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# Sampling of Surface Water and Spring Water in the Athabasca Oil Sands (In Situ) Area, Alberta, 1999-2001 – A Compilation of Protocols and Methods



Alberta Energy and Utilities Board  
Alberta Geological Survey

AGS

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Alberta Geological Survey

December 2002

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## Acknowledgments

This publication is a compilation of protocols and methods for the sampling of surface and spring water. None of these methods or protocols was developed originally by the Alberta Geological Survey. This document is a compilation of existing sampling and sample processing protocols based primarily on the work of the United States Geological Survey in Book 9 of the Techniques of Water-Resources Investigations series, with additional material compiled from the Handbook for Sampling and Sample Preservation of Water and Wastewater released by the United States Environmental Protection Agency, and from personal communications with Dr. S. Grasby from the Geological Survey of Canada; J. Fennell from Komex Environmental Ltd.; Dr. B. Rostron and Dr. J. Duke from the University of Alberta; Dr. I. Hutcheon, Dr. M. Wieser and S. Taylor from the University of Calgary; and Dr. Chris Holmden from the University of Saskatchewan. Dr. Holmden is also thanked for his review of the sampling protocols and for his suggestions on how to improve them. For additional information on sampling protocols, the reader is referred to the above sources.

These protocols were compiled in support of a project jointly funded by the Government of Alberta, through the Energy and Utilities Board, and by the Government of Canada, through the Ministry of Western Economic Diversification under the Western Economic Partnership.

## Abstract

Between 1999 and 2001, the Alberta Geological Survey (AGS) completed a water-sampling program in northeastern Alberta. Water samples were collected from springs issuing from Quaternary-Tertiary-aged aquifers exposed along the Athabasca River, as well as from springs believed to be issuing from Cretaceous and Devonian-aged strata along the Christina and Clearwater rivers. The goal of the sampling project was to collect high quality water samples. The results will be used to establish a baseline hydrogeochemistry dataset for these springs prior to large-scale industrial development in the area. All of the springs fall within the Alberta Energy and Utilities Board (EUB)-designated Athabasca Oil Sands (in situ) Area.

The sampling protocols documented in this Geo-Note are the result of a literature review and of personal communications with a number of research scientists involved in water sampling in the oil and gas industry. The protocols and methods include sections on: 1) site selection, preparation and setup; 2) collection of field measurements for pH, conductivity, temperature, oxidation-reduction potential, dissolved oxygen and alkalinity; 3) sampling for major, minor and trace elements, isotopes of O, H, C, B, S and Sr, organic acids, radionuclides, silica, Cl, Br and I; 4) quality control; and 5) site cleanup and equipment decontamination.



# 1 Introduction

Between 1999 and 2001, the Alberta Geological Survey conducted a spring-water sampling program in northeastern Alberta. The general purpose was to document baseline groundwater conditions in advance of extensive oil sands development in the area. Springwater samples were collected from springs issuing from Quaternary-Tertiary-aged strata along the Athabasca River and from springs believed to be issuing from Cretaceous or Devonian-aged strata along the Christina and Clearwater rivers. The goal of the spring sampling was to develop a high quality dataset for these units. This project was jointly funded by the Government of Alberta, through the Energy and Utilities Board, and by the Government of Canada, through the Ministry of Western Economic Diversification under the Western Economic Partnership Agreement. This Geo-Note is one in a series of Geo-Notes detailing the results of the project work completed.

The purpose of this document is to provide clear instructions for replication of the results of sample collection completed as part of this program. Sampling results are released in other Geo-Notes in this series. This document will also provide a basis for comparison of AGS reported samples cited above to samples that may be collected by others in the same area and under similar conditions. Otherwise, this compilation is being put into the public domain for information only, without comment or direction pertinent to the regulatory or administrative activities of the EUB or any other government agency in Alberta.

In order to document and standardize sampling methods, and to ensure that high quality samples were collected, a literature review of current sampling protocols was conducted. In addition, researchers currently engaged in water sampling activities were contacted. The result of this exercise was the compilation of sampling protocols and methods listed below.

A number of sources were consulted during this compilation. The primary reference was Book 9 of the Techniques of Water-Resources Investigations released by the United States Geological Survey (Wilde et al., 1998a to f). This reference was used to document methods and protocols for: 1) site preparation and equipment setup; 2) cleaning of equipment for water sampling; 3) sampling and processing of water samples; 4) the measurement of field parameters, such as pH, conductivity, temperature, oxidation-reduction potential, dissolved oxygen and alkalinity; and 5) the design of a quality assurance/quality control program. Additional information regarding the design of a quality assurance and quality control program was gathered from the Handbook for Sampling and Sample Preservation of Water and Wastewater released by the United States Environmental Protection Agency (Berg, 1982). Collection procedures for  $^{14}\text{C}$  were based upon personal communications with J. Fennell from Komex Environmental Ltd. Collection procedures for isotopes of oxygen (O) and hydrogen (H) were based upon personal communications with Dr. B. Rostron of the University of Alberta. Collection procedures for radionuclides, chloride (Cl), bromide (Br) and iodide (I) were based upon personal communications with Dr. J. Duke from the University of Alberta. Collection procedures for isotopes of carbon (C) and sulphur (S) were based upon personal communications with Dr. I. Hutcheon and S. Taylor from the University of Calgary and Dr. S. Grasby from the Geological Survey of Canada. Collection procedures for isotopes of boron (B) were based upon personal communications with S. Taylor and Dr. M. Wieser from the University of Calgary. Collection procedures for isotopes of strontium (Sr) were based upon personal communications with Dr. C. Holmden of the University of Saskatchewan.

This document is sectioned as follows: preparation for sampling, determination of field parameters, sample processing, quality control, and field equipment cleaning procedures. Within the section on water sample processing, each analytical sample type is treated separately and not as part of a coordinated

sampling program. This means that for each analytical sample type the complete list of steps necessary to collect that sample are listed. In a coordinated sampling program, a number of these steps can be omitted.

## 2 Equipment List

Supplies used during sampling and sample processing, and cleaning are listed in Appendix A. Field forms used as checklists and to record information are included in Appendix B.

## 3 Site Preparation

- 1) Set out safety equipment, such as traffic cones and signs. Park vehicles in a position to prevent sample contamination from vehicle and traffic emissions and the prevailing wind.
- 2) Examine the area for hazardous conditions.
- 3) Calibrate field-measurement instruments.
- 4) Select sampling method based on study objectives, budget, time constraints, etc.
- 5) Set up clean workspace and assemble equipment:
  - Organic compounds require equipment with fluorocarbon polymer, glass or metal components.
  - Inorganic constituents require equipment with components made of fluorocarbon polymer or other relatively inert and uncoloured plastics or glass.

## 4 Isokinetic Sampling Methods

Isokinetic sampling implies that the ambient stream velocity is equal to the water velocity as it passes into the sampler nozzle and that the sediment concentration in the stream is equal to the sediment concentration in the sample. Isokinetic sampling is used to obtain a discharge-weighted sample along a stream cross section.

### 4.1 Equal Discharge Increment Sampling Method

- 1) Visually inspect the stream from bank to bank and longitudinally, observing velocity, width and depth distribution. Note and document the location of stagnant water, eddies, backwater, reverse flows, areas of faster than normal flow, and other features along the cross-section.
- 2) Determine stream width.
- 3) Measure discharge at the cross section to be sampled or use an existing graph prepared from current or historical discharge measurements.
- 4) Determine volume of discharge that will be represented in each equal discharge increment (EDI), based on flow and stream channel characteristics along the cross section, volume of sample required, data objectives and variation in field measurements.
- 5) Divide the cross section into EDIs.
  - A minimum of four sampling increments is recommended.
  - The number of increments is usually less than 10.
- 6) Determine the location of the centroid of flow within each increment from the discharge measurement by
  - constructing a curve using cumulative discharge or cumulative percentage of discharge plotted against cross section stationing; and
  - determining EDI locations directly from the discharge measurement sheet.

Example:

If the stream cross section will be divided into five equal discharge increments, divide stream discharge by five to determine the discharge increment. Locate the centroid of the initial EDI, where cumulative discharge equals half the discharge increment (10%). This is the location of the vertical from which the first subsample is collected. Locate each of the remaining centroids by adding the discharge increment (20%) to the previous centroid discharge and determining where that cumulative discharge occurs along the cross section. The EDI centroids will correspond to locations of 10%, 30%, 50%, 70% and 90% of the cumulative discharge along the cross section (Figure 1).

#### **4.1.1 Equal Discharge Increment Transit Rate Method**

- 1) Determine the sampling depth and the mean stream velocity at the centroid of each equal discharge increment.
- 2) From tables (provided with the sampler), determine the transit rate (time the sampler spends submerged) for each centroid that will yield subsamples with approximately the same volume, using sampling depth, mean stream velocity and sampler configuration.
- 3) Transit rates vary from centroid to centroid in order to collect equal volumes.
- 4) Keep the transit rate unidirectional, constant and within the isokinetic transit range of the sampler.
- 5) Monitor transit rate and do not exceed the maximum transit rate.
  - Maximum rate is exceeded if the minimum sample volume associated with stream velocity and the selected nozzle and bottle size is not collected.
  - Exceeding the maximum transit rate will affect the concentration of particulates greater than or equal to 0.062 mm in size.

##### **4.1.1.1 Guidelines**

- 1) The descending and ascending transit rate must be constant in each direction and must be the same for each vertical.
- 2) Do not exceed the maximum allowable transit rate.
- 3) The transit rate must be sufficiently rapid to keep from overfilling the sampler. The sampler is overfilled when the water surface in the sampler container is above the bottom edge of the nozzle when the sampler is held in the sampling position.
- 4) The same size sampler nozzle and container must be used at all verticals along the cross section. If the total volume collected will exceed the recommended volume for the churn splitter, then a cone splitter should be used.

#### **4.1.2 Equal Discharge Increment Sample Collection Method**

- 1) Move to the first centroid and field-rinse equipment.
- 2) Field-rinse surface water sampler:
  - Put on appropriate disposable, powderless gloves.
  - Partially fill and rinse the sample with the water to be sampled.
  - Shake or swirl and then drain the rinse water from the sampler.
- 3) Record start time and gauge height.
- 4) Lower sampler at the constant transit rate until slight contact is made with the stream bed. Do not pause upon contacting the stream bed. Raise the sampler immediately at the same constant transit rate until sampler completes the vertical traverse.
  - Do not overfill the sample container.

