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PREFERRED METHODS OF ANALYSIS FOR CHEMICAL TRACERS IN MODERATE- AND HIGH-TEMPERATURE GEOTHERMAL ENVIRONMENTS

by

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December, 1984

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DISCLAIMER

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TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

INTRODUCTION

The collection and analysis of fluid samples have been important components of the hydrothermal injection research program sponsored by the Department of Energy at the Raft River, Idaho and East Mesa, California geothermal fields (Wright et al., 1984). In order to help quantify various physical and chemical parameters of a geothermal reservoir, we have been using the injection-backflow (huff-puff) technique as a tool to gather reservoir data. During injection-backflow tests, fluids spiked with chemical tracers have been injected into the geothermal reservoirs and then recovered after varying lengths of time. The concentrations of natural and artifical tracers contained in the recovered fluids provide basic data on the percentage of injectate that is recovered as a function of recovered volume (Capuano et al., 1983) and, from such mixing data estimates of the hydrologic properties of the reservoir can be made (Russell et al., 1983).

Chemical tracers are also used to detect breakthrough of fluids into one well that have been previously injected into a different well (Horne, 1982; Gudmundsson et al., 1983). In addition to tracer chemistry, analyses of major and minor species in geothermal fluids can also yield important reservoir information. This report describes the sampling and analytical techniques used for tracer analysis in the Raft River and East Mesa field tests. The collection procedures and sample preservation techniques, analytical methods and possible sources of contamination or error are discussed in detail.

SAMPLE COLLECTION AND PRESERVATION

Samples were collected at the geothermal sites from ports in the piping systems (Fig. 1). Both flashed and unflashed fluids were sampled using a stainless steel tubing that had been cut to a 45° angle and sealed in the sample port with the end of the tubing in the center of the pipe. The external tubing coils were immersed in ice water to bring the samples approximately to ambient temperature.

The samples were vacuum or pressure filtered through a 0.45 μ membrane filter. Pressure filtering is preferred because it is less likely to cause exsolution of gases or evaporation of the sample. pH was determined on the cooled, unfiltered sample immediately after collection. Alkalinity was determined at the collection site on a pressure-filtered aliquot. The remainder of the filtered sample was collected in plastic bottles which had been precleaned by soaking in 20% nitric acid and then rinsing thoroughly with demineralized water. Samples collected for inductively coupled argon plasma (ICP) spectrometry were stabilized with 20% nitric acid (v/v) whereas samples collected for SO_4 analysis were preserved with 1 or 2% hydrochloric acid (v/v).

Black bakelite or phenolic-resin caps contain a significant amount of readily leachable calcium and should not be used on sample bottles. It was found that molded polypropylene caps without paper liners were adequate. Sample bottles may be linear or conventional polyethylene or polypropylene.

Frequency of sampling was determined by the rate of change in one or more selected variables associated with fluid chemistry that could be easily monitored in the field. Sampling rate varied from one sample per minute to one sample per two hours. On-site monitoring was done with both an in-line

