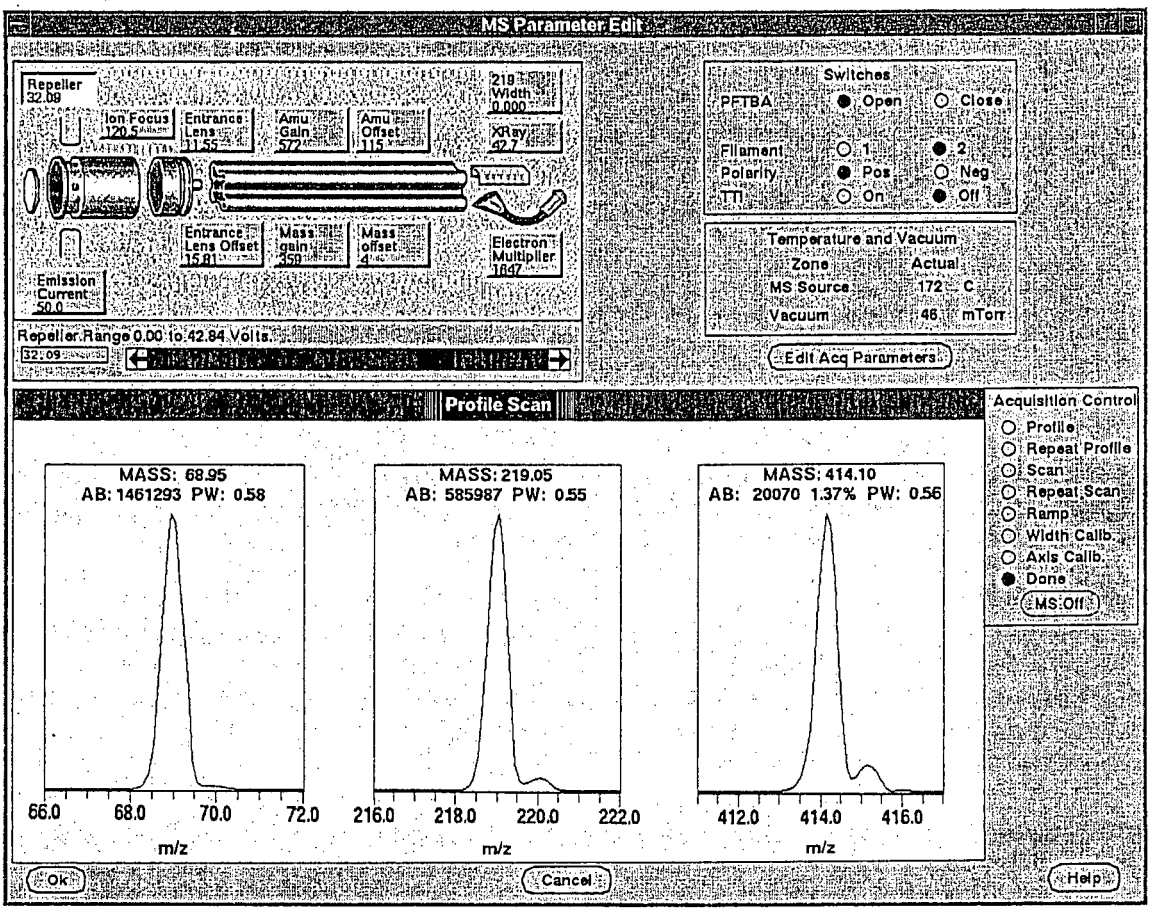


Figure 1 - MS Parameter Edit Window

8.1.2

MS background and interferences — Leaks of atmospheric air into the analyzer, or the presence of other compounds, might compromise instrument performance. A list of common air background and contaminant ions is found in table 3. Check the air background, and print the result, before beginning an analytical *batch* (the group of samples whose data are evaluated by the quality control samples associated with them) .

8.1.3 Determining when the MS source should be cleaned, or other MS maintenance performed — If the mass-axis, peak width, or the relative or absolute abundances described in table 2 are not met, the MS source may need to be cleaned, or other maintenance may be required. Other factors to observe are the repeller ramp and multiplier profiles. If they have changed significantly since the last cleaning and *continuing calibration verification* (CCV) criteria can not be met (section 8.8.3), then maintenance may be required. It is recommended that the injection port liner be changed when beginning a new batch.

Table 2 - Recommended PFTBA operating parameters

PFTBA ion (m/z)	Relative Abundance (%)	Absolute Abundance (area counts)	Peak Width Criteria (amu)	Mass Axis Criteria (amu)
69	100	≥2,000,000	0.5 ± 0.1	± 0.1
219	40-70	≥1,300,000	0.5 ± 0.1	± 0.1
414	2-7	≥110,000	0.5 ± 0.1	± 0.1

Table 3 - Typical MS background ions, their typical observed and maximum abundances when MS is tuned according to the criteria in 8.2.1.

Background m/z	Source	Typical Abundance	Maximum Abundance [1]
18	H_2O, atmosphere, carrier gas contamination	~2,000	Not greater than m/z 32
28	N_2, atmosphere, carrier gas contamination	~2,000	3 % of m/z 69 or 10,000 area counts
32	O_2, atmosphere, carrier gas contamination	~2,000	50% m/z 28
40	Ar, atmosphere, carrier gas contamination	~1,000	
44	CO_2, atmosphere, carrier gas contamination	~500	
446	Diffusion pump oil	~500	

1. Toleration of abundances greater than these values might shorten filament life, and may be habit-forming.

8.2 Analysis run sequence

8.2.1 *Ensuring a properly tuned instrument* — Performing a daily calibration of the instrument before sample analysis may not be required. The 5971 and 5972 instruments have demonstrated a very stable tune and calibration over time, as judged by the evaluation of CCV standards. Injection and subsequent analysis of a CCV before beginning a sample set indicates the accuracy of the active calibration curve. Recalibration is performed if CCVs repeatedly fail criteria (section 8.8.3).

8.2.2 Daily run sequence — A batch of environmental and quality control samples are placed in a particular order of analysis known as a *sequence*. A typical sequence for schedule 2001 might order the vials as shown in table 4. Samples must be bracketed by CCV's with acceptable results (see section 8.8.3). The number of samples that can thus be successfully analyzed between CCV's may vary.

Table 4 - Typical order of environmental sample and QC vials in an analytical sequence.

Vial	Description
1	CCV (0.4 ng/µL)
2	Instrument Detection Level Standard (IDL, at 0.04 ng/µL)
3	Preparation set method spike
4	Preparation set method blank
5-14	Samples (typically 10 samples for 2001, 20 for 2010)
15	CCV
16	Preparation set method spike
17	Preparation set method blank
18-27	Samples (typically 10 samples for 2001, 20 for 2010)
28-[...]	etc., samples bracketed with CCV's, blanks and spikes as indicated.
End vial	IDL

8.3 Data Acquisition Method

8.3.1 Data acquisition method name — There is no established convention for naming the acquisition method, except that the filename has a ".m" extension. If you are also working with other schedules or on other instruments, inclusion of the name of the schedule and the letter identifying the instrument in the file name would be beneficial; for example: "2001M.m".

8.3.2 MS run parameters are derived from the MS tune file. The MS run parameters used for sample data acquisition must be the same as those derived from the MS tuning process. Electron multiplier setting and other variable setpoints are established in the MS parameter Edit window (figure 1). The electron multiplier setting must be the same as that used in the MS tuning procedure, because this value can affect the MS tune. A Target dialogue window for setting the acquisition mode and tune file name is shown in figure 2.

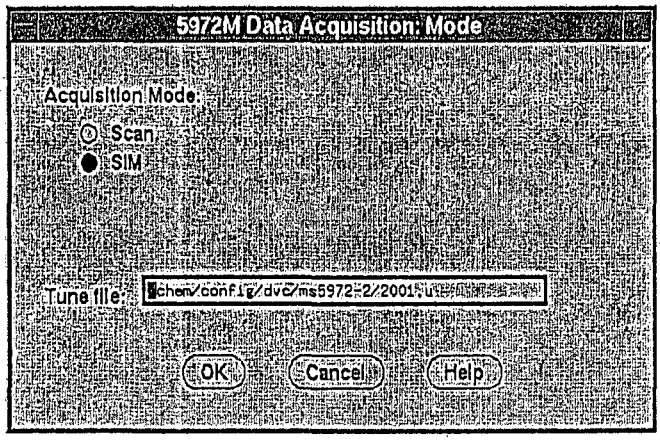


Figure 2: Data Acquisition: Mode

8.3.3 SIM data acquisition — Typically, twenty-three groups containing up to twenty ions are monitored in the method (table 1, appendix A). The dwell time of each ion is twenty milliseconds (ms), although a particular ion may appear more than once in a group. An example of part of a typical Target® Data Acquisition window for SIM analysis, (that is, a SIM table) is shown in figure 1 of appendix B. The individual character of a GC/MS instrument combination may require adjustment of the start time of particular ion groups and of the ions in those groups. Usually, the SIM ion tables are not created from scratch, but are copied from an existing 2001 or 2010 method and then modified to accommodate instrument character.

8.3.4 Batch directory naming convention — Following the convention established by the GC/MS section for naming analytical batches, the Target® directory names for batches follow the notation "ssssIyyjjj.b", where

Symbol	Description
ssss	4 numeral schedule name, e.g. "2001"
I	Instrument numeral, e.g. "P". This character is uppercase.
yy	Year, from the sample ID of the earliest sample in the batch.
jjj	Julian day, from the sample ID of the earliest sample in the batch.
.b	The Target® batch directory extension; the ".b" character is lowercase.

8.3.5 Data directory naming convention — The laboratory sample identification number is used. This directory name is of the form "yyjjjNnnn.d", where

Symbol	Description
yy	Year (last two digits)
jjj	Julian day
Nnnn	A number from 1 to 9999. Regular samples can be assigned a number from 1 to 7999, QC blanks from 8000 to 8999 (N = 8), and QC spikes from 9000 to 9999 (N=9).
.d	The Target® sample directory extension; the ".d" character is lowercase.

8.3.6 Data acquisition tips — Some hints to help in acquiring and analyzing data are:

- Modify the method before acquisition begins, e.g. update retention times.
- Save the sequence once it is completed.
- Backup and/or archive runs on tape or CD once they are analyzed.
- Don't modify the method in the batch if you're using it to acquire data. You'll lose your changes when the sequence finishes (however, you can stop the sequence and load the updated method).

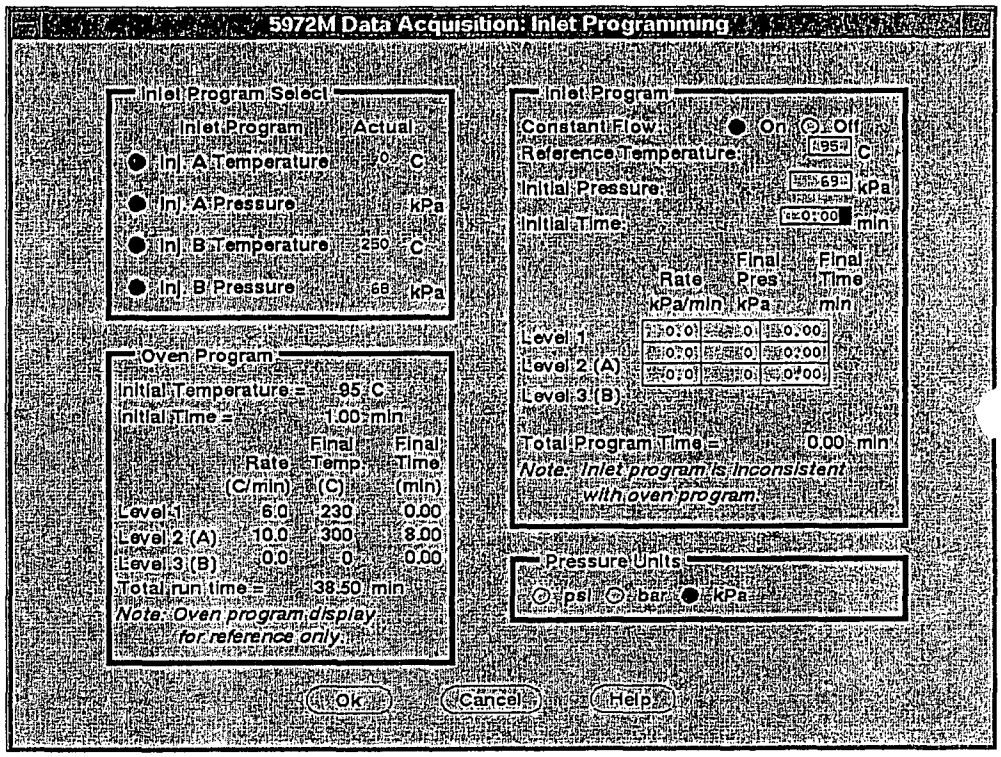
8.4 GC run parameters

Currently GC/MS systems are controlled through the data system through electronic pressure control (EPC). Typical settings are provided in the following examples from the GC/MS control software.

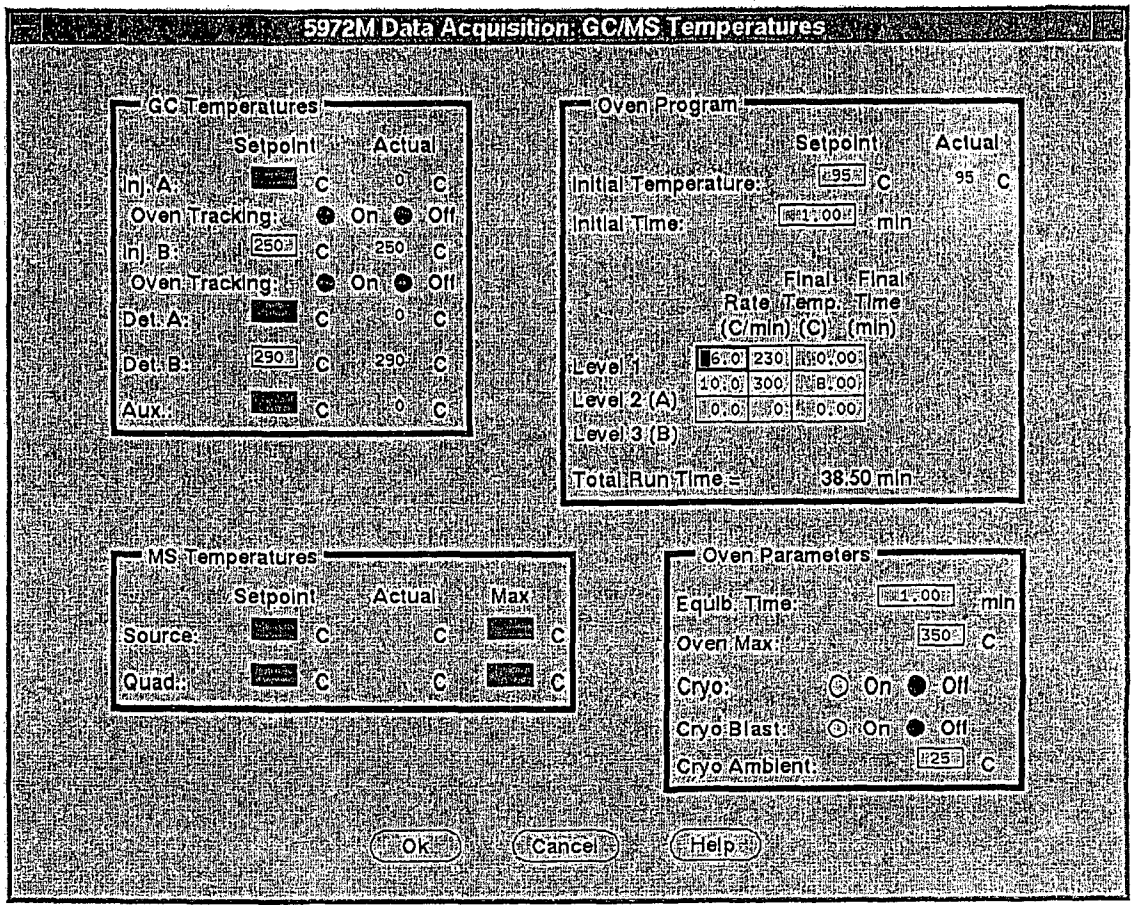
Table 5 - GC Instrument parameters

	GC Instrument Parameters
Column	25m x 0.3µm x 0.20mm 95% dimethyl -5% diphenyl polysiloxane, HP Ultra, or equivalent.
Carrier Gas	Helium 99.999% purity, or equivalent
Split vent flow	30 mL/min ± 3 mL/min
Septum purge	1 mL/min
Column flow	Nominal 0.65 mL/min, (30 cm/sec. linear velocity)

GC/MS control software windows with typical GC temperature and electronic pressure control setpoints:



GC Temperature window:



8.5 Integration Parameters

Different integration algorithms — such as "Falcon", "HP RTE", or "HP Genie" — can be selected in the method's configuration. LS2001 analysts have found little complaint with the default settings of the HP RTE integrator, although recent software revisions have let to improvements in the Falcon integrator that may make it the integrator of choice. These settings should be evaluated on an instrument by instrument basis (and from there compound by compound), particularly to insure reliable integration of low-level data. It has been discovered, however, that changing the integrator type can cause loss of calibration.

8.6 Data Processing Method

Post-data acquisition data processing usually occurs automatically at the end of analysis of each sample, using the method given in the sample sequence listing. After processing, the samples are ready for the analyst's inquisition using the Target Review program.

8.7 Initial Calibration

8.7.1 Number of calibration points, concentrations, exceptions — At least five calibration points need to be "enabled" for quantitation of each analyte, and at least eleven points (of the fourteen available levels) need to be described to establish calibration over the expected analytical range. These are 0.01, 0.02, 0.04, 0.1, 0.4, 1, 4, 10, 40, 100, and 200 ng/µL. The analyst should include zero as a point for the curve. Most analytes will fit a linear curve, but a few will probably be best represented by a quadratic fit (Figure 10, appendix B). The Internal Standard technique is used for calibration. Sample extract concentrations which are calculated to be greater than 40 ng/µL must be diluted and reshot in order to stay within the calibration range.

8.7.2 Calibration performance criteria — The quality of the curve should be judged on the correlation coefficient of the original curve, the linearity and accuracy of the check standards of third party check (TPC)

solutions, and the ability of the curve to generate correct values for known quality assurance samples. An r^2 value of 0.995 or better is the minimum acceptable level for calibration curves, but is not the sole criterion: The y-axis intercept should be less than ten times the method detection limit (MDL) of that analyte (that is to say, an analyte response of "zero" should indicate an on-column amount, and therefore a concentration, that is *less than* the MDL. This indicates that the MDL can be achieved). If data points are rejected, you must have a legitimate reason for dropping the point from the curve. These reasons might include a bad injection or a bad standard — *not* simply that the data didn't fit.

8.7.3 Calibration Tips — Not all calibration points need to be (or should be) enabled. Because the concentrations of most analytes in samples are low, points higher than 4 ng/µL can usually be disabled, with the exception of those analytes often found at higher concentrations. These are typically the corn herbicides alachlor, metolachlor, and atrazine; as well as simazine. Another tip is to reprocess a calibration standard's data file as an instrument spike to check the accuracy of the curve.

8.8 Quality Control

8.8.1 General Guidelines — Quality Control guidelines for organic analyses may be found in the "NWQL Organic Chemistry Program QA/QC Guidance Manual". QA/QC issues specific to LS 2001/2010 analyses which are not covered in the Guidance Manual may be addressed by this SOP. Questions concerning the interpretation of QA/QC issues should be brought to the attention of the unit supervisor.

8.8.2 Statistical Derivation of QC limits — Control limits for the relevant QC sample types (CCVs, spikes, and blanks) are derived from data accumulated over the calendar year. On or about March 1, these data are reviewed and compared to the limits derived from the previous year's data. The relevant Target sublists are updated, if required. See the QA/QC Guidance Manual for guidance on control limit calculations.

8.8.3 CCV Guidelines — For this schedule, the CCV concentration is defined to be 0.4 ng/µL. Schedule analysts have developed a convention that CCV frequency in a batch will consist (at a minimum) of a CCV at the first vial position, at every sample preparation set (e.g. after the set spike), and at the last vial. As a consequence, because there is more QC for a schedule 2001 sample set (10 samples) than 2010 samples (18 samples), there will be *more* CCVs run in a schedule 2001 batch.

Individual analytes in both of the CCV's immediately bracketing environmental samples in the analytical run sequence are relevant in the consideration of CCV acceptance criteria. All samples must be bracketed by acceptable CCVs. However, with 47 analytes in this schedule, failure at the 99th percentile does allow for an "occurrence of statistical anomaly" at the rate of about one analyte QC failure in two CCVs (i.e. 1 in 94). Therefore, some samples may *not* need to be re-run for failed CCVs. Definitions of CCV failures and subsequent corrective action may be found in the QA/QC Guidance Manual.

When system maintenance such as ion source cleaning or installation of a new chromatography column is performed, CCV failure will usually occur (or the accuracy of higher or lower level standards might be affected), and the instrument will need to be recalibrated.

See the QA/QC Guidance Manual for development of CCV performance criteria and guidelines of the compilation of multiple-instrument performance data.

8.8.4 Reagent spike performance criteria — Laboratory spike data are acquired and statistically evaluated to develop acceptance criteria on an on-going basis (see the QA/QC Guidance Manual). These data are entered into the Target® spike sample sublist. If a sample set contains a spike in which recovery results are unacceptable (as judged by the spike sublist), surrogate recovery in the associated samples and blank should be evaluated along with any observations recorded during sample preparation. If it is apparent that the poor recovery is due to laboratory process error, the possibility of the error adversely affecting the samples associated with that set must be considered.

Prometon recovery in spikes has recently been poor, but the addition of 100 mg of NaCl seems to have alleviated the problem. Diazinon may degrade if free chlorine is present in the matrix. Some compounds (e.g. deeethylatrazine) have typically poor recovery. Refer to OFR 95-181 for discussion of other problem analytes.

8.8.5 Internal standard performance criteria — Implementation of the initial tune criteria should insure achievement of a minimum response for the internal standard compounds. If internal standard peak areas are not within ± 50% of the mean internal standard area for the analytical set, the possibility of extract evaporation or other influences should be considered. Table 6 below identifies some of the more common symptoms describing internal standard problems, modes of failure, and corrective action.

Table 6: Internal Standard (IS) symptoms, causes, and corrective action

IS Symptoms	Probable cause	Corrective action
Low response of early eluting IS compounds relative to the mean response.	Loss of more volatile internal standards in TurboVap®	Probably affects analytes. Consider D-R of sample.
Variability of IS areas	Variability of sample extract volume	Bring to consistent volume.
Low response of all IS compounds	Not enough IS added in sample prep, poor injection; other possibilities...	Check surrogate recoveries. If unacceptable, D-R sample.
Loss of the last IS, Chrysene-d_{12}	Dirty column, MS source	Clean problem areas and reshoot.
Unsymmetrical IS quant-ion peak, other compound peak shapes OK	Matrix interference	Integrate appropriately, consider D-U of affected analytes.

8.8.6 Surrogate performance criteria — Surrogates are analytes intentionally added to a sample to assist in monitoring the process of sample preparation. Schedule 2001 uses two surrogates — alpha-HCH-d_6 and diazinon-d_{10} — to mimic the behavior of the organochlorine and organophosphate compound classes, respectively. Surrogate data are acquired and statistically evaluated (through the *bnared* program) to develop acceptance criteria on an on-going basis. Surrogate recoveries typically vary from 70 -130%. The criteria for surrogates are entered into the Target® spike sample sublist, which is used as a reference to evaluate sample data. If surrogate recovery results are unacceptable, surrogate recovery in the associated samples, spike, and blank should be evaluated along with any anomalous observations recorded during sample preparation (sometimes samples have twice the amount of surrogate added, or none at all). If it is apparent through this evaluation that the poor recovery is due to laboratory process error, then the possibility of adverse consequences to the sample must be considered. In general, if there are no indications of process failure other than those attributable to non-standard matrix problems or human error, the recovery failure may be attributed to matrix problems, and the results for any detected analytes might be flagged with the 'E' qualifier. The interpretation should be annotated on the Data Review Checklist (figure 9, appendix B), or other appropriate part of the data packet. See the Organic Program QA/QC Guidance Manual for assistance in specific situations.

The schedule of the samples needs to be taken into account when evaluating surrogate recovery performance. The LS2001 samples have surrogate added at the NWQL, while the surrogate for LS2010 samples are added (and extracted) in the field. Differences in surrogate lot numbers, cartridge "hold" times, equipment, technique, environmental temperature & humidity, etc. could all play a part in affecting the surrogate recoveries for LS2010 samples. Within a sample set, the surrogate recoveries could vary as much as the locations that the samples come from.

8.8.7 Method blank performance criteria — If method blanks associated with a sample set are determined to contain target analytes, the possibility of sample cross-contamination must be considered. Blank failure scenarios will consider an analyte's MRL and NDV (Non-Detect Value) in affected samples. See the QA/QC Guidance Manual for assistance in specific situations.

8.8.8 IDL performance criteria — The IDL (Instrument Detection Limit) is a test to determine if instrument sensitivity is sufficient for the determination of low analyte concentrations. For LS2001, the concentration of the IDL is 0.04 ng/µL (corresponding to 0.004 µg/L sample concentration). Only a single IDL is required in an analytical batch. If analytes cannot be *qualitatively* determined, the response of the instrument is suspect and maintenance may need to be performed. Affected samples will likely need to be re-analyzed.

8.8.9 Third Party Check (TPC) solutions — When a new calibration curve is created, an independent and separately prepared solution of known concentration, known as the TPC, is used to compare and verify the integrity of the curve. A mixture from Absolute Standards is currently used as the TPC for LS2001. TPC results should be within 20% of expected values. Failure of the TPC will probably be indicated by incorrect quantification of all analytes, not just a couple of analytes.

8.8.10 Quality control criteria for poorly performing analytes — Several LS2001 analytes have performed poorly over time. Five analytes are qualified with the E (estimated) flag, these are deethyl atrazine, carbaryl, carbofuran, methyl azinphos, and terbacil. However, other compounds might be flagged with the "E" qualifier if QC criteria are not met. These are described in table 7 (page 16).

8.9 Sample Data Analysis

8.9.1 Qualitative determination — A compound is identified based on retention time and a comparison of the background subtracted sample mass spectrum with the characteristic ions of a reference mass spectrum. Three or four characteristic ions are defined to be the ions that have the greatest relative intensity, or are desirable for their unique mass, occurring in the reference spectrum (table 1, appendix A).. Compounds should be identified as present when the following criteria are met (or as reason allows):

- **Retention time** — The intensities of the characteristic ions of a compound are at a maximum that should coincide within ± 0.05 minute of the target compound's retention time. For this schedule, the method is set (under Global →Compound ID) to choose the peak closest to the target peak retention time. In addition, the quantification ion and associated qualification ions should have their maxima within 0.01 minute of each other. However, matrix effects can have a significant influence on GC retention times, and retention time reproducibility can be highly compound dependent.
- **Spectra** — The identity of each target compound is verified by comparing the characteristic ions at the apex of the extracted ion profile of the quantitation ion with the (SIM) reference spectrum obtained from the standard for that compound. In particular, the relative ratios of the extracted ion profiles need to be within 20% of the relative ratios obtained on injection of a standard solution generated using the conditions of this method[1]. It is difficult to define explicitly which features of a sample mass spectrum must be present to consider the identification to be positive; in general, the sample spectrum should have the same base peaks, major fragmentation ions, significant isotope clusters, and molecular ion (where appropriate) as a standard spectrum (see the example Target® Review window in Figure 8, appendix B). Careful attention should be given to determine whether contribution to th target ion profiles are appropriate and have relative intensities that are consistent with the reference mass spectrum, or if they are due to interference ions, or are a result of contributions of target and interference ions. Experience and training are necessary for the analyst to recognize the salient features of individual mass spectra as well as potential interferences.

8.9.2 Peaks not meeting qualification criteria — It may be difficult to be completely confident about the identity of some peaks. In this situation, if the concentration of the analyte is calculated to be less than or equal to two times the MDL, the analyst may not choose to call it — raising the reporting level is not necessary. However, if the concentration is greater than two times the MDL and the analyst cannot state that it's not there, the detection level should be raised to that concentration.

Value	Report
≤2 times the MDL	<MDL (not called), altering MRL not required.
>2 times the MDL	raise the report level to that concentration.
can't determine	D-U

8.9.3 Qualitative determination tips — Identification is difficult when sample components are not resolved chromatographically and produce mass spectra containing more than one analyte. When chromatographic peaks obviously represent more than one sample component (a broadened peak, shoulders or a valley between two or more maxima), appropriate selection of analyte spectra and background subtraction is important. When analytes co-elute, identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the co-eluting analyte. Using the Data Analysis program to generate ion chromatograms may help in graphically separating the coeluting ions and correctly identifying possible hits.

8.9.4 Interferences — Contributions to the quanitation ion profile from compounds present in the sample matrix may make accurate measurement of the target analyte concentration difficult or impossible. The report level might

[1] OFR 95-181, page 20, section 11.1.2

be raised, or the compound reported with the U-DELETED flag (unable to determine due to interference). Consult with the unit supervisor for guidance with unusual circumstances.

8.9.5 Quantitative determination

8.9.5.1 Calculations — Analyte calibrations are performed by the Target software through use of regression equations. When a compound has been identified, the concentration of that compound will be based on the integrated area from the primary quantitation ion of that compound, and the regression line fitted to the initial calibration using response factors relative to the internal standard response factor (a graphic of the Target® window for part of the propachlor calibration curve is shown in Figure 10 of appendix B).

Where quadratic curves are used, the curve might sometimes acquire a negative slope past an inflection point. Curves with such parameters result in a formula for *decrease* in concentration when there's an *increase* in response. This nonsense situation can usually be corrected by adding an additional point to the calibration curve for that analyte. Note that the addition or removal of points on the calibration curve for a given analyte will necessitate reprocessing of the sample data. Be warned, however, that reprocessing requantifies concentrations for all analytes in the sample, not just the analyte of concern.

The method should be set up with usable formulas so that all the sample weights can be entered individually. This will make for easier electronic data transfer and form production. Following are the Target windows that can be found for the calculations:

Care must be taken to enter sample information from the sample preparation sheet correctly, as this is an obvious place to introduce errors into a sample's results. A typical sample preparation sheet is shown for LS2001 in

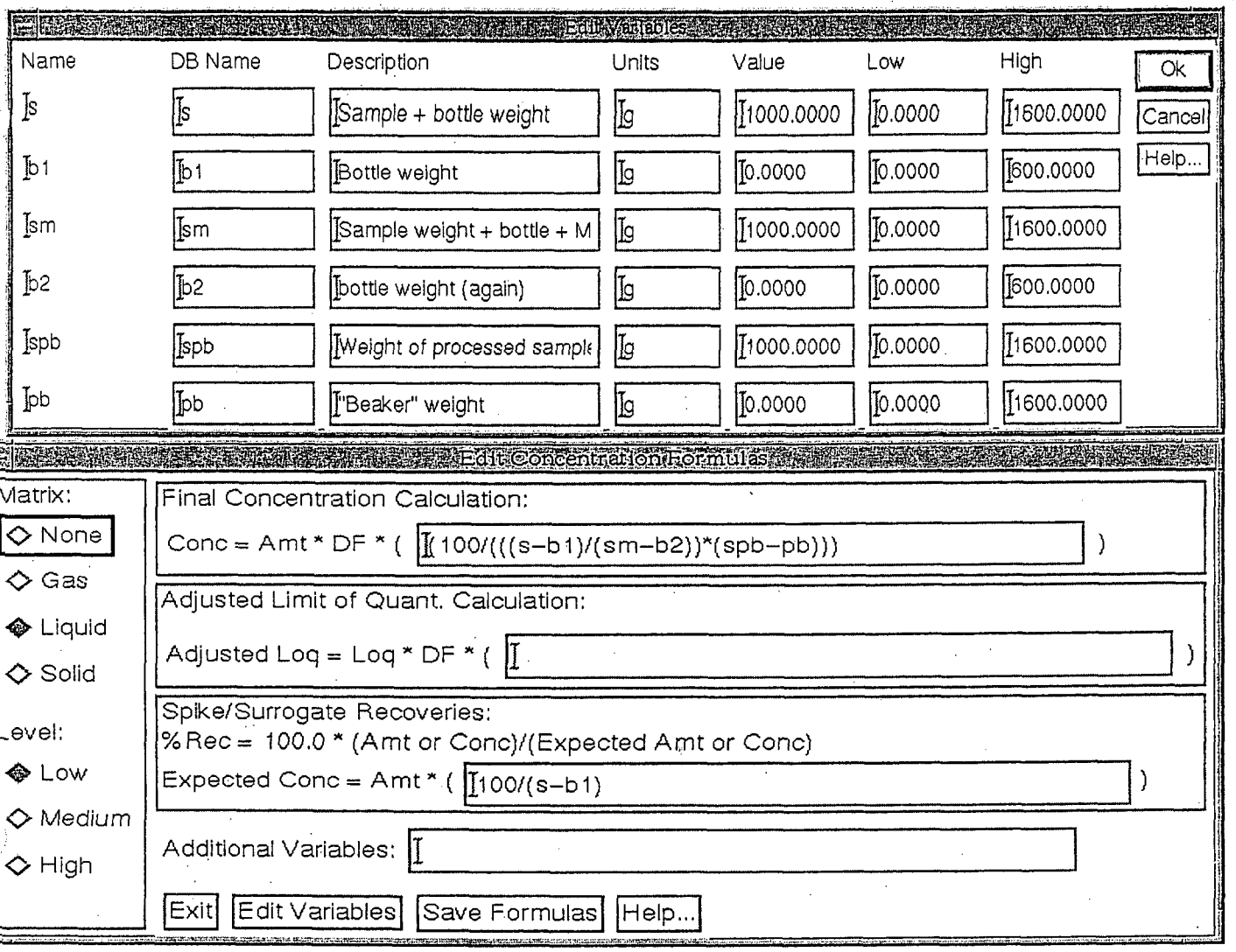


Figure 7 of appendix B.

8.9.6 Analysis of dilutions — Samples must be analyzed within the range of the calibration curve. Analyte concentrations in excess of the established curve (but below 40 ng/µL) may require the "enabling" of higher calibration points in the method. Analyte concentrations that are *over* 40 ng/µL should be to be brought within the range of the calibration curve through dilution of the extract. This is usually accomplished by performing a 1:5 dilution (with toluene) and the enabling of 100 and 200 ng/µL calibration points in the calibration table for that target analyte. The 100 and 200 ng/µL standards also have the internal standard at 1/5th the amount of the other calibration standards (while the analyte concentration is equivalent to a 20 and 40 ng/µL standard, respectively).

8.10 Data Report

8.10.1 Reporting units — For this schedule, the reporting units are in microgram per liter (µg/L).

8.10.2 Reporting level — The method detection limit of LS2001 is analyte dependent. However, the "E" flag will be used to qualify values (of qualitatively determined compounds) that are less than 0.004 µg/L or are less than the MDL, whichever is greater.

8.10.3 Significant figures — The number of significant figures is handled by the various data reporting programs. The Perkin Elmer LIMS system currently maintains two significant figures on values that are less than 0.01 µg/L, three significant figures for values between 0.01 to 10 µg/L, and two significant figures for values greater than 10 µg/L. Surrogate and spike results are reported as "percent recovery" with three significant figures.

8.10.4 Electronic data transmission — Transfer of data is done electronically. The *bnared* program is used to parse a sample's target.rp file to create a file (having a ".dat" extension) that can be interpreted by the LIMS. After the data have gone through a primary and secondary review, the file is transferred by FTP to the LIMS computer. On the night the data are sent to LIMS, the LIMS computer will generate a verification report and email it to the analyst. The analyst may use this report to verify against the original target.rp report for accuracy. If data is correct, do nothing. If data is incorrectly sent, notify *denorg* (NWQL's Denver organic chemistry program) to hold the data. Fi. in an update report form for any corrections and submit to ADP for re-processing.

Table 7 — 2001/2010 Problem Analytes — Major portion of this table from the Method of the Month (MoM) 5/16/94:ms. Compounds that always carry the E flag are marked "**E**".

Compound Name	Cal	Recovery	Other	Action
Deethyl atrazine		X		E
Phorate	X			E
Carbofuran	X			E
Terbacil	X			E (on probation, delete if not brought under control)
Carbaryl	X			E
Linuron				Monitor - may be coming under control. E if CCV criteria are not met. (Injection port liner problem?)
Methyl Azinphos	X			E
Permethrin			X	Previous standard solutions contained cis & trans isomers, should contain only cis (notify standard vendors). E if CCV criteria are not met. Report as cis-Permethrin.
Dimethoate		X		Deleted from the method
Propargite I&II				Use the sum of the areas of the two isomer peaks for calibration and quantitation. E if CCV criteria are not met.
"Fluralin" compounds	X			If initial batch CCV on a new liner, reshoot the CCV to "condition" the liner.
DDE		X	Blank contamination	Do not use a laboratory washed bottle - use a new bottle instead
Prometon		X spikes		No action yet — Diagnosis is ongoing

Disulfoton			X	Past problem with impure standard. Take care in handling (subject to oxidation). Recap standard solutions. E if CCV criteria are not met.
Tebuthiuron			X	Peak tailing problems - need to monitor integration to ensure consistent integration. E if CCV criteria are not met.
Terbufos			X	May co-elute w/terbuthylazine, with ions in common, corrupting cal curve at low conc. end. Seldom if ever detected, analysts be aware of potential problem. E if CCV criteria are not met.
Pronamide			X	May co-elute w/terbuthylazine, however should be resolved if system is performing correctly. E if CCV criteria are not met.
Pendimethalin			X	Standard solution problem, investigate. E if CCV criteria are not met.

