Field Methods for Hydrologic and Environmental Studies

Chapter 2

Water Quality Data Collection

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Water Quality – Introduction

Water quality is a *value judgement* that is related to the intended purpose of the water body and based on the physical, chemical, and/or biological attributes of the water body.
Water quality may be defined by a single or multiple characteristics.

History of Water Quality

Pre-historic	Realization of the importance of water and safe drinking water
3000 B.C.	Earliest record of central water supply and waste disposal in Nippur of Sumeria
98 A.D.	First books on water supply and treatment (Roman)
Early 1800's	First treatment of wastewater
1847	Outbreak of cholera in India caused examination of sewage systems
Late 1800's	Development of germ theory incorporated into water treatment
Early 1900's	Drinking water becomes safer through treatment by sand filtration and chlorination
1940-70	Focus on point source pollution discharges and wastewater from industry and municipalities
1970	First Earth Day
1970's	Interest begins on non-point source pollution discharges
1980's	Combined sewer overflows
1990's	Watershed and ecosystem approaches
	Chlorination by-product concerns
	Endocrine disruption
	Hypoxia issues
	Microbial concerns: pathogens, protozoans, viruses

What Affects Water Quality?

Stream hydraulics	Input sources
Geology	Climate
Geomorphology	Biology
Land use	Stream use
Atmosphere	Other?

Variability in Water Quality

Spatial - varies between different locations as a result of natural or anthropogenic factors, environmental conditions, and source locations.

Temporal - varies in time
- long-term changes (changes in land use, climate, assimilative processes...)
- seasonally (climatic variabiltiy, land-use practices...)
- daily (anthropogenic and natural processes)

Water Quality - Why?
- Characterize water bodies
- Identify changes or trends over time
- Identify specific existing or emerging problems or issues
- Determine compliance with regulations
- Determine effectiveness of pollution control actions or management practices
- Responses to emergencies, spills, or floods
- Research and modeling efforts
- Water resource management
- Determine fate and transport of pollutants

Water Quality - Who?
Regulatory interests - Federal, State, and Local agencies and the public
Research interests - Governmental, academic, scientific, corporate...
Management interests - Natural resource agencies, water authorities, lake managers, water suppliers, farmers...
Private entities- Volunteers, watershed associations, environmental groups, residents...

Water Quality - What?
Physical descriptors - Temperature, pH, dissolved oxygen, specific conductance, turbidity, alkalinity.
Nutrients - Nitrogen, phosphorus, silica, and others
Major ions - Calcium, carbonate, magnesium...
Trace elements - Metals, arsenic...
Organic compounds - Industrial, agrichemical, commercial
Sediment - Suspended and bottom material
Microbial - Bacteria, protozoans, viruses
Biological - Fish, algae, invertebrates, macrophytes, mollusks, biological indices (IBI)

Water Quality - HOW (the big question)

- Monitoring design
- Sampling network
- Collection frequency
- Collection methods
- Equipment
- Analytical requirements
- QA practices

Sample Collection Methods

Grab or Dip sample
Integrated sample
- width integrated
- depth integrated

Composite sample
- Time composited
- Flow composited

Point sample (specific location or depth)
End-of-pipe sample (point sources)
Continuous____sampling (probe measurments)

Other Sampling Considerations

- Whole sample versus filtered sample
- Sample processing methods
- Sample preservation methods

Selection of Sampling Site

Ideal sampling sites are seldom present. Selection of a sampling site should consider the following characteristics and the importance of each to the study objectives and how each may affect the quality of the sampling results, based on study objectives.

- At or near gaging station - discharge data for computing loads, relating QW to flow
- Straight reaches with uniform flows and even bottom contour
- Far enough above and below confluences and inputs to avoid poorly mixed sections
- Upstream from bridges and other structures that are potential contamination sources
- In sections of unidirectional flow
- At or near transect where other data are collected
- At a location where samples can be collected during all flow conditions.
- Confirm transect selection with field measurements at various locations across the sampling transect (may vary seasonally)

Section 2.1

PREPARATIONS FOR WATER SAMPLING

FIELD-PERSONNEL RESPONSIBILITIES

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

FIELD-TRIP PREPARATIONS

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

Before selecting sites or making other preparations:

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

Before selecting equipment:

- Understand the physical and chemical limitations of each piece of equipment, in order to meet data-collection objectives and data-quality requirements. Verify and test, if possible, the operational range of the sampling equipment to be used.

Before starting field work:

- Review site files and update and review the field folder for each site from which samples and ancillary data will be collected.
- Review the safety plan and be sure that you have the training needed if you will be working at sites designated as hazardous
- Plan ahead! Take adequate time to prepare.

DATA-QUALITY PLANS AND PREPARATIONS

Every study should have a written document that describes study objectives, data-quality requirements, and a quality-assurance plan.

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

Examine field and laboratory results as soon as possible, preferably before the next sample-collection field trip. Results indicating potential bias in the data will alert you to the changes needed in equipment, equipment-cleaning procedures, or field methods used.

Be prepared to collect additional blanks, replicates, or other field quality-control samples, based on your judgment of the effects of field conditions on sample collection. Field conditions are unpredictable, and adverse or unexpected conditions could necessitate additional steps to document data quality.

Quality-control samples are collected either in the office laboratory or at the field site, depending on their specific purpose. Field personnel must be familiar with the various types of quality-control samples and know how and when to collect them in order to comply with quality-assurance requirements.

In preparation for collection of quality-control samples, solutions of the appropriate type and quality must be obtained for blank and standard reference material samples. Laboratory certification should indicate that the blank water has target-analyte concentrations that are less than the method-detection limits.

Equipment blanks are processed through clean equipment in the controlled setting of an office laboratory. Process an equipment blank at least once a year for each set of sample-contacting equipment. This applies to new equipment to be used for the first time, to equipment that will be cleaned with a new cleaning procedure, and to equipment that has not been tested with an equipment blank for 1 year. Do not collect or process environmental samples until the annual equipment blank data have been reviewed.

The field personnel or other responsible party needs to ensure that the equipment blanks are either free of contamination or have concentrations small enough to be insignificant at the current analytical limits.

Collect field blanks at the field site under the same conditions as environmental samples. Field blanks can provide information on the efficacy of the equipment cleaning procedures used and on ambient atmospheric contamination.

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

SELECTION OF SAMPLING SITES

Before sample collection, sampling sites must be selected. For each sampling site, background files and a field folder should be established. Careful and complete documentation of site information and data collected should be input to appropriate files.

The study team is responsible for selecting sampling sites and conditions (such as time of year, flow rate or stage) that will yield samples representative of the aqueous system being studied. Each body of flowing and still surface water has a unique set of conditions that needs to be identified and considered in the site-selection process.

Field personnel should be trained in the correct and current water-quality data-collection procedures and must exercise judgment gained from field experience in order to make appropriate site selections.

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

<u>When selecting surface-water sampling sites:</u>

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

Flowing-Water Sites

Flowing-water sites refer to streams (fast or slow, intermittent, ephemeral, or perennial), canals, ditches, and flumes of all sizes and shapes, or to any other surface feature in which water moves unidirectionally. All or parts of reservoirs and estuaries that flow unidirectionally are considered to be flowing water.

