EUB/AGS Geo-Note 2002-11

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

Alberta Energy and Utilities Board
Alberta Geological Survey

AGS

Sampling of Formation Water 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

Published December 2002 by:
Alberta Energy and Utilities Board
Alberta Geological Survey
4th Floor, Twin Atria Building
4999 – 98th Avenue
Edmonton, Alberta
T6B 2X3

Tel: (780) 422-3767 (Information Sales)
Fax: (780) 422-1918

Web site: www.ags.gov.ab.ca

Contents

Tables

Figures

Acknowledgments

This publication is a compilation of protocols and methods for the sampling of formation water from oil and gas wells. 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; 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 gas wells completed in the Lower Cretaceous Viking Formation, Colony Member, Grand Rapids Formation, Clearwater Formation, Wabiskaw Member and McMurray Formation. Samples were also collected from wells completed in the Upper Devonian Nisku and Grosmont formations. 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 these formations within the Alberta Energy and Utilities Board (EUB)-designated Athabasca Oil Sands (in situ) Area.

The sampling protocols documented in this Geo-Note are the result of a subsequent literature review and of personal communication with a number of research scientists involved in formation-water sampling in the oil and gas industry. The protocols and methods include sections on: 1) site preparation and setup; 2) sampling for major, minor and trace elements, isotopes of O, H, C, B, S and Sr, organic acids, radionuclides, silica, Cl, Br and I; 3) quality control; and 4) site cleanup and equipment decontamination.

1 Introduction

Between 1999 and 2001, the Alberta Geological Survey (AGS) conducted a water-sampling program in northeastern Alberta. The purpose was to document baseline groundwater conditions in advance of extensive oil sands development in the area. In addition, formation water samples were collected from the Lower Cretaceous Viking Formation, Colony Member, Grand Rapids Formation, Clearwater Formation, Wabiskaw Member, McMurray Formation, and the Upper Devonian Nisku and Grosmont formations, in order to develop a high quality data set for these units. This project was jointly funded by the Government of Alberta through the Energy and Utilities Board, and by the Government of Canada through the Ministry of Western Economic Diversification under the Western Economic Partnership Agreement. This Geo-Note is one in a series of Geo-Notes detailing the results of the project work completed.

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

To document and standardize sampling methods, and to ensure 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., 1998 a to c). This reference was used to document methods and protocols for: 1) cleaning of equipment for water sampling; 2) processing of water samples; and 3) 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 the Handbook for Sampling and Sample Preservation of Water and Wastewater released by the United States Environmental Protection Agency (Berg, 1982). Collection procedures for isotopes of oxygen (O) and hydrogen (H) were based upon personal communications with Dr. B. Rostron of the University of Alberta. Collection procedures for radionuclides, chloride (Cl), bromide (Br) and iodide (I) were based upon personal communications with Dr. J. Duke from the University of Alberta. Water-sample collection procedures were based upon personal communications with Dr. B. Rostron from the University of Alberta and Dr. I. Hutcheon from the University of Calgary. Collection procedures for isotopes of carbon (C) and sulphur (S) were based upon personal communications with Dr. I. Hutcheon and S. Taylor from the University of Calgary and Dr. S. Grasby from the Geological Survey of Canada. Collection procedures for isotopes of boron (B) were based upon personal communications with S. Taylor and Dr. M. Wieser from the University of Calgary. Collection procedures for isotopes of strontium (Sr) were based upon personal communications with Dr. C. Holmden of the University of Saskatchewan.