8.10.5 Data packets — Set paperwork associated with a group of samples in a sequence are organized, along with the analytical set's QC data, into *data packets*. Data packets are filed in accordion folders labeled by sequence batch name (section 8.3.4), prep set(s), date, and analyst initials. Data packets should contain, at a minimum, the following information, in order:

Main: Tune, Air and Water check, sequence, Data Review Checklist.

QC: QC forms generated by *bnared*, spike.rp for CCVs and for laboratory set spikes, and spike.rp for the IDL.

Data: Sample ASRs, sample preparation sheets, and their associated target.rp files, stapled together. This is arranged by set (including the set's QC samples), with the set cover sheet in front.

Spectra not required since they are stored on the filesystem, or otherwise recoverable from a tape archive or other media.

8.10.6 Second Level Data Review — Data are reviewed according to the outline provided in the Data Review Checklist (Fig. 9, appendix B). QC acceptance criteria for most items are contained in the analysis reports generated by *bnared*, or are listed on the Data Review Checklist. Spectra may be checked on-line rather than storing hardcopies of spectra in the data packets. "Spot" checking of spectra is sufficient when reviewing data for experienced analysts.

9. Archiving and backups

9.1 Sample extracts — Sample extracts must be recapped and organized in vial storage boxes on which the year, schedule (2001 or 2010), and set number are indicated on the end. These are stored in a freezer forever.

9.2 Data packets — Data packets are filed in archive boxes and stored in the data archive room for 5 years (see data archiving SOP).

DDS tapes — After running a sequence, it would be prudent to *backup* the analytical batch onto tape. Use *tar* (the UNIX program) or the File Manager program (DAT tape format) to perform the transfer of batches onto tape. Label the tape accordingly. When the filesystem becomes full, a tape *archive* of sample data is created, and the sample data removed from disk.

10. References

1. Zaugg, et al, *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*, USGS Open-File Report (OFR) 95-181, 1995.
2. NWQL SOP OD0053; *Automated preparation of Schedules 2001 and 2010.*
3. NWQL SOP OX0098; *General Procedure for Data Acquisition and Analysis with Hewlett-Packard GC/MS Systems.*
4. *NWQL Organic Chemistry Program QA/QC Guidance Manual.*
5. Target Software Manuals.

Appendix A

Table 1 — Report limits and ions used for quantitation and verification for method compounds.
(MDL, Method Detection Limit; SIM, Selected Ion Monitoring; IS, Internal Standard)

Compound	MDL	Approximate Retention Time	Quantitation ion	2nd Confirmation ion	3rd Confirmation ion	4th Confirmation ion	SIM Group	IS
Diethylaniline	0.003	15.502	134	149	119	135	1	1st
EPTC	0.002	16.053	128	132	189	160	2	1st
Butylate	0.002	17.630	146	156	174	217	3	1st
Pebulate	0.004	18.334	128	160	132	203	4	1st
Tebuthiuron	0.010	19.711	156	171	157		5,6	1st
Molinate	0.004	20.379	126	187	98	127	6	1st
Propachlor	0.007	21.537	120	176	169	121	7	2nd
Ethalfluralin	0.004	21.942	276	316	292		7,8	2nd
Ethoprop	0.003	22.000	158	200	242	139	8	2nd
Trifluralin	0.002	22.191	306	264	307		8,9	2nd
Benfluralin	0.002	22.298	292	393	335		9	2nd
Atrazine, deethyl-	0.002	22.384	172	174	187	145	9	2nd
Phorate	0.002	23.208	75	231	260	97	10	2nd
HCH, alpha-	0.002	23.330	181	183	219	217	11	2nd
Prometon	0.018	23.810	210	183	225	168	11	2nd
Carbofuran	0.003	23.883	164	149	122	123	11	2nd
Simazine	0.005	23.982	201	186	173	138	11	2nd
Atrazine	0.001	24.105	200	215	173	138	11	2nd
Diazinon	0.002	24.680	137	153	179	152	12	2nd
Terbufos	0.013	24.741	231	186	153		12	2nd
HCH, gamma-	0.004	24.852	183	181	109	217	12,13	2nd
Pronamide	0.003	24.766	173	175	145	255	13	2nd
Fonofos	0.003	25.026	109	137	246		13	2nd
Terbacil	0.007	25.281	161	160	162	163	15	2nd
Disulfoton	0.017	25.351	88	153	186	89	14	2nd
Triallate	0.001	25.630	86	268	145	143	14	2nd
Propanil	0.004	26.442	161	163	217	219	15	2nd
Acetochlor	0.002	26.541	146	147	162	132	15	2nd
Metribuzzin	0.004	26.627	198	199	144	171	15	2nd
Parathion, methyl-	0.006	26.885	109	125	263		15	2nd
Alachlor	0.002	26.873	160	188	237	238	15	2nd
Malathion	0.005	27.790	173	127	125	158	17	2nd
Linuron	0.002	27.953	61	160	248	187	17	2nd
Cyanizine	0.004	28.171	225	240	173	172	18	2nd
Chlorpyrifos	0.004	28.196	197	199	314	316	18	2nd
Metolachlor	0.002	28.208	162	238	240		18	2nd
Thiobencarb	0.002	28.331	100	125	127		18	2nd
Dacthal	0.002	28.442	301	299	332	330	18	3rd
Parathion	0.004	28.479	291	109	137	139	18	3rd
Pendimethalin	0.004	29.283	252	281	162	191	19	3rd
Napropamide	0.003	30.800	128	115	100	271	20	3rd
DDE, p,p'-	0.006	31.123	246	248	318	316	20	3rd
Dieldrin	0.001	31.502	79	263	265	277	20	3rd
Propargite	0.013	32.876	135	173	150	201	21	3rd
Azinphos-methyl	0.001	34.716	160	132	77	104	22	3rd
Permethrin, cis-	0.005	35.807	183	163	165	184	23	3rd

HCH d_6, alpha-	N/a	23.490	224	222	226		11	2nd
Terbuthylazine	N/a	24.618	173	138	214		12	2nd
Diazinon-d_{10}	N/a	24.557	138	153	183	200	12	2nd
Acenaphthene-d_{10} (First IS)	N/a	17.364	162	164	160	163		
Phenanthrene-d_{10} (Second IS)	N/a	23.663	188	186				
Chrysene-d_{12} (Third IS)	N/a	34.900	240					

Appendix B

Figure 1— SIM acquisition window showing the first SIM group, "Group 1".

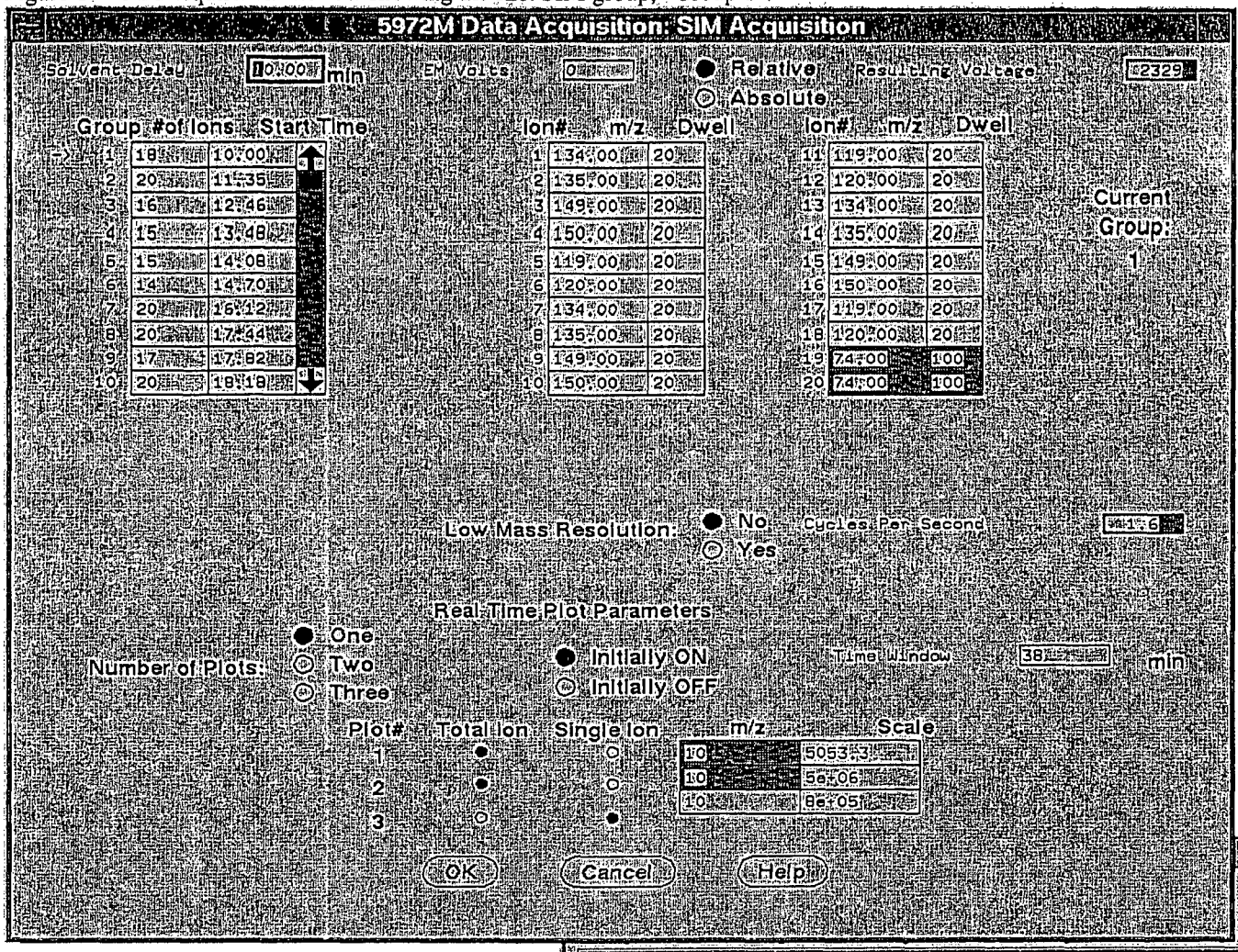


Figure 2— A Sequence Table.

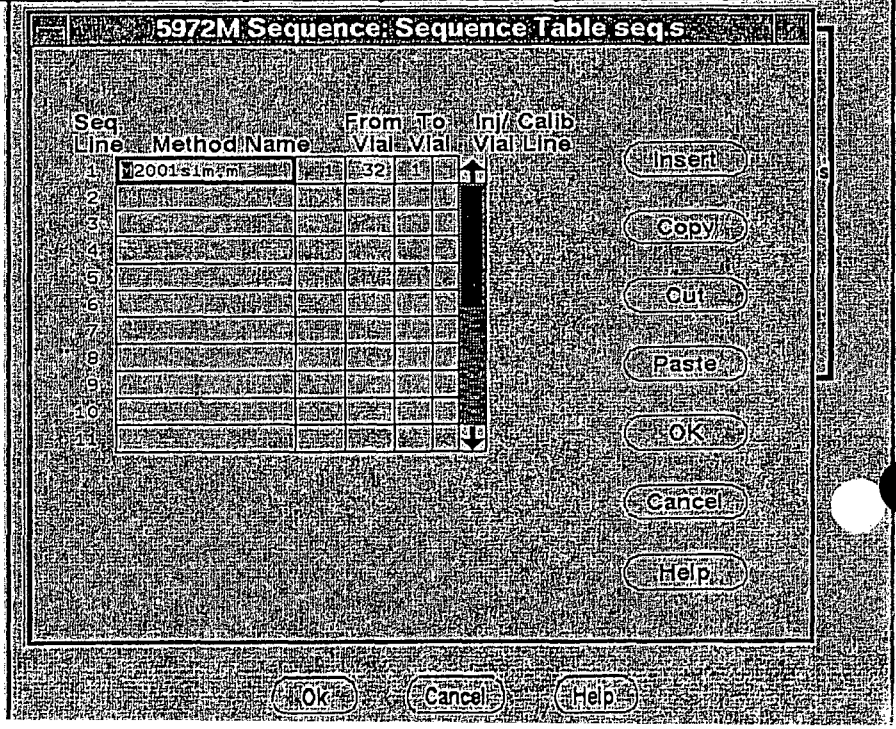


Figure 3 — Typical Target injector control window for GC/MS.

Figure 4 — A Typical LS2001 Acquisition Run Table.

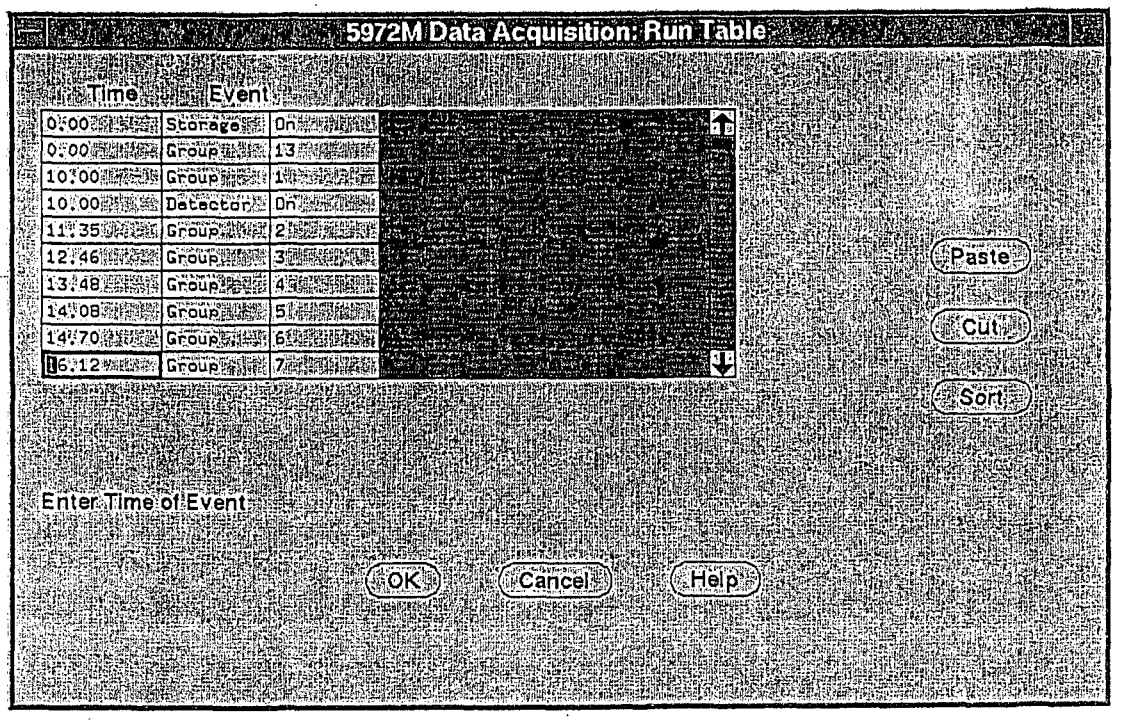


Figure 5 — Typical blank chromatogram for schedule 2001. Note the "steps" on the "total ion" chromatogram, indicating the SIM window changes. This chromatogram is of a blank; two of the three surrogates and the three internal standards are shown.

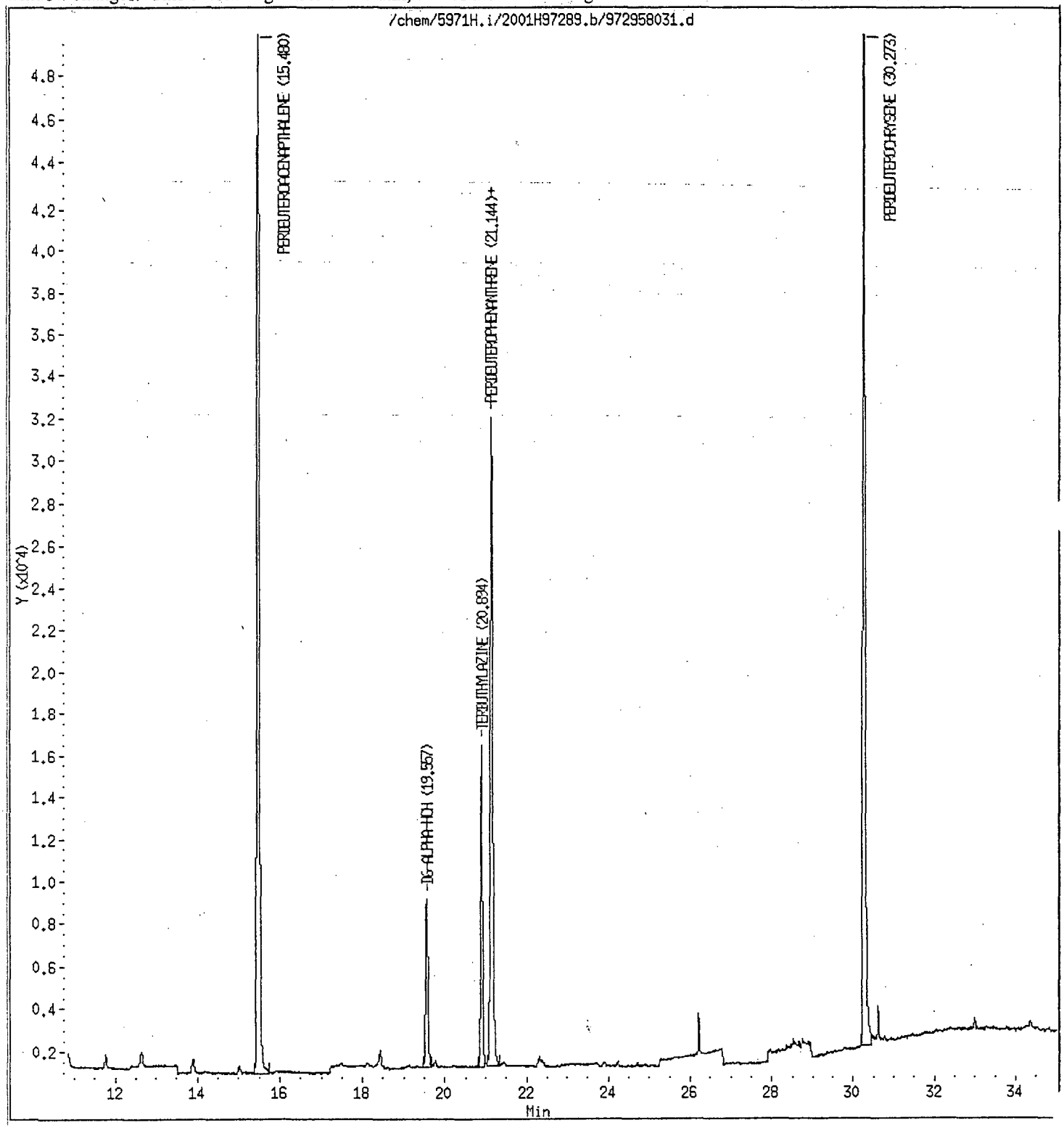


Figure 6 — Sequence Parameters dialog window:

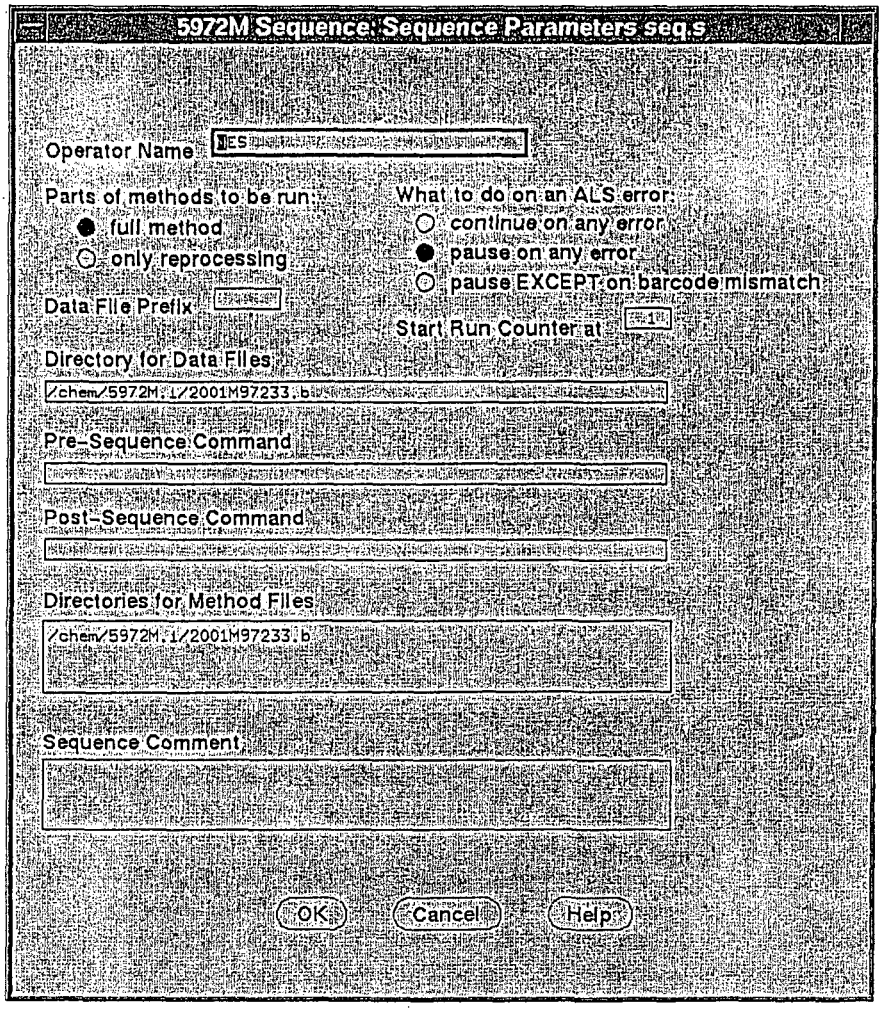


Figure 7: Sample Preparation form for a typical LS2001 sample. Of particular use on these forms are the bottle weights and any associated comments.
Figure 8: The Target Review window

Solid Phase Extraction - GC/MS Pesticides - Dissolved Water Lab Schedule 2001

Lab ID: 472400052 Set #: 4596 Date Received: 7/23

SPE Cartridge
Pump Position: 2-4
Dry wt. 3.316 gm.
Wt. after N_2 Drying: 3.309

Sample
Bottle + Sample Wt: 1316.2 gm.
Add 1% methanol: 8 ml
Bottle + Sample + MeOH: 3225 gm.

Surrogate
Solution ID: Ingall LOT # 1525
Volume added: 100 µl

~~QA Samples- Spike Mixture~~ LOT #: Supelco
Solution ID:
Volume added: µl

Sample through cartridge Date: 7/24
Sample + container: 437.6 gm.
Empty Bottle + cap: 437.4 gm.

SPE Elution + Vialing 2.0ml EtAc/Acetate Date: 7/25
Add ~~3.0 ml Hexane/Isopropanol (3:1)~~
Internal Standard (PAH -dn mixture in toluene keeper)

LOT # 55 17
Volume added: 100 µl

☑ Evaporate solvent - nitrogen (turbo-vap)
Pressure: 4 psi
Time: 15-20 min
☑ Evaporate solvent-nitrogen (N-Evap)
☑ Vialed 250 µl
☐ Analysis - Instrument ID.

Comments:

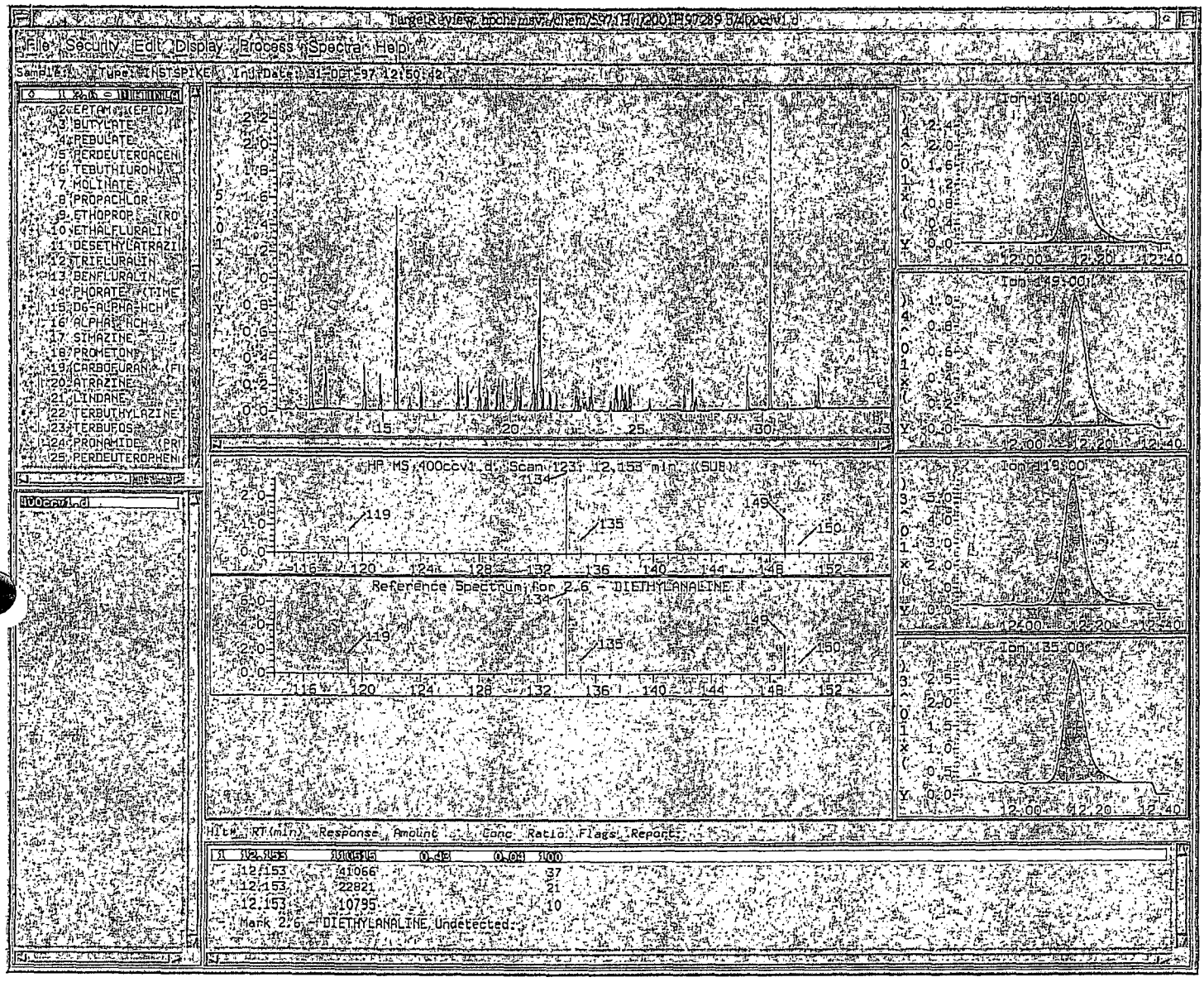

File Security Edit Display Process Spectra Help
HP MS 400ccv1.d Scan 1231 12.158 min (SUB)
Reference Spectrum for 2,6 - DIETHYLANALINE
Hits RT(min) Response Amount Conc Ratio Flags Report
12.153 41066 37
12.153 22821 21
12.153 10795 10
Mark 2,6 - DIETHYLANALINE Undetected.

Figure 9: The Schedule 2001/2010 Data Review Checklist

Schedule 2001/2010 Data Review Checklist rev 950919:ms

Analyst / Date: _____ Instrument ID: _____
Batch name: _____ Schedule(s): **2001, 2010**

Reviewer:_____ Date to ADP: _____

General Data

Analyst	Reviewer				
		1. Run Sequence list present and followed.[1]	Yes	No	
		2. MS Tune within criteria. [1]	Yes	No	If No, then note on report.
		3. Initial calibration summary a) All R^2 >= 0.995	Yes	No	If No, then note on report.
		4. Extended calibration curves	Yes	No	If Yes, note on sequence list as 'analyte (high conc.)'.

QC Data

		1. CCV Reports a) All analytes within criteria. [2]	Yes	No	If No, then note for each analyte on report and sequence list.
		2. Blanks - Positives < MRL.	Yes	No	If No, then note on report and sequence list.
		3. Lab Spikes a) All analytes within criteria. [2]	Yes	No	If No, then note on report and sequence list.
		4. Duplicates (if available)- meet criteria.	Yes	No	If No, then note on report and sequence list.
		5. MDL verification check			

Sample Data

For each sample check the following:

		1. Analysis Report Sheets			
		a. Sample ID			
		b. Internal Standard areas within criteria. [1]	Yes	No	If No, then note on report and sequence list.
		c. Surrogate Recoveries within criteria. [2]	Yes	No	If No, then note on report and sequence list.
		d. Sample Volume.			
		2. ASR's present.			
		3. Sample preparation sheets present.			
		4. Spectra for positive detects (spot check on data system).			
		5. Do positives make sense?			

1 - See back of this form for criteria.
2 - Criteria are printed on analysis report.
Documentation and / or corrective action are required if check is made in the shaded areas above.

Figure 9: The Schedule 2001/2010 Data Review Checklist, continued.

Comments:

Analysis Sequence

(Daily routine after initial calibration is run).

Inj.#	Material Injected
0	Check PFTBA tune, including air check
1	MRL Check, 0.04ng/ul (optional)
2	CCV, 0.4 ng/µl
3	Method reagent spike
4	Method reagent blank
5	Duplicate sample, if available.
6-13	Samples
14	CCV, 0.4 ng/µl
15	Method or solvent blank
16-25	Samples
26	CCV, 0.4 ng/µl
27	Method or solvent blank
28-37	Samples
38	CCV, 0.4 ng/µl
39	Method or solvent blank
40-49	Samples
50	CCV, 0.4 ng/µl
51	Method or solvent blank
52-61	Samples
62	CCV, 0.4 ng/µl
63	Method or solvent blank

Mass Spectrometer Tune Criteria (PFTBA calibration)

Abundance relative to m/z 69	m/z	Absolute Abundance
100	69	2 $X10^6$ +/- 50%
20-60 %	219	
0.5-12 %	414	

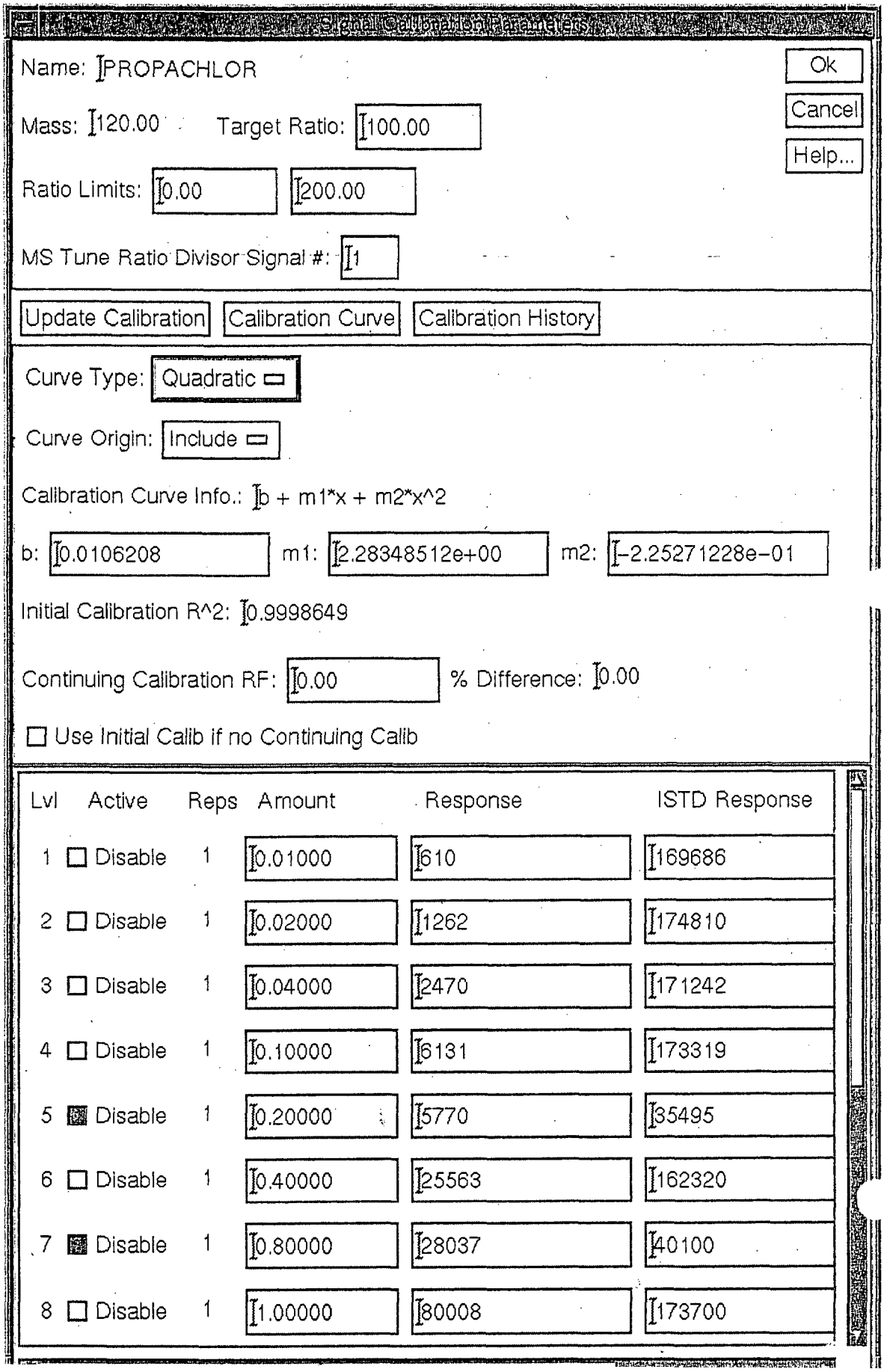
Surrogate Peak Area Criteria

Alpha HCH, d6		
Terbuthylazine		
Diazinon, d10		

1: E if detected. 2: E if CCV fails criteria. ==========>

	Report Levels	MRL	
1	2,6 - DIETHYLANALINE	< 0.003	
2	EPTAM (EPTC)	< 0.002	
3	BUTYLATE	< 0.002	
4	PEBULATE	< 0.004	
5	TEBUTHIURON	< 0.010	2
6	MOLINATE	< 0.004	
7	PROPACHLOR	< 0.007	
8	ETHOPROP (ROVOKIL)	< 0.003	
9	ETHALFLURALIN	< 0.004	1
10	DEETHYLATRAZINE	< 0.002	
11	TRIFLURALIN	< 0.002	
12	BENFLURALIN	< 0.002	
13	PHORATE (TIMET)	< 0.002	1
14	ALPHA HCH	< 0.002	
18	SIMAZINE	< 0.005	
19	PROMETON	< 0.018	
20	CARBOFURAN (FURANDAN)	< 0.003	1
21	ATRAZINE	< 0.001	
22	LINDANE	< 0.004	
23	**TERBUTHYLAZINE**	**SURR**	
24	TERBUFOS	< 0.013	2
25	PRONAMIDE (PROPYZAMID)	< 0.003	2
26	**PHENANTHRENE**	**INT STD**	
27	FONOFOS (DYFONATE)	< 0.003	
28	**DIAZINON d10**	**SURR**	
29	DIAZINON	< 0.002	
30	DISULFOTON (DISYSTON)	< 0.017	2
31	TERBACIL	< 0.007	2
32	TRIALLATE	< 0.001	
33	PROPANIL	< 0.004	
34	METRIBUZIN	< 0.004	
35	METHYL PARATHION	< 0.006	
36	CARBARYL (SEVIN)	< 0.003	1
37	ALACHLOR	< 0.002	
38	LINURON	< 0.002	2
39	MALATHION	< 0.005	
40	THIOBENCARB	< 0.002	
41	METOLACHLOR	< 0.002	
42	CYANAZINE	< 0.004	
43	CHLORPYRIFOS	< 0.004	
44	PARATHION	< 0.004	
45	DACTHAL	< 0.002	
46	PENDIMETHILAN (PROWL)	< 0.004	2
47	NAPROPAMIDE	< 0.003	
48	DDE	< 0.006	
49	DIELDRIN	< 0.001	
50	PROPARGITE I & II	< 0.013	2
51	CHRYSENE	INT STD	
52	METHYL AZIMPHOS	< 0.001	1
53	PERMETHRIN (AMBUSH)	< 0.005	2

Figure 10: Signal Calibration Parameters for the standard curve of propachlor.