Flowing-water sampling sites optimally are located:

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

After a tentative selection of a sampling site, develop a preliminary profile of field measurements at various locations along the cross section. The field-measurement profile is used to indicate reach homogeneity. Final site selection is based on a comparison of these field measurements with the data requirements of the study.

TECHNICAL NOTE*: The preferred sampling method and number of verticals to be sampled within the stream cross section that are needed to obtain a sample that is sufficiently representative depends on stream homogeneity as indicated by the field-measurement profile and stream-discharge or other data, as well as by study objectives. Also, it might be desirable to move to a sampling site upstream or downstream to adjust for seasonal variation or extreme flow conditions.*

The guidelines used for selecting sampling sites on ephemeral and intermittent streams are the same as those for perennial streams. Ephemeral and intermittent stream sites need additional planning and examination to account, for example, for conditions related to rapidly changing stage and discharge that can occur as a result of flash flooding or urban runoff.

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

Still-Water Sites

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

When locating still-water sampling sites:

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

Field Folders

Selected information that is needed for reference while at a surface-water site is kept in a field folder. The field folder contains information needed by trained personnel to locate and safely collect and process water samples. The field folder is taken along on each sampling trip. The folder should be customized according to study needs (table 1).

Table 1.

Section 2.2

EQUIPMENT FOR WATER-QUALITY SAMPLING

CHEMICAL COMPATIBILITY OF EQUIPMENT AND THE WATER SAMPLE

The materials used to construct equipment can directly affect sample. Equipment designed for water-quality work commonly is constructed of a combination of materials, the most inert being used for components that will contact the sample. Nonsample-wetted components also can be a source of sample contamination, and field personnel must use techniques to minimize potential contamination, implement quality-assurance procedures, and quantify potential effects by using quality-control sample analysis.

Materials used in equipment can include plastics, glass, and metals. Chemical reactivity varies widely within the same group of materials, depending on the chemical composition, the physical configuration, and the manufacturing process. Thus, regarding reactivity with water and most other chemical substances, plastics such as fluorocarbon polymers are less reactive than plastics such as polyethylene, and 316-type stainless steel (SS 316) is less reactive than brass, iron, or galvanized steel. For plastics and metals in general: The softer or more flexible forms of any plastic or metal are more reactive than the rigid forms. The more polished the surface, the less reactive the material tends to be. Table 2 provides general guidelines for selection of appropriate sampling equipment materials.

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

SURFACE-WATER SAMPLING EQUIPMENT

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

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

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

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

- Isokinetic depth-integrating samplers
- Nonisokinetic samplers

Isokinetic Depth-Integrating Samplers

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

Types and pertinent characteristics of isokinetic depth-integrating samplers recommended for sampling in flowing water are summarized in Table 3, illustrated on Figure 1, and described below.

For collection of an isokinetic sample,minimum stream velocity must begreater than 1.5 feet per second (ft/s) for a depth-integrating sampler with a rigid bottle, or 3.0 ft/s for a bag sampler.

The maximum allowable transit rate (Rt) relative to mean velocity (Vm) for a given sampler varies with nozzle size and sample-bottle size (table 2). **Do not exceed the listed Rt/Vm ratio for the given nozzle and bottle size.** A lower Rt/Vm is better for ensuring that a representative velocity-weighted sample is collected, but care must be taken to not overfill the sampler bottle.

The cap and nozzle assembly is available in fluorocarbon polymer and polypropylene. The same cap and nozzle can be used for the US DH-81, US D-95, and the US D-77. If the cap vent is plugged, the same cap and nozzle can be used for bag-type samplers. In addition, fluorocarbon polymer adapters are available to mate the cap to either 1-L or 3-L fluorocarbon polymer bottles.

Use the US DH-81, US D-95, US D-77, D-77 Bag, or Frame-Bag (FB) samplers to collect samples in flowing waters for all analyses except inorganic gases and volatile organic compounds.

- Samples of water for determination of metals and other trace elements (hereafter referred to collectively as “trace elements”) must contact only noncontaminating materials, typically flurocarbon polymer or polypropylene.
- Samples of water for determination of organic compounds must contact only noncontaminating materials, typically metal (such as stainless steel), fluorocarbon

polymers (such as TeflonTM), or ceramics (such as hard-fused microcrystalline alumina).

Do not use the US DH-48, US DH-59, US DH-76, US D-49, US D-74, US P-61, US P-63, and US P-72 samplers for collecting trace-element samples: they contaminate samples with measurable concentrations of trace elements.

- Some of these samplers may be acceptable for major ions, nutrients, and suspended sediments.
- Additional quality-control samples need to be collected if it is necessary to use any of these samplers.

Figure 1.

Hand-held samplers

The US DH-81 (Fig. 1-A) or US D-95 (Fig. 1-B) sampler is used to collect water samples where flowing water can be waded or where a bridge is accessible and low enough to sample from. The sampler components (cap, nozzle, and bottle) are interchangeable. Both inorganic and organic samples can be collected with either sampler as long as the construction material of the sampler components (Table 2) does not affect ambient concentrations of target analytes. Isokinetic depth-integrated samples for bacteria analysis also can be collected with these samplers because the cap, nozzle, and bottle can be autoclaved.

When using the US DH-81:

- Use a 1/4- or 5/16-in. nozzle.
- Make sure that flow velocity exceeds 1.5 ft/s (to collect an isokinetic sample).
- Use the 1-L bottle (not the 3-L bottle).

When using the US D-95:

- Use either a 3/16-, 1/4-, or 5/16-in. nozzle.
- Make sure that flow velocity exceeds 1.5 ft/s (to collect an isokinetic sample).
- Use the 1-L bottle.

Cable-and-reel samplers

Cable-and-reel samplers are used to collect water samples where flowing water cannot be waded. These include the US D-77, the D-77 Bag, and the Frame-Bag samplers. (Refer to Table 2 for sampler characteristics and sampling limitations.) Like the US DH-81 and US D-95, these samplers can be used for collecting inorganic and organic samples; however, sampler components (cap, nozzle, and bottle) must be selected so as not to bias concentrations of target analytes. Isokinetic depth-integrated samples for bacteria analysis also can be collected with these samplers because the cap, nozzle, bottle, and bags can be autoclaved.

The US D-77 sampler (Fig. 1-C) is used where water is less than 15 ft deep. The D-77 Bag and the Frame-Bag (FB) samplers (Fig.1-D, E) are designed to collect isokinetic depth-integrated samples at depths greater than 15 ft. The capability of collapsible bag-type samplers to collect isokinetic depth-integrated water-quality samples is being evaluated by the USGS.

Metal parts of the US D-77 Bottle sampler and D-77 Bag and Frame-Bag samplers must be coated with plastic ("plasti-dip") and recoated periodically to prevent possible sample contamination from metallic surfaces.

When using the US D-77 bottle sampler:

- Use a 5/16-in. nozzle.
- Make sure that flow velocity exceeds 1.5 ft/s.
- Use in water less than 15 ft deep for an isokinetic, depth-integrated sample.