This document has the following sections: preparation for sampling, sample processing, quality control and field equipment cleaning procedures. Within the section on water sample processing, each analytical sample type is treated separately and not as part of a coordinated sampling program. This means that for

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

2 Equipment List

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

3 Water Sampling Procedures

These protocols can be used to sample water from oil or gas wells. Certain factors should be taken into account when sampling from the different well types. A water cut of at least 40% is needed to easily separate oil from water without heating or the addition of de-emulsifiers. Alberta Energy and Utilities Board Guide 4 – Determining Water Production at Gas Wells states that water collected from a gas well with a total dissolved solids (TDS) value of less than 4000 ppm is water of condensation and not formation water. Both the EUB and Alberta Environment (AENV) define brackish water as having a TDS value in excess of 4000 mg/L. The water of condensation – formation water cutoff value is currently being reviewed to better define the difference between water of condensation and formation water. It is, therefore, uncertain if this water sample is truly representative of formation water or is water of condensation. TDS can be approximated using the relationship: TDS = AC, where C is the conductivity of the water sample, and A is a constant between 0.55 and 0.75. Water with a conductivity value below 7300 µS/cm could, therefore, represent water of condensation.

1) It is best to take the sample directly from the well head, if possible, not from separators or storage tanks.
   - A range of ¼, ½ and ¾-inch pipe thread reducers, L bends and fittings should be brought along.
   - A large adjustable wrench and a pipe wrench should also be brought.
2) It is best to sample wells that have no chemical injection.
3) Pools with water injection, N_2 floods, etc., should also be avoided if possible.
4) Fill an 8-L plastic container with hydrocarbon/water.
5) The water/oil mixture should separate immediately. If it does not, allowing the container to stand a few minutes to a few hours will often be sufficient for separation to occur.
   - De-emulsifier drops can be used if the emulsion refuses to break.
   - De-emulsifier acts on the oil phase only, so the water analyses should be unaffected.
   - De-emulsifier should be used only as the very last resort.
6) Filter the water sample to remove any fine particulate matter and oil droplets that would interfere with laboratory analyses.
   - Drain the water from the carboy into a plastic beaker. Care must be taken to avoid any excess hydrocarbon from draining into the beaker.
   - Place a 5 cm x 5 cm piece of glass wool in a funnel.
   - Pass the contents of the beaker through the funnel and glass wool into another plastic beaker.
   - This step is repeated 5 to 10 times until the water in the beaker is relatively free of hydrocarbon droplets and large particulate matter.
   - Document the number of times the water was passed through the glass wool.
   - Assemble the 0.45 µm filtration apparatus and connect the hand-vacuum pump to the filtration apparatus.
   - Pour the contents of the plastic beaker into the filtration apparatus.
   - The hand-vacuum pump should be pumped to a pressure of approximately 20”Hg.
7) The first filtered sample should be used for determining field parameters and alkalinity.

Remaining samples should be collected in a priority manner: trace metals, routine, organic acids, anions, silica, isotopes of oxygen, hydrogen, sulphur in sulphate and sulphide, boron and strontium, and radionuclides.

8) Collect the samples in the appropriate sample bottles and preserve according to the guidelines detailed below.
9) Measure the density of the formation water using hydrometers.
   - The field supplies should include hydrometers with the following ranges.
     0.940-1.010 gm/cm^3
     1.000-1.070 gm/cm^3
     1.060-1.130 gm/cm^3
     1.180-1.250 gm/cm^3
     1.240-1.310 gm/cm^3
   - Density can be measured to 0.0005 gm/cm^3.

4 Field Determinations

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

4.1 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.

4.1.1 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.

4.1.2 Measurement in Formation Water

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

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

4.2 Dissolved Oxygen (DO)

4.2.1 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 DO values be corrected for samples with high salinities.

4.2.2 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.

4.2.3 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.

4.2.4 Measuring DO in Formation Water

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) Measure and record DO.
3) Remove the sensor from the water and rinse with deionized or distilled water.

4.3 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.

4.3.1 Calibration

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

1) Inspect the instrument and the conductivity sensor for damage, and check the battery voltage.
2) Turn the instrument on and allow sufficient time for electronic stabilization.
3) Select the correct instrument scale for expected conductivity.
4) Select two conductivity standards that will bracket the expected sample conductivity.
5) Equilibrate the standard and the conductivity sensor to the temperature of the sample.
   - Allow 15 to 30 minutes for thermal equilibration.
6) Rinse the conductivity sensor, the thermometer and a container large enough to hold the sensor and thermometer.
   - Rinse the sensor, the thermometer and the container three times with deionized or distilled water.
   - Rinse the sensor, the thermometer and the container three times with the standard to be used.
7) Put the sensor and the thermometer into the rinsed container and pour in fresh calibration standard solution.
8) Measure water temperature to within 0.5^{o}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 solution 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 solution 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 solution.
    - Used to check instrument calibration over the range of the two solutions.
    - The difference from the first standard solution value should not exceed 5%.
    - If the difference is greater than 5%, repeat the entire calibration procedure.
14) Record calibration data for the second solution.

