



# Sampling of Groundwater from Wells in the Athabasca Oil Sands (In Situ) Area, Alberta, 1999-2001 – A Compilation of Protocols and Methods.



**Sampling of Groundwater  
from Wells in the Athabasca  
Oil Sands (In Situ) Area,  
Alberta, 1999-2001 – A  
Compilation of Protocols and  
Methods.**

T.G. Lemay

Alberta Geological Survey

December 2002

©Her Majesty the Queen in Right of Alberta, 2002

The Alberta Energy and Utilities Board/Alberta Geological Survey (EUB/AGS) and its employees and contractors make no warranty, guarantee or representation, express or implied, or assume any legal liability regarding the correctness, accuracy, completeness, or reliability of this publication. Any digital data and software supplied with this publication are subject to the licence conditions (specified in 'Licence Agreement for Digital Products'). The data are supplied on the understanding that they are for the sole use of the licensee and will not be redistributed in any form, in whole or in part, to third parties. Any references to proprietary software in the documentation, and/or any use of proprietary data formats in this release, do not constitute endorsement by the EUB/AGS of any manufacturer's product.

If this product is an EUB/AGS Special Report, the information is provided as received from the author and has not been edited for conformity to EUB/AGS standards.

When using information from this publication in other publications or presentations, due acknowledgment should be given to the EUB/AGS. The following reference format is recommended:

Lemay, T.G. (2002): Sampling of groundwater from wells in the Athabasca Oil Sands (in situ) Area, Alberta, 1999-2001 – A compilation of protocols and methods; Alberta Energy and Utilities Board, EUB/AGS Geo-Note 2002-10.

**Published December 2002 by:**

Alberta Energy and Utilities Board  
Alberta Geological Survey  
4<sup>th</sup> Floor, Twin Atria Building  
4999 – 98<sup>th</sup> Avenue  
Edmonton, Alberta  
T6B 2X3

Tel: (780) 422-3767 (Information Sales)

Fax: (780) 422-1918

Web site: [www.ags.gov.ab.ca](http://www.ags.gov.ab.ca)

# Contents

Acknowledgments .....	vi
Abstract.....	vii
<b>1 Introduction.....</b>	<b>1</b>
<b>2 Equipment List.....</b>	<b>2</b>
<b>3 Preparations Before Sampling.....</b>	<b>2</b>
<b>4 Measurement of the Water Level.....</b>	<b>2</b>
<b>5 Well Purging and Monitoring of Field Measurements.....</b>	<b>8</b>
5.1 Monitoring Wells .....	9
5.2 Water Supply Wells .....	10
<b>6 Field Determinations .....</b>	<b>11</b>
6.1 Temperature .....	12
6.1.1 Measurement in Air.....	12
6.1.2 Measurement in Groundwater .....	12
6.2 Dissolved Oxygen (DO) .....	13
6.2.1 Amperometric Method .....	13
6.2.2 Atmospheric Pressure Correction.....	13
6.2.3 Calibration in Air.....	13
6.2.4 Measuring DO in Groundwater .....	13
6.3 Specific Electrical Conductance (SC).....	14
6.3.1 Calibration .....	14
6.3.2 Measurement of the Conductivity of Groundwater in a Flow-Through Chamber .....	14
6.4 pH .....	15
6.4.1 Calibration .....	15
6.4.1.1 Calibration for Low-Conductivity Water .....	17
6.4.2 Measurement .....	17
6.4.2.1 Measurement of pH in Groundwater .....	17
6.4.2.2 Subsample Measurement.....	18
6.5 Reduction-Oxidation Potential (REDOX).....	18
6.5.1 Equipment Test Procedure .....	19
6.5.2 Measurement of Eh.....	20
6.5.3 Interferences and Limitations .....	21
6.6 Alkalinity .....	21
6.6.1 Calculation of Alkalinity Relationships .....	22
<b>7 Sample Withdrawal.....</b>	<b>23</b>
7.1 Sample Withdrawal Procedures .....	23
<b>8 Sample Processing .....</b>	<b>23</b>
8.1 Field-Rinsing Procedures.....	24
8.2 Common Organic Compounds .....	24
8.3 Major, Minor and Trace Elements .....	25
8.4 Silica .....	26
8.5 Anions.....	27
8.6 Radiochemicals.....	27
8.7 Stable Isotopes – $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ .....	28
8.8 Stable Isotopes – $^{13}\text{C}/^{12}\text{C}$ .....	29
8.9 Stable Isotopes – $^{34}\text{S}/^{32}\text{S}$ in Sulphide .....	30
8.10 Stable Isotopes – $^{34}\text{S}/^{32}\text{S}$ in Sulphate .....	30
8.11 Stable Isotopes – $^{34}\text{S}/^{32}\text{S}$ in Sulphide and in Sulphate .....	31
8.12 Stable Isotopes – $^{87}\text{Sr}/^{86}\text{Sr}$ .....	32
8.13 Stable Isotopes – $^{11}\text{B}/^{10}\text{B}$ .....	33

8.14 Radiogenic Isotopes – <sup>14</sup> C.....	33
<b>9 Cleaning Procedures.....</b>	<b>34</b>
9.1 Inorganic Sample Bottle Cleaning Procedures at the Laboratory (before heading to sample sites).....	34
9.2 Organic Sample Bottle Cleaning Procedures.....	34
9.3 Sequence for Cleaning of Equipment Used to Sample for Organic and Inorganic Constituents .....	34
9.3.1 Preparation.....	34
9.3.2 Detergent Wash and Water Rinse.....	34
9.3.3 Check Equipment for Metal Parts .....	35
9.3.4 Acid Rinse of Plastic Components .....	35
9.3.5 DIW or DW Rinse.....	35
9.3.6 Methanol Rinse.....	35
9.3.7 Air Drying or PBW Rinse .....	35
<b>10 Quality Control and Quality Assurance .....</b>	<b>35</b>
10.1 Goals in Quality Assurance .....	35
10.2 Blanks .....	36
10.2.1 Source Solution Blank .....	36
10.2.2 Equipment Blank .....	36
10.2.2.1 Procedure – Groundwater Samples Equipment Blank.....	36
10.2.3 Trip Blanks .....	37
10.2.4 Ambient Blanks .....	37
10.2.4.1 Procedure 1 .....	37
10.2.4.2 Procedure 2 .....	37
10.2.4.3 Procedure 3 .....	37
10.2.5 Field Blanks .....	38
10.3 Replicate Samples.....	38
10.3.1 Procedure for Processing Split Replicates .....	38
10.4 Spiked Samples.....	38
10.5 Reference Samples.....	39
10.6 Blind Samples .....	39
10.7 Designing a Quality Control and Quality Assurance Plan.....	39
<b>11 Conclusions.....</b>	<b>39</b>
<b>12 References.....</b>	<b>40</b>
<b>Appendix A Sample Equipment List.....</b>	<b>41</b>
<b>Appendix B Field Forms .....</b>	<b>48</b>

## Tables

Table 1 Stability criteria for field parameters during well purging (Wilde et al., 1998d).....	9
Table 2 Standard half-cell reference electrode potentials at various temperatures (Wilde et al, 1998f) .	19
Table 3 Eh of ZoBell’s solution as a function of temperature (Wilde et al., 1998f).....	20
Table 4 Alkalinity range, sample volume, titration cartridge normality and digit multiplier relationships.....	22
Table 5 Alkalinity relationships.....	22

## Figures

Figure 1 In-line sampling system (modified from Koterba et al., 1995) .....	3
Figure 2 Connection of sample tubing to the water source.....	4
Figure 3 Connection of the tubing from the water source to the sampling manifold (takes the place of the control valves and flow regulation valve in Figure 1) to the flow-through chamber and to the sample collection chamber.....	4

Figure 4	Close-up view of the sampling manifold.....	5
Figure 5	Field parameter measurement equipment (front from left to right: conductivity meter, pH-temperature meter and oxidation-reduction potential meter; rear: dissolved oxygen meter) .....	5
Figure 6	Sample collection chamber.....	6
Figure 7	Field equipment cleaning procedures flowchart (modified from Wilde et al., 1998f) .....	7

## Acknowledgments

This publication is a compilation of protocols and methods for the sampling of groundwater. 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 domestic wells, water-supply wells, observation wells and from piezometers. The goal of the sampling project was to collect high quality water samples. The results will be used to establish a baseline hydrogeochemical data set for the shallow groundwater in the area before resource development begins.

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 groundwater-sampling program in northeastern Alberta. The purpose was to document baseline groundwater conditions in advance of extensive oil sands development in the area. 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 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 the Province of 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) preparation for water sampling; 2) selection of equipment for water sampling; 3) cleaning of equipment for water sampling; 4) collection of water samples; 5) processing of water samples; and 6) the measurement of field parameters, such as pH, conductivity, temperature, oxidation-reduction potential, dissolved oxygen and alkalinity. Information regarding the design of a quality assurance and quality control program was gathered from Book 9 of the Techniques of Water-Resources Investigations released by the United States Geological Survey (Wilde et al., 1998d) and 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 <sup>14</sup>C samples were based on personal communications with J. Fennell of 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 communication with Dr. J. Duke from the University of Alberta. Collection procedures for isotopes of carbon (C) and sulphur (S) were based upon personal communication 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 communication with S. Taylor and Dr. M. Wieser from the University of Calgary. Collection procedures for isotopes of strontium (Sr) were based upon personal communication with Dr. C. Holmden of the University of Saskatchewan.