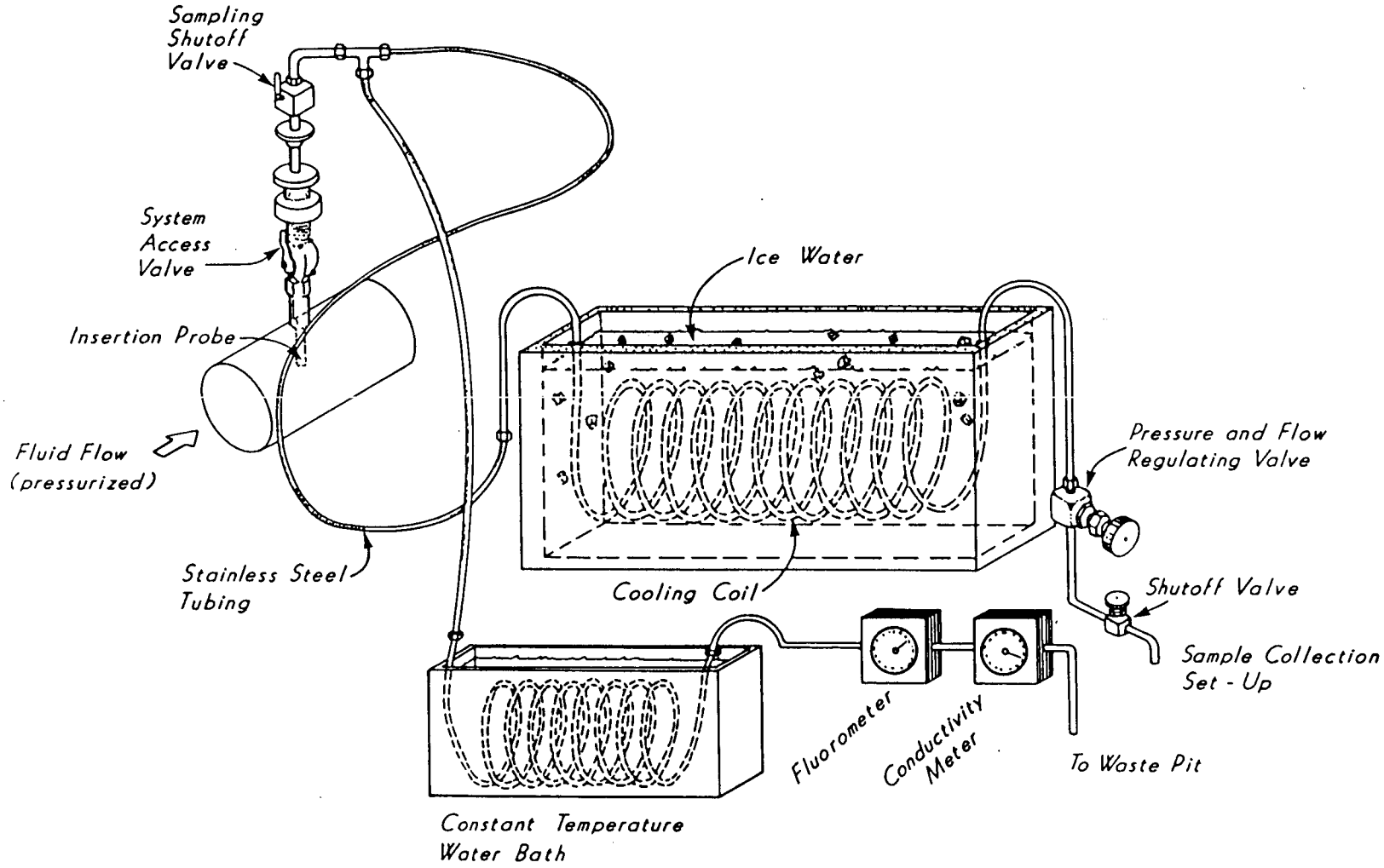

Figure 1. Sample Apparatus

fluorometer to measure concentration of organic dyes (fluorescein or rhodamine) and an in-line conductivity meter to measure specific electrical conductance, a quantity related to total amount of dissolved solids. Iodide, chloride, and alkalinity were also measured during backflow to help determine the sampling frequency.

SELECTION OF ANALYTICAL METHODS

The analytical methods chosen for the chemical determinations were based primarily on three factors: accuracy, precision and cost effectiveness. In many cases, more than one analytical method could be used. Wherever possible, each of the several different methods was evaluated. The preferred methods and associated sample preservation techniques are summarized in Table 1.

Accuracy was determined by analyzing carefully prepared standards. The precisions of the analytical determinations were obtained by measuring every tenth sample in duplicate. The relative percent difference (RPD), a measure of precision, was calculated from the analytical data using the relationship:

$$RPD = \frac{200}{n} \sum_{i=1}^{n} \frac{|S_{1i} - S_{2i}|}{(S_{1i} + S_{2i})}$$

where S_{1i} and S_{2i} are the first and second analytical values of the ith duplicate and n is the number of duplicate analyses.

As shown in Table 1, most of the major and minor elements of the waters were determined by ICP spectrometry. A comparison of analytical data for Na, K, and Ca (Table 2) indicate that the precision of the determinations by ICP techniques is substantially better for Na and K and only slightly less for Ca than by atomic absorption (AA) spectrometry. Tables 1 and 3 list the precision of the ICP analyses for the other major cations and SiO_2 present in the East Mesa and Raft River geothermal fluids. Because of the large number of elements that can be determined simultaneously, and the high levels of accuracy and precision possible by ICP techniques, this method was preferred to single-element techniques. A more complete discussion of the accuracy and precision of ICP spectrometry has been presented by Christensen et al. (1980).

TABLE 1. METHODS OF GEOTHERMAL WATER ANALYSIS.

SPECIES[a]	SAMPLE PREPARATION[b]		ANALYTIC TECHNIQUES	DETECTION[e] LIMITS	PRECISION (RPD %)
	Filtered[b,c]	Preservation[b]		(mg/l)	
Na	Yes	20% HNO_3	ICP[d]	1	0.7
K	Yes	20% HNO_3	ICP	2	1.0
Ca	Yes	20% HNO_3	ICP	0.2	1.2
Mg	Yes	20% HNO_3	ICP	0.5	4.5
Fe	Yes	20% HNO_3	ICP	0.1	1.9
B	Yes	20% HNO_3	ICP	0.1	2.1
SiO_2	Yes	20% HNO_3	ICP	1	1.0
Sr	Yes	20% HNO_3	ICP	0.01	0.9
Li	Yes	20% HNO_3	ICP	0.05	1.2
Cl^-	No	None	Mohr Titration	2	0.9
F^-	Yes	None	Specific Ion Electrode[f]	0.1	2.8
$SO_4^=$	Yes	1% HCl	Gravimetric	2	1.8
HCO_3^- , $CO_3^=$	Yes	None	H_2SO_4 Titration	1	1.4
I^-	No	None	Specific Ion Electrode[f]	0.1	2.8
I^-	No	None	Titration	0.5	1.6
Br^-	No	None	Titration	0.5	1.6
SCN^-	Yes	None	Colorimetric	0.2	2.3
pH	No	None	pH electrode[b]	±0.1	g
TDS	Yes	None	Gravimetric or fluorometric	5	0.5
Na_2Fluorescein	Yes	None	Colorimetric or fluorometric	0.02	g
Rhodamine-B	Yes	None	Colorimetric or fluorometric	0.02	g

a. For ions, analytical method is ion-specific; otherwise method gives total element.
b. Completed immediately after sample collection.
c. 0.45 μ membrane filter.
d. ICP = Inductively Coupled Argon Plasma Spectrophotometry.
e. The detection limit is defined as the point at which precision is approximately ± 100% of the given value with a confidence level of 95%. At ten times the detection limit the precision is ± 10% (Christensen et al., 1980).
f. Method of additions.
g. Not determined.