4.3.2 Measurement of the Conductivity of Formation Wwater

Measurements of formation-water conductivity should approximate aquifer conditions.

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

4.4 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.

4.4.1 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 (pH 7 buffer and either a pH 4 or pH 10). However, the use of three solutions ensures a more successful calibration.

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 the surface water source.
    - 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 that the pH buffer 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 buffer solution without further adjustment to the system.
5) Slope adjustment rinse
   - Rinse the electrode, thermometer or ATC sensor with deionized or distilled water.
   - Rinse a clean container, the electrode and thermometer or ATC sensor with the second buffer (pH 4 or pH 10) solution.
   - Pour the second buffer solution into a container; allow the temperature to equilibrate and then discard the buffer solution.
6) Slope adjustment. This step is automated in modern meters.
   - Pour a fresh portion of the second pH buffer solution into the container holding the electrode and thermometer or ATC sensor.
   - Stir slowly.
   - Measure the pH of the buffer solution; check the pH value of the solution on temperature coefficient tables and record the pH and temperature readings.
   - Adjust the slope to the value of the second pH buffer solution at known temperature and record the adjusted pH value.
   - Discard the used solution.
   - Repeat 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 solution.
   - Pour the third buffer solution into a container, allow the temperature to equilibrate and then discard the used solution.
10) Calibration range check
   - Pour a fresh portion of the third pH buffer solution into the container.
   - Stir slowly.
   - Measure the temperature of the buffer solution and check the temperature-adjusted pH value.
   - The pH should be within ±0.1 pH units.
   - If the system does not check over the entire range, recalibrate before measuring the sample pH.
   - Discard the used solution into a waste container.
   - Rinse the electrode and thermometer or ATC sensor with deionized or distilled water.

4.4.1.1 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 µS/cm.

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

4.4.2 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.

4.4.2.1 Measurement of pH in Formation Water

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

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

4.5 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 and higher.

Measurements of Eh are used to test and evaluate geochemical speciation models, particularly for suboxic and anoxic groundwater systems. Eh data can be useful for gaining insights on 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, to oxidized surface flow that becomes anaerobic after passing through stagnant organic rich systems, to mine drainage discharges.

4.5.1 Equipment Test Procedure

1) Follow the manufacturer's recommendations for instrument warm up and operation.

- Set the scale to the desired millivolt range.
- Record the type of reference electrode being used.

2) Unplug the fill hole. Shake the electrode gently to remove air bubbles from the sensing tip of the electrode and check the level of the filling solution.
   - The filling solution level must be at least 2.5 cm above the level of solution being measured.
   - Use only specified filling solutions.
3) Rinse the electrode, thermometer and measurement beaker with deionized or distilled water. Blot dry.
4) Pour ZoBell's solution into a measurement beaker containing the electrode and temperature sensor.
   - Add enough solution to cover the reference junction.
   - Allow 15 to 30 minutes for the solution and sensors to equilibrate to ambient temperature.
5) Stir slowly to establish equilibrium between the electrode(s) and the solution. Switch the meter to the millivolt function, allow the readings to stabilize (±5 mV) and record the ambient temperature and the millivolt value.
6) Look up the half-cell reference potential in Table 1 for the electrode being used. Add this value to the measured potential to obtain the Eh of ZoBell's at ambient temperature.
   - If the value is within 5 mV of the theoretical ZoBell Eh at the measured water temperature (Table 2) then the equipment is ready for field use.
   - If the value is not within 5 mV, check meter operation or electrode operation, and make sure the ZoBell solution has not expired or become contaminated.
7) Rinse off the electrodes and the thermometer thoroughly with deionized or distilled water.

