

**COLLECTION AND FIELD ANALYSIS
OF
WATER QUALITY SAMPLES**



**U.S. SECTION
INTERNATIONAL BOUNDARY AND WATER COMMISSION
ENVIRONMENTAL MANAGEMENT DIVISION**

August 1997

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INTRODUCTION

This manual has been prepared by the Environmental Management Division (EMD) of the U.S. Section of the International Boundary and Water Commission (USIBWC), to provide detailed guidelines for the collection of water and sediment samples and field analysis of water quality samples. The procedures described herein were extracted from manuals of agencies of recognized authority in the fields of water quality sampling and analysis, including the U.S. Environmental Protection Agency (EPA), the U.S. Geological Survey (USGS), the Texas Natural Resource Conservation Commission (TNRCC), and the Arizona Water Resources Research Center (AWRRC).

Although the procedures described in the manual are applicable to most water quality sampling studies proposed by the USIBWC, it should be recognized that each sampling study may have unique characteristics and problems not fully covered by these guidelines. Should procedural questions arise that are not covered in this manual, the EMD should be contacted for clarification and instructions.

PART I - SAMPLING

Before a water quality investigation can be conducted, information about the sampling locations, sampling parameters and methods that will be used is needed. This information is required for writing federal or state sampling plans. In addition, sampling cannot proceed until a plan has been developed that specifies the locations, number of samples, kind of samples, numbers and kinds of quality assurance/quality control (QA/QC) samples, and desired quality of the data. The samplers are responsible for collecting and handling samples and keeping records in accordance with the sampling plan.

1. SAMPLING PLAN

The intent of the sampling plan is to ensure that complete and consistent sampling procedures have been developed before any sampling takes place. A complete sampling plan protects the sampling agency from errors and omissions that could compromise or invalidate sampling results. Water quality sampling is expensive and time consuming, so be certain before you start, that samples will serve the project goals.

This manual will provide guidance for ongoing USIBWC sampling activities. EMD will provide a sampling plan for special projects.

2. SITE SELECTION

If the investigator has primary responsibility for station selection, he or she should consult with the appropriate individuals and review all available information in order to establish the sampling locations based on the following:

- the location should allow samples to be obtained throughout the entire year (i.e., take into consideration seasonal wells and all discharges)
- the location should allow for the collection of representative samples (to measure a site's regional or local water quality depending on the objectives of the sampling)
- existing sampling locations should, if possible, be incorporated in the sampling program
- the sampling array should be efficient (over sampling as well as under sampling should be avoided)
- the sample size should be adequate for obtaining statistically valid results

If samples are collected that do not truly reflect the composition or condition of the water body, errors may be introduced. The extent to which a single small sample can adequately represent a large water body will depend upon several factors, the chief of which is the homogeneity of the water body and the manner and care in which the sample is collected.

Most water bodies are not completely homogenous; consequently, the collection of a representative sample will depend upon the method of sampling and the number and size of samples collected.

A. SURFACE WATERS - RIVERS AND STREAMS

Sampling programs for flowing water bodies must be designed so that samples collected represent the entire flow of the stream at that location and that instant in time. For this reason, sampling stations should not be established at locations where mixing is not complete or where significant cross-sectional variations exist in water quality composition. If new stations are being added, describe their number, type, location and construction before continuing the sampling process. At least three visits may be required to establish new stations to do the following:

Select and examine the potential station through reconnaissance to ensure that the surface water body is the optimum location to provide water quality data. At a river, for example, find a section where the channel is smoothest, straightest, accessible and uniform in depth, at least 30 meters (100 feet), or more depending on backwater conditions, upstream from a confluence, and near a landmark, such as a bridge, large boulder or tree. If the river is flowing, measure its temperature, pH, electrical conductivity, or dissolved oxygen at regular intervals and depths across the channel to test the degree of mixing of the flowing water. The variability in these parameters will help you decide how many vertical sections will be needed to accurately sample this stream. A well-mixed channel requires fewer samples to be composited than one showing distinct change from one location to another. Other major siting considerations are the location of upstream or downstream sources of contamination and their impact on water quality, and whether or not you can access the station at all discharges.

For some specific purposes, a single point sample may be desired if that point differs significantly in composition from the rest of the stream. Such a point may be the area of issuance of a spring in the river channel or a point directly below a waste outfall. In such cases, the sample should be adequately identified so as to lessen the chance of misinterpretation.

Samples should be taken during a period when stream stage is near normal and has been relatively stable for the preceding week. When samples are collected during abnormally high or low flow as during rising or falling stages, the abnormal conditions should be recorded in the field notebook and on the observation lines of the sample data form.

Sites which are impacted by oxygen-demanding wastes or excessive nutrients, such as downstream of waste outfalls or storm drains, should be sampled for physico-chemical parameters as close to dawn as possible to determine the dissolved oxygen minimum. Special studies may require that sampling be performed under specific conditions, such as wet-weather monitoring.

Metals-in-water samples collected for trend monitoring should not be collected during periods of abnormally high turbidity, since such samples are unstable in terms of soluble metals and it is difficult to collect a representative sample. For stream samples, the centroid of flow should be accessible (except for rare locations, discharge-weighted samples should be collected) for sampling physicochemical parameters, either by bridge, boat or wading. The least preferable site in general is the shoreline.

B. SURFACE WATERS - LAKES AND RESERVOIRS

Selection of sampling sites on lakes and reservoirs depends upon the degree of accuracy acceptable in determining the composition of the water body and upon the degree of mixing which occurs in the lake. It is generally better to sample at the midpoint of the reservoir at approximately mid-depth, so as to represent as nearly as possible the average of the water mass. When the prime consideration is the suitability of stored water for downstream use, the sampling station may be located at the point of discharge.

In general, final selection of sample stations for a standing water body should be made after a thorough review of existing data, maps, and an on-site visitation. The number of stations needed to adequately define a water body will depend upon the number of influent streams and the lake's size and shape. Evaporation in long bays, inlets, and backwaters may significantly alter the water composition. Each major tributary should be sampled as near the reservoir as possible, and above backwater effects in an area of measurable flow.

C. DOMESTIC SUPPLY

Generally, the purpose of sampling a domestic supply system is to evaluate its suitability for drinking water. Several factors enter into the choice of sampling location. The longer the system, the less residual dissolved chlorine is available at the farthest point from the chlorinators. As the chlorine residual is diminished, the possibility of bacteriological regrowth is enhanced. Consequently, for bacteriological considerations, the farthest point of the distribution system may be the most favorable.

When sampling for dissolved metals in the source water, samples should be collected from as near to the source as possible and preferably before chlorination. When sampling for dissolved metals in a domestic supply, allow the system to sit overnight. The next morning, collect the first draw from the system.

As domestic water taps are frequently handled, the chance for bacteriological contamination from the tap, rather than from the water source, is an important consideration. Special precautions may be necessary to disinfect the tap before a bacteriological sample is collected. Discussions of techniques for sterilization are provided in the discussion of bacteriological sampling under Domestic Supply in Section 5.D.

3. PREPARATION

A. PRELIMINARY PLANNING

After selection of a sampling site and prior to initiating the sampling program, the program coordinator or field supervisor should visit each station with the individual responsible for collection of the samples, and give any additional instructions that may be necessary. Such instructions may include the exact location, depth, and manner of sampling. The optimum sampling time and the

conditions which will affect the sampling should be discussed. The reading of staff gages and other field observations should be described, and the format for reporting this information on the sample tags should be explained.

At the time of this pre-sampling visitation, the necessary construction, removal of obstacles for easy access, cutting of brush, etc., should be accomplished. It should be borne in mind that at the next visitation, the collector will be encumbered with field equipment and sample bottles, and the slight obstacles encountered on the preliminary visitations may be greatly increased if the sample collector is encumbered. Small foot bridges of a single plank across boggy areas and the removal of low-hanging limbs may greatly facilitate access to the sampling location.

The sample collector should, prior to the sampling trip, make all possible preparations and equipment checks a few days in advance of the trip. All equipment should be cleaned and stored in appropriate transport containers. Field meters should be checked and calibrated, reagents and sample preservatives checked and replaced, sample bottles obtained and sample tags prefilled in advance if possible, and any miscellaneous sampling equipment assembled and checked for shortages and operational conditions. Obtaining a representative sample means being careful in your choice of equipment. If you are sampling for the presence of heavy metals, do not use samplers with metal components. When sampling for organics, avoid using samplers with plastic components, as the plastic may absorb and/or contaminate the samples. Most important, always decontaminate, wrap inorganic equipment in plastic and other equipment in aluminum foil for transport to the site.

Table No. 1 is a check list that should be reviewed as part of the planning for any sampling activity.

The proper handling of water quality samples also includes wearing gloves. Gloves not only protect field personnel, but also prevent potential contamination to the water sample. Always wear powderless, disposable gloves. When sampling for inorganics, wear latex gloves. Nitrile gloves are appropriate for organics. Certain organics, such as solvents, will dissolve latex gloves.

B. SAMPLE CONTAINERS

Clean sample containers, preservatives and coolers are generally provided by the laboratory. Contact the laboratory about a month before the sampling date to schedule analyses and container shipment or pickup. Use chain-of-custody procedures when cooler and containers are prepared, sealed and shipped. They should remain sealed until used in the field. When making arrangements with the laboratory, make sure you request enough containers, including those for blank and duplicate samples. Order extra sample bottles to allow for breakage or contamination in the field.

Some samples require low temperature storage and/or preservation with chemicals to maintain their integrity during shipment and before analysis in the laboratory. The most common preservatives are hydrochloric, nitric, sulfuric and ascorbic acids, sodium hydroxide, sodium thiosulfate, and biocide. Many laboratories provide pre-preserved bottles filled with measured amounts of preservatives. Although most federal and state agencies allow the use of pre-preserved sample containers, some may

require either cool temperatures or added preservatives in the field.

When the containers and preservatives are received from the laboratory, check to see that none have leaked. Be aware that many preservatives can burn eyes and skin, and must be handled carefully. Sampling bottles should be labeled with type of preservative used, type of analysis to be done and be accompanied by a Material Safety Data Sheet (MSDS). Make sure you can tell which containers are pre-preserved, because extra care must be taken not to overfill them when collecting samples in the field. Check with the laboratory about quality control procedures when using pre-preserved bottles.

Coolers used for sample shipment must be large enough to store containers, packing materials and ice. Obtain extra coolers, if necessary. Never store coolers and containers near solvents, fuels or other sources of contamination or combustion. In warm weather, keep coolers and samples in the shade.

C. SHIPPING PROCEDURES

The following instructions should be followed when preparing samples for shipping. Prior to sampling, make arrangements for sample pick-up or delivery with a shipping company, such as FEDEX or UPS or pick-up by the laboratory to ensure the samples reach the laboratory within the holding time and while the temperature inside the container is still below 4° Celsius.

1. Preserve samples immediately after collection by placing them on crushed ice and by storing them away from direct sunlight. Follow the preservation procedures included for each sample type included in this manual. Sufficient crushed ice should be used to lower the sample temperature to less than 4° Celsius within 45 minutes after time of collection.
2. Prepare the samples for shipment by placing them in a **sturdy**, plastic cooler to ensure the sample temperature will be maintained at a temperature less than 4° Celsius until delivered to the laboratory. Blue Ice; frozen cubitainers with caps securely tightened or other non-leaking forms of ice should be used to ship the samples. **DO NOT** use “dry ice” since dry ice may freeze the samples and cause them to break. Crushed ice should only be used to cool samples immediately after collection. Once all samples have been securely packed for shipping, seal the container with tape. You may need to purchase durable, sturdy coolers for shipping water quality samples. Make sure you label the coolers with indelible ink with your name and return address. The laboratory will return the cooler to you after each shipment.
3. Attach the properly completed shipping documents and ship to the designated laboratory.

D. FIELD SAFETY AND FIRST AID

Before you attempt to collect water quality samples, you must be aware of the applicable health and safety requirements. Since sample collection may occur at contaminated sites or in remote, rugged country far from immediate medical attention:

1. Receive prior training in personal safety at a level appropriate for the types of chemicals or contamination likely to be encountered.
2. Consult with the safety officer.
3. Avoid going alone to the field. If you must go alone, notify your supervisor of your itinerary and schedule
4. Determine the location of the nearest hospital, clinic or physician beforehand.
5. Receive the appropriate immunizations. Vaccinations for tetanus, Hepatitis A and B, and typhoid fever is recommended when working near contaminated waters.
6. Notify others of your itinerary and whereabouts.
7. Take precautions against hunters, poisonous reptiles, scorpions and sudden floods.
8. Carry identification. If possible, take a two-way radio or cellular telephone with you.
9. Be aware of all bridge safety regulations. Check with the USGS bridge sampling protocol for guidelines.
10. When handling sample preservatives such as acid, always wear splash-proof goggles and non-contaminating gloves.

Water samples are collected under a variety of conditions, some of which may pose a hazard to the incautious or untrained. A knowledge of some of the dangers that may be encountered, and means of preventing them, may minimize these hazards and provide greater safety for sample collectors.

Surface water samples collected from bridges, piers, boats, cableways, or by wading from the shore, always present the possibility of falling into deep water. The inability to swim, or becoming encumbered in sampling equipment in such a fashion as to restrict the sampler's swimming ability, are the most serious hazards in water quality field work.

The USGS, in its Water Supply Paper 1454, "Methods for Collection and Analysis of Water Samples," presents comments in regard to sampling safety. Appendix A contains information abstracted from the Water Supply Paper 1454.