This document is broken up into the following sections: preparation for sampling, purge procedures and field measurements monitoring, sample withdrawal, sample processing, quality control, and field equipment cleaning procedures. Within the section on groundwater-sample processing, each analytical sample type is treated separately. This means that for each analytical sample type, the complete list of steps necessary to collect that sample is listed. If the sampling program will be collecting water samples for more than one type of analysis, then some of these steps can be omitted.

## 2 Equipment List

Supplies used during water level measurement, 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 Preparations Before Sampling

- 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 the field-measurement instruments.
- 4) Spread clean plastic sheeting around the well to keep sampling equipment and sample tubing clean.
- 5) Prepare area to be used for field-cleaning of equipment.
- 6) Put on latex or nitrile disposable gloves.
- 7) An inline sampling equipment setup similar to that of Koterba et al. (1995) is recommended (Figures 1-6).
- 8) Set up equipment ensuring sample collection and preservation chambers are in a clean workspace.
- 9) If connecting to an existing system, connect sample tubing as close to the wellhead as possible.
  - There must be no chemical disinfection or water softening systems between the pump and the tap, faucet or other means of connection.
  - Select a tap, faucet or other means of connection without an aerator.
  - Use connectors and sample tubing that are compatible with the target analytes and that will not contaminate the sample. Clean before use.
  - Connect a length of sample tubing between the water source and the sampling manifold.
  - Connect sample tubing from the sampling manifold to the flow-through chamber, to the processing chamber, and to waste discharge.
  - Keep tubing for sample and field measurement lines as short as possible and protected from direct sunlight and extreme temperatures.
- 10) If sampling from a monitoring well or piezometer, connect sample tubing from the pump to the manifold and from the manifold to the flow-through chamber, processing chamber and to waste discharge.
  - Keep tubing for sample and field measurement lines as short as possible and protected from direct sunlight and extreme temperatures.

Tubing that transfers sample to the processing chamber must be of non-contaminating material, such as fluorocarbon polymer or stainless steel (grade SS316 and higher).

## 4 Measurement of the Water Level

- 1) Using a weighted steel or electric tape in a non-pumping well, measure water level to the nearest 0.5 cm (for wells <60 m to water).
- 2) Repeat measurement until precision is within 0.10 m.
- 3) At deep wells, calculate the compensation factor to account for tape stretching and thermal effects.
  - The stretch correction and thermal effects can be calculated following the methods described in Garber and Koopman (1968)

$$C = (L_c^2 WS)/2 + PLS$$

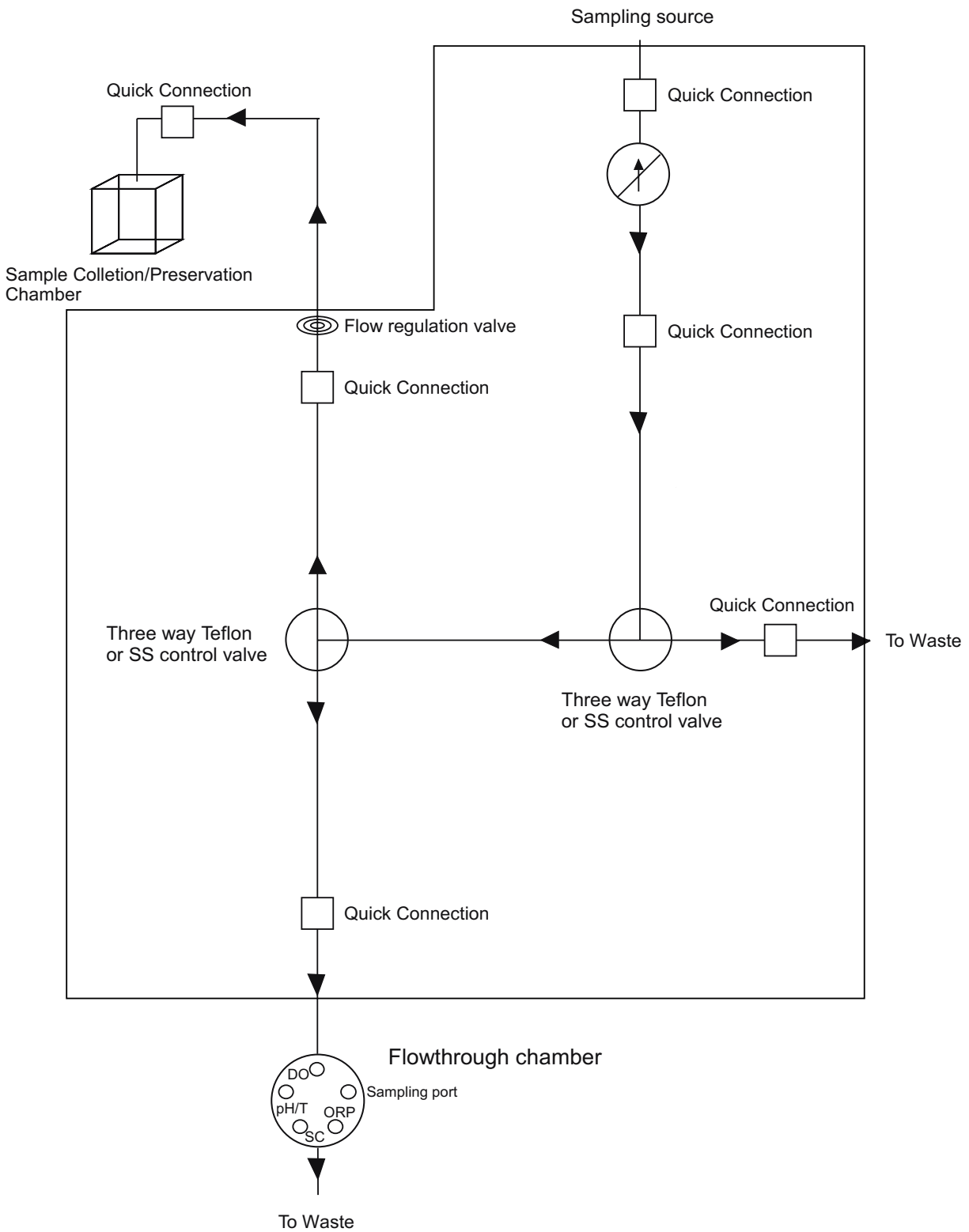


Figure 1. In-line sampling system (modified from Koterba et al., 1995).



Figure 2. Connection of sample tubing to the water source.

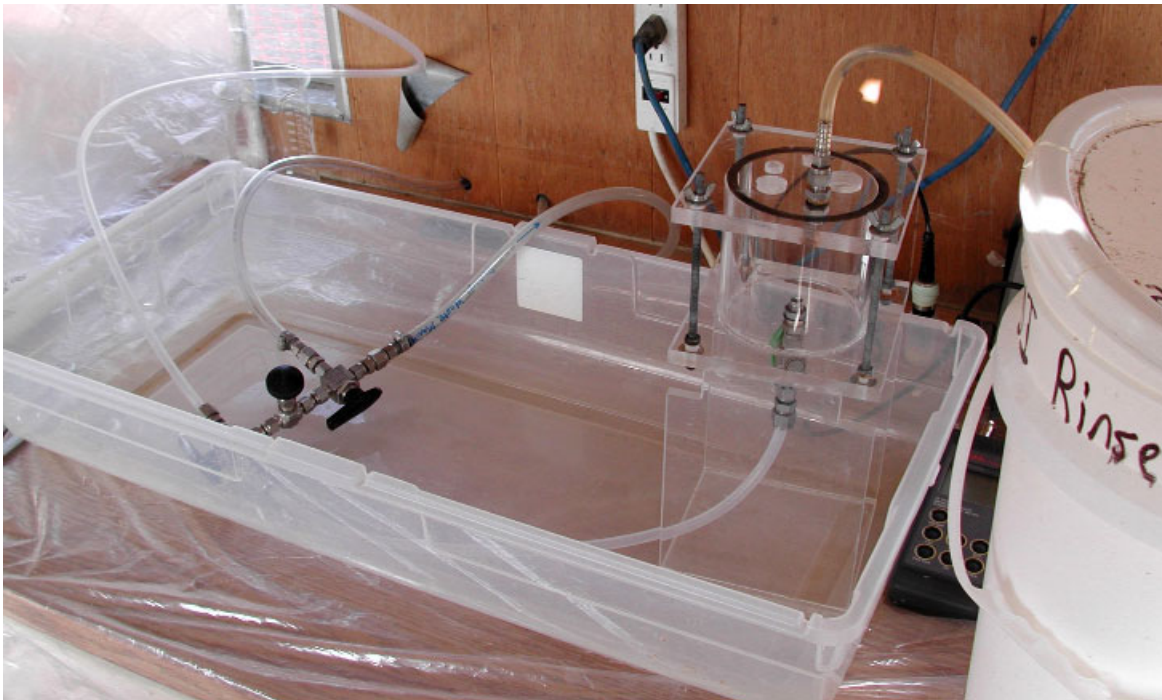


Figure 3. In-line sampling system (modified from Koterba et al., 1995).