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

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

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

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
Temperature (°C)	**Eh (mV)**

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

Temperature (°C)	Eh (mV)
30	418
32	416
34	407
36	402
38	397
40	393

4.5.2 Measurement of Eh

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

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

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

4.5.3 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.

4.6 Alkalinity

Alkalinity applies to the acid-neutralizing capacity of solutes in a water sample. It consists of the sum of the titratable carbonate and noncarbonate chemical species in a filtered water sample. Alkalinity is used routinely in checking the charge balance of a solution and to gain insights on the evolution of aqueous systems. Any substance in the water sample that reacts with the strong titrant acid can contribute to the

water's acid neutralizing capacity. Important noncarbonate contributors include organic ligands and ions of hydroxide, phosphate, ammonium, silicate, sulphide, borate and arsenate. Noncarbonate ionized contributors generally are not present in large enough quantities to affect alkalinity. Alkalinity is independent of exchange with carbon dioxide and other atmospheric gases. However, atmospheric gas exchange can alter concentrations of individual species, such as bicarbonate. Also, aeration of a sample during filtration can cause mineral precipitation on the filter, altering alkalinity, especially in water systems closed to the atmosphere under ambient conditions.

1) Filter the samples along with the other anion samples.
2) Fill and securely cap two 250-mL sample bottles with the sample to ensure there is enough sample to repeat the titration, to preserve the integrity of the second aliquot after the first has been opened, and to avoid losing the volume of sample needed to spillage.
3) Prevent agitation of the sample or prolonged exposure to air 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. See Table 3.
2) Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.
3) Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
4) Use a graduated cylinder or pipette to measure the sample volume. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100 mL mark with deionized or distilled water if necessary.
5) Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix. Four drops of Phenolphthalein Indicator Solution may be substituted for the pillow.
6) If the solution turns pink, place the delivery tube tip into the solution and swirl the flask while titrating with sulphuric acid. Titrate to a colourless end point. Record the number of digits required.
7) Calculate and record mg/L $CaCO_3$ phenolphthalein alkalinity.
   - mg/L $CaCO_3$ Alkalinity = digits required x digit multiplier
8) Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the flask and swirl to mix. Four drops of Methyl Purple Indicator Solution or Bromcresol Green-Methyl Red Indicator Solution can be substituted for the powder pillow.
9) Continue the titration with sulphuric acid to a light greenish blue-grey (pH 5.1), a light violet-grey (pH 4.8), or a light pink (pH 4.5).
10) Calculate and record mg/L $CaCO_3$ Total Alkalinity.
    - mg/L $CaCO_3$ = total digits required x digit multiplier

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

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (H_2SO_4)	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

4.6.1 Calculation of Alkalinity Relationships

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

Table 4. Alkalinity relationships

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 equal to Total Alkalinity	Total Alkalinity	0	0
Phenolphthalein Alkalinity less than one half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus two times Phenolphthalein Alkalinity
Phenolphthalein Alkalinity equal to one half of Total Alkalinity	0	Total Alkalinity	0
Phenolphthalein Alkalinity greater than one half of Total Alkalinity	2 times the Phenolphthalein Alkalinity minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

Example:

A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity. If we move through the result of titration column in Table 4 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.

Hydroxide alkalinity = 2 x 170 mg/L – 250 mg/L = 90 mg/L

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

Carbonate alkalinity = 2 x (250 mg/L – 170 mg/L) = 160 mg/L

Bicarbonate alkalinity is zero.

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

5 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 (most isotope samples are collected outside the processing chamber)

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

5.2 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., (1998b) 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. Cover bench or table with a sheet of aluminum foil to make a clean work surface.
2) Assemble necessary equipment and supplies on the work surface, and remove aluminum foil from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
3) Place bottles and other equipment into processing chamber.
4) Change gloves if necessary.
5) If necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Load the filter, wet with pesticide-grade blank water. Connect the filter assembly.