Table No. 1

WATER SAMPLING SUPPLIES CHECKLIST

FIELD SURVIVAL

- ☐ Map of station locations
- ☐ Business card or ID
- ☐ Authorizations (letter, etc.)
- ☐ Field Notebook
- ☐ Waterproof pens, markers, and pencils
- ☐ Masking tape and rubber bands
- ☐ Trip routing forms
- ☐ Road Log
- ☐ Photo log forms
- ☐ Field data forms
- ☐ Chain of custody forms
- ☐ Other forms
- ☐ Keys or security codes for gates and locks
- ☐ Graphite lubricant (not oil or WD-40) for locks and well caps
- ☐ First aid kit, knife
- ☐ Insect repellent (wash hands thoroughly after applying)
- ☐ Hat, sunscreen, drinking water
- ☐ Sunglasses or safety glasses
- ☐ Leather gloves
- ☐ Steel-toed boots, rubber boots and/or waders
- ☐ Rain gear
- ☐ Toolbox with basic tools
- ☐ Tape measure
- ☐ Flashlight and extra batteries
- ☐ 2-way radio/cellular phone
- ☐ Binoculars
- ☐ Weather radio
- ☐ Uniform
- ☐ Rope
- ☐ Fire extinguisher (Type B)
- ☐ Helmet or hard hat

SPECIALIZED HEALTH AND SAFETY

- ☐ Tyvex suits, non-contaminating gloves, tape, goggles, respirator, extra filters
- ☐ Explosivity meter or photoionization meter

FIELD PARAMETER MEASUREMENT

- ☐ Stopwatch
- ☐ Calculator
- ☐ Non-mercuric thermometers (2)
- ☐ pH meter and buffers, pH indicator strips
- ☐ Turbidimeter
- ☐ Rain gage
- ☐ Temperature, Conductivity, Redox and DO meters, probes and batteries
- ☐ Appropriate Hach kit(s)
- ☐ Flow-through cell
- ☐ Copies of manufacturers manuals for field equipment
- ☐ 1.8 m (6-ft) wooden engineers ruler

SURFACE WATER

- ☐ Flow meter, rod and tape measure
- ☐ DH-81 sampler (with Teflon nozzle and gasket for VOCs)
- ☐ Van Dorn or Kemmerer bottle and string
- ☐ D-77 for large streams
- ☐ Glass mason jars, 1-quart
- ☐ Churn splitter
- ☐ Decontaminated spade
- ☐ Life jacket

TABLE No. 1 (continued)

PHYSICAL POSITIONING

- ☐ Camera, film
- ☐ Topographic map
- ☐ Tape measure
- ☐ Aerial photograph (optional)
- ☐ Global positioning system (optional)

MICROBIAL SAMPLING

- ☐ Ziploc plastic bags (1 gallon size)
- ☐ Disposable nitrile gloves
- ☐ Filtration equipment, tubing, pump, flowmeter
- ☐ Sterilized Whirl-pak bags (for fecal coliform and E. Coli samples)
- ☐ Teflon tweezers
- ☐ Bactericidal soap
- ☐ Bacteria sample rack
- ☐ Sterile and buffered water

CLEANING AND DECONTAMINATION

- ☐ Alconox non-phosphate detergent
- ☐ Carboy-tap water (1 gallon per well)
- ☐ Carboy-deionized water (2 gallons per well)
- ☐ Carboy-HPLC grade, organic-free water (0.5 gallon per well)
- ☐ Squeeze bottle for DI water
- ☐ 0.1N nitric acid rinse (when sampling for metals)
- ☐ Pesticide-grade solvent, such as hexane (when sampling for volatile or non-volatile compounds)
- ☐ 10% sodium thiosulfate solution (0.25 gallon for viral sampling)
- ☐ Chlorine bleach (5% for 20 minutes for decontaminating viral sampling equipment)
- ☐ Hand-pump sprayers for washing fluids
- ☐ Decontamination vessel (plastic garbage can)
- ☐ Aluminum foil
- ☐ Plastic garbage bag for disposable equipment

GROUND WATER

- ☐ Electric water level probe or graduated (3mm/0.01 foot) tape with water indicator paste, gel, non-ferro- cyanide chalk or 'popper'
- ☐ Clear plastic bailer (for oil)
- ☐ Interface probe
- ☐ Containers for purged water
- ☐ Pipe wrench
- ☐ Pump and tubing
- ☐ Compressed air for pump
- ☐ Pipe threader, pipe adapters, faucets or valves
- ☐ Calibrated bucket

SAMPLING

- ☐ Sealed coolers and sample containers
- ☐ Bags of ice
- ☐ Maximum/minimum non-mercuric thermometers (one per cooler)
- ☐ Folding table
- ☐ Polyethylene plastic sheets (1 per station)
- ☐ Paper towels, KIM-wipes, oil sorbent pads
- ☐ Teflon-lined screw caps (for radon volatile and semi-volatile organics)
- ☐ Sodium thiosulfate or ascorbic acid for volatile organics if chlorine is present)
- ☐ Preservatives (i.e. HNO_3 , HCl , H_2SO_4 , HgCl_2)
- ☐ Residual chlorine test kit
- ☐ Glass vials (for radon and volatile organics)
- ☐ Amber glass bottle (for semi-volatile organics)
- ☐ Concentrated sulfuric acid (for phenols, oil and grease)
- ☐ Precleaned sample containers (for metals)
- ☐ Precleaned sampling tubes (for metals)
- ☐ Metals-free deionized water (for metals)
- ☐ Filter cartridges (for metals)
- ☐ Peristaltic pump
- ☐ Disposable powder free latex or nitrile gloves

4. RECORD KEEPING

A. MINIMUM SET OF DATA ELEMENTS

On October 29, 1992, the EPA approved the establishment of the minimum set of data elements (MSDE) for ground water quality. The purpose of the MSDE is to share and manage water-quality information effectively at the federal, state, county and local levels of government.

The MDSE consists of 21 data elements. Items 1 through 10 and 17 through 21 below also are applicable to surface water quality sampling.

IDENTIFICATION

1. Data Source: Name of the organization to which questions regarding the following data can be directed.

LOCATION

2. Latitude: A coordinate representation that indicates a location on the surface of the earth using the earth's equator as the latitudinal origin, reported in degrees, minutes, seconds, and fractions of a second in decimal format (if fractions of a second are available). A "+" (plus) symbol represents latitudes north of the equator. A "-" (minus) symbol represents latitudes south of the equator.
3. Longitude: A coordinate representation that indicates a location on the surface of the earth using the prime meridian as the longitudinal origin, reported in degrees, minutes, seconds, and fractions of seconds (if fractions of a second are available). A "+" (plus) symbol represents longitudes "east" of the prime meridian.
4. Method Used to Determine Latitude and Longitude: The procedure used to determine the latitude and longitude coordinates, the standard used for three dimensional and horizontal positioning, and the date on which the coordinates were determined.
5. Description of Entity: A textual description of the entity (e.g., sampling station) to which the latitude and longitude coordinate refers.
6. Accuracy of Latitude and Longitude Measurement: The quantitative measurement of the amount of deviation from true value presents in a measurement (estimate of error). It describes the correctness of a measurement.
7. Altitude: The vertical distance from the National Reference Datum for Altitude to the land surface or other measuring point in meters (or feet). If the measuring point is above the National Reference Datum for altitude, a "+" (plus) sign shall precede the reported altitude value. If the measuring point is below the National Reference Datum for Altitude a "-" (minus) sign shall precede the reported altitude value.
8. Method Used to Determine Altitude: The method used to determine the altitude value, the National Reference Datum on which the altitude measurement is based, and the date the measurement was taken.

9. **State FIPS Code:** A Federal Information Processing Standard (FIPS) alphabetic or numeric code to indicate the state (or its equivalent such as territory or province) in which the station or well is located.

10. **County FIPS Code:** An FIPS numeric code to indicate the location of the county (or county equivalent such as territory or province) in which the station or well is located.

WELL INFORMATION

11. **Well Identifier:** A unique well indicator assigned by the responsible organization.

12. **Well Use:** The principal current use of the well; if the well is not currently in use, the original or principal purpose for its construction.

13. **Type of Log:** The type of record-keeping log(s) available for a well.

14. **Depth of Well of Completion:** The depth of the completed well below the land surface or other measuring point, in meters (or feet).

15. **Screened/Open Interval:** The depth below the measuring point to the top and bottom of the open section in a well reported as an interval in meters (or feet). The open section may be a well screen, perforated casing or open hole.

16. **Depth to Water:** The vertical distance between the measuring point and the water surface level at a well, corrected to land surfaces, where the measuring point is not the land surface. Report this distance in meters (or feet), along with the data and time of measurement.

SAMPLE INFORMATION

17. **Sample Identifier:** A unique number for each water quality sample collected which references the date, the depth at which each sample is taken reported in meters (or feet) (if the sample was taken from a well), and the time the sample was taken.

18. **Constituent or Parameter Measured:** Measurement of a physical, chemical or biological component is referred to as a constituent or parameter.

19. **Concentration/Value:** The analytical results value, the units of measure used, and the analytical methods applied.

20. **Analytical Results Qualifier:** Qualifying information that will assist in the interpretation of the concentration/value, such as whether the level is below the detectable limit or if the constituents (or parameters) of interest are present but cannot be quantified.

21. **Quality Assurance Indicator:** The quality assurance of the field protocol plan and laboratory QA/QC procedures.

B. KEEPING FIELD NOTES

Modern sample collection in the field requires adequate documentation for quality assurance and control. Maintain a separate file in the office for each station. The sampling station file may contain detailed written notes describing how samples were taken, field measurements, previous laboratory analyses, permission forms, chain-of-custody records, maps, photographs and correspondence. Because of the importance of official and legal documents, make these as legible and complete as possible.

The recording process is more efficient if one person performs the sampling while the other takes field notes. The following items shall be recorded in indelible ink:

- Samplers' identity
- Time and date of sampling
- Significant weather conditions, current and recent
- Sample description (type, volume, grab or composite)
- Site location (preferable cadastral and lat/long coordinates)
- Sample identification (well number, project number)
- Name and address of site/well owner
- Pertinent site/well data (well construction data, pumping schedule & method, waste types, etc.)
- Method and results of field measurements; appearance of the sample
- Sample method(s)
- Reason for sampling
- Type of analysis for which samples are collected
- Signatures of persons making log entries
- Volume of water purged from the well, including the date and time from start to completion of purging
- Preservation methods
- Observations and comments (accessibility, calibration results, divergence from protocols, safety hazards encountered, aquatic organisms present, wildlife, bank conditions, anthropogenic activities, stream-bed composition, photographs, QA/QC methods used, etc.)
- Duplicate sample location
- Field meter calibration results

Remarks - The observations and comments of the samples at the time of collection may be extremely important in the interpretation of the subsequent chemical analysis. The importance of submitting in writing along with the sample, the source of the sample and conditions under which it was collected, cannot be over emphasized.

Recent weather conditions should be recorded. Heavy rainfall leading to recent runoff will greatly alter the chemical composition and bacteriological concentration of surface waters. Cloud conditions will affect not only the composition of the dissolved gas species in the water by diminishing the rate of carbon affixation by chloroplast but may also alter the appearance of a river. It may appear murky and polluted on a cloudy day and clean and clear on a sunny day.

Water quality in small to medium streams and in the headwaters of many lakes is influenced by runoff during

and immediately after rainfall events. This influence is site specific and poorly studied. As part of a new initiative to understand and regulate the adverse effects of runoff, we would like to associate recent rains or melted snow with ambient water quality, using a parameter defined as "days since last significant precipitation." Record the number of days, rounded to the nearest whole number, since rain has occurred that, in your professional judgement, may have influenced water quality. If it is raining when the sample is collected, or has rained within the last 24-hours, report a value of <1. If you know that it has been a long time since significant rain, record this as greater than that particular value, i.e., >15 days. If you have no confidence about the recent history of precipitation, draw a line through the space on the data form.

The stream's appearance and such conditions as slimes, alga blooms, muddy water, turbidity, color, oil slicks, debris, etc. should be noted in the remarks section of the tags and on the field analyses sheet.

Report changes in river stage, whether rising or falling, if known, and also that of tributaries above the sampling station. Activities which may affect stream composition should be noted if observed. Dredging will increase turbidity and possibly redissolve phosphorous or metals from the bottom sediments. The presence of cattle, wildlife, or aquatic wildfowl may greatly alter the bacteriological and nutrient levels in the immediate area. Bathers upstream from the sampling station may also affect the samples.

Catastrophic conditions such as fish kills and oil spills should be recorded on sample tags and appropriate officials notified.

5. WATER SAMPLE COLLECTION

A. RIVERS AND STREAMS

Collection of samples from rivers and streams involves transporting all necessary items to the sampling station and setting up field notes, instrumentation, filtration equipment (if required), sample containers and decontamination washes near the river or stream. The first step is to measure all field parameters and then measure stream flow.

1. Field Parameters - Measure and record the following field parameters: temperature, electrical conductivity, pH and dissolved oxygen in aliquot of water used for water quality analyses. Other parameters may be measured, if desired.

2. Streamflow Measurement - Before collecting water quality samples, record the stream's flow rate at the selected station. The flow rate measurement is important for estimating contaminant loading and other impacts. Follow USIBWC standard procedures for stream flow measurements.

3. Grab sampling should only be used when uniform mixing in the river or stream channel is assured, when point samples are desired, when sample degassing may occur, or when the water is too shallow for composite sampling. Record any decision to use grab sampling in the field notes.

When collecting a grab sample by hand, place the sample bottle neck down into the water and rotate to an upright position below the surface, while slowly moving the sample bottle upstream. Water samples should be collected away from debris or scum and in such a manner that no bedload sediment is disturbed

and mixed with the water sample.

Samples should be collected in the flowing portion of the stream away from stagnant areas or areas affected by eddies created by channel configuration or by upstream obstructions to the flow. It is recommended that water samples be collected directly into the sampling bottle. It is often convenient to use a bucket to obtain the sample, which then may be poured into the sample bottle. The bucket should be decontaminated before using at each sampling location.

4. Composite sampling is the preferred method to collect samples for water quality and is intended to produce a water quality sample representative of the total stream discharge. If your sampling plan calls for composite sampling, use a depth-integrating sampler, such as the DH-81. However, the DH-81 uses different nozzle sizes depending on the velocity and the size of the container. Consult the DH-81 documentation or your project manager for the appropriate size to use in your sampling program.

