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SPECIAL TECHNIQUES FOR DETERMINING CHEMICAL PROPERTIES OF GEOTHERMAL WATER

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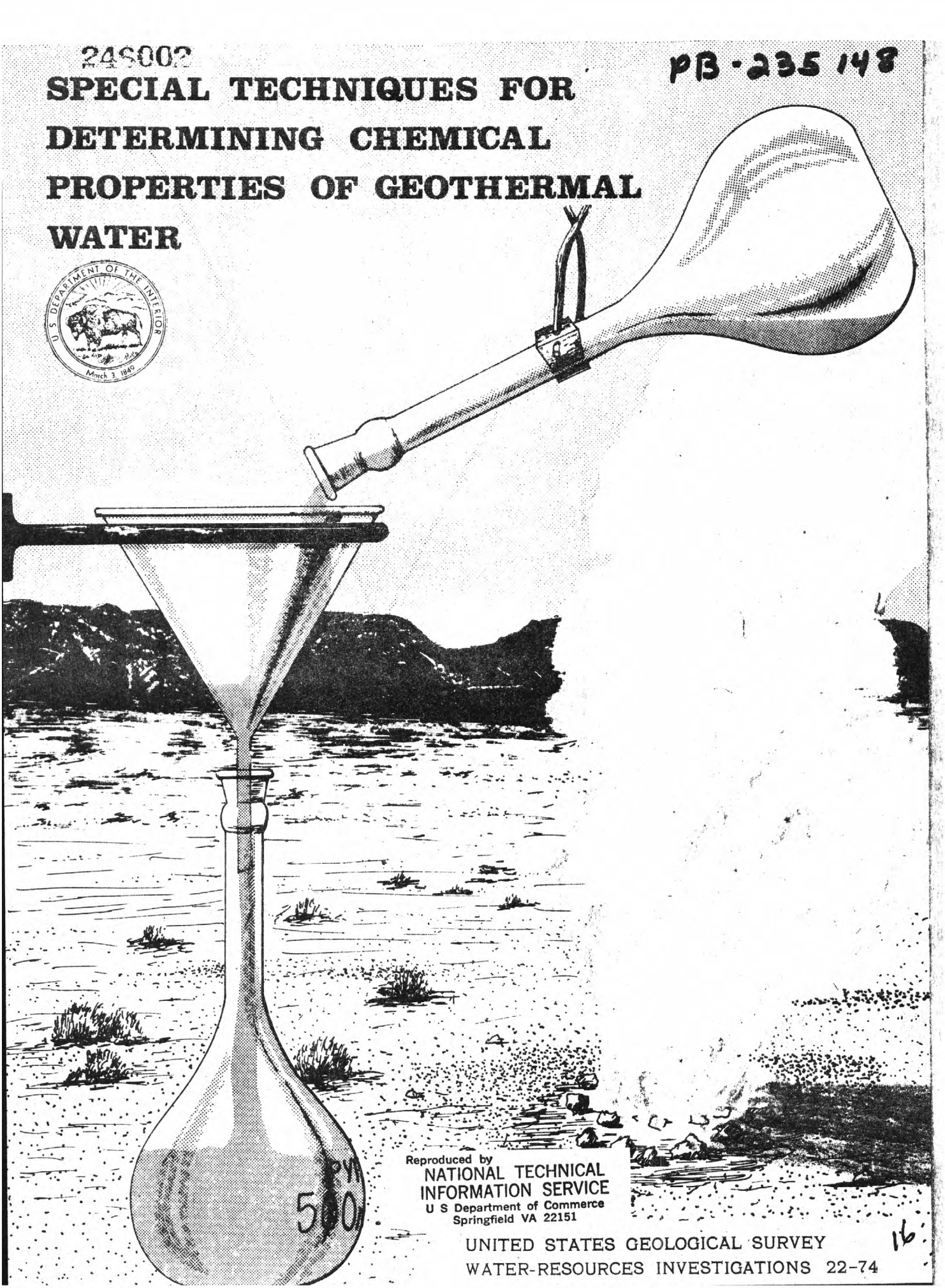

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SPECIAL TECHNIQUES FOR DETERMINING CHEMICAL PROPERTIES OF GEOTHERMAL WATER

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ABSTRACT

A reliable determination of the chemical composition of geothermal fluids may require special sampling and preservation techniques. A sample collected without pretreatment is usually adequate for the analysis of sodium, potassium, and chloride. Other constituents may require further treatment or even analysis in the field, depending on the data requirements. The collection and preservation methods described permit accurate results for 31 chemical variables, including major and minor chemical constituents.