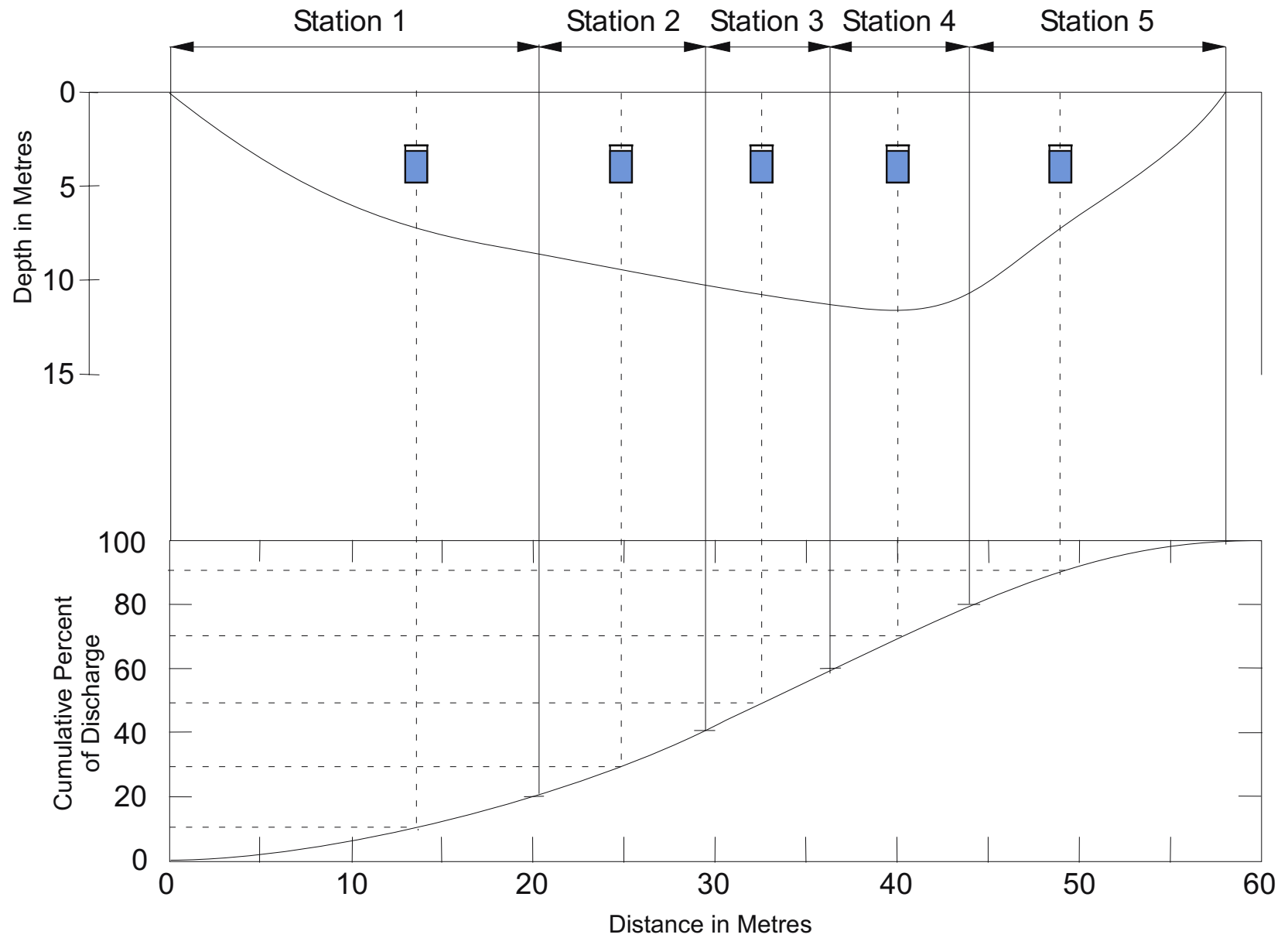


Figure 1. Equal discharge increment sampling (modified from Wilde et al., (1998d)).

- Overfilled samples could be enriched with heavy particulates because of secondary circulation of water through the sampler, biasing particle size distribution toward heavier and larger particulates.
  - Do not underfill the sample container.
  - Underfilled samples are not isokinetically collected.
- 5) Inspect each subsample as it is collected, looking for overfilling or underfilling as well as anomalously large amounts of particulates.
    - If any of these conditions occurs, discard the sample and resample.
  - 6) Depending on study objectives, either process and/or analyze the subsample collected at the initial centroid as a separate sample, composite this subsample with other subsamples collected along the cross section, or split the subsample for further processing.
  - 7) Move sampling equipment to the next vertical.
  - 8) Repeat steps 3 to 7 for the remaining verticals along the cross section.
  - 9) Record necessary information after all samples have been collected:
    - sampling end time
    - ending gauge height
    - field observations

## 4.2 Equal Width Increment Sampling Method

- 1) Visually inspect the stream from bank to bank and longitudinally, observing velocity, width, and depth distribution. Note and document the location of stagnant water, eddies, backwater, reverse flows, areas of faster than normal flow, and other features along the cross section.
- 2) Determine stream width.
- 3) Determine the width of the increments. The number of increments must be a whole number (Figure 2):
  - based on study objectives, variation in field measurements and flow, and stream channel characteristics along the cross section
  - for cross sectional width greater than or equal to 1.5 m, use a minimum of 10 equal width increments.
  - for cross sectional width less than 1.5 m, use as many increments as practical, but equally spaced a minimum of 0.10 m apart.

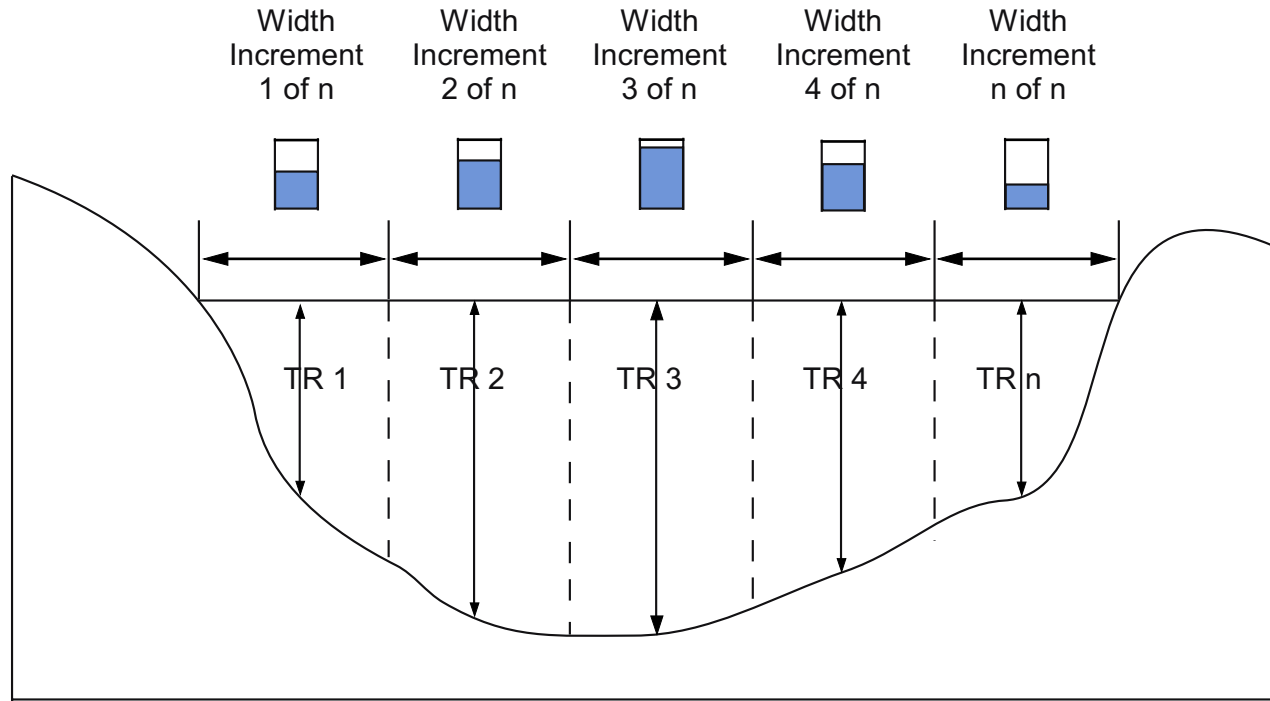
Make adjustments to sampling locations to avoid sampling where the flow is affected by a pier or other obstructions.

### 4.2.1 Equal Width Increment Transit Rate Method

- 1) Locate the equal width increment containing the largest discharge by sounding for depth and either measuring or estimating velocity.
- 2) Determine the minimum transit rate at this vertical for the type of sampler, size of nozzle, and the desired sample volume:
  - Approximate the mean velocity of the vertical in feet per second by timing a floating marker as it travels a known distance; divide the distance by the time and multiply by 0.86.
  - Using sampler type, nozzle size, mean velocity and stream depth, determine the transit rate from tables.

Make sure the transit rate does not exceed the maximum allowable transit rate to be used at any of the remaining verticals along the cross section.

Samples are collected at the center of each increment



TR = Transit Rate, where:  
 $TR\ 1 \neq TR\ 2 \neq TR\ 3 \neq TR\ 4 \neq TR\ n$

↑ ↓ Sampling Path of  
each Equal-Width  
Increment

Figure 2. Equal width increment sampling (modified from Wilde et al., (1998d)).

#### 4.2.1.1 Guidelines

- 1) The descending and ascending transit rate must be constant in each direction and must be the same for each vertical.
- 2) Do not exceed the maximum allowable transit rate.
- 3) The transit rate must be sufficiently rapid to keep from overflowing the sampler. The sampler is overflowed when the water surface in the sampler container is above the bottom edge of the nozzle when the sampler is held in the sampling position.
- 4) The same size sampler nozzle and container must be used at all verticals along the cross section.
- 5) If the total volume collected will exceed the recommended volume for the churn splitter, then a cone splitter should be used.

#### 4.2.2 Equal Width Increment Sample Collection Method

- 1) Move to the first vertical and field-rinse equipment.
- 2) Field-rinse surface water sampler.
  - Put on appropriate disposable, powderless gloves.
  - Partially fill and rinse the sample with the water to be sampled.
  - Shake or swirl and then drain the rinse water from the sampler.
- 3) Record start time and gauge height.
- 4) Lower the sampler at the constant transit rate until slight contact is made with the stream bed. Do not pause upon contacting the stream bed. Raise the sampler immediately at the same constant transit rate until sampler completes the vertical traverse.
  - Do not overflow the sample container.
  - Overflowed samples could be enriched with heavy particulates because of secondary circulation of water through the sampler, biasing particle distribution toward heavier and larger particulates.
  - Do not underfill the sample container.
  - Underfilled samples are not isokinetically collected.
- 5) Inspect each subsample as it is collected, looking for overflowing or underfilling, as well as anomalously large amounts of particulates.
  - If any of these conditions occurs, discard the sample and resample.
- 6) Move sampling equipment to the next vertical.
- 7) Maintain the selected transit rate.
- 8) Continue to the next vertical until no more samples can be collected without overflowing the sample container.
- 9) Empty the subsample into a field-rinsed churn or cone splitter.
- 10) Repeat sample collection in the same manner until all subsamples have been collected at all the verticals.
- 11) Record necessary information after all samples have been collected at all verticals:
  - sampling end time
  - ending gauge height
  - field observations

## 5 Nonisokinetic Sampling Methods

Nonisokinetic sampling implies that the ambient stream velocity is different from the velocity in the sampler nozzle or intake, and that the sediment concentration in the stream is different from that in the sample. Most nonisokinetic samplers cannot be used to collect representative discharge-weighted samples from streams that transport sand or larger sized particles.