The equal-width-increment (EWI) method is used to obtain a discharge-weighted composite sample. To employ the EWI method, use a tape to measure the bank-to-bank width of flowing water in the channel. Divide the width into equal increments, using a minimum of ten increments for streams as much as 1.5 meters (5 feet) wide, to a maximum of twenty increments for wide channels. This will assure enough spacing to allow for discrete sampling at each vertical.

Next, determine the appropriate 'transit rate'; go to the deepest part of the channel, face upstream and slowly lower the sampler to the streambed at a constant rate; then immediately raise it back to the surface at a constant transit rate. At the correct transit rate the quart jar is about 3/4 full when it returns to the surface. If the jar becomes completely full while lowering the sampler, you must empty it and start over until you find the best transit rate. This may require some practice.

Once you have determined the transit rate, empty the sampler and return to the first vertical. Using the appropriate transit rate, lower and raise the sampler at successive verticals. Hand the jar to your co-worker (who is wearing clean disposable gloves). The co-worker will then pour the sample into the sample containers or a churn splitter. The churn splitter is a polyethylene vessel that slowly mixes the composited sample with a polypropylene disk. Sample the remaining verticals until enough samples have been collected for your needs, and add all the required preservatives. Because the churn splitter requires from 3 to 8 liters of composite water, verticals in a narrow stream may have to be sampled more than once. It is important, however, that all verticals be sampled the same number of times. It is also important to churn while drawing samples from the splitter.

Do not use a churn splitter to composite samples collected for volatile organics, organic carbon, oil and grease, pesticides, herbicides or bacteria, because its plastic components have the potential for adsorbing and contaminating the samples. Instead, use baked glass containers for sampling these parameters with the grab sampling method.

B. LAKES AND RESERVOIRS

Routine water samples for monitoring water quality of lakes and reservoirs are generally collected in the same manner as river grab samples and at a specific location and depth, usually one foot below the surface.

If the water sample is to be used to determine reservoir stratification or other purposes which may be affected by non-uniform composition, samples may be collected at selected depths.

When samples are collected from lakes and reservoirs that are not part of a routine ongoing monitoring program, it is best to take composite samples taken using a technique similar to the EWI sampling. Determine a transit rate sufficient to fill the sample bottle 3/4 full. If the bottle is too full on recovery, try a different transit rate.

1. Field Parameters - As in river and stream sampling, measure temperature, electrical conductivity, pH, and dissolved oxygen to assess the three-dimensional variability and stratification of water quality in ponds, lakes and large springs. If a boat is available, measure the change of these parameters throughout the lake with depth by slowly lowering and raising the probes at specified locations. Note the depth and location of the readings as accurately as possible. If the lake or pond is stratified, record the depth and thickness of the upper layer (epilimnion), transition zone (methalimnion), and lower layers (hypolimnion). If no boat is available, non-representative measurements can be made as a last resort at several accessible locations along the shore.

2. Onshore Sampling - If no boat is available, collect a surface sample using a clean one-quart jar. Record the sampling depth and distance from shore in the field log book.

3. Offshore sampling - Water samples from lakes and ponds may be obtained with Kemmerer or Van dorn (Alpha Bottle) samplers. Peristaltic pumps with weighted hoses also may be used. Use containers and pumps made of materials compatible with the parameters to be analyzed and carefully decontaminate before use. In general, rinse the samplers with lake water before collection, and obtain samples with the lowest concentrations (e.g., top before bottom) first. If samples are to be taken for chlorophyll, DO NOT acid wash the sampler as the acid quickly destroys chlorophyll.

In shallow lakes (those with fairly uniform dissolved oxygen concentrations with depth), take samples near the center of the lake at 30 cm (1 foot) depth. In deep lakes that are stratified, obtain samples at a minimum of three depths: 30 cm below the surface, at the top of the hypolimnion, and another at the base of the hypolimnion, approximately 1 meter (3 feet) above the lake bottom. Be sure not to mix the sample with bottom sediments. (EPA, August 1990, Monitoring Lake and Reservoir Restoration: EPA Office of Water, Washington, D.C. 20460, EPA 440/4-90-007).

Record the physical parameter measurements, location and depth of each sample taken. Carefully decontaminate the sampler before reuse.

C. GROUNDWATER

Well samples should only be collected after the well has been purged sufficiently to insure that stagnant water has been displaced by water from the aquifer. Generally, this can be achieved by purging the well until three successive measurements of field parameters (temperature, pH, conductivity and turbidity) have stabilized.

Sampling Monitoring Wells - collecting water quality samples from wells involves a careful process of

physically acquiring the best possible sample for the intended analysis, characterizing the environment from which the sample was drawn, and handling the sample so as to protect its value for its intended purpose. The goal of sample collection and field measurements is to accurately represent the water resource being sampled at that time. This means obtaining a series of measurements (field parameter or in-situ measurements) in a prescribed manner, preserving and maintaining water quality and QA/QC samples according to established guidelines, and observing chain of custody requirements.

Obtaining a representative sample means being careful in your choice of equipment. If you are sampling for the presence of heavy metals, do not use samplers with metal components. When sampling for organics, avoid using samplers with plastic components, as the plastic may adsorb and/or contaminate the samples. Most important, always decontaminate equipment before use. When sampling more than one well on a site, be sure to decontaminate all equipment before using it in another well. When weighting lines, do not use lead weights. In addition, do not use ferrocyanide chalk (blue) as this could introduce contaminants to the water quality sample.

The proper handling of water quality samples also includes wearing gloves. Gloves not only protect field personnel, but also prevent potential contamination to the water sample. Always wear powderless, disposable gloves. When sampling for inorganics, wear latex gloves. Nitrile gloves are appropriate for organics.

a. Open the well and check for trapped vapors - hold the probe of a photo-ionization meter or explosive gas meter at nose level and take vapor readings around and over the well. If volatile levels **in the breathing zone** are more than 5 ppm, at least level C protection is required. This level of personal protection requires wearing a Tyvek suit, air-purifying mask, nitrile or viton gloves, and over boots. **Consult your personal safety officer before testing or sampling this well.** Next, open the well by unlocking or unscrewing the well cap and take vapor readings.

If the reading in the breathing zone is less than 5 parts per million (ppm) volatile (Modified Level D) then insert a photoionization meter or explosive gas probe into the well casing to measure the degree of personal hazard from trapped vapors.

b. Measure the well - first, describe the well's condition and location in the field log book. Is the casing or cap bent, cracked or damaged in any way? Does the well appear to be secure against people or contamination? Are there nearby structures from which its location can be measured? If so, make a plan view sketch showing the distance from the well to these features to the nearest meter (or a foot). If a global positioning system is available, determine the well's latitude and longitude in degrees, minutes and seconds to the nearest fraction of a second. In the field log book, record the following information: Well number; date; your name; casing diameter; casing and screen material (if known); and description of the measurement point to be used.

In most wells, this is the inner edge of the well's top of casing. If there is an inner and outer casing, use the casing that is highest. If the top of the casing is not horizontal, use the edge that is highest above the ground and mark it with an arrow either scratched into the surface or drawn in waterproof ink. With a decontaminated tape or ruler, measure and record the measuring point's vertical height above the land surface to the nearest 3 cm (0.1 feet). This is called the well's 'stickup'.

c. Measure water level - measure the depth to water below the measuring point to the nearest 3 mm (0.10 feet). The objectives of this task are to determine: 1) the altitude of the water table for flow direction studies; and 2) the correct pump size and length of tubing for well purging and water quality sampling. Make sure the sampling pumps are turned off for an appropriate period before measuring the water level (at least 3 hrs for small diameter (2 in) to several days for large wells) and that pumping from adjacent wells (within ½ mile for large wells) is not influencing the water level at the sampling site. In most cases, a graduated steel or fiberglass tape or electric sounder is recommended. Cover the bottom of the tape with a water indicator paste, gel or non-ferrocyanide chalk that changes color when wet, or attach a metal cup, or “popper” that make a “pop” sound when it hits the water’s surface.

Electric sounders indicate water contact with either a light, meter or buzzer. After the first water contact, gently raise and lower the probe until the light, meter or buzzer activates. Record the reading at the measuring point. Electric sounders usually are ineffective if there is floating product in the well, such as a layer of petroleum products that may have leaked from underground storage tanks, etc. Other methods such as a tape, interface probe or clear bailer must be used. If you have any doubt about the accuracy of your water depth measurement, repeat it as many times as necessary until you get an unambiguous and reproducible reading.

Before you put an expensive probe into an unfamiliar well, use a non-lead weight of the same size as the probe to verify that you have sufficient access.

d. Plumb well depth - if you use an electric sounder, make sure the switch is turned off. Lower the weighted tape or sounding cable all the way to the bottom of the well. Continue reeling out until it feels limp in your hands. Raise and lower the tape or cable several times to ensure that the weight or probe has not become ‘hung up’ on the casing or screen joints. After you are confident that the maximum depth has been reached, slowly take up the slack. Record the depth below this measuring point to the nearest 3 mm (0.10 feet).

Reel up the tape or cable, and decontaminate it and the reel before its reuse in the next well. Some electric depth sounders allow the complete removal of their electronic components before cleaning so that the entire reel and cable can be safely immersed in decontaminating fluids.

Determining the finished well depth enables you to compare it to drillers’ log information, to assess the extent of in-screen filling by fine sediments (and therefore the efficiency of well development and the actual open length of the screen interval), to help determine the well’s condition for sampling, and to measure the length of cable and tubing necessary to place the pump at the optimum depth.

e. Purge and sample the monitoring well - removing or ‘purging’ stale water from the well, pump and tubing to ensure that the sample is representative of aquifer water at the monitored depth is one of the most important aspects of sample collection. Select the method of purging and sampling based on site-specific conditions and goals described in the sampling plan.

The low-flow purging method is an effective approach when compared to other methods. However, it is not officially approved by the EPA at this time. Recent studies by the EPA and others regarding sampling for metals and colloidal-associated contaminants recommend both purging and sampling with a single pump

at rates of 0.2 to 0.5 liters per minute. The low-flow purge and sample method causes less agitation in the well, and reduces excess turbidity that can affect water quality. It also greatly reduces the volume of purge water, which may be difficult or expensive to dispose of.

To use the low-flow purging method, set the pump intake approximately in the middle of the well screen or open interval. Measure the water level in the well to the nearest 3 mm (0.01 ft) before turning on the pump, and record it in your notebook or form. Generally, stabilization criteria for parameter trend analysis are established before groundwater sampling takes place. Purge the well at a low flow rate until field parameters such as turbidity and dissolved oxygen stabilize. Recommended purging criteria are less than 10% change for turbidity or 5% for dissolved oxygen more than three successive readings three to five minutes apart.

It is also important to monitor drawdown in the well during purging because excess drawdown from pumping may create locally high entrance velocities of ground water around the well, and increase turbidity. If drawdown exceeds about 0.15 m (0.5 ft), the purge rate is too high, and should be gradually reduced. Record the pumping rate and water levels in your field notes.

Once the field parameters have stabilized, fill the sample bottles directly from the end of the tubing at a flow-rate of about 0.1 liters/min. Allow the discharge to flow gently down the inside of the bottle, and cap immediately. However, when sampling for radon, VOC's and other analyses that quickly degrade by aeration, an alternative method is to insert the tubing into the sample bottle and draw the tubing up as the surface of the water rises.

After sampling, carefully remove the pump assembly from the well. The Teflon-lined polyethylene tubing can be dedicated to each well by sealing it in a plastic garbage bag and labeling it with the monitoring well number. If possible, store the tubing onsite until the next round of sampling. This will ensure the tubing has not been exposed to contamination from other sources.

Various physical parameters, measured before and during well purging and sampling, provide both scientific and legal evidence that the sample is representative of aquifer conditions. Measurements are made with sensitive probes placed in a flow-through cell, such as a Hydrolab, that are either above or below the pump intake or on the ground surface. These parameters include temperature, electrical conductivity, pH, dissolved oxygen, redox and turbidity. Others (such as specific contaminants) may be measured according to program objectives. Several manufacturers offer probes and meters that are connected to data loggers for easy downloading into computer databases.

Pumps most commonly used and recommended for both purging and sampling are electric submersible, bladder, and gas piston types that are constructed with stainless steel and Teflon components. Many types of pumps are available for dedicated sampling programs, where the pump, wiring and tubing remains in the well over the life of the sampling program. Initial equipment decontamination is necessary.

Bailers are not recommended for purging or sample collection because they artificially induce chemical changes in the sample and water column by agitation, mixing and aeration. The use of bailers may give you non-conservative water quality parameters, high turbidity, and degassing of VOC's. If bailers must be used for purging and sampling, measure the turbidity and dissolved oxygen of bailed water at three to five minute

intervals and clearly describe the collection method.

D. DOMESTIC SUPPLY

Before collecting samples from domestic supply lines the system should be flushed of stagnant water by discharging a sufficient quantity to insure that the sample collected will be representative of the source of supply. A knowledge of the length of the system and diameter of the pipe will be necessary to calculate the quantity to be wasted.

When sampling from a water tap, open the tap slowly to provide a water stream smaller than the diameter of the mouth of the sample bottle. Collect the stream three or four inches below the tap, while avoiding splashing the water onto the tap surfaces. Tap surfaces frequently have high concentrations of soap and cleanser residues, which might affect subsequent analyses.

When sampling for bacteriological levels of domestic supplies, it is frequently necessary to sterilize the tap by either washing in alcohol or flaming it with a propane torch prior to sampling. These procedures are, in addition, to the sterile sampling techniques normally employed in bacteriological sampling.

6. *SAMPLING PROCEDURES FOR COMMON CONTAMINANTS AND SPECIFIC ANALYSES*

After field physico-chemical measurements have been recorded, collect water chemistry and bacteriological samples at the same location. The sample preservation and storage for the various sample types are listed in Table 2 at the end of this section.