When using the D-77 Bag sampler:

- Use a 1/4- or 5/16-in. nozzle.
- Make sure that flow velocity exceeds 3 ft/s (to collect an isokinetic sample). Isokinetic capability decreases at flow
- velocities less than 3 ft/s.
- Use in water with depth greater than 15 ft for an isokinetic, depth-integrated sample.
- Make sure that a clean, noncontaminating object such as a glass (not rubber) bottle stopper is in the bag.
- Water temperature must be above 8°C.

The D-77 Bag sampler uses a collapsible ReynoldsTM oven or fluorocarbon polymer bag that is placed in a special slotted 3-L bottle with a US D-77 cap and nozzle assembly in which the vent is plugged. The Frame-Bag sampler uses a collapsible bag that is placed in a special slotted 3- or 8-L bottle (Fig. 1-E) with a US D-77 cap and nozzle assembly in

which the vent is plugged. The slotted bottle is held in a plastic-coated metal frame to which various sizes of sounding weights can be attached. The size of the weight depends on the stream velocity along the cross section that will be sampled. The advantages of the Frame-Bag sampler over the D-77 Bag sampler are that the Frame-Bag sampler can be used to collect a larger sample volume and, therefore, to sample greater depths; and it can be used to collect samples in streams with greater velocities because heavier weights can be attached to maintain proper orientation of the sampler in the stream. Another advantage of the D-77 Bag sampler over the Frame-Bag sampler is that use of the D-77 Bag sampler results in a smaller unsampled zone (distance between the nozzle and the bottom of the sampler).

When using the Frame-Bag sampler:

- Use a 3/16-, 1/4- or 5/16-in. nozzle (not a 1/8-in. nozzle).
- Make sure that flow velocity exceeds 3.0 ft/s (to collect an isokinetic sample).
- Keep a clean, noncontaminating object such as a glass bottle stopper or a fluorocarbon polymer-coated magnetic stirring bar in the bag. Do not use a rubber stopper.
- Water temperature must be above 8°C.

Nonisokinetic Samplers

Open-mouth samplers

Open-mouth samplers used for the collection of water samples include the hand-held bottle, the weighted-bottle sampler, the BOD sampler, and the VOC sampler (Fig. 2).

The ***hand-held bottle sampler*** is the simplest type of open-mouth sampler. A bottle is dipped to collect a sample (Fig. 2-A) where depth and velocity are less than the minimum requirements for depth-integrated samplers.

The ***weighted-bottle sampler*** is available in stainless steel (US WBH-96) (Fig. 2-B) or polyvinyl chloride. The weighted-bottle sampler can be used to collect samples where flow velocities are less than the minimum requirement for isokinetic depth-integrating samplers and where the water body is too deep to wade. An open bottle is inserted into a weighted holder that is attached to a handline for lowering. Sampling depth is restricted by the capacity of the bottle and the rate of filling.

The ***biochemical oxygen demand (BOD) sampler and the volatile organic compound (VOC) sampler*** (Fig. 2-C,D), are open-mouth samplers designed to collect nonaerated samples. The BOD sampler accommodates 300-mL glass BOD bottles specifically designed to collect samples for dissolved-oxygen. The VOC sampler is specifically designed to collect nonaerated samples in 40-mL glass septum vials for determination of volatile organic compounds.

Thief samplers

Thief samplers are used to collect instantaneous discrete (point) samples. Thief samplers have been used primarily to collect samples from lakes, reservoirs, and some areas of estuaries. Smaller versions, designed to collect ground-water samples, also have been used in still and flowing surface water. The most commonly used thief samplers are the Kemmerer sampler, Van Dorn sampler, and double check-valve bailer with bottom-emptying device (Fig. 3). These samplers are available in various sizes, mechanical configurations, and in various types of construction material (such as stainless steel, glass, polyvinyl chloride, fluorocarbon polymer). Disposable fluorocarbon polymer bailers also are available.

Figure 2.

Figure 3.

Automatic samplers and pumps

Automatic pumping samplers with fixed-depth intake(s) are sometimes used to collect samples at remote sites; from ephemeral, small streams; or from urban storm drains where stage rises quickly. These samplers can be programmed to collect samples at preset time intervals or at selected stages, thus reducing the personnel requirements for time-intensive sampling. Whenever automatic samplers or pumps are used, the sample is considered to be a point or grab sample.

Pumps used for water sampling are grouped into two general categories: suction-lift pumps and submersible pumps. Pumps can be used to collect water samples from lakes, reservoirs, and.

SAMPLE PROCESSING

Water samples must be processed as quickly as possible after collection. The equipment most commonly used for sample processing includes sample splitters, filtration units or assemblies, solid-phase extraction systems, and chambers in which samples are processed and treated with chemical preservatives. Having several available sets of cleaned processing equipment is recommended.

SAMPLE SPLITTERS

The collection of surface water generally results in a single composite sample. A ground-water sample generally is not composited; instead the sample is pumped directly into separate bottles for designated analyses. There are exceptions. For example, a ground-water sample can be composited when the sample is collected using a nonpumping method (bailer or thief sampler).

Once a sample has been composited, the sample is often subdivided (split) into subsamples for analysis. Each whole-water subsample should contain suspended and dissolved concentrations of target analytes that are virtually equal to those in every other subsample.

Churn Splitter.

An 8 or 14-L plastic churn splitter is recommended to composite and split surface-water samples for trace-element analysis (Figure 4). Stainless steel and glass containers are used to composite samples for organic analysis. To avoid sample contamination, do not collect or extract samples for trace-element analyses from a metal container, or samples for organic-compound analysis from a nonflurocarbon-polymer plastic container.

Advantages of the churn splitter:

- Simple to operate.
- Easy to clean.

Limitations of the churn splitter:

- Although it can be used to split samples with particle sizes 250 µm and suspended-sediment concentrations 1,000 mg/L, splitting accuracy becomes unacceptable for particle sizes >250 µm and
- suspended-sediment concentrations >1,000 mg/L.
- Sample volumes less than 3 L or greater than 13 L cannot be split for whole-water subsamples.
- Plastic (nonfluorocarbon polymer) churn splitters should not be used to composite samples for determination of organic compounds.
- Samples for bacteria determinations are not to be taken from a churn splitter because the splitter cannot be autoclaved.

Cone Splitter

The cone splitter is a pour-through device constructed entirely of fluorocarbon polymers (Figure 5). The cone splitter may be used to process samples with particle sizes 250 µm and suspended-sediment concentrations 10,000 mg/L. Its primary function is to split the sample simultaneously into as many as 10 equal-volume samples. Some cone splitters have a 2-µm mesh screen in the reservoir funnel to retain large debris, such as leaves and twigs, that could clog or interfere with the splitting process. Below the funnel is a short standpipe that directs sample water in a steady stream, into a splitting chamber that contains a notched, cone-shaped splitting head with 10 equally spaced exit ports around its base. There should be no ridges, benches, or surfaces inside the splitting chamber that could retain material or interfere with the splitting process. The cone splitter is supported either by tripod legs or with an adjustable clamp and stand.

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

Advantages of the cone splitter:

- Used to process samples with suspended-sediment concentrations from 1,000 to 10,000 mg/L.
- Samples as small as 250 mL can be split into 10 equal subsamples.
- Samples greater than 13 L can be processed.
- Samples to be analyzed for organic compounds (except for volatile organic compounds) can be processed through the fluorocarbon polymer cone splitter.
- Samples containing sediment particles ranging in size from very fine clay and silt (1 to 10 µm) to sand-size particles (250 µm) can be split.