Nonisokinetic sampling methods are used when:

- Velocity of flow is high and an isokinetic sampler cannot be lowered properly or safely.
- Low flow conditions make using an isokinetic sampler impractical.
- Sampling is being done in remote sites.
- Sampling of time-dependent events such as floods must be accomplished.
- Cold conditions cause the isokinetic sampler nozzle to freeze.

## 5.1 Nonisokinetic Sample Collection Method

- 1) Review data objectives to ensure they will be met at the sampling location(s) selected.
- 2) Measure discharge at the cross section where samples will be collected.
- 3) Locate the centroid of flow if distribution of streamflow and the field measurement data indicate the section is well mixed.
- 4) Move to the first sampling location and field-rinse equipment.
- 5) Field-rinse surface water sampler:
  - put on appropriate disposable, powderless gloves.
  - partially fill and rinse the sample with the water to be sampled.
  - shake or swirl and then drain the rinse water from the sampler.
- 6) Record start time and gauge height.
- 7) Lower field-rinsed sampler using the method selected:
  - If a vertical traverse is made to collect the sample, do not pause when contact with the stream bed occurs, but raise the sampler immediately until the traverse is completed.
  - If a discrete sample is to be collected, lower the sampler to the desired depth, then sample.
  - If a pump is used to collect a sample, lower the pump intake to the desired depth and pump about three sample-tubing volumes to field-rinse sample tubing before collecting the sample.
- 8) Move sampling equipment to the next vertical.
- 9) Record the time, and repeat sample collection at next vertical.
  - Inspect each sample, looking for anomalously large amounts of particulates that might have been captured because of excessive stream bed disturbance during sample collection; discard the sample if such conditions are observed.
- 10) Either composite the samples collected, or set aside each sample to be independently processed and analyzed.
  - Ensure that all particulates in the sampler are transferred.
  - After all the samples have been collected, record necessary information, including sampling end time, ending gauge height and any field observations.

### 5.1.1 Nonisokinetic Sampling Methods - Dip Sampling Method

Dip sampling involves dipping a narrow-mouthed bottle or other container into a water body. The error introduced by dip sampling can be significant if the target analytes are sorbed onto suspended materials that are not uniformly distributed along the cross section.

- 1) Wade to where the sample(s) will be collected and immerse a hand-held, narrow-mouthed bottle or other sample container at the centroid of flow or at multiple locations along a cross section.
- 2) To sample with a hand-held sampler, stand downstream of the sampler while it is being filled.
- 3) To collect a dip sample where water is too deep to wade, lower a weighted-sampler at the centroid of flow or at multiple locations along a cross section.



### **5.1.2 Nonisokinetic Sampling Methods - Discrete Sampling Method**

Discrete point sampling involves either (1) lowering a sampler to a specified depth and collecting a sample by first opening then closing the sampler, or (2) using a single-stage sampler, which fills when stream stage rises to a predetermined height.

### **5.1.3 Nonisokinetic Sampling Methods - Pump Sampling Method**

Pump sampling involves either suction lift or submersible pump systems designed to collect water samples.

- Portable pump samplers are used to collect a point sample by lowering the pump to a selected depth.
- A portable pump can be used to collect a nonisokinetic, depth-integrated sample by continuously pumping at a constant rate as the intake is being lowered through the vertical.

### **5.1.4 Nonisokinetic Sampling Methods – Still Water Method**

- 1) Locate the first sampling site (vertical section) and maintain a sampling platform at the site.
- 2) Record the depth to bottom.
- 3) Make field measurements in situ to obtain a vertical profile of field measurement variation.
- 4) Measure light penetration, if applicable.
- 5) Select and record sampling depth(s) based on study objectives and the variation in field measurements in the vertical.
- 6) Field-rinse sampling equipment.

#### **5.1.4.1 Thief-Type Sampler**

- 1) Lower opened sampler to the desired depth while minimizing disturbance of the water column.
- 2) Isolate the sample by activating the mechanism that closes the sampler.
- 3) Raise the sampler from the water body.
- 4) Dispense water to sample bottle or compositing/splitting device:
  - Drain sample through bottom-emptying device.
  - Ensure all particulates in the sampler are transferred with the sample.
- 5) Repeat steps 1 to 4 if more sample is needed from the same depth for that vertical section.
- 6) Repeat steps 1 to 5 for each depth to be sampled in that vertical section.  
Move to the next site if another vertical section will be sampled. Repeat steps 1 to 6.

#### **5.1.4.2 Pump Sampler**

- 1) Lower the pump or pump-sample tube to the desired depth.
- 2) Turn on the pump and pump about three sample-tubing volumes to field-rinse the pump, tubing, and other sample-collection or processing equipment. Discard rinse water.
- 3) Direct sample-flow into collection container(s) until sufficient sample volume has been collected.
- 4) Repeat steps 1 to 3 if another depth and/or another vertical section is to be sampled.

## **6 Field Determinations**

Field measurements should be made as soon as possible once the sample has been obtained.

## **6.1 Temperature**

Measurements of water and air temperatures at the field site are essential for water-data collection. Determinations of dissolved oxygen concentrations, conductivity, pH, rate and equilibria of chemical reactions, biological activity, and fluid properties rely on accurate temperature measurements.

### **6.1.1 Measurement in Air**

- 1) Read air temperature with a dry, calibrated thermometer.
- 2) Place the thermometer about 1.5 m above the ground in a shaded area protected from strong winds, but open to air circulation.
- 3) Allow 3 to 5 minutes for the thermometer to equilibrate; record temperature and time of day.
- 4) Measure the air temperature as close as possible to the time when the water temperature is measured.
- 5) Report routine air temperature measurements to the nearest 0.5°C.

### **6.1.2 Measurement in Surface Water**

Measure temperature with a thermometer that has been calibrated within the temperature range to be encountered.

- 1) Prepare the instrument.
- 2) Immerse the thermometer in the water.
- 3) Allow the thermometer sensor to equilibrate with the water for 5 minutes; record the reading.
- 4) Remove and clean the thermometer.

## **6.2 Dissolved Oxygen (DO)**

### **6.2.1 Amperometric Method**

The DO concentration in water is determined with a temperature-compensating instrument or meter that works with a polarographic, membrane-type sensor. Atmospheric pressure, water temperature and water conductivity must be known to determine the theoretical amount of oxygen that can be dissolved in water.

The higher the atmospheric pressure and the lower the temperature and conductivity, the more oxygen can be dissolved in the water. Degassing, mineral precipitation and other chemical, physical and biological reactions can cause the DO concentration of a water sample to change significantly. The solubility of oxygen in water decreases as salinity increases, requiring that DO values be corrected for samples with high salinities.

### **6.2.2 Atmospheric Pressure Correction**

- 1) Check the accuracy of all field barometers before each field trip and record results.
- 2) Use a calibrated, pocket altimeter-barometer to determine ambient atmospheric pressure to the nearest 1 mm of mercury.

### **6.2.3 Calibration in Air**

Determine the proper calibration point for the local barometric pressure. Consult the manufacturer's instructions to determine the calibration value for a given barometric pressure and calibration procedures.

## 6.2.4 Measuring DO in Water

If possible, the water being measured should not contact air. If possible, throughout the measurement, use equipment that avoids aeration and operate equipment to mitigate losses or gains of dissolved gases.

- 1) Calibrate the DO system on site.
- 2) Measure and record DO.
- 3) Remove the sensor from the water and rinse with deionized or distilled water.

## 6.3 Specific Electrical Conductance (SC)

Specific electrical conductance of water is a measure of the capacity of the water to conduct an electrical current. It is a function of the types and quantities of dissolved substances in water.

### 6.3.1 Calibration

Conductivity systems normally are calibrated with at least two standards. It is suggested that sensors should be calibrated against a standard that approximates sample conductivity and a second standard as a calibration check.

- 1) Inspect the instrument and the conductivity sensor for damage, and check the battery voltage.
- 2) Turn the instrument on and allow sufficient time for electronic stabilization.
- 3) Select the correct instrument scale for expected conductivity.
- 4) Select two conductivity standards that will bracket the expected sample conductivity.
- 5) Equilibrate the standard and the conductivity sensor to the temperature of the sample.
  - Allow 15 to 30 minutes for thermal equilibration.
- 6) Rinse the conductivity sensor, the thermometer and a container large enough to hold the sensor and thermometer:
  - Rinse the sensor, the thermometer and the container three times with deionized or distilled water.
  - Rinse the sensor, the thermometer and the container three times with the standard to be used.
- 7) Put the sensor and the thermometer into the rinsed container and pour in fresh calibration standard.
- 8) Measure water temperature to within 0.5°C.
- 9) Agitate a submersible-type sensor up and down under the solution surface to expel air trapped in the sensor. Agitate until consecutive readings are the same.
- 10) Record the instrument reading and adjust the instrument to the known standard value.
- 11) Record the temperature of the standard solution, the known and measured conductivity of the standard solution and the temperature correction factor, if using a non-temperature-compensating conductivity instrument.
- 12) Discard the used standard into a waste container. Rinse the sensor, thermometer and container with deionized or distilled water.
- 13) Repeat steps 6 to 12 with the second conductivity standard.
  - This is used to check instrument calibration over the range of the two standards.
  - The difference from the standard value should not exceed 5%.
  - If the difference is greater than 5%, repeat the entire calibration procedure.
- 14) Record calibration data for the second standard.

### 6.3.2 Measurement of the Conductivity of Surface Water

Measurements of springwater conductivity will approximate aquifer conditions.

- 1) Calibrate the conductivity instrument system on site.

- Bring standard solutions to the temperature of the water to be sampled, allowing at least 15 minutes for temperature equilibration.
  - Check the temperature of the standards and the water.
  - Use a calibrated thermometer.
  - After calibration, rinse the conductivity sensor and thermometer thoroughly with deionized or distilled water.
- 2) Measure and record the conductivity and associated temperature values.

## 6.4 Measurement of pH

The pH of an aqueous solution is controlled by interrelated chemical reactions that produce or consume hydrogen ions. Water pH is a useful index of the status of equilibrium reactions in which water participates. The pH of water directly affects physiological functions of plants and animals, and it is, therefore, an important indicator of the health of a water system.