7) Change gloves if necessary.
8) Filter sample and pour into 1-L amber glass bottles.
9) If the filter becomes clogged, replace with a new filter.
10) 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.
11) Label and chill immediately to 4°C or below without freezing.
12) Disassemble processing chamber. Discard chamber cover, aluminum foil, gloves, filter and wastewate.
13) Field-clean all equipment while equipment is still wet and before going to the next site.

5.3 Major, Minor and Trace Elements

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

1) Put on latex or nitrile disposable gloves. Cover bench or table with a 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 necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) Field-rinse bottles.
   - Collect only 25 mL of water to be sampled.
   - Rinse bottle and discard rinse water to waste.
8) Collect sample filtrate in two 500-mL polyethylene bottles.
9) Cap and place in a corner of the collection chamber until filtering is complete. Once complete, transfer to the preservation chamber.
10) Uncap and add HNO_3 to the minor and trace elements sample until pH < 2.0. Recap minor and trace element sample and label both bottles.

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

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

5.4 Silica

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

1) Put on latex or nitrile disposable gloves. Cover bench or table with a 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 necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) Field-rinse bottles.
   - Collect only 25 mL of water to be sampled.
   - Rinse bottle and discard rinse water to waste.
8) Collect sample filtrate in a 30 or 40-mL polyethylene bottle. Label.

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

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

5.5 Anions

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

1) Put on latex or nitrile disposable gloves. Cover bench or table with a 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 necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) Field-rinse bottles.
   - Collect only 25 mL of water to be sampled.
   - Rinse bottle and discard to waste.
8) Collect sample filtrate immediately into a 250-mL field-rinsed polyethylene bottle.

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

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

5.6 Radiochemicals

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

1) Put on latex or nitrile disposable gloves. Cover bench or table with a 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 necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) Collect sample filtrate immediately into 1-L polyethylene bottles. Fill to shoulder.
8) Cap and place in corner of the collection chamber until filtering is complete. Once complete, transfer to the preservation chamber.
9) Uncap and add HNO_3 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.

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

5.7 Stable Isotopes – $^{18}O/^{16}O$ and $^{2}H/^{1}H$

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

1) Put on latex or nitrile disposable gloves. Cover bench or table with a 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 necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) Collect sample immediately into 20-mL vacu-tubes.
8) 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.

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

5.8 Stable Isotopes – $^{13}C/^{12}C$

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

1) Put on latex or nitrile disposable gloves. Cover bench or table with a 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 necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) 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.
8) Wrap the self-sealing top with parafilm and label. Do not allow any atmospheric 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.

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

5.9 Stable Isotopes – $^{34}S/^{32}S$ in Sulphide

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

1) Put on latex or nitrile disposable gloves. Cover bench or table with a 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 necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) Collect sample filtrate immediately into 1-L amber glass bottles.
8) Cap and label sample. Move to the sample preservation chamber.
9) Uncap the 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.

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

5.10 Stable Isotopes – $^{34}S/^{32}S$ in Sulphate

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

1) Put on latex or nitrile disposable gloves. Cover bench or table with a 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 necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) Collect sample filtrate immediately into 125-mL amber glass bottles.
8) Cap and label sample. Move to the preservation chamber.
9) Uncap the sample. Acidify sample to pH<2 with HCl. Add 1 to 2 scoopula scoops of barium chloride to water sample to precipitate $BaSO_4$. Recap and store.

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

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

5.11 Stable Isotopes – $^{34}S/^{32}S$ in Sulphide and in Sulphate

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

1) Put on latex or nitrile disposable gloves. Cover bench or table with a 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 necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) Collect sample filtrate immediately into 1-L amber glass bottle.
8) Cap and label sample. Move to the sample preservation chamber.
9) Uncap the sample. Add 1 to 2 scoopula scoops of cadmium acetate to water to precipitate CdS. Recap and store.

10) Once the precipitate has formed, filter sample, dry precipitate, place filter paper in a secure container and label it.
11) Pour filtered water into 125-mL amber glass bottle and add 1 to 2 scoopula scoops of barium chloride to the water sample to precipitate $BaSO_4$.
12) 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.