Limitations of the cone splitter:

- Accuracy of the volume equivalents must be verified before using a new or modified cone splitter
- Splitter is awkward to operate and clean in the field.
- Sample is vulnerable to contamination from atmospheric sources or from improper operation.
- Splitting capability for sediment particles >250 μm must be quantified.
- Samples for bacteria determinations are not to be collected with the cone splitter because the splitter cannot be adequately sterilized.
- The cone splitter must be level for proper operation.

PROCESSING AND PRESERVATION CHAMBERS

Processing and preservation chambers reduce the possibility of random atmospheric contamination during sample splitting, filtration, and preservation. These chambers are required for samples for trace-element determinations. The processing chamber can serve also as a collection chamber for pumped samples. There is no standard design for either fixed or portable chambers; however, to prevent contamination of inorganic samples with metals, the materials used in their construction should be either nonmetallic or completel covered by or embedded in nonmetallic material. Plastic components have been tested and do not emit volatile substances that might contaminate a VOC sample. This can be further documented by collecting an ambient blank in the chamber(s).

Fixed chambers can be enclosures permanently installed in a field vehicle for the sole purpose of sample collection, processing, or preservation. Fixed chambers must not be used as a storage area. The portable chamber illustrated is inexpensive and easily constructed with 1/2-in. white polyvinyl chloride (PVC), tubes which are used to support a clear plastic bag (Fig. 6). The transparent bag forms a protective tent to work within while collecting, processing, or preserving samples. Another option is to purchase or construct a fixed or portable glove box. The glove box also should have no exposed metal parts. Glove boxes that can be filled with inert gas should be used for samples to be excluded from contact with atmospheric gases.

Figure 4.

Figure 5.

Figure 6.

FILTRATION SYSTEMS

Filtration separates particulate substances (solid-phase and biological materials) from the solute or aqueous phase of a water sample. Water samples are filtered for analysis of inorganic constituents, organic compounds, and biological materials to help determine the environmental fate and quantify the transport of these target analytes.

For surface water, the most common filtration system consists of a reversible, variable-speed battery-operated peristaltic pump or a metering pump that forces the whole-water sample through tubing into a filter assembly. For ground water, the sample ordinarily is pumped through a sample line directly into a filter assembly. If the sample is collected by bailer, the sample generally is emptied through a valve with fluorocarbon polymer tubing and is transferred to the filter assembly by means of a peristaltic pump. Some bailers can be directly fitted with a filter and hand-pump system.

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

The filter assembly to be used depends on the type of target analytes, which are discussed in the following sections. Membrane filters commonly used to filter inorganic samples generally are made of cellulose nitrate, polycarbonate polymers, or polyethersulfone-based media. These filter media are not suitable for filtering samples to be analyzed for organics; glass microfiber is the media used for filtering most organic samples (silver filters are used for dissolved-organic compound samples).

A filtered sample is defined operationally by the nominal pore size of the filter media used.

- The filter pore size selected depends on study objectives, data requirements, and industry standards.
- The standard pore sizes of filter media used by the USGS are:
    - μm for pesticides, most other organic compounds, and some bacteria.
    - 0.45 μm for inorganic constituents (including major ions, radiochemicals, and trace elements), some bacteria, and dissolved organic carbon.
    - 0.2 μm or less for trace-element samples to be analyzed for some geochemical applications and interpretive studies and for nutrient samples for which exclusion of bacteria at the 0.2-μ threshold is desirable.

Inorganic Constituents

Samples for analyses of inorganic constituents are filtered by use of either a disposable capsule-filter assembly or a plate-filter assembly. **Construction materials of filtering systems must not be a source of sample contamination with respect to the substances for which the sample will be analyzed.**

Disposable capsule filter

The protocol for filtering a sample for analysis of inorganic constituents (inorganic sample) is to use a disposable capsule filter such as the Gelman 12175 ground-water sampling capsule (Figure 7). Use of a disposable capsule filter eliminates the potential for contamination from a reusable filter assembly (such as the plate filter) and also eliminates time-consuming field-cleaning procedures that are required for a reusable assembly after each sample is filtered.

Advantages of the disposable capsule filter compared to the plate-type filter:

- Capsule filters are sealed units; hence, the likelihood of contamination is reduced because the filter itself is not handled.
- Surface area of the capsule filter is roughly three times that of the 142-mm plate filter and is less subject to clogging.
- Cleaning the filter between samples is not necessary because each capsule filter is used only once and then discarded.

Plate-filter assembly

Before 1994, the most common filtration assembly used for USGS studies for filtering inorganic samples was the nonmetallic backflushing plate-filter assembly designed to hold a 142-mm filter. Two screens support the filter media (one above and one below) and allow water flow in either direction without disruption of the membrane. A smooth-tipped plastic forceps is needed to transfer the filter media to the plate of the filter assembly.

Types of plate-filter assemblies for inorganic samples include:

- Plastic backflushing assembly (described above), available for 47-mm, 142-mm, and 293-mm filters (Figure 8).
- Plastic vacuum filter assembly for 47-mm-diameter filter; used with either a hand vacuum pump or a peristaltic pump.
- Fluorocarbon polymer filter assembly designed for 47-mm-diameter filters; can be used for in-line filtering of inorganic or organic samples by changing to the appropriate filter media.

The plate-filter assembly is no longer recommended for routine filtration of samples for analysis of inorganic constituents, but is still used to filter samples for analysis of major ions, nutrients, stable isotopes, and radiochemicals.

Figure 7.

Figure 8.

Trace Organic Compounds

Filtering whole-water samples isolates suspended solid-phase substances from the aqueous phase, thus allowing separate determinations of organic compounds in each phase.

As preparation for determining organic compounds that partition onto suspended matter (hydrophobic compounds)--Filtering primarily concentrates suspended materials on the filter, enhancing extraction efficiency and lowering analytical detection limits. This is especially useful for whole-water samples with small concentrations of suspended material where large volumes of sample (4 to 40 L) must be filtered to provide an analyzable mass of suspended materials.

As preparation for determining organic compounds that are more water soluble (hydrophilic)--Filtering is used to remove suspended material, because it often contains interfering constituents that are co-extracted with target analytes.

Filtering also helps to preserve samples for organic determinations because microorganisms that could degrade compounds in the sample are removed (Ogawa and others, 1981).

Equipment needed to filter samples for determination of organic includes a positive displacement pump, an aluminum plate-filter assembly (Figure 9), the filter media, and metal forceps. Various filter assemblies may be required, depending on the specific analyses to be done. All equipment and components used for filtering whole-water samples for organic determinations should be made of materials that will not contaminate the sample or sorb analytes and that are suitable for use with organic cleaning solvents. Such materials include stainless steel or aluminum, fluorocarbon polymer, glass, and nonporous ceramics (hard-fused microcrystalline alumina). Other materials can be used, but they must not introduce contaminants or cause sorptive losses, and they must be sufficiently resistant to degradation by cleaning solvents. Use of plastics, rubber, oils and other lubricants are to be avoided because they can result in sample contamination, analytical interference, and (or) sorptive losses.