Lvl	Active	Reps	Amount	Response	ISTD Response
1	☐ Disable	1	0.01000	610	169686
2	☐ Disable	1	0.02000	1262	174810
3	☐ Disable	1	0.04000	2470	171242
4	☐ Disable	1	0.10000	6131	173319
5	■ Disable	1	0.20000	5770	35495
6	☐ Disable	1	0.40000	25563	162320
7	■ Disable	1	0.80000	28037	40100
8	☐ Disable	1	1.00000	80008	173700

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

By Steven D. Zaugg, Mark W. Sandstrom, Steven G. Smith, and Kevin M. Fehlberg

U.S. Geological Survey

Open-File Report 95-181

Denver, Colorado
1995

U.S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, *Secretary*

U. S. GEOLOGICAL SURVEY

Gordon P. Eaton, *Director*

For additional information
write to:

Chief, National Water Quality Laboratory
U.S. Geological Survey
Box 25046, Mail Stop 407
Federal Center
Denver, CO 80225

Copies of this report can be
purchased from:

U.S. Geological Survey
Open-File Reports Section/ESIC
Box 25286, Mail Stop 517
Federal Center
Denver, CO 80225

CONTENTS

FIGURES

TABLES

CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
centimeter (cm)	3.94×10^{-1}	inch
gram (g)	3.52×10^{-2}	ounce
kilogram (kg)	3.53×10^{-1}	ounce, avoirdupois
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch
liter (L)	2.64×10^{-1}	gallon
meter (m)	3.28×10^{0}	foot
microliter (µL)	2.64×10^{-7}	gallon
micrometer (µm)	3.94×10^{-5}	inch
milligram (mg)	3.53×10^{-5}	ounce
milliliter (mL)	2.64×10^{-4}	gallon
milliliter per minute (mL/min)	3.38×10^{-2}	ounce per minute
millimeter (mm)	3.94×10^{-2}	inch
nanogram (ng)	3.53×10^{-11}	ounce

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

The following abbreviations are used in this report:

dc	direct current	ng/µL	nanogram per microliter
µg/L	microgram per liter	lb/in^2	pound per square inch
min	minute	V	volt
ng/L	nanogram per liter		

The following terms are used in this report:

C-18	octadecyl	PFA	perfluoralkoxy
EDOC	electronic documents system	PFTBA	perfluorotributylamine
ETFE	ethylenetetrafluoroethylene	SIM	selected-ion monitoring
GC	gas chromatography	SPE	solid-phase extraction
GCC	glass bottle, amber	USGS	U.S. Geological Survey
GC/MS	gas chromatograph/mass spectrometer		
HIP	hexane-isopropanol		
HPLC	high-performance liquid chromatography		
ID	inside diameter		
MDL	method detection limit		
NAWQA	National Water-Quality Assessment program		
NWQL	National Water Quality Laboratory		
OD	outside diameter		
PAH	polyaromatic hydrocarbon		

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

By Steven D. Zaugg, Mark W. Sandstrom, Steven G. Smith, and Kevin M. Fehlberg

ABSTRACT

A method for the isolation and analysis of 41 pesticides and pesticide metabolites in natural-water samples is described. The pesticides are isolated by C-18 solid-phase extraction and determined by capillary-column gas chromatography/mass spectrometry with selected-ion monitoring. Water samples are filtered to remove suspended particulate matter and then are pumped through disposable solid-phase extraction columns containing octadecyl-bonded porous silica to extract the pesticides. The columns are dried using carbon dioxide or nitrogen gas, and adsorbed pesticides are removed from the columns by elution with hexane-isopropanol (3:1). Extracted pesticides are determined by capillary-column gas chromatography/mass spectrometry with selected-ion monitoring of three characteristic ions. The upper concentration limit is 4 micrograms per liter (µg/L) for most pesticides, with the exception of widely used corn herbicides--atrazine, alachlor, cyanazine, and metolachlor--which have upper concentration limits of 20 µg/L. Single-operator method detection limits in reagent-water samples range from 0.001 to 0.018 µg/L. Recoveries in reagent-water samples ranged from 37 to 126 percent for most pesticides. The estimated holding time for pesticides after extraction on the solid-phase extraction columns was 7 days. An optional on-site extraction procedure allows for samples to be collected and processed at remote sites where it is difficult to ship samples to the laboratory within the recommended pre-extraction holding time.

INTRODUCTION

Pesticides are widely used in the United States to increase production of agricultural products by controlling weeds, insects, and other pests in a wide variety of settings (Gianessi and others, 1986). They are frequently detected in surface water and ground water in the United States (Hallberg, 1989) and Europe (Leistra and Boesten, 1989). The traditional methods for determining residues of pesticides in natural-water samples involve liquid-liquid

extraction with an organic solvent followed by analysis by gas chromatography (GC) with nitrogen-phosphorus or electron-capture detection, using two columns to confirm pesticide identity.

Recently, methods for pesticide analysis using solid-phase extraction (SPE) as an alternative to liquid-liquid extraction have been described (Bagnati and others, 1988; Bellar and Budde, 1988; Eichelberger and others, 1988; Junk and Richard, 1988; Battista and others, 1989; Brooks and others 1989; DiCorcia and others, 1989; Sandstrom, 1989; Thurman and others, 1990). These SPE methods are attractive because they are rapid, efficient, use less solvents than liquid-liquid extraction, and consequently have lower laboratory expenses. The SPE methods can be conducted onsite, which enables processing of samples with labile compounds, or at remote sites. In addition, the SPE methods can be automated by using laboratory robotic systems that do all or part of the sample-preparation steps. Some of these SPE methods also incorporate the use of a gas chromatograph/mass spectrometer (GC/MS) operated under a selected-ion monitoring (SIM) mode for confirmation and quantitation of pesticides. The GC/MS SIM is more specific than either the nitrogen-phosphorus or electron-capture detector, and more sensitive than the nitrogen-phosphorus detector.

This report describes a method for determining a broad range of pesticides in natural-water samples. It was developed by the U.S. Geological Survey (USGS) for use in the USGS National Water Quality Laboratory. The method combines octadecyl (C-18) SPE for pesticide isolation and GC/MS operated in the SIM mode for selective confirmation and quantitation of the pesticides. It is rapid, more efficient, and can detect lower concentration levels (in nanograms per liter) compared to other USGS methods (Wershaw and others, 1987). The method supplements other methods of the USGS for determination of organic substances in water that are described by Wershaw and others (1987) and by Fishman (1993). The method was implemented in the National Water Quality Laboratory (NWQL) in October 1992.

This report provides a detailed description of all aspects of the method, including the equipment, reagents, sampling protocol, instrument calibration, and SPE procedure required for sample analysis. Method performance (precision and accuracy) and estimated method detection limits for 47 pesticides are presented.

The scope of the report includes determination of method performance in ultrapure water samples and two natural-water types--a ground water and a surface water from the Denver, Colorado, region. Method performance was determined at two concentration levels--0.1 and 1.0 µg/L--in each water type. Method detection limits were determined according to an accepted statistical procedure (U.S. Environmental Protection Agency, 1992). Holding times of SPE columns before extraction and the use of an automated evaporation

system for solvent reduction also were evaluated. An optional on-site SPE procedure is described, and an optional laboratory automated procedure is briefly described in Supplements A and B to the report. The method was tested on surface-water samples from the midcontinent of the United States in 1991. During 1992, four study units of the National Water-Quality Assessment (NAWQA) program tested the on-site isolation procedure.

ANALYTICAL METHOD

Organic Compounds and Parameter Codes: Pesticides, dissolved, gas chromatography/mass spectrometry, O-1126-95 (see table 1)

1. Scope and application

This method is suitable for the determination of low-level concentrations (in micrograms per liter and nanograms per liter) of pesticides and pesticide metabolites in natural-water samples. The method is applicable to pesticides and metabolites that are (1) efficiently partitioned from the water phase onto an octadecyl (C-18) organic phase that is chemically bonded to a solid inorganic matrix, and (2) sufficiently volatile and thermally stable for gas chromatography. Suspended particulate matter is removed from the samples by filtration, so this method is suitable only for dissolved-phase pesticides and metabolites.

The compounds include some of those in the NWQL Laboratory Services Catalog (Timme, 1994), as well as newer pesticides determined to be of national importance for the NAWQA program (table 1). The method was developed in response to the request for a broad spectrum pesticide method for use in determining their occurrence and distribution as monitored by the NAWQA program. Pesticides were selected initially because of their widespread use in the United States, according to information in Resources for the Future database (Gianessi and Puffer, 1990, 1992a, and 1992b) and compatibility with the general analytical plan. Other criteria included published studies of pesticide fate and occurrence of metabolites, responses from NAWQA Study Unit personnel regarding pesticides of local significance, and U.S. Environmental Protection Agency health advisories. Finally, restrictions in the analytical software on the number of ions scanned for specific time intervals limited the number of pesticides chosen for testing in the method to about 50.

Table 1.--*Compound name, use, pesticide class, codes,and registry numbers*

[NWQL, National Water Quality Laboratory; CAS, Chemical Abstract Service; MW, molecular weight; USE, annual national use of active ingredient (a.i.) in thousand kilograms (kg) (a.i./1,000 kg, Gianessi and Puffer, 1990, 1992a, 1992b); H, herbicide; AMID, Cl-acetamide; TRI, triazine; --, metabolite or pesticide no longer registered for use; MET, metabolite; I, insecticide; OP, organophosphate; DNA, dinitroaniline; CB, carbamate; OC, organochlorine; UREA, phenyl urea; PYR, permethrin; MISC, miscellaneous; URAC, uracil]

Compound (common chemical name)	Use	Class	NWQL code	Parameter code	CAS registry number	MW	USE (a.i/ 1,000 kg)
Alachlor (Lasso)	H	AMID	4001	46342	15972-60-8	269.8	25,055
Atrazine	H	TRI	4003	39632	1912-24-9	215.7	29,163
Atrazine, desethyl-[1]	–	MET	4002	04040	6190-65-4	152.1	–
Azimphos-methyl (guthion)[1]	I	OP	4004	82686	86-50-0	317.1	1,125
Benfluralin (Benefin)	H	DNA	4005	82673	1861-40-1	335.3	560
Butylate (Genate Plus, Suntan +)	H	CB	4006	04028	2008-41-5	217.4	8,675
Carbaryl (Sevin)[1]	I	CB	4007	82680	63-25-2	201.2	44
Carbofuran (Furandan)[1]	I	CB	4008	82674	1563-66-2	236.3	1,459
Chlorpyrifos	I	OP	4009	38933	2921-88-2	350.6	7,593
Cyanazine	H	TRI	4010	04041	21725-46-2	240.7	10,394
Dacthal (DCPA, chlorthal-dimethyl)	H	OC	4011	82682	1861-32-1	332.0	1,007
DDE, *p,p'*-	I	OC	4012	34653	72-55-9	318.0	–
Diazinon	I	OP	4013	39572	333-41-5	304.3	776
Dieldrin	I	OC	4015	39381	60-57-1	380.9	–
Diethylanaline, 2,6-	–	MET	4016	82660	579-66-8	149.2	–
Dimethoate[2]	I	OP	4017	82662	60-51-5	229.3	1,344
Disulfoton	I	OP	4018	82677	298-04-4	274.4	1,388
EPTC (Eptam)	H	CB	4019	82668	759-94-4	189.3	16,885
Ethalfluralin (Sonalan)	H	DNA	4020	82663	55283-68-6	333.3	1,597
Ethoprop (Mocap, ethoprophos)	I	OP	4021	82672	13194-48-4	242.3	743
Fonofos (Dyfonate)	I	OP	4022	04095	944-22-9	246.3	1,834
HCH, *alpha*-	I	OC	4023	34253	319-84-6	290.8	–
HCH, *gamma*- (Lindane)	I	OC	4025	39341	58-89-9	290.9	30
Linuron (Lorox, Linex)	H	UREA	4026	82666	330-55-2	249.1	1,191
Malathion	I	OP	4027	39532	121-75-5	330.3	1,447
Metolachlor (Dual)	H	AMID	4029	39415	51218-45-2	283.8	22,570
Metribuzin (Lexone, Sencor)	H	TRI	4030	82630	21087-64-9	214.3	2,189
Molinate (Ordram)	H	CB	4031	82671	2212-67-1	187.3	2,001
Napropamide (Devrinol)	H	AMID	4032	82684	15299-99-7	271.4	317
Parathion	I	OP	4033	39542	56-38-2	291.3	1,293
Parathion, methyl- (Penncap-M)	I	OP	4028	82667	298-00-0	263.2	3,692
Pebulate (Tillam)	H	CB	4034	82669	1114-71-2	203.3	296
Pendimethilan	H	DNA	4035	82683	40487-42-1	281.3	5,685
Permethrin, *cis*-	I	PYR	4036	82687	54774-45-7	391.3	509
Phorate (Thimet)	I	OP	4037	82664	298-02-2	260.4	2,171
Prometon	H	TRI	4039	04037	1610-18-0	225.3	–
Pronamide (Kerb) (Propyzamid)	H	AMID	4038	82676	23950-58-5	256.1	113
Propachlor (Ramrod)	H	AMID	4040	04024	1918-16-7	211.7	1,811
Propanil (Stampede)	H	AMID	4041	82679	709-98-8	218.1	3,412
Propargite (Omite) (alkyl sulfite)	I	MISC	4042	82685	2312-35-8	350.5	1,719
Simazine (Aquazine, Princep)	H	TRI	4043	04035	122-34-9	201.7	1,800
Tebuthiuron (Spike)	H	UREA	4045	82670	34014-18-1	228.3	276
Terbacil (Sinbar)[1]	H	URAC	4046	82665	5902-51-2	216.7	175,
Terbufos (Counter)	I	OP	4047	82675	13071-79-9	288.4	3,277
Thiobencarb (Bolero)	H	CB	4044	82681	28249-77-6	257.8	617
Triallate (Avadex BW, Far-Go)	H	CB	4049	82678	2303-17-5	304.7	1,593
Trifluralin (Treflan)	H	DNA	4050	82661	1582-09-8	335.5	12,312

[1]These pesticides are qualitatively identified and reported with an E code (estimated value) because of problems with gas chromatography or extraction.

[2]Pesticide shows small and variable recovery because of incomplete extraction. This pesticide was deleted from the method in June 1994.

The calibration range is equivalent to concentrations from 0.001 to 4.0 µg/L for most pesticides. Widely and abundantly used corn herbicides--atrazine, metolachlor, cyanazine, and alachlor--have upper concentration limits of 20 µg/L. Method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the compound concentration is greater than zero (Wershaw and others, 1987). The MDL is compound dependent and dependent on sample matrix and instrument performance and other operational sources of variation. For the listed pesticides, MDLs vary from 0.001 to 0.018 µg/L. Analytical results are not censored at the MDL; if a pesticide meets the detection criteria (retention time and mass spectra compared to that of a reference standard, as defined in section 11.1), the result is calculated and reported.

2. Summary of method

2.1 The samples are filtered at the collection site using glass-fiber filters with 0.7-µm pore diameter to remove suspended particulate matter. The procedure for filtration of samples for organic analysis is described by Sandstrom (1995). Filtered water samples are pumped through disposable, polypropylene SPE columns containing porous silica coated with an octadecyl (C-18) phase that is chemically bonded to the surface of the silica. The SPE columns are dried using a gentle stream of carbon dioxide or nitrogen to remove residual water. The adsorbed pesticides and metabolites then are removed from the SPE columns by elution with hexane-isopropanol (3:1). The eluant is further evaporated using a gentle stream of nitrogen. Extracts of the eluant are analyzed by a capillary-column GC/MS operated in the SIM mode.

3. Interferences

Organic compounds having gas-chromatographic retention times and characteristic ions with a mass identical to those of the pesticides and metabolites of interest may interfere.

4. Apparatus and instrumentation

4.1 *Cleaning and elution module for SPE columns*; Supelco, Inc., Visiprep Solid Phase Extraction Vacuum Manifold and Visidry Drying Attachment or equivalent.

4.2 *SPE pump, ceramic-piston, valveless pump*, capable of pumping 0 to 30 mL/min, with fittings for 3.18-mm outside diameter (OD) tubing; Fluid

Metering Inc., Model QSY - 2 CKC or equivalent. For on-site SPE, an SPE pump powered by a 12-V dc motor is needed; Fluid Metering Inc., Model RHB - 0 CKC or equivalent.

4.3 *Teflon-perfluoralkoxy (PFA) tubing*, 3.18-mm OD; Cole-Parmer Instrument Co., CL-06375-01 or equivalent.

4.4 *Tefzel-ethylenetetrafluoroethylene (Tefzel-ETFE) female Luer connector* with 1/4-28 thread, Tefzel-ETFE union with 1/4-28 thread, and Tefzel-ETFE nut with 1/4-28 thread and 3.18-mm OD tubing connector; Upchurch Scientific or equivalent.

4.5 *Pump control box* (optional) for 12-V dc pumps, fitted with a 4-amp fuse, toggle switch, and 10-ohm 1.58-amp variable resistor.

4.6 *Sample-preparation workstation* (optional) for cleaning SPE column; Zymark Inc., Benchmate Workstation or equivalent.

4.7 *Bottle-top solvent dispenser*, adjustable from 2 to 10 mL; Brinkman Dispensette, Van Waters & Rogers (VWR) Scientific or equivalent.

4.8 *Luer stopcocks* (optional), flow control valves or on-off valves, constructed of inert materials; Burdick & Jackson (B&J) Inert PTFE flow control valve, Baxter Diagnostics, Inc. or equivalent.

4.9 *Vacuum pump*--Any vacuum pump with sufficient capacity to maintain a slight vacuum of 1.5 to 3 kPa in the cleaning/elution module.

4.10 *Micropipets*--50- and 100-µL, fixed- and variable-volume micropipets with disposable glass capillaries; VWR Scientific or equivalent.

4.11 *Analytical balances*--Capable of accurately weighing 1,200 g ±1 g and 10.000 g ±0.001 mg. An optional procedure for weighing the SPE columns requires a balance capable of accurately weighing 10.000 g ±0.001 g.

4.12 *Fused-silica capillary column* that provides adequate resolution, capacity, accuracy, and precision. A 25-m x 0.20-mm inside diameter (ID) fused-silica capillary column coated with a 0.33-µm bonded film of polyphenylmethylsilicone was used; Hewlett-Packard Ultra II or equivalent.

4.13 *Automated solvent evaporator*--The heat-bath temperature needs to be maintained at 25°C, and the nitrogen gas pressure at 27.5 kPa (4 lb/in^2); Zymark Inc., TurboVap LV or equivalent.

4.14 *GC/MS bench-top system*; Hewlett-Packard, Model 5971 or equivalent.

4.14.1 GC conditions: Oven, 100°C (hold 5 minutes), then program to 300°C at 6°C/min, then hold for 5 minutes; injection port, 250°C; carrier gas, helium; injection volume, 2 µL, splitless injection.

4.14.2 MS conditions: Interface, 290°C; source, 200°C; analyzer, 100°C; dwell time 20 milliseconds; mass ions monitored are listed in table 2 (see section 9, Calibration).

4.14.3 The apparatus and equipment required for the automated SPE method are listed below; specific sources and models used during the development of this method also are listed, where applicable:

4.14.3.1 *AutoTrace SPE Workstation* configured for 3-mL SPE columns; Zymark Inc. or equivalent. The set-up conditions and processing steps for this method using the AutoTrace Workstation are listed in Supplement B at the end of this report.

NOTE 1: In the automated method, environmental and quality-control samples are extracted in batches of six. The time required for extraction is 58 minutes. One operator typically can process 30 samples in an 8-hour day using this apparatus.

5. Reagents and consumable materials

5.1 *Helium carrier gas* (99.999 percent) as contaminant free as possible.

5.2 *Carbon dioxide gas* for drying, ultrapure.

5.3 *Nitrogen gas* for evaporation, ultrapure.

5.4 *SPE columns* packed with 500 mg of silica coated with a chemically bonded C-18 hydrocarbon phase and end-capped to reduce polar secondary interactions associated with surface silanol groups, Isolute C-18 (EC) end-capped or equivalent; International Sorbent Technology, Ltd. or equivalent. The solid packing material is held in place with stainless-steel frits.

NOTE 2: Similar columns obtained from Varian Sample Preparation Products, Bond-Elut 1212-4025, were used during initial testing of the method but were replaced by the Isolute columns because of their superior quality (see Method Performance section).

5.5 *Test tubes*, borosilicate glass, 16 mm x 100 mm, baked at 450°C for 2 hours; Kimax Brand, VWR or equivalent.

5.6 *Glass-fiber filters*, 0.7-µm nominal pore diameter (GF/F grade), baked at 450°C for 2 hours; Whatman, Inc. or equivalent.

5.7 *Glass bottles, amber,* 1,000-mL, 33-mm neck, baked at 450°C for 2 hours, fitted with Teflon-lined screw caps; NWQL GCC or equivalent.

5.8 *Solvents*: Hexane, toluene, isopropanol, methylene chloride, and methanol; B&J Brand ultrapure pesticide quality or equivalent.

5.9 *Reagent water*, ultrapure, B&J Brand for HPLC or equivalent.

5.10 Detergent solution: Prepare a dilute mixture (0.2 percent) of laboratory-grade phosphate-free liquid detergent; Liquinox, Alconox Inc. or equivalent.

6. Sampling methods, sample-collection equipment, and cleaning procedures

6.1 *Sampling methods:* Use sampling methods capable of collecting water samples that accurately represent the water-quality characteristics of the surface water or ground water at a given time or location. Detailed descriptions of sampling methods used by the U.S. Geological Survey for obtaining depth- and width-integrated surface-water samples are given in Edwards and Glysson (1988) and Ward and Harr (1990). Similar descriptions of sampling methods for obtaining ground-water samples are given in Hardy and others (1989).

6.2 *Sample-collection equipment:* Use sample-collection equipment, including automatic samplers, that are free of tubing, gaskets, and other components made of nonfluorinated plastic material that might leach interferences into water samples or sorb the pesticides and metabolites from the water. Material suitable for sample-collection equipment includes fluorinated plastics (Teflon, ETFE), metals (stainless steel, aluminum), and ceramics.

6.3 *Cleaning procedures:* Wash all sample-collection equipment with phosphate-free detergent, rinse with distilled or tap water to remove all traces of detergent, and finally rinse with ultrapure methanol (contained in a Teflon squeeze-bottle). Clean all sample-collection equipment before each sample is collected to prevent cross-contamination of the samples.

NOTE 3: Methanol needs to be collected and disposed of in accordance with local regulations.

7. Standards

7.1 *Stock standard solutions:* Obtain the pesticides, metabolites, internal standards, and surrogates as pure materials from commercial vendors. If pure materials are obtained, prepare standard solutions of about

2,000 ng/μL by accurately weighing, to the nearest 0.001 mg, 10 mg of the pure material in a 5-mL volumetric flask and dilute with ethyl acetate. Transfer the stock solutions to clean vials and store in a refrigerator. The stock solutions are stable for about 6 months.

7.2 *Primary fortification standard solution* (stock): Prepare a 40-ng/μL concentration primary fortification standard solution by combining appropriate volumes of the individual stock standard solutions in a 2- or 5-mL volumetric flask. Use adjustable micropipet (0-50 μL or 0-100 μL) to dispense an appropriate volume into the volumetric flask and dilute with toluene. Transfer the primary fortification standard solution to a clean vial and store in a refrigerator. This solution is stable for about 6 months.

7.3 *Primary dilution standard solution* (working): Prepare low-concentration (1 ng/μL) and high-concentration (10 ng/μL) primary dilution standard solutions by combining appropriate volumes of the primary fortification standard solution in a 2- or 5-mL volumetric flask and dilute with methanol. Add a 100-μL aliquot of either primary dilution standard solution to a 1-L water sample to obtain a concentration of 0.1 or 1 μg/L for the method performance-evaluation studies.

7.4 *Polyaromatic hydrocarbon (PAH) internal standard solution* (stock): Prepare a 50-ng/μL concentration of PAH internal standard solution by combining appropriate volumes of the individual stock standard solutions of acenapthalene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} in a 2-mL volumetric flask. Use an adjustable micropipet (0-100 μL) to dispense an appropriate volume into the volumetric flask and dilute with toluene. Transfer the primary dilution standard to a clean vial and store in a refrigerator. This solution is stable for about 6 months.

7.5 *PAH internal standard solution* (working): Dilute part of the PAH internal standard stock solution to 1 ng/μL. Use an adjustable micropipet (0-100 μL) to dispense 100 μL into a 5-mL volumetric flask and dilute with toluene. Transfer the PAH internal standard solution to a clean vial and store in a refrigerator where it is stable for about 6 months.

7.6 *Surrogate solution*: Prepare a solution of Diazinon-d_{10}, *alpha*-HCH-d_6, and terbuthylazine from the stock standard solutions in methanol at a concentration of 1 ng/μL.

7.7 *Calibration solutions.* Prepare a series of calibration solutions in toluene that contain all pesticides and metabolites at concentrations from 0.01 to 40.0 ng/μL (0.01, 0.02, 0.04, 0.10, 0.20, 0.40, 1.0, 2.0, 4.0, 10, 20, 40 ng/μL) and the PAH internal standard solution at a constant concentration of 1.0 ng/μL. Prepare these calibration solutions by appropriate dilutions of the 10 and 40 ng/μL primary fortification and dilution standard solutions. For the

widely and abundantly used corn herbicides--atrazine, metolachlor, cyanazine, and alachlor--prepare a calibration solution at a concentration of 200 ng/µL and the internal standard at 1.0 ng/µL. Prepare this calibration solution by appropriate dilution of the stock standard solutions.

8. Gas chromatograph/mass spectrometer performance

8.1 Gas chromatograph performance evaluation

8.1.1 The gas chromatograph performance normally is indicated by peak shape and by the variation of the selected-compound (pesticide or metabolite) response factors relative to response factors obtained using a new capillary column and freshly prepared calibration solutions. An example of the separation and peak shape of the pesticides and metabolites is shown in a total ion chromatogram of a 1.0 ng/µL standard solution in figure 1. If peak shape deteriorates or if response factors fail to meet the calibration criteria, either change the injection liner or perform maintenance on the capillary column to bring the gas chromatograph into compliance. Part of the inlet end of the capillary column can be removed to restore performance. Specifically, a loss in response greater than 30 percent for pesticides and metabolites susceptible to loss on injection--Linuron or Carbaryl--indicates a need for immediate action.

8.2 Mass spectrometer performance evaluation

8.2.1 Check the mass spectrometer prior to analysis for the presence of water and air which indicate leaks in the vacuum. If detected, locate and fix leaks. Also, check the instrument every 24 hours during a series of analyses to ensure mass spectrometer performance according to the perfluorotributylamine (PFTBA) tuning criteria outlined below. In addition, initially adjust the mass spectrometer to ensure that the established reporting level for each selected compound can be achieved.

8.2.2 Tune the mass spectrometer daily using the procedure and standard software supplied by the manufacturer. Parameters in the tuning software are set to give ±0.15 atomic mass unit resolution at masses 69, 219, and 414 in the spectrum of PFTBA. Adjust the electron multiplier voltage to get an area of 2,000,000 counts for the mass 69 ion. Manually adjust the resolution so that the mass 69 ion has 100 percent abundance, mass 219 ion is 40±20 percent, and mass 414 ion is 6.2±5.7 percent relative abundance. Check mass assignments to ensure accuracy to ±0.15 atomic mass unit and that mass peak widths measured at one-half the peak height range from about 0.53 to 0.59 atomic mass unit.

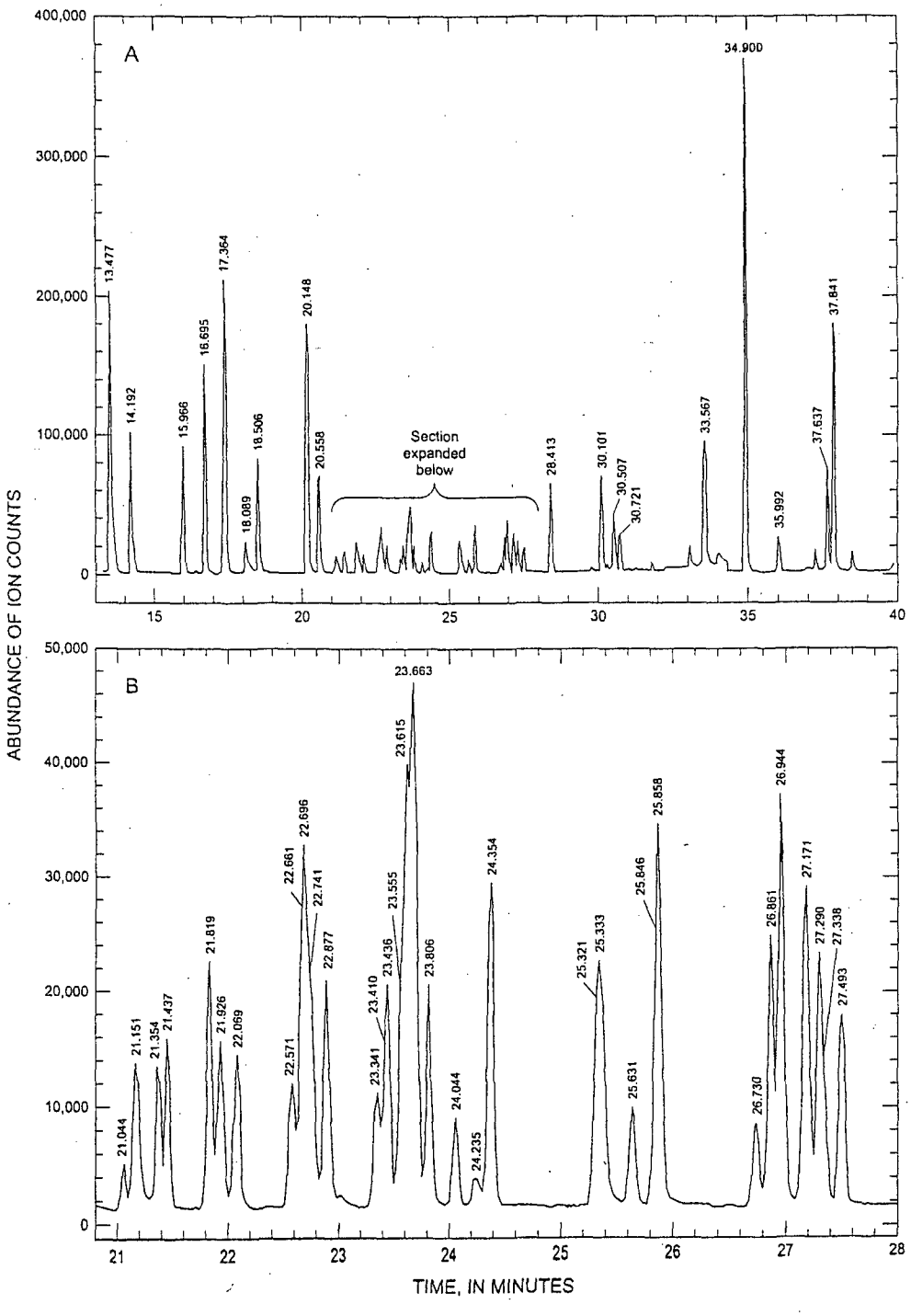


Figure 1.–A, Chromatogram of total ions of pesticides and metabolites in 1.0-nanogram-per-microliter standard solution; B, expanded view of the 21- to 28-minute time interval shown in figure 1A. Retention times shown above each peak correspond to compounds listed in table 2.

Calibration

9.1 Acquire initial calibration data by using a new capillary column and freshly prepared calibration solutions. Use these data in subsequent evaluation of the GC/MS performance.

9.2 Prior to the analysis of each sample set and every 10 samples thereafter during a series of analyses, analyze and evaluate a calibration solution (or solutions) containing all of the selected compounds to ensure that the GC/MS performance is in compliance with the established criteria.

9.3 Acquire data for each calibration solution by injecting 2 µL of each solution into the GC/MS according to the GC/MS conditions already described. Calculate the relative retention time for each selected compound and the surrogate compounds (RRT_c) in the calibration solution or in a sample as follows:

$$RRT_c = \frac{RT_c}{RT_i} \qquad (1)$$

where RT_c = uncorrected retention time of the quantitation ion of the selected compound or surrogate compound, and
RT_i = uncorrected retention time of the quantitation ion of the internal standard (acenapthalene-d_{10}, phenanthrene-d_{10}, or chrysene-d_{12}, table 2).

9.4 Calculate a response factor (RF_c) for each selected compound and the surrogate compounds in each calibration solution as follows:

$$RF_c = \frac{A_c \times C_i}{C_c \times A_i} \qquad (2)$$

where A_c = GC peak area of the quantitation ion for the selected compound or surrogate compounds;
C_i = concentration of the internal standard, in nanograms per microliter;
C_c = concentration of the selected compound or surrogate compounds, in nanograms per microliter; and
A_i = GC peak area of the quantitation ion for the internal standard.

9.5 See table 2 for the respective quantitation ions and internal-standard reference used in these calculations.

Table 2.--*Retention time, relative retention time, quantitation ion, and confirmation ions for selected compounds, surrogate compounds, and internal standards*

[Compounds are listed in order of retention time. min, minutes; m/z, mass per unit charge; IS, internal standard; --, not used]

Compound	Retention time (min)	Relative retention time	Quantitation ion (m/z)	Second confirmation ion (m/z)	Third confirmation ion (m/z)	Internal standard reference
Diethylanaline, 2,6-	13.477	0.766	134	149	119	IS1
EPTC	14.191	.817	128	132	189	IS1
Butylate	15.966	.919	146	156	174	IS1
Pebulate	16.695	.962	128	57	132	IS1
Tebuthiuron	18.089	1.042	156	171	88	IS1
Molinate	18.506	1.066	126	187	55	IS1
Ethalfluralin	20.044	.889	276	316	292	IS2
Ethoprop	20.558	.869	158	200	97	IS2
Propachlor	21.148	1.160	120	176	93	IS1
Atrazine, desethyl-	21.151	.894	172	174	187	IS2
Trifluralin	21.354	.902	306	264	248	IS2
Benfluralin	21.437	.906	292	318	264	IS2
Phorate	21.819	.922	75	121	231	IS2
HCH, *alpha-*	22.069	.933	181	183	219	IS2
Dimethoate	22.571	.954	125	87	93	IS2
Prometon	22.661	.958	210	183	225	IS2
Simazine	22.696	.959	201	186	173	IS2
Carbofuran	22.741	.961	164	149	127	IS2
Atrazine	22.877	.967	200	173	138	IS2
HCH, *gamma-*	23.341	.986	183	181	109	IS2
Terbufos	23.436	.990	153	186	231	IS2
Pronamide	23.555	.989	175	173	145	IS2
Fonofos	23.615	.997	109	137	246	IS2
Diazinon	23.805	1.006	137	179	153	IS2
Disulfoton	24.044	1.016	88	153	186	IS2
Terbacil	24.235	1.027	161	117	--	IS2
Triallate	24.354	1.029	86	268	145	IS2
Propanil	25.321	1.072	161	163	217	IS2
Metribuzin	25.333	1.072	198	199	144	IS2
Parathion-methyl	25.631	1.083	109	125	263	IS2
Carbaryl	25.846	1.092	144	115	116	IS2
Alachlor	25.858	1.093	160	188	237	IS2
Linuron	26.730	1.130	61	160	248	IS2
Malathion	26.861	1.135	173	127	125	IS2
Thiobencarb	26.944	1.139	100	257	125	IS2
Metolachlor	27.171	1.148	162	238	240	IS2
Cyanazine	27.278	1.153	225	240	173	IS2

Table 2.--*Retention time, relative retention time, quantitation ion, and confirmation ions for selected compounds, surrogate compounds, and internal standards*--Continued

Compound	Retention time (min)	Relative retention time	Quantitation ion (m/z)	Second confirmation ion (m/z)	Third confirmation ion (m/z)	Internal standard reference
Chlorpyrifos	27.290	1.153	197	199	314	IS2
Parathion	27.338	1.165	109	291	125	IS2
Dacthal	27.493	1.162	301	299	332	IS2
Pendimethalin	28.413	.814	252	281	162	IS3
Napropamide	30.101	.862	128	171	271	IS3
DDE, *p,p'*-	30.506	.874	246	248	318	IS3
Dieldrin	30.721	.880	79	263	265	IS3
Propargite	33.567	.962	135	173	81	IS3
Azimphos-methyl	35.992	1.034	160	132	77	IS3
Permethrin, *cis*-	37.637	1.078	183	163	165	IS3
		Surrogates				
HCH-d_6, *alpha*-	21.926	0.927	224	222	226	IS2
Terbuthylazine	23.412	.989	173	138	231	IS2
Diazinon-d_{10}	23.663	1.363	138	153	183	IS2
		Internal Standards				
Acenapthalene-d_{10} (IS1)	17.364	1	162	164	160	--
Phenanthrene-d_{10} (IS2)	23.663	1	188	--	--	--
Chrysene-d_{12} (IS3)	34.900	1	240	--	--	--

9.6 Initial calibration data acquired using a new capillary column and fresh calibration solutions are acceptable if the relative standard deviation is less than or equal to 35 percent for response factors calculated across the working concentration range for each selected compound or surrogate compounds.