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

5.12 Stable Isotopes – $^{87}Sr/^{86}Sr$

If the $^{87}Sr/^{86}Sr$ 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 filter can be omitted.

1) Put on latex or nitrile disposable gloves.
2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
3) Place bottles and other equipment into processing chamber.
4) Change gloves if necessary.
5) If necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse the filter.
   - Keep a slow rate of flow through the filter.
7) Collect sample immediately in a 250-mL polyethylene bottle.
8) Cap and label. Move to preservation chamber.
9) Uncap the sample. Acidify the sample to pH<2 with HNO_3. Recap and store.

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 and filters.
11) Field-clean all equipment while equipment is still wet and before going to the next site.

5.13 Stable Isotopes – $^{11}B/^{10}B$

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

1) Put on latex or nitrile disposable gloves.
2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
3) Place bottles and other equipment into processing chamber.
4) Change gloves if necessary.
5) If necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.

6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
7) Collect sample immediately in a 250-mL polyethylene bottle.
8) 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.

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

5.14 Radiogenic Isotopes – ^{14}C

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

1) Put on latex or nitrile disposable gloves.
2) Assemble necessary equipment and supplies on the work surface, and remove plastic wrapping from pre-cleaned equipment. Attach processing chamber cover (recommended but not mandatory).
3) Place bottles and other equipment into processing chamber.
4) Change gloves if necessary.
5) If necessary, formation water can be prefiltered through glass wool to remove any hydrocarbon or suspended sediment.
6) Field-rinse filter.
   - Keep a slow rate of flow through the filter.
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.
   - If air is trapped inside the sample bottle, discard water sample and repeat sampling procedure
   - If no air is trapped inside the sample bottle, turn bottle right side up, wrap tape around cap and bottleneck to ensure no atmospheric gases enter sample.
9) Label sample and chill immediately.
10) Once filtering and preservation for all samples is complete, disassemble processing and preservation chamber. Discard chamber covers, gloves, wastewater and filters.
11) Field-clean all equipment while equipment is still wet and before going to the next site.

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

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

6 Cleaning Procedures

6.1 Inorganic Sample Bottle Cleaning Procedures

1) Put on powderless, disposable vinyl or latex gloves.
2) Fill each bottle about one quarter full with DIW or DW and cap.
3) Shake vigorously and decant DIW or DW.
4) Repeat the DIW or DW rinse two more times.

5) Fill each bottle half full with DIW or DW and cap the bottle.
6) Store in doubled plastic bags.

6.2 Organic Sample Bottle Cleaning Procedures

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

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

See Figure 1 for a flowchart of the steps involved in equipment cleaning.

6.3.1 Preparation

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

6.3.2 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 the equipment thoroughly with water to remove detergent residue.
5) Change gloves if necessary.

6.3.3 Check Equipment for Metal Parts

6.3.4 Acid Rinse of Plastic Components

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

6.3.5 DIW or DW Rinse

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

6.3.6 Methanol Rinse

1) Change gloves if necessary.
2) Place cleaned equipment into a clean stainless steel or solvent-resistant 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.