Filtration assemblies

The filtration equipment described in the following list includes various types of plate-filter assemblies, one of which is used for solid-phase extraction.

- The most common plate-filter assembly consists of two machined aluminum or stainless steel plates, designed to hold a 142-mm-diameter filter, which are held together by locking bolts or a locking ring.
- The plates have fluorocarbon polymer-coated silicone or VitonTM O-rings set in grooves to seal the filter assembly. A stainless steel screen on the lower plate supports the filter.

- A valve is built into the upper plate to exhaust trapped air. Connectors are built into the center of the top and bottom plates so that inlet and outlet fluorocarbon polymer tubing can be attached.

- Plate-filter assemblies are available for filters with diameters ranging from 13 to 293 mm. The size selected is determined by the sample volume to be filtered and the concentration of suspended materials in the sample.

Filter media

Tortuous-path depth filters made of borosilicate glass fibers are used to filter most samples for organic determination because the filter materials are basically inert and can be precleaned with organic solvents or baked at 450°C for at least 2 hours. Depth filters also can process larger fluid volumes than membrane filters without clogging**. Membrane filters (cellulose or polycarbonate polymers) commonly used to process samples for determination of nutrients and other inorganic constituents are not suitable for filtering samples for organic determinations, mainly because they are not resistant to organic solvents used to preclean sampling and processing equipment**. Membrane filters made of silver metal with a 0.45-µm pore size are resistant to organic solvents, but they become clogged too quickly for filtering the relatively large sample volumes (1 to 5 L) often needed for determination of organic compounds.

Use only filters without binders. (Acrylic resin binders can leach and contaminate samples, or might not be completely combusted when baked at 450°C.) Binder-free glass-fiber filters are available in various diameters ranging from 13 to 293 mm.

Dissolved and Suspended Organic Carbon

A stainless steel or fluorocarbon polymer pressure filter assembly fitted with a 47-mm, 0.45-µm-pore-size silver membrane filter is used to separate dissolved from suspended phases of organic carbon (Fig. 10).

- Use a hand-pressure pump, peristaltic pump, or an organic-free nitrogen gas tank fitted with clean tubing to apply pressure to filter dissolved organic carbon (DOC) from suspended organic carbon (SOC) samples.
- Maintain gas pressure applied to the filter assembly at less than 15 lb/in2.
- Ensure that the gas is clean by way of gas-purveyor certification or by attaching an in-line 0.2-mm Gelman Acro 50 hydrophobic membrane filter disk. Do not use any other type of filter.
    - Because the sample does not contact the in-line gas-filter disk, the disk can be used to filter gas used to process multiple samples, or until the disk clogs or is contaminated.
    - Store in-line filter disk in a resealable plastic bag between uses.

Pump Tubing

Pump tubing refers to the sample lines used with peristaltic, metering, and submersible pumps. Field personnel are cautioned to evaluate possible artifacts in a sample associated with pump tubing and tubing connections.

- Silicone tubing is suitable when sampling for inorganic analytes only, and only after appropriate cleaning.
- C-FlexTM tubing is made from a thermoplastic elastomer and is suitable for use when sampling for all inorganic analytes.
- Fluorocarbon polymer tubing is recommended when sampling for most inorganic and organic analytes.Fluorocarbon polymer tubing is available in corrugated, convoluted, and straight-wall configurations.
- Polyvinyl chloride (PVC) tubing (TygonTM) is suitable for inorganic samples only, and it must be appropriately cleaned prior to contact with inorganic samples.
- NorpreneTM tubing is made from a thermoplastic elastomer (a polypropylene base with USP mineral oil) and is suitable when sampling for inorganic analytes only. It must be appropriately cleaned prior to contact with samples collected for inorganic analysis.

Figure 9.

Figure 10.

Section 2.3

CLEANING OF EQUIPMENT FOR WATER SAMPLING

Equipment for water samples be properly cleaned before contacting the sample and that the effectiveness of cleaning procedures be quality. The goal of equipment cleaning is to help ensure that the equipment is not a source of foreign substances that could affect the ambient concentrations or chemistry of target analytes in samples. Standard procedures are described in this chapter for when, where, and how to clean equipment constructed of various materials and to collect equipment blanks and field blanks for quality control. Space is commonly dedicated in an office laboratory for equipment cleaning and for storage of cleaning supplies.

> ***Equipment cleaning (decontamination):*** *applying cleaning solutions to the surfaces of equipment or using other nondestructive procedures (such as stream cleaning) to remove foreign substances that could affect the concentrations of analytes in samples.*

- Clean all sample-collection and sample-processing equipment before use.
  - Manufacturing residues must be removed from new equipment.
  - Dust and any other foreign substances must be removed from equipment that has been in storage.
  - Substances adhering to equipment from previous sampling must be removed.

Prevent cross contamination between sampling sites by rinsing equipment with deionized water (DIW) while equipment is still wet, and then clean equipment as prescribed in this chapter before transporting it to the next site.

Do not substitute field rinsing with sample water for the equipment-cleaning procedures described in this chapter.

Collect equipment blanks and field blanks for quality control. A minimum of one equipment blank per year is required for each piece of equipment. The frequency of collecting blanks normally is based on study objectives and site conditions.

For inorganic analyses, basins, brushes and other items used to clean sampling equipment should be constructed of a suitable nonmetallic material such as uncolored or white polypropylene or other plastic. For analyses of organic substances, cleaning equipment should be constructed of metal, glass, or plastic materials. Do not use substances or detergents that might leach, sorb, or leave residues that might interfere with the analyses.

Some of the commonly used cleaning solutions include (also see Table 4):

8. Acid solution. A 5-percent, by volume hydrochloric acid solution is used to remove constituents (particularly metals) adhered to sampler and processing equipment surfaces.
9. Distilled/deionized water. Distilled or deionized water is used to wash and rinse equipment.
10. Detergent. Nonphosphate laboratory soap is used to scrub equipment.
11. Inorganic blank water. Water free of inorganic constituents. Used to rinse equipment and process inorganic blank quality-control samples.
12. Organic blank water. Water free of organic constituents. Used to rinse equipment and process blank organic quality-control samples.
13. Methanol. An organic solvent used to remove organic compounds from equipment.