NOTE 4: The concentration range suitable for the quantitation of pesticides and metabolites in this method is from 0.01 to 40 ng/µL, equivalent to 0.001 to 4.0 µg/L in a 1-L sample. Atrazine, alachlor, metolachlor, and cyanazine have an additional higher concentration standard solution, resulting in a high concentration quantitation limit of 20 µg/L.

9.7 Subsequent daily response factors calculated for the majority of compounds need to agree within ±20 percent of the average response factor for the selected compound of interest. Analyze at least one calibration solution with each sample set, and analyze a standard near or at the detection limit at least once weekly to verify that the detection limits are being achieved.

9.8 Add the latest response factors to prior response factors and calculate a new average response factor, provided the latest data meet the criteria given above, and the relative standard deviation for all of the response-factor data is less than or equal to 35 percent.

9.9 Calibration-curve fitting routines also can be used, provided back calculation of the calibration-standard concentration agrees within ±20 percent of the expected value.

10. Procedure

10.1 *Weighing SPE columns* (optional): Weigh the SPE columns (±0.0001 g) and record the weight on the column using waterproof ink.

NOTE 5: Recording the weight on the SPE columns helps to determine when the columns are dry after extraction and drying steps.

10.2 *Precleaning SPE columns*: Preclean the SPE columns by rinsing with 3 mL of the elution solvent (hexane-isopropanol 3:1). Allow the solvent to drain by gravity, then completely remove all solvent from the column by either nitrogen positive pressure or vacuum. Use a vacuum/elution apparatus to remove solvent by vacuum. Attach the SPE columns to the Luer-Lok fittings and twist counterclockwise to open the fittings. An optional Benchmate Workstation also can be used for automated cleaning of the columns in batches of 50. Store the clean columns in 40-mL glass vials until used.

10.3 *Precleaning extraction apparatus*: Set up the solid-phase-extraction pumping apparatus as shown in figure 2. Use a 50-mL glass graduated cylinder to contain the cleaning solutions and prevent contamination of the inlet tubing. Rinse the Teflon-PFA tubing and pump with about 50 mL of detergent solution, followed by about 100 mL of tap water and 50 mL of methanol. Turn on the pump and adjust the flow rate of the pump to 20 to 25 mL/min using a graduated cylinder to measure the volume through the SPE column. Ensure there are no leaks in any of the fittings. Keep the clean inlet tubing of the pump in the glass cylinder to avoid contamination of the tubing while preparing the sample and SPE column. For longer storage, wrap the tubing in aluminum foil.

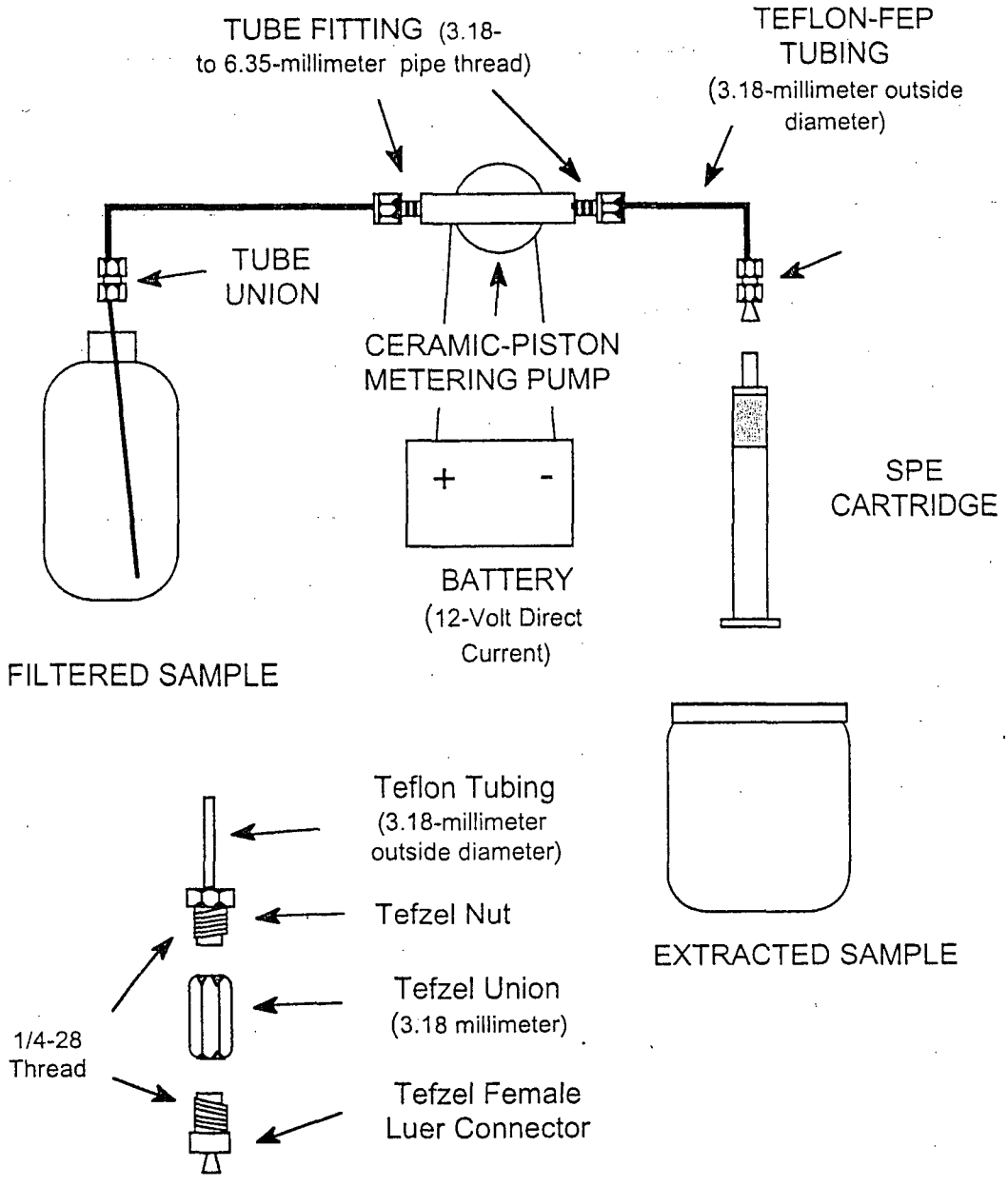


Figure 2.--Manual solid-phase-extraction pumping apparatus.

10.4 *SPE column conditioning*: Immediately before sample extraction, add 3 mL of methanol to the SPE column and allow the methanol to partially drain through the column by gravity. An optional Luer flow-control valve attached to the male Luer fitting of the SPE column can be used to control the flow of fluids through the SPE column. Conditioning is needed to solvate the C-18 phase attached to the silica particles in the SPE column. This conditioning ensures maximum interaction of the C-18 phase with the sample.

NOTE 6: Do not allow the columns to go dry once conditioning has started. Maintain levels of fluids by adding additional fluid or by closing Luer-Lok fittings or flow-control values.

10.5 *SPE column equilibration*: Replace the methanol in the SPE column with ultrapure water to equilibrate the column with the sample matrix. Add 3 mL of ultrapure water and allow the water and methanol to partially drain through the column by gravity. About 5 minutes is required for each volume of the water and methanol to drip through the column.

10.6 *Sample preparation*: Water samples must have been previously filtered (Sandstrom, 1995). Weigh the sample and bottle and record the gross sample weight (±1 g). To the sample, add methanol equivalent to 1 percent of the sample volume (about 9 mL) as a conditioner, and record the gross sample weight. Add a 100-µL aliquot of the surrogate solution (1 ng/µL) using a micropipet with a disposable glass bore. (This should result in a concentration of 0.1 µg/L for the surrogates in a 1-L sample.) Swirl the sample in the bottle to thoroughly mix.

NOTE 7: Allow surrogate and spike solutions to come to room temperature before adding to samples.

10.7 *Sample extraction*: Weigh a 1,000-mL plastic beaker that will be used to collect the volume of sample processed through the column. Place the inlet end of the Teflon-PFA tubing into the sample container, making sure tubing end is positioned in lowest spot of the bottle, and turn on the pump. After all air is displaced from the tubing, attach the SPE column to the outlet fitting of the pump tubing, and collect the sample that is pumped through the column. Ensure that there are no leaks or sources of bubbles in the system. Small bubbles might form as the sample is pumped through the tubing, but they will not cause any problems if they accumulate in the pump head. Large air bubbles are a problem because they can displace the methanol conditioner in the column or cause uneven flow through the column.

NOTE 8: To avoid contaminating the sample, do not handle the outside of the clean section of tubing that is placed in the sample bottle. A piece of tape attached to the top of the tubing helps to indicate which section of the tubing can be handled and which is clean and will be in contact with the sample.

10.8 Pump all of the sample through the SPE column and turn off the pump when completed. Disconnect the column from the pump system and remove residual interstitial water with a positive pressure of air. Weigh the extracted water sample, and record the final weight of the sample processed through the column. Discard the extracted sample, weigh the empty sample bottle, and record the tare weight.

10.9 Clean the pump and Teflon-PFA tubing with detergent solution, water, and methanol (see section 6.3) to prepare for the next sample.

10.10 *SPE column drying*: Attach a universal adapter to the large, open end of the SPE column. Next attach the adapter to the male Luer-Lok fitting on the gas-pressure module of the SPE vacuum manifold, and then dry the column using a positive pressure (138 kPa or 20 lb/in^2 for 20 minutes) of ultrapure carbon dioxide to remove all interstitial water. Ultrapure nitrogen gas also can be used to dry the column, but the drying time might be longer. Optional: Verify that all water is removed from the column by periodically weighing the column and comparing the weight to the pre-extraction weight.

NOTE 9: Do not dry the column for excessive periods of time. Pesticides and metabolites might evaporate and be removed in the gas phase.

10.11 *Elution of compounds*: Label a 16- x 100-mm culture tube with sample identification and place in a holding rack. Add 100 µL of the internal standard PAH solution (1 ng/µL) to the culture tube using a micropipet or syringe. Place the dried SPE columns in the appropriate culture tube. The open end of the SPE column rests on the edge of the culture tube, keeping the male Luer end of the SPE column raised a few centimeters above the bottom of the culture tube. Add 3 mL of HIP (3:1) to the SPE column and allow the solvent to drain by gravity into the culture tube (about 5 minutes). Air pressure (using a 50-mL glass syringe) can be used to gently force interstitial solvent remaining in the column into the vial.

10.12 *Evaporation of solvent:* Preheat the TurboVap evaporator water bath to 30°C, and adjust the gas pressure to 34.5 kPa (5 lb/in^2). Place culture tubes in the TurboVap evaporator for about 15 minutes and concentrate the eluant to about 100 µL under a gentle stream of nitrogen. Periodically check the sample volumes. At no time should the eluant be allowed to evaporate completely, because this might result in loss of compounds.

10.13 *Transfer to vials*: Using a baked disposable glass Pasteur pipet, withdraw eluant into pipet, and transfer eluant to appropriately labeled GC vial containing a 200-µL insert for GC/MS analysis.

NOTE 10: A glass syringe fitted with a short length of silicone tubing to attach the glass Pasteur pipet is the preferred procedure for withdrawing eluant into the pipet. Solvent vapors in contact with rubber or latex pipet bulbs might contaminate the eluant with plasticizers.

10.14 Rinse the culture tube with 50 µL of toluene, using a syringe to dispense the solvent, and taking care not to allow the tip of the syringe to contact the walls of the culture tube. If the tip does contact the culture tube, rinse with solvent. Vortex the culture tube, ensuring the solvent reaches the height of the original 3-mL solvent volume. Transfer the toluene rinse into the GC vial insert. Cap GC vial, and refrigerate until analysis by GC/MS.

NOTE 11: Using a pipet or squeeze bottle to rinse the culture tube is not good practice because this might result in excess solvent added and require additional evaporation.

10.15 *Sample analysis and data evaluation*: Ensure that GC/MS conditions for the analysis of the selected compounds in sample extracts are the same as those used in the analysis of the calibration solutions. Prior to the analysis of any sample extracts, ensure that the PFTBA mass-spectral performance criteria have been met, and that the selected-compound calibration data conform to the criteria set forth above. In addition, optimize the system so the reporting level for each selected compound can be achieved. Inject 2 µL of the sample extract and acquire data using the GC/MS conditions described in sections 4.14.1 and 4.14.2.

11. Calculation of results

11.1 Qualitative identification

11.1.1 The expected retention time (RT) of the GC peak of the quantitation ion for the selected compound of interest needs to be within ±6 seconds of the expected retention time based on the RRT_c obtained from the internal-standard analysis. Calculate the expected retention time as follows:

$$RT = RRT_c \times RT_i \qquad (3)$$

where RT = expected retention time of the selected compound or surrogate compound,
RRT_c = relative retention time of the selected compound or surrogate compound, and
RT_i = uncorrected retention time of the quantitation ion of the internal standard.

11.1.2 Mass-spectral verification for each selected compound is done by comparing the relative integrated abundance values of the three significant ions monitored with the relative integrated abundance values obtained from calibration solutions analyzed by the GC/MS according to procedures given above. The relative ratios of the three ions need to be within ±20 percent of the relative ratios of those obtained on injection of a 1-ng calibration solution in the absence of any obvious interferences.

11.2 Quantitation

11.2.1 Calculate the weight of sample processed as follows:

$$W = (W_a - W_c) \times \frac{W_s - W_b}{W_m - W_b} \quad (4)$$

where W = weight of sample, in grams;
W_a = weight of sample and container after SPE, in grams;
W_c = weight of container used to collect sample that passes through SPE column, in grams;
W_s = weight of bottle and sample, in grams;
W_b = weight of empty sample bottle, in grams; and
W_m = weight of sample, methanol, and bottle, in grams.

11.2.2 If a selected compound has passed the aforementioned qualitative identification criteria, calculate the concentration in the sample as follows:

$$C = \frac{C_i \times A_c \times 1000}{F_c \times A_i \times W} \quad (5)$$

where C = concentration of the selected compound or surrogate compound in the sample, in micrograms per liter;
C_i = mass of the corresponding internal standard, in micrograms per sample;
A_c = area of the quantitation ion for the selected compound or surrogate compound identified;
F_c = response factor for each selected compound or surrogate compound calculated above;
A_i = area of the quantitation ion for the internal standard; and
W = volume of the sample, in milliliters (assume 1.0 g = 1.0 mL).

11.2.3 The percent recovery of the surrogate compounds is calculated as follows:

$$R = \frac{C_i \times A_c}{RF_c \times A_i \times C_s \times V_s} \times 100 \qquad (6)$$

where R = percent recovery of the surrogate compound;
C_i = mass of the corresponding internal standard, in nanograms per sample;
A_c = area of the quantitation ion for the surrogate compound;
RF_c = response factor for the surrogate compound;
A_i = area of the quantitation ion for the internal standard;
C_s = concentration of the surrogate compound in the surrogate standard solution added to the sample, in nanograms per microliter; and
V_s = volume of the surrogate standard solution added to the sample, in microliters.

11.3 Reporting of results

This method was designed for use in studies of pesticide occurrence and transport, for which the best possible information about the presence and concentration of a pesticide is needed even if the standard error is relatively high. Consequently, results are not censored at a low reporting level. Concentrations of pesticides are reported as follows: If the concentration is less than the MDL listed in table 9, report the concentration to three significant figures, using the "E" code to alert the user that the result is less than the statistically determined MDL; if the concentration is greater than the detection limit, report the concentration to three significant figures; if the concentration is greater than the highest concentration standard, report the result as "greater than the highest standard," for example, >4 µg/L.

METHOD PERFORMANCE

A reagent-water sample, a surface-water sample collected from the South Platte River near Henderson, Colo., and a ground-water sample collected in Jefferson County, Colo. (monitoring well near building 15, Denver Federal Center) were used to test the method performance. Each of the three samples was split into 14 1-L subsamples. One set of seven subsamples was fortified with 0.1 µg/L of each compound and the other set of seven subsamples was fortified with 1.0 µg/L of each compound. In addition, unfortified samples of the surface water and ground water were extracted and analyzed to determine background concentrations of the pesticides. All subsamples were analyzed in one laboratory (the National Water Quality Laboratory) using one GC/MS.

Each sample set was extracted and analyzed on different days during September 1992, so comparison of different matrices and concentrations includes bias from day-to-day variation. Accuracy and precision data from the analyses are listed in tables 3 through 8.

Rejection of outlier samples: If the concentration of more than one replicate determination from a subsample was consistently high or low, it was assumed there was a systematic error with that sample, and the data were not included in calculating the method performance. One replicate was rejected in both the 0.1-µg/L concentration in the reagent-water data set and in the 1.0-µg/L concentration in the ground-water data set, so only six replicates were used to evaluate method performance.

Rejection of individual compound outliers: If the relative standard deviation for any concentration-matrix specific data set was greater than 10 percent, extreme values were tested as outliers using a standard Student's *t*-test (American Society for Testing and Materials, 1993). Outliers were rejected if the *t*-value exceeded the critical *t*-value [$t = 2.14$, 7 degrees of freedom, α=0.01 (99-percent confidence level)]. Using this approach, two results were rejected as outliers (tables 4 and 9).

Corrections for background concentrations: The ground-water sample did not require correction for background concentrations of compounds. The surface-water sample contained low concentrations of atrazine (0.043 µg/L), simazine (0.022 µg/L), Terbufos (0.059 µg/L), pronamide (0.074 µg/L), Diazinon (0.062 µg/L), Carbaryl (0.18 µg/L), and tebuthiuron (0.12 µg/L). These concentrations are subtracted from values determined to give corrected results in tables 5 and 6.

Method detection limits: The MDL is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the compound concentration is greater than zero (Wershaw and others, 1987). MDLs were determined according to procedures outlined by the U.S. Environmental Protection Agency (1992). Seven replicate samples of reagent water fortified at 0.1 µg/L were analyzed to determine a preliminary estimated MDL (table 3).

The MDL was calculated using the following equation:

$$MDL = S \times t_{(n-1,\ 1-\alpha=0.99)}$$

where S = standard deviation of replicate analyses, in micrograms per liter, at the lowest concentration;

n = number of replicate analyses; and

$t_{(n-1,\ 1-\alpha = 0.99)}$ = Student's *t*-value for the 99-percent confidence level with $n-1$ degrees of freedom (U.S. Environmental Protection Agency, 1992).

Table 3.--*Recovery and precision data from six determinations of the compounds at 0.1 microgram per liter in reagent water*

[conc., concentration; µg/L, microgram per liter; MDL, method detection limit; E code, estimated value; --, MDL not determined for surrogates]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)	Preliminary estimated MDL (µg/L)
Alachlor	0.086	0.003	3	86	0.009
Atrazine	.089	.005	6	89	.017
Benfluralin	.046	.004	9	46	.013
Butylate	.080	.002	3	80	.008
Chlorpyrifos	.083	.002	2	83	.005
Cyanazine	.096	.004	4	96	.013
Dacthal	.082	.001	2	82	.004
DDE, *p,p'*-	.048	.003	6	48	.010
Diazinon	.077	.002	3	77	.008
Dieldrin	.067	.003	4	67	.008
Diethylanaline, 2,6-	.073	.002	3	73	.006
Disulfoton	.072	.003	4	72	.008
EPTC	.080	.002	2	80	.005
Ethalfluralin	.054	.004	8	54	.013
Ethoprop	.080	.004	5	80	.012
Fonofos	.075	.002	3	75	.008
HCH, *alpha*-	.077	.002	3	77	.007
HCH, *gamma*-	.077	.003	4	77	.011
Linuron	.126	.012	10	126	.039
Malathion	.090	.005	5	90	.014
Metolachlor	.092	.003	3	92	.009
Metribuzin	.042	.004	9	42	.012
Molinate	.082	.002	3	82	.007
Napropamide	.083	.003	4	83	.010
Parathion	.083	.007	9	83	.022
Parathion-methyl	.073	.011	15	73	.035
Pebulate	.079	.003	4	79	.009
Pendimethalin	.046	.006	13	46	.018
Permethrin, *cis*-	.037	.005	13	37	.016
Phorate	.077	.003	4	77	.011
Prometon	.077	.003	3	77	.008
Pronamide	.076	.003	4	76	.009
Propachlor	.079	.005	6	79	.015
Propanil	.096	.005	5	96	.016
Propargite	.059	.002	3	59	.006
Simazine	.076	.003	3	76	.008
Tebuthiuron	.088	.005	6	88	.015
Terbufos	.074	.004	5	74	.012
Thiobencarb	.085	.003	3	85	.008
Triallate	.075	.003	4	75	.008
Trifluralin	.047	.004	8	47	.012

Table 3.--*Recovery and precision data from six determinations of the compounds at 0.1 microgram per liter in reagent water*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)	Preliminary estimated MDL (µg/L)
Pesticides having poor performance and reported with an E code					
Atrazine, desethyl-	0.012	0.001	8	12	0.003
Azimphos-methyl	.078	.012	15	78	.038
Carbaryl	.151	.014	10	151	.046
Carbofuran	.108	.004	4	108	.013
Terbacil	.075	.010	13	75	.030
Pesticide deleted from method in November 1994					
Dimethoate	0.011	0.008	68	11	0.024
Surrogates					
HCH-d_6, *alpha*-	0.905	0.015	2	90	--
Diazinon-d_{10}	.876	.024	3	88	--
Terbuthylazine	1.000	.022	2	100	--

Table 4.--*Recovery and precision data from seven determinations of the compounds at 1.0 microgram per liter in reagent water*

[conc., concentration; µg/L, microgram per liter; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.861	0.039	5	86
Atrazine	.840	.046	5	84
Benfluralin	.483	.033	7	48
Butylate	.769	.035	5	77
Carbaryl	2.020	.204	10	202
Carbofuran	1.261	.066	5	126
Chlorpyrifos	.784	.053	7	78
Cyanazine	.901	.047	5	90
Dacthal	.829	.046	6	83
DDE, *p,p'*-	.371	.049	13	37
Diazinon	.779	.041	5	78
Dieldrin	.600	.030	5	60
Diethylanaline, 2,6-	.694	.038	6	69
Disulfoton	.757	.034	5	76
EPTC	.780	.035	5	78
Ethalfluralin	.532	.035	7	53

Table 4.--*Recovery and precision data from seven determinations of the compounds at 1.0 microgram per liter in reagent water*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Ethoprop	0.793	0.027	3	79
Fonofos	.777	.033	4	78
HCH, *alpha*-	.739	.030	4	74
HCH, *gamma*-	.766	.032	4	77
Linuron[1]	1.173	.032	3	117
Malathion	.961	.047	5	96
Metolachlor	.891	.044	5	89
Metribuzin	.345	.018	5	35
Molinate	.753	.027	4	75
Napropamide	.718	.027	4	72
Parathion	.905	.056	6	90
Parathion-methyl	.924	.052	6	92
Pebulate	.762	.032	4	76
Pendimethalin	.521	.036	7	52
Permethrin, *cis*-	.343	.064	19	34
Phorate	.737	.028	4	74
Prometon	.671	.046	7	67
Pronamide	.842	.042	5	84
Propachlor	.786	.028	4	79
Propanil	.908	.048	5	91
Propargite	.506	.050	10	51
Simazine	.612	.033	5	61
Tebuthiuron[1]	.936	.052	6	94
Terbufos	.714	.033	5	71
Thiobencarb	.841	.047	6	84
Triallate	.733	.038	5	73
Trifluralin	.489	.033	7	49
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.091	0.006	6	9
Azimphos-methyl	.889	.051	6	89
Carbaryl	2.020	.204	10	202
Carbofuran	1.261	.066	5	126
Terbacil	.577	.032	6	58
Pesticide deleted from method in November 1994				
Dimethoate	0.052	0.005	10	5
Surrogates				
HCH-d_6, *alpha*-	0.954	0.042	4	95
Diazinon-d_{10}	1.002	.058	6	100
Terbuthylazine	1.075	.060	6	107

[1]Six replicates were used for accuracy and precision data after rejection of one concentration (linuron, 1.400 µg/L; tebuthiuron, 0.465 µg/L) as an outlier based on Student's *t*-test (American Society for Testing and Materials, 1993).

Table 5.--*Recovery and precision data from seven determinations of the compounds at 0.1 microgram per liter in surface water (South Platte River near Henderson, Colo.)*

[conc., concentration; µg/L, microgram per liter; --, no data; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.095	0.006	6	95
Atrazine[1]	.060	.007	12	60
Benfluralin	.060	.006	9	60
Butylate	.085	.010	11	85
Chlorpyrifos	.080	.008	10	80
Cyanazine	.066	.003	5	66
Dacthal	.087	.007	8	87
DDE, *p,p'*-	.045	.007	15	45
Diazinon[1]	.068	.009	13	68
Dieldrin	.062	.005	9	62
Diethylanaline, 2,6-	.067	.006	9	67
Disulfoton	.141	.005	3	141
EPTC	.083	.004	5	83
Ethalfluralin	.068	.006	9	68
Ethoprop	.096	.011	12	96
Fonofos	.073	.005	7	73
HCH, *alpha*-	.077	.005	7	77
HCH, *gamma*-	.072	.005	7	72
Linuron	.037	.002	5	37
Malathion	.085	.006	7	85
Metolachlor	.087	.004	5	87
Metribuzin	.056	.004	7	56
Molinate	.081	.004	5	81
Napropamide	.079	.004	5	79
Parathion	.068	.006	8	68
Parathion-methyl	.071	.006	8	71
Pebulate	.081	.004	5	81
Pendimethalin	.064	.004	7	64
Permethrin, *cis*-	.039	.006	16	39
Phorate	.105	.005	5	105
Prometon	.098	.011	11	98
Pronamide[1]	.046	.010	22	46
Propachlor	.082	.006	7	82
Propanil	.083	.008	10	83
Propargite	.056	.005	9	56
Simazine[1]	.058	.005	8	58
Tebuthiuron[1]	--	--	--	--
Terbufos	.046	.004	9	46
Thiobencarb	.076	.006	8	76
Triallate	.071	.005	7	71
Trifluralin	.063	.004	7	63

Table 5.--*Recovery and precision data from seven determinations of the compounds at 0.1 microgram per liter in surface water (South Platte River near Henderson, Colo.)*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.019	0.002	9	19
Azimphos-methyl	.042	.006	14	42
Carbaryl	.010	.032	335	10
Carbofuran	.119	.006	5	119
Terbacil	.125	.010	8	125
Pesticide deleted from method in November 1994				
Dimethoate	0.034	0.006	17	34
Surrogates				
HCH-d_6, *alpha*-	0.844	0.044	5	84
Diazinon-d_{10}	.851	.057	7	85
Terbuthylazine	.789	.042	5	79

[1]Corrected for background concentrations of compound in surface water.

Table 6.--*Recovery and precision data from seven determinations of the compounds at 1.0 microgram per liter in surface water (South Platte River near Henderson, Colo.)*

[conc., concentration; µg/L, microgram per liter; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.827	0.036	4	83
Atrazine[1]	.769	.028	4	77
Benfluralin	.619	.058	9	62
Butylate	.853	.023	3	85
Chlorpyrifos	.671	.040	6	67
Cyanazine	.629	.034	5	63
Dacthal	.821	.035	4	82
DDE, *p,p'*-	.397	.051	13	40
Diazinon[1]	.763	.027	4	76
Dieldrin	.577	.045	8	58
Diethylanaline, 2,6-	.738	.018	2	74
Disulfoton	.746	.020	3	75
EPTC	.861	.022	3	86
Ethalfluralin	.645	.046	7	65

Table 6.--*Recovery and precision data from seven determinations of the compounds at 1.0 microgram per liter in surface water (South Platte River near Henderson, Colo.)*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Ethoprop	0.835	0.028	3	84
Fonofos	.738	.019	3	74
HCH, *alpha*-	.654	.016	2	65
HCH, *gamma*-	.756	.022	3	76
Linuron	.257	.023	9	26
Malathion	.761	.037	5	76
Metolachlor	.880	.033	4	88
Metribuzin	.430	.017	4	43
Molinate	.845	.024	3	85
Napropamide	.803	.010	1	80
Parathion	.680	.032	5	68
Parathion-methyl	.619	.030	5	62
Pebulate	.864	.023	3	86
Pendimethalin	.647	.054	8	65
Permethrin, *cis*-	.316	.047	15	32
Phorate	.742	.018	2	74
Prometon	.670	.061	9	67
Pronamide[1]	1.147	.040	3	115
Propachlor	.816	.035	4	82
Propanil	.770	.031	4	77
Propargite	.566	.067	12	57
Simazine[1]	.657	.028	4	66
Tebuthiuron[1]	.653	.060	9	65
Terbufos	.696	.025	4	70
Thiobencarb	.761	.029	4	76
Triallate	.703	.022	3	70
Trifluralin	.635	.057	9	64
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.100	0.006	6	10
Azimphos-methyl	.233	.024	10	23
Carbaryl	.747	.039	5	75
Carbofuran	.925	.031	3	93
Terbacil	.833	.027	3	83
Pesticide deleted from method in November 1994				
Dimethoate	0.066	0.009	14	7
Surrogates				
HCH-d_6, *alpha*-	0.771	0.025	3	77
Diazinon-d_{10}	.809	.053	6	81
Terbuthylazine	.739	.039	5	74

[1]Corrected for background concentrations of compound in surface water.

Table 7.--*Reocvery and precision data from seven determinations of the compounds at 0.1 microgram per liter in ground water (Denver Federal Center Well 15)*

[conc., concentration; µg/L, microgram per liter; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.089	0.003	3	89
Atrazine	.079	.002	3	79
Benfluralin	.045	.005	10	45
Butylate	.077	.003	3	77
Chlorpyrifos	.074	.005	6	74
Cyanazine	.079	.003	4	79
Dacthal	.079	.003	4	79
DDE, *p,p'*-	.051	.012	23	51
Diazinon	.070	.002	3	70
Dieldrin	.063	.008	13	63
Diethylanaline, 2,6-	.065	.003	4	65
Disulfoton	.132	.003	2	132
EPTC	.077	.001	2	77
Ethalfluralin	.043	.003	7	43
Ethoprop	.073	.003	4	73
Fonofos	.065	.002	3	65
HCH, *alpha*-	.070	.002	2	70
HCH, *gamma*-	.076	.003	4	76
Linuron	.042	.006	14	42
Malathion	.072	.004	5	72
Metolachlor	.082	.004	4	82
Metribuzin	.041	.003	6	41
Molinate	.082	.003	4	82
Napropamide	.080	.005	6	80
Parathion	.054	.004	7	54
Parathion-methyl	.047	.002	5	47
Pebulate	.079	.003	3	79
Pendimethalin	.046	.005	11	46
Permethrin, *cis*-	.040	.009	23	40
Phorate	.089	.003	4	89
Prometon	.050	.002	4	50
Pronamide	.098	.004	4	98
Propachlor	.083	.004	4	83
Propanil	.073	.003	4	73
Propargite	.055	.006	11	55
Simazine	.073	.003	4	73
Tebuthiuron	.071	.002	3	71
Terbufos	.094	.005	5	94
Thiobencarb	.074	.003	4	74
Triallate	.067	.003	4	67
Trifluralin	.044	.004	9	44

Table 7.--*Recovery and precision data from seven determinations of the compounds at 0.1 microgram per liter in ground water (Denver Federal Center Well 15)*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.014	0.001	6	14
Azimphos-methyl	.054	.005	9	54
Carbaryl	.094	.007	8	94
Carbofuran	.100	.005	5	100
Terbacil	.110	.005	5	110
Pesticide deleted from method in November 1994				
Dimethoate	0.025	0.005	21	25
Surrogates				
HCH-d_6, *alpha*-	0.824	0.030	4	82
Diazinon-d_{10}	.998	.035	4	100
Terbuthylazine	.853	.025	3	85

Table 8.--*Recovery and precision data from six determinations of the compounds at 1.0 microgram per liter in ground water (Denver Federal Center Well 15)*

[conc., concentration; µg/L, microgram per liter; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.893	0.034	4	89
Atrazine	.766	.027	4	77
Benfluralin	.568	.050	9	57
Butylate	.699	.011	2	70
Chlorpyrifos	.690	.054	8	69
Cyanazine	.733	.045	6	73
Dacthal	.809	.045	6	81
DDE, *p,p'*-	.506	.035	7	51
Diazinon	.742	.069	9	74
Dieldrin	.624	.051	8	62
Diethylanaline, 2,6-	.639	.017	3	64
Disulfoton	.739	.037	5	74
EPTC	.697	.016	2	70
Ethalfluralin	.528	.038	7	53

Table 8.--*Recovery and precision data from six determinations of the compounds at 1.0 microgram per liter in ground water (Denver Federal Center Well 15)*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Ethoprop	0.750	0.036	5	75
Fonofos	.701	.032	5	70
HCH, *alpha-*	.586	.021	4	59
HCH, *gamma-*	.740	.041	6	74
Linuron	.330	.164	50	33
Malathion	.707	.027	4	71
Metolachlor	.786	.030	4	79
Metribuzin	.429	.020	5	43
Molinate	.736	.007	1	74
Napropamide	.732	.081	11	73
Parathion	.572	.020	4	57
Parathion-methyl	.530	.017	3	53
Pebulate	.712	.011	2	71
Pendimethalin	.550	.036	6	55
Permethrin, *cis-*	.418	.043	10	42
Phorate	.584	.016	3	58
Prometon	.459	.022	5	46
Pronamide	.996	.036	4	100
Propachlor	.762	.007	1	76
Propanil	.714	.033	5	71
Propargite	.900	.124	14	90
Simazine	.683	.023	3	68
Tebuthiuron	.532	.052	10	53
Terbufos	.605	.015	2	60
Thiobencarb	.710	.035	5	71
Triallate	.713	.039	5	71
Trifluralin	.541	.034	6	54
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.122	0.007	5	12
Azimphos-methyl	.519	.041	8	52
Carbaryl	.864	.073	8	86
Carbofuran	.881	.046	5	88
Terbacil	.763	.022	3	76
Pesticide deleted from method in November 1994				
Dimethoate	0.098	0.011	12	10
Surrogates				
HCH-d_6, *alpha-*	0.885	0.050	6	89
Diazinon-d_{10}	.934	.034	4	93
Terbuthylazine	.874	.045	5	87

Table 9.--*Method detection limit calculated from precision data for seven determinations of the compounds in reagent water fortified at initial detection limits estimated in table 3*

[MDL, method detection limit; conc., concentration, µg/L, microgram per liter; E code, estimated value]

Compound	MDL expected conc. (µg/L)	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)	Method detection limit (µg/L)
Alachlor	0.01	0.011	0.0005	4	113	0.002
Atrazine[1]	.01	.010	.0004	4	98	.001
Benfluralin	.02	.010	.0005	5	51	.002
Butylate	.01	.008	.0005	6	84	.002
Chlorpyrifos	.01	.012	.0013	11	116	.004
Cyanazine	.02	.014	.0013	9	71	.004
Dacthal	.01	.016	.0005	3	156	.002
DDE, *p,p'*-	.03	.034	.0019	6	113	.006
Diazinon	.02	.017	.0007	4	84	.002
Dieldrin	.03	.027	.0004	1	90	.001
Diethylanaline, 2,6-	.01	.005	.0010	20	47	.003
Disulfoton	.30	.247	.0053	2	82	.017
EPTC	.01	.008	.0005	6	84	.002
Ethalfluralin	.02	.020	.0013	6	102	.004
Ethoprop	.02	.017	.0010	6	84	.003
Fonofos	.02	.016	.0008	5	80	.003
HCH, *alpha*-	.03	.029	.0005	2	95	.002
HCH, *gamma*-	.03	.030	.0012	4	100	.004
Linuron	.05	.011	.0007	6	22	.002
Malathion	.03	.021	.0017	8	71	.005
Metolachlor	.01	.011	.0006	5	110	.002
Metribuzin	.04	.023	.0012	5	57	.004
Molinate	.02	.018	.0012	6	90	.004
Napropamide	.02	.025	.0010	4	124	.003
Parathion	.03	.017	.0014	8	58	.004
Parathion-methyl	.03	.014	.0018	13	46	.006
Pebulate	.03	.023	.0013	5	78	.004
Pendimethalin	.04	.017	.0014	8	42	.004
Permethrin, *cis*-	.05	.025	.0016	6	50	.005
Phorate	.02	.015	.0008	5	76	.002
Prometon	.04	.018	.0058	32	45	.018
Pronamide	.03	.021	.0010	4	71	.003
Propachlor	.01	.010	.0021	21	100	.007
Propanil	.02	.015	.0011	8	73	.004
Propargite	.04	.026	.0040	16	64	.013
Simazine	.03	.028	.0017	6	94	.005
Tebuthiuron	.03	.032	.0030	10	106	.010
Terbufos	.03	.042	.0040	10	139	.013
Thiobencarb	.03	.027	.0008	3	91	.002
Triallate	.01	.009	.0004	4	91	.001
Trifluralin	.02	.012	.0008	6	59	.002

Table 9.--*Method detection limit calculated from precision data for seven determinations of the compounds in reagent water fortified at initial detection limits estimated in table 3*--Continued

Compound	MDL expected conc. (µg/L)	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)	Method detection limit (µg/L)
Pesticides having poor performance and reported with an E code						
Atrazine, desethyl-	0.05	0.008	0.0007	8	16	0.002
Azimphos-methyl	.03	.004	.0000	0	13	.001
Carbaryl	.03	.007	.0011	15	24	.003
Carbofuran	.02	.006	.0011	18	31	.003
Terbacil	.03	.012	.0022	19	39	.007
Pesticide deleted from method in November 1994						
Dimethoate	0.07	0.013	0.0014	11	19	0.004

[1]Six determinations were used for mean concentration and standard deviation after rejection of one concentration (0.016 µg/L) as an outlier based on a Student's *t*-test (American Society for Testing and Materials, 1993).