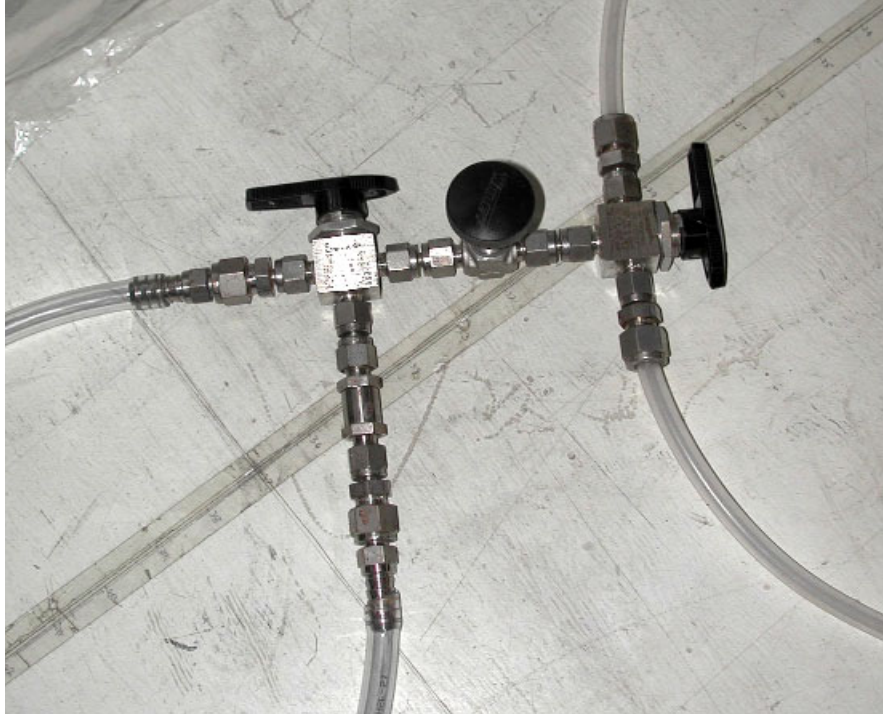


Figure 4. Close-up view of the sampling manifold.



Figure 5. Field parameter measurement equipment (front from left to right: conductivity meter, pH-temperature meter and oxidation-reduction potential meter; rear: dissolved oxygen meter).



Figure 6. Sample collection chamber.

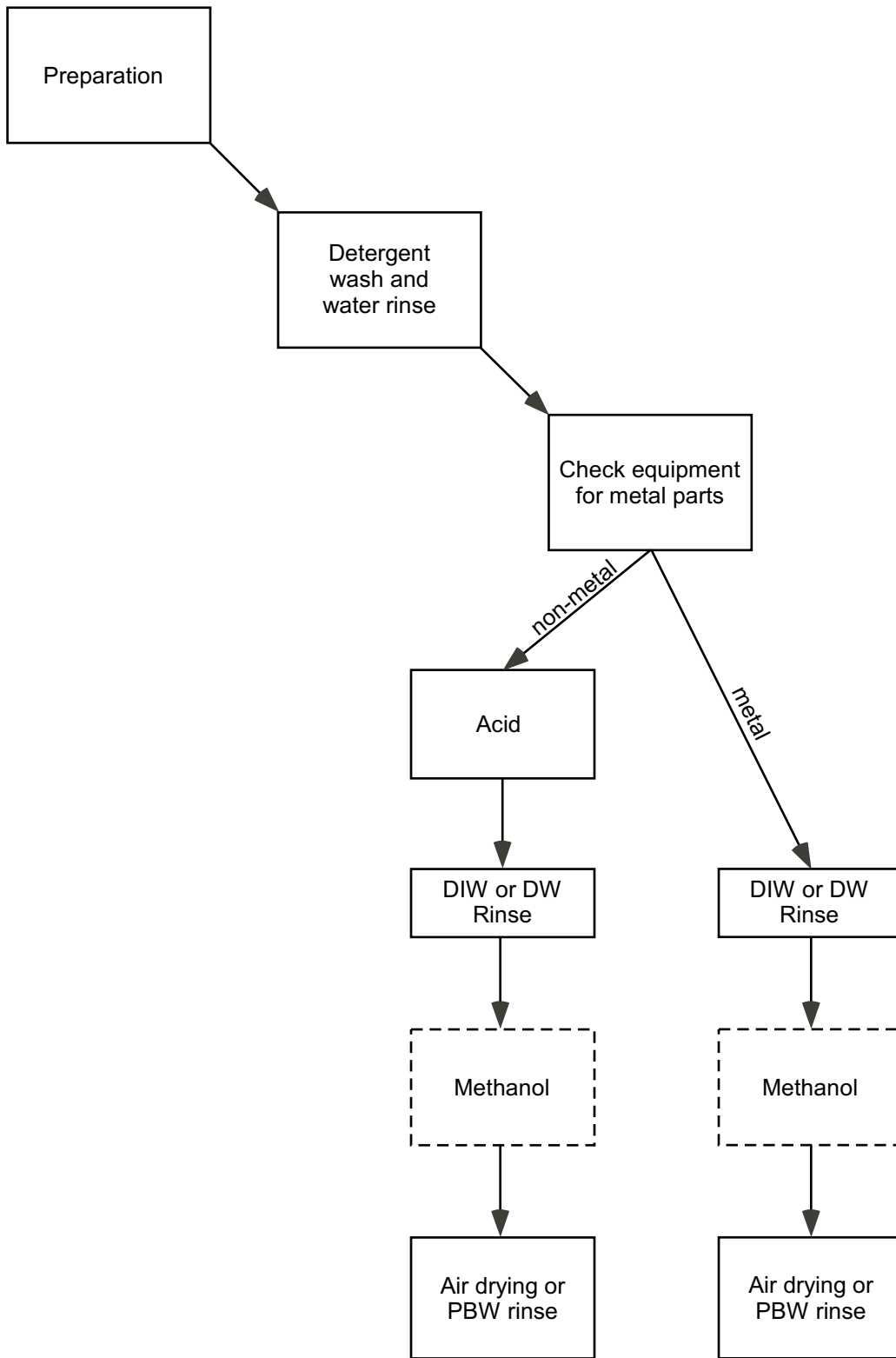


Figure 7. Field equipment cleaning procedures flowchart (modified from Wilde et al.,1998c).

Where: C = stretch correction

$L_c$  = corrected length of suspended tape (corrected for thermal effects)

W = weight of tape per unit of length

S = coefficient of stretch (provided by the tape manufacturer)

P = mass of the weight

- Thermal effects are calculated using the following formula

$$L_c = D - ((D \times (T_{ave} - T_{ref}) \times T_{coef}))$$

Where:  $L_c$  = corrected depth (corrected for thermal effects)

D = measured depth

$T_{ave}$  = average temperature (average of the surface temp. and downhole temp.)

$T_{ref}$  = reference temperature provided by the manufacturer

$T_{coef}$  = temperature coefficient provided by the manufacturer

- 4) Record water-level measurements.

Note:

- 1) Care must be taken not to entangle the well tape in the pump discharge pipe or intake.
- 2) An unweighted tape might be necessary if the weight cannot fit past the pump apparatus.
- 3) At some supply wells, the water level can only be estimated using the air-line method.
  - A summary of the air-line method is presented in Garber and Koopman (1968) and Driscoll (1986).

## 5 Well Purging and Monitoring of Field Measurements

Standard purge procedures involve removal of at least three well volumes of standing water. Field measurements, water level, pumping rate and the volume of water removed are recorded as a function of time.

Calculate a purge volume using the height of the water column to the bottom of the well. This minimizes the effects on groundwater chemistry from (1) vertical and/or horizontal exchange of water in the open or screened interval with the aquifer, (2) diffusion of oxygen from air above the water column into the column of standing water within the open or screened interval.

Exceptions to the three well volume rule:

- 1) A supply well to be sampled has been pumped continuously, or long enough to have removed three casing volumes of water before sampling.
- 2) The sample-collection interval is sealed with packers and, therefore, only the packed interval requires purging.
- 3) Drawdown occurs rapidly, but recovery to ~90% cannot be achieved before samples are collected.
- 4) Purging will disturb sediment at the bottom of the well.
- 5) The well to be sampled is equipped with a dedicated sampling device and the intake is within the open or screened interval.
- 6) A purge minimization device, or low-flow purging techniques, are used.



Low-flow (micropurge) purging minimizes the volume of purge water. This technique is applicable to sites at which the pump intake is to be located within the screened/open interval and a low rate of flow can be maintained without compromising sample integrity.

A sufficient volume has been purged from the well when the variability in sequentially monitored field measurements is within the prescribed criteria for stability.