A. ROUTINE WATER CHEMISTRY SAMPLE

The chemistry sample should be collected at a depth of 30 cm (1 foot) by one of the following procedures. Rinse the sampling device and sample containers at least once with native water before filling:

1. Prerinsed sewage sampler
2. Prerinsed Kemmerer bottle
3. Prerinsed Van Dorn bottle
4. Prerinsed submersible pump
5. Submerging a sample container by hand
6. Prerinsed plastic bucket

Collect a minimum of three one-liter samples of native water. Care should be taken at all times during sample collection, handling and transport to prevent exposure of the sample to direct sunlight. If a bucket is used, extreme care should be taken to avoid drips from the rope on the bridge. Preserve samples immediately after collection by placing on crushed ice in the dark. Sufficient crushed ice will be used to lower the sample temperature to less than 4°C within 45 minutes after time of collection. Sample temperature will be maintained at a temperature less than 4°C until delivered to the laboratory. Blue ice or frozen cubitainers can be used to ship samples, but crushed ice must be used to cool samples immediately after collection. All excess air should be excluded from the sample container.

Immediately after sample collection, acidify one sample to reduce the pH to less than 2 with two ml of concentrated, analytical reagent grade, H_2SO_4 to one liter of sample and invert about 20 times, then return to the ice and dark where it should be maintained at a temperature less than 4°C until delivered to the laboratory. The other two one-liter samples are not acidified.

B. METALS-IN-WATER SAMPLES

When deciding to measure total and dissolved metals, you must consider the purpose of the sampling. Water quality standards that apply to the protection of aquatic life were determined for the dissolved form of heavy metals. However, in order to budget inputs, transport, and accumulation of metals, it is necessary to know total metals in the water column, sediments, effluent, etc. Metals-in-water samples should not be collected during periods of abnormally high turbidity since the turbidity typically has certain metals associated with it and metal concentration varies with the turbidity. Of course, the exception to this is special purpose sampling for example, wet weather sampling is likely to include high turbidity samples.

Metals-in-water undergo exchange between the dissolved form and adsorption onto suspended particles. Dissolved metals are defined as those constituents (metal) of an unacidified sample that pass through a 0.45 micron membrane filter. Immediate filtration of the sample after collection results in a partition most representative of ambient conditions. The sample should be collected using a sampling pump and in-line filter set up and pump the filtered sample directly into the sample container.

Collect the Metals-in-water sample at a depth of 30 cm (1 foot) using a peristaltic pump. In most streams, near-surface water is representative of the water mass. Samples are pumped directly into the sample container. This minimizes contamination by using no intermediate sampling device. Powder-free latex gloves should be worn during sampling. The sample containers should be new, clean, 1-liter, unused plastic bottle or cubitainer (acid washed and thoroughly rinsed before use). Precleaned, preacidified sample containers are commercially available for scientific suppliers.

Companion samples for Metals-in-water

- a. Collect a hardness sample whenever Metals-in-water are to be analyzed. A minimum of 250 ml of water is required. Label the sample container "total hardness only." Sample holding time for unpreserved samples is two days under refrigeration.
- b. If you are collecting a total metals sample, submit a sample for TSS if you are not already requesting this analysis in a companion sample for "routine chemical." Sample holding time, under refrigeration, is seven days.

C. DISSOLVED METALS-IN-WATER

Before going to the field, be prepared to filter the samples before sending them to the laboratory. Determine what will be needed to filter the samples. The equipment/supply list includes: powder free latex gloves, precleaned sample containers, preservatives, precleaned sampling tubes, metals-free deionized water and filter cartridges. Precleaned sampling tubes should be obtained from the laboratory performing the analysis or from a scientific supplier.

One to two liter containers with metals-free deionized water must be taken into the field for making filter blanks. Metals-free deionized water can be obtained from scientific suppliers or a laboratory performing metal analysis. One filter blank should be taken for every "batch" or box of filters. The deionized water containers should also be kept clean and dust-free on the outside, perhaps by wrapping in a plastic bag. Metals-free filter cartridges with the capacity to filter several liters are commercially available.

To assemble the pump apparatus, put the precleaned tube into the pumphead, then remove the plastic protection from the tube ends. Put a new in-line filter onto the tube. Each sample requires its own new filter and precleaned tube. Wear powder-free latex gloves and be careful not to get the tube ends contaminated. Immerse the intake tube into the sample or directly into the water and flush about 500 ml to 1000 ml of ambient water while holding the filter upright. Fill the sample container with 600-1000 ml of filtrate leaving some head space.

Preserve the sample in the sample container with a 1:1 HNO₃/H₂O preservative solution made from metals-free nitric acid and deionized water (if not using a preacidified container). Freshwater samples require two ml of acid preservative and estuarine samples require 4 ml of acid preservative. Ultrex grade acid is factory analyzed for contaminants. For practical purposes, it is metals-free. Take care to avoid contaminating the acid. Acid with questionable purity can be used, however, only for soaking or cleaning labware. Holding time for acid-preserved samples is six months.

Label each sample container with the tag number and some other information about the location, or type of blank. Your request for analysis form should note the preservation method. If you filtered the sample, write "field filtered" on the container. In the space for special instructions on the request for analysis form, indicate that you have "field filtered and acidified" the sample.

D. TOTAL METALS-IN-WATER

The whole-water sample can be collected directly into the sample container or with the pump to avoid loss of acid. When using preacidified sample containers it is best to collect the sample with the pump. Follow the same procedure used for dissolved metals-in-water but exclude the filter. Samples are preserved with metals-free nitric acid as described above. Submit 600-1000 ml of sample for analysis. Holding time for preserved samples is six months.

E. HEXAVALENT CHROMIUM

Acidification alters the hexavalent form of chromium, so you must submit a separate sample if you want this analyzed. Filter and submit a minimum of 200 ml of water. Sample holding time is 24 hours, on ice.

F. CYANIDE

If you want cyanide analyzed, you must submit a separate sample and request "free cyanide" or "cyanide amenable to chlorination." Submit one liter of whole water (unfiltered) that has been preserved with a few ml of NaOH solution, or tablets, to make the pH greater than 12. If there is a chance that the sample has residual chlorine, add approximately 0.6 grams of ascorbic acid. The sample holding time is 14 days, under refrigeration. Cyanide is not usually run on filtered samples.

G. ORGANICS-IN-WATER SAMPLE

1. Collect the organic sample at a depth of 30 cm (1 foot) by one of the following procedures:
 - a. Kemmerer bottle (prerinsed with deionized water)
 - b. Van Dorn bottle (prerinsed with deionized water)
 - c. Sewage samplers (prerinsed with deionized water or hexane)
 - d. Submerging sample container by hand
2. The sampling device and sample container should not be rinsed with native water before being filled (organic compounds tend to concentrate on the surface of the sampling device or container).
3. Use three sample containers.
 - a. The sample container for insecticides and herbicides should be a new, clean, unused amber glass bottle with a teflon-liner inside the cap, both of which have been prerinsed with pesticide-grade hexane, acetone, or methylene chloride. Collect one liter of water. Minimize the air space in the top of the jar. Preserve immediately after collection by placing on ice in the dark. Make sure laboratory liquid extraction starts within five days. Label "Insecticides and Herbicides."
 - b. The sample container for semivolatile organic is the same kind of glass jar. Fill and preserve the same way. Label "Semivolatiles."
 - c. The sample containers for volatiles are two VOA vials. Fill with no headspace and preserve on ice. Label "VOA."
 - d. Phenols - use the same procedure as for insecticides and herbicide except preserve with sufficient concentrated sulfuric acid to reduce sample pH to <2.
 - e. Oil and grease - use the same procedure as for insecticides and herbicides except preserve with 5 ml of concentrated sulfuric acid.
 - f. Viruses -
 - 1) Fill out information on one, 1-gallon ziploc bag with a waterproof pen
 - 2) Assemble clean sampling equipment in the following order: inlet hose, portable pump, connecting hose, filter, housing unit, connecting hose, flow meter, and outlet hose. If the well has a pump, then connect the equipment (without the portable pump) to the faucet tap. Be sure the outlet hose is far from the inlet hose;
 - 3) Pump 40 to 1,000 liters (10 to 250 gallons) of water through the filter at approximately 4 liters per minute.
 - 4) Wearing non-contaminating gloves, carefully unscrew the filter housing and remove the filter with tweezers;
 - 5) Place the filter in a ziploc bag along with the remaining water left in the housing unit and seal bag tightly;
 - 6) Seal this bag in another ziploc bag;
 - 7) Store bag in ice-filled cooler;

- 8) Ship to the laboratory within 24 hours;
- 9) Decontaminate all equipment in contact with sample water by circulating a solution of 5% chlorine bleach for at least 20 minutes, followed by a solution of 10% sodium thiosulfate and 0.1-micron filtered water to neutralize the chlorine, followed by flushing with 100 gallons of water; and
- 10) Take an equipment blank sample from the final flush water and have it analyzed for viruses (check with lab for required volume).

4. Measure chlorine residual using a separate water sub-sample. Free chlorine will oxidize organic compounds in the water sample even after it is collected. If chlorine residual is above a detectable level, (i.e., the pink color is observed upon adding the reagents) immediately add 100 mg of sodium thiosulfate to the sample and invert until sodium thiosulfate is dissolved. Record chlorine residual concentration in field notebook. If chlorine residual is below detectable levels, no additional sample treatment is necessary.

H. ROUTINE WATER SUPPLY SAMPLE

1. Collect the Routine Water Supply sample at a depth of 30 cm (1 foot) by one of the following procedures:
 - a. Kemmerer bottle (prerinse with native water)
 - b. Van Dorn bottle (prerinse with native water)
 - c. Sewage sampler (prerinsed with native water)
 - d. Submerging sample container by hand (prerinse with native water)
2. The sample container should be a new, clean, 1-liter, unused polyethylene cubitainer or glass bottle.
3. Rinse the sampling device and sample container at least once with native water before filling.
4. Collect one liter of water. Preserve immediately after collection by placing on ice in the dark.
5. The sample container should be labeled with the station number and date of collection. It should also be labeled, "Routine Water Supply."

I. RESERVOIR BOTTOM WATER SAMPLE

Reservoir bottom water samples should be collected at stations specifically designated for this type of collection. These additional chemical data are needed in order to make inferences about the nutrient budget of the reservoirs. These samples should be collected even if the lake appears mixed top and bottom.

1. If the depth of the designated station is less than or equal to 3 meters (10 feet), do not collect a bottom water sample. Stations which are always this shallow should be dropped from the schedule of bottom water stations.
2. Collect the reservoir bottom water sample at a depth of approximately 1 meter (3 feet) above the bottom of the reservoir with a Kemmerer bottle (prerinsed with reservoir water) or a Van Dorn bottle (prerinsed with reservoir water).

3. The sample containers should be new, clean, one liter, unused polyethylene cubitainer. Rinse the sample containers at least once with native water before filling.
4. The bottom water samples should be representative of the hypolimnion. They should also be representative of the near bottom water when the lake is vertically mixed. Samples should not contain resuspended sediment. A good way to avoid stirring up the mud when probing the depth is to attach a weight with a 1 meter (3 feet) length line to the water sampler. The sampler can be tripped when the weight touches the bottom. An alternate way to avoid disturbing the sediment is to track the sampler position (depth), relative to the bottom with the depth sounder. Trip the sampler a meter or so above the bottom.
5. Collect three one-liter cubitainers. If you are unable to collect enough samples for the three cubitainers with one cast, composite several casts in a bucket and then withdraw the samples. (If this step is necessary, ensure the bucket with composite samples is kept out of direct sunlight at all times). Preserve all cubitainers immediately after collection by placing on ice in the dark. As soon as is reasonably and safely possible, two ml of concentrated H_2SO_4 (adequate to reduce $\text{pH} < 2$) to one cubitainer and label it, "TKN, ____ml H_2SO_4 added." A second cubitainer should also be preserved with H_2SO_4 and labeled, "____ml H_2SO_4 added" indicating the amount of H_2SO_4 added.

Minimum sample volumes for the cubitainers:

- a. TKN sample, preserved with H_2SO_4 -- 200 ml (in a separate cubitainer)
- b. Routine chemical parameters, preserved with H_2SO_4 -- slightly less than 1 quart cubitainer
- c. Routine chemical parameters, cooled -- 1 full quart cubitainer.