TABLE 2

COMPARISON OF PRECISION[a] OF ANALYSES FOR Na, K, AND C BY ATOMIC ABSORPTION SPECTROPHOTOMETRY[b] AND INDUCTIVELY COUPLED PLASMA SPECTROMETRY[c]

Sample	AA ppm Na	AA RSD %	ICP ppm Na	ICP RSD %	AA ppm K	AA RSD %	ICP ppm K	ICP RSD %	AA ppm Ca	AA RSD %	ICP ppm Ca	ICP RSD %
A-18	614	±1.8	623	±0.96	24.2	±1.8	23.4	±1.6	6.2	±1.1	6.0	±3.3
A-35	618	±1.2	629	±0.57	24.1	±1.8	23.8	±1.5	6.0	±1.4	5.9	±4.4
A-71	749	±2.3	747	±0.90	269	±4.5	249	±1.4	2.5	±3.3	2.4	±3.5
A-115	1816	±2.4	1852	±0.97	46.6	±5.3	44.6	±1.4	16.2	±1.7	15.2	±2.4
A-125	1811	±2.9	1846	±0.87	45.6	±4.6	43.8	±1.9	16.7	±2.3	16.0	±3.1
A-183	1476	±2.8	1496	±1.0	40.1	±4.7	38.7	±2.2	13.8	±1.5	15.5	±3.1

a. Calculated as Relative Standard Deviation (RSD) from the relationship: $\frac{\sigma}{\bar{X}} \times 100$ where σ = 1 standard deviation and $\bar{X}$ = average.

b. Atomic Absorption analyses were done 5 times on 4 different days.

c. ICP analyses were done 12 times over a period of 4 days. All procedures used were standard method analyses at ESL, as of December, 1983.

TABLE 3

ESTIMATES OF PRECISION[a] OF ANALYSES FOR Mg, SiO_2, Sr, Li and B BY INDUCTIVELY COUPLED PLASMA SPECTROMETRY[b]

	ICP ppm Mg	ICP RSD	ICP ppm SiO_2	ICP RSD	ICP ppm Sr	ICP RSD	ICP ppm Li	ICP RSD	ICP ppm B
A-18	ND		175	±2.0%	0.79	±1.0%	0.47	±1.6%	1.0
A-35	ND		177	±2.0%	0.77	±1.1%	0.48	±2.0%	0.95
A-71	ND		183	±2.2%	0.47	±1.1%	0.57	±1.4%	159
A-115	2.46	±10.1%	98.3	±1.7%	2.44	±1.2%	1.99	±0.9%	9.1
A-125	2.70	±10.0%	94.8	±1.9%	2.62	±1.1%	1.98	±1.3%	8.8
A-183	1.88	±14.9%	119	±1.1%	2.07	±0.8%	35.8	±1.6%	6.5

a. Calculated as Relative Standard Deviation (RSD) from the relationship: $\frac{\sigma}{\bar{X}} \times 100$ where σ = 1 standard deviation and $\bar{X}$ = average.

b. ICP analyses were done 12 times over a period of 4 days. All procedures used were standard method analyses at ESL, as of December, 1983.

The tracers, iodide, bromide and thiocyanate were each analyzed by several different methods. Iodide was analyzed by ion chromatography (INEL[1] and Chemical Criteria), titration (ESL[2] and UBTL[3]), and specific ion electrode (on site and ESL). In the absence of interferences, titration is the most accurate method followed in turn by specific ion electrode and ion chromatography. Because the titration involves an oxidation - reduction reaction, it cannot be used if other tracers that will interfere are present. At East Mesa, thiocyanate was present with iodide so the specific ion electrode was used for iodide.

Bromide was analyzed by titration and ion chromatography. Titration is the preferred method because it is more accurate.

Thiocyanate was analyzed colorimetrically and by ion chromatography. The colorimetric method developed at ESL is preferred because it is more accurate and precise, and is about one-tenth the cost of ion chromatography.

A detailed discussion of the preferred techniques for each of the species commonly determined in our injection research efforts is presented in the appendix to this report. We have discussed sample preservation, detection limit, range, precision, analytical procedures, calculations, and reagents required and have given references to appropriate literature.

[1] Idaho National Engineering Laboratory
[2] Earth Science Laboratory
[3] Utah Biomedical Test Laboratory

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Wright, P. M., Capuano, R. M., Adams, M. C., and Moore, J. N., 1984, Uses of geochemistry with injection-backflow testing in geothermal reservoir studies: Geoth. Res. Council, Trans., v. 8, p. 349-354.

APPENDIX

DETAILED DISCUSSION OF ANALYTICAL METHODS

Terms Used in This Appendix

Detection Limit - The point at which precision is approximately ± 100% of the given value with a confidence level of 95% (Christensen et al., 1980).

Precision - Given by the Relative Percent Difference (RPD), where

$$RPD = \frac{200}{n} \sum_{i=1}^{n} \frac{|S_{1i} - S_{2i}|}{(S_{1i} + S_{2i})}$$

where S_{1i} or S_{2i} are the first and second analytical values of the ith duplicate and n is the number of duplicate analyses.

TOTAL DISSOLVED SOLIDS

Sample preservation - filter through 0.45 μ filter paper.

Stability - variable. Analysis should be completed as soon as possible.

Detection limit - 5 mg/l

Range - 2 to 5000 mg/l for 50 ml sample. A smaller aliquot should be used if TDS is higher.

Precision - RPD = 0.5%

Discussion

Total dissolved solids in water may be measured by evaporating a carefully measured portion of filtered water and weighing the dried residue. Care must be taken to avoid loss from splattering caused by boiling. Bicarbonate is quantitatively changed to carbonate with the loss of water and carbon dioxide, according to the reaction

$$2\ (HCO_3^-)\ \rightarrow\ CO_3^{=} + H_2O\uparrow + CO_2\uparrow\ .$$

This weight loss must be accounted for in comparing measured and calculated TDS.