The preliminary estimated MDLs ranged from 0.004 to 0.039 µg/L (table 3). According to the U.S. Environmental Protection Agency (1992) procedure, the fortified concentrations should be no more than five times the estimated MDL. Because the fortified concentration (0.1 µg/L) was more than five times the estimated MDLs for many of the pesticides in table 3, another MDL determination was conducted by fortifying seven replicates with the compounds at the estimated MDLs determined in table 3. The MDLs calculated from this procedure range from 0.001 to 0.018 µg/L (table 9). The MDLs in table 9 are used as the default reporting value when no peak is observed at the characteristic retention time.

The MDLs do not account for sample matrix. With clean environmental samples, it might be possible to detect compound concentrations less than the MDL; conversely, in complex samples, it might not be possible to detect compounds at concentrations greater than the MDL.

Recovery at different concentrations: For each sample matrix, samples were grouped by concentration and compared using the nonparametric Kruskal-Wallis test (reagent water) or Mann-Whitney test (ground water or surface water) to examine the null hypothesis that the mean recoveries were equal in each concentration (Miller and Miller, 1988). The *F*-test was used to compare the variance of recovery in each concentration to examine the null hypothesis that the precision was different in the two concentrations (Miller and Miller, 1988).

In reagent-water samples, mean recoveries were comparable at 1.0 µg/L (table 4), 0.1 µg/L (table 3), or 0.01 µg/L (table 9) for most compounds. For some compounds (Malathion, Parathion-methyl and pronamide), the mean recoveries were significantly lower (p <0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L set. For other compounds (cyanazine, *p,p'*-DDE, dieldrin, 2,6-diethylaniline, metribuzin, molinate, naproamide, prometon, propargite, and simazine), the mean recoveries were significantly higher (p <0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L set. These differences were relatively small (4 to 15 percent) and might also be the result of variation in instrument performance because each sample set was analyzed at different time periods. Similarly, in the 0.01-µg/L sample set (table 9), mean recoveries of some compounds (2,6-diethylaniline, chlorpyrifos, dacthal, EPTC, linuron, molinate, propachlor, prometon, propargite, Terbufos) were significantly greater (p <0.05; Kruskal-Wallis test) than in the 0.1- and 1.0-µg/L sample sets (tables 3 and 4). However, this 0.01-µg/L sample set was prepared from a different primary fortification solution than that for the 0.1- and 1.0-µg/L samples, so these differences might be the result of differences in the solution mixtures, as well as sample preparation and instrument calibration.

The average recovery and precision of all compounds in tables 3 and 4 were combined to calculate average recovery and precision in reagent water. The average short-term, single-operator precision in reagent water at the 0.1- and 1.0-µg/L level is 7 percent, and the average recovery is 73 percent. From table 9, the average precision of all compounds in reagent water at 0.01 µg/L is 8 percent, and the average recovery is 83 percent.

In the Denver Federal Center Well 15 ground-water samples, mean recoveries were comparable at 0.1-µg/L (table 7) and 1.0-µg/L (table 8) concentration levels for most compounds. As in the case of reagent water, mean recoveries of prometon and simazine were significantly higher (p <0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L sample set. A few additional compounds (disulfoton, α-HCH, phorate, tebuthiuron, Terbufos) had significantly higher recoveries (p <0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L sample set.

In surface-water samples from South Platte River, mean recoveries were comparable at 0.1 µg/L (table 5) and 1.0 µg/L (table 6) concentration levels for most compounds. As in the case of reagent-water and ground-water samples, mean recovery of prometon was significantly higher (p < 0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L sample set. Other compounds (alachlor, chlorpyrifos, disulfoton, α-HCH, ethoprop, Linuron, Malathion, metribuzin, Parathion-methyl, phorate) had significantly higher recoveries (p < 0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L sample set. In addition, the relative

standard deviations of some compounds (ethoprop, pronamide, prometon, chlorpyrifos, Diazinon) in the 0.1-µg/L sample set (table 5) were significantly higher ($p < 0.05$; *F*-test for comparison of variance) (10 to 22 percent) than in the reagent-water sample set (2 to 5 percent). Pronamide and Diazinon were among those compounds corrected for background concentration in samples from South Platte River.

Recovery in different matrices: The mean recovery of most compounds was higher in the reagent-water sample sets (tables 3, 4, and 9) compared to samples of surface water (tables 5 and 6) or ground water (tables 7 and 8). Pronamide had significantly higher recoveries ($p < 0.05$; Mann-Whitney test) (98 and 100 percent) in the Denver Federal Center Well 15 ground-water sample sets compared to reagent water (76 and 84 percent). In surface-water samples from South Platte River, mean recoveries of ethoprop and the dinitroaniline class of herbicides (benfluralin, ethafluralin, pendemethilin, trifluralin) were significantly higher ($p < 0.05$; Mann-Whitney test) (62 to 68 percent) than in reagent-water samples (46 to 54 percent).

Qualification or elimination of some compounds: A few compounds produced poor performance in all matrices and all concentrations. Dimethoate demonstrated small and variable recovery (7 to 25 percent) in all sample-matrix types as a result of breakthrough on the SPE columns. Breakthrough of Dimethoate in 10-L water samples using 10-g C-18 SPE columns was observed by Foreman and Foster (1991). This compound has the highest water solubility (20,000 mg/L) of the compounds tested, and apparently is not well retained by the C-18 phase. Breakthrough is a function of the volume of sample processed. Because the volume of sample processed is variable, the precision of this compound tends to be unacceptably high and variable. As a result of this poor performance, Dimethoate was deleted from the method in November 1994.

Desethylatrazine also demonstrated small recovery (9 to 19 percent) in all sample-matrix types because of poor retention on C-18 phase at 1-L sample volumes. However, because of the national importance of this metabolite, the compound was not deleted from the method, but the result is qualified by reporting an "E" code.

Carbofuran, Carbaryl, terbacil, and azimphos-methyl demonstrated variable performance because of problems in the GC/MS procedure, either as a result of injector or coelution and integration problems. These compounds are reported with an "E" code to qualify the result and caution the user that concentrations are estimated and need to be evaluated carefully because of variable performance. Carbofuran and Carbaryl, in particular, are subject to variable performance because of contamination of injection liners. Early method-performance evaluation (tables 3-8) was studied using Bond-Elut SPE columns that resulted in a white precipitate after elution from the SPE

column which contaminated the injection liner. Changing to Isolute SPE columns largely eliminated the precipitate and resulted in improved performance of carbofuran and Carbaryl (compared to results listed in tables 3-8). Despite the improvement in performance with the Isolute columns, these compounds are reported with an "E" code because of the potential for variable performance.

Estimated holding time: The estimated holding time of samples after extraction of the SPE column and storage at room temperature was estimated using a mathematically defined procedure (ASTM Procedure D-4841-88) (American Society for Testing and Materials, 1993). The maximum holding time is defined as the 90-percent lower confidence limit of a specified critical time. The critical time is defined as the time that a change in 10 percent of the compound concentration from day zero occurred and when precision of the method allowed that 10-percent change to be a statistically significant difference at the 90-percent confidence level.

The relative standard deviation of analysis of samples fortified at 1.0 µg/L (table 4) was used to estimate the number of samples needed to evaluate a significant change in concentration over time. The number of replicates (table 10) was calculated according to the following equation:

$$n = \left(\frac{t \times RSD}{D}\right)^2 \qquad (8)$$

where n = number of replicates;
t = Student's t-value, 3.707, based on seven replicates used in table 4;
RSD = relative standard deviation (table 4); and
D = 15 percent, maximum variation from mean to be tolerated.

For most compounds, n was less than 3 (table 10), so this value was selected for the holding-time study.

Reagent-water samples were fortified at 1.0 µg/L, extracted on day zero, and stored at room temperature. Triplicate samples were eluted from the SPE columns at discrete (3, 12, 14, and 28 days) time intervals over 28 days. All samples were analyzed in one batch at the end of the experiment. Table 10 lists the tolerable variation d, calculated from the following formula:

Table 10.--*Summary of statistical data used to determine estimated holding time of compounds on solid-phase-extraction columns held at 25 degrees Celsius*

[Reagent water samples were fortified at 1.0 µg/L, and triplicate samples were analyzed on days 3, 12, 14, and 28. *n*, number of replicates; *d*, determination; µg/L, micrograms per liter; conc., concentration; r^2, regression coefficient; --, estimated holding time could not be determined because compound did not decrease in concentration over 28-day test period; E code, estimated value]

Compound	Calculated holding time replicates (*n*)	Tolerable variation (*d*) (99 percent) (µg/L)	Extrapolated day zero conc. (µg/L)	Slope coefficient	Intercept (*d*)	Regression coefficient (r^2)	Estimated holding time (days)
Alachlor	1	0.084	1.2	-0.00195	1.083	0.07	43
Atrazine	2	.098	1.1	-.00364	.984	.15	27
Benfluralin	3	.071	.6	.00197	.541	.22	--
Butylate	1	.075	.9	-.00035	.865	.006	213
Chlorpyrifos	3	.113	1.0	-.00321	.884	.12	35
Cyanazine	2	.102	1.0	-.00792	.936	.58	13
Dacthal	2	.099	1.2	-.0027	1.090	.08	37
DDE, *p,p'*-	11	.105	.4	.01294	.283	.51	--
Diazinon	2	.087	1.0	-.01229	.952	.68	7
Dieldrin	2	.065	.9	.00717	.856	.45	--
Diethylanaline, 2,6-	2	.082	.9	-.00692	.810	.43	12
Disulfoton	1	.074	1.1	-.00694	1.055	.60	11
EPTC	1	.076	1.0	-.00039	.907	.01	194
Ethalfluralin	3	.074	.7	.00102	.620	.02	--
Ethoprop	1	.059	1.2	-.00255	1.103	.13	23
Fonofos	1	.070	1.0	-.00284	.975	.17	25
HCH, *alpha*-	1	.065	1.1	-.00241	1.030	.09	27
HCH, *gamma*-	1	.068	1.1	-.00267	1.027	.13	25
Linuron	3	.194	.4	.00111	.253	.04	--
Malathion	1	.100	1.1	-.00024	.992	.001	418
Metolachlor	2	.095	1.1	-.00265	1.039	.14	36
Metribuzin	2	.039	.4	-.00199	.395	.17	20
Molinate	1	.058	1.0	-.00205	.930	.20	28
Napropamide	1	.058	1.0	.00574	.971	.37	--
Parathion	2	.119	1.0	-.00145	.876	.04	82
Parathion-methyl	2	.112	1.0	-.00259	.866	.18	43
Pebulate	1	.068	1.0	-.00095	.899	.05	71
Pendimethalin	3	.077	.7	.00697	.641	.49	--
Permethrin, *cis*-	21	.136	.2	.00749	.110	.39	--
Phorate	1	.059	1.1	-.00621	1.011	.48	10
Prometon	3	.099	.7	-.00327	.641	.17	30
Pronamide	1	.089	1.1	-.00661	1.016	.30	13
Propachlor	1	.059	1.0	-.00383	.959	.44	15
Propanil	2	.104	1.2	-.00232	1.087	.23	45
Propargite	6	.107	.6	-.00844	.524	.46	13
Simazine	2	.070	.7	-.00293	.710	.24	24
Tebuthiuron	2	.110	1.0	-.00363	.655	.24	109
Terbufos	1	.071	1.0	-.00576	.916	.60	12
Thiobencarb	2	.100	1.1	-.00177	1.011	.04	56

Table 10.--*Summary of statistical data used to determine estimated holding time of compounds on solid-phase-extraction columns held at 25 degrees Celsius*---Continued

Compound	Calculated holding time replicates (*n*)	Tolerable variation (*d*) (99 percent) (µg/L)	Extrapolated day zero conc. (µg/L)	Slope coefficient	Intercept (*d*)	Regression coefficient (r^2)	Estimated holding time (days)
Triallate	2	0.081	1.0	-0.0022	0.923	0.11	37
Trifluralin	3	.071	.6	-.00137	.568	.15	9
Pesticides having poor performance and reported with an E code							
Atrazine, desethyl-	2	0.012	0.1	-0.00006	0.093	0.002	204
Azimphos-methyl	2	.108	.7	-.00548	.600	.36	20
Carbaryl	6	.437	.7	-.00983	.219	.32	44
Carbofuran	2	.141	.6	-.00856	.469	.38	16
Terbacil	2	.069	.6	-.00798	.511	.64	9
Pesticide deleted from method in November 1994							
Dimethoate	7	0.011	0.1	-0.00121	0.080	0.57	9
Surrogates							
HCH-d_6, *alpha*-	1	0.090	1.1	-0.00132	0.965	0.03	68
Diazinon-d_{10}	2	.124	1.0	-.01247	.873	.76	10
Terbuthylazine	2	.128	1.1	-.00239	.993	.07	54

$$d = \pm \frac{t \cdot s}{\sqrt{n}} \qquad (9)$$

where d = range of tolerable variation from initial concentration;
t = Student's *t*-value, 3.707, based on seven replicates used in precision study;
s = standard deviation (table 4); and
n = 3, number of replicates.

Linear curves were fit to the data and the day-zero intercept was calculated from the regression line. The estimated *d* value, in micrograms per liter, then was subtracted from the day-zero value to give the lower tolerable range of variation from the day-zero concentration. The intercept of the linear fit of the concentration in relation to the time line with the lower tolerable range concentration gives the estimated holding time. Diazinon, terbacil, Dimethoate, phorate, Diazinon-d_{10}, and trifluralin had estimated

holding times of 10 days or less (table 10). The shortest is Diazinon at 7 days, which is the maximum allowable holding time of the SPE columns after extraction for the method.

Automation--The method is ideally suited for automation using laboratory systems to prepare samples. The method, with minor modifications, has been successfully used with an AutoTrace SPE Workstation. An example of the procedure and parameter set-up used with the AutoTrace SPE Workstation is shown in Supplement A.

On-site extraction--The method also can be used with an optional on-site extraction procedure, which allows samples to be collected and processed at remote locations. This procedure reduces potential problems of exceeding the estimated pre-extraction holding-time limit of 4 days and avoids complications and expense of overnight shipping of samples to the laboratory.

CONCLUSIONS

From the data presented in this report, SPE and determination by GC/MS is shown to be a sensitive and reliable method for the determination of low concentrations of a broad range of pesticides in water samples. This report presents a method for routine analysis of 41 pesticides and metabolites in natural-water samples. Method detection limits range from 0.001 to 0.018 µg/L. Average short-term single-operator precision in reagent-water samples is 7 percent at the 0.1- and 1.0-µg/L levels and 8 percent at the 0.01-µg/L level. Mean recoveries in reagent-water samples are 73 percent at the 0.1- and 1.0-µg/L levels and 83 percent at the 0.01-µg/L level.

Because of GC or SPE problems, five compounds (desethylatrazine, azimphos-methyl, Carbaryl, carbofuran, and terbacil) demonstrated variable performance and are reported as estimated values. One compound, Dimethoate, was deleted from the method because of variable recovery by SPE.

REFERENCES CITED

American Society for Testing and Materials, 1992, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 8-13.

_____1993, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 31-44.

Bagnati, R., Benfenati, E., Davoli, E., and Fanelli, R., 1988, Screening of 21 pesticides in water by a single extraction with C-18 silica bonded phase columns and HRGC-MS: Chemosphere, v. 17, no. 1, p. 59-65.

Battista, Massimo, DiCorcia, Antonio, and Marchetti, Marcello, 1989, Extraction and isolation of triazine herbicides from water and vegetables by a double trap tandem system: Analytical Chemistry, v. 61, no. 9, p. 935-939.

Bellar, T.A., and Budde, W.L., 1988, Determination of nonvolatile organic compounds in aqueous environmental samples using liquid chromatography/mass spectrometry: Analytical Chemistry, v. 60, no. 19, p. 2076-2083.

Brooks, M.W., Jenkins, Jeffrey, Jimenez, Miguel, Quinn, Theresa, and Clark, J.M., 1989, Rapid method for the determination of alachlor, atrazine and metolachlor in groundwater by solid-phase extraction: Analyst, v. 114, p. 405-406.

DiCorcia, Antonio, Marchetti, Marcello, and Samperi, Roberto, 1989, Extraction and isolation of phenoxy acid herbicides in environmental waters using two adsorbants in one minicartridge: Analytical Chemistry, v. 61, no. 13, p. 1363-1367.

Edwards, T.K., and Glysson, G.D., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.

Eichelberger, J.W., Behymer, T.D., and Budde, W.L., 1988, Method 525--Determination of organic compounds in drinking water by liquid-solid extraction and capillary GC/MS, *in* Methods for the determination of organic compounds in drinking water: Cincinnati, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, p. 325-356.

Fishman, M.J., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Foreman, W.T., and Foster, G.D., 1991, Isolation of multiple classes of pesticides from large-volume water samples using solid phase extraction cartridges, *in* Mallard, G.E., and Aronson, D.A., eds., U.S. Geological Survey toxic substances hydrology program--Proceedings of the technical meeting, Monterey, California, March 11-15, 1991: U.S. Geological Survey Water-Resources Investigations Report 91-4034, p. 530-533.

Gianessi, L.P., Peskin, H.M., and Puffer, C.A., 1986, A national data base of nonurban nonpoint source discharges and their effect on the Nation's water quality: Report prepared for the U.S. Environmental Protection Agency, Office of Standards and Regulations under Cooperative Agreement CR 811858-01-0, 14 p.

Gianessi, L.P., and Puffer, C.A., 1990 (revised 1991), Herbicide use in the United States: Washington, D.C., Resources for the Future, December 1990 (Revised April 1991), 128 p.

Gianessi, L.P., and Puffer, C.A., 1992a, Fungicide use in U.S. crop production: Washington, D.C., Resources for the Future, November 1992.

Gianessi, L.P., and Puffer, C.A., 1992b, Insecticide use in U.S. crop production: Washington, D.C., Resources for the Future, August 1992.

Hallberg, G.R., 1989, Pesticide pollution of groundwater in the humid United States: Agriculture, Ecosystems and Environment, v. 26, p. 299-367.

Hardy, M.A., Leahy, P.P., and Alley, W.M., 1989, Well installation and documentation and ground-water sampling protocols for the pilot National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 89-396, 36 p.

Junk, G.A., and Richard, J.J., 1988, Organics in water--Solid-phase extraction on a small scale: Analytical Chemistry, v. 60, no. 5, p. 451-454.

Leistra, M., and Boesten, J.J.T.I., 1989, Pesticide contamination of groundwater in Western Europe: Agriculture, Ecosystems and Environment, v. 26, p. 369-389.

Miller, J.C., and Miller, J.N., 1988, Statistics for analytical chemistry (2d ed.): New York, Ellis Horwood Limited, 227 p.

Sandstrom, M.W., 1989, Field method for isolation of herbicides in surface and ground water using solid-phase extraction, *in* Pederson, G.L., and Smith, M.M., eds., U.S. Geological Survey second national symposium on water quality--Abstracts of the technical sessions, Orlando, Florida, November 12-17, 1989: U.S. Geological Survey Open-File Report 89-409, p. 82.

Sandstrom, M.W., in press, Filtration of water-sediment samples for determination of organic compounds: U.S. Geological Survey Water-Resources Investigations Report 95-4105.

Sandstrom, M.W., Wydoski, D.S., Schroeder, M.P., Zamboni, J.L., and Foreman, W.T., 1992, 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.

Thurman, E.M., Meyer, M.M., Pomes, M., Perry, C.E., and Schwab, A.P., 1990, Enzyme-linked immunosorbent assay compared with GC/MS for the determination of herbicides in water: Analytical Chemistry, v. 62, no. 18, p. 2043-2048.

Timme, P.J., 1994, National Water Quality Laboratory 1994 services catalog: U.S. Geological Survey Open-File Report 94-304, 103 p.

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.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., eds., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, 80 p.

U.S. Environmental Protection Agency, 1992, Guidelines establishing test procedures for the analysis of pollutants (App. B, Part 136, Definition and procedures for the determination of the method detection limit): U.S. Code of Federal Regulations, Title 40, revised as of July 1, 1992, p. 565-567.

Supplement A--Automated Solid-Phase Extraction Procedure Using AutoTrace Workstation

Zymark AutoTrace Extraction Workstation 1.20

[mL, milliliter]

AutoTrace Extraction Procedure: 2001 CONDITIONING/EXTRACTION 9/8/94
Estimated time for samples : 57.8 minutes
Date : 8 Sep 94
Step 1: Process 6 samples using the following procedure:
Step 2: Condition column with 3 mL of METHANOL into SOLVENT WASTE
Step 3: Condition column with 6 mL of WATER into SOLVENT WASTE
Step 4: Load 1,000 mL of sample onto column
Step 5: Dry column with gas for 4 minutes
Step 6: Pause and alert operator, resume when CONTINUE is pressed
Step 7: Clean each sample path with 50 mL into SOLVENT WASTE
Step 8: Clean each sample path with 50 mL into SOLVENT WASTE
Step 9: Clean each sample path with 100 mL into AQUEOUS WASTE
Step 10: Dry column with gas for 0.1 minute
Step 11: END

Setup Parameters

[mL/min, milliliters per minute; mL, milliliter]

AutoTrace Extraction Workstation

FLOW RATES (mL/min)		SOLID-PHASE EXTRACTION PARAMETERS	
Condition flow:	25	Push delay:	2 seconds
Load flow:	25	Air factor:	0.5
Rinse flow:	25	Autowash volume:	0.00 mL
Elute flow:	5		
Condition air push:	25	WORKSTATION PARAMETERS	
Rinse air push:	25	Maximum elution volume:	12.0 mL
Elute air push:	5	Exhaust fan on:	Y Y=Yes N=No
		Beeper on:	N Y=Yes N=No

Name Solvents

Solvent 1 : Water
Solvent 2 : Methanol
Solvent 3 : Solvent 3
Solvent 4 : Solvent 4
Solvent 5 : Solvent 5

Supplement B--On-site Solid-Phase Extraction Procedure

Solid-Phase Extraction, GC/MS Analysis, Filtered Water Schedule 2010

Instructions for On-Site Processing Using Solid-Phase Extraction (SPE)

1. Gather the equipment and supplies needed for on-site SPE listed in table 11.

2. Record the precleaned SPE column type, lot number, and weight on the field form. Prepare the SPE column by conditioning with about 2 mL of methanol, followed by about 2 mL of water to remove excess methanol. Allow the methanol and water to flow by gravity through the column. AT NO TIME SHOULD THE COLUMN GO DRY ONCE CONDITIONING HAS STARTED (If it does, add methanol then water to recondition again). Maintain the water in the column bed by replacing the water that drains through, or by using an on-off valve to stop all water from draining out of the column.

3. Tare the weight of the amber glass 1-L sample bottle. Collect, split, and filter samples using appropriate procedures (Sandstrom, 1995). Collect about 1 L of the sample in the 1-L sample bottle (do not completely fill the bottle; leave about a 2-cm headspace to add conditioner and surrogate).

4. Weigh and record the amount of sample collected. Add about 10 mL of the methanol using the bottle-top dispenser. Weigh and record the sample-plus-methanol weight.

5. Add the surrogate solution (1.25 ng/µL) contained in the 2-mL amber screw-cap vial (refer to Spike Kit Instruction Manual for more detailed information on use of micropipet). Use the 100-µL micropipet and a clean glass bore. Withdraw the solution into the glass bore, then put the tip into the sample bottle, below the surface of the sample (tip the bottle on the side if needed to reach below the surface with the tip of the micropipet), and press the plunger to deliver the surrogate to the sample. Withdraw the micropipet, remove and discard the glass bore, and rinse the orange-colored Teflon tip with methanol. Swirl the sample to mix. Detailed instructions on use of the micropipet are contained in the spike kit.

6. Obtain a plastic 1-L beaker for collecting the extracted water.

7. If necessary, adjust the pump flow rate to 20 to 25 mL/min using the cleaning solutions and graduated cylinder or beaker to measure volume.

8. Insert the inlet end of the Teflon-PFA tubing from the SPE pump into the sample bottle. Turn on the pump and allow the air to be rinsed from the Teflon tubing, then attach the Luer tip of the SPE column to the outlet end of the pump tubing. Invert the column to discard any conditioning water remaining in the SPE reservoir and begin collecting extracted water that passes through the column into the plastic beaker. Pump sample through the column at 20 to 25 mL/min. After sample has been pumped through column, turn off pump, disconnect SPE column, and record final weight of sample processed through the column.

9. Remove excess water from SPE column using a syringe to blow out water. Write sample ID on side of column, and store in 40-mL glass ampule. Store columns in cool place (between 4-25°C).

CLEANING PROCEDURE

Clean all equipment after use by rinsing with a laboratory detergent (Liquinox solution, 0.2 percent), followed by rinses with about 30 mL of tap or distilled water to remove the detergent; finally, rinse with about 30 mL of methanol. Wrap all openings of cleaned material with aluminum foil.

Samples (and any materials added to samples) should contact only glass, Teflon, ceramic or stainless steel (or other metal).

QUALITY-ASSURANCE SAMPLES

Field equipment blank: Process a sample of pesticide-grade water (available from NWQL, through DENSUPL section) exactly as the samples. This includes sample bottles, compositing, splitting, and filtration equipment as well as the SPE system. Process the field-equipment blank at the start of sampling, and then after about every 10 to 15 samples. More frequent blanks are always helpful.

Field matrix spikes: Collect duplicate samples and add the 2.0-ng/µL spike solution to one sample. Use the 100-µL micropipet to add the spike solution, which is contained in a 2-mL glass vial, after about every 20 samples. Add the surrogate to every spiked sample.

FURTHER INFORMATION

Contact Frank Wiebe (EDOC - FWWIEBE; 303-467-8178), Mark Sandstrom (EDOC - SANDSTRO; 303-467-8086), or Steve Zaugg (EDOC - SDZAUGG; 303-467-8207) for additional information.

Table 11.--*Equipment and supplies required for broad spectrum pesticide analysis (Schedule 2010) by onsite solid-phase extraction*

[mm, millimeter; in., inch; mL, milliliter; SPE, solid-phase extraction; µL, microliter; g, gram; µm, micrometer; mg, milligram; L, liter; ng/µL, nanogram per microliter]

Item	Number per sample
Equipment	
Filter Unit, 147-mm diameter, aluminum, and FMI Model QB-1 CKC pump and 1/4-in. diameter convoluted Teflon tubing	1
Teflon squeeze bottle, 250 mL, for methanol	1
Valveless, piston-type metering pump for SPE; FMI Model RHB 0CKC	1
Fixed volume (100-µL) micropipet	1
Portable balance (1,200.0 g)	1
Filters, 147-mm diameter, 0.7-µm pore diameter, precleaned	1-5
Bottle-top dispenser, 1-5 mL, for methanol	1
Teflon squeeze bottle, 250 mL, for pesticide-grade water	1
Supplies	
SPE columns, Analytichem C-18, 500 mg, precleaned[1]	1
Sample bottles, 1-L, amber	1
Disposable glass bores, for 100-µL micropipet[1]	1
Surrogate mixture, 1.25 ng/µL, 2-mL vial[1]	1
Liquinox detergent, 0.2-percent solution, 4-L	1
B&J methanol, 4-L	1
B&J water, 4-L	1
Aluminum foil, roll	1
Gloves, disposable, nonpowdered, medium	1-5
Spike kit, including Instruction Manual[1]	1
Spike mixture, 1-10 ng/µL, 2-mL vial[1]	1

[1]Supplies obtained through NWQL DENSUPPL.

Solid-Phase Extraction, GC/MS Analysis, Filtered Water
Schedule 2010

Station ID or Unique Number: _____ Station Name _____
Date: _____ Time _____ Collector: _____
Telephone Number of Collector: _____
Comments: _____

NWQL INFORMATION

SPE Cartridge
Type: _____
Lot #: _____
Dry Wt.: _____ g

FIELD INFORMATION

Filter Sample 0.7-µm glass fiber filter Date filtered:_
SPE Cartridge Conditioning: Date of SPE procedure:_____
Methanol (2 mL): _____ mL
Organic-free water (2 mL): _____ mL
(DO NOT LET CARTRIDGE GO DRY ONCE CONDITIONING STARTED)

Sample
Sample + bottle: _____ g
(-) bottle tare wt.: _____ g
= Sample wt.: _____ g
Add 1% methanol: _____ mL
Sample + bottle + MeOH: _____ g

Surrogate
Solution ID: _____
Volume added: _____ µL

QA Samples - Spike Mixture
Solution ID: _____
Volume added: _____ µL

Sample through cartridge
Sample + plastic beaker: _____ g
plastic beaker: _____ g
Flow rate: Start time: _____ hr:min
Finish time: _____ hr:min

Remove excess water - Write station ID, date, time on cartridge - Store in 40-mL vial @ 4°C

NWQL INFORMATION

Lab ID: _____ Set #: _____ Date Received_____

Dry cartridge with CO_2: Date:
Pressure: _____ lb/in^2
Time: _____ min
SPE cartridge wt.: _____ g

SPE Elution Date:
add 1.8 mL HIP (3:1) _____ mL

Internal Standard (PAH-d_n mixture in toluene keeper)
Solution ID: _____
Volume added (100 µL): _____ µL

Evaporate solvent - nitrogen Date:
Pressure: _____ lb/in^2
Time: _____ min

Analysis - Instrument ID: _____ Date:

Comments:

Attachment E

ATTACHMENT E

U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY ORGANIC CHEMISTRY PROGRAM

QA/QC GUIDANCE MANUAL

SAC1

U.S. Geological Survey
National Water Quality Laboratory

Organic Chemistry Program

QA/QC Guidance Manual

TABLE OF CONTENTS

LIST OF FIGURES

TABLES

Appendices

1. Preface

1.1 Introduction

The "Organic Quality Assurance Committee" (OQAC) of the National Water Quality Laboratory (NWQL) identified two elements, Acceptance Criteria and Corrective Action, as the most critical elements to address in a comprehensive Quality Assurance/Quality Control (QA/QC) program. A subcommittee of OQAC, consisting of representatives from the Organic Program (including all supervisors), Quality Management Program staff, Method Research and Development staff, and the Chief Chemist of the WRD, was formed in 1996 to prepare a guidance document setting acceptance criteria and corrective actions for Organic Program analyses. Contributing authors of this document include Mike Schroeder, Brooke Connor, Ron Brenton, Duane Wydoski, Ralph White, Alan Bumgartner, Merle Shockey, Tom Maloney, Jeff Pritt, Kim Pirkey, Bill Foreman, and Pete Rogerson. The guidance document not only standardizes internal NWQL policy for setting and applying acceptance criteria and corrective action, but also fulfills requirements of auditing organizations by identifying processes and corrective action policies. Although written for the Organic Program analytical chemist, the document addresses concepts and limitations of specific QA/QC data that might prove valuable to the environmental data user as an interpretive aid.

1.2 NWQL policy for establishing acceptance criteria for organic analytical methods

In concurrence with the U.S. Geological Survey policy on collecting data of known quality, the NWQL will produce organic analytical data under controlled quality assurance and quality control conditions, including process control acceptance criteria. This document defines the policies established for the use and interpretation of QA/QC data for the Organic Program of the NWQL.

1.3 Scope and application

The guidance document is used to set acceptance criteria and to standardize corrective actions for quality control failures. It is organized such that future revisions or additions can be inserted or deleted without replacing the entire document. The document includes five parts: I) introductory material, II) quality-control design, III) introduction to acceptance criteria and corrective actions, IV) quality control acceptance criteria, establishment guidelines, and corrective actions for continuing calibration verification standards, surrogate standards, reagent spikes and method blanks, and V) the appendices containing reference materials.

2. Quality control design

The assessment of the quality of analytical data is attained through specific indicators. Currently, the Organic Program uses standard quality control samples for specific applications. Standard operating procedures (SOP) outline and document the method-specific processes and standards personnel must follow to produce comparable data over time. Instrument performance is assessed with tools such as calibration standards, continuing calibration verification standards (CCVs), performance evaluation mixes, internal standards, and method blanks. Analytical standard quality may be determined through third-party check standards, external performance audits, comparison to previous calibrations, careful gravimetric determination, and verification of measuring devices. Sample preparation may be controlled through reagent spikes, certified reference materials, method blanks, surrogate standards, and replicate samples. Data reporting and electronic data transfer are verified through second- and third-level review by qualified personnel. If any aspect of a quality control sample fails selected criteria, then troubleshooting and/or corrective actions as outlined in this document must be implemented and all affected personnel notified.

2.1 Analytical run sequence

The analytical run sequence is the order in which calibration standards, QC samples, and environmental samples are analyzed on an instrument. The order in which samples are analyzed assures the quality of the data by controlling the sources of error due to carryover and instrument performance. For example, bracketing samples with acceptable CCVs assures the analyst that calibration is accurate and precise for the enclosed samples. Analyzing a method blank and reagent spike before analyzing the samples may prevent unnecessary analysis of a ruined sample set. Checking instrument contamination periodically throughout an analytical run sequence assures the integrity of the samples by checking instrument contamination.

The analytical run sequence is minimally designed to: 1) calibrate the instrument, or 2) verify the calibration, 3) verify the accuracy of the calibration, and 4) verify that the instrument is not contaminating the samples.

A typical sequence might be:

- Calibration standards or continuing calibration verification standards (CCV)
- Performance evaluation mix (if applicable)
- Third-party check of the calibration standards
- Method blank
- Reagent spike
- Samples
- CCV
- Samples (including additional method blanks or reagent spikes)

- CCV
- Samples (including additional method blanks or reagent spikes)
- CCV
- Performance evaluation mix

The exact number of calibrants, placement of QC samples, number of samples in each bracket of CCVs, and the number of repetitions of the cycles are all method specific. Refer to individual SOP for limitations of each method for these concerns.

2.2 Types of failures

The following sections outline general concepts meant to act as guidance in the interpretation of recovery failures. Other possible scenarios may arise - consult with your supervisor or other responsible individuals for assistance in interpretation. This is intended to distinguish among the possible failure modes in order to proceed to the appropriate corrective action(s). There are five kinds of recognized failure, 1) matrix-induced, noncorrectable lab, correctable lab, process, and catastrophic.

2.2.1 **Matrix induced failure** - Failure of surrogates, internal standards or calibration check standards instrument due to degradation of the analytical instruments may be caused by the accumulation of detrimental matrix interferences or materials. If a failure is matrix-induced, then it may not be beneficial to reanalyze the guilty sample(s) unless the sample is further processed to remove the problem. It is necessary however to rerun other affected samples once the instrument has been restored to meet acceptance criteria.

Symptoms of matrix associated surrogate recovery failure:

- Surrogate recoveries in QC samples (blank, spike, etc.) indicate that the process is in control.
- Troublesome matrix indicated by results of previous analysis or other analytical method, historical site data, field notes from the ASR, or type of project.
- Sample preparation notes and / or other evidence indicate preparation or analysis problems associated with physical characteristics of the sample matrix - e.g., color, odor, viscosity, precipitation, emulsions.
- Indications during instrumental analysis of an unusual matrix - e.g., major interferences, retention time shifts, baseline perturbations, and chromatographic peak distortions.
- Inappropriate sample type submitted for the method employed.

2.2.2 Noncorrectable laboratory failure – Laboratory problems that adversely affect sample data quality, and cannot be corrected or adequately documented to recover all or part of the data are considered noncorrectable. Every effort should be made to correct the problem in order to avoid future recurrence.

Symptoms of noncorrectable laboratory failure:

- Sample preparation notes indicate errors resulting in sample / surrogate losses.
- Similar surrogate recovery failure pattern in sample(s) and blank and/or spike. Surrogate recovery failures in QC samples (blank, spike, etc.) are strong indicators, but not absolute indicators of process failure for samples, if all or most sample surrogate results are in control.
- Empty chromatogram (normal noise not present) verified by re-injection of the sample extract.
- Sample not prepared according to method / SOP.
- Evidence that the sample was stored improperly or deteriorated in storage due to faulty container or excessively long storage time.

2.2.3 Correctable laboratory failure - Laboratory problems in which sample analyte data quality is not affected are considered correctable. The preponderance of evidence implies that whatever went wrong would not negatively affect sample quality - results can be legitimately corrected and documented to recover data. An example might include a sample which was double-surrogated, exhibiting almost 200 percent surrogate recovery. Every effort should be made to correct these problems in order to avoid future recurrence before analyses continue.

