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GUIDE TO WATER SAMPLING

by

Ruth L. Kroneman

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Earth Science Laboratory
University of Utah Research Institute
420 Chipeta Way, Suite 120
Salt Lake City, Utah 84108

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Introduction

The stability of natural water with respect to dissolved species has been the source of many publications and much study. No one method of sampling or sample handling is ideal for all types of water or analytical schemes. This guide is written with a two-fold purpose: one is to give a general understanding of the problems involved in collecting and preserving water samples; the second is to specify the treatment of samples necessary for analysis by the Earth Science Laboratory. Because of our instrument capability (an Inductively Coupled Plasma Emission Spectrograph with a 37 element array), our requirements are somewhat different from laboratories with only atomic absorption and UV-visible spectrophotometers.

Many factors affect solubility. Perhaps the two most important factors influencing gas solubility are temperature and pressure. Since it is difficult to maintain either of these conditions after the samples are collected, it is imperative to analyze for dissolved gasses at the time of collection. Mineral solubilities are affected primarily by pH, temperature, and concentrations of other dissolved species. Some of the dissolved elements and ions can be stabilized after filtration. The addition of acid is commonly used to prevent precipitation of sulfate and metals.

Collection and Sample Preservation

Cleanliness of equipment and storage bottles is very important. In the field, equipment that must be reused should be rinsed immediately after use with demineralized or distilled water. If sample water dries on the equipment or containers, they must be acid washed prior to reuse. Sample bottles (polyethylene or polypropylene) must be soaked for at least 2 hours, preferably overnight, in 20% HNO_3 then rinsed 3 times with demineralized water. After draining (dry or nearly dry), bottles should be capped tightly to prevent recontamination. This procedure must be followed for new as well as reused bottles. Polyseal caps, which provide a good airtight seal, cannot be soaked in acid but should be washed briefly in an acid bath and immediately rinsed several times with demineralized water. Molded polypropylene caps may be used if they give an airtight seal; this can be checked by capping an empty bottle and squeezing to check for air leakage. Polypropylene caps should be cleaned in the same manner as bottles. Contamination, particularly with Na, K, Ca or trace metals may occur if this procedure is not followed. Contamination may result as well if any sample collection or handling equipment is made of metal.

It should be decided prior to sample collection what analyses are needed. If these analyses include some which must be done immediately, field procedures or test kits should be acquired. These should always be tried in a laboratory prior to field use. Hach Chemical Co., Ames, Iowa makes a number of field kits, most of which are adequate. However, it is wise to try all kits or procedures on accurately prepared standards or known water samples. The expected range of sample concentrations should be tested. As an example,

the Hach alkalinity test kit gives instructions for two ranges. The kit instructions do not give an alkalinity figure at which the low-range test should be used. Assuming a possible error of one drop, it becomes apparent that a 10% error (1 grain/gallon) is likely at 10 grains/gallon, with the error increasing as alkalinity decreases. To minimize this error the low range (15 ml) procedure should be used for 10 grains/gallon or less. A one-drop error is then reduced to 0.4 grains/gallon. It is also wise to check the accuracy of volumes used in measuring devices.

If accurate temperature measurement is important, be certain the thermometer is accurate by checking all thermometers in the laboratory. Even mercury thermometers are not necessarily accurate. Do not use a "total immersion" thermometer for "partial immersion" application. If hot waters are to be sampled, a maximum indicating thermometer is usually necessary. A digital thermometer may be a good investment.

Accurate pH measurement is often difficult to obtain. An adequate understanding of your pH meter requires reading the manufacturer's instructions. A meter and electrode in good condition should not change (need calibration adjustment) by more than a few hundredths of a pH unit if checked over several days. Calibration should be done with 2 buffers. Nearly all meters have a calibration adjustment and a slope adjustment. Always use pH 7 buffer to adjust the calibration knob. Slope adjustment is done with a second pH standard, usually pH 4 or 10. Notice the drift before a stable pH is reached with the buffer solution. This drift is usually more lengthy in natural waters. The electrode should be rinsed with demineralized water and blotted dry before immersing in the buffer. A hydrous silica layer on the

glass sensing tip is necessary for proper operation and it can be damaged or destroyed by dry storage. Always fill the electrode end cap before putting it on the electrode. Water, KCl solution or pH 7 buffer may be used.

Filtration of water samples is normally done with 0.45 micron pore size filter. This may be very difficult if the water contains a considerable volume of suspended solids. Prefiltration with a coarser filter (5 or 1 micron) may be necessary. Filtration can be done with either vacuum or pressure. Vacuum filtration will usually degas the sample and may (especially if the sample is hot or muddy) concentrate the dissolved minerals due to evaporation. Pressure filtration may introduce O_2 or CO_2 from the air but is less likely to change the sample composition appreciably. Pressure filtration is therefore recommended, especially for alkalinity determination. The simplest apparatus is a large (50 to 100 cc) plastic syringe with a swinnex filter holder, available from most laboratory supply houses. Larger plexiglass pressure filters can be machined or purchased. These can use a valved rubber bulb, a tire pump, cylinder gas (N_2 or Ar) or a peristaltic pump for pressure.

Since there is some degree of uncertainty in all analytical procedures, it is a good practice to submit an occasional blind duplicate sample (same sample with different number or name designation). This gives a good indication of the quality of analytical work you are getting. Field procedures should also be repeated to test their repeatability.