Procedure

1. Heat 60-ml porcelain evaporating dish to 165°C in a drying oven. Cool in a dessicator, weigh on an analytical balance, and record the weight.
2. Pipet 50 ml of water into evaporating dish, tared as described in step 1.
3. Evaporate the water without boiling. A drying oven at about 95°C works well. When the dish is completely dry, raise the oven temperature to 165°C for at least 2 hours.
4. Cool in a dessicator for at least 1 hour. Weigh quickly on an analytical balance and record the weight. If significant concentrations of salts are

present, heat at 165°C again for several hours, cool as before and reweigh until a constant weight is attained.

Calculations

$$\text{mg/l TDS} = \frac{[\text{wt of crucible + residue (g)}] - \text{wt of crucible (g)} \times 10^6}{\text{sample volume (mls)}}$$

Reference

EPA Methods for Chemical Analysis of Water and Wastes, March, 1979: United States Environmental Protection Agency, Cincinnati, Ohio 45268, pp. 160.2, 1-3.

TOTAL ALKALINITY/pH

Sample preservation - may be pressure filtered or unfiltered.

Stability - pH should be done at the time of collection, if possible. At a later time, pH may be significantly different. Surprisingly, total alkalinity appears to be very stable, even after one or more months.

Detection limit - 2 mg/l

Range - 2-2500 mg/l. Higher concentrations may be determined using a smaller sample volume.

Precision - RPD = 1.4%

Discussion

Carbonate and bicarbonate ions are determined by neutralizing the sample with standardized dilute sulfuric acid to a pH of 4.5. A pH meter is used to monitor the pH change during titration. If the sample pH is greater than 8.2, carbonate is present. The carbonate content is determined by titrating the sample to a pH of 8.2:

$$H_2SO_4 + CO_3^{=} \rightarrow CO_2\uparrow + H_2O + SO_4^{=} . \qquad (1)$$

Continued titration to a pH of 4.5 allows determination of the bicarbonate content according to:

$$H_2SO_4 + HCO_3^{-} \rightarrow CO_2\uparrow + H_2O + HSO_4 . \qquad (2)$$

Procedure

1. Calibrate the pH meter using pH 7 and pH 4 buffers. If sample pH is greater than 8.2, check calibration at a pH of 9 or 10.
2. Standardize dilute H_2SO_4 by titrating 5 ml of 1000 ppm HCO_3^{-} standard to a

pH of 4.5. This standardization should be done in duplicate. Results should agree within 0.02 ml.

3. Measure the sample pH, preferably in the original sample container to avoid any pH change caused by mixing with air. Record the pH and temperature of the sample.
4. Titrate the sample to a pH of 8.2 if the pH is greater than 8.2. Record the acid volume.
5. Continue titration to a pH of 4.5. Record the volume of acid used from a pH of 8.2 to a pH of 4.5. The sample should be stirred during the titration; however, stirring should only be sufficient to mix the sample and acid completely but not form a vortex or mix air into the sample.

Calculations

$$\text{mg/l } CO_3^{=} = F(CO_3^{=}) \frac{\text{ml acid (step 4)}}{\text{sample volume, ml}}$$

$$\text{mg/l } HCO_3^{-} = F(HCO_3^{-}) \frac{\text{ml acid (step 5)}}{\text{sample volume, ml}}$$

where

$$F(CO_3^{=}) = \frac{491.8 \times 5}{\text{ml } H_2SO_4 \text{ soln (to pH 4.5)}}$$

$$F(HCO_3^{-}) = \frac{1000 \times 5}{\text{ml } H_2SO_4 \text{ soln (to pH 4.5)}}$$

Reagents

Standard 1000 ppm HCO_3^{-} (491.8 ppm $CO_3^{=}$): Dry primary standard Na_2CO_3 at 110°C for at least 2 hours. Weigh 0.8686 gm and dissolve in CO_2-free water (demineralized water boiled for 15 minutes and cooled.) Dilute to 1 liter with CO_2-free water.

Dilute H_2SO_4: Thoroughly mix 0.5 ml concentrated H_2SO_4 with approximately 1 liter water. Standardize daily as described in step 2.

References

ASTM-D1293-78, 1978, pH of Industrial Water and Industrial Waste Water: pp. 1-12.

USGS Paper 1454, 1960, Method for Collection and Analysis of Water Samples: pp. 93-95 and 237, 238.

ICP ANALYSIS OF WATERS

Sample preservation - filter through 0.45 μ filter paper and acidify to 20% (v/v) with HNO_3 (v/v).

Stability - 3 to 4 months.

Detection limit - see Table 1.

Range - see Table 1.

Precision - see Tables 1 and 2.

Discussion

Multielement analyses are performed on an Applied Research Laboratories inductively coupled argon plasma emission spectrograph (model ICPQ). The spectrograph is a fixed-slit, direct-reading, computer-controlled (Dec PDP 11/05) instrument with 38 channels for 37 elements. There are 2 channels for iron to cover the range of values encountered in both solid and water samples.

The wide linear range of the ICP (3 to 4 orders of magnitude) makes dilutions unnecessary except in cases of water with TDS contents greater than 1%. Sample preparation is limited to filtration and acidification of the water, thereby eliminating the possible dilution errors.