### 6.4.1 Calibration

Calibrate and check the operation of a pH instrument system at the field site. A minimum of two pH buffer solutions are needed to properly calibrate the pH system (pH 7 and either a pH 4 or pH 10).

- 1) Temperature equilibration of equipment
  - Not needed if using an automatic compensating meter.
  - Allow 15 to 30 minutes for the buffers to adjust to the sample temperature.
  - Place buffer bottles in a bucket or bag and suspend them in the water.
- 2) Inspect the pH electrode.
  - Check for damage.
  - Rinse any precipitate off of the electrode with deionized or distilled water.
  - Slide the protective sleeve up or down to uncover the filling hole.
  - Shake or tap the electrode to dislodge and remove air bubbles trapped in the sensing tip of the electrode and to remove excess deionized or distilled water.
- 3) Calibration rinse
  - Rinse the electrode, thermometer or automatic temperature compensating (ATC) sensor and a container large enough to hold the sensors with pH 7 buffer solution.
  - Discard the used buffer solution.
- 4) Calibration – Bullets 4, 5 and 6 are not needed for auto-compensating meters.
  - Pour fresh pH 7 buffer solution into the container that holds the electrode and thermometer or ATC sensor so the solution covers the reference junction.
  - Swirl the sample gently or stir carefully with the electrode.
  - Measure the temperature of the buffer solution and then remove the thermometer.
  - Determine the theoretical pH of the buffer solution from temperature-correction tables.
  - Note and record the pH temperature readings and adjust the meter reading to the pH value using the standardize function on the meter.
  - Repeat the calibration steps using fresh portions of reference buffer solution until two successive readings are obtained at the adjusted pH value for pH 7 buffer solution without further adjustment to the system.
- 5) Slope adjustment rinse
  - Rinse the electrode, thermometer or ATC sensor with deionized or distilled water.
  - Rinse a clean container, the electrode and thermometer or ATC sensor with the second buffer solution (pH 4 or pH 10).

- Pour the second buffer solution into a container; allow the temperature to equilibrate and then discard the buffer solution.
- 6) Slope adjustment. This step is automated in modern meters.
    - Pour a fresh portion of the second pH buffer solution into the container holding the electrode and thermometer or ATC sensor.
    - Stir slowly.
    - Measure the pH of the buffer solution; check the pH value of the solution on temperature coefficient tables and record the pH and temperature readings.
    - Adjust the slope to the value of the second pH buffer solution at known temperature and record the adjusted pH value.
    - Discard the used solution.
    - Repeat bullets 1 through 5 using the same buffer solution until two successive readings are obtained without further adjustment.
  - 7) Rinse the electrode and thermometer or ATC sensor with deionized or distilled water.
  - 8) If using a non-compensating or non-automated meter, repeat the calibration rinse and calibration procedures to ensure the slope adjustment did not affect the calibration adjustment.
    - If adjustment is needed, repeat the entire calibration adjustment.
  - 9) Calibration check rinse
    - Rinse the electrode and thermometer or ATC sensor with deionized or distilled water.
    - Rinse a clean container, the electrode and the thermometer or ATC sensor with a third buffer solution (pH 4 or pH 10) and then discard the used solution.
    - Pour the third solution into a container, allow the temperature to equilibrate and then discard the used solution.
  - 10) Calibration range check
    - Pour a fresh portion of the third pH buffer solution into the container.
    - Stir slowly.
    - Measure the temperature of the buffer solution and check the temperature-adjusted pH value.
    - The pH should be within  $\pm 0.1$  pH units.
    - If the system does not check over the entire range, recalibrate before measuring the sample pH.
    - Discard the used solution into a waste container.
    - Rinse the electrode and thermometer or ATC sensor with deionized or distilled water.

#### 6.4.1.1 Calibration for Low-Conductivity Water

Proper calibration of the pH instrument system with standard buffer solutions does not guarantee accurate pH measurement in water with conductivity less than 100  $\mu\text{S}/\text{cm}$ .

- 1) After calibration with pH 4, 7 and 10 buffer solutions, check electrode performance daily in an appropriate sulphuric acid standard solution with conductivity less than 20  $\mu\text{S}/\text{cm}$ .
  - Check sulphuric acid standard solution for contamination by measuring conductivity.
- 2) Check electrode performance with deionized or distilled water saturated with an analyzed nitrogen-carbon dioxide gas mixture having a carbon dioxide mole fraction of less than 0.5%.
- 3) Rinse the electrode at least three times, preferably with a portion of the sample to be measured.
- 4) Calibrate and measure pH in quiescent solutions after the sample has been homogenized by stirring.
- 5) Check the electrode performance before using the readings at pH 7 and pH 4. Keep a record of the electrode slope and millivolt readings.

## 6.4.2 Measurement

The pH of a water sample can change significantly within hours or even minutes after sample collection as a result of: 1) degassing (such as loss of carbon dioxide, hydrogen sulphide and ammonia); 2) mineral precipitation (such as formation of calcium carbonate); 3) temperature change; and 4) other chemical, physical and biological reactions.

Field conditions, including rain, wind, cold, dust and direct sunlight, can cause measurement problems. To the extent possible, shield the instrument and measurement process from the weather.

### 6.4.2.1 Measurement of pH in Surface Water

Measurements will approximate aquifer conditions. Measure the pH as soon as possible once the sample has been collected.

- 1) Calibrate the pH instrument system onsite.
  - After calibration, rinse the pH electrode and other equipment used with deionized or distilled water.
- 2) Measure and report the pH.

## 6.5 Reduction-Oxidation Potential (REDOX)

Determining the reduction-oxidation potential of water should not be considered routine. Measurement of redox potential or Eh measurement is not recommended in general because of the difficulties inherent in its theoretical concept and its practical measurement. Determinations of redox using the platinum electrode method are valid only when redox species are electroactive and present in the solution at concentrations of about  $10^{-5}$  molal and higher.

Measurements of Eh are used to test and evaluate geochemical speciation models, particularly for suboxic and anoxic groundwater systems. Eh data can be useful for gaining insights into the evolution of water chemistry and for estimating the equilibrium behaviour of multivalent elements relative to pH for an aqueous system. Eh can delineate redox gradients in environments as diverse as stratified lakes and rivers with an anaerobic zone, oxidized surface flow that becomes anaerobic after passing through stagnant organic rich systems, and mine drainage discharges.

### 6.5.1 Equipment Test Procedure

- 1) Follow the manufacturers' recommendations for instrument warm up and operation.
  - Set the scale to the desired millivolt range.
  - Record the type of reference electrode being used.
- 2) Unplug the fill hole. Shake the electrode gently to remove air bubbles from the sensing tip of the electrode and check the level of the filling solution.
  - The filling solution level must be at least 2.5 cm above the level of solution being measured.
  - Use only specified filling solutions.
- 3) Rinse the electrode, thermometer and measurement beaker with deionized or distilled water. Blot dry.
- 4) Pour ZoBell's solution into a measurement beaker containing the electrode and temperature sensor:
  - Add enough solution to cover the reference junction.
  - Allow 15 to 30 minutes for the solution and sensors to equilibrate to ambient temperature.
- 5) Stir slowly to establish equilibrium between the electrode(s) and the solution. Switch the meter to the millivolt function, allow the readings to stabilize ( $\pm 5$  mV), and record the ambient temperature and the millivolt value.

- 6) Look up the half-cell reference potential in the table below (Table 1) for the electrode being used. Add this value to the measured potential to obtain the Eh of ZoBell's at ambient temperature.
  - If the value is within 5 mV of the theoretical ZoBell Eh at the measured water temperature (Table 2) then the equipment is ready for field use.
  - If the value is not within 5 mV, check meter operation, or electrode operation, and make sure that the ZoBell solution has not expired or become contaminated.
- 7) Rinse off the electrodes and the thermometer thoroughly with deionized or distilled water.

**Table 1. Standard half-cell reference electrode potentials at various temperatures (Wilde et al., 1998f)**

Temp °C	Silver:Silver Chloride			Calomel			
	3M KCl	3.5M KCl	Saturated KCl	3M KCl	3.5M KCl	4M KCl	Saturated KCl
10	220 mV	215 mV	214 mV	260 mV	256 mV	-	254 mV
15	216 mV	212 mV	209 mV	-	-	-	251 mV
20	213 mV	208 mV	204 mV	257 mV	252 mV	-	248 mV
25	209 mV	205 mV	199 mV	255 mV	250 mV	246 mV	244 mV
30	205 mV	201 mV	194 mV	253 mV	248 mV	244 mV	241 mV
35	202 mV	197 mV	189 mV	-	-	-	238 mV
40	198 mV	193 mV	184 mV	249 mV	244 mV	239 mV	234 mV

**Table 2. Eh of ZoBell's solution as a function of temperature (Wilde et al., 1998f)**

Temperature (°C)	Eh (mV)
10	467
12	462
14	457
16	453
18	448
20	443
22	438
24	433
25	430
26	428
28	423
30	418
32	416
34	407
36	402
38	397
40	393

### 6.5.2 Measurement of Eh

To obtain accurate results, it is necessary to prevent losses and gains of dissolved gases in solution. Chemical, physical and biological reactions can cause the Eh of water to change significantly within minutes or even seconds after the collection of a sample. Water samples cannot be preserved or stored for the Eh measurement.

Measure Eh as soon as possible once the sample has been collected:

- 1) Record the type of reference electrode system being used.
- 2) Check for the correct electrode filling solution. If working in very hot or boiling waters, change the reference electrode filling solution daily.
- 3) Keep the electrode surface brightly polished.
- 4) Immerse the electrodes and temperature sensors in the sample water.
- 5) Allow the sensors to reach thermal equilibrium with the aqueous system being measured and record the time lapsed.
- 6) Switch the meter to the millivolt function.
  - Allow the reading to stabilize ( $\pm 5$  mV).
  - Record the value and temperature.
- 7) After the measurements have been completed for the day, rinse the electrode(s) thoroughly with deionized or distilled water.
- 8) Record all data and calculate Eh.
- 9) For quality control purposes, the measurement can be repeated.

### 6.5.3 Interferences and Limitations

Organic matter and sulphide may cause contamination of the electrode surface, salt bridge, or internal electrolyte, which can cause drift or erratic performance.

Hydrogen sulphide can produce a coating on the platinum electrode that interferes with the measurement if the electrode is left in sulphide-rich water for several hours.

The platinum, single and combination redox electrodes may yield unstable readings in solutions containing chromium, uranium, vanadium or titanium ions and other ions that are stronger reducing agents than hydrogen or platinum.

Do not insert redox electrodes into iron-rich waters directly after electrode(s) contact with ZoBell's.