**Table 1. Stability criteria for field parameters during well purging (Wilde et al., 1998d)**

Field Measurement	Stability Criteria
pH	±0.1 standard units
Temperature (°C)	± 0.2 °C for thermistor thermometers ± 0.5 °C for liquid in glass thermometers
Specific electrical conductance (SC) (µS/cm)	± 5% for SC ≤ 100 µS/cm ± 3 % for SC > 100 µS/cm
Dissolved Oxygen (DO) (mg/L)	± 0.3 mg/L

## 5.1 Monitoring Wells

Groundwater samples commonly are collected from monitoring wells using portable sampling equipment. Submersible pumps are recommended in general, but site characteristics can place limitations on the practical use of various types of sampling equipment.

### To field-rinse the sampler

- 1) Put on latex or nitrile disposable gloves.
- 2) Lower the sampler carefully through the water column in the well to the selected depth interval for sampling. Take care to minimize disturbance to the water column and to sediments.
  - If using a pump sampler, run water continuously through the pump and sample tubing to waste to achieve the equivalent volume of three equipment rinses.
  - Field-rinsing can be achieved with well purging if the well is purged with the same equipment that will be used for sampling.
  - If using a bailer or other point or thief sampler, lower sampler smoothly and allow sampler to fill and then withdraw.
  - Shake water in sampler vigorously to rinse all interior surfaces then drain water from sampler. Repeat filling, rinsing and draining at least two more times.
  - Discard or contain the purge water used for field-rinsing, as appropriate.
- 3) Calculate the well volume.
  - $V$  of the well in  $m^3 = 7.854 \times 10^{-5} \times H_{wc} \times D^2$
  - $H_{wc}$  = Height of the water column from the bottom of the well in metres
  - $D$  = Diameter of the well in centimetres
- 4) The volume can be converted to litres by multiplying  $V$  in  $m^3$  by 1000  $L/m^3$ , to cubic feet by multiplying  $V$  in  $m^3$  by 35.3  $ft^3/m^3$  and to gallons by multiplying  $V$  in  $m^3$  by 264.2 gallons/ $m^3$ .
- 5) Lower a submersible pump, followed by a water-level sensor, to the desired location of the pump intake.
- 6) Move the equipment slowly and smoothly through the water column to avoid stirring up particulates.
- 7) The intake can either be lowered continually while purging to the final depth, or placed immediately in final position.

- Position the pump intake at least 0.9 m below static water surface and a minimum distance above the top of the screened/open interval of 10 times the well diameter.
  - Place the water-level sensor a maximum of 0.3 m below the water surface.
  - Do not exceed 0.3 m of drawdown.
- 8) Start the pump, channelling initial discharge to waste.
  - 9) Gradually increase and/or adjust the pumping rate to limit drawdown to between 0.15 m and 0.3 m.
    - Do not use a flow-splitting valve to adjust flow rate.
  - 10) Discharge water to waste until sediment is cleared from the flow.
  - 11) Begin flow through the flow-through chamber.
  - 12) Record the start and end times of purging, the purging rate, water levels, and the location of the pump intake.
  - 13) Calculate the flow rate.
  - 14) Purge a minimum of three well volumes.
  - 15) As the final well volume is removed, record at least five sets of field measurements at regularly spaced intervals, and check data against stability criteria.

Sampling equipment can be dedicated for use at a specific well or can be installed permanently for the duration of the study. If the same equipment is used for several wells, a substantial risk of cross contamination exists.

- Select equipment that will not alter the chemical composition of the sample.
- Use only clean equipment.
- Quality assure the sampling equipment with an equipment blank(s) to verify that the equipment is suitable for the purpose of the study.

## 5.2 Water Supply Wells

A water supply well that is in regular service and has been operating long enough to have removed three casing volumes of water within several hours of sample collection should not require the purging of three well volumes. Sample tubing needs to be flushed with sample, and the field measurements monitored before sampling. It is recommended the water level in the well be maintained above the screened or open interval to ensure a representative sample.

- 1) Begin the discharge of water to waste.
- 2) Open any additional valves or taps/faucets to ensure the pump will operate continuously and to reduce the possibility of backflow of water stored in plumbing lines.
- 3) Begin to calculate the three well volumes after discharging the initial volume of water to waste until sediment is cleared from the flow.
- 4) Calculate the well volume.
  - $V$  of the well in  $m^3 = 7.854 \times 10^{-5} \times H_{wc} \times D^2$
  - $H_{wc}$  = Height of the water column from the bottom of the well in metres
  - $D$  = Diameter of the well in centimetres
- 5) The volume can be converted to litres by multiplying  $V$  in  $m^3$  by 1000  $L/m^3$ , to cubic feet by multiplying  $V$  in  $m^3$  by 35.3  $ft^3/m^3$  and to gallons by multiplying  $V$  in  $m^3$  by 264.2  $gallons/m^3$ .
- 6) Record the start and end times of purging, the purging rate, water levels and the location of the pump intake.
- 7) Begin the flow through the flow-through chamber for field measurements. Adjust the flow to the chamber from the pump.
- 8) Once flow is constant, begin monitoring field measurements.

- 9) Calculate and record the final pumping rate.
- 10) Record at least five sets of field measurements at regularly spaced intervals, and check data against stability criteria.

Notes:

- 1) Adjust the flow rate at the pump, or use a manifold with a flow-regulating valve, to prevent backpressure and air bubbles from building in the line.
- 2) The pump should produce a smooth, solid stream of water without air or gas bubbles and without pump cavitation during field measurements.
- 3) Contain and dispose of purge water as required by regulations. Discharge the water far enough away from a well or well cluster so as not to affect water quality in the well.
- 4) Flow should not be halted or the flow rate changed suddenly during the final phases of purging and sampling.
- 5) Do not use a flow-splitting valve to adjust flow rate.
- 6) The final pumping rate used during the final five sets of field measurements also should be used during sample collection.

Do not sample the well if it is not possible to bypass any holding tank or chemical treatment system.

Advantages of sampling water supply wells over monitoring wells

- Cost of well and pump installation is not a factor.
- Samples from domestic and municipal wells are collected directly from the resource being studied.
- Pumps are dedicated to the site.
  - Cross contamination of other wells from pumping equipment is not a problem.
  - Field time and effort expended in operating and cleaning portable pumps can be allocated to other tasks.
- In-service supply wells require minimal amount of purging at time of sampling.

Disadvantages

- The well and open or screened intervals might not isolate the aquifer zone where information is needed.
- Materials of construction of well and pump could affect concentrations of analytes.
- Pumps with high capacities can alter the water chemistry of a sample through
  - contact with lubrication fluids; or
  - aeration and degassing caused by high-velocity pumping, suction-lift and cavitation.
- Access for water-level measurements might be unavailable, or access might be indirect.

## 6 Field Determinations

More accurate field measurements can be made through a flow-through chamber for groundwater samples. Where in situ sampling is not possible, a thief-type sampler, such as a bailer, can be used.

A flow-through chamber is an airtight, transparent vessel with a pressure-relief valve and either (1) ports to accommodate individual sensors or (2) a multiparameter instrument.

When setting up a flow-through chamber:

- 1) Test and calibrate field instruments.
- 2) Install the chamber in-line from the pump and as close to the wellhead as possible.
  - Keep the chamber, field measurement instruments and tubing off the ground, shaded from direct sunlight and shielded from the wind.
  - Keep tubing as short as possible.
- 3) Turn on the pump; adjust flow to the desired purge rate and record rate and time purging began. Direct initial flow to waste to avoid introducing sediment into the chamber.
  - Adjust the flow into the chamber so a constant stream of water is maintained at the rate required for dissolved-oxygen measurements.
  - Correct any backpressure conditions; tilt the chamber to expel trapped air.
  - Allow sensors to equilibrate.
- 4) Record and monitor sequential sets of field measurement readings during withdrawal of final purge volume.
  - After two or more well volumes are purged, and before the final five or more readings are made, adjust the flow rate to be used for sampling flow; flow must be sufficient for dissolved oxygen measurements.
- 5) If stabilization criteria are being met, record at least five measurements at intervals of three to five minutes or more. If stabilization criteria are not being met, extend purge time and document the problem in the field notes.
- 6) Report the median of the last five or more readings and the time of measurement.
- 7) Field determinations include temperature (T), dissolved oxygen (DO), specific electrical conductance (SC), pH, oxidation-reduction potential (ORP) and alkalinity measurements.

## 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 three to five minutes for the thermometer to equilibrate, record the 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 Groundwater

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

- 1) Prepare the instruments for the flow-through chamber system.
- 2) Immerse the thermometer in the chamber. Keep the tubing from the well to the chamber as short as possible, out of direct sunlight, and off the ground.
- 3) Begin water withdrawal from the well.
- 4) Allow the thermometer sensor to equilibrate with the well water for five minutes; record the readings and time intervals throughout the period of purging.