INTRODUCTION

The purpose of sampling and analysis of a natural fluid is to determine the properties of the fluid itself in its natural state. Some constituents in natural fluids are unstable and change with time. The changes result from the difference in conditions within the natural environment before sampling compared to those within the sample container in storage. Changes in temperature and partial pressures of gases, especially oxygen, carbon dioxide, and hydrogen sulfide are particularly likely to occur. Experience has shown that plastic bottles are permeable to oxygen as shown by continued oxidation of iron from ferrous to ferric in tightly closed plastic sample bottles. Plastic sample bottles are also permeable to hydrogen sulfide, as shown by the odor in storage cabinets containing tightly capped plastic bottles of samples of water containing hydrogen sulfide. Some constituents, such as sodium, potassium, and chloride, are usually stable and show no change upon storage. Sulfate is also stable in dilute samples in the absence of hydrogen sulfide.

Depending upon the purpose and nature of the study, changes in constituents upon collection and storage of samples may or may not be a problem. No one sample collection procedure will be satisfactory for all purposes. The information needed for a particular study and the desired accuracy should be established first; then appropriate sampling techniques should be selected. This paper suggests sample treatment and field analysis techniques appropriate for minimizing errors that may result from changes in water samples between time of collection and time of analysis. Methods for analysis of the samples in the laboratory are given in standard reference publications (Brown and others, 1970, and American Public Health Association, 1971).

STABILITY OF CONSTITUENTS

The most commonly observed changes in untreated samples are in pH, iron, manganese, bicarbonate, ammonia, hydrogen sulfide, calcium, and sulfate. Silica concentrations in excess of 100 mg/l (milligrams per liter) may lead to difficulties owing to precipitation and polymerization. Polymeric silica is not reactive in the ammonium molybdate method that is often used for laboratory determination of silica.

The changes in sample composition result from loss of carbon dioxide to the air space, oxidation and precipitation of iron and manganese, oxidation of hydrogen sulfide to sulfate, oxidation of ammonia, loss of calcium ion as calcium carbonate precipitates, and precipitation of silica. Waters inoculated with diatoms may also lose silica. Once a precipitate forms, there is no accurate way to restore

the initial composition of the solution. Constituents that will probably be unaffected by storage include sulfate (if no hydrogen sulfide was originally present), lithium, sodium, potassium, magnesium, fluoride, chloride, bromide, iodide, and boron.

SAMPLE TREATMENT AND FIELD ANALYSIS

Samples for determination of stable constituents require no pretreatment. A sample of adequate size, usually 2 liters, is collected in a carefully cleaned bottle, generally of glass or polyethylene. The bottle should be rinsed with the source water and then filled, leaving an air space for expansion, tightly stoppered, and designated Ru (raw, untreated).

Samples for determination of iron, manganese, calcium, and magnesium should be filtered and acidified at the time of collection, preferably with hydrochloric acid. Nitric acid and sulfuric acid cause interferences in analyses. Iron may be present as fine particles of ferric hydroxide, some of which pass 0.45μm (micrometer) filters but not 0.1μm filters. To maximize the probability (although not to make certain) of obtaining only the iron in solution, 0.1μm or finer filters should be used. Lightweight filter kits using air pressure have been found useful for field filtration. The filtration rarely takes as much as 15 minutes. A volume of 200 ml (milliliters) of filtrate acidified to pH 2 as indicated by pH paper is adequate for determining these cations by direct aspiration in the atomic absorption spectrophotometer.

If results of a high degree of accuracy are required, several precautions must be taken in the field to insure an adequately preserved sample for laboratory analysis. Polyethylene bottles with polyseal caps are recommended as sample containers. The bottles prior to use should be rinsed first with 10 percent nitric acid and second with several washings of distilled deionized water. A filtering apparatus using compressed nitrogen and a 0.1μm or 0.45μm membrane filter is preferred. The apparatus should be rinsed with distilled deionized water immediately prior to use. The first liter of filtered sample is used to rinse the collection bottles and is discarded. One liter of sample is then filtered, collected, and designated Fu (filtered, untreated) for anion analysis. One liter of sample is also filtered, collected, and acidified with high purity acid to a pH of approximately 1.5 as indicated either by pH paper or a pH meter and designated Fa (filtered, acidified) for cation analysis. Complete information on sample sizes recommended for various constituents is given in the table at the end of the paper. For trace element analysis in the part per billion range a set of more rigorous procedures is needed and will not be covered here.