TABLE 2**SAMPLE PRESERVATION AND STORAGE**

PARAMETER(S)	CONTAINER(S)	SAMPLE MAXIMUM VOLUME (ml)	PRESERVATION	HOLDING TIME
Bacteria Fecal Coliform	sterile whirlpack bags sterile plastic or glass bottles	80-100	Cool to 4°C-if residual chlorine detected, add sodium thiosulfate	6 hours
Routine Water Chemistry Sample				
Alkalinity	cubitainer or glass	100	Cool to 4°C, dark	14 days
TSS	cubitainer or glass	400	Cool to 4°C, dark	7 days
VSS	cubitainer or glass	150	Cool to 4°C, dark	7 days
TDS	cubitainer	250	Cool to 4°C, dark	7 days
Chloride	cubitainer or glass	75	Cool to 4°C, dark	28 days
Sulfate	cubitainer or glass	75	Cool to 4°C, dark	28 days
Specific Conductance	cubitainer or glass	100	Cool to 4°C, dark	28 days
Ortho- phosphorous	cubitainer or glass	150	Cool to 4°C, dark	Filter ASAP 2 days
Nitrate	cubitainer or glass	150	Cool to 4°C, dark	48 hours
Nitrite	cubitainer	50	Cool to 4°C, dark	48 hours
Ammonia	cubitainer or glass	150	Conc. H ₂ SO ₄ to pH < 2 and cool to 4°C, in dark	28 days
Total Phosphorous	cubitainer or glass	150	Conc. H ₂ SO ₄ to pH < 2 and cool to 4°C, in dark	28 days
Total Organic Carbon	cubitainer or glass	50	Conc. H ₂ SO ₄ to pH < 2 and cool to 4°C, in dark	28 days

PARAMETER(S)	CONTAINER(S)	SAMPLE MAXIMUM VOLUME (ml)	PRESERVATION	HOLDING TIME
Cyanide in water	cubitainer	1000	NaOH added to pH >12, 0.6 g ascorbic acid if residual Cl ₂ , cool to 4° C, in dark.	14 days
BOD	cubitainer	>4000	Cool to 4°C, dark add 1 g FAS crystals per liter if Cl ₂ is detected	2 days
COD	cubitainer	110	Conc. H ₂ SO ₄ to pH < 2 and cool to 4°C, dark	28 days
VOC	2-40 ml VOA vials	80	Cool to 4°C; doarc; or 2-4 drops HCL to pH<2, Cool to 4°C for BTEX	14 days
Metals in Sediment	glass with Teflon lid liner (rinsed with 10% HNO ₃)	500 g	Cool to 4°C, dark	14 days
Organics-in-Sediment	glass with Teflon lid liner (rinsed with hexane, acetone or methylene chloride)	500 g	Cool to 4°C, dark	14 days
Conventionals in Sediment	glass with Teflon lid liner	500 g	Cool to 4°C, dark	14 days

NOTE:

Containers, preservatives and holding times for chemical constituents are taken from the EPA guidelines, Table II, page 28, of the Federal Register (1984)

PARAMETER(S)	CONTAINER(S)	SAMPLE MAXIMUM VOLUME (ml)	PRESERVATION	HOLDING TIME
Total Kjeldahl Nitrogen	cubitainer or glass	200	Conc. H ₂ SO ₄ to pH < 2 and cool to 4°C, in dark	28 days
Chlorophyll	cubitainer or glass	1000	Cool to 4°C, dark	Filter within 48 hours - frozen filters up to 30 days
Metals-in-Water				
Total Metals	HNO ₃ -cleaned quart plastic bottle	1000	Preacidified with HNO ₃ to pH < 2	6 months
Dissolved Metals	HNO ₃ -cleaned quart plastic bottle	1000	Filter at sample site with 45 micron in-line filter into HNO ₃ preacidified container, pH < 2. Cool to 4° C dark.	6 months
Total Mercury	HNO ₃ -cleaned quart plastic bottle	600	Preacidified with 5 ml conc. HNO ₃ to pH <20 Cool to 4° C, dark.	28 days
Hexavalent Chromium	Cubitainer or glass (notify lab)	600	Cool to 4°C, dark (in line filter)	24 hours
Organics-in-Water	glass with Teflon-lined lids (2 jars)	2000	Cool to 4°C, dark	7 days until extraction
Routine Water Supply	cubitainer	1000	Cool to 4°C, dark	14 days
Hardness	cubitainer	250	Cool to 4°C, dark	2 days (optimum time)
Oil and grease in water	glass with Teflon lined lids	900	2 ml conc. H ₂ SO ₄ to pH < 2 and cool to 4° C, in dark.	28 days
Phenols in water	glass with Teflon lids	750	2 ml conc. H ₂ SO ₄ to pH < 2 and cool to 4° C, in dark.	28 days

7. QUALITY CONTROL SAMPLES

Both federal and state QA/QC offices require the collection of additional samples called equipment blanks, field blanks, travel blanks, duplicates, and split samples. These samples are used to check the quality of decontamination, collection, and handling procedures to verify that they have not affected sample water quality.

EPA, Region 9 guidance states that all three types of blanks do not have to be collected every day; instead, one blank per day is sufficient with the order of preference being: equipment, field and travel blanks. Travel blanks are mostly used for VOC analyses. All QA/QC samples should be sent to the laboratory. That is, that the sample should not be identified as a blank, but rather, the sample should be given a fictitious sample number similar to the other samples being collected. The fictitious number should be identified and recorded in the field notes for easy identification when the results are received.

The Lab QC Sample is collected for each 10 samples collected or one per week, whichever is greater. This sample is not an additional sample, but a special designation for an existing one. Collect a double volume sample (i.e., twice as many containers as a normal sample). Containers must clearly be identified as a lab QC sample.

Equipment blanks consist of containers filled with the final rinse water from equipment decontamination. Once analyzed, they reveal the effectiveness of cleaning of field equipment. Collect equipment blanks after sampling the surface water or ground water station with the highest contamination. One per day of sampling is sufficient.

Field blanks are containers of deionized water that are filled at the sampling station, then labeled, package, sealed and shipped to the laboratory like other samples. They check for contamination in the laboratory and for cross-contamination during the collection and shipment of the samples. One field blank for each day of sampling is sufficient.

Travel blanks are containers of deionized water prepared by the laboratory. They are kept in the same sample cooler as the other samples at every stage of the collection, handling and shipment process. Back at the lab they are analyzed for VOC parameters. If contaminants are found, they could be attributed to contamination that occurred during sample transport, storage or in the lab. At least one for each sample shipment is required.

Duplicate samples are used to check the precision of field collection or laboratory analyses. Duplicates are collected at the same time as the water quality sample at a rate of one in every ten or 10 percent per day, whichever is greater. Collect a duplicate sample from a station that is believed to have elevated levels of a particular compound.

Split samples are additional water quality samples that are collected and handled identically as the others in the field, but are sent to a different laboratory or as a blind sample for analyses to the same lab, as a check on laboratory handling and procedures. Split samples are often most collected at a facility during compliance monitoring.

Background samples are collected to check the results of site evaluation sampling. Background samples are used to establish the background conditions, and are obtained hydraulically up gradient from contaminant sources.

PART II - FIELD ANALYTICAL TECHNIQUES

Multi probes, such as the Hydrolab, are the preferred equipment for conducting field measurements for temperature, pH, dissolved oxygen, specific conductance, alkalinity, and turbidity. To ensure the accuracy of the results measured in the field, the operating procedures provided by the instrument's manufacturer should be strictly followed. All calibration and maintenance activities should be performed prior to departing to the sampling location. All calibration and maintenance activities should be recorded in the project's notebook.

1. TEMPERATURE

Water temperatures ideally should be taken in the stream as small volumes may change temperature rapidly after being removed from the stream. Larger volumes of water will maintain temperatures nearly that of the stream for fairly long periods. Temperature readings on bucket samples are permissible if the measurement is begun promptly. No special sampling precautions are required for temperature sampling.

2. TURBIDITY

Water samples collected for the measurement of turbidity should be from a well-mixed area at the center of flow. As the suspended sediment carried by a stream is a function of the velocity and depth, turbidity samples should be collected in the upper portion of the water column. Samples should be maintained intact until the turbidity measurement is made.

3. pH (HYDROGEN ION)

The pH samples should be taken in a well-mixed area representative of the stream composition. No special sampling precautions are needed in collections of the sample other than to ensure the cleanliness of the container. Sample containers should be rinsed several times with native water before the sample is collected.

The pH will change with time under the influence of increases or reductions of dissolved gases. For this reason the measurement should not be duly delayed.

4. DISSOLVED OXYGEN

The dissolved oxygen concentration should be recorded for each water quality monitoring sampling visit. Preferably, D.O. is measured directly in stream. The D.O. probe will be allowed to equilibrate for at least 90 seconds before D.O. is recorded to the nearest 0.1 mg/l. Care must be taken at profile stations to insure that the reading is stable for each depth. Since dissolved oxygen takes the longest to stabilize, record this parameter after temperature, conductivity and pH. If the D.O. probe has an operable, automatic stirrer attached, the D.O. probe does not have to be manually stirred. However, if the probe is not equipped with an automatic stirrer, manual stirring must be provided by raising and lowering the probe at a rate of one foot/sec without agitating the water surface. (If the stream velocity

at the sampling point exceeds one foot/sec, the probe membrane can be pointed upstream into the flow and manual stirring can be avoided).

If D.O. cannot be measured in stream, it should be measured in the container used for collection of water samples.

5. SPECIFIC CONDUCTANCE

The specific conductance (conductivity) should be recorded for each water quality monitoring sampling visit. Preferably, conductivity is measured directly in stream. Allow the conductivity probe to equilibrate for at least one minute before conductivity is recorded to three significant figures (if the value exceeds 100). The primary physical problem in utilizing an operable conductivity meter is entrapment of air in the conductivity probe chambers. The presence of air in the probe is indicated by unstable conductivity values fluctuating up to +100 $\mu\text{mhos/cm}$. The entrainment of air can be minimized by slowly, carefully inserting the probe assembly into the water; and when the probe assembly is completely submerged, quickly shoving it through the water; and by frequency cleaning of the probe assembly. If specific conductance cannot be measured in stream it should be measured in the container used for collection of water samples.

6. ALKALINITY

Alkalinity is the ability of salts in the water to neutralize acids. Water that is alkaline has a pH greater than seven. Analysis for this parameter should be done in the field, or if impractical, by a laboratory within 14 days of sample collection.

PART III - ADDITIONAL WATER QUALITY CONSIDERATIONS

1. OIL SPILLS

A. DISCUSSION

Oil, grease, and other immersible floating substances are objectionable in both fresh and marine waters. The material may concentrate on beaches or banks to form an unsightly and odorous deposit. When present in a thin layer on the water surface of the water, the slick will reduce oxygen uptake by reaeration.

Wildfowl exposed to oil-contaminated waters will lose the flotation and insulation property of their feathers as the oil mats these and reduces air pockets between and beneath the feathers. Lack of insulation and the loss of both swimming and flying ability make these birds readily susceptible to chill exposure, disease, and attack by predators.

Oil and grease contaminating waterways may come from many sources. Small amounts are released constantly by poorly operating wastewater treatment plants. Gasoline-powered craft will contribute quantities both through normal operations and the inevitable small spills. However, it is the large major spill or purposeful dump of oily material which creates the major concern. The USIBWC has developed a contingency plan to cope with these major spills and to alleviate their impact upon the environment.

B. REPORTING PROCEDURE

When a spill is detected, contact at once the designated "On-Scene Coordinator" or Incident Commander assigned to that segment of the river. The on-scene coordinator has the responsibility of implementing the USIBWC oil spill contingency plan and taking wherever steps possible to minimize the effects of the spill. On-scene coordinators will be designed from among the USIBWC employees living in the vicinity of their area of responsibility. It will be the responsibility of field personnel to maintain a list of on-scene coordinators and their phone numbers and area of coverage.

Spills above the reportable quantity must be reported to the appropriate authorities within 24 hours. Since different materials have different reportable quantities, when in doubt, report the spill. The following is a list of agencies responsible for handling spill investigations:

Arizona

Arizona Department of Environmental Quality	(602) 257 -2330
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California

California Regional Water Quality Control Board (Imperial Co.)	(760) 346-7491
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California Regional Water Quality Control Board (San Diego Co.)	(619) 467-2952
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New Mexico

New Mexico Environment Department

(505) 827-9329

Texas

Texas Natural Resource Conservation Commission

(800) 832-8224

Alternately, call the local fire department. Please note that these numbers must be updated periodically.

C. SAMPLING

For purposes of identification of the source of spills, assessing responsibility, and providing physical evidence that may be required in a court case to impose fines and levy charges for cleanup costs, it is often necessary to collect a sample from the spill area. The optimum sample container for such purposes is a wide-mouth jar which will allow the oil layer to be skimmed from the surface. Lacking this, a narrow-mouthed bottle may be substituted. Extreme care should be taken in filling out the sample tag. The exact location, including the relationship to entering drains, should be specified. The exact time of sampling on a spill may be of great importance. The volume of spilled material will be difficult to estimate by anyone not thoroughly knowledgeable in the dispersion characteristics of oil wastes; consequently, the depth of the slick and its aerial coverage should be determined. If a camera is available, several pictures should be taken from various angles and locations.

At the time of detection, the location at which the spill occurred may sometimes be determined by signs of the oil's passage or by the presence of residual oily material along the river course. Later, these signs may be washed away, so attempt to gather as much information as possible at the time of discovery and to relay this information to the on-scene coordinator when he or she arrives.

2. FISH KILLS

A. DISCUSSION

Fish kills are the result of many causes, whether consisting of a single fish dying from old age or disease, or a catastrophic decimation of the entire fish population of a given area.

Fish kills may result from natural events, such as acute temperature changes, decomposition of natural materials which results in oxygen depletion, changes in salinity, bacterial or viral epidemics, or in the natural order, such as the spawning deaths of the salmonoids. As these kills relate directly to water quality conditions or by their occurrence affecting these conditions, their causes and results should be reported.

Fish kills, through the actions of man may be attributed to municipal and industrial waste discharges, thermal pollution by waste cooling waters, or to toxic chemicals used in agricultural activities.

By definition, one dead fish in a stream may be described as a fish kill, some basis should be developed to describe fish kills and their severity. "Standard Methods" offers the following definitions for a large

stream, about 60 m (200 ft.) wide and two m (6 ft.) deep. For streams of other dimensions, adjustments should be made in the adjective qualifiers.

1. Minor kill: 1 to 100 dead or dying fish confined to a small area of stream stretch. If recurrent, it could be significant and should be investigated.
2. Moderate kill: 100 to 1,000 dead or dying fish of various species in a mile or so of stream or equivalent area of a lake or estuary.
3. Major kill: 1,000 or more dead or dying fish of many species in a reach of stream up to 16 km (10 miles) or greater, or equivalent area of a lake or estuary.

In using the above guidelines, it should be remembered that any fish kill is significant if it affects sports fish or fish of commercial value, or if the kill is the result of negligent discharge or the malfunction of a wastewater treatment facility.

B. REPORTING PROCEDURE

The following is a list of agencies responsible for handling fish kill investigations:

Arizona

Arizona Game and Fish Department (800) 352-0700

California

California Regional Water Quality Control Board (Imperial Co.) (760) 346-7491

California Regional Water Quality Control Board (San Diego Co.) (619) 467-2952

New Mexico

New Mexico Environment Department (505) 827-9329

Texas

Texas Natural Resource Conservation Commission (800) 832-8224

Alternately, any local game warden may take the report of fish kills and assist in field sampling.