- 5) Toward the end of purging, record five measurements, spaced at increments of three to five minutes or more.
  - There should only be slight fluctuation with the 0.5°C interval for liquid in glass thermometers and 0.2°C for thermistor thermometers.
  - Report the median of the final five measurements.
  - If the stability criterion has not been met, extend the purge time and report the last five or more sequential measurements and record any instability on field forms.
- 6) 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, temperature of the water and conductivity of the water 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 Groundwater**

The water being measured must not contact air. 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) Install the DO equipment in the flow-through chamber.
  - Install the DO sensor through an airtight sensor port and check that the sensor is properly immersed.
  - Flush air bubbles from the tubing walls and chamber.
  - Check for and eliminate backpressure from the chamber.
- 3) Keep flow passing the DO sensor laminar and constant.
- 4) Measure and record DO at regular intervals throughout purging.
- 5) Check the stability of DO toward the end of purging.

- Stability criteria have been met when five consecutive readings made at regularly spaced intervals for three to five minutes are within 0.3 mg/L.
  - If the criterion is not met, lengthen the purge period and continue to record measurements at regularly spaced time intervals.
- 6) Report sample DO as the median of the final five DO readings recorded.
  - 7) 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 sensors 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) If necessary, 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.
  - 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 Groundwater in a Flow-Through Chamber

Measurements of groundwater conductivity should represent 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 of the water.
  - Use a calibrated thermometer.
  - After calibration, rinse the conductivity sensor and thermometer thoroughly with deionized or distilled water.
- 2) Install the conductivity sensor into the flow-through chamber.
    - Install chamber as close to the well as possible, and shield the system from direct sunlight.
    - Direct flow to the chamber after an initial discharge to waste to clear sediment from the sample line.
    - Release any air trapped in the chamber.
    - Agitate the conductivity sensor to remove air from the system until consecutive readings of conductivity are identical.
  - 3) During purging
    - Keep flow constant; and
    - Allow the sensors to equilibrate with groundwater temperatures for five minutes or more at the flow rate to be used for sampling.
  - 4) Measure conductivity and associated temperature at regular intervals during purging. Record the conductivity values and associated temperatures.
  - 5) Check the variability of the conductivity values toward the end of purging.
    - The stability criterion is met when five readings taken at regularly spaced intervals of three to five minutes or more are within 5% for waters with conductivities  $\leq 100 \mu\text{S}/\text{cm}$  and within 3% for waters with conductivities  $> 100 \mu\text{S}/\text{cm}$ .
    - If the criterion is not met, extend the purge period and continue to record measurements at regularly spaced time intervals, and record the difficulty in the field notes.
  - 6) Report conductivity.
    - Record the final five values.
    - Report the median value of the final five measurements as the sample conductivity.
    - If the values exceed the stability criterion, report the range of values and the median of the final five or more values.

## 6.4 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. Two pH buffer solutions are needed to properly calibrate the pH system. However, calibration using three buffer solutions provides a greater level of confidence in the calibration. Standard buffer solutions include pH 7, pH 4 and pH 10 buffer solutions.

- 1) Temperature equilibration of equipment
  - Not needed if using an automatic compensating meter.
  - Allow 15 to 30 minutes for the buffer solutions to adjust to the sample temperature.
  - Place buffer bottles in a bucket or bag and suspend them in a bucket or other container overflowing with water being pumped from the well.

- 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 pH 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 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 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 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 solution at known temperature and record the adjusted pH value.
  - Discard the used buffer solution.
  - Repeat steps 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 buffer solution.
  - Pour the third buffer solution into a container, allow the temperature to equilibrate and then discard the used buffer 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 buffer 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, before using.
- 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 Groundwater

Measurements must represent aquifer conditions. Measure the pH as close to the source as possible. Streaming potentials in the flow-through chamber can result in biased pH values. Make the final measurement in quiescent water.

- 1) Calibrate the pH instrument system on site.
  - After calibration, rinse the pH electrode and other equipment used with deionized or distilled water.
- 2) Install the pH monitoring system for sample measurement.
  - Install the chamber system as close to the well as possible, and shield the chamber and tubing from direct sunlight.
  - The electrode fill hole should be open to the atmosphere.
  - The reference junction should be entirely submerged.
- 3) During purging, keep flow constant and laminar, and allow the sensors to equilibrate with the groundwater for five minutes or more at the flow rate to be used for collecting samples.

- 4) Record pH values at regularly spaced time intervals throughout purging, and compare the variability with the stability criterion.
  - The criteria are met when five readings made at regularly spaced time intervals of three to five minutes or more are within 0.1 standard pH units or less.
  - If the criteria are not met, extend the purge period.
- 5) Measure and report the pH.
  - Divert the flow from passing into the flow-through chamber after recording the other field measurements.
  - Measure the sample pH in the chamber as soon as the water is still.
  - Take several readings to be sure that the system has stabilized.
  - Report the final value measured on a no-flow sample.
  - If stability is not met, record the range of values and report the median of the final five or more values observed.

#### **6.4.2.2 Subsample Measurement**

The pH measurements reported from bailed or other discrete samples must be carefully collected and documented.

- 1) Calibrate the pH system on site.
- 2) Draw off a subsample through a bottom-emptying device.
  - Collect three subsamples to check precision.
  - Rinse the sample bottle three times with sample.
  - If the samples need to be stored for a short time, or if several subsamples will be measured, collect sample aliquots in separate bottles, fill them to the brim, cap tightly and maintain them at ambient temperature until they can be measured.
- 3) Rinse the pH electrode, thermometer or ATC sensor, and measurement container thoroughly with deionized or distilled water.
  - Follow the deionized or distilled water rinse with a sample water rinse.
- 4) Immerse the electrode and thermometer or temperature sensor in the sample water, and allow at least 60 seconds for temperature equilibration.
- 5) Pour fresh aliquot of the sample water into the container with the electrode and thermometer or ATC sensor.
- 6) Measure and record the initial temperature.
- 7) Establish equilibrium between the electrode(s) and the sample by stirring slowly.
- 8) Record the pH and temperature measurements.
- 9) Repeat steps 6 through 9 with at least two fresh subsamples. Report the median values measured.
- 10) Rinse the electrode and thermometer or ATC sensor with deionized or distilled water.
- 11) Discard the used sample.

#### **6.5 Reduction-Oxidation Potential (REDOX)**

The determination of the reduction-oxidation potential of water should not be considered a routine determination. 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 or 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 qualitatively strong 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 manufacturer's recommendations for instrument warm up and operation.
  - If necessary, 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 2 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 3) 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 water.

**Table 2. 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 3. 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 in situ with a submersible instrument or use a flow-through system.

- 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) Select an in situ or closed system sampling method. 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) Take readings of the sample temperature and potential every few minutes for the first 15 to 20 minutes.
  - It is best to stop the flow of the sample while the reading is being taken to prevent streaming potential effects.
  - After 15 to 20 minutes, begin to record the time, temperature and potential in plus or minus millivolts about every 10 minutes. Continue until 30 minutes have passed from the initial measurement and until the measurements indicate a constant potential.
- 8) After the measurements have been completed for the day, rinse the electrode(s) thoroughly with deionized or distilled water.
- 9) Record all data and calculate Eh.

10) 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 is 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 4).
- 2) Insert a clean delivery tube into the titration cartridge.
- 3) Attach the cartridge to the titrator body.
- 4) Turn the delivery knob to eject a few drops of titrant.
- 5) Reset the counter to zero and wipe the tip.
- 6) Use a graduated cylinder or pipette to measure the sample volume.
- 7) Transfer the sample into a clean 250-mL Erlenmeyer flask.

- 8) Dilute to about the 100 mL mark with deionized or distilled water, if necessary.
- 9) 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).
- 10) 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.
- 11) Calculate and record mg/L CaCO<sub>3</sub> Phenolphthalein Alkalinity.
  - mg/L CaCO<sub>3</sub> Alkalinity = digits required x digit multiplier
- 12) 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).
- 13) 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).
- 14) Calculate and record mg/L CaCO<sub>3</sub> Total Alkalinity.
  - mg/L CaCO<sub>3</sub> = total digits required x digit multiplier

**Table 4. 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 the following table (Table 5).

**Table 5. Alkalinity relationships**

Result of Titration	Hydroxide Alkalinity Is equal to:	Carbonate Alkalinity Is equal to:	Bicarbonate Alkalinity Is equal to:
Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
Phenolphthalein Alkalinity = Total Alkalinity	Total Alkalinity	0	0
Phenolphthalein Alkalinity < ½ Total Alkalinity	0	2 x the Phenolphthalein Alkalinity	Total Alkalinity – 2 x Phenolphthalein Alkalinity
Phenolphthalein Alkalinity = ½ Total Alkalinity	0	Total Alkalinity	0
Phenolphthalein Alkalinity > ½ Total Alkalinity	2 x the Phenolphthalein Alkalinity - Total Alkalinity	2 x (Total Alkalinity - 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 the above table we see that:

- 1) The phenolphthalein alkalinity does not equal zero.
- 2) The phenolphthalein alkalinity does not equal total alkalinity.
- 3) The phenolphthalein alkalinity is not less than one half of total alkalinity.
- 4) The phenolphthalein alkalinity is not equal to one half of total alkalinity.
- 5) 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 Withdrawal

### 7.1 Sample Withdrawal Procedures

Flow should be constant and uninterrupted during purging and sampling. Regulate flow at the pump if possible.

- 1) Wearing latex or nitrile disposable gloves, check that the sample tubing is properly secured within the processing chamber.
- 2) Direct the sample flow through the sample tubing to the collection chamber immediately after the final field measurements have been recorded.