The choice of acid for the acidification step is very important because several of the analyses performed in the laboratory are subject to interferences from these acids. Hydrochloric acid interferes with the analysis of silver and lead because insoluble chlorides may be formed. Hydrochloric acid free from metal contaminants is not readily available. Sulfuric acid interferes with the analysis of calcium and magnesium and some of the heavy metals. Nitric acid interferes with the analysis of strontium and calcium. However, nitric acid is the acid of choice for the heavy metal analyses because it is readily available at high purity, all metal nitrates are soluble, and it is an oxidizing acid. It is recommended that the sample for calcium and strontium analysis be acidified with hydrochloric acid and the sample for heavy metal analysis be acidified with nitric acid. Therefore, if a 1-liter sample is filtered and acidified with nitric acid for heavy metals, an additional 100 ml sample should be filtered and acidified with hydrochloric acid. If only iron, manganese, calcium, and magnesium are needed, filter and acidify two 100 ml bottles, one with hydrochloric acid and one with nitric acid. Each bottle should be labeled with the type of acid used for acidification.

If the water is expected to contain a high concentration of silica, a 1:10 dilution made in the field is desirable, as polymers may form in the concentrated sample. Ninety ml of deionized water is measured accurately and placed in a 125 ml plastic bottle prior to going into the field. At the sample site 10 ml of the sample is pipetted into the prepared bottle.

Field determination of pH and alkalinity

To obtain reliable values, pH and bicarbonate must be determined in the field (Barnes, 1964). For normal waters, two pH buffers are put in the cup of a combination electrode, or other suitable container, each is brought to the temperature of the water source, and the meter is calibrated. The stepwise procedure is:

1. Put pH 7 buffer in cup and immerse cup electrode in water source.

2. When pH reading is steady, use calibrate knob to adjust meter to pH 7.00.

3. Rinse cup, add pH 4 buffer and immerse cup electrode in water source.

4. When reading is constant, use temperature knob on pH meter to adjust meter to pH 4.00. The meter is now direct reading at temperatures near 25°C. In any event, record the observed pH of the pH 4 buffer so true pH values may be calculated later.

5. Rinse electrode and immerse in water source.

6. Record pH when reading is steady. The indicated pH of the 4 and 7 buffers and the pH of the water and the temperature are all needed for calculation of the true pH.

7. Fill buret with standard acid (usually 0.05 N H_2SO_4) for bicarbonate titration.

8. While pH electrode is immersed in water, pipet an aliquot (usually 100 ml) of water into a beaker. Add three drops methyl purple.

9. Transfer electrode to beaker. The pH of the aliquot will almost always be different from the pH of the water source owing to trivial losses of carbon dioxide. This will not affect the titration of bicarbonate significantly.

10. Run acid into beaker while stirring until indicator changes to gray (pH = 5.1).

11. Record at least three pairs of acid volumes and pH readings from the color change through the range to 1 full pH unit below the color change.

Bicarbonate and carbonate will be computed from a titration curve using the data pairs, the temperature, and the pH of the buffers and the water.

For hot springs there should be two pH calibrations, one in the spring (pH of water and two buffers) and one at ambient temperature (pH of water and two buffers, and titration data). The pH of the spring is computed from the high temperature data and the bicarbonate and carbonate from the low temperature data.

Field determination of ammonia

Ammonia can be determined in the field, using a millivolt meter or pIon meter with specific ion electrodes. Additional equipment and reagents needed include 1, 10, and 100 mg/l NH_3 standards (100 ml each), a small bottle of 10 N NaOH, and four graduated plastic beakers. The procedure is:

1. Put a measured volume of unknown into a beaker (usually 25 ml).

2. Add 10 N NaOH to sample, at the rate of 1 ml NaOH/100 ml sample (one drop $\sim$ 0.05 ml).

3. Immediately place electrode in the solution. Set meter to determine millivolts. Measure sample, recording millivolts.

4. Repeat the above steps with standards, measuring millivolts of the most dilute standard first.

5. Read mg/l ammonia of sample from calibration curve prepared from standards.

Direct reading ammonia scales are not recommended because the required amplification makes the meter unstable under field conditions.