Symptoms of correctable laboratory failure:

- Sample preparation notes and / or other evidence indicates that wrong or improperly prepared, stored, or expired surrogate solution was used. Other QC data are in control.
- Evidence that an incorrect amount (including none) of surrogate or internal standard solution was added to the sample(s). Incorrect amount may have been added due to out of calibration dispenser or multiple additions of the solution. Other QC data are in control.
- Identified equipment failures (e.g. injection or CCV failure) that may be corrected by reinjection or other limited reprocessing of the sample.

2.2.4 Process failure – Any failure that indicates that the representative process (as opposed to an individual sample) is out-of-control for the associated samples is considered a process failure.

Symptoms of a process failure:

- All samples and quality control samples that encountered the same process fail or err in the same direction (all high or all low - not necessarily all exceed control limits however).
- Identified equipment failure is noted.
- Process representative surrogates fail for all samples that encounter the same process.

2.2.5 Catastrophic failure - An out-of-bounds condition indicated by some QC indicator that is an unequivocal indication that sample data quality is compromised. Catastrophic-failure bounds should be predefined according to method specific issues. Catastrophic failure requires reanalysis.

2.2.6 Statistical anomaly – If QC criteria are based on a statistical diagnosis of historical performance, there is an associated probability of failure, based on the normal distribution of expected results. At the 99 percent confidence interval, 1 percent of the results will fail due to statistical anomaly even when nothing is actually wrong with the process or the controls. In methods with frequent tests or large compound lists, the frequency of failure may be often enough to expect a failure in every analytical sequence (i.e. in methods with 50 compounds, at least one will fail every other time). It is the goal of the Organic Program to limit reanalysis to the above failures, and to attempt to identify statistical anomalies by ruling out other failures.

3. Introduction to acceptance criteria and corrective actions

3.1 Acceptance criteria and corrective actions for the NWQL Organic Program

The major quality-control sample types (continuing calibration verification standards, method blanks, reagent spikes, and surrogate standards) are evaluated for process control in a similar manner. Each is quantifiable and therefore subject to statistical evaluation. Each can have tabulated results, and each can be standardized. Each has a set of acceptance criteria applied, either statistically or based on other data quality objectives, to judge acceptance or rejection of associated sample data. QC criteria are the numeric bounds used to determine the acceptability of analytical data. Criteria for the various QC sample types are typically developed from data generated from QC samples analyzed in conjunction with routine sample analyses. The data are compiled using appropriate software over a given interval based on time or data set size. Prior to implementation, the criteria are calculated and reviewed relative to prior method performance and data-quality objectives. A general goal is to use nonparametric statistics over parametric statistics to develop QC criteria as appropriate for each QC sample type. Each criterion has associated corrective actions.

3.2 Non-parametric statistics

The term non-parametric statistics refers to data evaluation methods in which no assumptions are made about the statistical distribution of the data. In particular, one does not need to test or assume that the data are normally distributed in order to apply the calculation and interpretation techniques of non-parametric statistics. Non-parametric techniques are recommended for most of the statistical calculations described in this manual because they lend themselves to easier data manipulation and more meaningful interpretation of the results. Although data for most organic analyses are normally distributed, anomalous results in a data set may skew the distribution, leading to erroneous confidence intervals and improper data interpretation. Non-parametric statistics are more resistant to perturbation by anomalous results because only the inner 50 percent of the data are used for calculations. Additionally, the median is used instead of the mean as the 'measure of central tendency'[1]. F-pseudosigma is used to express the spread of the data, analogous to the standard deviation in normal statistics. The capability to apply the non-parametric techniques recommended here is highly dependent on the software used to manipulate analytical data – if the software to apply non-parametric techniques is not available, then use the corresponding normal distribution statistical techniques (such as mean and standard deviation), or discuss with your supervisor the most appropriate course of action. See appendix B.1 for a more thorough description of non-parametric statistics.

[1] Miller, Miller, Statistics for Analytical Chemistry, Ellis Horwood Limited, 1993

4. Continuing Calibration Verification Standards (CCVs)

4.1 Definition - CCVs

Continuing calibration verification standards (CCVs) are standard solutions used in instrumental analysis to check instrument stability of all method analytes (exceptions may include multicomponent standards such as toxaphene, or method specific restrictions such as fraction appropriate mixes) in relationship to the calibration curve. CCVs are prepared from the same materials and in the same manner as calibration standards are prepared. The concentration of the CCV should be chosen to allow easy review by the analyst and is typically in the mid-range of the calibration curve.

4.2 Calculations - CCVs

Determination of whether a CCV result is acceptable is based on the comparison of the calculated result with the theoretical value, which can take the form:

$$D = 100 \times \left\{ \frac{(CCV_o - CCV_t)}{CCV_t} \right\}$$

Where:

D = percent difference from theoretical value
CCV_o = observed CCV value
CCV_t = theoretical CCV value

The actual method for the determination and evaluation of the difference from the theoretical value may differ from method to method based on the measurement and the data system used.

4.3 Application - CCVs

An analyst must bracket environmental samples in an analytical run sequence with CCVs according to the accepted analytical run sequence convention for each method (refer to the appropriate SOP). Thus, there are at least two CCV's in each analytical run sequence. Evaluation of the two CCV's that bracket a series of samples is used to determine whether the results for the bracketed environmental samples are acceptable. In general, for a given analyte detected in a sample to be properly reported, the results for that analyte in both bracketing CCV's must be within the acceptance criteria (see corrective action guidance, Table 1j). The goal for the Organic Program is to use statistical data to develop acceptance criteria, or to validate existing criteria. CCV's are used principally to evaluate quantitative reliability; they may also be used to update retention times and spectra as well as to evaluate chromatographic or other instrument performance criteria.

4.3.1 Establishing Acceptance Criteria for CCVs

The following tables list options for methods of establishing acceptance criteria. The format of these tables is repeated in this guidance document for each quality control section. Each heading (e.g. - data compilation) lists components that need to be individually defined for each method. If multiple options are listed for addressing a given topic, then the most appropriate option for a given analysis may selected. When a single option is listed, then the listed option is the standard for the Organic Program. If this option is unworkable for a specific method, then an alternate choice must be justified.

Table 1a. Data compilation – CCV
Description of the data used to develop criteria

	Option Number	Options
Composition of the QC standard material	1	CCV mix includes all method analytes at a single concentration for a given analysis. Separate mixes may be appropriate.
Data used for statistical compilation	1	Compile data for the FIRST CCV in analytical batches as defined by the accepted analytical sequence.
Options defining the size of the data set for statistical criteria	1	Sliding n; e.g. $n \geq 30$. Data may be acquired until n is reached, then determine criteria; or add/drop points, recalculate criteria with constant n.
	2	Compile all data over a defined timeframe.
	3	Provisional criteria: $7 \leq n < 30$; Accepted: $n \geq 30$
	4	Pool data for all analytes into a single data set for overall performance criteria. (Test to see how this might work.)
Dual column data considerations	1	Compile data independently for each column.
	2	Choose the lower result of the two columns

Table 1b. Multi-instrument analyses – CCV
How to handle data for multi-instrument analyses.

	Option Number	Options
Compile first CCV data for individual or pooled instrument data	1	Individual - CCV performance is an individual instrument attribute.
	2	Pooled from all instruments performing this analysis
Dual-column considerations	1	Compile first CCV data for each column separately, for each instrument or pool instruments
	2	Pool first CCV data from both columns, for each instrument or pool instruments

Table 1c. Review or Update Frequency – CCV
Interval for evaluation of QC criteria with possible update of criteria – this may coincide with the data compilation interval.

	Option Number	Options
Based on a defined time interval	1	Defined time interval, e.g., quarterly. Data should be reviewed at least annually.
Based on data set size	1	Based on sliding n, e.g. $n \geq 30$.
Other considerations	1	When significant change occurs in process that may affect data.

Table 1d. Acceptance Criteria for CCVs

Determination of QC criteria - results outside of criteria require corrective action.

	Option Number	Options
Statistical Criteria *(Goal: non-parametric statistical criteria)*	1	Base on the median and F-pseudosigma f(σ), or theoretical value (TV) and standard deviation (SD): Warning limits: Median ± 2 f(σ) Control limits: Median ± 3 f(σ) -or- Warning limits: TV ± 2 SD Control limits: TV ± 3 SD $\overline{X}$ should be within ± Z% of TV (define per method)
Initial (provisional) criteria	1	Initial criteria when developing data: control limit = (TV) ± 20% (define per method)
Maximum limits for control limit criteria	1	Maximum limits for control limit criteria (statistical or otherwise): TV ± 45%; $\overline{X}$ should be within ± Z% of TV (or evaluate by *t*-test) (define per method)
Options for dual column analyses	1	For dual column analysis, develop criteria independently for each column.
Other considerations	1	Set criteria at value determined from statistical data - change only if method changes, or other legitimate reason.
Non-statistical options	1	Fix criteria at (non-statistical) value determined from data quality objectives defined by method, project, etc.

Table 1e. Data Presentation – CCV
Options for presenting data for short and long term data evaluation.

	Option Number	Options
Graphical display options generally used for longer term interpretation	1	Plot data on control charts for all CCV compounds
	2	Plot data on control charts for key compounds
Tabular data generally used for daily, on-line evaluation.	1	Tabular recovery data for all CCV compounds

Table 1f. Outlier Test CCV
Options for outlier testing and rejection.

	Option Number	Options
Non-parametric statistics, the preferred option.	1	Use non-parametric statistical evaluation of data. Results for CCV's that have failed due to an identifiable cause (e.g. failed injection, wrong standard solution, etc.) should not be included in the data set for QC criteria calculation.
Other options if non-parametric techniques are not available.	1	Reject only if legitimate, documentable failures, e.g. failed injection, wrong standard solution, etc.
	2	For large data sets single pass reject of data outside ± 3 SD, then recalculate criteria once.

Table 1g. Corrective Action Synopsis for CCVs

	Option Number	Options
More specific information regarding corrective actions follows this table.	1	See CCV Table 1h below for actions to take for most CCV failure scenarios.
Use of data qualifiers	1	Qualify ("E") data for specific analytes whenever detected if they are documented to be chronic poor performers.
Other considerations	1	Reagent spike data are treated in the same way as environmental sample data for the purposes of CCV corrective action interpretation.
	2	If CCV fails upon rerun, qualify the results with "E", or other qualifier.

4.3.2 Evaluation of CCV data

If an analyte is detected in an environmental sample (or in a reagent spike), then the data for that analyte must be acceptable in both of the CCV's analyzed just before and after the sample in the accepted analytical sequence. If data for the analyte are out of control for either of the bracketing CCV's, then perform maintenance as necessary on the equipment to return to acceptable CCV performance, and reanalyze the affected samples according to the approved analytical sequence. If a similar CCV failure occurs upon rerunning the samples, then further reanalysis should be reconsidered before proceeding to determine if the failure is an uncontrollable matrix effect. Depending on the severity of the failure, qualify these results with "E" (estimated value), delete the results due to interference, or use some other appropriate qualifier. If analytes are not detected and a CCV failure occurs, reanalysis is generally not required, unless there is a loss of detection capability. See table 1i for a summary of sample data interpretation guidance relative to CCV results. Exceptions to rerunning include failures in a CCV due to statistical anomaly (see 4.3.3) and permanently qualified compounds (flakes). Analyst judgment and knowledge of the performance characteristics of the method compounds are important components of the decision-making process.

If a CCV analyte is outside of current control limits, refer to table 1h for data-reporting strategies.

Table 1h. CCV corrective action summary[1]
[read as a control chart. Substitute the correct acceptance criteria if other than two and three f-psuedosigma are used (e.g. – if standard deviation or other criteria are used instead). f(σ), f-pseudosigma; TV, true value]

	No Analytes Detected In the samples	Analyte(s) Detected In the samples
Control Limits + 3 f(σ) ▼	**Report Data[2] Investigate cause**	***RERUN***[3]
Warning Limits + 2 f(σ) ▼	**Report Data**	**Report Data, Document**[4]
▲ TV (= $\overline{X}$) ▼	**Acceptable Results**	
▲ — 2 f(σ) Warning Limits	**Report Data**	**Report Data, Document**
▲ — 3 f(σ) Control Limits	***RERUN***[5]	***RERUN***

2. Corrective action must be considered in the context of other QC data and the historical performance of the method and equipment; check with supervisor when in doubt. The supervisor may determine that other corrective action is necessary. Criteria that have been derived by non-statistical means should be interpreted in the same fashion as control limits (±3 f(σ)).
3. This failure mode may be indicative of a method, equipment or other problem requiring attention if it occurs frequently and/or the results are significantly out of bounds.
4. Perform maintenance as necessary on equipment to return to acceptable performance (may require recalibration), reanalyze only affected samples (extracts), with bracketing CCV's according to approved analytical sequence.

5. Documentation may entail the use of qualifiers on the data review checklist, or elsewhere in the data packet.
6. If a test standard is analyzed to demonstrate that the minimum report level can be determined, then rerun of the affected samples may not be required. For dual-column chromatography methods analytes must be detected in the low level test standard on both columns.

4.3.2.1 Interpretation of CCV data for dual-column GC

Interpretation of dual-column chromatography data is based on the convention that the lower of the two results for an environmental sample is reported. Table 1i is a synopsis of the corrective action for dual-column chromatographic analysis in which the CCV failure occurs on column A whereas the result for column B is acceptable. To correctly interpret this situation, the analyst must determine if the failure mode is out-of-control high or out-of-control low compared to the expected result. The reason for the distinction between high and low failure is to maintain consistency with the convention of reporting the lower of the two column results. Additionally, the distinction between high and low failure is to protect against reporting bias due to CCV failure. Simultaneous CCV failure for both columns is interpreted according to the conventions in Table 1h.

Table 1i. CCV Corrective action for dual-column analyses (no interference present)

Failure mode of CCV on Column A	Column A sample	Column B sample	Corrective Action
High	High	Low	**Report B results**
High	Low	High	**Rerun**
Low	Low	High	**Rerun**
Low	High	Low	**Report B results**
Low	No Detect	Detect	**Rerun**

4.3.3 Statistical anomaly diagnosis - CCVs

For statistically-determined acceptance criteria there is a 1 percent probability (assuming the 99 percent confidence interval is used for control limits) that an individual result will be out of control, even in a "well-behaved" data set. Therefore, as the number of compounds determined in a method increases, the likelihood of a compound failure in a CCV attributable to statistical occurrence increases in proportion to the number of compounds[2]. To prevent reanalyses, the analyst must distinguish statistical failures from process failures.

The following may be indicative of a statistically anomalous out-of-control CCV:

- The CCV failure is marginal and observed on a normally stable key compound
- The CCV failure is not indicative of process failure (see 2.2.3)
- The compound does not fail CCV criteria frequently (statistically approximately 1 in 100 determinations), and it is not a canary (see the glossary, appendix A).

The following are examples of CCV indicated process-failures and may not (even if within the permissible number of compounds to fail CCV criteria, table 1j) be construed as statistically anomalous:

- Instrumental degradation of labile compounds
- Instrumental enhancement of signal
- Calibration changes
- Loss of resolution

If acceptance criteria are not statistically derived, then the evaluation for statistically anomalous results does not apply.

Table 1j provides a description of the number of allowable analyte failures in a CCV that may be considered a statistically anomalous condition, given the above guidelines:

Table 1j. Maximum permissible number of compounds to fail per CCV

Number of analytes determined in a method	Permissible number of failed analytes
1-5	0
6-20	1
>20	≤ 5%

[2] Provost, Elder, "Choosing Cost Effective QA/QC Programs for Chemical Analysis", USEPA report no. EPA/600/4-85/056, 1985.

If a CCV failure is determined to be a statistical CCV failure, then report sample results and document conclusions in the data packet – reanalysis is not necessary. Note that if the failure is unequivocally determined to be a statistically anomalous failure, then it is not necessary to consider whether analytes are present in any associated samples. Also, note that a statistical anomaly should be rare. If the CCV failure is not due to a statistical failure, then determine corrective actions according to Table 1h, "CCV Corrective Action Summary".

5. Surrogate standards

5.1 Definition – Surrogate standards

Surrogates are compounds similar in physical and chemical properties to the compounds of interest in a given method and are therefore expected to behave similarly. Surrogates are added to all environmental samples, reagent spikes, blanks and other relevant quality control samples at a specific point in the process to monitor process performance. A surrogate is a compound not normally found in environmental samples and might be isotopically labeled fluorinated or brominated. The number of surrogate compounds used varies with each method; surrogates are not used in gross non-chromatographic methods such as total phenols or organic carbon determinations. Surrogate solutions are prepared and added to samples independently of other spike solutions. Implementation of new surrogate solutions should be kept in synchrony with calibration standards in order to avoid undesirable data shifts. Concentration of the surrogate should be selected such that recovery losses can be clearly discerned (generally in the mid-range of the calibration curve), and to allow easy review by the analyst.

5.2 Calculations – Surrogate standards

Calculation of surrogate percent recovery is of the form:

$$R = \left(SS_o / SS_t \right) \times 100$$

Where:

R = percent recovery of surrogate standard (SS)
SS_o = observed SS value
SS_t = theoretical SS value

Statistical acceptance criteria are developed for minimum and maximum percent recovery from both the reagent spikes and from the method blank surrogate results. The actual method for the determination and evaluation of surrogate data may differ from method to method based on the measurement and the data system used.

5.3 Application – Surrogate standards

Surrogate recoveries monitor gross sample processing errors and matrix effects. Surrogate recoveries should not be used to correct analyte concentrations in samples. Changing a surrogate compound within a method is considered an SOP change and not a method change because the change will not affect sample data quality. However, the interpretation of sample data quality may be affected. Data supporting the change must be acquired and evaluated, and customers and others concerned should be informed of the ramifications.

Surrogate standards are added to every sample in a process to monitor process performance. Multiple surrogates may be added to evaluate certain failure modes indicative of whole or partial process failures. Some surrogates are used to evaluate method performance for a class of compounds. Redundant surrogates (surrogates that monitor the same function) are added to reduce the probability of out-of-control results due to statistical failure (assigned to 1 percent) rather than process failure.

In order to determine how to interpret surrogate recovery results the purpose for each surrogate must be defined according to whether it is added to –

1. Monitor the whole or a defined portion of the process.
   and
2. Represent the performance of all or a subset of specific compounds.

Specific surrogates may be required by some methods (e.g., EPA methods) for unspecified reasons. In such cases, follow the method requirements for interpretation of recovery results. If the method documentation is unclear regarding the interpretation of surrogate recovery results, assign a purpose and interpret the results according to the guidelines described here. It may also be appropriate in some cases just to monitor the performance of a surrogate without using it for any corrective action purposes. The method standard operating procedure (SOP) should contain a description of which parts of the method and which analytes are related to each surrogate.

5.3.1 Establishing acceptance criteria for surrogate standards

The following tables list options for methods of establishing acceptance criteria. The format of these tables is repeated in this guidance document for each quality control tool. Each heading (e.g. - data compilation) lists components that need to be individually defined for each method. If multiple options are listed for addressing a given topic, then the most appropriate option for a given analysis may selected. When a single option is listed, then the listed option is the standard for the Organic Program. If this option is unworkable for a specific method, then an alternate choice must be justified.

Table 2a - Data compilation – Surrogate standards
Description of the data used to develop criteria

	Option Number	Options
Composition of the QC standard material	1	Fix surrogate concentration at a single concentration for data compilation.
	2	Use of multiple surrogates inserted at various points in the sample preparation process may be desirable.
Data used for statistical compilation	1	Compile surrogate recovery data for spikes and blanks only, for statistical criteria.
Options defining the size of the data set for statistical criteria	1	Sliding n; e.g. $n \geq 30$. Data may be acquired until n is reached, then determine criteria; and/or add/drop points, recalculate criteria with constant n.
	2	Compile all data over a defined time period. (see Review/Update section).
	3	Provisional criteria: $7 \leq n < 30$; Accepted: $n \geq 30$
Dual column data considerations	1	For dual column analysis compile data independently for each column.
	2	For dual column analyses compile data from blank and spike surrogate recoveries, use the lower of the two results. Compile data into a single data set.

Table 2b - Multi-instrument analyses – Surrogate standards
How to handle data for multi-instrument analyses.

	Option Number	Options
Compile for individual or pooled instrument data	1	Compile results from individual instruments
	2	Pool results for all instruments used in the analysis.
Dual column considerations	1	For dual-column data analysis compile data independently for each column.
	2	Record lowest result of data from either column.
	3	Use results from primary column only

Table 2c - Review or Update Frequency – Surrogate standards
Interval for evaluation of QC criteria with possible update of criteria – this may coincide with the data compilation interval.

	Option Number	Options
Based on a defined time interval	1	Defined time interval, e.g. quarterly. Data should be reviewed at least annually.
	2	Use longer/shorter time intervals withdifferent evaluation purposes.
Based on data set size	1	Based on sliding $n \geq 30$ - when one data point added, oldest is deleted.
	2	Sliding block of n data points - when n new points are acquired, add to data set, delete n oldest data points.
Other considerations	1	When significant change occurs in process that may affect data.
	2	Statistically evaluate old versus new data (t, F- tests, P = 0.05) at update interval to determine whether new criteria are necessary.

Table 2d. - Acceptance Criteria for Surrogate standards

Determination of QC criteria - results outside of criteria require corrective action.

	Option Number	Options
Statistical Criteria *(Goal: non-parametric statistical criteria)*	1	Base on median (or mean) % recovery ($\bar{X}$), and F-pseudosigma (f(σ)), or standard deviation (SD):
		Warning limits: $\bar{X} \pm$ 2(f(σ)or 2 SD Control limits: $\bar{X} \pm$ 3f(σ) or 3 SD
Initial (provisional) criteria	1	± 20 percent or based on analyst judgment
Maximum limits for control limit criteria	1	Goal for control limit maximum values (statistical or otherwise): 60% ≤ $\bar{X}$ ≤120% , SD ≤15%.
Options for dual column analyses	1	Develop separate criteria for each column.
	2	Develop criteria based on the lower of the two column results.
Other considerations	1	Set criteria at values determined from statistical data - change only if method change, or other legitimate reason.
	2	Set criteria at values within (but not necessarily equivalent to) statistical data - change only if method change, or other legitimate reason.
	3	Trend analysis - see table "Test for Special Causes" in the appendix as an aid in diagnosing some types of problems. Select representative subset of analytes to test for data trends.
Non-statistical options	1	Set criteria at (possibly non-statistical) value determined from data quality objectives defined by method, project, etc.

Table 2e. - Data Presentation – Surrogate standards
Options for presenting data for short and long term data evaluation.

	Option Number	Options
Graphical display options generally used for longer term interpretation	1	Plot data on control charts for all surrogates.
	2	Precision chart - plot standard deviation.
	3	Control chart bias and precision for short and long term.
Tabular data generally used for daily, on-line evaluation.	1	Tabular recovery data for all surrogates.

Table 2f. - Outlier Test – Surrogate standards
Options for outlier testing and rejection.

	Option Number	Options
The preferred option.	1	Use non-parametric statistical evaluation of data.
Other options if non-parametric techniques are not available.	1	Reject only if legitimate, documentable failure, e.g. failed injection, wrong standard solution, etc.
	2	For large data sets single pass reject of data outside ± 3 SD, then recalculate criteria once.

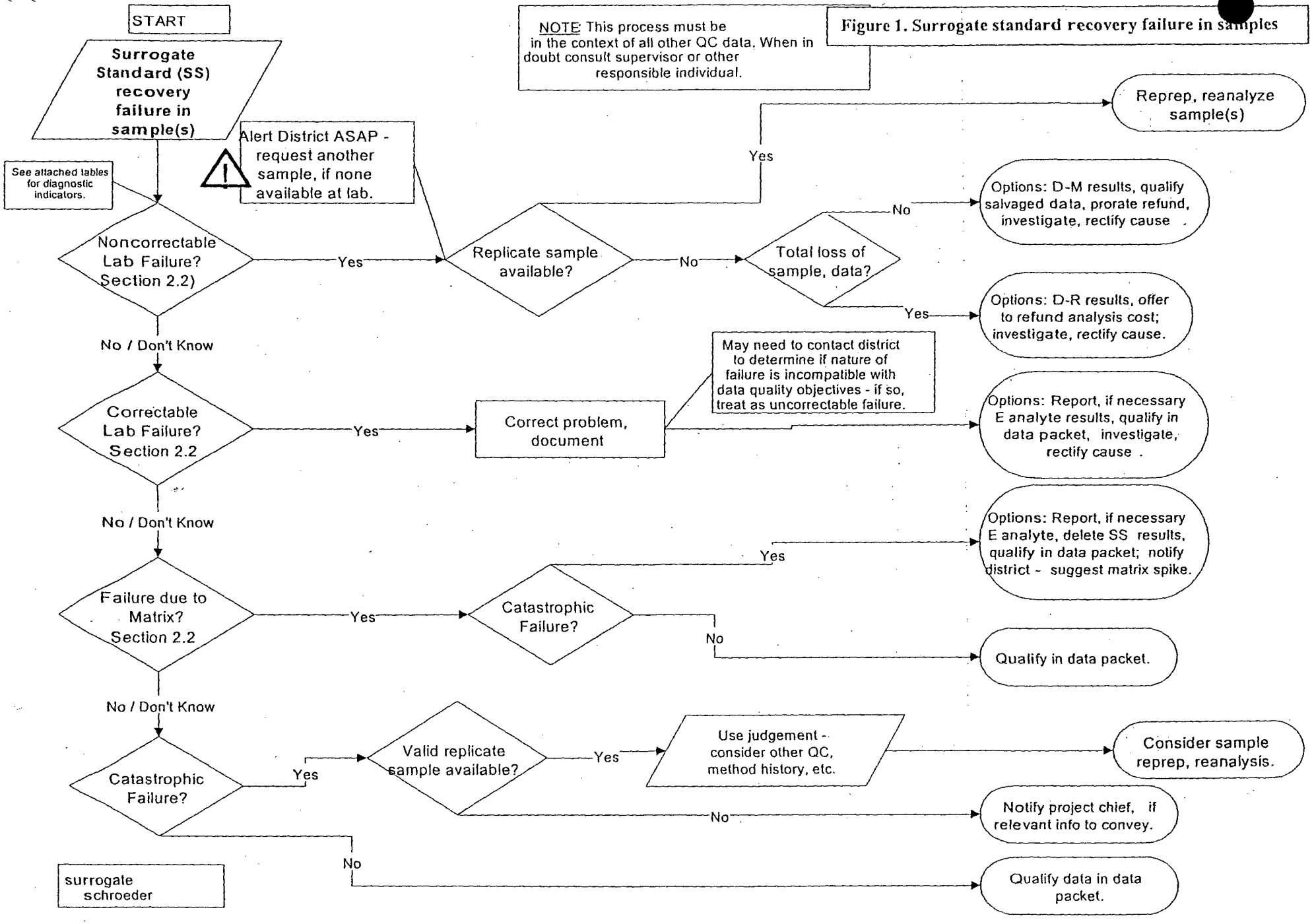
Table 2g. Corrective Action Synopsis – Surrogate standards

	Option Number	Options
More specific information regarding corrective actions follows this table.	1	See the enclosed flow chart and table for corrective action for most surrogate recovery failure scenarios.
Use of data qualifiers	1	Do not use "E" (estimated value qualifier) for surrogate results unless quantitation is questionable.
Other considerations	1	Do not raise analyte report levels corresponding to low surrogate recoveries. (Report levels may need to be adjusted for other reasons that result in low surrogate, like spills, but not solely for low surrogate recoveries).

5.3.2 Surrogate recovery failure evaluation

Surrogate recovery failure is defined as recovery of any surrogate outside of (≥ or ≤) the defined control limits. The accompanying flowchart (fig. 1) provides a description of the surrogate recovery failure evaluation process. The corrective action options described on the right side of the flowchart depend on the nature and scope of the surrogate recovery failure – whether the failure is due to a known correctable or noncorrectable lab failure, or matrix effect. If the cause for the failure cannot be deduced, then the degree of failure – whether catastrophic or not – is used to determine the proper corrective action.

Figure 1. Surrogate standard recovery failure in samples



5.4 Surrogate recovery process failures for methods with multiple surrogates

The following is included to assist in the interpretation of process failures for methods that incorporate the use of multiple surrogates. The definition of a process failure, when employing multiple surrogates, depends on a surrogate's assigned purpose, and the number of surrogates assigned to a given purpose. Process failure requiring corrective action is generally determined by any of the following conditions:

1. Recovery is out-of-control for a single surrogate, if only a single surrogate is assigned to represent performance for a given purpose. The process failure and resulting corrective action may apply only to the affected compounds.
2. Recoveries that are out-of-control in the same mode (high or low) for two or more surrogates assigned to the same purpose. Failure of one of several surrogates at a rate greater than that anticipated due to statistical anomalies (e.g. in several samples in a set) is an indication that the surrogates do not represent the same method performance characteristics and are not valid for interpretation as redundant surrogates - a process failure may actually be indicated. General guidance for failure of redundant surrogates in different (alternating) high/low modes is not practical - method specific factors relative to the matrix must be considered.

Example:

A method has five surrogates A, B, C, D, E with the following purposes assigned:

A,B: Whole procedure, all compounds
C,D : Step 1, compounds of class "C and D"
E : Whole procedure, compound class "E"

The following are some of the interpretations that can be made relative to surrogate performance in this example:

- Entire process failure for all compounds is defined if both surrogates A and B are out of control in the same mode (high/low).
- Results for compounds of class "C and D" only are flagged as failed if both surrogates C and D are out of control in the same mode.
- Compounds of class "E" only are flagged as failed if only surrogate E recovery is out of control.

5.5 Corrective action – Surrogate standards

If a process failure is based on surrogate recovery for any or all of the compounds in a method, then follow the surrogate recovery corrective action flowchart (fig. 1) to determine what action to take. Corrective action for process failures linked to specific compounds applies only to the affected compounds.

In many cases, the use of surrogates to monitor specific method steps may be only for troubleshooting particular method problems. For the purpose of corrective action it may be irrelevant whether a specific portion of a method has failed, the interpretation is the same as though the entire method is determined to have failed.

6. Reagent spikes

6.1 Definition – Reagent spike

A reagent spike is a synthetic matrix fortified with known concentrations of all, or a representative selection of, the method compounds. The synthetic matrix usually is the same as that used in the method blank, for example, organic-free water or sodium sulfate. For interpreting the corrective action guidelines described in this document, a reagent spike failure is defined as an out of control recovery for any relevant spiked analyte. Synonyms include laboratory spike, set spike, method spike, and laboratory fortified blank (EPA drinking water methods).

Key compounds – Key compounds are reagent spike compounds whose recoveries are used to diagnose the possibility of catastrophic failure (see section 2.2) during sample processing, which may potentially affect all analytes in all samples in a set. Key compounds are generally solid performers with relatively good recovery precision and accuracy. There is ideally a correlation between key compound and surrogate standard performance such that inferences regarding sample processing may be made based on surrogate performance. In order to reduce the likelihood of statistically anomalous failures there should be at least two key compounds used to represent process performance for all, or a given class of compounds.

Flakes – Method flakes are reagent spike compounds that do not perform ideally in a given method, typically with large standard deviations, or frequent performance problems. Flakes are generally identified as compounds with mean recoveries outside of 60 – 120 percent, and/or standard deviations greater than 15 percent.

6.2 Calculations – Reagent spike

Calculation of reagent spike percent recovery is of the form:

$$R = \left({}^{RS_o}\!/_{RS_t} \right) \times 100$$

Where:

R = percent recovery of reagent spike

RS_o = observed reagent spike concentration

RS_t = theoretical reagent spike concentration

Statistical acceptance criteria are developed for minimum and maximum percent recovery. The actual method for the determination and evaluation of reagent spike data may differ from method to method based on the measurement and the data system used.

6.3 Application – Reagent spike

The reagent spike is used to monitor performance over the entire method. The reagent spike verifies the method accuracy of each sample set. Over time, analysis of many reagent spike samples provides method precision data. The results of the reagent spike should be reported to the database as percent recovery. Reagent spike recoveries should not be used to correct analyte concentrations in environmental samples.

The reagent spike solution should be from the same stock as the method calibration solutions and prepared at similar times in order to prevent data shifts. Field and lab projects that require a field spike should use the same reagent spike solution, and reagent spike solution lot numbers should be kept synchronous between lab and field as much as possible.

One reagent spike is required per set of processed samples or as required by the method. Reagent spike concentration should be set at the range of minimum method variability and such that recovery losses can be clearly discerned - usually around the mid-calibration point for the method.

6.3.1 Establishing acceptance criteria for reagent spikes

The following tables list options for methods of establishing acceptance criteria. The format of these tables is repeated in this guidance document for each quality control tool. Each heading (e.g. - data compilation) lists components that need to be individually defined for each method. If multiple options are listed for addressing a given topic, then the most appropriate option for a given analysis may selected. When a single option is listed, then the listed option is the standard for the Organic Program. If this option is unworkable for a specific method, then an alternate choice must be justified.

Table 3a. Data compilation – Reagent spikes
Description of the data used to develop criteria

	Option Number	Options
Composition of the QC standard material	1	Fix reagent spike at single concentration for data compilation.
	2	All analytes for a given method should be contained in the reagent spike.
Data used for statistical compilation	1	All reagent spikes that did not experience a known process failure (e.g., spilled extract, didn't inject, wrong solution used)
Options defining the size of the data set for statistical criteria	1	Sliding n; e.g. $n \geq 30$. Data may be acquired until n is reached, then determine criteria; and/or add/drop points, recalculate criteria w/ constant n.
	2	Compile all data over a defined time period.
	3	Provisional criteria: $7 \leq n < 30$; Accepted: $n \geq 30$
Dual column data considerations	1	For dual column analyses compile data from results determined according to the procedure used to report sample results.
	2	For dual column analysis compile data independently for each column.

Table 3b. Multi-instrument analyses – Reagent spikes

How to handle data for multi-instrument analyses.

	Option Number	Options
Compile for individual or pooled instrument data	1	Compile results from individual instruments
	2	Pool results for all instruments used in the analysis.
Compile for individual or pooled instrument data	1	Pool results for all instruments used in the analysis.
Dual column considerations	1	For dual-column data analysis compile data independently for each column.
	2	Record lowest result of data from either column.
	3	Use results from primary column only

Table 3c. Review or Update Frequency – Reagent spikes

Interval for evaluation of QC criteria with possible update of criteria – this may coincide with the data compilation interval.

	Option Number	Options
Based on a defined time interval	1	Defined time interval, e.g. quarterly. Data should be reviewed at least annually.
	2	Use longer/shorter time intervals with different evaluation purposes.
Based on data set size	1	Based on sliding $n \geq 30$ - when one data point added, oldest is deleted.
	2	Sliding block of n data points - when n new points are acquired, add to data set, delete n oldest data points.
Other considerations	1	When significant change occurs in process that may affect data.
	2	Statistically evaluate old versus new data (t, F - tests, $P = 0.05$) at update interval to determine whether new criteria are necessary.

Table 3d. Acceptance criteria for reagent spikes

Determination of QC criteria - results outside of criteria require corrective action.

	Option Number	Options
Statistical Criteria *(Goal: non-parametric statistical criteria)*	1	Base on median or mean % recovery ($\bar{X}$), and F-pseudosigma (f(σ)or standard deviation (SD): Warning limits: $\bar{X} \pm 2$ f(σ) or SD Control limits: $\bar{X} \pm 3$ f(σ) or SD
Initial (provisional) criteria	1	Mean ± 30 percent or other limit (70-130%) based on QC objectives.
Maximum limits for control limit criteria	1	Goal for maximum values for control limit criteria (statistical or otherwise): $60\% \leq \bar{X} \leq 120\%$, SD ≥ 15%.
Options for dual column analyses	1	Dual column GC analysis - develop separate criteria for each column.
	2	Develop criteria based on the lower of the two column results
Other considerations	1	Set criteria at values determined from statistical data - change only if method change, or other legitimate reason.
	2	Trend analysis - see table "Test for Special Causes" as an aid in diagnosing some types of problems. Select representative subset of analytes to test for data trends.
Non-statistical options	1	Set criteria at (possibly non-statistical) value determined from data quality objectives defined by method, project, etc.

Table 3e. - Data Presentation – Reagent spike
Options for presenting data for short and long term data evaluation.

	Option Number	Options
Graphical display options generally used for longer term interpretation	1	Plot data on control charts for compounds that are used for control purposes.
	2	Precision chart - plot standard deviation.
	3	Control chart bias and precision short, long term for different interpretation purposes.
Tabular data generally used for daily, on-line evaluation.	1	Tabular recovery data for all analytes in the reagent spike.

Table 3f. - Outlier Test – Reagent spike
Options for outlier testing and rejection.

	Option Number	Options
The preferred option.	1	Use non-parametric statistical evaluation of data.
Other options if non-parametric techniques are not available.	1	Reject only if legitimate, documentable failures, e.g. failed injection, wrong standard solution, etc.
	2	For large data sets single pass reject of data outside ± 3 SD, then recalculate criteria once.