Note: The rate of flow for filling sample bottles should not exceed 500 mL/min for bottles 250 mL or greater in volume, and should not exceed 150 mL/min for bottles 40 mL or less in volume

- 3) If using a thief-type sampler, lower and raise the sampler smoothly at a constant rate, keeping the suspension line clean and off the ground.
  - A bailer or other thief-type sampler is not recommended for trace-element sampling.
  - Composite the bailed sample. Wilde et al., (1998e) discuss compositing methods in detail.

## 8 Sample Processing

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.
- Field-rinse as required.

Order:

- 1) organics
- 2) trace metals
- 3) separate treatment constituents and major cations
- 4) major anions
- 5) radiochemicals and isotopes

## 8.1 Field-Rinsing Procedures

- 1) Use filtrate for filtered samples and whole-water for raw samples. Use only 25 mL of filtrate for bottle rinse for the filtered sample.
- 2) Rinse twice with deionized water or distilled water (DIW or DW) onsite, followed by one field-rinse with the water to be sampled. DIW is preferred, but DW can be used. If DW is used, it should be noted.
- 3) Capsule filters 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.

## 8.2 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 safe guard against contamination of the sample by the plastic covering the work area, the bench or table can be covered with a sheet of aluminum foil to make a clean work surface. Ensure foil is removed before sampling for trace elements takes place.
- 2) Assemble necessary equipment and supplies on the work surface. Attach processing chamber cover (recommended but not mandatory) (See Appendix A for a photograph and parts list.)
- 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.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn the filter so the outlet is pointing up so that trapped air is forced out.



- Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Filter samples into 1-L amber glass bottles.
  - 9) 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.
  - 10) Label and chill immediately to 4°C or below without freezing.

If sampling only for organics, 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, changing gloves if necessary.

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

### 8.3 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 plastic sheet 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Field-rinse bottles.
  - Collect only 25 mL of water to be sampled.
  - Rinse two 500-mL bottles and discard rinse water to waste.
- 9) Collect sample filtrate.
- 10) Cap and place bottles in a corner of the collection chamber until filtering is complete. Once complete, transfer the bottles to the preservation chamber.
- 11) Uncap and add HNO<sub>3</sub> to the minor and trace element sample until pH < 2.0. Recap minor and trace element sample and label both bottles.

When 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, changing gloves if necessary.

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

#### **8.4 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 capsule filter or peristaltic pump (if using a thief-type sampler), can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a plastic sheet 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Field-rinse bottles.
  - Collect only 25 mL of water to be sampled.
  - Rinse bottle and discard rinse water to waste.
- 9) Collect sample filtrate in a 30-mL or 40-mL polyethylene bottle. Cap and label.

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

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

## 8.5 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 capsule filter or peristaltic pump (if using a thief-type sampler), can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a plastic sheet 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Field-rinse bottles.
  - Collect only 25 mL of water to be sampled.
  - Rinse bottle and discard rinse water to waste.
- 9) Collect sample filtrate immediately into a 250 mL field-rinsed, polyethylene bottle.

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

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

## 8.6 Radiochemicals

If the radiochemicals sample is the first sample to be collected then begin sample processing with step 1. If not, then move to step 3, changing gloves if necessary. Already completed steps, such as field-rinsing of the capsule filter or peristaltic pump (if using a thief-type sampler), can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a plastic sheet 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-ml vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Collect sample filtrate immediately into 1-L polyethylene bottles. Fill to shoulder.
- 9) Cap and place in corner of the collection chamber until filtering is complete. Once complete, transfer to the preservation chamber.
- 10) 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, changing gloves if necessary.

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

### 8.7 Stable Isotopes – <sup>18</sup>O/<sup>16</sup>O and <sup>2</sup>H/<sup>1</sup>H

If the <sup>18</sup>O/<sup>16</sup>O and <sup>2</sup>H/<sup>1</sup>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 capsule filter and peristaltic pump (if using a thief-type sampler), can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a plastic sheet 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Collect sample filtrate immediately into 20-mL vacu-tubes.

- 9) 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, changing gloves if necessary.

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

### **8.8 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 capsule filter and peristaltic pump (if using a thief-type sampler), can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a plastic sheet 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) 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.
- 9) 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, changing gloves if necessary.

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

## 8.9 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 capsule filter and peristaltic pump (if using a thief-type sampler), can be omitted. See Sections 8.10 and 8.11 for other methods.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a plastic sheet 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Collect sample filtrate immediately into 1-L amber glass bottles.
- 9) Cap and label sample. Move to the sample preservation chamber.
- 10) Uncap sample, add 1 or 2 scoopula scoops of cadmium acetate to water to precipitate CdS, 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, changing gloves if necessary.

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

## 8.10 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 capsule filter and peristaltic pump (if using a thief-type sampler), can be omitted. See Sections 8.9 and 8.11 for other methods.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a plastic sheet 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Collect sample filtrate immediately into 125-mL amber glass bottles.
- 9) Cap and label sample. Move to preservation chamber.
- 10) Uncap sample. Acidify sample to pH<2 with HCl. Add 1 or 2 scoopula scoops of barium chloride to water sample to precipitate BaSO<sub>4</sub>. 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, changing gloves if necessary.

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

### 8.11 Stable Isotopes – <sup>34</sup>S/<sup>32</sup>S in Sulphide and in Sulphate

This method can be used instead of the two methods listed above to collect <sup>34</sup>S/<sup>32</sup>S in sulphide and sulphate. If the <sup>34</sup>S/<sup>32</sup>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 capsule filter and peristaltic pump (if using a thief-type sampler), can be omitted.

- 1) Put on latex or nitrile disposable gloves. Cover bench or table with a plastic sheet 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.

- Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Collect sample filtrate immediately into 1-L amber glass bottle.
  - 9) Cap and label sample. Move to sample preservation chamber.
  - 10) Uncap sample. Add 1 or 2 scoopula scoops of cadmium acetate to water to precipitate CdS. Recap and store.
  - 11) Once precipitate has formed, filter sample, dry precipitate, place filter paper in a secure container and label it.
  - 12) Pour filtered water into 125-mL amber glass bottle and add 1 or 2 scoopula scoops of barium chloride to the water sample to precipitate BaSO<sub>4</sub>.
  - 13) 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, changing gloves if necessary.

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

### 8.12 Stable Isotopes - <sup>87</sup>Sr/<sup>86</sup>Sr

If the <sup>87</sup>Sr/<sup>86</sup>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 capsule filter and peristaltic pump (if using a thief-type sampler), 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Collect sample immediately in a 250-mL polyethylene bottle.
- 9) Cap and label the sample. Move the sample to preservation chamber.
- 10) Uncap sample. Acidify the sample to pH<2 with HNO<sub>3</sub>. 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, changing gloves if necessary.



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

### 8.13 Stable Isotopes – $^{11}\text{B}/^{10}\text{B}$

If the  $^{11}\text{B}/^{10}\text{B}$  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 capsule filter and peristaltic pump (if using a thief-type sampler), 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump to pump water through the filter. Field-rinse both the filter and the pump tubing.
- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Field-rinse the capsule filter.
  - Ensure sample line is full of sample and free of bubbles.
  - Keep a slow rate of flow through the filter.
  - Turn filter so outlet is pointing up so trapped air is forced out.
  - Stop as soon as the capsule filter is full of sample and all air in the capsule filter has been expelled.
- 8) Collect sample immediately in a 250-mL polyethylene bottle.
- 9) Cap 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, changing gloves if necessary.

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

### 8.14 Radiogenic Isotopes – $^{14}\text{C}$

If the  $^{14}\text{C}$  sample is the first sample to be collected, begin sample processing with step 1. If not, move to step 3, changing gloves if necessary.

- 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) If using a thief-type sampler and compositing device, field-rinse with the water to be sampled. Use a peristaltic pump and field-rinse the pump tubing.

- 6) Direct the sample flow through the sample line into the processing chamber.
  - Waste initial sample through chamber drain for the sample-line rinse.
  - Flow should not exceed 150 mL/min when filling 40-mL vials or 500 mL/min when filling larger bottles.
- 7) Collect sample immediately in a 1-L certified organics clean amber glass bottle to overflowing.
- 8) Cap sample and turn upside down to ensure no air bubbles are visible.
- 9) If air is trapped inside the sample bottle, discard water sample and repeat sampling procedure.
- 10) 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.
- 11) Label sample and chill immediately.
- 12) Once sampling is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater, PVC flexible tubing and filters.
- 13) Field-clean all equipment while equipment is still wet and before going to the next site.

## 9 Cleaning Procedures

### 9.1 Inorganic Sample Bottle Cleaning Procedures at the Laboratory (before heading to sample sites)

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

### 9.2 Organic Sample Bottle Cleaning Procedures

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

### 9.3 Sequence for Cleaning of Equipment Used to Sample for Organic and Inorganic Constituents

See Figure 7 for a flowchart of the steps involved in equipment cleaning.

#### 9.3.1 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.

#### 9.3.2 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 washbasin.

- 4) Rinse equipment thoroughly with water to remove detergent residue.