## 6.6 Alkalinity

Alkalinity applies to the acid neutralizing capacity of solutes in a water sample. It consists of the sum of the titratable carbonate and noncarbonate chemical species in a filtered water sample. Alkalinity is used routinely in checking the charge balance of a solution and to gain insights on the evolution of aqueous systems. Any substance in the water sample that reacts with the strong titrant acid can contribute to the water's acid neutralizing capacity. Important noncarbonate contributors include organic ligands and ions of hydroxide, phosphate, ammonium, silicate, sulphide, borate and arsenate. Noncarbonate ionized contributors generally are not present in large enough quantities to affect alkalinity. Alkalinity is independent of exchange with carbon dioxide and other atmospheric gases. However, atmospheric gas exchange can alter concentrations of individual species, such as bicarbonate. Also, aeration of a sample during filtration can cause mineral precipitation on the filter, altering alkalinity, especially in water systems closed to the atmosphere under ambient conditions.

- 1) Filter the samples along with the other anion samples.
- 2) Fill and securely cap two 250-mL sample bottles with the sample to ensure there is enough sample to repeat the titration, to preserve the integrity of the second aliquot after the first has been opened, and to avoid losing the volume of sample needed to spillage.
- 3) Prevent agitation of the sample or prolonged exposure to air in order to avoid oxidation of hydrogen sulphide, ferrous iron, manganous manganese and prevent precipitation of mineral phases.



- 4) Begin the titration as soon as possible.
  - If titration is delayed, maintain the samples at the temperature of their ambient environment.
  - If there is a tendency for mineral precipitation, collect and process the sample in an inert gas atmosphere.

The next steps are specific to the Hach Model 16900 Digital Titrator:

- 1) Select the sample volume and sulphuric acid titration cartridge corresponding to the expected alkalinity concentration as mg/L calcium carbonate (Table 3).
- 2) Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.
- 3) Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
- 4) Use a graduated cylinder or pipette to measure the sample volume. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100 mL mark with deionized or distilled water, if necessary.
- 5) Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix. Four drops of Phenolphthalein Indicator Solution may be substituted for the pillow.
- 6) If the solution turns pink, place the delivery tube tip into the solution and swirl the flask while titrating with sulphuric acid. Titrate to a colourless end point. Record the number of digits required. If the solution does not turn pink, proceed to point 8.
- 7) Calculate and record mg/L CaCO<sub>3</sub> Phenolphthalein Alkalinity.
  - mg/L CaCO<sub>3</sub> Alkalinity = digits required x digit multiplier
- 8) Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the flask and swirl to mix. Four drops of Methyl Purple Indicator Solution, or Bromcresol Green-Methyl Red Indicator Solution, can be substituted for the powder pillow.
- 9) Continue the titration with sulphuric acid to a light, greenish blue-grey (pH 5.1), a light violet-grey (pH 4.8), or a light pink (pH 4.5).
- 10) Calculate and record mg/L CaCO<sub>3</sub> Total Alkalinity.
  - mg/L CaCO<sub>3</sub> = total digits required x digit multiplier

**Table 3. Alkalinity range, sample volume, titration cartridge normality and digit multiplier relationships**

Range (mg/L as CaCO <sub>3</sub> )	Sample Volume (mL)	Titration Cartridge (H <sub>2</sub> SO <sub>4</sub> )	Digit Multiplier
10-40	100	0.1600	0.1
40-160	25	0.1600	0.4
100-400	100	1.600	1.0
200-800	50	1.600	2.0
500-2000	20	1.600	5.0
1000-4000	10	1.600	10.0

### 6.6.1 Calculation of Alkalinity Relationships

Total alkalinity primarily includes hydroxide, carbonate and bicarbonate alkalinities. The concentration of these alkalinities in a sample may be determined when the phenolphthalein and total alkalinities are known. The various concentrations can be calculated from Table 4.

**Table 4. Alkalinity relationships**

<b>Result Of Titration</b>	<b>Hydroxide Alkalinity Is equal to:</b>	<b>Carbonate Alkalinity Is equal to:</b>	<b>Bicarbonate Alkalinity Is equal to:</b>
Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
Phenolphthalein Alkalinity less than one half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus two times Phenolphthalein Alkalinity
Phenolphthalein Alkalinity equal to one half of Total Alkalinity	0	Total Alkalinity	0
Phenolphthalein Alkalinity greater than one half of Total Alkalinity	2 times the Phenolphthalein Alkalinity minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

Example:

A sample has 170 mg/L as CaCO<sub>3</sub> phenolphthalein alkalinity and 250 mg/L as CaCO<sub>3</sub> total alkalinity. If we move through the result of titration column in Table 4, we see that

- The phenolphthalein alkalinity does not equal zero.
- The phenolphthalein alkalinity does not equal total alkalinity.
- The phenolphthalein alkalinity is not less than one half of total alkalinity.
- The phenolphthalein alkalinity is not equal to one half of total alkalinity.
- The phenolphthalein alkalinity is greater than one half of total alkalinity.

Therefore, the resulting concentrations of the hydroxide, carbonate and bicarbonate alkalinities are determined using the final row of the table.

Hydroxide alkalinity is given by 2 x phenolphthalein alkalinity - total alkalinity.

$$\text{Hydroxide alkalinity} = 2 \times 170 \text{ mg/L} - 250 \text{ mg/L} = 90 \text{ mg/L}$$

Carbonate alkalinity is given by 2 x (total alkalinity – phenolphthalein alkalinity).

$$\text{Carbonate alkalinity} = 2 \times (250 \text{ mg/L} - 170 \text{ mg/L}) = 160 \text{ mg/L}$$

Bicarbonate alkalinity is zero.

Hydroxide alkalinity+carbonate alkalinity+bicarbonate alkalinity = 250 mg/L = Total Alkalinity

## 7 Sample Processing

Surface water samples normally are composited and processed through sample-splitting devices and then filtered. Two types of water-sample splitters used for this purpose are the polypropylene churn splitter and the fluorocarbon polymer cone splitter. By convention, the churn usually is used only for inorganic

constituents, whereas the cone splitter can be used for either inorganic or organic samples. Samples were not composited as part of AGS sampling activities. Guidelines regarding compositing samples can be found in Wilde et al., (1998d).

### **To split a composite sample**

- 1) Put on appropriate disposable, powderless gloves.
- 2) Place splitter inside sample collection chamber. Remove splitter from protective covering.
- 3) Install cone splitter.
- 4) Field-rinse cone splitter and the appropriate sample bottles with the water to be sampled.
- 5) Place bottles for raw samples under outlet tubes.
  - Begin with bottles for organic samples.
  - End with bottles for inorganic samples.
- 6) Gently shake or agitate sample for at least 10-15 seconds to resuspend any particulate matter present in the sample bottle. Pour or pump sample into cone splitter.
  - Maintain a head of water above the splitter standpipe to prevent air from entering the splitting block while transferring the sample.
- 7) Avoid exposing samples to direct sunlight or freezing conditions.
- 8) Close cover.
- 9) After flow has stopped, tap the cone splitter to dislodge adhering drops.
- 10) Cap sample bottles immediately and transfer to the preservation chamber.
- 11) Preserve samples as required.

### **Recommended sequence for processing samples**

#### Organic compounds

- Raw samples first, followed by filtered.
- Do not field-rinse bottles.
- Chill immediately.

#### Inorganic constituents, radiochemicals and isotopes

- For groundwater, filtered samples first, followed by raw samples.
- For surface water, raw samples first, followed by filtered samples.
- Field-rinse as required.

Order:

- 1) Organics
- 2) Trace metals
- 3) Separate treatment constituents and major cations
- 4) Major anions
- 5) Radiochemicals and isotopes

### **7.1 Field-Rinsing Procedures**

- 1) Use filtrate (the liquid that passes through a filter) for filtered samples and whole-water for raw samples. Use only 25 mL of filtrate for bottle rinse for the filtered sample.

- 2) If bottles were rinsed and half-filled with deionized water (DIW) or distilled water (DW), discard DIW or DW and rinse only once with the water to be sampled.
- 3) If bottles were not pre-rinsed with DIW, rinse twice with DIW or DW onsite, followed by one field-rinse with the water to be sampled.
- 4) Glass-fibre filters for organic compound samples are rinsed with 10 mL to 20 mL of pesticide-grade blank water and conditioned with 100 to 125 mL of sample.
- 5) Filters for inorganic samples are rinsed with 1 L of DIW or DW. Residual DIW or DW is removed and the filters are then conditioned with 25 mL of sample.

## 7.2 Common Organic Compounds

The protocols listed below are appropriate for the collection of samples to be analyzed for common organic compounds, dissolved organic carbon, total organic carbon and suspended organic carbon. Wilde et al., (1998e) discuss sampling for specific organic compounds with emphasis placed on volatile organic compounds, semivolatile organic compounds, pesticides, organonitrogen herbicides, polychlorinated biphenyls and phenols.

- 1) Put on latex or nitrile disposable gloves. As an additional safeguard against contamination of the sample by the plastic sheet covering the work area, the bench or table can be covered with a sheet of aluminum foil to make a clean work surface. Ensure the foil is removed before sampling for trace elements.
- 2) Assemble necessary equipment and supplies on the work surface, and remove aluminum foil from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) If at any time the disposable gloves appear to have been contaminated, change gloves.
- 5) Connect the filter assembly and vacuum pump.
- 6) Rinse filter assembly with DIW or DW.
- 7) Drain as much DIW or DW from the filter.
- 8) Field-rinse the filter assembly.
- 9) Filter sample into 1-L amber glass bottles.
- 10) If the filter becomes clogged, replace with a new filter.
- 11) Consult with the analytical laboratory for appropriate preservatives for the organic compounds of interest. If sampling for organic acids, add a few drops of chloroform to 1-L container.
- 12) Label and chill immediately to 4°C or below without freezing.

If sampling is complete, proceed with the cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 13) Disassemble processing chamber. Discard chamber cover, aluminum foil, gloves, filter and wastewater.
- 14) Field-clean all equipment while equipment is still wet and before going to the next site.

## 7.3 Major, Minor and Trace Elements

If the major, minor and trace element samples are the first samples to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a sheet of plastic to make a clean work surface.

- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Field-rinse bottles.
  - Collect only 25 mL of water to be sampled.
  - Rinse bottles and discard rinse water to waste.
- 7) Collect sample filtrate in two, 500-mL polyethylene bottles.
- 8) Cap and place in a corner of the collection chamber until filtering is complete. Once complete, transfer to the preservation chamber.
- 9) Uncap minor and trace elements bottle and add HNO<sub>3</sub> to sample until pH < 2.0. Recap minor and trace elements bottle and label both bottles.

If sampling is complete, proceed with cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 10) Once all filtering and preservation is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 11) Field-clean all equipment while equipment is still wet and before going to the next site.