C. SAMPLING

Field investigation of fish kills consists of visual observations, sampling of water, physical measurements, and collection of dead or distressed fish.

The first observer on the scene should survey the area to determine if a fish kill has in fact occurred. After the determination has been made that a kill has occurred, observers should dispatch someone to

report the kill to the appropriate state authorities. If no one is available, the observer himself or herself should make the report if he or she can leave and return to the scene within a relatively short time, say one hour. When reporting the incident, advise the agency that a water quality monitoring team is on-site with equipment and is collecting samples. Request the agency to furnish any specific instructions they wish carried out before their field personnel can arrive.

After ensuring that the appropriate agencies are being advised, immediately start fish collection, since the preservation of dying and recently dead fish is critical in assessing the causes of fish kills.

Place individual fish in well-labeled bags, specifying location and time of collection, and preserve by icing until the fish can be quick-frozen for transport to the laboratory in dry ice.

Collect water samples from the polluted area and from the area above the source of pollution, if this can be ascertained. If the source of pollution is known, such as a drainage pipe or influent discharge ditch, collect a sample from this source also. Field measurements of pH, temperature, dissolved oxygen, conductivity, stream velocity, and depth should be made on each sampled site. Observations on the water appearance, color and turbidity should be recorded. Record also any circumstance appearing at the site of the kill that may be useful in establishing the cause of the kill, such as presence of oil slicks, foam, and the present or past weather conditions.

When the field representative of the regulatory agency appears on the scene, turn over all samples and field notes. Guide the official(s) around the scene, explaining what actions you have taken and pointing out specific locations where living, but distressed, fish were observed.

PART IV - SEDIMENT

After water samples have been collected, the sediment samples should be collected. Sediment samples for metals and organics are submitted in separate glass jars which are cleaned with acid or solvent, respectively.

Sediment chemistry samples give information on both trend contaminant loading and the potential for adverse effects on sediment and water biota. In order to compare samples over time and from site to site, they must be collected in a consistent manner. If a suitable site for collecting sediment cannot be found at a station, the sampling personnel should not collect the sediment sample. Attempt to reschedule and collect the sample.

1. CHARACTERISTICS OF MATERIALS TO BE COLLECTED

Many of the chemical constituents of concern are adsorbed onto fine particles. An objective in selecting a sample site, and collecting the sample, is to obtain recently deposited fine sediment. Avoid hard clay, bank deposits, gravel, and disturbed and filled areas. Any sediment that resists being scooped by a dredge is not fine, recently deposited material.

2. CHARACTERISTICS OF AN IDEAL SITE

Quiescent areas are conducive to the settling of finer materials. Choose a sampling site with lower hydrologic energy, such as the inner (depositional) side of bends or eddies where water movement may be slower. Reservoirs and estuaries are generally depositional environments.

3. SAMPLE COLLECTION

Sediment chemistry samples should be collected with a clean, washed, Ekman dredge (pre-rinsed with native water.) Wash the dredge between samples, removing all sediment from previous samples. The dredge should also be used in streams that are wadable, since it allows a relatively undisturbed sample to be collected.

Materials to be collected will vary from site to site and perhaps from time to time at a particular site. In areas of frequent scouring, such as occur in most rivers and streams, there may not be sufficient sediment for collection during or following periods of high flow. Attempts to collect sediment during these times may prove unsuccessful and re-sampling should be scheduled. When the suspended load in rivers and streams precipitates due to reduction of velocity, most of the resulting sediment will be "fresh". In such instances, the whole bite from the dredge sub-sample may be used. In areas where very little scouring normally occurs such as estuaries and reservoirs, the sediment will be vertically stratified. Often the sediment is consolidated enough to be extruded into a flat pre-rinsed plastic or Teflon pan as a cube-shaped block of mud. Vertical stratification can then be observed. Typically, there may be light brown silt on top, followed by a gray colored aerobic zone overlying a typically black anaerobic layer. Because the thickness of these layers is variable, it is difficult to prescribe a certain thickness representing "recent deposits" to be sampled. The aerobic layer should be sampled,

because this zone represents more recent deposits and is where most of the benthic fauna live. If the sediment does not have an aerobic zone, then the top 2 cm should be collected for analysis. If the aerobic zone is deeper than 5 cm, collect the sample for analysis from the top 5 cm of three or more grabs to obtain the most recently deposited sediments.

In summary, for routine monitoring purposes, the portion of the sediment sample selected to be analyzed must be consistent at a particular site from time to time. Choose the most appropriate part of the dredge sample to be analyzed at a site and be consistent thereafter.

After choosing an appropriate site for collection, collect the sample using the following procedure:

a. Slowly lower the dredge to the bottom with a minimum of substrate disturbance. Retrieve the closed dredge at a moderate speed (less than two ft/sec). Upon retrieval, examine the grab to ensure that the sediment surface is undisturbed. The grab should be rejected if it does not meet these criteria:

- Mud surface must not be pressing out of the top of the sampler. If it is, you must lower the dredge more slowly.
- Overlying water must not be leaking out along the sides of the sediment in the dredge, so that the superficial sediment is not washed out.
- Sediment surface should be flat and level in the sampler. If it is not level, the dredge had tilted over before closing.

b. The water overlying the sediment in the dredge should be very gently decanted by slightly tipping the dredge with the lid closed until the water runs out the top. The decanting process should remove all of the overlying water but not remove the superficial sediments. The laboratory reports percent water for sample, so overlying water should not be included in the sample container.

c. The sediment should be examined for depth of penetration, color and thickness of top aerobic zone, and texture. These observations should be recorded in the log book.

For stream samples, the entire grab may be composite (remember - the pan must be cleaned as the dredge, otherwise, exclude the bottom-most layers).

Composite the grabs by transferring an equal portion of successive grabs (minimum of three) to the sample container with a clean plastic scoop. Do not transfer rocks, large leaves or sticks to the sample container. The minimum volume is about one-third quart (500 g), but one-half to three-quarters of a quart is preferred.

d. The sediment sample should be placed in a properly cleaned, one-quart glass jar with a Teflon liner. For organics in sediment, the sample jar and Teflon liner should be pre-rinsed with pesticide-quality hexane, acetone, Freon or methylene chloride. Disposable plastic spoons may dissolve when rinsed with some organic solvents. For metals in sediment, the sample jar and Teflon liner must

be pre-rinsed or soaked in a 10% solution of nitric acid, and then rinsed with distilled water.

e. Seal the jar with the Teflon linear in the lid.

f. The jar should be labeled with the station ID and date of collection, as well as the type of analysis requested. i.e., metals or pesticides.

g. Immediately place the labeled jar on ice ($< 4^{\circ}\text{C}$) in the dark until delivery to the laboratory. Holding times for sediment samples are provided in Table 2.

4. RECORDS

Record the depth at the location where the sample was taken in the field notebook and on the data form. Record a gross description of the sample, i.e., color, texture, number of grabs, depth of penetration, and depth of aerobic zone that was composited. This information should be reported as comments with the sediment analytical results. When sediment samples are collected for Organics and/or metals, you should also request the analysis of sediment conventionals.

GLOSSARY OF TERMS

ADEQ	Arizona Department of Environmental Quality
AWRRC	Arizona Water Resources Research Center
BOD	Biological Oxygen Demand
cfs	cubic feet per second
COD	Chemical Oxygen Demand
D.O.	Dissolved Oxygen
DI water	Deionized water
EMD	Environmental Management Division
EPA	United States Environmental Protection Agency
EWI	Equal With Increment
FIPS	Federal Information Processing Standard
H ₂ SO ₄	Sulfuric Acid
HCl	Hydrochloric Acid
HgCl ₂	Mercuric Chloride
HNO ₃	Nitric Acid
JTU	Jackson turbidity units
ml	milliliters
MSDE	Minimum Set of Data Elements
MSDS	Material Safety Data Sheets
NaOH	Sodium Hydroxide
NTU	Nephelometric turbidity units
PAO	Phenylarsineoxide
ppm	Parts Per Million
QA	Quality Assurance
QC	Quality Control

TDS	Total Dissolved Solids
TNRCC	Texas Natural Resource Conservation Commission (Formerly Texas Water Commission (TWC))
TSS	Total Suspended Solids
USGS	United States Geological Survey
USIBWC	United States Section, International Boundary and Water Commission
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compounds

REFERENCES

- 1) **Arizona Water Resources Research Center, 1995, "Field Manual For Water Quality Sampling", ADEQ TM-94-3, March 1995.**
- 2) **Texas Water Commission, "Water Quality Monitoring Procedures Manual", October 1991.**
- 3) **Texas Natural Resource Conservation Commission, "Surface Water Quality Monitoring Procedures Manual", June 1997**

APPENDIX A

ABSTRACT FROM USGS WATER SUPPLY PAPER 1454

Methods for Collection and Analysis of Water Samples

Wading is one of the easiest methods to collect samples from many streams and also affords the collector the best opportunity to "size up" the flow and decide where to collect the samples. Rubber boots or breast-high waders are standard equipment. A wading rod or similar probing instrument is essential to safe wading. By probing ahead, the collector can estimate the current and locate holes, benches, and even quicksand. In shallow water the most satisfactory method of extricating oneself from quicksand is to fall flat on the bed and crawl to firmer ground; in deep water one's effective weight in the sand can be lessened by swimming motions. In a swift sandy-bottom stream or where the bottom is covered with ooze, the wader may find that his or her feet slowly sink into the bottom if he or she stands in one position too long. Lake or pond bottoms may be more treacherous than the beds of flowing streams.

A general rule of thumb is that wading should not be attempted if the depth of the water in feet multiplied by the water velocity in feet per second equals 10 or more, but this criterion must be modified by many factors peculiar to the site and to the season of the year. The depth as related to the velocity of water that can be waded safely is closely associated with the body weight. They should always attach a rope or tag line securely to the bank or have his or her partner hold it.

Traffic is the most serious hazard when working from bridges. Sometimes the bridges have walkways for pedestrian traffic or catwalks suspended at the side or beneath the bridge, but more often than not, the collector must work in the traffic lanes. Warning signals and signs of various kinds are some protection when sampling from a bridge. Commonly used, signals include flags, signs, and red lights. Even with all prescribed traffic warnings installed, the collector still must keep an eye on approaching vehicles--there are always drivers unwilling to cooperate. When working on railroad bridges, a knowledge of train schedules is essential, and at no time should the collector use equipment that cannot be removed quickly.

The principal hazards of cableways are not the possibilities of their structural failure, but rather those that attend the operation of the cable car. Proper instruction of inexperienced personnel in cable-car operation may prevent many accidents. Before releasing a car from its mooring, check to see if the car puller is in the car and that it has adequate lining. Once the car is rolling free on the cable, no attempt should be made to retard its speed by use of hands or car pullers until it has slowed almost to a standstill. If there is any danger of the car continuing across the stream and crashing into the cable mooring on the opposite bank, the sample collector should case the car out from the landing platform with the car puller or brake and never allow the car to run free.

The degree of hazard involved in collecting from boats is generally dependent on the selection and operation of the boat. Life jackets are essential equipment. Much of the hazard in sampling large streams, lakes, and reservoirs is related to the seaworthiness of the craft and to changing weather.

Only an experienced person can judge the roughness in the center of the reservoir from the breeze on the shore. In many parts of the country, the wind often follows a rather definite pattern during any 24-hour period, depending on the season of the year. Check the weather forecast before planning an extended sample collection trip on a large lake or reservoir. All work should be done at a safe distance from spillways, "glory holes," and other areas of water discharge.

Collection of groundwater samples offers a different series of hazards from those encountered in stream sampling. Dangers may include losses or rotten well coverings, unfriendly dogs, poisonous snakes, dangerous cattle or the hazards of pumping equipment such as encounters with flywheels, belts or drive shafts.

Members of the field party should be prepared to render first aid to themselves or each other. By definition, first aid is the immediate and temporary care of an injury until competent medical attention can be obtained. Each field party should be equipped with a standard first aid kit designed to provide equipment to treat commonly encountered problems and a first aid manual providing instructions for the treatment of more serious accidents.

APPENDIX B

FIELD ANALYTICAL TECHNIQUES

TEMPERATURE

Water temperatures ideally should be taken in the stream as small volumes may change temperature rapidly after being removed from the stream. Larger volumes of water will maintain temperatures nearly that of the stream for fairly long periods. Temperature readings on bucket samples are permissible if the measurement is begun promptly. No special sampling precautions are required for temperature sampling.

Temperature measurements may be made with a multi probe (Hydrolab) or any good grade of mercury-Celsius thermometer. As a minimum, the thermometer should have a scale marked for every 0.1° Celsius. Markings should be etched on the capillary glass. The thermometer should be checked against a known standard prior to usage. For field use, the thermometer should be provided with a metal case to prevent breakage. Temperature readings should be made while the bulb is immersed in the sample and after equilibrium has been reached.

Alternatively, a thermistor may be used for temperature measurements. The manufacturer's instructions would be carefully followed when using electronic meters. Report temperatures to the nearest 0.1 Degree Celsius.

TURBIDITY

Water samples collected for the measurement of turbidity should be from a well-mixed area at the center of flow. As the suspended sediment carried by a stream is a function of the velocity and depth, turbidity samples should be collected in the upper portion of the water column. Samples should be maintained intact until the turbidity measurement is made upon an aliquot removed from a freshly shaken bottle so that the ratio of particulate matter to water volume is unchanged.

An alternative procedure is to measure turbidity in situ with a visibility extinction device such as a Secchi disk.

Methods of measuring water turbidity generally fall into one of three categories:

A. LIGHT SCATTERING EFFECT

A beam of light striking particles in suspension will be scattered at different angles. The ratio of light intensity of the incident light to that reflected at right angles is measured (Tyndall effect).