### **9.3.3 Check Equipment for Metal Parts**

### **9.3.4 Acid Rinse of Plastic Components**

- 1) Rinse with a 5% (v/v) HCl solution to remove organic films and inorganic deposits.
- 2) Using a peristaltic pump, rinse exterior of equipment and tubing.
- 3) With a sponge, scrub equipment surfaces.
- 4) Dispose of acid rinse fluid into a dedicated container.
- 5) Neutralization of the solution must be done prior to disposal of the acid rinse.
  - Neutralization can be accomplished through dilution with large volumes of water, or through addition of a neutralizing agent, such as lime or marble chips, to the acid rinse pail.
  - Disposal methods should be discussed with the local waste management authorities.

### **9.3.5 DIW or DW Rinse**

- 1) Place equipment into the DIW or DW washbasin.
- 2) Pump DIW or DW through equipment.
- 3) Pour discharge DIW or DW into the neutralizing container.
- 4) Continue rising until the rinse water pH is  $>6$  or the original DIW or DW pH is reached.

### **9.3.6 Methanol Rinse**

- 1) Change gloves if necessary.
- 2) Place cleaned equipment into the methanol rinse washbasin.
- 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 discharge methanol into an appropriate waste container.
- 8) Dispose of gloves.

### **9.3.7 Air Drying or 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.
- 4) Place equipment into storage containers.

## **10 Quality Control and Quality Assurance**

### **10.1 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, and sample blanks, replicate samples, spiked samples, reference samples and blind samples should be taken.

## **10.2 Blanks**

### **10.2.1 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.

Pesticide-grade Blank Water (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.

### **10.2.2 Equipment Blank**

An equipment blank is a water sample is processed under controlled conditions in the laboratory and 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; and
- 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.

#### **10.2.2.1 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-quality 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.

### 10.2.3 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.

### 10.2.4 Ambient Blanks

An ambient blank is used to answer the question, “To what extent could exposure of the sample to its environment contaminate the sample?” There are three different procedures to create an ambient blank. The choice of procedure is not as critical as documentation of which procedure was chosen.

#### 10.2.4.1 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 samples are being processed.
- 9) Cap blank samples.

#### 10.2.4.2 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.

#### 10.2.4.3 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.

### 10.2.5 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 preservative from the same lot number for the entire sampling trip for both the environmental and quality control samples.
- 4) Collect the field blanks in the same order, manner, and with the same quality control measures and checks associated with obtaining, processing, preserving and storing environmental samples.

### 10.3 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.

#### 10.3.1 Procedure for Processing Split Replicates

- 1) Wearing disposable, powderless gloves, and working 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.

### 10.4 Spiked 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.

## 10.5 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.

## 10.6 Blind Samples

With a blind sample, the submitter knows the source and chemical composition of the blind sample, but not 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.

## 10.7 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, available knowledge of the study area and analyte concentrations.

A general 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 five well sites minimally.
  - Replicates (2) taken at five well sites minimally.
- 2) Commonly present but not in all areas – trace elements, radionuclides and organic acids
  - Trace elements
    - Field blanks taken at between five and seven well sites minimally.
    - Three standard reference solutions analyzed per season.
    - Replicates (2) taken at between five and seven well sites minimally.
  - Radionuclides
    - Replicates (2) taken at between five and seven well sites minimally.
  - Organic acids
    - Field blanks taken at between four and five well sites minimally.
    - One trip blank per season
    - Field-spiked replicates (2) made up at four well sites minimally.

## 11 Conclusions

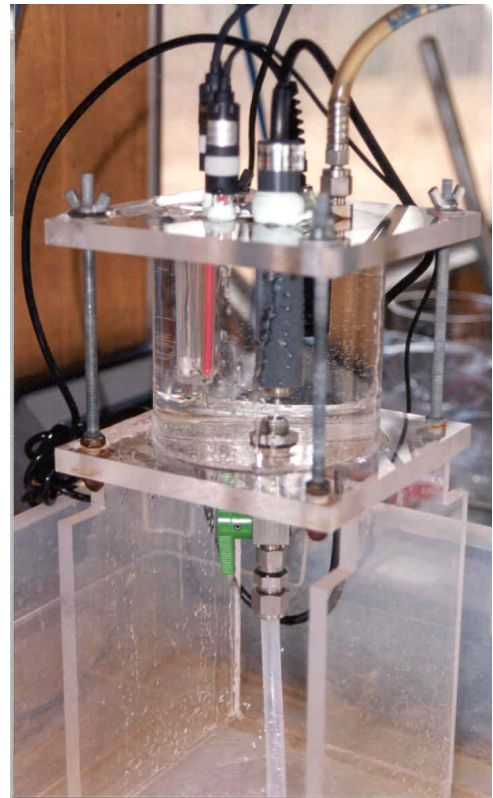
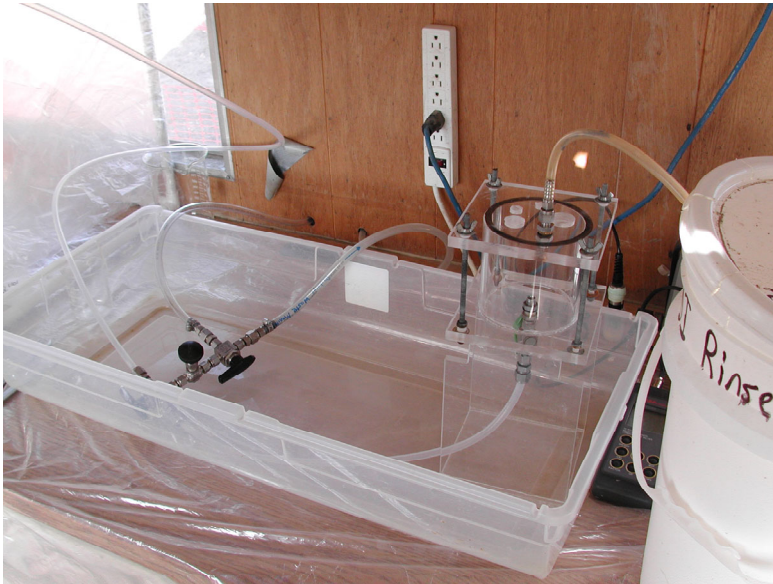
Groundwater sampling protocols are necessary to a sampling program. They ensure the same sampling steps are followed at each sample location. By using non-contaminating materials in the design of the sampling equipment, the risk of outside contamination is minimized. Careful calibration of field equipment 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 data set can be understood and accounted for. Changes in sampling methods can then be made to ensure that any abnormalities are addressed.

## 12 References

- Berg, E.L. 1982. Handbook for sampling and sample preservation of water and wastewaters. Environmental Protection Agency, Report No. EPA-600/4-82-029.
- Driscoll, F.G. 1986. Groundwater and wells - Second Edition. Johnson Filtration Systems Inc., St. Paul, MN, 1089 p.
- Garber, M.S. and Koopman, F.C. 1968. Chapter A1. Methods of measuring water levels in deep wells, United States Geological Survey, Techniques of Water-Resources Investigations of the United States Geological Survey, Book 8 Instrumentation.
- Koterba, M.T. Wilde, F.D. and Lapham, W.W. 1995. Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program – collection and documentation of water-quality samples and related data: United States Geological Survey, Open-File Report 95-399.
- Wilde, F.D. Radtke, D.B. Gibs, J. and Iwatsubo, R.T. (editors) 1998a. Chapter A1. Preparations for water sampling, United States Geological Survey, Techniques of Water-Resources Investigations, Book 9 Handbooks for Water-Resources Investigations, National Field Manual for the Collection of Water-Quality Data.
- Wilde, F.D., Radtke, D.B. Gibs, J. and Iwatsubo, R.T. (editors) 1998b. Chapter A2. Selection of equipment for water sampling, United States Geological Survey, Techniques of Water-Resources Investigations, Book 9 Handbooks for Water-Resources Investigations, National Field Manual for the Collection of Water-Quality Data.
- Wilde, F.D., Radtke, D.B. Gibs, J. and Iwatsubo, R.T. (editors) 1998c. Chapter A3. Cleaning of equipment for water sampling, United States Geological Survey, Techniques of Water-Resources Investigations, Book 9 Handbooks for Water-Resources Investigations, National Field Manual for the Collection of Water-Quality Data.
- Wilde, F.D., Radtke, D.B. Gibs, J. and Iwatsubo, R.T. (editors) 1998d. Chapter A4. Collection of water samples, United States Geological Survey, Techniques of Water-Resources Investigations, Book 9 Handbooks for Water-Resources Investigations, National Field Manual for the Collection of Water-Quality Data.
- Wilde, F.D., Radtke, D.B. Gibs, J. and Iwatsubo, R.T. (editors) 1998e. Chapter A5. Processing of water samples, United States Geological Survey, Techniques of Water-Resources Investigations, Book 9 Handbooks for Water-Resources Investigations, National Field Manual for the Collection of Water-Quality Data.
- Wilde, F.D., Radtke, D.B. Gibs, J. and Iwatsubo, R.T. (editors) 1998f. Chapter A6. Field measurements, United States Geological Survey, Techniques of Water-Resources Investigations, Book 9 Handbooks for Water-Resources Investigations, National Field Manual for the Collection of Water-Quality Data.