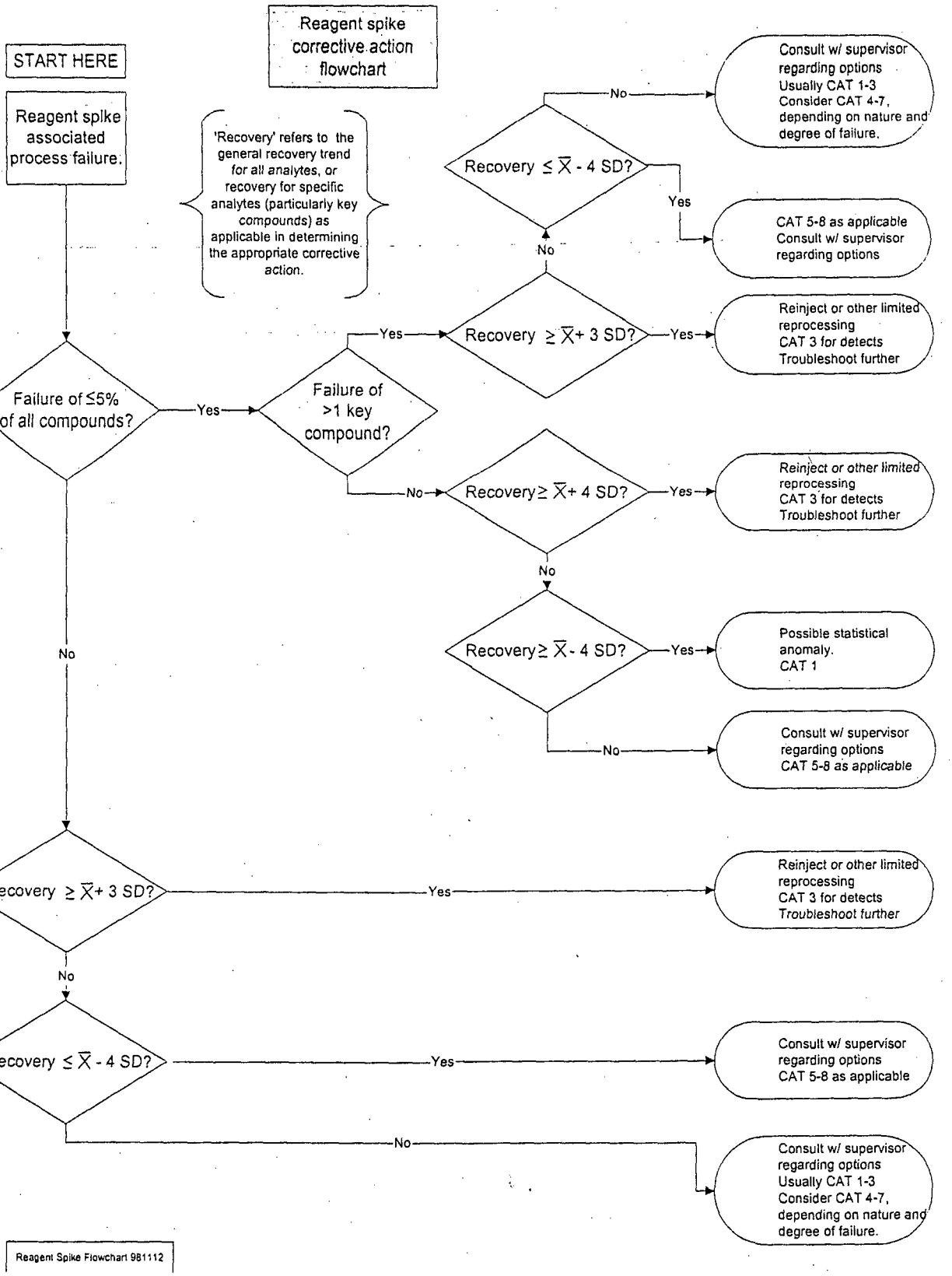
Table 3g. Corrective action synopsis – Reagent spike

	Option Number	Options
More specific information regarding corrective actions follows this table	1	See the enclosed flow chart and table for corrective action for most reagent spike recovery failure scenarios.
Use of data qualifiers	1	Do not use "E" (estimated value qualifier) for reagent spike results unless quantitation is questionable.

6.3.2 Reagent spike recovery failure evaluation

For most methods, process failures may occur that affect samples – including QC samples – independently of one another. Therefore, the ramifications of reagent spike recovery failure may be difficult to determine, particularly for multi-analyte methods. The approach described below is to first determine whether there is evidence that the process failure may have affected only the reagent spike, or correspondingly that the environmental sample data are not adversely affected (fig. 2 and tables 3h, 3i, and 3k). Ancillary QC data (particularly surrogate recoveries) and preparation notes are crucial to this evaluation. If it cannot be determined that only the reagent spike was the victim of a process failure, then the severity of the failure must be evaluated in order to determine the corrective action to take (fig. 2 and tables 3h and 3i). The recommended corrective action types (CAT) are dependent on the number and types of analytes with unacceptable recoveries, as well as the severity of the recovery failures. Key compounds are used as the primary indicators of process failure because they are selected to represent the performance of other method analytes, and their recoveries will ideally correlate well with recoveries of relevant surrogate standards so that inferences may be made regarding the possible effects on samples.

Figure 2. – Reagent spike corrective action flowchart



Sections 6.3.2.1 and 6.3.2.2 below are to be used with the reagent spike recovery failure flowchart. These are general concepts meant to act as guidance in the interpretation of reagent spike recovery failures. Other possible scenarios may arise - consult with your supervisor or other responsible individuals for assistance in interpretation. This is intended to distinguish among the possible reagent spike recovery failure modes in order to proceed to the appropriate corrective action(s). The fundamental distinction to be made is whether the failure is indicative of a process error associated only with the reagent spike, or a process failure affecting sample data quality.

6.3.2.1 Direct evidence of reagent spike only failure

Direct evidence of laboratory process problems in which the preponderance of evidence indicates that only the results of the reagent spike are affected and that sample data quality is not adversely affected. Reagent spike results may legitimately be corrected and documented to recover data, or deleted if the data are inappropriate for storage in the reagent spike recovery database. Every effort should be made to correct the problem in order to avoid future recurrence. Examples of evidence include:

- Sample preparation notes and/or other evidence indicate that improperly prepared, stored, or expired reagent spike solution was used. Other QC data are in control.
- Evidence that an incorrect amount (including none) of the reagent spike or internal standard solution was added to the spike matrix. An incorrect amount may have been added due to an out of calibration dispenser or multiple additions of the solution. Other QC data are in control.
- Identified equipment failures (e.g. injection or CCV failure) or concentrated or diluted extract that may be corrected by re-injection or other limited reprocessing of the sample. Other QC data are in control.

6.3.2.2 Evidence that sample data are acceptable

If there are indicators that processing of the environmental samples was acceptable, even when there are one or more failed compounds in the reagent spike, then sample data may be reported. All of the conditions below should be met in order to consider sample processing to have been acceptably performed. Consult with your supervisor if you have any doubt as to how to interpret the results. If you determine that a sample-processing problem was encountered, then every effort should be made to correct the problem in order to avoid future recurrence. Examples of evidence include:

- Acceptable recoveries of representative surrogates in sample(s) and/or blank. Refer to section 5 regarding "Surrogate Standards" for guidance on the interpretation of surrogate standard recoveries.
- Acceptable recoveries in matrix spikes, field spikes, standard reference materials (SRM), certified reference materials (CRM), other spiked samples, if present in the sample preparation set.

- Absence of a pattern of failures in recent sample sets (check control charts, other analyst's results).
- Normal indicators of instrumental analysis of a sample matrix are present - baseline noise, typical matrix perturbations, etc., (as opposed to a blank chromatogram - normal noise not present); verified by re-injection of the sample extract if necessary.
- Confidence that the method and SOP were properly followed and that there were no errors resulting in sample / reagent spike losses; the absence of preparation and / or analysis notes or remarks indicating problems.

6.4 Corrective action – Reagent Spike

Figure 2 and tables 3h and 3i provide corrective action guidance for environmental samples associated with a failed reagent spike - corroborative information (particularly surrogate recoveries) indicates that a process failure has occurred that may affect analyte recoveries in some or all of the samples, as well as the reagent spike. In general, the severity of the corrective action escalates as the number of analyte recovery failures increases, and as their recoveries become poorer (especially lower). Recoveries of key compounds are used as the primary indicators of process failure, in conjunction with the percentage of all the analytes with unacceptable recoveries. The table was developed under the assumption that most analyte recovery failures will occur in the same mode – all high or low - it may be conceivably possible to have some analyte recoveries fail high and others simultaneously low. Analysts should consult with their supervisors to determine what corrective actions to take for these and other unforeseen circumstances. Note also that the corrective action options for many conditions are the same; it is up to the analyst and supervisor to determine which among the several possible options to implement relative to the severity of the failure.

Table 3h – Number of allowable Key Compound failures and other compound failures per reagent spike based on total number of compounds per method

	Number of failed analytes			
	≤ 5%		> 5%	
Key Failures ⇒	**0, 1**	**> 1**	**0, 1**	**> 1**
Reagent Spike Recovery: ⇓				
≥ $\bar{X}$ + 4sd	Consult with supervisor regarding options: • Reinject or other limited reprocessing • Troubleshoot further • CAT 3 for detects	Consult with supervisor regarding options: • Reinject or other limited reprocessing • Troubleshoot further • CAT 3 for detects	Consult with supervisor regarding options: • Reinject or other limited reprocessing • Troubleshoot further • CAT 3 for detects	Consult with supervisor regarding options: • Reinject or other limited reprocessing • Troubleshoot further • CAT 3 for detects
≥ $\bar{X}$ + 3sd and ≤ $\bar{X}$ + 4sd	Possible statistically anomalous recovery. See statistical anomaly diagnosis guidance below. CAT 1	Consult with supervisor regarding options: • Reinject or other limited reprocessing • Troubleshoot further • CAT 3	Consult with supervisor regarding options: • Reinject or other limited reprocessing • Troubleshoot further • CAT 3	Consult with supervisor regarding options: • Reinject or other limited reprocessing • Troubleshoot further • CAT 3
≤ $\bar{X}$ - 3sd and ≥ $\bar{X}$ - 4sd	Possible statistically anomalous recovery. See statistical anomaly diagnosis guidance below. CAT 1	Consult with supervisor regarding options: • Usually CAT 1-3 • Consider CAT 4-7 depending on nature and degree of failure.	Consult with supervisor regarding options: • Usually CAT 1-3 • Consider CAT 4-7 depending on nature and degree of failure.	Consult with supervisor regarding options: • Usually CAT 1-3 • Consider CAT 4-7 depending on nature and degree of failure.
≤ $\bar{X}$ - 4sd or ≤ ½ LCL (lower control limit)	Consult with supervisor regarding options: CAT 5 - 8 as applicable	Consult with supervisor regarding options: CAT 5 - 8 as applicable	Consult with supervisor regarding options: CAT 5 - 8 as applicable.	Consult with supervisor regarding options: CAT 5 - 8 as applicable

Table 3i. List of Corrective Action Types (CAT)

CAT	Description	Refund?[1]	Should data go into WATSTORE?
1	Qualify sample data in data pack with standardized qualifiers as applicable.	No	Yes
2	D-R affected QC results	No	---
3	Qualify sample data in data base (E or other similar data qualifier[2]) as well as in data pack.	No	Yes
4	Qualify sample data by memo to customer as well as in data pack.	No	Yes
5	Re-prepare sample, re-evaluate, if replicate is available.	No	Yes [3]
6	Adjust analyte report levels [4], qualify sample data in data pack.	Probably not	Yes
7	CAT 4 plus D-M [5] affected analytes in sample results.	Maybe	Maybe
8	CAT 4 plus D-R [6] affected analytes in sample results.	Yes	No

Footnotes:

1. Prorate refund according to the degree of loss as applicable.
2. Under normal circumstances the "E" (estimated result) qualifier should not be applied to reagent spike results, although it may be applicable to the environmental sample results.
3. Report replicate results to WATSTORE if associated QC results are acceptable.
4. Adjust analyte report levels for non-detected compounds in direct proportion to the (unacceptable) recovery: $RL_2 = 100 * (RL_1)/(R_{\%})$; where RL_1, RL_2 are the old and new report levels respectively, and $R_{\%}$ is the analyte percent recovery in the spike in question. This is intended to be an expeditious way to flag the results, pending the availability of more appropriate data qualifiers.
5. D-M: Data quality is inappropriate for WATSTORE, but may be of use to the customer when sufficiently qualified.
6. D-R: Data are non-existent or completely uninterpretable.

6.5 Statistical anomaly diagnosis – Reagent spike

As the number of analytes determined in a method increases, the likelihood of an analyte failure in a reagent spike attributable to statistical occurrence increases[3]. Therefore, it is necessary to distinguish between statistical and process failures because false out of control signals may lead to unnecessary reanalyses. It is important that analysts use their judgment in interpreting results - if it looks like a process failure, then determine the action to take according to the corrective action guidance. The following conditions are used to classify analyte failure in a reagent spike as a statistical anomaly:

- Reagent spike performance evaluation criteria were derived from statistical data as described in the reagent spike criteria development guidelines, and
- observed marginal reagent spike failure of a stable compound., and/or
- reagent spike failure of the compound in question is generally not indicative of process failure, and/or
- the analyte in question does not fail reagent spike criteria frequently (statistically approximately 1/100 determinations).

Table 3j provides a description of the number of allowable analyte failures in a reagent spike to be considered a statistically anomalous condition, given the above guidelines:

Table 3j. Number of permissible failed compounds in a reagent spike if due to statistical anomaly

Number of compounds determined	Permissible number of failed compounds
1-5	0
6-20	1
>20	≤ 5%

[3] Provost, Elder, "Choosing Cost Effective QA/QC Programs for Chemical Analysis", USEPA report no. EPA/600/4-85/056, 1985.

7. Method Blank

7.1 Definition – Method blank

A method blank consists of a representative matrix with minimal analyte interferences that is carried through the entire sample preparation and analytical procedure. All reagents are added in the same volumes or same proportions as the environmental samples. For most water samples, analyte-free water is the synthetic matrix used as the method blank matrix. An exception is the determination of organochlorine compounds by gas chromatography with electron capture detection. In this case, it is difficult to prepare interference-free water, so the method blank consists of the extraction solvent and reagents placed into a sample bottle. For tissue and sediment samples, sodium sulfate is used as the synthetic matrix blank. There are many different types of blanks used for the evaluation of potential sample contamination during sampling, transport, storage, and laboratory analysis. For the purpose of this discussion, only blanks used for routine laboratory process control will be considered. Synonyms include set blank, reagent blank, laboratory reagent blank, method reagent blank, blank control sample.

7.2 Calculation – Method blank

Quantitate detections in method blanks and tabulate. The actual method for the determination and evaluation of blank data may differ from method to method based on the measurement and the data system used. There are two options for blank record keeping. Record nondetections (<NDV or <MRL) in the blank as zero for calculation purposes. Alternatively, record all quantitated results, regardless of identification criteria. This will assure that blanks are not censored because of failed identification criteria, when slightly higher concentration sample results are recorded (identification criteria are met in sample and fail in blank) and skew the data. Keep historical records in the same data set for as long as the process is producing similar data. An ideal data set will include over 100 method blanks. The 95^{th} percentile concentrations will determine the concentration of a "normal" blank. For most organic methods, the blank amount must <u>not</u> be subtracted from the amount detected in an environmental sample. The blank amount may, however, be used as a censoring level, when historical blank levels are separated from true environmental sample detections. In some cases, the method blank amount may be included as the zero amount in a calibration curve.

7.3 Application – Chronic and nonchronic method blank contaminants

The method blank is used to identify contamination from the laboratory during sample preparation and analysis. There are two types of blank contaminants defined for sample data reporting – chronic and nonchronic blank contaminants.

Chronic blank contaminants are interpreted as if they are always present, even if they are not detected in samples and/or blanks, or if the calculated background concentration varies. Chronic blank contaminants are frequently detected in blanks (greater than 10 percent) and samples due to process contamination. Because their presence is frequent, it is difficult to determine if similar concentrations of the contaminant found in the environmental samples are true. For that reason, chronic blank contaminants are conservatively judged as if they are always present in all environmental samples at a concentration equal to the 95th percentile concentration.

Nonchronic blank contaminants are treated as found in daily blanks, that is, negative results are recorded as nondetections, and positive results are recorded and used to interpret sample results. Sample data are adjusted for positive detections in the daily method blank. Nonchronic blank contaminants are rarely detected in blanks (less than 10 percent) and therefore are judged, when not present in the blank, to be absent in samples.

For a method blank to be acceptable, the concentration of each compound should be undetected, or detected at less than the MRL or NDV. If a compound is detected in the method blank, an attempt is made to identify the source of contamination and to take corrective action. Data reporting strategies are outlined for chronic contaminants differently than for nonchronic contaminants. Refer to fig. 3 for guidance.

7.3.1 Establishing acceptance criteria – Method blank

The following tables list options for methods of establishing acceptance criteria. The format of these tables is repeated in this guidance document for each quality control tool. Each heading (e.g. - data compilation) lists components that need to be individually defined for each method. If multiple options are listed for addressing a given topic, then the most appropriate option for a given analysis may selected. When a single option is listed, then the listed option is the standard for the Organic Program. If this option is unworkable for a specific method, then an alternate choice must be justified.

Table 4a. Data compilation – Method blanks
Description of the data used to develop criteria

	Option Number	Options
Composition of the QC standard material	1	"Clean" matrix – best available matrix as analyte free as possible.
	2	Reagents, surrogates, internal standards, etc. are added as appropriate.
Data used for statistical compilation	1	Compile recovery data for all method blanks. Delete data for known process failures. Report analytes detected < MRL, flag with E code. If unknown interference, raise MRL in proportion to the interference, if appropriate.
Options defining the size of the data set for statistical criteria	1	Ideally $n \geq 100$; compile data continuously. Process changes affecting blank performance may necessitate development of a new data set.
	2	Compile all data over a defined time period.
	3	For $n < 100$ evaluate data frequently; use judgment to develop interim criteria based on criteria development guidelines.
Dual-column data considerations	1	For dual column analyses compile data from results determined according to the procedure used to report sample results.
	2	For dual column analysis compile data independently for each column including interferences.

Table 4b - Multi-instrument analyses – Method blanks
How to handle data for multi-instrument analyses.

	Option Number	Options
Compile for individual or pooled instrument data	1	Pool results for all instruments used in the analysis.
Dual column considerations	1	For dual-column data analysis compile data independently for each column.
	2	Record lowest result of either column data.
	3	Record interferences as well

Table 4c. Review or Update Frequency – Method blanks
Interval for evaluation of QC criteria with possible update of criteria – this may coincide with the data compilation interval.

	Option Number	Options
Based on a defined time interval	1	Defined time interval, e.g. quarterly. Data should be reviewed at least annually.
	2	Use longer/shorter time intervals with different evaluation purposes.
Based on data set size	1	Data should be evaluated frequently for $n < 100$ to determine whether potential chronic blank contamination occurs.
Other considerations	1	When significant change occurs in process that may affect data.
Other considerations	2	The main concern is bias, precision may be an issue if blank interference concentration is relatively constant – a constant blank contaminant may introduce a bias that may affect MDL determination.

Table 4d. Acceptance criteria for method blanks

Determination of QC criteria - results outside of criteria require corrective action.

	Option Number	Options
Statistical Criteria *(Goal: non-parametric statistical criteria)*	1	*Chronic blank contaminant*: an analyte that is detected in ≥ 10 % of historical blanks ($n \geq 100$). Calculate the 95th percentile concentration (C_{95}) for chronic blank contaminants using all detections and substituting a zero value for all non-detections (see calculation instructions below.
Initial (provisional) criteria	1	No detections above MRL or NDV
	2	For $n < 100$ evaluate data frequently; use judgment to develop interim criteria. Calculate or estimate C_{95} value if chronic blank contamination condition is apparent.
Maximum limits for control limit criteria	1	$C_{95} \leq$ NDV; NDV should be redetermined if C_{95} > NDV.
Options for dual column analyses	1	Treat single column interferences as blank contaminants so these peaks do not cause false confirmation of detection.
Other considerations	1	It may be apparent early in the development of the blank data that chronic contamination is occurring; consult and use judgment to determine how to develop criteria and interpret sample data.
Non-statistical options	1	For non-chronic blank contaminants and limited historical data set size (n <100) use set blank for data interpretation.

Table 4e. Data Presentation – Method blank
Options for presenting data for short and long term data evaluation

	Option Number	Options
Graphical display options	1	Use box plots to display concentration distribution of blank contamination.
	2	Chart concentration vs. time for possible data trend evaluation.
Tabular data generally used for daily, on-line evaluation.	1	Use tables to document historical blank data, include zero as the value for nondetection. Tabular reports are important for short-term data evaluation of small historical data sets.

Table 4f. Outlier Test – Method blank
Options for outlier testing and rejection.

	Option Number	Options
Definition of blank data set outliers	1	Reject only if legitimate, documentable failure, e.g. known contamination incident, contaminated reagents, etc.

Table 4g. Corrective action synopsis – Method blank

	Option Number	Options
More specific information regarding corrective actions follows this table.	1	Blank detections above MRL are process failures. Follow the flowchart for other scenarios.
Use of data qualifiers	1	Raise report levels when the blank and sample result are similar. Use "E" for estimated when blank values are much lower than sample results. Use "V" for chronic blank contaminant when the sample result is less than ten times the C_{95} result and greater than the blank value.
Other considerations	1	For $n < 100$ interpret data as non-chronic (if appropriate) using the method blank data interpretation flowchart.

7.4 Method blank failure evaluation

Any blank detection greater than NDV or MRL is indicative of a potential process failure. Determination of a blank-contamination related process failure is a method specific interpretation process that is dependent on the number of contaminating analytes (or nondescript background contaminants) and their concentrations. A process failure for a blank requires investigation as to the cause and the effect. Corrective action must be taken to correct the source of contamination and to mitigate the effects.

Blank detections below the NDV or MRL require different strategies for sample data interpretation. Based on the frequency of detections in historical blank data, each analyte in a method is classified as a chronic (frequency $\geq$ 10%) or non-chronic ($<$ 10%) blank contaminant. This classification determines how relevant an individual set blank is relative to its associated samples. Individual set blank data are generally not immediately relevant for analytes determined to be chronic blank contaminants, unless the concentration is abnormally high enough to indicate a process failure. Chronic blank contaminants are treated as though the analyte were detected in every blank, whether actually detected or not detected in any given blank. Thus, the main concern for chronic blank contaminants is the amount of analyte in the sample relative to the chronic blank contaminant amount (C_{95}) and the non-detection value (NDV) or MRL. C_{95} is used as the blank contamination amount to compare to the amount of analyte detected in samples, in lieu of the individual set blank data.

The C_{95} value was selected to represent the chronic blank contamination amount because the majority of actual blank concentrations are, as a rule, in the undetectable portion of the data distribution; i.e. the actual detections are just the tip of the blank data iceberg. Thus the typical values used to characterize data, such as mean and median, would not appropriately characterize the data. Note that it is crucial to ensure that non-detections are included in the blank data set, by assigning them a value of zero, in order to properly represent the data and calculate the 95^{th} percentile value. Alternatively, non-detections can be entered as the calculated concentration to assure that censoring blank detections does not skew interpretation of low-concentration environmental sample contaminants.

The individual blank results for non-chronic blank contaminants are immediately relevant to their associated sample data to evaluate process failures and environmental sample results. Blank data are used to evaluate the presence/absence and amounts of non-chronic contaminants in all of the samples in the associated sample set.

Details for the interpretation of chronic and non-chronic corrective action options are provided in the method blank data interpretation flowchart, fig. 3.

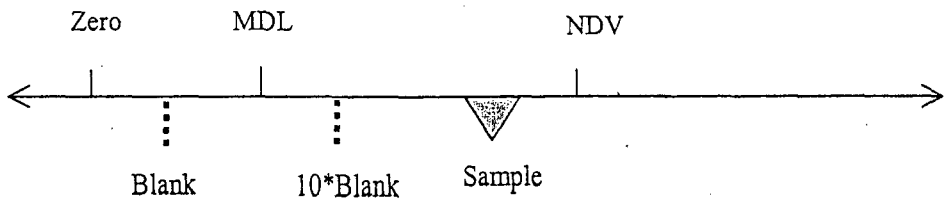
7.4.1 Special considerations – Method Blank – Dual-column analyses

Dual-column analyses generally require compound detection confirmation by the presence of a peak on each of two dissimilar columns at the correct relative retention times. If an analyte detected in the method blank is verified on both analytical columns, then interpret sample data according to the general guidance given above. For correct blank interpretation, any peak that is detected at the target compound retention time in both the blank and samples needs to be considered a possible interference, even if not verified on both columns. The analyst must not interpret the interference peak as confirmation of a target compound in the samples, if there is a confirming peak on the other column. For confirmation in samples with an interference peak, the calculated amount of the interference peak needs to be at least equal to the sum of amount of the interference plus the amount of target compound in order to be considered a confirmation. The amount quantitated on the uninterfered column should be the value reported to the data user. Alternatively, confirmation can be obtained in some other manner – mass spectrometry, third-column identification, standard addition, or fractionation.

7.5 Corrective Action – Method blank

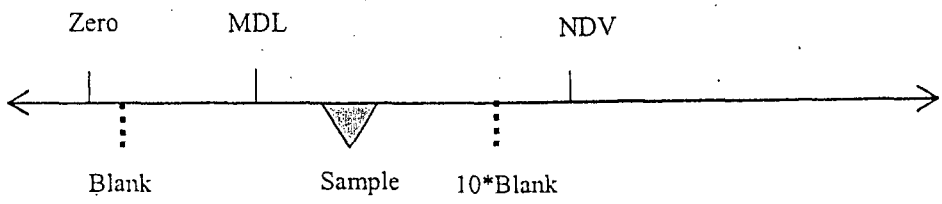
If the daily method blank is greater than NDV for any contaminant (chronic or nonchronic), treat the situation as a process failure. Any time a sample detection of a contaminant is similar in concentration to the blank concentration, the sample detection is suspect. All other situations should address blank contaminant concentrations below the NDV according to fig. 3 and the following examples:

A. If the blank is **less than** NDV
and the sample is **less than** NDV
but the sample is **greater than** 10 times the blank



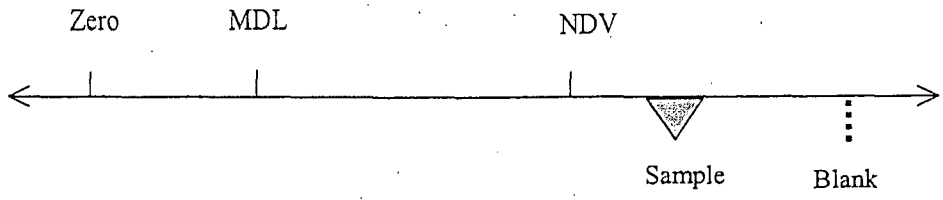
Then: Report the sample result with an "E" remark code

B. If the blank is **less than** NDV
and the sample is **less than** NDV
but the sample is less than 10 times the blank



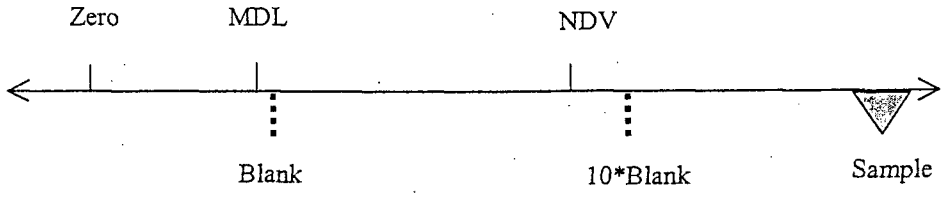
Then: Report < NDV

C. If the blank is **greater than** NDV
and the sample is **greater than** NDV
and the blank is **greater than** the sample



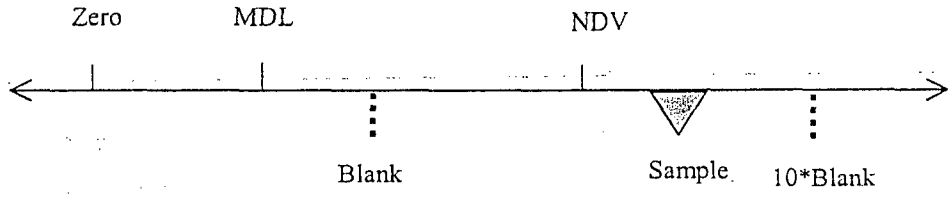
Then: Raise the report level in the sample to the sample result

D. If the blank is **less than** NDV
and the sample is **greater than** the NDV
and the sample is **greater than** or equal to 10 times C_{95} (chronic contaminants)
OR the sample is **greater than** or equal to 10 times the daily blank (nonchronic)



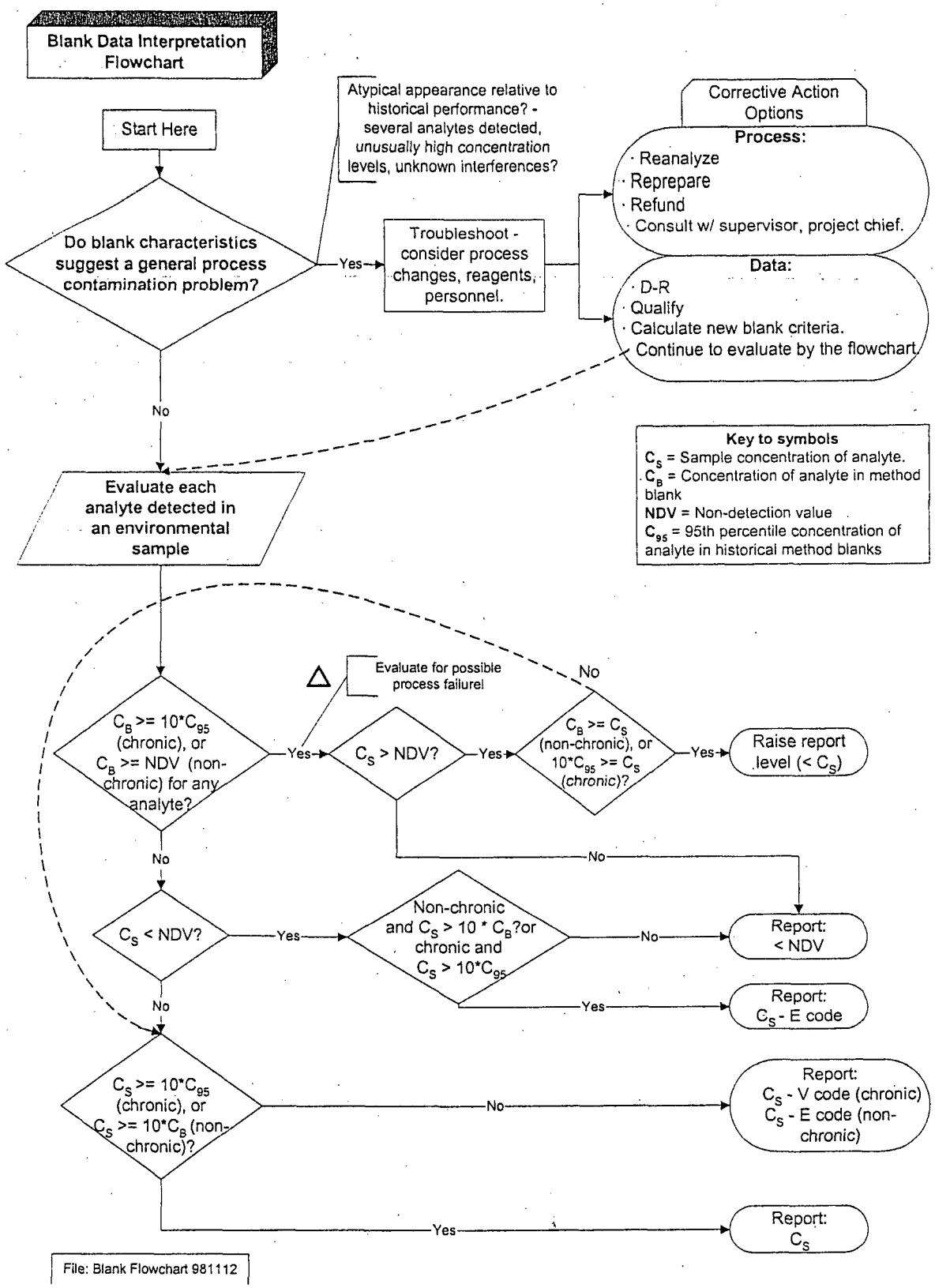
Then: Report the sample concentration as found

E. If the blank is **less than** NDV
and the sample is **greater than** the NDV
and the sample is **less than** or equal to 10 times C_{95} (chronic contaminants)
OR the sample is **less than** or equal to 10 times the daily blank (nonchronic)



Then: Report the sample with a V code for chronics
Report the sample with an E code for nonchronics

Figure 3. Blank data interpretation flowchart



Appendices

Appendix A - Glossary

Batch - one or more sample sets treated together using the same QC data for determination of acceptance or rejection of data.

Calibration –the process of standardizing an analytical instrument in order to equate instrument response to the amount of the material in question.

Calibration standard – standards used to create a calibration curve and define the concentration range of analysis.

Canaries – compounds that are sensitive to possible processing errors and may be indicative of specific failures.

Catastrophic failure - an out of bound condition that is an unequivocal indication that sample data quality is compromised. See section 5.3.2.

Chronic blank contaminant – compounds that are detected in collective method blanks greater than or equal to 10 percent of the time.

Continuing calibration verification standard (CCV) – A standard solution used in instrumental analysis to check instrument stability in relationship to the calibration standard curve.

Control limits – the bounds against which QC data are evaluated to determine whether corrective action is necessary. The upper and lower control limits are typically calculated as the mean value of the QC data set plus and minus three standard deviations (or *f*-pseudo sigma), respectively.

Corrective action – the action taken on a failed quality-control result.

Correctable laboratory failure - Laboratory problems wherein sample data quality is not affected. The preponderance of evidence is that the failure will not affect some or all aspects of data quality. Results can be legitimately corrected and documented to recover data.

Data qualifiers – codes attached to numeric results that intend to modify the meaning of the result.

Flakes – compounds that do not perform ideally in a given method, typically with large standard deviations, or frequent performance problems. Flakes are generally identified as

compounds with mean recoveries outside of 60 – 120%, and/or standard deviations greater than 15%.

Internal Standard - Internal standard (IS) quantitation is a procedure used in chromatographic methods in which a known amount of a standard material (the IS) is added to each calibration standard, sample, blank or spike analyzed. The IS is added to serve as a retention time (RT) reference to improve qualitative certainty and/or as a reference amount on which analyte quantitation is based.

Key compounds - Reagent spike compounds whose recoveries are used to diagnose the possibility of catastrophic failure during sample processing. See section 7.1.

Method blank - A representative matrix with minimal analyte interferences processed through the entire sample preparation and analytical procedure - used to assess contamination due to the laboratory procedure.

Nonchronic blank contaminant – compounds that are detected in collective method blanks less than 10 percent of the time.

Noncorrectable laboratory failure – A laboratory problem that adversely affects data quality, and cannot be corrected or adequately documented to recover all or part of the data.

Non-parametric statistics – Statistical data evaluation method, in which no assumptions are made about the distribution of the data. In particular, one does not need to test or assume that the data are normally distributed in order to apply the calculation and interpretation techniques of non-parametric statistics.

Outlier test – A statistical assessment of a population to determine if certain values are not part of the same population.

Performance evaluation mix – a standard solution injected into an analytical instrument for assessing specific indicators of instrument performance, such as sensitivity and resolution.

Process failure – An occurrence in sample processing that yields unacceptable QC results.

Reagent spike – a synthetic matrix fortified with known concentrations of all or a representative selection of, the method analytes.

Run sequence – The order in which environmental and QC samples are sequentially processed during instrumental analysis.

Sample set - a group of samples processed identically under the same QC for determination of acceptance or rejection of data.

Sequence (see run sequence) –

Statistical anomaly – an out of control QC result that may be attributed to statistical performance of the data rather than the process, e.g. at the 99th percent confidence interval, one in one-hundred determinations will fail statistically.

Surrogate standard - compounds similar in physical and chemical properties to the compounds of interest in a given method. Surrogates are added to all environmental samples, reagent spikes, method blanks and other relevant QC samples for applicable methods. Surrogate recoveries provide QC information to monitor gross sample processing errors and matrix effects.

Third-party check standard – An independently prepared standard solution used to verify accuracy of the calibration solution. Must be from a different lot and prepared by a different manufacturer (or person).

Warning limits – The upper and lower warning limits are typically calculated as the mean value of the QC data set plus and minus two standard deviations (or *f*-pseudo sigma), respectively. QC results that are between the warning and control limits are generally taken to be an indication that process failure is imminent.