B. LIGHT TRANSMITTING EFFECT

A beam of light striking particles in suspension will be reduced in intensity proportional to the quantity of particles encountered. The ratio of the light transmitted through a solution in a straight line to the intensity of the incident light is measured.

C. PROCEDURES FOR MEASURING DEPTH

The first instrument and procedure to gain wide acceptance was the Jackson Candle Turbidimeter which since shortly after the turn of the century has been considered to be the preferred instrument for turbidity measurements. The Jackson Turbidimeter is based on the second category above and although careful control is required of several variables, low levels of turbidity cannot be determined, and the measurement rests on the subjective evaluation of the operator, this instrument is still used occasionally especially for highly turbid samples.

More recently, other instruments, simpler in operation and relying less upon operator interpretation has been developed. The USGS and the EPA now use the Hach Model 2100 turbidimeter as their standard laboratory instrument, primarily because of its sensitivity to low turbidity levels and because of its reproducibility and comparability between laboratories. This instrument uses the first method of measurement discussed above.

Since there are no direct methods of comparison of results between the methods of measurement described above even when using the same synthetic standards, there is no valid purpose in calibrating a nephelometer which utilizes right angle scattering principles in candle units. To distinguish between methods and units of turbidity, the results from nephelometer are expressed as nephelometric turbidity units (NTU) and from the light absorption method as Jackson turbidity units (JTU).

Manufacturers' instructions accompanying the instruments should be referred to for specific information on each turbidimeter's operation. The third category of turbidity measurement is represented by the Secchi visibility disk. This 20 cm, weighted plate with quadrants alternatively painted black and white is lowered into the water column until just visible. The depth at which the disk disappears from sight is recorded in inches. Measurements should be made in the open sunlight with no shadows falling across the sampled area. The sampler should try to position himself or herself in such a location as to prevent self shadowing when viewing the disk.

SECCHI DISC TRANSPARENCY (METERS)

Secchi disc transparency should be recorded for each water quality monitoring sampling visit.

A. Sampling Equipment.

- a. Secchi disc, 20 cm in diameter. Secchi disc should be clean, weighted and suspended with chain, wire or Dacron line (the line used for suspending the Secchi disc should not be nylon or cotton because these lines may stretch and cause erroneous readings).

- b. Measuring tape (measuring tape is not necessary if the line used for suspending the disc is accurately and permanently marked at a minimum of 0.5 meter intervals).

B. Sampling Procedures.

- a. Preferably, Secchi disc transparency is measured directly in-stream wherever conditions allow.

- 1) The Secchi disc should be lowered vertically in allocation shielded from direct sunlight. Glare from the water's surface will affect the accuracy of the measurement. Don't wear sunglasses or photo greys unless you must.
- 2) Slowly lower the disc until it disappears from view. The person viewing the disc should maintain an eye level of less than two meters above the water's surface. Note the depth at which the disc disappears from view.
- 3) Slowly raise the disc until it becomes visible. Note the depth at which the disc reappears.
- 4) Compute the mathematical average of the two depths noted and record the average value to two significant figures in the field notebook. The recorded average value is the Secchi disc transparency.

- b. In streams with very high turbidity, high velocity, and/or poor access, it may be necessary to measure Secchi disc transparency in a bucket.

- 1) Fill the bucket from the centroid of flow being careful not to disturb the substrate.
- 2) Follow steps above for measuring the Secchi disc depth within 30 seconds after raising filled bucket from water's surface. Or, re-suspend the solids by stirring, then quickly make the measurement.
- 3) Record Secchi disc transparency to two significant figures.

- c. Some bodies of water will be so clear and shallow that it will not be possible to lower the Secchi disc until it disappears from view.

- 1) Measure and record the depth at the deepest point accessible.
- 2) Report Secchi disc transparency as greater than the deepest depth measured.

EXAMPLE: South Fork Rocky Creek is a small (<1 cfs) clear stream. The stream in the vicinity of the sampling site was less than one meter deep and the bottom was clearly visible everywhere. However, a pool was located in the stream next to a bridge. The maximum depth of the pool was 2.6 meters at which depth the Secchi disc was still visible. Therefore, Secchi disc transparency for South Fork Rocky Creek was recorded as >2.6 m.

pH (HYDROGEN ION)

The pH samples should be taken in a well-mixed area representative of the stream composition. No special sampling precautions are needed in collections of the sample other than to ensure the cleanliness

of the container. Sample containers should be rinsed several times with the native water before the sample is collected.

The pH will change with time under the influence of increases or reductions of dissolved gases. For this reason the measurement should be delayed.

DISSOLVED OXYGEN (mg/l)

The dissolved oxygen concentration should be recorded for each water quality monitoring sampling visit. Oxygen can be measured by Winkler titration (iodometric titration) or with a dissolved oxygen meter (polarographic electrodes).

A. Sampling Equipment

a. Dissolved oxygen meter

b. Winkler titration kit:

- Two 300 ml BOD bottles with stoppers
- One sewage sampler
- Manganous sulfate power pillows
- Alkaline-iodide-azide reagent powder pillows
- Sulfamic acid powder pillows
- 10-ml pipettes
- 200 or 250-ml graduated cylinder
- One 300 ml Erlenmeyer flask
- 0.025 N PAO (phenylarsineoxide) (replace annually or as often as necessary in field kit)
- Stable starch reagent indicator solution. Starch solution is stable for one month under field conditions. It should be renewed from stock which is stable for up to a year in the refrigerator.
- Scissors or knife for opening power pillows.

B. Sampling procedure:

a. Water quality monitoring personnel should always carry a complete Winkler titration kit when making water quality monitoring sampling visits.

b. Preferably, D.O. is measured directly in-stream. The D.O. probe will be allowed to equilibrate for at least 90 seconds before D.O. is recorded to the nearest 0.1 mg/l. Care must be taken at profile stations to insure that the reading is stable for each depth. Since dissolved oxygen takes the longest to stabilize, record this parameter after temperature, conductivity and pH. If the D.O. probe has an operable, automatic stirrer attached, the D.O. probe does not have to be manually stirred. However, if the probe is not equipped with an automatic stirrer, manual stirring must be provided by raising and lowering the probe at a rate of one foot/sec without agitating the water surface. (If the stream velocity at the sampling point exceeds one foot/sec, the probe membrane can be pointed upstream into the flow and manual stirring can be avoided).

c. If D.O. cannot be measured in-stream, it should be measured in the container used for collection of water samples, i.e., a bucket using the precautions outlined above for the measurement of temperature. During equilibration and reading, water should be moved past the membrane surface at a velocity of one ft/sec. , either by automatic stirrer or manual stirring. If stirred manually in a bucket, the water's surface should not be agitated.

d. If the electronic D.O. meter is inoperable, D.O. should be measured by Winkler titration. A sample for titration is collected by placing a 300-ml BOD bottle in a sewage sampler and lowering the top of the sewage sampler to a depth of one foot. The sewage sampler will fill in 30 to 45 seconds. The sampler is filled with water when it ceases bubbling. The sewage sampler should not be withdrawn until it has completely filled. The sampler should be carried upright until the BOD bottle is removed.

- 1) Remove BOD bottle from sewage sampler carefully. The bottle should be filled to the top of the lip. Gently pour the upper 3-4 ml out of the flared mouth of the bottle.
- 2) Add the contents of one manganous sulfate powder pillow to the full bottle.
- 3) Add the contents of one alkali-iodide-azide powder pillow to the full bottle.
- 4) "Inclining the bottle slightly, introduce the glass stopper with a quick twisting thrust, thereby removing all bubbles." (Eckblad, 1978). Sometimes it works well, just to touch the top of the liquid with the stopper tip and then drop it into position.
- 5) Invert the bottle about 20 times to mix and set the bottle aside out of direct sunlight.
- 6) When the floc has settled so the upper one-third of the bottle is clear or after waiting two minutes, repeat the mixing procedure. Allowing the floc to settle twice ensures reaction of the chemicals with all of the dissolved oxygen present. The floc will settle very slowly in sea water. A minimum of two minutes reaction time is required for sea water. Results will not be affected if the floc refuses to settle or if some of the reagent powder does not dissolve.
- 7) When the floc has settled so the upper one-third of the bottle is clear or after waiting two minutes, add the contents of one sulfuric acid powder pillow.
- 8) Re-stopper and gently invert the bottle about 20 times. The solution should be clear and straw-colored in appearance. The intensity of the yellow color is directly related to the original concentration of D.O. in the sample. A clear, pale solution suggests very low original D.O. levels. A dark, clear, yellow solution suggests high original D.O. levels.
- 9) Samples prepared through the addition of sulfuric acid may be stored for four hours before completion of the Winkler titration. Samples can be stored for a maximum of

six hours in the dark if the bottle is stored at the temperature of collection or water-sealed by putting water around the lip, and kept at 10-20 degrees Celsius.

10) As soon as the precipitate has completely dissolved as a result of acidification, the sample is ready to titrate. Transfer 200 ml of the solution to a 300-ml Erlenmeyer flask (a 300-ml BOD bottle may be substituted for this purpose). Alternately, pour 100 ml from the BOD bottle into a graduated cylinder and use the remaining 200 ml in BOD bottle for the titration.

11) Titrate with 0.025N PAO until the solution is pale yellow in color. The PAO titrant is not affected by bacterial action, however, it is affected by ultraviolet radiation and should be protected from direct sunlight. An opened bottle of PAO should be discarded after one year in a regularly used field kit and after two years if it is stored in the stockroom. Unopened bottles have a shelf life of about five years. The strength of the solution can be checked using an Iodate-Iodide Standard solution which is equivalent to 10.00 mg/l as dissolved oxygen. Repeat steps g. - m. using the Iodate-iodide Standard solution in place of the sample. The volume of PAO used to titrate should be 10 ml. If more than 10.5 ml of PAO is required to reach the endpoint, the PAO should be discarded. Alternatively, the D.O. value from a well-mixed body of water can be titrated using both a fresh bottle of PAO and the bottle in question. If the old solution requires 0.2 ml more to reach the endpoint in several titrations it should be discarded.

12) Add two ml of stable starch reagent and note the blue color which indicates the presence of iodine. The starch solution degrades rapidly at high temperatures. Monthly renewal of the supply in the field kit is recommended. Opened bottles should be stored in the refrigerator and discarded after two years. Unopened bottles have a shelf life of about five years when protected from high temperatures. A few drops should give the blue indicator color (not gray). If it takes more than one or two ml to produce the color, the sample titration results should be rejected and the starch solution replaced.

13) Continue the titration until the blue color just disappears. Titration should be completed against a white background. This step requires vigorous swirling to ensure that the titration endpoint is accurate. Disregard the reappearance after a few minutes of the blue color.

14) The total number of milliliters of PAO used in the titration is equal to the D.O., expressed in mg/l. The D.O. (mg/l) value obtained from the titration should be recorded in the field notebook.

C. Correcting D.O. Measurements Made with Polarographic Oxygen Probe

a. Dissolved Solids exert a "salting out effect" on dissolved oxygen in water. This permits the concentration of dissolved oxygen (mg/l) to decrease while the partial pressure (and thus the apparent D.O. sensed by the probe) can remain the same. The effect of dissolved solids

(measured as specific conductance) on the solubility of oxygen has been determined empirically. Measurements made the Winkler titration do not need to be corrected since this method measures actual concentration (weight/volume) of dissolved oxygen and yields a direct and accurate value, regardless of salinity, altitude, temperature, etc.

b. Field D.O. values measured with meters that are not salinity compensated and that is measured in waters with conductivities exceeding 1800 $\mu\text{mhos/cm}$, must be corrected. An easy way to make the correction is to multiply the field D.O. values by a correction factor.

The factor is computed from the formula:

$$F = 1 - (.003439 + \frac{.361}{(22.1 + T)^2}) * (C) / 1000$$

Where: F = the adjustment factor
T = water temperature in $^{\circ}\text{C}$
C = specific conductance ($\mu\text{mhos/cm}$)

Therefore: corrected D.O. = field D.O. value x F

c. The corrected D.O. value should be recorded in the field notebook.

EXAMPLE: D.O. measured in the field with the air-calibrated Hydrolab = 5.4 mg/l. The field temperature = 18.1 $^{\circ}\text{C}$ and field conductivity = 15,200 $\mu\text{mhos/cm}$.

$$\text{Therefore: } F = 1 - (.003439 + \frac{.361}{(22.1 + 18.1)^2}) * (15,200) / 1000$$

$$F = 1 - (.003439 + .00022339)(15.2) \\ F = 0.94433174$$

Therefore: corrected D.O. = 5.4 x .94
corrected D.O. = 5.1 mg/L

SPECIFIC CONDUCTANCE ($\mu\text{mhos/cm}$)

The specific conductance (conductivity) should be recorded for each water quality monitoring sampling visit.

A. Sampling Equipment - Conductivity meter (Hydrolab)

B. Sampling Procedures

- a. Preferably, conductivity is measured directly in-stream. Allow the conductivity probe to equilibrate for at least one minute before conductivity is recorded to three significant figures (if the value exceeds 100). The primary physical problem in utilizing an operable conductivity meter is entrapment of air in the conductivity probe chambers. The presence of air in the probe is indicated by unstable conductivity values fluctuating up to +100 $\mu\text{mhos/cm}$. The entrainment of air can be minimized by slowing, carefully inserting the probe assembly into the water; and when the probe assembly is completely submerged, quickly shoving it through the water; and by frequency cleaning of the probe assembly.
- b. If specific conductance cannot be measured in-stream it should be measured in the container used for collection of water samples, i.e., a bucket using the precautions outlines above for the measurement of temperature.

SALINITY (ppt)

The value for salinity is computed from chloride concentration (measured by titration) or conductivity (measured with a conductivity cell). The calculation assumes a nearly constant ratio for major ions in an estuary when sea water is diluted by river water. This assumption does not hold for salinities less than about three parts per thousand and salinity determinations at such low values are only approximate. Do not report salinity from freshwater or inland (brine) locations. In estuarine waters, salinity is a relevant and meaningful parameter. Often the salinity may be low, approaching that of freshwater. Nevertheless, this is useful information.