Water samples are acidified to 20% v/v with concentrated nitric acid, by diluting 20 ml of acid to 100 ml with sample water. The actual volume of water required for this is not 80 ml but 82 ml because of the volume loss caused by mixing. This acid concentration has a two-fold purpose. The first is to match the calibration matrix of the ICP. This is important because the type of acid and acid concentration affect element sensitivities. The second reason for this high acid concentration is sample stability. Silica in the ranges often found in geothermal waters may precipitate in samples acidified

to 2% or less. Low-concentration elements (a few ppm or less) may adsorb on container walls, even at acid concentrations as high as 10%. Stability appears to be good for 3 or 4 months at this acid concentration.

Procedure

Blanks are analyzed at the beginning of each set and subsequently every 12 samples. One or two standards or standardized natural waters are analyzed every 6 samples through the set as well as after the last sample. Standards are chosen to be as close to the samples in composition as possible. All normalizations, drift and interference corrections have been computerized.

Reagents

Blank: 20 ml of reagent grade HNO_3 diluted to 100 ml with high-purity demineralized water. If possible, blank acid is from the same bottle used to acidify samples.

Standards: Single-element stock standards are prepared from known high-purity metals whenever possible, or from stable salts. Dilutions for working mixed standards are prepared from these in needed concentrations with acid concentrations the same as for the unknown samples.

Calculations

None.

SULFATE: DETERMINATION BY BARIUM SULFATE PRECIPITATION

Sample preservation - filter, acidify with 1% HCl (v/v), or 2% HCl if needed to prevent precipitation.

Stability - 1-4 months.

Detection limit - 2 mg/l

Range - 2 to ~ 2000 mg/l. For samples > 1000 mg/l, rerun with smaller volume

Precision - RPD = 1.8%

Discussion

This procedure is based on the formation of insoluble barium sulfate when barium chloride is added to a solution containing sulfate ions. The formation of barium sulfate is described by the reaction:

$$BaCl_2 + SO_4^{=} \rightarrow BaSO_4 + 2Cl^{-}.$$

The precipitation is carried out in a slightly acid medium. This increases the solubility of barium sulfate slightly but is necessary to prevent the precipitation of other barium salts, such as carbonate, phosphate and hydroxide. The acid condition also promotes the formation of larger and therefore filterable barium sulfate crystals. It is necessary that the precipitation be made with both solutions near boiling as supersaturation is minimized at this temperature.

The coprecipitation of other barium salts may be further minimized by having the sample and barium chloride as dilute as possible and by adding the barium chloride solution rapidly.

An additional error may be introduced during burning of the filter paper. While pure barium sulfate is not decomposed by heating in air until the temperature reaches about 1400°C, it is easily reduced to the sulfide by

carbon formed when the paper is charred. This can be avoided by burning the paper off slowly at a low temperature with free access of air. Final temperature should not exceed 900°C.

Procedure

1. Accurately measure 200 ml of filtered water into a 400 ml beaker. For samples containing > 1000 ppm SO_4 it is preferable to use 100 ml, diluting to about 200 ml with demineralized water.
2. If samples are not already acidifed, add 2 ml concentrated HCl.
3. Cover with watch glasses and heat nearly to boiling. The sample should be perfectly clear. If any precipitate is visible at this time, samples should be refiltered before adding $BaCl_2$.
4. At the same time, heat a 10% $BaCl_2$ solution nearly to boiling.
5. Add 10 ml of 10% $BaCl_2$ solution to each sample.
6. If possible keep samples warm for several hours. (This helps prevent the formation of very small difficult-to-filter precipitate.)
7. Filter through Whatman #44 or S&S Blue Ribbon filter paper, pouring all but a few milliliters of the supernatent liquid through before disturbing the precipitate. Wash the precipitate into the filter paper with a fine stream of hot water from a wash bottle. Scrub the beaker with a rubber policeman to loosen any remaining precipitate from the beaker. Be sure all precipitate is washed into the filter paper. Examining the beaker against a dark background is recommended.

   NOTE: Fold filter paper in quarters, tear off one corner and seat papers in long stemmed fluted funnels. Retain torn off corner for wiping beaker lip. If paper is properly seated, the funnel stem should hold a column of water.

8. After all precipitate is washed into the paper, wash precipitate and paper 8 to 10 times with hot water, allowing all water to drain between each rinse. Wash water should be squirted at the top of the paper, starting with the 3-thickness side, going completely around the paper and rewashing the folded side for each rinse.

   Completeness of washing may be checked by running a drop or two of rinse water from the funnel stem into a solution of $AgNO_3$. Cloudiness indicates the presence of Cl and the need for additional rinsing.

9. Carefully remove the filter paper from the funnel, fold and place in a numbered Denver fire clay annealing cup. Press down into the cup.

10. Place in a muffle furnace and heat slowly with the door propped open (≈ 75°C intervals to 600°C). When all carbon is burned off, close door and raise temperature to about 850°C.

11. Remove crucibles, cool to room temperature, brush precipitate out into tared balance pan and weigh. A stencil brush is useful for brushing precipitate out of the crucible. Care must be taken to avoid scratching the crucible.

Calculations

gravimetric factor for $BaSO_4 \rightarrow SO_4 = 0.41158$

$$\frac{\text{wt } BaSO_4 \text{ (g)} \times 0.41158 \times 10^6}{\text{sample volume (ml)}} = \text{mg/liter } SO_4^{=}$$

Reagents

10% $BaCl_2$: Dissolve 50 g $BaCl_2 \cdot 2H_2O$ in demineralized water. Dilute to 500 ml.

Reference

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of Quantitative Inorganic Analysis, 3rd ed.: The MacMillan Co., New York, pp. 322-335.

THIOCYANATE: DETERMINATION BY COLORIMETRY

Sample preservation - filter through 0.45 μ filter paper.