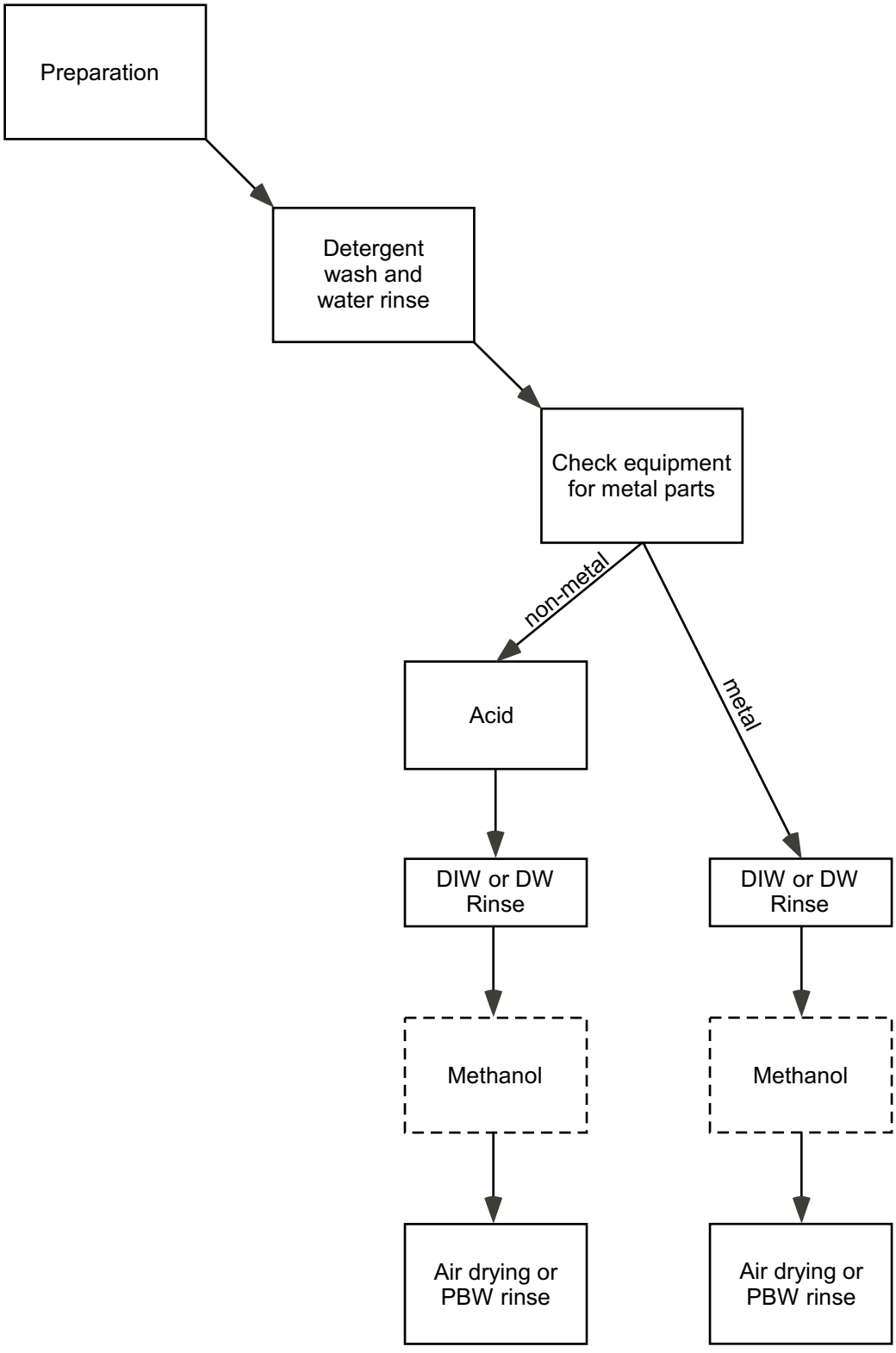

Figure 1. Field equipment cleaning procedures flowchart (modified from Wilde et al., 1998a).

6) Pour discharge methanol into an appropriate waste container.
7) Dispose of gloves.

6.3.7 Air Drying or Pesticide-Grade Blank Water 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.

Cover all equipment orifices with fluorocarbon polymer bags. Place equipment into sealable storage bags.

7 Quality Control and Quality Assurance

7.1 Goals in Quality Assurance

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

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

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

7.2 Blanks

7.2.1 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.

7.2.2 Equipment Blank

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

An equipment blank is required:

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

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

7.2.2.1 Procedure – Groundwater Samples Equipment Blank

Equipment system blank

- Put on disposable, powderless latex or nitrile gloves.
- Attach filter.
- Precondition the filter using the source water.
- Use IBW to test cleaning of inorganic contaminants.
- Use PBW to test cleaning of organic contaminants.
- Filter the required volume of source water 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.

7.2.3 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.

7.2.4 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.

7.2.4.1 Procedure 1

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

7.2.4.2 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.

7.2.4.3 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.

7.2.5 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.

7.3 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.