Extraction of aluminum

Aluminum must be extracted from samples in the field. The authors know of no way to store water samples and get reliable aluminum-in-solution results. Data on aluminum in solution are required for studies of the reactions of aluminosilicates.

Filter each sample immediately after collection through a 0.1µm membrane filter to remove coarse particulate matter. Extract aluminum immediately upon filtration if only monomeric or readily reactive polymeric forms are to be determined. For total aluminum in the filtered sample acidify to pH 2 and allow to stand about 2 weeks to convert the larger polynuclear aluminum species to a more reactive form.

Prepare a series of standards containing 0, 5, 10, and 20µg (micrograms) Al^{+3} in 400 ml distilled, deionized water. Carry standards through the entire procedure. Detection limit is approximately 2 µg/l (0.002 mg/l). Transfer 400 ml of a sample containing less than 20 µg Al^{+3} and less than 0.4 mg Fe to a 500 ml separatory funnel. Add 10 to 15 drops of phenol red indicator and 2 ml of 5 percent 8-hydroxyquinoline. Swirl to mix. Raise the pH to about 8 by adding ammonium hydroxide dropwise, while swirling to mix, until the solution turns red. Immediately add 5 ml buffer solution and 15 ml methyl isobutyl ketone (MIBK). Shake vigorously for at least 10 seconds but no more than 30 seconds if only dissolved and readily reactive species of aluminum are to be determined. Allow the phases to separate. Drain off the aqueous phase and discard. Collect the MIBK extract, stopper tightly, refrigerate, and save for the atomic absorption measurement of aluminum.

If a greenish-black precipitate forms with 8-hydroxyquinoline as the pH is raised, the sample probably contains a large amount of iron. Discard the sample and start with a new 400 ml aliquot. Add 5 ml of 20 percent hydroxylamine hydrochloride, 5 ml of 1 percent 1,10-phenanthroline, adjust the pH to about 4, and swirl to mix. Allow the sample with added reagents to stand at least 30 minutes to reduce the iron from

ferric to ferrous and continue with the procedure beginning with the addition of the ammonium hydroxide indicator. If the orange-red color of the ferrous phenanthroline complex tends to mask the red end point of the phenol red indicator, a pH meter equipped with a combination electrode may be used to monitor the pH during the addition of the ammonium hydroxide.

Preservation of sulfide

Sulfide should be determined in the field, but for those who find this impossible, the following procedure may be used for preservation of the sulfide for periods of less than 24 hours.

Reagents:

∿0.8 N zinc acetate: Dissolve 17.6 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in deionized water and dilute to 100 ml with deionized water. Place in dropping bottle (20 drops = 1 ml).

∿1 N sodium hydroxide: Dissolve 4 g NaOH in deionized water and dilute to 100 ml with deionized water. Place in dropping bottle (20 drops = 1 ml).

Collect two 100 ml portions of filtered untreated sample in separate containers. To each container immediately add 1 ml 0.8 N $Zn(C_2H_3O_2)_2$ solution followed by 1 ml 1 N NaOH solution. Swirl the bottles and wait for a precipitate to form. The solution must be analyzed within the next 24 hours. One ml of 0.8 N $Zn(C_2H_3O_2)_2$ will preserve as much as 270 mg/l H_2S.

Field determination of sulfide

Reagents:

∿0.8 N zinc acetate

∿1 N sodium hydroxide

Hydrochloric acid, concentrated

0.01 N iodine (standardized against thiosulfate)

0.01 N sodium thiosulfate, standard solution of known normality (standardized against potassium iodide)

Starch solution: Dissolve 1 g soluble starch in 2 ml hot deionized water and dilute to 100 ml with hot deionized water. Add 1 ml chloroform as a preservative.