Stability - several months.

Detection limit - 0.2 ppm

Range - 0.1 to 20 mg/l. Dilution to this range is necessary for higher concentration.

Precision - RPD = 2.3%

Discussion

The thiocyanate ion forms a soluble red complex with ferric iron. The color intensity is proportional to the thiocyanate concentration in a slightly acid solution and can be measured spectrophotometrically at 480 nm. This method appears to be specific and interference-free.

Procedure

1. Using a reagent blank, set 100% transmittance on the spectrophotometer at a wavelength setting of 480 nm.
2. Add 1 ml of ferric iron solution and 0.1 ml concentrated HCl to 25 ml of sample. Mix thoroughly and read absorbance immediately.
3. Prepare and analyze a series of standards with SCN^- concentrations of 1, 5, 10, 20 ppm.

Calculations

$$\text{mg/l } SCN^- = F \times \text{sample absorbance} \times \text{dilution factor}$$

where the slope F is given by

$$F = \frac{\mu g \text{ of standard}}{\text{absorbance}}$$

Reagents

1000 ppm SCN^- stock solution: Dissolve 0.1396 g of dried NaSCN in demineralized water. Dilute to 100 ml. Dilute as necessary for lower concentration solutions.

Ferric iron solution: Dissolve 4.84 g $FeCl_2 \cdot 6H_2O$ in 100 ml of demineralized water.

Reference

Snell, F. D., and Snell, C. T., 1949, Colorimetric Methods of Analysis, Vol. 2, D. Van Nostrand Co., Inc., New York, p. 783.

FLUORIDE: DETERMINATION BY METHOD OF ADDITIONS

Sample preservation - may be filtered or unfiltered.

Stability - several months.

Detection limit - 0.1 mg/l (lower detection limits are possible if needed.)

Range - 0.1 to 2.5 mg/l. Dilution is necessary for higher concentrations.

Precision - RPD = 2.8%

Discussion

The activity of fluoride ions in a solution is determined using a fluoride specific ion electrode and meter. At the fluoride concentrations of most natural waters, the concentration of uncomplexed fluoride is equal to its activity. The addition of a releasing agent destroys fluoride complexes making complexed fluoride measurable with an electrode.

Procedure

1. Check the slope adjustment of the meter by reading two different concentrations of standard solution. (Orion model 407 or 407A with combination fluoride electrode is used at UURI.)
2. Pipet an aliquot of sample (10 to 50 ml) into a 50 ml beaker. Add about 0.5 g $(NH_4)_2HC_6H_5O_7$ (ammonium citrate). TISAB buffer may be used according to manufacturer's instructions. The solution should be mixed thoroughly by swirling or with a magnetic stirrer.
3. Adjust meter exactly to center scale with calibration control. The reading should be stable, not drifting.
4. Add exactly 1/100 the sample volume of 100 ppm fluoride standard (i.e. 0.1 ml for 10 ml of sample).
5. Stir to mix completely. Read concentration from green additions scale.

If samples with varying F concentrations are being analyzed it is often helpful to determine approximate values by direct reading. The same procedure can be used for higher concentration samples using 1000 ppm standard for the addition and multiplying the meter reading by 10.

Reagents

1000 ppm F standard: dissolve 0.2210 g dried NaF (reagent grade or higher purity) in 100 ml demineralized water. The solution should be stored in a plastic bottle. Dilute the solution as needed for lower concentrations.

Ammonium citrate: Reagent grade $(NH_4)_2HC_6H_5O_7$

Reference

Orion Research Incorporated Fluoride Electrode Instruction Manual, 1982, 36 pp.

CHLORIDE: DETERMINATION BY MOHR TITRATION

Sample preservation - no treatment; may be filtered or unfiltered.

Stability - no known limit.

Detection limit - 2 mg/l

Range - 2 mg/l to saturation.

Precision - RPD = 0.9%

Discussion

This procedure is based on the formation of insoluble silver chloride when a solution containing chloride is titrated with a silver solution. The chromate ion of the indicator also forms a precipitate with silver. Silver chromate is slightly more soluble than silver chloride; therefore the chloride is preferentially precipitated. Stable silver chromate is only formed after all chloride is precipitated. The silver chromate is brick red in color which gives a visible end point. Since a slight excess of silver must be added to form the colored compound, a blank must be analyzed to determine this titer volume.

The following equations show these reactions:

$$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3 \quad (1)$$

$$K_2CrO_4 + 2AgNO_3 \rightarrow Ag_2CrO_4\downarrow + 2KNO_3 \quad (2)$$

$$2NaCl + Ag_2CrO_4 \rightarrow 2AgCl\downarrow + Na_2CrO_4 \quad (3)$$

pH and temperature adjustment are necessary because these affect the solubility of both silver chloride and silver chromate. Silver chloride solubility is negligible at temperatures near or below room temperature. At higher temperatures the precipitate begins to dissolve and only reforms as

excess silver is added. This gives erroneously high results.

Silver chloride forms and precipitates over a wide pH range including strongly acid conditions. Silver chromate formation, however, is inhibited by the presence of hydrogen ions. Therefore, the pH must be above 6.5. In samples such as natural waters, a pH as high as 9.5 is permissible.