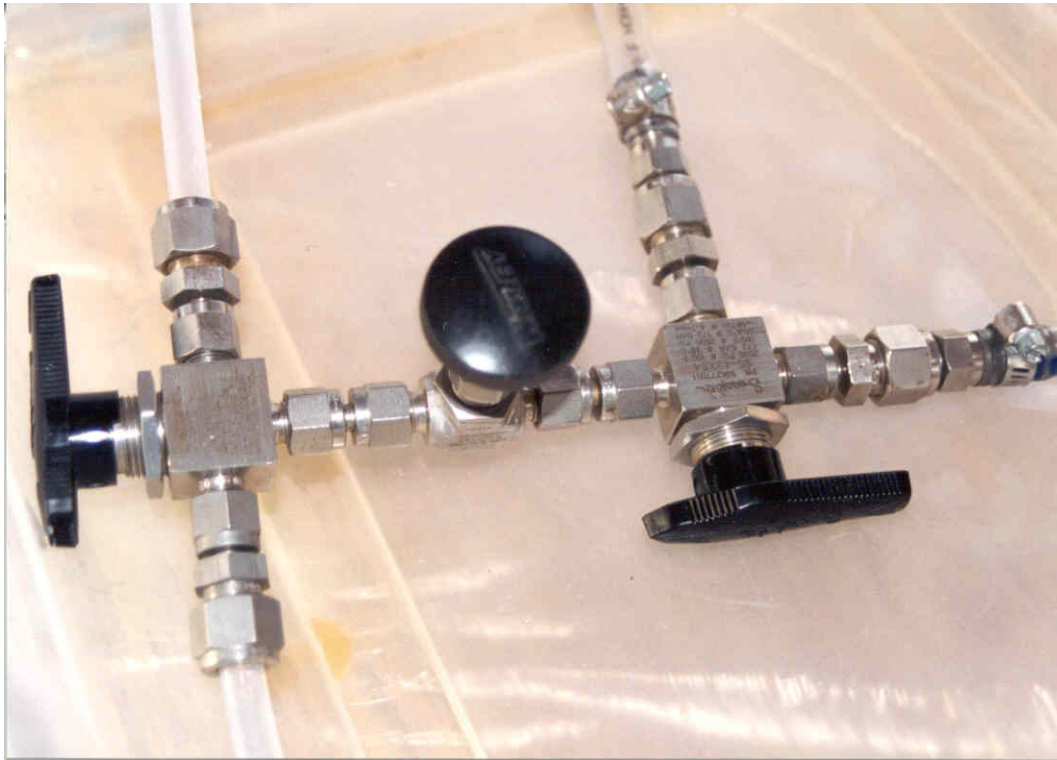


## Appendix A, Sample Equipment List – Flow-Through Cell







Supplies List	Supplier
Acrylic tube 10.8 cm OD, height ~12.7 cm	Industrial plastics supplier
Acrylic sheeting thickness ~0.635 cm for base, top and sides	Industrial plastic supplier
Acrylic sheet cement	Industrial plastic supplier
316 stainless steel 0.635 cm bulkhead fittings	Valve and fitting supplier
316 stainless steel 0.635 cm ball valve	Valve and fitting supplier
316 stainless steel 0.635 cm tubing fitting	Valve and fitting supplier
0.635 cm threaded rod	Hardware supplier
0.635 cm nuts, washers and wingnuts	Hardware supplier
12.7 cm diameter rubber gasket	Hardwater supplier

## Appendix A, Sample Equipment List - Sampling Manifold



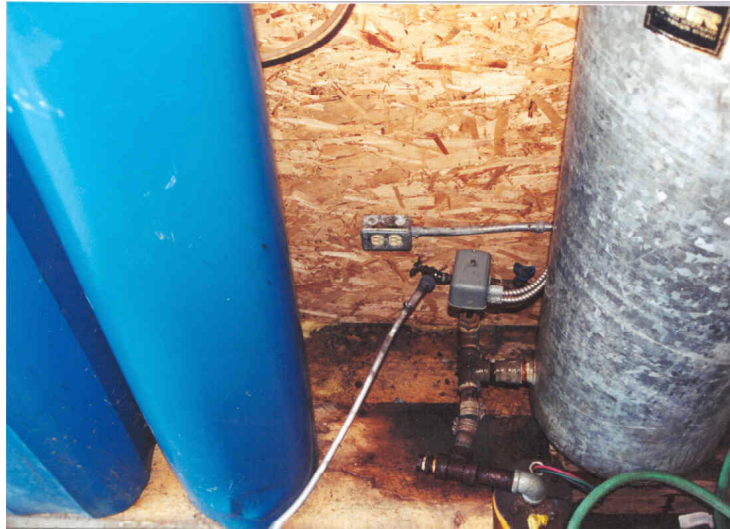
Supplies List	Supplier
5 x 0.635 cm Swaglock™ 316 stainless steel fittings	Valve and fitting supplier
4 x short pieces of 0.635 cm steel tubing 2 placed between the ball valves and the needle valve, 1 placed between the ball valve and the check valve and one placed between the check valve and the Swaglock™ fitting	Valve and fitting supplier
2 x 0.635 cm 316 stainless steel ball valves	Valve and fitting supplier
0.635 cm 316 stainless steel needle valve	Valve and fitting supplier
0.635 cm 316 stainless steel check valve	Valve and fitting supplier
0.635 cm 316 stainless steel tubing fittings	Valve and fitting supplier
~ 3 m of 0.95 cm OD Teflon™ tubing	Valve and fitting supplier
2 x hose clamps to attach incoming PVC tubing	Hardware supplier

## Appendix A, Sample Equipment List - Pumps and Sampling Devices

Sampling Device	Photos	
Grundfos Redi-Flo2 Pump		
Whale Pump		
Bennett Sampling Pump		
Point Source Bailer	Photo Not Available	

The sampling and purging system used to sample and purge wells and piezometers was selected based on considerations such as water level depth, site accessibility, well condition and construction, and budget. Each system has advantages and disadvantages that should be factored into its selection as the sampling and purging system for each particular site.

## Appendix A, Sample Equipment List - Equipment Necessary to Connect to Existing Water Supply Systems



Equipment	Supplier
Male and female hose fittings	Hardware supplier
Hose clamps	Hardware supplier
PVC flexible tubing 0.95 cm ID	Groundwater industry supplier
Garden hose to carry waste water	Hardware supplier

## Appendix A, Sample Equipment List - Field Determination Equipment



Meters and Equipment	Supplier
2 x Accumet™ Model AP15 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 HI9331 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

## Appendix A, Sample Equipment List - Sample Processing and Preservation



<b>Sample Processing and Preservation Chambers</b>	
<b>Equipment</b>	<b>Supplier</b>
~ 15 m of PVC pipe 1.3 cm OD	Hardware supplier
16 x 1.3 cm OD side outlet elbow PVC fittings	Hardware supplier
Roll of plastic sheeting	Hardware supplier
Tape	Hardware supplier
<b>Bottles and sampling containers</b>	
<b>Equipment</b>	<b>Supplier</b>
Nalgene 30 mL, 125 mL and 1 L high density polyethylene Boston round bottles	Scientific equipment supply company
500 mL polyethylene 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</b>	
<b>Equipment</b>	<b>Supplier</b>
Disposable capsule filter 0.45 µm	Scientific equipment supply company
Qualitative filter paper 2.5 µm	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

## Appendix A, Sample Equipment List - Cleaning Supplies

Equipment	Supplier
Sponges	Hardware supplier
Acid and solvent resistant basins	Hardware supplier
5 20 L storage pails with lids	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

## Miscellaneous Equipment

Equipment	Supplier
Graduated cylinders – 10 mL or 20 mL	Scientific equipment supply company
Disposable pipettes	Scientific equipment supply company
Latex or nitrile powderless disposable gloves	Scientific equipment supply company or hardware supplier
Parafilm	Scientific equipment supply company
Lab coats	Scientific equipment supply company
Safety glasses	Scientific equipment supply company or hardware supplier
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
Ground cloth	Hardware supplier
Electric water level tape (length will vary depending on expected hydraulic heads)	Groundwater equipment supply company
Cooler and ice	Hardware supplier
Distilled or deionized water	Analytical laboratory
Packing material (bubble wrap, sturdy cardboard boxes)	Hardware supplier
Tools – wrenches, screwdrivers, scissors, utility knives	Hardware supplier

## Appendix B, Field Forms - Record of Well Purging

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

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

WELL PURGING METHOD AND PUMP TYPE(describe): \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

TIME (hh:mm)	WATER LEVEL (m to c)	DRAW- DOWN (m)	TEMPER- ATURE (°C)	CONDUCT- TIVITY (µS/cm)	DISSOLVED OXYGEN (mg/L)	pH	e <sub>mf</sub> (mV)	APPROX PUMPING RATE





## 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		
Well purged and readings taken		
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		
-------------------	--	--

Additional comments:

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

## Appendix B, Field Forms - 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 ~2mL 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.