Procedure:

Prepare a blank of 100 ml deionized water and carry it through the determination with the sample. Pipet a volume of filtered, untreated sample (100 ml maximum) into a 250 ml disposable plastic beaker and adjust the volume to approximately 100 ml with deionized water. Immediately add 1 ml 0.8 N $Zn(C_2H_3O_2)_2$ and then 1 ml 1 N NaOH solution. Swirl the beaker and wait for a precipitate to form. The solution may be kept at this point and run within the next 24 hours. If the temperature of the sample is higher than 25°C, let the sample cool in the open beaker until 25°C is reached (a cold water bath may be used) before continuing the determination. Add 10 ml concentrated HCl followed immediately by 10.0 ml 0.01 N I_2. Place the beaker on the magnetic stirrer and titrate the excess iodine (yellow color) with 0.01 N $Na_2S_2O_3$, adding approximately 1 ml of starch when the color has decreased to a pale yellow color. Continue titrating until the blue starch color has disappeared (this color will return upon standing owing to air oxidation). If no iodine is liberated from the acidified sample (no yellow color), prepare a smaller sample volume or a dilution of the sample. For calculation of mg/l hydrogen sulfide, record the number of milliliters of sodium thiosulfate used for the sample and for the blank and the normality of the sodium thiosulfate solution.

Calculations:

$$\text{Mg/l } H_2S = \frac{1{,}000}{\text{ml of sample taken}} \times 17.04 \times N\ Na_2S_2O_3 \times \left(\begin{matrix} \text{ml blank} \\ \text{titrant} \end{matrix} - \begin{matrix} \text{ml sample} \\ \text{titrant} \end{matrix} \right).$$

Size of sample required

Sample sizes cannot be arbitrarily specified. The volumes listed in table 1 are only an approximate guide. If the sample is highly concentrated much smaller volumes may suffice for some determinations depending on the necessity for dilutions. If the sample is relatively dilute, larger volumes will be needed, never smaller.

Table 1.--Guidelines for analyses performed in the laboratory

Constituent	Volume[1/]	Detection limit using only this volume	Method
pH	20 ml Ru or Fu	-	Meter
Specific conductance	25 ml Ru or Fu	0.1 μmho	Meter
Alkalinity as HCO_3	50 ml Ru or Fu	1 mg/l	Automatic titration
H_2S	200 ml Ru or Fu	.5 mg/l	Titration (Iodine-thiosulfate)
NH_4(N)	25 ml Ru or Fu	.1 mg/l	Specific ion electrode
SiO_2	25 ml Fu	10 mg/l	Atomic absorption
SiO_2	50 ml Fu	.1 mg/l	Colorimetric (molybdate blue)
Na	25 ml Fa or Ru or Fu	.1 mg/l	Atomic absorption
K	25 ml Fa or Ru or Fu	.1 mg/l	Do.
Ca	25 ml Fa	.1 mg/l	Do.
Mg	25 ml Fa	.1 mg/l	Do.
Cl	200 ml Fu	1.0 mg/l	Specific ion electrode titration
Cl	150 ml Fu	10 mg/l	Mohr titration
SO_4	100 ml Fu	1.0 mg/l	Colorimetric (thorin)
F	20 ml Fu	.1 mg/l	Specific ion electrode
B	25 ml Fu or Fa or Ru	.02 mg/l	Colorimetric
Sr	25 ml Fa	.1 mg/l	Atomic absorption
Li	20 ml Fa or Fu or Ru	.01 mg/l	Do.

Table 1.--Guidelines for analyses perfomed in the laboratory--Continued

Constituent	Volume[1/]	Detection limit using only this volume	Method
Cs	20 ml Fa or Fu or Ru	0.1 mg/l	Atomic absorption
Rb	20 ml Fa or Fu or Ru	.01 mg/l	Do.
As	20 ml Fa or Fu or Ru	5 mg/l	Do.
Sb	20 ml Fa or Fu or Ru	.1 mg/l	Do.
Heavy metals			
Ag	20 ml Fa	.02 mg/l	Atomic absorption
Au	20 ml Fa	.1 mg/l	Do.
Cd	20 ml Fa	.01 mg/l	Do.
Co	20 ml Fa	.05 mg/l	Do.
Cu	20 ml Fa	.02 mg/l	Do.
Fe	20 ml Fa	.05 mg/l	Do.
Mn	20 ml Fa	.01 mg/l	Do.
Ni	20 ml Fa	.05 mg/l	Do.
Pb	20 ml Fa	.1 mg/l	Do.
Zn	20 ml Fa	.01 mg/l	Do.

[1/] Ru = raw untreated

Ra = raw acidified

Fu = filtered untreated

Fa = filtered acidified

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