Sampling Procedure

Instruction	Reason
1. Assemble filtering apparatus, test equipment, sampling container, storage bottles, etc. Calibrate pH meter. If water is pumped, allow time for the pump to flush before sampling.	Rapid handling & testing of water sample minimizes changes in composition.
2. If possible, measure pH and temperature in the spring, stream or other water source.	Changes caused by sampling are avoided.
3. Fill sample collection container with water sample, then discard.	To prevent contamination (from previous sample or any foreign material which might have gotten in the container) or dilution with residual distilled water.
4. To remove particulate matter, filter (pressure if possible) sufficient sample to fill necessary sample bottles, filling & capping bottles as quickly as possible. <u>SAMPLES MUST BE VISIBLY CLEAR</u> ; if not, check filter membrane and apparatus. Unclear samples must be refiltered <u>prior</u> to acidification. The following splits should be taken depending upon the analyses required. a) 60 ml (2 oz) acidified to 20% with reagent grade HNO ₃ <u>for ICP analysis</u> . This includes <u>37</u> elements. See appendix A. This is most easily done by measuring the true volume of the bottle in the lab and adding the measured amount of acid to the clean bottle. The bottle is then filled with filtered water at the sample location - full, but not overflowing.	Acidification of unfiltered water may dissolve particulate material. This would change water composition. Particulates also interfere with analyses (ICP, SO ₄ , TDS). This acid concentration has a two-fold purpose. (1) Both major cations including SiO ₂ and trace metals remain in solution with no apparent degradation of sample for a month or more. (2) This matrix matches the matrix of calibration solutions for the ICP and is necessary for accurate analysis.

We strongly recommend the use of variable volume dispenser bottles for acid addition. This is fast & repeatable. Please submit a sample of the HNO₃ for blank determination (60 ml conc.). If acid in bottle is discolored, discard.

b) 500 ml (8 oz) acidified to 1% with concentrated HCL. This split is used for SO₄ analysis. Acid can be added to bottles in the lab as done for split a. This bottle is also filled full but not overflowing with filtered H₂O.

1% HCL prevents SO₄ precipitation and is useful for gravimetric determination.

c) 500 ml (8 oz) filtered with no additive. This split is used for TDS, Cl, and F determinations.

Any additives would interfere with analysis.

This split may not be stable. If possible, it should be kept close to the temperature of the water at its source and delivered to ESL as soon as possible.

Since solubilities are affected by temperature, cold waters should be kept cold (an ice chest) but hot waters should not be refrigerated.

5. If isotope determination is required, a glass bottle of unfiltered, untreated sample should be collected.

Filtering may reduce isotope fractionation across the paper.

6. Collect additional sample for any field analyses necessary, i.e., alkalinity (pressure filtered only), dissolved O₂, H₂S, etc.

Carbonate mineral particles may react with alkalinity titration acid. CO₂ may be lost during vacuum filtration.

These analyses should be done as quickly as possible.

Samples may degas very rapidly.

7. Rinse all equipment in demineralized H₂O. A minimum of a squeeze bottle can be carried to sample location.

This prevents sample drying on equipment. Dried water residue may contaminate the next sample.

8. Check to be sure field notes and sample labels are accurate. Site location on topographic map or areal photo is best. Be sure acidified samples are labeled.

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APPENDIX A

ELEMENTS AND DETECTION LIMITS

ELEMENT	CONCENTRATION (PPM)
Na	1.25
K	2.5
Ca	0.25
Mg	0.5
Fe	0.025
Al	0.625
Si	0.25
Ti	0.125
P	0.625
Sr	0.013
Ba	0.625
V	1.25
Cr	0.05
Mn	0.25
Co	0.025
Ni	0.125
Cu	0.063
Mo	1.25
Pb	0.25
Zn	0.125
Cd	0.063
Ag	0.05
Au	0.1
As	0.625
Sb	0.75
Bi	2.5
U	6.25
Te	1.25
Sn	0.125
W	0.125
Li	0.05
Be	0.005
B	0.125
Zr	0.125
La	0.125
Ce	0.25
Th	2.5

APPENDIX B

POSSIBLE INFORMATION SUPPLIED BY GEOCHEMICAL FLUID STUDIES

- I Range in composition and homogeneity of hot fluids in overall system.
- II Subsurface temperatures and pressure.
- III Type of system: vapor vs. liquid dominated.
- IV Subsurface alteration associated with the fluids.
- V Origin of hot fluids, direction of fluid flow, turnover time of the fluid, and permeability.
- VI Mineral deposition potential of the fluid (scaling problems likely to be encountered).
- VII Natural heat flow.
- VIII Zones of upflow permeability.
- IX Fluid constituents which could have economic value (metal recovery).
- X Feasibility of reinjecting the fluid back into the system to eliminate local thermal and chemical pollution.

APPENDIX C

ACCURACY CHECKS

- I. CALCULATE THE CATION - ANION BALANCE.

TOTAL CATIONS EQUALS TOTAL ANIONS IN MEQ/ L

- II. ASSUME THAT THE WATER DOES NOT CONTAIN UNDETERMINED SPECIES WHICH CAN PARTICIPATE IN THE BALANCE, AND THAT THE FORMULA AND CHARGE OF ALL ANIONS AND CATIONS ARE KNOWN.

FOR MODERATE CONCENTRATIONS (250 - 1000 mg/l) ERROR = 1 to 2%
FOR CONCENTRATIONS LESS THAN 250 OR GREATER THAN 1000 mg/l,
ERROR = 2 to 10%.

- III. COMPARE TDS (CALCULATED) WITH THE TDS (MEASURED), THEY SHOULD AGREE TO WITHIN A FEW MG/L.