CLEANING PROCEDURES

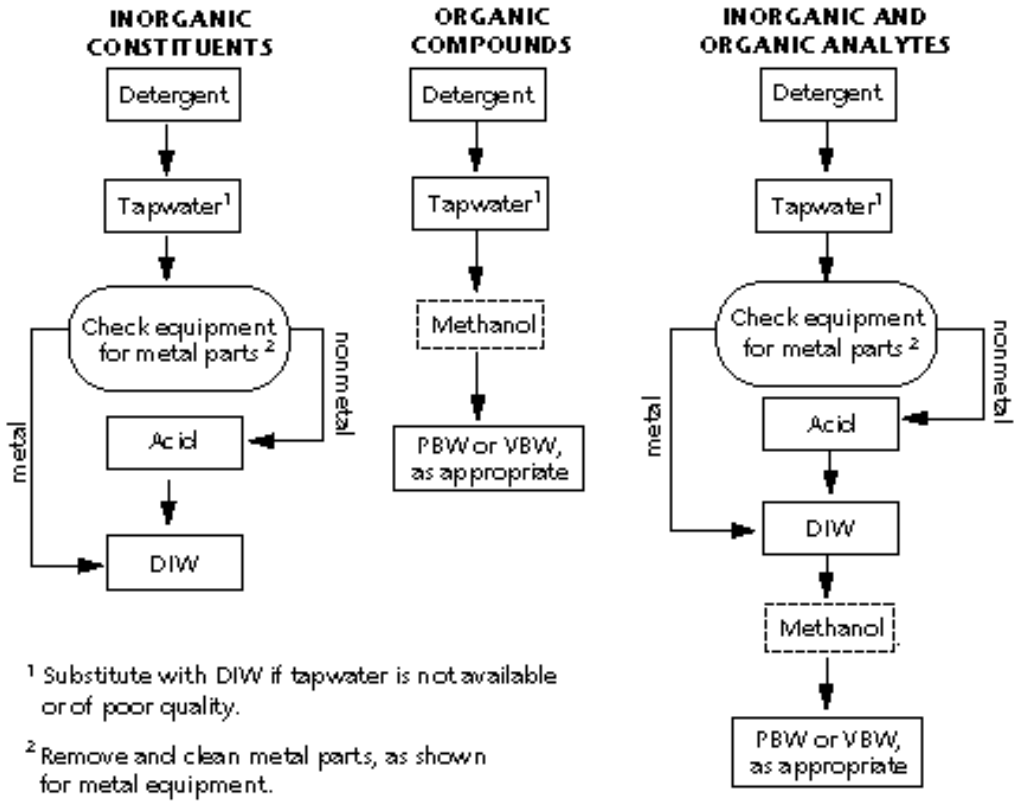
The cleaning procedure to be used depends on the type(s) of water samples that will be collected and processed. Figure 11 summarizes the sequence of cleaning procedures for equipment used to collect samples for inorganic and (or) organic analytes.

Table 4. Supplies for cleaning equipment used for water-sampling activities

[ACS, American Chemical Society; DIW, distilled/deionized water; µS/cm, microsiemens per centimeter at 25 degrees Celsius; PBW, pesticide-grade blank water; VBW, volatiles and pesticide-grade blank water; IBW, inorganic-grade blank water; L, liter; cm, centimeter; TOC, total organic carbon; DOC, dissolved organic carbon; SOC, suspended organic carbon; NFM, *National Field Manual*; PVC, polyvinyl chloride; IBW, inorganic-grade blank water]

Item	Description and Comments
Acid solution[1]	Hydrochloric: ACS trace-element grade (5 percent by volume in DIW). Nitric: ACS trace-element grade (10 percent by volume in DIW).
Aluminum foil	Organics only: Heavy duty, for work surfaces and equipment.
Bags, plastic or fluorocarbon polymer	Sealable bags with uncolored closure strips, various sizes. Recyclable trash bags are recommended for large equipment storage.
Noncolored plastic sheeting	Clean sheeting used to provide a clean work surface.
Brushes and sponges	Uncolored; plastic components needed for inorganic work.
Distilled/deionized water (DIW)	Maximum specific electrical conductance, 1 µS/cm (usually District produced; Office of Water Quality Memorandum 92.01).
Office-produced organic-grade deionized water	Usable only as a cleaning solution and only as specified in the text. Must not be used to substitute for PBW or VBW.[2]
Detergent	Nonphosphate laboratory soap (for example, LiquinoxTM).
Gloves, disposable	Powderless, noncolored vinyl, latex, or nitrile (latex or nitrile for use with methanol), assorted sizes.
Inorganic-grade blank water (IBW)[2]	Blank water with certificate of analysis prepared and (or) quality assured by the analyzing laboratory. IBW is required for blank samples.
Jerricans or carboys	For waste solutions and as neutralization container. Neutralization container: 25- to 30-L, polyethylene, wide-mouth, with layer of marble chips. Methanol waste container: Appropriate for flammable liquid.
Methanol	ACS pesticide grade. Methanol is the organic solvent in common use for equipment cleaning, but study requirements might dictate use of a different ACS pesticide-grade solvent.
Neutralization materials	Marble landscape chips (1- to 2-cm chips recommended).[3]
Pesticide-grade blank water (PBW)[2] ; volatile-grade blank water (VBW)[2]	Blank water prepared and (or) quality assured by the analyzing laboratory; required for collecting blank samples as follows: PBW for pesticide analysis; VBW for volatile compounds analysis and pesticide analysis; and either PBW or VBW for TOC, DOC, and SOC analyses.
Safety equipment and guidelines	For example, Material Safety Data Sheets (MSDS), safety glasses, chemical spill kit, apron, emergency phone numbers.
Standpipes for submersible pump	Plastic, glass, or other suitable material; for example, pipette jars or capped PVC casing; one standpipe labeled for blank water and one each for each cleaning solution. (Do not use PVC for methanol.)
Tapwater	If quality is questionable, substitute DIW. Tapwater is more effective for initial and rapid removal of detergent residue.
Tissues	Laboratory grade, lint free, various sizes (for example, KimwipesTM).
Wash bottles (dispenser or squeeze)	Labeled to indicate contents (for example, ACID, DIW, TAP). Fluorocarbon polymer needed for methanol, PBW, VBW, and IBW.

[1]Hydrochloric acid is required if analyzing for nitrogen species; otherwise, nitric acid is acceptable.
[2]PBW and VBW can be obtained from the USGS National Water Quality Laboratory (NWQL). IBW can be obtained from the USGS Quality of Water Service Unit.
[3]Agricultural limestone, soda ash, baking soda, and crushed shells are not recommended (Horowitz and others, 1994).



EXPLANATION

DIW	Distilled/deionized water
methanol	Current protocol includes methanol rinse for most types of equipment except that used with samples for organic-carbon analyses. However, this protocol is under review. SAFETY ALERT: Methanol is highly flammable; fumes can be hazardous to human health.
PBW	Pesticide-grade blank water
VBW	Volatiles- and pesticide-grade blank water

Figure 11. General sequence for cleaning equipment before sampling for inorganic and (or) organic analytes.

Section 2.4

FIELD ANALYSES

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

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

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

TEMPERATURE

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

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

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

Water temperatures should represent the mean temperature of the stream at the time of observation. A horizontal and vertical cross-section profile will determine the variability, if any, that exists. Streams with highly variable temperature profiles should have several readings averaged to use as the mean and those variations should be documented. Streams with a fairly uniform temperature (less than 2^0 C variance 95 percent of the time) generally will have one measurement that can be made and reported as the stream temperature. Make this measurement by suspending (from a weighted line) or placing a thermistor in midstream. Shade the thermistor probe to prevent erroneous readings caused by direct solar radiation. The thermistor should be immersed in the stream for a minimum of 1 minute prior to making measurements. Report all routine temperature measurements to the nearest $0.5\ ^0$ C. For special studies where more precision is required, verify the accuracy and report temperatures to the requested precision.

SPECIFIC CONDUCTANCE

Conductance is the reciprocal of resistance in ohms and is a measure of the capacity of water or other substance to conduct an electrical current. Specific conductance is the conductance measured at 25^0 C and is reported in microsiemens per centimeter at 25 ^{0} C. The specific conductance of water is determined by the types and quantities of dissolved substances in the water. Thus, specific conductance indicates the concentration of dissolved solids in water.