Procedure

1. Prepare a blank with about 50 ml of demineralized water and 2 or 3 drops of K_2CrO_4 solution. Titrate with $AgNO_3$ solution to the first visible color change from clear yellow to orange. This should require less than 0.05 ml of 0.1 N $AgNO_3$.
2. Pipet an appropriate aliquot of sample into a Erlynmeyer flask. This should contain between 3000 and 20,000 μ grams of Cl.
3. Adjust the pH to between 6.5 and 8.5 if it is outside this range. To make a sample more basic use a small amount of Cl-free Na_2CO_3 or $NaHCO_3$. Very basic samples may be adjusted with dilute HNO_3 solution.
4. Titrate the sample to the first permanent color change from clear yellow, mixing during $AgNO_3$ addition. The intensity of the red-orange color must be the same as the blank.
5. Prepare duplicate chloride standards and titrate using the same procedure as used for samples. This should be done on a daily basis.

NOTE: Br, I and SCN are titrated by this method. If present, they should be determined by an alternate method (see below) and subtracted out.

H_2S also interferes but can be removed by boiling.

Calculations

$$\text{mg/l Cl} = \frac{[\text{ml } AgNO_3 \text{ (sample titration)} - \text{ml } AgNO_3 \text{ (blank)}] \times F}{\text{sample volume (ml)}}$$

$$F = \frac{\text{ppm Cl (in standard) x ml standard}}{\text{ml } AgNO_3 - \text{blank ml } AgNO_3}$$

Reagents

~ 0.1 N $AgNO_3$: Dissolve 16.989 g reagent grade $AgNO_3$ in 1 liter of demineralized water. Store in a brown bottle out of the light.

10,000 ppm Cl standard: Dissolve 1.6485 g high purity dried (105°) NaCl in water. Dilute to 100 ml.

Potassium chromate indicator: Dissolve about 50 g KC_2O_4 in 100 ml water.

Reference

Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of Quantitative Inorganic Analysis: The MacMillan Co., New York, pp. 451-453 and 542-543.

BROMIDE: DETERMINATION BY SODIUM THIOSULFATE TITRATION

Sample preservation - no treatment necessary.

Stability - no known limit.

Detection limit - 0.5 mg/l

Range - 1.0 mg/l to saturation.

Precision - RPD = 1.6%

Discussion

This procedure uses sodium hypochlorite to oxidize bromide to bromate according to the reaction:

$$Br^- + 3NaOCl \rightarrow BrO_3^- + 3H^+ + Cl^-.$$

Addition of potassium iodide to the solution will liberate iodine in an amount equivalent to the bromate by the reaction:

$$BrO_3^- + 6I^- + 6H^+ \rightarrow Br^- + 3H_2O + 3I_2.$$

The liberated iodine is titrated with standardized sodium thiosulfate solution using starch as an indicator as shown by the reaction:

$$I_2 + 2S_2O_3^{=} \rightarrow S_4O_6^{=} + 2I^-.$$

Because iodide, if present, is determined as bromide, iodide must be determined independently and subtracted from the amount determined by titration.

Iron, manganese, and organic material interfere but may be removed by adding calcium oxide and filtering the sample. Chloride does not interfere.

Procedure

1. If necessary, add 1 g of CaO (in excess) to 100 ml of sample. Stir the sample for 1 hour and filter through a folded, dry retentive filter paper, discarding the first portion of filtrate. In the case of waters containing high metal concentrations, it may be necessary to stir samples and CaO overnight to remove the interference completely. Prepare a blank in the same manner.
2. Pipet an aliquot of the sample, containing 1 to 20 mg of bromide into a 270 ml Erlenmeyer flask and bring the total volume to 50 ml with distilled water.
3. Neutralize the sample by adding 50% HCl drop-wise.
4. Add a) 8 ml of 1 N NaOCl (sodium hypochlorite) solution in 0.1 N sodium hydroxide
   b) 0.5 ml of 50% HCl acid.
   c) enough $CaCO_3$ to give an excess of 0.1 to 0.2 g.
5. Heat to a gentle boil and boil for 8 minutes.
6. Remove the flask from the hot plate and add 4 ml of 50% (w/v) $CHNaO_2$ (sodium formate).
7. Heat for an additional 8 minutes and rinse the flask with distilled water.
8. Cool to room temperature.
9. Add a) 3 drops of 1% (w/v) $(NH_4)_6\ Mo_7O_{24} \cdot 4H_2O$ (ammonium molybdate)
   b) 1 g of $KF \cdot 2H_2O$
   c) 0.5 g KI
   d) 10 ml of 25% (v/v) H_2SO_4.
10. Titrate with 0.05 N $Na_2S_2O_3$, (sodium thiosulfate) adding a starch indicator just before the end point.
11. Prepare and run a series of standards in the same manner.

Calculations

$$Br\ (mg/l) = 13{,}320\ \left(\frac{ml\ Na_2S_2O_3 \times Normality}{vol\ sample\ (ml)}\right)$$

Iodide (ppm) x 0.6297 = equivalent Br.

Subtract equivalent bromide (mg/l) from bromide to correct for iodide present in the sample.

Reagents

CaO: Reagent grade. If reagent grade CaO is not available, it may be prepared by heating $CaCO_3$ to 900°C.

50% HCl: Dilute 50 ml concentrated reagent grade HCl to 100 ml with demineralized water.

~ 1 N NaOCL: Add 1 g NaOH to 500 ml of commercial bleach (5.25% NaOCl).

50% Sodium formate: Dissolve 50 g $CHNaO_2$ in water. Dilute to 100 ml.

1% Ammonium molybdate: Dissolve 1 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water. Dilute to 100 ml.

$CaCO_3$: Reagent grade

$KF\cdot 2H_2O$: Reagent grade

KI: Reagent grade

Starch solution: Prepare an emulsion of 10 g of soluble starch in a mortar with a small quantity of demineralized water. Pour this emulsion into 1 liter of boiling water. Let settle overnight.