#### 7.4 Silica

If the silica sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a sheet of plastic to make a clean work surface.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Field-rinse bottles.
  - Collect only 25 mL of water to be sampled.
  - Rinse bottle and discard rinse water to waste.
- 7) Collect sample filtrate in a 30-mL or 40-mL polyethylene bottle. Label.

If sampling is complete, proceed with cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 8) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 9) Field-clean all equipment while equipment is still wet and before going to the next site.

## 7.5 Anions

If the anions sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a sheet of plastic to make a clean work surface.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Field-rinse bottles.
  - Collect only 25 mL of water to be sampled.
  - Rinse bottle and discard rinse water to waste.
- 7) Collect sample filtrate immediately into a 250-mL field-rinsed, polyethylene bottle.

If sampling is complete, proceed with cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 8) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 9) Field clean all equipment while equipment is still wet and before going to the next site.

## 7.6 Radiochemicals

If the radiochemicals sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as cleaning and field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a sheet of plastic to make a clean work surface.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Collect sample filtrate immediately into 1-L polyethylene bottles. Fill to shoulder.
- 7) Cap and place in corner of the collection chamber until filtering is complete. Once complete, transfer to the preservation chamber.
- 8) Uncap and add HNO<sub>3</sub> to the sample until pH<2. Recap and label.

If sampling is complete, proceed with cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 9) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 10) Field-clean all equipment while equipment is still wet and before going to the next site.

### 7.7 Stable Isotopes – $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$

If the  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$  sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a sheet of plastic to make a clean work surface.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Collect sample immediately into 20-mL vacu-tubes.
- 7) Wrap the self-sealing top with parafilm and label.

If sampling is complete, proceed with cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 8) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 9) Field-clean all equipment while equipment is still wet and before going to the next site.

### 7.8 Stable Isotopes – $^{13}\text{C}/^{12}\text{C}$

If the  $^{13}\text{C}/^{12}\text{C}$  sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a sheet of plastic to make a clean work surface.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Collect sample with a syringe into a 20-mL draw vacu-tube. Vacu-tubes should already contain ~ 2 mL of an ammoniacal, strontium chloride solution.
- 7) Wrap the self-sealing top with parafilm and label. Do not allow any atmospheric  $\text{CO}_2$  to enter the tube.

If sampling is complete, proceed with cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 8) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 9) Field-clean all equipment while equipment is still wet and before going to the next site.

### 7.9 Stable Isotopes – $^{34}\text{S}/^{32}\text{S}$ in Sulphide

If the  $^{34}\text{S}/^{32}\text{S}$  in sulphide sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a sheet of plastic to make a clean work surface.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Collect sample filtrate immediately into 1 L amber glass bottles.
- 7) Cap and label sample. Move to the sample preservation chamber.
- 8) Uncap the sample. Add 1 or 2 scoopula scoops of cadmium acetate to water sample to precipitate CdS. Recap and store.

If sampling is complete, proceed with the cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 9) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 10) Field-clean all equipment while equipment is still wet and before going to the next site.

### 7.10 Stable Isotopes – $^{34}\text{S}/^{32}\text{S}$ in Sulphate

If the  $^{34}\text{S}/^{32}\text{S}$  in sulphate sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a sheet of plastic to make a clean work surface.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Collect sample filtrate immediately into 125-mL amber glass bottles.
- 7) Cap and label sample. Move to the preservation chamber.
- 8) Uncap the sample. Acidify sample to  $\text{pH} < 2$  with HCl. Add 1 to 2 scoopula scoops of barium chloride to water sample to precipitate  $\text{BaSO}_4$ . Recap and store.



If sampling is complete, proceed with cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 9) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 10) Field-clean all equipment while equipment is still wet and before going to the next site.

#### 7.11 Stable Isotopes – $^{34}\text{S}/^{32}\text{S}$ in Sulphide and in Sulphate

If the  $^{34}\text{S}/^{32}\text{S}$  in sulphide and sulphate sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a sheet of plastic to make a clean work surface.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Collect sample filtrate immediately into 1-L amber glass bottle.
- 7) Cap and label sample. Move to the sample preservation chamber.
- 8) Uncap the sample. Add 1 to 2 scoopula scoops of cadmium acetate to water sample to precipitate CdS. Recap and store.
- 9) Once the precipitate has formed, filter sample, dry precipitate, place filter paper in a secure container and label it.
- 10) Pour filtered water into 125-mL amber glass bottle and add 1 to 2 scoopula scoops of barium chloride to the water sample to precipitate  $\text{BaSO}_4$ .
- 11) Cap, label sample and store.

If sampling is complete, proceed with cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 12) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 13) Field clean all equipment while equipment is still wet and before going to the next site.

#### 7.12 Stable Isotopes - $^{87}\text{Sr}/^{86}\text{Sr}$

If the  $^{87}\text{Sr}/^{86}\text{Sr}$  sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.

- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Collect sample immediately in a 250-mL polyethylene bottle.
- 7) Cap and label. Move to preservation chamber.
- 8) Uncap the sample. Acidify the sample to pH<2 with HNO<sub>3</sub>. Recap and store.

If sampling is complete, proceed with the cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 9) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 10) Field-clean all equipment while equipment is still wet and before going to the next site.

### 7.13 Stable Isotopes – <sup>11</sup>B/<sup>10</sup>B

If the <sup>11</sup>B/<sup>10</sup>B sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.
- 6) Collect sample immediately in a 250-mL polyethylene bottle.
- 7) Cap and label.

If sampling is complete, proceed with the cleaning procedures. If additional sampling for other constituents will be done, continue to step 3 of the appropriate section without following the cleaning steps; change gloves if necessary.

- 8) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 9) Field-clean all equipment while equipment is still wet and before going to the next site.

### 7.14 Radiogenic Isotopes – <sup>14</sup>C

If the <sup>14</sup>C sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the filter, can be omitted.

- 1) Put on latex or nitrile disposable gloves.
- 2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
- 3) Place bottles and other equipment into processing chamber.
- 4) Change gloves if necessary.
- 5) Field-rinse the filter.
  - Keep a slow rate of flow through the filter.

- 6) Collect sample immediately in a 1-L certified organics-clean amber glass bottle to overflowing.
- 7) Cap sample and turn upside down to ensure no air bubbles are visible.
  - If air is trapped inside the sample bottle, discard water sample and repeat sampling procedure.
  - If no air is trapped inside the sample bottle, turn bottle right side up, wrap tape around cap and bottleneck to ensure no atmospheric gases enter sample.
- 8) Label sample and chill immediately.
- 9) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
- 10) Field-clean all equipment while equipment is still wet and before going to the next site.

## **8 Cleaning Procedures**

### **8.1 Inorganic Sample Bottle Cleaning Procedures**

- 1) Put on powderless, disposable vinyl or latex gloves.
- 2) Fill each bottle about 25% full with deionized water (DIW) or distilled water (DW) and cap.
- 3) Shake vigorously and decant DIW or DW.
- 4) Repeat the DIW or DW rinse two more times.
- 5) Fill each bottle half full with DIW or DW and cap the bottle.
- 6) Store in doubled plastic bags.

### **8.2 Organic Sample Bottle Cleaning Procedures**

Omit any cleaning procedure for sample bottles for organic compounds. Bottles for organic analyses arrive from the laboratory capped and ready for use.

### **8.3 Sequence for Cleaning Equipment Used to Sample Organic and Inorganic Constituents**

See Figure 3 for a flowchart of the steps involved in equipment cleaning.

#### **8.3.1 Preparation**

- 1) Prepare a contaminant-free space for cleaning and drying the cleaning supplies and sample collection and processing equipment.
  - Cover the area with plastic sheeting.
  - Put on disposable, powderless gloves.
  - Prepare the detergent solution using nonphosphate, laboratory-grade detergent (0.1 to 0.2% (v/v)).
- 2) Clean the items used to clean the equipment.
- 3) Disassemble the sample collection and sample processing equipment.

#### **8.3.2 Detergent Wash and Water Rinse**

- 1) Rinse equipment exterior and interior with detergent solution.
- 2) Scrub the exterior and interior of equipment surfaces, excluding tubing, with a firm sponge or soft brush.
- 3) Place equipment into the water wash basin.
- 4) Rinse the equipment thoroughly with water to remove detergent residue.
- 5) Change gloves if necessary.

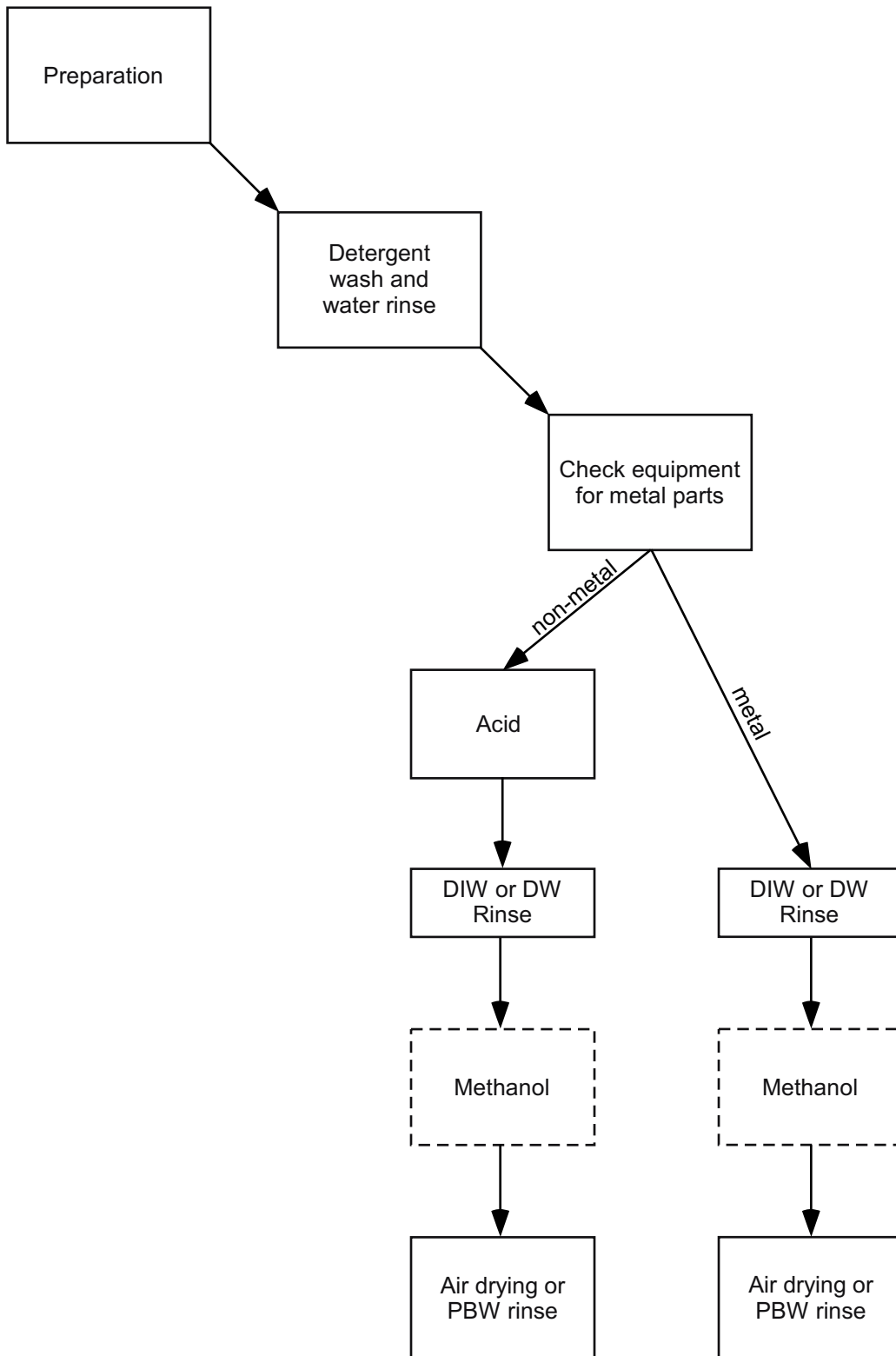


Figure 3. Field equipment cleaning procedures flowchart (modified from Wilde et al., (1998c)).