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

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

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

Calibration

Specific-conductance standards, 10 to 50,000 uS/cm at 25^0 C, are for meter calibration. Prior to every water-quality field trip and again onsite, standards should be used to calibrate the meter and to check meter calibration. Document calibration checks in the instrument log. Used standards should not be returned to the stock container.

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

- Presoak electrode in DIW at least overnight.
- Choose two specific-conductance standards that will bracket the expected value of the sample to be measured.
- The standards should be approximately the same temperature as the sample to be measured. Standards are affected by temperature and standard values should be adjusted to the temperature of the sample (Table 5).
- Use the calibration standard closest to the expected value of the sample to be measured. Rinse the container and electrode with standard. Pour calibration standard into container holding the electrode. Allow a minute or two for equilibration and then discard the standard.
- Calibration setting: Pour fresh calibration standard into the container holding the electrode. The electrode should not touch the sides or bottom of the container. Note the meter reading and ADJUST meter to the known standard value.
- Discard calibration standard into a waste container.

- Rinse electrode and container with the second standard. The second standard will bracket the range of expected stream conductance. Pour check standard into rinsed container holding the electrode. Allow to equilibrate, and then discard check standard into a waste container.
- Calibration check: Pour second standard into the rinsed container holding the electrode. This check reading should be within 5 percent of the known standard value. If not, repeat entire calibration procedures. Electrode cleaning or replacement, a different meter, or both might be needed.

NOTE: Switching meter calibration range will require recalibrating.

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

Measurement

Measurements of specific conductance at stream sites should be made from an unfiltered subsample from the cone splitter. If a direct in-stream measurement is made, several readings are necessary (vertically and horizontally) in the cross section to determine a mean value. Conductivity measurements are reported as specific conductance and are expressed as microsiemens per centimeter at 25^0 C. Results are reported to three significant figures, whole numbers only.

Table 5.

pH

The pH of a solution is a measure of the effective hydrogen-ion concentration (activity). In aqueous solutions, pH is controlled primarily by the hydrolysis of salts of strong bases and weak acids or vice versa. The pH is expressed in logarithmic units using a scale from 0 to 14. Solutions having a pH of less than 7 are described as acid; solutions with a pH of more than 7 are described as basic or alkaline. Dissolved gases, such as carbon dioxide, hydrogen sulfide, and ammonia, appreciably affect pH. Degasification (for example, loss of carbon dioxide), precipitation [for example, calcium carbonate ($CaCO_3^{-1}$)], and other chemical, physical, and biological reactions may cause the pH of a water sample to change significantly within several hours or even minutes after sample collection. Immediate analysis of a pH in the field is REQUIRED if dependable results are to be obtained.

Some important features of the meters and electrodes include the following:

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

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

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

Calibration

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

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

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

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

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

Measurement

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

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

ALKALINITY, BICARBONATE, AND CARBONATE

Alkalinity refers to the capacity of water to neutralize an acid by means of chemical buffering. In most waters, alkalinity is caused primarily by the presence of bicarbonate (HCO_3^{-1}) and carbonate (CO_3^{-2}) ions. Some noncarbonate contributors to alkalinity include hydroxide, silicate, borate, and organic ligands, especially acetate and propionate. Because bicarbonate and carbonate predominate in most waters, their determination is essential in studies involving carbonate-chemistry and equilibrium calculations. Alkalinity is commonly used in the determination of the cation/anion balance of a water sample.

Degasification, precipitation, and other chemical and physical reactions can cause the concentrations of bicarbonate and carbonate to change significantly within several hours or even minutes after sample collection. Consequently, field determinations of alkalinity, bicarbonate, and carbonate are needed in addition to laboratory determinations. Determine alkalinity, bicarbonate, and carbonate concentrations on a FILTERED sample. The section on filtration describes the proper method.

Several methods can be used to determine total alkalinity, bicarbonate, and carbonate. All of the methods involve titrating a water sample with a standard solution of sulfuric acid and monitoring the change in pH as the acid is added to the sample. The presence and quantity of hydroxide (if sample pH is 10.4 or greater), carbonate (sample pH is approximately 8.3 or greater), and bicarbonate (sample pH approximately 4.5 or greater) is determined by the pH of the sample and the quantity of acid added. The two methods commonly used are the

fixed end-point and incremental methods. Figure 12 summarizes the general procedure for alkalinity determinations.

Fixed end-point method

The fixed end-point method determines bicarbonate and carbonate by preselecting end points that correspond to true equivalence points under ideal conditions. Using sulfuric acid for titration, the sample pH is lowered to 8.3 for carbonate and 4.5 for bicarbonate. This method is not preferred because it is less accurate than the incremental method.

Incremental method

The incremental method, which determines alkalinity, bicarbonate, and carbonate values more accurately than the fixed end-point method. Rather than assuming the equivalence points to be at pH 8.3 and 4.5, the incremental method determines the actual equivalence points by constructing a titration curve (plotting pH and the volume of sulfuric acid) and selecting the inflection point of the curve as the end point. The end point also can be determined by plotting the change in pH divided by the change in volume of sulfuric acid added, noting the maximum rate of change of pH per volume of acid added. The dilute-acid titrant should be added using a digital titrator.

The incremental method for alkalinity using the digital titrator cosists of the following steps (example given in table 5 and figure 12):

- Calibrate pH meter (see section on pH).
- Depending upon the expected alkalinity, select the sample volume and the appropriate strength titrant cartridge, 0.160 normal (N) or 1.600N sulfuric acid.
- Assemble the digital titrator by placing the titrant cartridge into the titrator and inserting a clear delivery tube into the cartridge. Turn delivery knob to release a few drops of titrant (into a waste container) from the end of the delivery tube, gently blot any droplets adhering to the end of the tube, and set digital counter to a ZERO reading. Inspect the delivery tube; if air bubbles are present, continue to turn knob, expelling the acid until bubbles are removed. Always make sure the delivery tube is below the water surface when dispensing acid into the sample.
- With a volumetric pipet put selected volume of FILTERED sample (50 or 100 mL) into a clean beaker containing a thermistor and a small Teflon-coated, magnetic stirring bar. Record volume of sample that will be titrated on the field notes.
- Place pH electrode (previously rinsed with DIW) into sample to be titrated and place beaker on a magnetic stirrer.
- Measure temperature, remove thermistor, and set meter temperature to sample temperature.
- Turn on stirrer and adjust stirring rate to low (do not create a vortex). Turn on pH meter, allow reading to stabilize, and then read and record initial pH value.

NOTE: IF SAMPLE pH IS LESS THAN 8.3, OMIT STEP 8.

- If sample pH is greater than 8.3, add sulfuric acid by small increments (1 to 3 digital counts at a time) until the pH of the sample is below 8.0. Record pH and digital-counter reading after each addition of acid. Allow 15 to 20 seconds for equilibration between incremental additions. Sample should be gently stirred with a magnetic stirrer or appropriate stirring device.