7.3.1 Procedure for Processing Split Replicates

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

7.4 Spike Samples

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

7.5 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.

7.6 Blind Samples

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.

7.7 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

8 Conclusions

Formation water 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. 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 any abnormalities are addressed.

9 References

Alberta Energy and Utilities Board (1990): Determining water production at gas wells; Alberta Energy and Utilities Board, EUB Guide 4.

Berg, E.L. (1982): Handbook for sampling and sample preservation of water and wastewaters; Environmental Protection Agency, Report No. EPA-600/4-82-029.

Wilde, F.D., Radtke, D.B. Gibs, J. and Iwatsubo, R.T. (ed.) (1998a): 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. (ed.) (1998b): 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. (ed.) (1998c): 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, Equipment List

Sampling Equipment

Equipment	Supplier
Plastic container ~ 8-L in volume	Grocery store, scientific equipment supply company
Range of ¼, ½ and ¾ inch pipe thread reducers, L bends, and fittings	Plumbing supply company
Tools (pipe wrenches, adjustable wrenches)	Hardware supply company

Formation water sampling set up

Cleaning Supplies

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

Sample Processing and Preservation

Bottles and sampling containers	
Equipment	**Supplier**
Nalgene 30-mL, 250-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
Filters and Filtering Equipment	
Equipment	**Supplier**
Disposable filter 0.45 μm	Scientific equipment supply company
Qualitative filter paper	Scientific equipment supply company
Hand vacuum pump	Scientific equipment supply company
Glass wool	Scientific equipment supply company
Funnel	Scientific equipment supply company

Preservation Materials

Equipment	**Supplier**
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

Field Determination Equipment

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

Miscellaneous Equipment

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

Appendix B, Field Forms - Site Checklist

Site location and description:_____
Date:_____

Activity	Y/N	Comments
Vehicle parked, signs setup if needed, safety check		
Equipment calibrated		
Sampling equipment setup		
Tubing and manifold systems connected		
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		
^{18}O and ^{2}H samples taken		
$^{13}C/^{12}C$ samples taken		
^{14}C sample taken		
$^{34}S/^{32}S$ for sulphide sample taken and preserved		
$^{34}S/^{32}S$ for sulphate sample taken and preserved		
$^{11}B/^{10}B$ sample taken		
$^{87}Sr/^{86}Sr$ 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 - Record of Water Sampling and Field Parameters

DATE:_____ RECORDED BY:_____

SITE ID:_____STATION NAME:_____OTHER ID:_____

WATER SAMPLING METHOD (describe):_____
_____
_____

TIME (hh:mm)	TEMPER-ATURE (°C)	CONDUC-TIVITY (µS/cm)	DISSOLVED OXYGEN (mg/L)	pH	e_{mf} (mV)

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_3. 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_3 to bring pH to < 2	Use filtered water.
^{18}O and ^{2}H	20-mL vacutainer tube	No	None	Use filtered water.
^{13}C in DIC	20-mL vacutainer tube pre-filled with ~2 mL ammoniacal SrCl	No	Ammoniacal SrCl already in vial	Use filtered water.
$^{34}S/^{32}S$ in sulphate (Method 1)	125-mL glass amber bottle	No	Dilute HCl and excess $BaCl_2$	Use filtered water. Store in a dark place
$^{34}S/^{32}S$ in sulphide (Method 1)	1-L amber glass bottle	No	Excess CdAc	Use filtered water.
$^{34}S/^{32}S$ 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.
$^{34}S/^{32}S$ in sulphate (Method 2)	125-mL amber glass bottle	No	Excess $BaCl_2$	Use filtrate from $^{34}S/^{32}S$ in sulphide (Method 2) procedure. Store in a dark place.
$^{87}Sr/^{86}Sr$	250-mL polyethylene bottle	No	Vial of dilute HNO3. One 5-mL vial per bottle.	Use filtered water.
$^{11}B/^{10}B$	250-mL polyethylene bottle	No	None	Use filtered water.
^{14}C	1-L amber bottle from the laboratory	No	None	Do not use filtered water. Fill bottle to overflowing.