### 8.3.3 Check Equipment for Metal Parts

### 8.3.4 Acid Rinse of Plastic Components

- 1) Rinse in a 5% (v/v) HCl solution to remove organic films and inorganic deposits.
  - Using a wash bottle, rinse exterior of equipment and tubing.
  - Using a peristaltic pump, pump acid solution into a neutralization container with marble chips covering the bottom; replenish chips as needed.

### 8.3.5 DIW or DW Rinse

- 1) Place equipment into the water wash basin.
- 2) Pump DIW or DW through equipment.
- 3) Pour discharged DIW or DW into the neutralization container.  
Continue rising until rinse water pH > 6 or original DIW or DW pH is achieved.

### 8.3.6 Methanol Rinse

- 1) Change gloves if necessary.
- 2) Place cleaned equipment into a clean stainless steel or solvent-resistant wash basin.
- 3) Use pesticide-grade methanol dispensed from a fluorocarbon wash bottle or pumped through tubing.
- 4) Rinse equipment exterior and interior with a minimum amount of methanol.
- 5) Rinse only the interior of the pump tubing with methanol.
- 6) Place equipment and tubing on a clean surface.
- 7) Pour discharged methanol into an appropriate waste container.
- 8) Dispose of gloves.

### 8.3.7 Air drying or Pesticide-Grade Blank Water (PBW) Rinse

- 1) Allow methanol-rinsed equipment to air-dry in an area free from dust and potential airborne contaminants.
- 2) If it is not practical to let the equipment air-dry, dry by blowing inert gas through the equipment or rinse methanol from the equipment with pesticide-grade blank water.
- 3) Cover all equipment orifices with fluorocarbon polymer bags.
- 4) Place equipment into sealable storage bags.

## 9 Quality Control and Quality Assurance

### 9.1 Goals in Quality Assurance

- 1) Keep the measurement error variance to less than 10% of the total variance between measurements.
- 2) Keep the measurement error standard deviation to less than 25% of the total between measurement standard deviation.

In quality assurance, procedures are specified for the survey in an attempt to keep measurement errors, measurement bias and measurement error variance small.

The principal independent sources of random error must be specified. To obtain an unbiased measure of the internal consistency of the samples, samples should be labelled with a code number; sample blanks, replicate samples, spiked samples, reference samples and blind samples should be taken.

## 9.2 Blanks

### 9.2.1 Source Solution Blank

The source solution must be produced and certified by a laboratory to have analyte concentrations that do not exceed a specific method detection limit.

Inorganic-grade Blank Water (IBW) is required for blanks that will be analyzed for inorganic constituents.

PBW is required for blanks that will be analyzed for organic constituents.

Collect a sample of the source solution, or solutions used, in a designated clean, draft-free area, such as under a laminar-flow hood or laminar-flow bench.

### 9.2.2 Equipment Blank

An equipment blank sample is water (IBW or PBW) that is processed under controlled conditions in the laboratory and is passed sequentially through each component of the sample collection and processing equipment.

An equipment blank is required

- 1) Annually;
- 2) when a cleaning procedure is followed for the first time; or
- 3) when new equipment will be used for the first time.

Collect the equipment blank in a designated clean area of the office laboratory. It is recommended the equipment blank be collected at least four weeks before fieldwork begins.

#### 9.2.2.1 Procedure – Groundwater Samples Equipment Blank

- 1) Pump blank
  - Put on disposable, powderless latex or nitrile gloves.
  - After cleaning the pump, rinse a precleaned, noncontaminating standpipe with source water and discard rinse water.
  - Use IBW to test cleaning of inorganic contaminants.
  - Use PBW to test cleaning of organic contaminants.
  - Place the submersible pump, or pump intake, into the standpipe and pour in source water.
  - Keep water level above the pump intake.
  - Insert discharge end of the pump into the sample collection chamber.
  - Circulate source water through the pump and tubing to waste.
  - Pump the required volume of source water into the sample bottle.
- 2) Equipment system blank
  - Put on disposable, powderless latex or nitrile gloves.
  - After cleaning the pump, attach filter to the discharge tubing.
  - Precondition the filter using the source water.
  - Use IBW to test cleaning of inorganic contaminants.
  - Use PBW to test cleaning of organic contaminants.

- Pump the required volume of source water from the standpipe through the filter assembly into the sample bottle.

Analyze the equipment system blank before collecting and processing the first water sample. Sampling can proceed if the equipment system blank does not indicate contamination. If contamination is indicated, the remaining equipment blank samples and the source solution blank must be submitted to determine the cause of contamination. In this situation, the equipment or cleaning procedures must be changed or modified before sampling can continue.

### **9.2.3 Trip Blanks**

A trip blank is a blank sample prepared by the laboratory. Carry the trip blank as received from the laboratory to the field site. Label appropriately. Do not open, but store with the environmental samples collected for the same target analyte. Submit the trip blanks with the environmental samples.

### **9.2.4 Ambient Blanks**

An ambient blank answers the question, “To what extent could exposure of the sample to its environment contaminate the sample?”

#### **9.2.4.1 Procedure 1**

- 1) Put on disposable, powderless latex or nitrile gloves.
- 2) Fill sample bottles with appropriate blank water in the designated clean area of the office laboratory.
- 3) Cap and label appropriately.
- 4) Discard gloves.
- 5) Transport the sample to the field.
- 6) Put on disposable, powderless latex or nitrile gloves.
- 7) Place bottles in the collection or preservation chamber.
- 8) Open the blank sample bottle for the period of time in which the environmental samples are being processed.
- 9) Cap blank samples.

#### **9.2.4.2 Procedure 2**

- 1) Put on disposable, powderless latex or nitrile gloves.
- 2) Work in the area to be tested.
- 3) Pour blank water from the source solution container directly into the sample blank bottle.
- 4) Cap and label the bottle.

#### **9.2.4.3 Procedure 3**

- 1) Put on disposable, powderless latex or nitrile gloves.
- 2) Work in the area to be tested.
- 3) Fill a clean, wide-mouthed container with source solution water.
- 4) Leave open to the atmosphere for the testing period.
- 5) Pour the blank water into a clean sample bottle.
- 6) Cap and label the bottle.

### 9.2.5 Field Blanks

Field blanks are collected and processed at the field site. Field samples are processed through clean equipment and provide information on the contamination of the samples by the equipment used to collect the sample.

- 1) Process field blanks through clean equipment.
- 2) Process field blanks onsite under the same conditions as the environmental samples.
- 3) Record the date and lot number of the IBW and PBW and of the preservatives used.
  - If possible, use preservatives from the same lot numbers for the entire sampling trip for both the environmental and quality control samples.
- 4) Collect the field blanks in the same order, manner and quality control measures and checks associated with obtaining, processing, preserving and storing environmental samples.

### 9.3 Replicate Samples

Replicate samples are collected to identify and/or quantify the variability in all or part of the sampling and analysis system.

Concurrent replicates are simultaneously collected samples of water. They can be collected by using two sampling devices of the same type simultaneously, or by filling separate sample compositing containers concurrently using the same sampling device.

Sequential replicates are collected consecutively. They can be designed to assess sample variability from inhomogeneities in the system being sampled by spacing samples over short or long time periods.

Split replicates are samples divided into two or more equal subsamples. Each is submitted to one or more laboratories for the identical analysis. Split replicates are used to assess the variability from sample processing and preservation.

#### 9.3.1 Procedure for Processing Split Replicates

- 1) Wearing disposable, powderless gloves and work inside the collection chamber
  - Start with a full sample bottle of water.
- 2) Transfer contents of the first bottle to the second bottle.
- 3) Cap the second bottle and thoroughly shake.
- 4) Pour entire contents of the second bottle to the first bottle.
- 5) Pour one half of the sample from the first bottle back into the second bottle.
- 6) Cap both bottles.

### 9.4 Spike Samples

Spiked samples are used to determine the loss or gain of target analytes that occurred because of water-matrix characteristics, field processing, shipping or handling, holding time, or laboratory analytical procedures. Samples are spiked by adding a mixture of target compounds obtained from a laboratory as a sample. As a rule, an unspiked sample must accompany each spiked sample.

### 9.5 Reference Samples

Reference samples are used to determine the bias and variability associated with field handling, shipping and laboratory procedures. Samples are commonly submitted as blind samples and as split replicate



samples. Samples should be prepared before leaving for the field site, and processed in a clean environment at the office laboratory.

## 9.6 Blind Samples

The submitter knows the source and chemical composition of the blind sample, but not to the laboratory. These samples are used to determine the bias and variability introduced by the procedures used within a single laboratory or among laboratories. Blanks and reference samples are commonly used as blind samples.

## 9.7 Designing a Quality Control and Quality Assurance Plan

The number of QA/QC samples should be based on how precise one wants the estimate of variance to be. This depends on the degrees of freedom of the estimate. The percentage of the total sampling effort allocated to QA/QC will depend on factors such as the size of the project, project budget, available knowledge of the study area and analyte concentrations.

A recommended guideline for the minimum number of QA/QC samples necessary is provided below.