- Titrate RAPIDLY to approximately pH 5.5. Allow 15 to 20 seconds for equilibration and record the digital-counter reading.
- Add acid by small increments (1 to 3 digital units at a time) from pH 5.5 to 4.0. Allow 15 to 20 seconds for equilibration between incremental additions of acid and record pH and digital-counter readings.
- Construct a titration curve plotting the digital counts of titrant (sulfuric acid) as a function of pH. The end points are the inflection points of the curve (near 8.3 or 4.5), the points at which the pH changes are greatest for volume of acid added. An alternate method is to plot the rate of change of pH with the change in digital counts to determine the inflection points as follows:

$$\frac{\text{change in pH}}{\text{change in digital count}}$$

- Use the digital count at the maximum rate of pH change that represents the appropriate end points to determine the following:

<u>For 1.600N acid titration</u>:
Carbonate (mg/L as CO_3^{-2}) = 2.40 x DCA [50-mL sample]
= 1.20 x DCA [100-mL sample]
Bicarbonate (mg/L as HCO_3^{-1}) = 2.44 x (DCB-2 x DCA) [50-mL sample]
= 1.22 x (DCB-2 x DCA) [100-mL sample]

<u>For 0.160N acid titration</u>:
Carbonate (mg/L as CO_3^{-2})= 0.240 x DCA [50-mL sample]
= 0.120 x DCA [100-mL sample]
Bicarbonate (mg/L as HCO_3^{-1}) = 0.244 x (DCB-2 x DCA) [50-mL sample]
= 0.122 x (DCB-2 x DCA) [100-mL sample]

<u>where</u>
DCA is digital count near end point 8.3 pH and
DCB is digital count near end point 4.5 pH.

Alkalinity (mg/L as HCO_3^{-1}) = [(CO3-2/30)+(HCO_3^{-1}-1/61)]x50

- Report concentrations of alkalinity as equivalent calcium carbonate as CaCO3, in milligrams per liter, bicarbonate as HCO_3^{-1}, in milligrams per liter, and carbonate as CO_3^{-2}, in milligrams per liter, as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

Figu re 12.

Table 6.

Figure 13.

DISSOLVED OXYGEN

Oxygen dissolved in stream water is derived from the air and from the oxygen given off by aquatic plants in the process of photosynthesis. The solubility of oxygen in water is dependent upon the partial pressure of oxygen in the air, the temperature of the water, and the mineral content of the water.

The field method most commonly used for measuring dissolved oxygen in water is the cathode/electrometric method, which uses a membrane-type electrode. Oxygen passes through a membrane at a rate relative to the partial pressure of oxygen outside the membrane. When oxygen diffuses through the membrane, it is rapidly consumed at the gold cathode. The consumption of oxygen causes a current to flow through the cell. The current is directly proportional to the quantity of oxygen consumed and can be converted to concentration units. The membrane is permeable to gases other than oxygen; therefore, halogens, hydrogen sulfide, sulfur dioxide, and helium will interfere with the ability of the probe to give correct readings. Several new methods for determining in-stream dissolved oxygen are equally dependable. Follow the instructions provided by the manufacturer for calibration and measurements when using other methods for determining dissolved oxygen.

Calibration

Keep a log of calibration information for each meter and probe.
Calibrate the barometer with information from the nearest weather station or airport. The barometric-pressure readings reported by a weather station are adjusted to sea level, however, and must be converted to the elevation of the field site to enable comparison among location readings (see Table 7 and Figure 14.)
There are several methods used to calibrate dissolved-oxygen meters. These methods may vary with specific instrumentation. Users should calibrate meters according to manufacturer specifications.

Measurement

Dissolved-oxygen measurements should represent the mean dissolved-oxygen concentration at the time of measurement. Cross-sectional profiles will help to determine if the stream has a fairly uniform dissolved-oxygen concentration. If the stream cross section has uniform dissolved-oxygen concentrations, a single measurement can be made (usually at the centroid of flow). If the stream does not have uniform dissolved concentrations, or if a cross-sectional measurement has not been made, make several measurements and report an average (discharge-weighted average is preferred) concentration. Dissolved-oxygen measurements should not be made in or directly below stream sections with turbulent flow or in still water (near the streambank) because these conditions generally do not represent the majority of water flowing along the stream reach.

The dissolved oxygen should be measured with the probe immersed directly in the stream. If the stream velocity at the point of measurement is less than 1 ft/s, use a stirrer or raise and lower the probe at a rate of approximately 1 ft/s (do not break the surface of the water). If the stream velocity is so high that the probe will not submerged, attach the probe to a small weight on a separate line.

- Turn on the dissolved-oxygen meter to any operational 1 hour before use to ensure stability of operation. Leave meter on until final measurement for the day is completed.
- Turn operation switch to the range used during calibration.

- Read and record the dissolved-oxygen values after the reading on the meter has stabilized (at least 2 minutes).
- Remove the probe from the water, rinse with DIW, and store the probe tip in a storage bottle that contains a damp towel or immerse in DIW. Protect the probe from freezing.
- Turn the operation switch to the OFF position after the final measurement of the day.
- Report dissolved-oxygen concentrations to the nearest 0.1 mg/L.

To express the results as percent saturation, use the following equation:

$$\text{DO (\% saturation)} = \frac{\text{measured DO (mg/L)}}{\text{DO at saturation (mg/L)}} \times 100$$

where DO is dissolved oxygen.

DOCUMENTATION

Field activities should be documented on field.

Table 7.

Figure 14.

Table 8.

Table 8 .

Section 2.5

QUALITY ASSURANCE AND QUALITY CONTROL

Quality Assurance / Quality Control

Quality Assurance – Assesses processes and procedures

- Techniques and methods

Quality Control - Means to check accuracy and quality

- QC samples

Water Quality QC samples

- Identify **contamination** from: collection, processing, shipping, or environment.
- Quantify the **variability** and **bias** resulting from: collection, processing, shipping, and analysis.

Blank samples - samples of water known to be free of target analytes.
Purpose - to identify potential sources of contamination and to evaluate the magnitude of the contamination with respect to the concentration of the target analytes.

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

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

- Field blank – processed in the field
- Lab blank – processed in the laboratory
- Source-solution blank - processing water
- Equipment blank - sampling and processing equipment
- Trip blank - environment

Replicate Samples - environmental samples collected in duplicate, triplicate..., and are considered to be identical in composition.
Purpose - To identify / quantify the variability from the sample collection, processing, and analysis procedures

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

- *Concurrent replicates* - simultaneous
- *Sequential replicates* - one follows the other
- *Split replicates* - sample divided into two or more equal subsamples (generally following processing)

Spikes- Environmental samples spiked with known concentrations of target analytes.
Purpose - to (1) assess recoveries from field matrices and (2) assist in evaluating the precision of results for the range of target analytes in different matrices.

A field-matrix spike is prepared by adding a standard spike solution to a split of sample water processed in the same way as the regular pesticide analysis..

- Used to measure the loss or gain of analyte due to water matrix, processing, shipping, or analysis
- Must be accompanied by an unspiked sample
- Measured loss or gain must be assessed in light of analysis precision.

Reference Samples - Samples with known concentrations of target analytes

- Used to assess variability and bias associated with processing, shipping, and analysis
- Generally submitted as blind samples or duplicate samples

Section 2.6

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