Appendix B - Robust statistics and description of F-pseudosigma

The routine summary statistics for a sample consisting of n observations, $x_1, x_2, x_3, \ldots, x_n$, are the sample mean given by

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i,$$

and sample variance given by

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x-\bar{x})^2.$$

The sample standard deviation is the square root of the sample variance. Statisticians generally refer to the mean and variance as measures of location and spread of the data. In quality control, the mean is the process average and the standard deviation is the process variability (or precision). If the process average is different than the desired or expected process average, there is bias in the process. If the process is exhibiting greater variability than expected, there is greater chance for the process to lack control. Both situations are indications of an out-of-control process.

For exploratory purposes and for determining initial process control limits, it is advantageous to use simple summaries based on sorting and counting (ranking). The summaries can be robust; that is, a change in a small part of the sample can have only a small effect on the summary statistics. The sample mean and variance do not behave in this way. A single wild datum can have a substantial effect on the calculated mean and variance. The robust statistical parameter for location is the median, or 50th percentile ($P_{.50}$). The median is determined by sorting and ranking the data in order of magnitude (smallest to largest value). For n data values, after sorting and ranking, x_1 is the smallest and x_n is the largest data value. For an odd number of observations, the median is the data value, which has an equal number of observations above and below it. For an even number of observations, the median is the average of the two central observations. The median is given by

$$median = x_{(n+1)/2}$$

when n is odd, and

$$median = \frac{1}{2}(x_{(n/2)} + x_{(n/2)+1})$$

when n is even.

The most common robust measure of spread in the interquartile range (IQR). This is the range of the central 50-percent of the data. Determination of the IQR is not influenced by the magnitude of the data values found in the 25-percent of the data on each end. The IQR is defined as the 75th percentile subtracted by the 25th percentile. The 75th, 50th (median), and 25th percentiles split the ranks of data

into four equal-numbered quarters. Twenty-five percent of the data lie below the 25th percentile and 25 percent of the data lie above the 75th percentile.

Another common measure of data spread is the F-spread or fourth spread. The F-spread is calculated from the depth of fourths. This is similar to the interquartile range in that the ranked data are divided into equal sized fourths. The depth of the data value is the smaller of its upward rank and its downward rank. The fourths are values taken directly from the ranked data set. Therefore, unlike the percentiles, which can be a calculated value. The depth of fourth is given by

$$\text{depth of fourth} = \frac{[\text{depth of median}]+1}{2}$$

Sometimes the depth of fourth is also refered to as the hinge, ie., the lower hinge is the lower depth of fourth and the upper hinge is the upper depth of fourth. For large data sets (n>/=30, the 25th percentile, the lower depth of fourth, and the lower hinge are approximately the same (as are the 75th percentile, upper depth of fourth, and upper hinge). Computer statistical applications usually provide and option to calculate the interquartile range and the median in a statistical summary.

F-pseudosigma

How does one distinguish data values that may not appear to be part of the population short of knowing the history of obtaining the data?

It would be useful if we could identify outliers corresponding to different underlying behavior for certain values as compared with that of the bulk of the data. The explanation for the difference may lie in how the quantity we are studying truly behaves, how we measured it, or how we mishandled the measurements. Identifying outliers with certainty is not possible. The best we can do is cut off some values for special attention. Many of the values outside the cutoffs will not be outliers as they may have been produced under the same underlying conditions as the bulk of the data. We want assurance that we can separate the true outliers without sacrificing too much of the data that accurately describe the behavior of the majority of the data. To do this we rely on the central portion of the data rather than the extremes of the data to describe behavior.

To examine a data set for outlying values, a measure of spread that is insensitive to outliers is needed. The IQR or F-spread provide such a measure, whereas, standard deviation and mean do not. The F-spread or IQR single out the central 50 percent of the data leaving tail areas of 25 percent on either side.

When we otherwise think of standard deviation or variance, we can obtain a robust analogue by asking what a standard deviation or variance for a normal distribution need to be in order to yield the same F-spread as the data. The fourths of a normal distribution are $\mu - 0.6745\sigma$ and $\mu + 0.6745\sigma$ yielding an F-spread of 1.349σ.

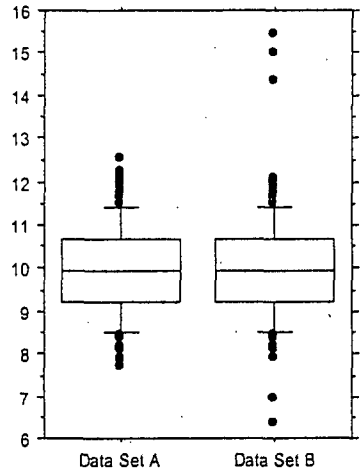
F-pseudosigma would then be

$$\frac{F-spread}{1.349} = \frac{IQR}{1.349}$$

This ratio is known as F-pseudosigma, and its square (analogous to variance) is the F-pseudovariance.

When the data appear to be normally distributed (the usual case), the F-pseudosigma is an estimate of sigma and its value is close to the sample standard deviation. Using the robust F-pseudosigma, in addition to, or instead of the standard deviation has advantages, particularly when the data are close to being normally distributed except for a few extreme observations. If the two estimates differ, the F-pseudosigma may be the preferred estimate.

For quality control purposes, the assumptions of repeated measures of a process characteristic should expect the measurements to be normally distributed. If the assumptions of normality are accepted, then F-pseudosigma is acceptable as an alternative to standard deviation. Conversely, if normality assumptions do not apply, then neither F-pseudosigma, nor standard deviation is a good estimator of process spread, so some other measure may be more appropriate. F-pseudosigma can replace standard deviation in quality control applications, especially for obtaining initial estimates of process variability. This can be shown using the following examples. Data set A is approximately normally distributed while data set B has 5 percent of the observations that do not fit the normal distribution. Box plots and descriptive statistics for the two data sets are presented in figure 1.



	Mean	Std. Dev.	Median	IQR	F-pseudosigma
Data Set A	9.961	1.058	9.924	1.427	1.058
Data Set B	10.016	1.353	9.924	1.427	1.058

Figure 1.—Box plots and descriptive statistics for two data sets. Data set A is approximately normal and data set B is the same data except 5 data values were replaced with extreme values.

Appendix C - Changes and additions

Revision notes

Revision 1.0 – May 22, 1998.

Part IV includes four major quality-control components:

- Continuing calibration verification standards
- Surrogate standards
- Reagent spikes
- Method blanks

ATTACHMENT F

FIELD DATA SHEETS
AND EXAMPLE FIELD AUDIT CHECKLIST

ATTACHMENTS
F

U.S. GEOLOGICAL SURVEY, WRD, SURFACE-WATER QUALITY FIELD NOTES

BQA-1 3/92 (3rd printing, 1st ed.)

Proj. Name, No. _____ Date _____

Station _____ Sta.No. _____

Sampled By _____ Mean Time _____ SMS Cntrl. No. _____

Record No. _____ Sample Purpose (71999) :

SAMPLES COLLECTED

Nutrients ☐ TOC ☐
Major Ions ☐ DOC ☐
SOC ☐ Vol. Filt. _____mL
BOD ☐ Turbidity ☐
COD ☐ _____ ☐
_____ ☐

ORGANICS / TR. ELEMENTS
Pesticide ☐ Unfiltered ☐
VOC ☐ Filtered ☐
BNA ☐ Suspended ☐
_____ ☐ Bottom ☐

Sediment Conc. ☐
Sediment Size ☐
Sed. Bot. Material ☐
Sand Split/Break ☐
Radiochemical ☐
Isotope ☐
☐

LABORATORY SCHEDULES

Lab Schedules Req. (or copy of lab request form attached ☐)

Lab Codes Add (A) Delete (D) :

FIELD MEASUREMENTS

Q. Inst. (00061)	_____	cfs	meas. rating est.	Alkalinity ( )	_____ mg/L
Gage Ht (00065)	_____	ft.		Bicarbonate ( )	_____ mg/L
Temp. Water (00010)	_____	°C		Carbonate ( )	_____ mg/L
Temp. Air (00020)	_____	°C		Hydroxide ( )	_____ mg/L
pH (00400)	_____	units		E. Coli (31633)	_____ col./100 mL; Rmk
Sp. Cond. (00095)	_____	µS/cm 25 °C		FC (31625)	_____ col./100 mL; Rmk
Dis. Oxy. (00300)	_____	mg/L		FS (31673)	_____ col./100 mL; Rmk
DO Sat. (00301)	_____	%		Other:	
Bar. Press. (00025)	_____	mm Hg			

SAMPLING CONDITIONS

Location: Wading, cable, ice, boat, bridge, upstr., downstr., side bridge _____ft mile, above, below gage, and

Sampling site: Pool Riffle Open Channel Braided Backwater Sampler Type _____

Sample Method: EWI EDI OTHER _____ Sampler ID _____

Nozzle size _____ Nozzle Made of _____ Bottle type, size _____

Sample Split: Churn Cone Other _____ Made of _____

LB_____ RB_____ Stream Width_____ Sampling Pts. _____ _____ _____

_____ _____ _____ _____ _____ _____ _____ _____ _____

_____ _____ _____ _____ _____ _____ _____ _____ _____

Bottom: Bedrock Rock Cobble Gravel Sand Mud Concrete Other _____

Stage Conditions:
A Not Determined **4** Stable, low **5** Falling **6** Stable, high **7** Peak **8** Rising **9** **Stable, normal**

Hydrologic Event: **9** **Routine samp.** **A** Spg. breakup **B** Ice Cover **1** Drought **2** Spill **3** Reg. Flow **4** Snowmelt **7** Flood

Other _____ Ice Thickness _____ Ice cover _____

Stream color(s): brown green blue gray other _____

Stream Mixing: Excellent Good Fair Poor Clarity/Turbidity: _____

Weather: Clear Partly Cloudy Cloudy Light Medium Heavy Snow Rain Calm Light Breeze Very Gusty Windy Very Cold Warm Hot Other

Other Observations

_____

_____

_____

_____

_____

(Cont. p. 3,4)

Checked by _____ Date _____

Observations:

(Codes: 0-none 1-mild 2-moderate 3-serious 4-extreme)

(option: LEAVE BLANK IF NONE)

Floating debris	(01345) :	____
Floating garbage	(01320) :	____
Floating algae mats	(01325) :	____
Fish kill	(01340) :	____
Detergent suds	(01305) :	____
Turbidity	(01350) :	____
Atms. Odor	(01330) :	____
Oil-grease	(01300) :	____

Sampling	GHT	
Start Time	_____	_____
Mean Time =	_____	_____
	_____	_____
End Time	_____	_____

TEMPERATURE

Lab Tested Thermometer used? ☐ Yes ☐ No — If NO, explain in remarks

Thermometer Checked w/ASTM within ± 0.5 °C; Date

AMPULE LOT NUMBERS:
nitric acid _____ mercuric chloride _____
nitric acid/potassium dichromate

pH

Mtr W-no. METER Make/Model

electrode no. electrode type

pH Buffer	pH Buffer Temp °C	Initial Reading	Adj. Reading	Remarks
___.___ ___				
___.___ ___				
___.___ ___				
___.___ ___				

☐ unfiltered sample ☐ filtered sample

Temp correction factors for buffers applied? ☐ YES ☐ NO

stirrer used? ☐ YES ☐ NO

if yes, ☐ magnetic stirrer ☐ manually stirred

pH subsample from or pH measurement location : Churn sample bottle single point at _____sta_____depth vertical avg of _____ points

x-sec average of _____points

Sample Temp = _____ °C

FIELD pH = **USE :**

SPECIFIC CONDUCTANCE

Mtr W-no. METER Make/Model

probe no.

standard value	Temp Std °C	Initial Reading	Adj. Reading	Remarks

correction factor applied? ☐ YES ☐ NO

☐ auto temp compensated meter

☐ manual temp compensated meter

corr. factor = _____

SC subsample from or SC measurement location : Churn sample bottle single point at _____sta_____depth vertical avg of _____ points

x-sec avg of _____points

FIELD CONDUCTANCE = **USE :**

DISSOLVED OXYGEN

W-no. _____ METER Make/Model _____

D.O. measurement location or D.O. subsample from : single point at _____sta_____depth vertical avg of _____ points x-sec avg of _____points

Calibration : BOD bottle

☐ Air Calibration in Water ☐ Air Calibration Chamber in Air

☐ Air-Saturation Deionized Water ☐ Calibration by Winkler Titration (attach Supplementary Winkler page)

D.O. Zero Check (using zero D.O. solution) ☐ YES ☐ NO

Thermister Check ☐ YES ☐ NO

BAR. PRESS _____ mm Hg; (mm = in. X 25.4)

Salinity Corr. Factor _____ H_2O Temp. _____ °C

Chart D.O. Sat. _____ mg/L stirrer used? ☐ YES ☐ NO if yes, ☐ magnetic stirrer ☐ manually stirred

Meter D.O. Sat. _____ mg/L; Adjusted to _____ (if corr. factor applicable)

DISSOLVED OXYGEN IN STREAM =

QUALITY ASSURANCE SAMPLES

Were quality assurance samples collected?

☐ YES ☐ NO If YES indicate type(s) :

	Organic-free	DI	water from sampling site
Replicate	☐	☐	☐
Spike	☐	☐	☐
Field Blank	☐	☐	Supplementary page w/additional
Trip Blank	☐	☐	QA sample info attached ☐

Other ☐ Indicate Type(s) :

Calibration Notes and Remarks

ALKALINITY

pH	△ pH	Vol acid DC or mL	△Vol acid DC or mL	△ pH / △ Vol acid

Acid: 1.60 N 0.1600 N 0.01639N OTHER ________

Acid Lot No. : ________

Sample Volume : ________ mL

☐ Filtered ☐ Unfiltered

Sample stirred : ☐ magnetically ☐ manually

pH: Start ________ End ________

DC (Digital Counts) or
Vol. titrated at End Point near pH 8.3 : ________

Digital Counts or
Vol. titrated at End Point near pH 4.5 : ________

☐ Incremental Equivalence ☐ Fixed End Point ☐ Gran Titration

Date ________ Time ________

CALCULATIONS :

$$CO_3^{-2} = A \times \frac{F_1}{\text{mL sample}} \times CF^{*}$$

$$HCO_3^{-1} = [B - 2(A)] \times \frac{F_2}{\text{mL sample}} \times CF;^{*}$$

$$\text{ALKALINITY as } CaCO_3 = B \times \frac{F_3}{\text{mL sample}} \times CF^{*}$$

A = DC or mLs acid from initial pH to endpoint near 8.3 = ________

B = DC or mLs acid from initial pH to endpoint near 4.5 = ________

* APPLY CORRECTION FACTOR (CF) IF ACID USED FOR BURETTE TITRATION HAS NONSTANDARD NORMALITY– CF = corr. factor = H_2SO_4 normality/0.01639

FACTORS	DIGITAL COUNT TITRATION (DC) Using 0.1600 normal	Using 1.60 normal
F_1	12.0	120
F_2	12.2	122
F_3	10.0	100

FACTORS	BURETTE TITRATION (mL)* Using ml of 0.01639 normal H_2SO_4
F_1	983.5
F_2	1000
F_3	820.2

(IMPORTANT : CF NOT APPLICABLE FOR THE DIGITAL TITRATION FACTORS SHOWN; use only with nonstandard normality BURETTE titration)

ALKALINITY ( ) ________ mg/L as $CaCO_3$

BICARBONATE ( ) ________ mg/L as HCO_3^{-1}

CARBONATE ( ) ________ mg/L as CO_3^{-2}

NOTE: ATTACH OUTPUT COPY IF ALKALINITY VALUES ARE CALCULATED USING A COMPUTER PROGRAM

OBSERVATIONS/CALCULATIONS :

E. COLI (31633)

Time collected : _____

Time in @ 35°C : _____ Date : _____

Time in @ 44.5°C : _____

Time out : Date :

Vol. (mL)	Count	Used in calculation?	Remarks *
Blank			
Blank			

* Remarks 1 = Less than 2 = Greater than 0 = Est. ct. K = non ideal ct.

Incub. Time 2 hrs @ 35°C followed by :

filt. size _____ 20-24 hrs @ 44.5°C

Ideal count 20-80 col.

E. COLI COUNT /100 mL_____; Rmk____

FECAL STREPTOCOCCI (31673)

Time collected : _____

Time in : _____ Date : _____

Time out : Date :

Vol. (mL)	Count	Used in calculation?	Remarks *
Blank			
Blank			

* Remarks 1 = Less than 2 = Greater than 0 = Est. ct. K = non ideal ct.

Incub. Time 46-50 hrs filt. size _____

Ideal count 20-100 col. Incub. Temp 35°C

FS COUNT / 100 mL_____; Rmk____

FECAL COLIFORM (31625)

Time collected : _____

Time in : _____ Date : _____

Time out : Date :

Vol. (mL)	Count	Used in calculation?	Remarks *
Blank			
Blank			

* Remarks 1 = Less than 2 = Greater than 0 = Est. ct. K = non ideal ct.

Incub. Time 22-26 hrs filt. size _____

Ideal count 20-60 col. Incub. Temp 44.5°C

FC COUNT / 100 mL_____; Rmk____

CALCULATIONS

Miscellaneous Section (Notes/Sketches/Calculations/X-Sec. & Etc.)

CROSS SECTIONAL MEASUREMENTS

STA	FT FROM L BANK (00009) or R. BANK (72103)	TIME	DEPTH 81903	pH 00400	T°C 00010	SC 00095	DO 00300	DO Sat 00301	GHT 00065	SUB Q (INST)

Surface-Water Water-Quality Field Form

U.S. GEOLOGICAL SURVEY

DISTRICT REVIEW FORM FOR FIELD AND LABORATORY

WATER QUALITY PROCEDURES: SURFACE WATER EDITION

REVIEW OF

_____DISTRICT,_____OFFICE

FIELD AND LABORATORY REVIEW CONDUCTED BY

_____*

_____

_____

* LEAD REVIEWER

FIELD TECHNIQUES REVIEWED AT:

Station No._____

Station Name_____

Date _____

DISTRICT REVIEW FORM FOR FIELD AND LABORATORY

WATER-QUALITY PROCEDURES: SURFACE WATER EDITION

I. FIELD SERVICE LABORATORY OR PREPARATION UNIT

Schedule sufficient time during the review to physically examine the field service laboratory or preparation unit. Because these preparation areas tend to have multiple uses, upkeep can sometimes be a problem. Stress during the review that a clean and orderly lab helps reduce the possibility of contamination.

Hood(s)

1. Are hoods present?
   a. To protect the sample? Y N NA
   b. To protect the user? Y N NA

2. Do the hoods work correctly (e.g. sufficient draw, ventilates outdoors, etc.)? Y N NA

3. Does the cup sink work? Y N NA

4. Does the hood appear to be a possible source of contamination (rust, paint flakes, etc.)? Y N NA

5. Remarks _____

_____

_____

Refrigerator(s)

1. Is a working refrigerator present? Y N NA

2. Is it labeled "FOR LAB USE ONLY, NO FOOD OR DRINK"? Y N NA

3. Are water samples stored in it? Y N NA
   Are the samples dated? Y N NA

4. If chemicals are stored in it, is the storage proper (do the chemicals require it be vapor or explosion proof)? Y N NA

5. Are precautions taken to minimize cross contamination of chemicals or water sample contamination by chemical vapors? Y N NA

Other Equipment

1. Are incubators, ovens, pressure cookers and similar equipment in good working order? Y N NA

2. Is a maintenance log kept for balances, and pH and specific conductance meters? Y N NA

3. Does the DI storage bottle look clean and free of biological growth? Y N NA

4. Remarks _____

_____

_____

Chemicals and solutions

1. Are chemicals dated and disposed of upon expiration of shelf life? Y N NA

2. Are all bottles and containers capped? Y N NA

3. Are solutions and standards dated? Y N NA

4. Are material safety data sheets available? Y N NA

5. Are calibration standards available for pH, and specific conductance? Y N NA

6. Is good quality deionized or distilled water available? Y N NA

7. Remarks _____

_____

_____

House Keeping

1. Are bench tops clear? Y N NA
   Is lighting acceptable? Y N NA

2. What is the general appearance: (excellent good fair poor)

3. Are all solutions, reagents, and equipment stored in a safe and orderly manner? (e.g., oxidizing agents separate from organic solutions) Y N NA

4. Are cabinets and drawers labeled for contents? Y N NA

5. Are fire extinguishers, first aid kits, exits, etc., clearly marked and readily accessible? Y N NA

6. Are EXITS clearly marked and lighted in case of power failure? Y N NA
   Note number of EXITS:_____

7. Test the safety equipment to ensure proper working condition (eye wash, etc.)

8. Are written descriptions of all field techniques and related office procedures maintained in the field preparatory unit? Y N NA

9. Remarks_____

II. FIELD VEHICLE

Field Folders

1. Is a WQ field folder available for routine stations? Y N NA

2. Does the field folder:

   a. Contain historical data for the station? Y N NA

   b. State where samples are normally collected? (e.g., for surface water sites, where samples are collected for various stages) Y N NA

   c. Contain directions to the site? Y N NA

   d. Station description? Y N NA

   e. Contain a list of samples to collect and those already collected for the current year? Y N NA

3. Remarks _____

_____

_____

Vehicle

1. Does the vehicle appear to be in good working condition? Y N NA

2. Are goggles, fire extinguisher, gloves and similar items stored in the vehicle and readily accessible? Y N NA

3. Are all equipment and supplies stored safely and securely? (e.g. not loose in back of the vehicle) Y N NA

4. Are easily damaged meters and equipment adequately cushioned during transport? Y N NA

5. Are traffic cones, road-signs, flags and orange safety vests available for work off bridges and near roads? Y N NA

6. Is there a checklist for all water-quality equipment necessary for the sampling trip? Y N NA

7. How is the housekeeping in general (excellent good fair poor)

8. Is there a satisfactory work area for processing samples and performing field measurements? (e.g., one which contributes to the quality of field measurements while minimizing risk of contaminating the samples.) Y N NA

9. If a boat is used, does it appear to be in good working condition? Y N NA
Is trailer in good condition? Y N NA

10. If a boat is used, is all the necessary safety equipment (PFDs, fire extinguishers, radio, lights, etc.) available and properly stored and/or used? Y N NA

11. Remarks_____

_____

III. SURFACE-WATER SAMPLE COLLECTION PROCEDURES

Sampling site and cross section

1. Is the WQ data collector the person primarily responsible for the upkeep of the gage? Y N NA
Is gage well maintained and free of clutter? Y N NA

2. When applicable, are traffic cones, road signs and/or flags positioned before work begins? Y N NA

3. Does sampling location appear to satisfy Water Resource Division criteria? Y N NA

Distance from gaging station is _____ ft
NOT APPLICABLE - NO GAGE _____
If there is no gage, is a streamflow measurement made? Y N NA

4. Does the cross section satisfy the requirements for gradually varying depth and velocity distributions? Y N NA

5. Are samples collected using water-sediment depth integrating samplers? Y N NA
IF NO EXPLAIN (Dip samples may be necessary if the flow is excessively shallow or if stream velocities are too slow to use a sampler.)_____

_____

_____

IV. SURFACE WATER SAMPLING EQUIPMENT

1. Is the appropriate sampler used? Y N NA
Condition of sampler: Good___ Fair___ Poor___

2. What kinds of samplers and support equipment does field person have available?

DH-81___
DH-95___
D-77___
D-95___
Other___
Weighted Bottle Sampler___ (Plastic___ Stainless Steel ___)
NOZZLES: 1/4"___3/16"___1/8"___OTHER___ (Plastic___ Teflon___)

REELS:
A__B__D__E__OTHER__

CRANES:
Type A___
TYPE B___
OTHER___
HANDLINES___

3. Is Plasti-Dip or epoxy coating on sampler in good condition? Y N NA

4. Does the field person have AT LEAST one hand held sampler, one cable type sampler and one reel, depending on the type of field conditions he/she encounters? Y N NA

5. Are reels and cranes in good working condition? Y N NA

6. Are equipment manuals kept with the equipment? Y N NA

7. Is cableway and cable car in good working condition? Y N NA

8. What type of splitter was used to process samples? churn___ cone___ other___

LIST ANY EQUIPMENT DEFICIENCIES:_____

_____

_____

9. Is all work from bridges and cableways done safely (e.g. cranes assembled and used correctly, brakes used on cableways, etc.) and according to Water Resource Division procedures? Y N NA

IF NO, EXPLAIN DEFICIENCIES:_____

_____

_____

V. SURFACE-WATER SAMPLING METHODOLOGY

In order to collect representative water quality and suspended sediment samples, an appropriate sampling technique must be used. Unless conditions warrant otherwise, depth and width integrated samples are normally collected. Two integrating sampling methods are most commonly used by the U.S. Geological Survey: The equal discharge increment (EDI) method and the equal width increment (EWI) method. The equal width increment method is also referred to as the equal transit rate (ETR) method. Only one sampling method is to be used for a given site visit.

Indicate which sample collection procedure is used: EWI SAMPLING METHOD__
EDI SAMPLING METHOD____ OTHER____ IF OTHER, EXPLAIN

_____

_____

A. Checklist for EWI (Equal Width Increment) sampling method:
(*Items 2, 3, 6, 7, 8, 9, 10 also apply to EDI method)

1a. Is the transit rate established in the deepest swiftest section of the stream? Y N NA

1b. Is this transit rate in the allowable range for the sampler? Y N NA

2.* Is the sampler lowered and raised at constant rate? Y N NA

3.* Does the sampler disturb the streambed? Y N NA

4. Are factors such as total stream width, velocity and depth distributions, and the minimum/maximum volumes for the sampler/transit rate taken into consideration when establishing sampling interval? Y N NA

5.* Before use, were the churn splitter/cone splitter and sample collection bottle used in the sampler rinsed with stream water at the site in addition to being properly cleaned and stored before going to the field? Y N NA

6.* Is the clean hands/dirty hands technique used? Y N NA

7.* Are appropriate measures taken to protect samples from contamination during sample collection ? Y N NA

8.* While pouring the water-sediment mixture from the sampler's collection container to the churn or cone splitter, does the field person swirl the sample to ensure complete sediment transfer? Y N NA

9.* Is the churn or cone splitter covered except when samples are added? Y N NA

10. Is the gage height recorded immediately prior to and immediately after sample collection, and is the time of sample collection noted? Y N NA

B. Checklist for EDI Sampling

1. Is the EDI (Equal Discharge Increment) method appropriate for this site? (e.g. does the site meet EDI method requirements for channel and rating curve stability?) Y N NA

2. Are graphs of cumulative discharge, in percent of total discharge versus distance from the left or right bank stored in the gage house or prepared on site from a discharge measurement? Y N NA

3. Using the graphs mentioned above, are samples obtained at the centroids of equal discharge increments? Y N NA

4. Is the number and location of verticals sampled adequate for the flow conditions and volume requirements? Y N NA

5. Is the transit rate correctly established for each vertical? Y N NA

6. Is the ratio of transit rate to stream velocity checked to see if it is in the correct range? Y N NA

7. Are items no. 2, 3, 6, 8, 9, and 10 from the EWI checklist performed? Y N NA

C. Pesticide and Organic Samples

1. Are samples collected using __ a single vertical near the centroid of the flow OR __ using multiple verticals? (depends on sampling constraints)

2. Are the sampler bottle, cap, and nozzle made from materials appropriate for sampling organics? Y N NA

3. Are samples labeled and preserved as required? Y N NA

4. Are dissolved and suspended organic carbon samples correctly processed using silver membrane filters under pressure with a peristaltric pump or carbon-free nitrogen gas? Y N NA

5. Remarks_____

_____

_____

VI. PROCESSING THE SAMPLE

1. Are samples processed in a clean area, protected from contamination? Y N NA

2. If churn splitter is used, is the sample churned at a uniform rate of about 9 inches per second, touching the bottom of the churn every stroke and without breaking water surface when filling unfiltered sample bottles? Y N NA

3. If churn splitter is used, is the sample churned for at least 10 strokes before any subsamples are withdrawn and is the constant churning rate maintained while unfiltered samples are drawn off? Y N NA

4. If cone splitter is used, are splits calculated and done correctly? Y N NA

5. Is filtration performed AFTER drawing off the raw samples and the samples needed for field measurements? Y N NA

6. Is filtration accomplished with a peristaltic pump using 0.45 micron filters? (plate___capsule___other___) Y N NA

IF NO EXPLAIN METHOD_____

_____

_____

7. Is the filter rinsed to remove surfactants prior to collecting any samples by drawing at least 1L of deionized water through the filter? Y N NA

8. Are sample bottles labeled to identify sample type, time and date of collection, and site ID? Y N NA

9. Are sample bottles filled and preserved in the correct order? Y N NA
(trace elements; mercury; nutrients; major ions; alkalinity; radiochemicals; others)

10. Are samples preserved using the correct ampules, and/or chilling the samples? Y N NA

11. Are bottles labeled in a manner such that the writing will still be readable when the samples reach the lab? Y N NA

12. Are ampules handled safely and disposed of properly? Y N NA

13. Are gloves and eye protection worn at all times when handling ampules? Y N NA

VII. FIELD MEASUREMENTS

Does a visual inspection of field meters indicate any of the following problems? (indicate which meter has the problem)

Excessive wear_____ Damaged probes or electrodes_____

Excessive age_____ Inappropriate for given use_____

Remarks_____

_____

_____

A. Temperature

1. Is water temperature measured in centroid of streamflow or by wading into stream as far as possible? Y N NA

IF NO EXPLAIN METHOD_____

_____

_____

2. Is thermometer or thermister accuracy periodically checked with an ASTM certified thermometer? Y N NA

3. Is air temperature measured? Y N NA

B. Dissolved Oxygen

1. Is dissolved oxygen meter calibrated in field using water temperature and barometric pressure? Y N NA

IF NO EXPLAIN METHOD_____

_____

_____

2. Are all calibration procedures properly followed? Y N NA

3. Prior to use, is the D.O. membrane inspected to ensure there are no air bubbles under it? Y N NA

4. Is dissolved oxygen measured in the center of flow if possible with probe in downstream direction to avoid damaging the membrane? Y N NA

5. In low velocity streams, is the probe moved slowly from side to side or a stirrer used to avoid inaccurate readings due to oxygen depletion? Y N NA

C. pH and Alkalinity

1. Is the pH meter calibrated in the field using the standard two-point calibration method? Y N NA

2. Are the bottles of buffer solution that are used for calibration submerged in container of stream water or brought to approximate sample temperature by an acceptable method? Y N NA

3. Is the electrode rinsed with buffer solution before that buffer is measured? Y N NA

4. Does the electrode calibrate to within +/-.1 pH units on the third check buffer solution? Y N NA

5. Is pH measured using an unfiltered sample? Y N NA
From Composite___ In Stream___

6. Is the pH reading confirmed by repeated measurements using at least two aliquots? Y N NA

7. Is the electrode rinsed and carefully blotted dry (not rubbed) between measurements? Y N NA

8. Is alkalinity measured on a filtered sample? Y N NA

9. Is the incremental titration method used to determine carbonate and bicarbonate concentrations? Y N NA

IF NO EXPLAIN METHOD_____

_____

10. Is a burette_____ or Hach titrator_____ used?
Is the normality of the sulfuric acid noted? Y N NA

11. Is the volume of sample used in the titration recorded? Y N NA

12. If a Hach titrator is used, are air bubbles cleared from the delivery tube prior to beginning the titration? Y N NA

13. Is a clear delivery tube used? Y N NA

14. Is the tip of the delivery tube below the water surface while increments of acid are added to the sample? Y N NA

15. Are increments of sulfuric acid added in a manner that clearly defines the endpoint for carbonate and bicarbonate? Y N NA

16. Remarks_____

_____

Specific Conductance

1. Does the type of meter used require field calibration? Y N NA
IF NO EXPLAIN_____

_____

2. Is the performance of the specific conductance meter checked by measuring 2-3 standard solutions? Y N NA

3. Is the specific conductance reading confirmed by repeating the measurement in at least two aliquots? Y N NA

4. Is temperature compensation applied? Y N NA

5. Remarks_____

_____

_____

VIII. MICROBIOLOGICAL ANALYSES

1. Check-off the microbiological methods being used by the District Office:

_____total coliform _____fecal coliform _____fecal streptococcus

_____E. coli _____enterococci_____other_____

2. How many samples per year of each test are analyzed by the District?

_____total coliform _____fecal coliform _____fecal streptococcus

_____E. coli _____enterococci_____other_____

3. What kind of projects are samples collected for?

___water-quality assessment (indicate type: **NASQAN___ NAWQA___ BASIC DATA___OTHER___**)

___discharge permit work ___other (list)_____

A. Equipment for Microbiological Analysis:

___autoclave ___steam sterilizer ___uv sterilizer ___waterbath incubator
___alcohol lamp ___dry-heat incubator ___D-77 sampler ___DH-81 sampler
___other sampler ___pipettes ___dilution bottles ___microscope ___forceps
___syringes ___hand-held magnifier ___graduated cylinders
___0.45 ___0.65um pore-size filters ___absorbent pads ___sterile filtration system

B. Media, Buffered Water, and Preparation:

1. Are holding times and expiration dates observed for media and buffer? Y N NA

2. Was the agar stored in a desiccator? Y N NA

3. Was the media prepared according to the instructions that came with the media kit? Y N NA

4. For fecal coliform analysis; is the rosolic acid added to the agar after boiling? Y N NA

5. For E. coli, is the agar autoclaved after boiling? Y N NA

6. For fecal strep, is the TTC added after cooling the agar to 60 degrees °C? Y N NA

7. Are bottles of sterile buffer dilution chilled at 4°C until needed in a manner which minimizes the possibility of contamination from melting ice? Y N NA

8. Are sterile bacteria plates chilled at 4°C in the same manner? Y N NA

9. Are all parts of the filtration apparatus sterilized prior to use at each site (or for each sample)? This includes filter funnel, filter holder base, graduated cylinders and pipettes. Y N NA

C. Sample Collection:

1. What technique is used to collect the bacteria sample?
depth-width integration ___single vertical ___point at centroid of flow

2. What type of sample-collection equipment is used? D-77___ DH-81___ weighted bottle___ BOD___ DH-95___ D-95___ Dip___ Other_____

Is the sample:

3. Collected in a sterile bottle? Y N NA

4. Chilled on ice between collection and filtration? Y N NA

5. Processed within 6 hours of collection? Y N NA

D. Plating

1. Vigorously shaken (15 times) before each sample volume is withdrawn? Y N NA

2. Was the membrane filter technique correctly used? Y N NA

3. Are sample volumes filtered from smallest to largest? Y N NA

4. Is vacuum applied to filters no more than 15 psi? Y N NA

5. Is an appropriate range of sample volumes used for filtration to maximize probability of obtaining ideal colony counts? Y N NA

6. Are the forceps sterilized before transferring each filter to the filtration unit? Y N NA

7. For sample volumes of 10 mL or less is at least 10 mL of the buffer dilution sample poured into the filtration apparatus before pipetting the sample? Y N NA

8. Is the filtration unit thoroughly rinsed with buffer solution after each bacteria sample is drawn through the unit? Y N NA

9. Does the field person transfer the filter from the filtration unit to the petri dish using good technique and without introducing contamination? Y N NA

10. Is the filter apparatus sterilized using an approved method? Y N NA

11. Is left-over dilution water discarded at the end of the day? Y N NA

12. Are petri dishes labeled with site ID, sample volume, date and time, and sample type? Y N NA

13. Are sample incubation start and end times recorded? Y N NA

14. Are petri dishes incubated promptly at the correct temperature, with the filter inverted? Y N NA

15. Is there evidence that bacteria colonies have been counted after the correct incubation periods and that the total counts per 100 mL have been correctly tabulated in the past? (Examine previous results for the site) Y N NA

E. Safety Practices

1. Are petri dishes sterilized prior to disposal? Y N NA

2. Are aseptic techniques used in all parts of the procedure? For example, samples should not be counted in an office or area where beverages or food are ingested. Y N NA

3. Are all steps completed in an appropriate laboratory or field vehicle area that is cleaned with bactericidal solutions, including the counting and enumeration steps? If not, are all surfaces wiped clean with bactericidal solutions (e.g. alcohol) after use? Y N NA

4.Are pipettors used when needed for small volume samples? (never pipet by mouth) Y N NA

F. QC Specifically For Microbiological Analyses:

(studies have indicated more errors are associated with bacteria analysis then any other field measured WQ parameter, so extra attention is warranted).

1. Are incubators tested for temperature settings and tolerances by use of an independent, ASTM or NIST traceable thermometer? Y N NA

2. Are the correct temperature, pressure, time settings being used for autoclaves and sterilizers? Y N NA

3. Are records kept of the above? Y N NA

4. Are blank samples analyzed with each new batch of dilution water or with every 10 samples? Y N NA

5. Are samples analyzed in duplicate to estimate precision at a frequency of once in every 10 to 20 samples? Y N NA

6. Are the data obtained in preceding duplicate analysis recorded and used? Y N NA

7. Are countable plates re-examined and counted by another experienced person periodically? Y N NA

8. Are quality control samples of pure cultures used as a positive control periodically? Y N NA

9. List the reference documents used as part of the test method and collection method.

____TWRI ____EPA Manual ____Standard Methods ____other

11. Remarks _____

WRAPPING UP

Is the field form filled out completely, including any remarks regarding conditions at the time sample was collected, whether the water was clear or muddy, any unusual conditions, or problems etc.? _____

Notes or Final Remarks

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____