Values between 2.0 ppt and 1.0 ppt should be reported as <2.0 ppt rather than the actual value and values less than 1.0 ppt should be reported as <1.0 ppt. The Hydrolab Surveyor II computes salinity from specific conductance and temperature, and displays the value in parts per thousand. Report salinity values above 2.0 ppt to the nearest 0.1 ppt.

ALKALINITY

Alkalinity is the ability of salts in the water to neutralize acids. Water that is alkaline has a pH greater than seven. If possible, analysis for this parameter should be done in the field, or if impractical, by a laboratory within 14 days of sample collection.

Common methods for measuring total alkalinity, bicarbonate and carbonate in water samples include the Fixed End-Point Method and the Incremental Method. Both involve adding a standard solution of sulfuric acid to the sample with a buret or digital titrator and monitoring the change in its pH. The Incremental Method is considered to be more accurate. This procedure, however, requires special equipment. Alkalinity samples are much less subject to changes in the dissolved gas concentration than are dissolved oxygen samples and the care taken in their collection is much less. A clean, well-mixed sample free from sediment is necessary for alkalinity measurements as the acid titrant may react with the sediment particles and produce erroneous results. If the water has appreciable turbidity, it may be necessary to let it settle for a while after collection before doing the analysis.

Alkalinity is measured by titrating a water sample with a standard solution of strong acid to predetermined end points. Traditionally the end points have been chosen as those inflection points encountered in the titration of sodium carbonate. These values are 8.3 and 4.5 pH units. The upper value represents the point where all carbonate ions in the system have been converted to the bicarbonate form. The lower value is the point where all bicarbonate ions have been converted to the undissociated bicarbonate or back to carbon dioxide and water.

If the volume of titrant used for the first titration is exactly the same as in the second, then the alkalinity of the sample was due entirely to carbonates.

If the volume of the titrant for the first titration exceeds that of the second, then hydroxide ions were present.

For most natural water systems, the titrations for bicarbonate will be the largest or the sole contribution to the alkalinity.

Without a pH meter, an approximation of the above end points may be achieved for purposes of titrations by the use of visual indicators: phenolphthalein for the upper and methyl orange for the lower pH range. Report alkalinity concentrations below 1000 mg/l to whole numbers and above 1000 mg/l to three significant figures.

CHLORIDE

There are no restrictions imposed on sampling by the analytical procedures normally employed in measuring chloride ion. Colored solutions or high turbidities may interfere with the visual detection of titration endpoints. Two chloride analytical procedures are adaptable to field measurements, both of which employ a visual endpoint to a titration procedure.

The first of these, the long-established Mohr method, relies upon the insolubility of silver chloride as its basis. When titrating a chloride solution with silver nitrate, the silver will combine with the chloride ions and be removed from the solution. When all the chloride ions are removed, excess silver ions will react with a potassium dichromate solution to form silver chromate, a red precipitate which may be visually detected. Detection is enhanced by viewing the color change through a yellow filter to mask out the color of the indicator alone.

A newer procedure is the mercurimetric analysis which has many points in common with the Mohr method. In this procedure, mercury replaces the silver in the titrant, and the stable complex which removes chloride ions from solution is mercuric chloride. Excess mercury ions, after all chloride ions are removed, are detected by adding a small amount of diphenylcarbazone to the sample, which forms a blue-violet complex with the un-reacted mercury.

The choice of method between the Mohr and the mercurimetric methods depends upon the concentrations of chloride expected in the water samples. The Mohr method will have application at higher chloride levels at least above 10 mg/l and preferably above 100 mg/l, while the mercurimetric analysis is applicable in ranges down to 0.1 mg/l.

FECAL COLIFORM (TNRCC, 1997)

Preparation

Filter a minimum of two subsamples of different volumes from each sample collected. The objective is to filter a sample volume that will result in the optimum number of 20-60 fecal coliform colonies on the filter. The volume(s) filtered will depend on the source of the sample(s). The more contaminated the sample the smaller the volume filtered. This is the reason for multiple subsamples

Prepare petri dishes with absorbent pads and M-FC media.

A minimum supply of two petri dishes per sample plus one petri dish for a blank are needed.

Add the contents of one M-FC media ampule to each petri dish containing a sterile, absorbent pad. You may wish to pour off some, but not all of the excess media. Immediately cover petri dish base with petri dish lid.

Bacterial Media: Refrigerate until expired; avoid warm temperatures of vehicles.

Label the top lid of each petri dish with the appropriate station identifier and number of milliliters of sample to be filtered. If samples are run on successive days, it may also be helpful to add the date.

Filter Sample

Based on your experience, filter the least contaminated samples first.

Assemble filtration equipment apparatus and connect vacuum pump.

Rinse the filter assembly thoroughly with sterile rinse water by pulling several rinses through the filter apparatus. This will remove traces of alcohol and formaldehyde generated by the sterilization procedure.

Place a sterile, 0.45 μm , membrane filter on filter apparatus using sterilized forceps. Sterilize forceps each time before they are used to move the filter. Forceps are sterilized by dipping the tips into methanol, then burning the methanol off. The flame merely burns off the methanol, the methanol acts as the disinfectant. The forceps should grasp the filter near the filter's outside edge without extending onto the area covered by the filtered sample.

Wet the filter with a few milliliters of sterile buffer water; this will aid in distributing the bacteria onto the filter.

If the sample volume to be filtered is less than 10 ml, add at least 10 to 50 ml of sterile buffer water to the filter funnel.

Shake the sample vigorously 25 times and quickly pipet desired volume into filter funnel. The airspace

in the bag helps mix the sample. Bacteria are associated with particles in the water. By vigorously shaking the sample, these particles are broken up and the bacteria are dispersed. Five to ten milliliters of air in the Whirl-pak bag will facilitate the mixing.

Apply a moderate vacuum to filter the sample.

Rinse down the filter funnel twice with sterile buffer water.

Release vacuum from filter apparatus and remove the filter from the filter apparatus to a labeled petri dish containing absorbent pad saturated with M-FC media.

Place new filter on filter apparatus and repeat the filtration steps with another subsample of the same sample.

Repeat the procedure with each additional sample. Discard used pipette and use a new, sterile pipette for each additional sample. Place labeled petri dishes, upside down, in an incubator set at an incubation temperature of 44.5 °C. When the plates are upside down, condensation does not form on the lid and the pad is less likely to dry out. Record beginning incubator temperature in the log book.

Reassemble filter apparatus without a filter and rinse down thoroughly (a minimum of three rinses) with sterile buffer water.

Filter a blank following the procedure above but use about 20 ml of sterile buffer water. The blank allows you to monitor the effectiveness of your technique. If colonies appear on the blank, all data from samples that were filtered at the same time as the blank should be discarded. If you chose to run blanks between samples, discard the data from samples filtered since the last blank with no colonies.

Sterilization of Filter Apparatus

The best procedure is to routinely perform this step when finished filtering for the day. If the apparatus has been sterilized in this manner before storage, then this step does not need to be done at the beginning of the next filtering exercise.

Remove the stainless steel beaker from the filter assembly.

Saturate the asbestos wick around the base of the filter assembly with methanol.

Ignite the methanol on the asbestos wick and allow to burn for 30 seconds.

Place the stainless steel beaker tightly over the filter assembly and leave in place for 15 minutes or until the next time the apparatus is used. The oxygen is consumed by burning, and formaldehyde is produced by incomplete combustion. About 15 minutes is necessary ensure sterilization.

Record Keeping

Record the volume of sample filtered each time, the time and date samples were collected and filtered,

and initial temperature of incubator. The information can be recorded in the field the logbook or bacteriological raw data log sheets.

The log should contain the following information:

- * Sampling station number and location
- * Date and time of sample collection
- * Volume of sample filtered
- * Time of sample filtration
- * Number of fecal coliform colonies counted on each filter
- * Pertinent observations, i.e. confluent growth; abnormal coloration
- * Incubator temperature at beginning and end of incubation period
- * Date and time filter removal from incubator
- * Initials of individual preparing and analyzing samples

Sample Incubation (APHA, 1985)

Incubate fecal coliform samples for 22-24 hours at $44.5^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$.

Counting the Colonies

At end of incubation period, record incubator temperature and the time samples were removed from the incubator.

Count and record the number of individual, distinct, round, blue colonies on each filter. Counting colonies is preferably accomplished with a dissecting microscope or a hand-held magnifying lens. The ideal number of colonies on the plate is 20 to 60. Often in the summer months, a pink thermophilic bacteria may overgrow the coliform colonies. The only way to cope with this is to reduce the volume filtered, to perhaps 5 ml. Occasionally, the culture plate will produce many very small blue colonies, ranging from 1/50 to 1/10 the size of coliform colonies. Do not count these pretenders.

Data Reporting

Calculate the concentration of fecal coliform bacteria in the original sample and record the value as number of colonies/100 ml.

Report the fecal coliform bacteria concentration according to the following guidelines:

EXAMPLE 1: If each of the two filters prepared from a sample had 20-60 fecal coliform colonies, the ideal range of colonies per plate, report a fecal coliform concentration based on the combined results of this sample.

filter a: 5 ml filtered, 20 colonies .

filter b: 20 ml filtered, 55 colonies

$\frac{20 \text{ colonies}}{5 \text{ ml}} + \frac{55 \text{ colonies}}{20 \text{ ml}} = \frac{75 \text{ colonies}}{25 \text{ ml}}$
$\frac{75 \text{ colonies}}{25 \text{ ml}} = 3 \text{ colonies/ml}$
$3 \text{ colonies/ml} \times 100 \text{ ml} = 300 \text{ colonies/100 ml}$
Report 300 colonies per 100 ml.

EXAMPLE 2: If one of the two filters prepared from a sample had 20-60 fecal coliform colonies and the other filter had less than 20 or more than 60 colonies, report the concentration calculated from the filter with 20-60 colonies.

EXAMPLE 3: If each of the two filters prepared from a sample had less than 20 fecal coliform colonies, calculate and report a combined fecal coliform concentration for the sample.

filter a: 10 ml filtered, 0 colonies

filter b: 20 ml filtered, 3 colonies

$\frac{0 \text{ colonies}}{10 \text{ ml}} + \frac{3 \text{ colonies}}{20 \text{ ml}} = \frac{3 \text{ colonies}}{30 \text{ ml}}$
$\frac{3 \text{ colonies}}{30 \text{ ml}} = 0.1 \text{ colonies/ml}$
$0.1 \text{ colonies/ml} \times 100 \text{ ml} = 10 \text{ colonies/100 ml}$
Report 10 colonies per 100 ml

EXAMPLE 4: If each of the two filters prepared from a sample had greater than 60 fecal coliform colonies, make the following evaluations:

*If you can make an accurate count of discrete fecal coliform colonies on one or both filters, calculate and report the concentration of fecal coliform colonies. Usually when the density on the filter exceeds 100 colonies, competition for space and nutrients suppresses growth, giving erroneously low counts. Thus the count should be expressed 'greater than' whatever the count reveals.

*If the growth is confluent, report a minimum estimated value by assuming a count of 60 coliform

colonies based on the smallest volume filtered (Rawson, 1982).

filter a: 1 ml filtered, > 60 colonies filter b: 10 ml filtered, > 60 colonies

Use the smaller volume filtered
$\frac{> 60 \text{ colonies}}{1 \text{ ml}} > 60 \text{ colonies/ml}$
$> 60 \text{ colonies/ml} \times 100 \text{ ml} = > 6000 \text{ colonies/100ml}$
Report > 6000 colonies per 100 ml.

EXAMPLE 5: If no colonies appear on the plates, report a value, dependent upon the volume filtered, that represents the detection limit. Combine the two volumes filtered in order to maximize the sample size. Report the fecal coliform concentration as less than the value you calculated by this procedure, using the symbol "<" for less than the detection limit. When the actual values (rounded) of low counts are reported, it will allow us to use the uncensored data in making calculations and reporting statistics.

filter a: 10 ml, no colonies

filter b: 50 ml, no colonies

$\frac{\leq 1 \text{ colony}}{10 \text{ ml} + 50 \text{ ml}}$	$\frac{\leq 1 \text{ colony}}{60 \text{ ml}}$	$< 0.017 \text{ colonies/ml}$
$< 0.017 \text{ colonies/ml} \times 100 \text{ ml} = < 1.7 \text{ colonies/100 ml}$		
Report < 2 colonies/100 ml		

Remember to report fecal coliform concentrations as a whole number. Always report the concentration to two significant rimes.

EXAMPLE 6: For fecal coliform concentrations < 100 colonies/ 100 ml, report the concentration to the nearest whole number. For fecal coliform concentrations > 100 colonies/100 ml, always report the concentration to two significant figures.

NOTE: The fecal coliform test is performed according to a universally standard procedure. The data are useful only for comparison to other data obtained using the same procedure or to standards criteria. If the test cannot be performed successfully, then no result should be reported. The analyst may indicate on the reporting form that the test was attempted by noting "interference by competing organisms", "exceeded holding time", "exceeded incubation time", "incubator failure," etc.

EMERGENCY TELEPHONE NUMBERS TO REPORT SPILLS AND FISH KILLS

Arizona

Arizona Game and Fish Department (Fish Kills)	(800) 352-0700
Arizona Department of Environmental Quality (Spills)	(602) 257-2330

California

California Regional Water Quality Control Board (Imperial Co.)	(760) 346-7491
California Regional Water Quality Control Board (San Diego Co.)	(619) 467-2952

New Mexico

New Mexico Environment Department	(505) 827-9329
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Texas

Texas Natural Resource Conservation Commission (Fish Kills and Spills)	(800) 832-8224
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Alternately, call the local fire department to report spill and any local game warden to report of fish kills.