- 1) Commonly present constituents in measurable concentrations – major ions and anions
  - Field blanks taken at a minimum of 5 well sites.
  - Replicates (2) taken at a minimum of 5 well sites.
- 2) Commonly present but not in all areas – trace elements, radionuclides and organic acids

### Trace elements

- Field blanks taken at a minimum of 5 to 7 well sites
- 3 standard reference solutions analyzed per season
- Replicates (2) taken at a minimum of 5 to 7 well sites

### Radionuclides

- Replicates (2) taken at a minimum of 5 to 7 well sites

### Organic acids

- Field blanks taken at a minimum of 4 to 5 well sites
- 1 trip blank per season
- Field-spiked replicates (2) made up at a minimum of 4 well sites

## 10 Conclusions

Sampling protocols are necessary to a sampling program. They ensure the same sampling steps are followed at each sample location. By using non-contaminating materials in the design of the sampling equipment, the risk of outside contamination is minimized. Careful calibration of field equipment and subsequent observations of field measurements provide information on the completeness of water well purging and of aquifer conditions. Combined with quality control-quality assurance measures, sources of variability within the dataset can be understood and accounted for. Changes in sampling methods can then be made to ensure that any abnormalities are addressed.

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## Appendix A – Equipment List

### Sampling Equipment

Equipment	Supplier
Nonisokinetic sampler (open-mouth bottle sampler, weighted bottle sampler, BOD sampler, VOC sampler)	Surface water scientific equipment supply company
Isokinetic sampler (US DH-1, US D-77, US D95, D-77, frame bag sampler)	Surface water scientific equipment supply company
Crane	Surface water scientific equipment supply company
Reel, hanger bars and pins	Surface water scientific equipment supply company
Sounding weight	Surface water scientific equipment supply company
Thief sampler	Surface water scientific equipment supply company
Pumping sampler	Surface water scientific equipment supply company

The sampling system used to sample surface water should be selected on considerations such as surface water conditions, site accessibility, water depth, current velocity and budget. Each system has its advantages and disadvantages that should be factored into its selection as the sampling system for each particular site.

### Cleaning Supplies

Equipment	Supplier
Sponges	Hardware supplier
Acid and solvent resistant basins	Hardware supplier
5 x 20- L storage pails	Hardware supplier
Neutralizing agent such as marble chips or lime	Scientific equipment supply company or hardware supplier
Flexible silicone peristaltic pump tubing	Scientific equipment supply company
Peristaltic pump	Scientific equipment supply company
Distilled or deionized water	Analytical laboratory
Phosphate-free detergent	Scientific equipment supply company
Hydrochloric acid (Trace metal grade)	Scientific equipment supply company
Methanol (Pesticide grade)	Scientific equipment supply company

## Field Determination Equipment

Meters and Equipment	Supplier
2 x Accumet Model AP 15 portable waterproof pH/mV meters, 1 with an Accumet combination temperature/pH electrode and 1 with an Accumet platinum Ag/AgCl ORP combination electrode	Scientific equipment supply company
Hanna Instruments Model HI 9331 waterproof conductivity meter with conductivity probe	Scientific equipment supply company
YSI Model 52 dissolved oxygen meter with dissolved oxygen probe	Scientific equipment supply company
Hach Model 16900 digital alkalinity titrator and associated supplies	Scientific equipment supply company
Calibration Solutions	Supplier
ZoBell solution	Scientific equipment supply company
Conductivity standard 1413 $\mu$ S	Scientific equipment supply company
pH 4, 7 and 10 buffers	Scientific equipment supply company



Field determination equipment setup

## Sample Processing and Preservation

<b>Sample Processing and Preservation Chambers</b>	
<b>Equipment</b>	<b>Supplier</b>
~ 15 m of PVC pipe 1.9 cm OD	Hardware supplier
16 x 1.9 cm OD side outlet elbow PVC fittings	Hardware supplier
Roll of plastic sheeting	Hardware supplier
Tape	Hardware supplier
<b>Sample Splitters</b>	
<b>Equipment</b>	<b>Supplier</b>
Churn splitter	Surface water scientific equipment supply company
Churn carrier	Surface water scientific equipment supply company
Cone splitter	Surface water scientific equipment supply company
<b>Bottles and sampling containers</b>	
<b>Equipment</b>	<b>Supplier</b>
Nalgene 30-mL, 250-mL and 1-L high density polyethylene Boston round bottles	Scientific equipment supply company
500-mL polypropylene round bottles	Analytical laboratory
1-L amber glass bottles (certified clean)	Analytical laboratory
1-L amber glass bottles	Scientific equipment supply company
125-mL amber glass bottles	Scientific equipment supply company
20-mL draw Vacutainer™ test tubes	Scientific equipment supply company
Vacutainer™ needles	Scientific equipment supply company
Vacutainer™ needle holders	Scientific equipment supply company
<b>Filters and Filtering Equipment</b>	
<b>Equipment</b>	<b>Supplier</b>
Disposable filter 0.45 mm	Scientific equipment supply company
Qualitative filter paper	Scientific equipment supply company
Hand vacuum pump	Scientific equipment supply company
<b>Preservation Materials</b>	
<b>Preservation agent</b>	<b>Supplier</b>
Nitric acid (Trace metal grade)	Analytical laboratory or Scientific equipment supply company
Hydrochloric acid (Trace metal grade)	Scientific equipment supply company
Chloroform (HPLC grade)	Scientific equipment supply company
Barium chloride (Certified)	Scientific equipment supply company
Cadmium acetate (Certified)	Scientific equipment supply company
Ammoniacal strontium chloride	Analytical laboratory



Disposable filter 0.45 $\mu$ m



Capsule filters



**Sampling Chamber**

## Miscellaneous Equipment

Equipment	Supplier
Graduated cylinders	Scientific equipment supply company
Disposable pipettes	Scientific equipment supply company
Latex or nitrile powderless disposable gloves	Scientific equipment supply company
Parafilm	Scientific equipment supply company
Lab coats	Scientific equipment supply company
Safety glasses	Scientific equipment supply company
MSDS sheets for chemicals	Scientific equipment supply company
Plastic bags, garbage bags	Hardware supplier
Tape (packing, duct, masking)	Hardware supplier
Labels for samples and safety labels	Scientific equipment supply company
Pens, markers and paper	Office supply company
Traffic cones, safety signage	Safety supply company
Tools (wrenches, screwdrivers, scissors, utility knives)	Hardware supply company
Ground cloth	Hardware supply company
Cooler and ice	Hardware supply company
Packing material (bubble wrap, sturdy boxes)	Hardware supply company
Distilled or deionized water	Analytical laboratory

## Appendix B – Field Forms

### Site Checklist

Site location and description: \_\_\_\_\_

Date: \_\_\_\_\_

Activity	Y/N	Comments
Vehicle parked, signs setup if needed, safety check		
Equipment calibrated		
Sampling equipment setup		
Tubing and manifold systems connected		
Organic acid sample taken and preserved		
Trace metal sample taken and preserved		
Alkalinity samples taken		
Anions sample taken		
Silica sample taken		
Routine sample taken		
<sup>18</sup> O and <sup>2</sup> H samples taken		
<sup>13</sup> C/ <sup>12</sup> C samples taken		
<sup>14</sup> C sample taken		
<sup>34</sup> S/ <sup>32</sup> S for sulphide sample taken and preserved		
<sup>34</sup> S/ <sup>32</sup> S for sulphate sample taken and preserved		
<sup>11</sup> B/ <sup>10</sup> B sample taken		
<sup>87</sup> Sr/ <sup>86</sup> Sr sample taken and preserved		
Radionuclides sample taken and preserved		
Equipment cleaned and wash materials disposed of appropriately		
Blanks processed		
Equipment packed up		
Final site inspection		



Photographs taken		
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Additional comments:

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# Record of Water Sampling and Field Parameters

DATE: \_\_\_\_\_

RECORDED BY: \_\_\_\_\_

SITE ID: \_\_\_\_\_ STATION NAME: \_\_\_\_\_ OTHER ID: \_\_\_\_\_

WATER SAMPLING METHOD(describe): \_\_\_\_\_

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TIME (hh:mm)	TEMPER- ATURE (°C)	CONDUC- TIVITY (μS/cm)	DISSOLVED OXYGEN (mg/L)	pH	e <sub>mf</sub> (mV)

## Sampling Protocol Summary for Specific Elements

Analyte	Bottle Type	Field Rinse	Preservatives	Comments
Organic Acids	1-L amber bottle from the laboratory	No	Chloroform. Cool to 4°C or less but not to freezing	Use a filtered sample and make sure and leave a headspace.
Trace elements	500-mL polyethylene bottle from the laboratory	Yes	Vial of dilute HNO <sub>3</sub> . One 5-mL vial per 500-mL bottle	Use a filtered sample and fill to shoulder of bottle.
Anions (Cl, Br and I) for NAA	250-mL polyethylene bottles	Yes	None	Use a filtered sample and fill to shoulder of bottle.
Silica	30-mL polyethylene bottle	Yes	None	Either use 5 mL of filtered sample water and dilute with 20 mL of deionized water or fill sample bottle with filtered water.
Routine	500-mL polyethylene bottle from the laboratory	Yes	None	Use filtered water.
Radiochemicals	1-L polyethylene bottle	Yes	Vial of dilute HNO <sub>3</sub> to bring pH to < 2	Use filtered water.
<sup>18</sup> O and <sup>2</sup> H	20-mL vacutainer tube	No	None	Use filtered water.
<sup>13</sup> C in DIC	20-mL vacutainer tube pre-filled with ~2 mL ammoniacal SrCl	No	Ammoniacal SrCl already in vial	Use filtered water.
<sup>34</sup> S/ <sup>32</sup> S in sulphate (Method 1)	125- mL glass amber bottle	No	Dilute HCl and excess BaCl <sub>2</sub>	Use filtered water. Store in a dark place
<sup>34</sup> S/ <sup>32</sup> S in sulphide (Method 1)	1-L amber glass bottle	No	Excess CdAc	Use filtered water.
<sup>34</sup> S/ <sup>32</sup> S in sulphide (Method 2)	1-L amber glass bottle	No	Excess CdAc	Use filtered water. Once precipitate forms (after approximately 24 hours) filter water sample and dry precipitate. Ship filter paper for analysis.
<sup>34</sup> S/ <sup>32</sup> S in sulphate (Method 2)	125-mL amber glass bottle	No	Excess BaCl <sub>2</sub>	Use filtrate from <sup>34</sup> S/ <sup>32</sup> S in sulphide (Method 2) procedure. Store in a dark place.
<sup>87</sup> Sr/ <sup>86</sup> Sr	250-mL polyethylene bottle	No	Vial of dilute HNO <sub>3</sub> . One 5-mL vial per bottle.	Use filtered water.
<sup>11</sup> B/ <sup>10</sup> B	250-mL polyethylene bottle	No	None	Use filtered water.
<sup>14</sup> C	1-L amber bottle from the laboratory	No	None	Do not use filtered water. Fill bottle to overflowing.