25% H_2SO_4: Slowly pour 25 ml concentrated H_2SO_4 into about 60 ml water with stirring. Dilute to 100 ml.

0.05 N Sodium Thiosulfate: Dissolve 3925 g $Na_2S_2O_3$ in water. Dilute to 1 liter.

Reference

Kolthoff, I. M. and Elving, Treatise on Analytical Chemistry, Part II: Vol. 7, pp. 403-404.

IODIDE: DETERMINATION BY METHOD OF ADDITIONS

Sample preservation - filter through 0.45 μ filter paper.

Stability - several months.

Detection limit - 0.1 mg/l (lower detection limits are possible if necessary.)

Range - 0.1 to 2.5 mg/l. Dilution is necessary for higher concentrations.

Precision - RPD = 2.8%

Discussion

The activity of iodide ions in a solution is determined using an iodide specific ion electrode and meter. At the concentrations encountered in most natural waters, the activity of uncomplexed iodide is equal to its concentration. The addition of a releasing agent destroys iodide complexes making it measurable with an electrode.

Procedure

1. Check the slope adjustment of the meter by reading two different concentrations of standard solution. (Orion model 407 or 407A using an iodide electrode with a reference electrode used at UURI.)
2. Pipet an aliquot of sample (10 to 50 ml) into a 50 ml beaker. Add about 0.5 g NH_4NO_3 or $NaNO_3$. ISA buffer may be used according to the manufacturer's instructions. The solution should be mixed thoroughly by swirling or with a magnetic stirrer.
3. Adjust meter to exactly center scale with calibration control. The reading should be stable, not drifting.
4. Add exactly 1/100 the sample volume of 100 ppm iodide standard (i.e. 0.1 ml for 10 ml of sample).
5. Stir to mix completely. Read concentration from green additions scale.

If samples with varying iodide concentrations are being analyzed it is often helpful to determine approximate values by direct reading. The same procedure can be used for higher concentration samples using 1000 ppm standard for the addition and multiplying the meter reading by 10.

Reagents

1000 ppm iodide standard: dissolve 0.1308 g dried KI (reagent grade or higher purity) in 100 ml demineralized water. The solution should be stored in a plastic bottle. Dilute the solution as needed for lower concentrations.

Ammonium nitrate: Reagent grade (NH_4NO_3)

Reference

Orion Research Incorporated Halide Electrodes Instruction Manual, 1982, 28 pp.

IODIDE: DETERMINATION BY SODIUM THIOSULFATE TITRATION

Sample preservation - filter through 0.45 μ filter paper.

Stability - several months.

Detection limit - 0.5 mg/l

Range - 1.0 mg/l to saturation.

Precision - RPD = 1.6%

Discussion

This procedure uses bromine in a buffered solution to oxidize iodide to iodate; the excess bromine is then removed by adding sodium formate by the reaction:

$$I^- + 3Br_2 + 3H_2O \rightarrow IO_3^- + 6HBr.$$

Iodine is then liberated by addition of potassium iodide to the solution as described by the reaction:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O.$$

The liberated iodine is titrated with standardized thiosulfate solution using starch as an indicator, according to the reaction:

$$I_2 + 2S_2O_3^{=} \rightarrow S_4O_6^{=} + 2I^-.$$

Iron, manganese, and organic material which interfere may be removed by adding calcium oxide and filtering.

Procedure

1. If necessary, add 1 gram of CaO in excess to 100 ml of sample. Stir the sample for 1 hour and filter through a folded, dry retentive filter paper, discarding the first portion of filtrate. Prepare a blank in the same

manner.

2. Pipettte an aliquot of the sample, containing 0.2 to 5.0 mg of iodide, into a 500 ml Erlenmeyer flask and dilute to 100 ml.
3. Add 15 ml of 2 M C_2H_3NaO (sodium acetate) followed by 5 ml of 2 M CH_3COOH (acetic acid) and then 4 ml of bromine water, or enough to give a pale yellow color due to excess bromine.
4. Mix and let stand 10 minutes.
5. Add 2 ml 25% (w/v) $NaHCO_2$ (sodium formate) solution, blow out any excess bromine and rinse down sides of flask with distilled water.
6. When the bromine has been reduced, add 1g $KF \cdot 2H_2O$, 0.5 g KI and 10 ml 25% (v/v) H_2SO_4.
7. Titrate with 0.01 N $Na_2S_2O_3$ (sodium thiosulfate), adding a starch indicator just before the end point.
8. Prepare and analyze a series of standards in the same manner.

Calculations

$$I^- \text{ (mg/l)} = 2{,}150 \left(\frac{0.01N\ Na_2S_2O_3\ ,\ ml}{ml\ sample} \right)$$

Reagents

CaO: Reagent grade

2 M Sodium acetate: Dissolve 164 g C_2H_3NaO in water. Dilute to 1 liter.

2 M Acetic acid: Dilute 11.4 ml of glacial CH_3COOH to 100 ml with water.

Bromine water: Dissolve about 1 ml bromine in water.

25% Sodium formate: Dissolve 25 g $NaHCO_2$ in water. Dilute to 100 ml.

$KF \cdot 2H_2O$: Reagent grade

KI: Reagent grade

25% H_2SO_4: Slowly add 25 ml concentrated H_2SO_4 to about 75 ml H_2O with

rapid stirring. Cool. Dilute to 100 ml.

0.01 N sodium thiosulfate: Dissolve 0.7905 g $Na_2S_2O_3$ in water. Dilute to 1 liter.

Starch solution: Prepare an emulsion of 10 g of soluble starch in a mortar with a small quantity of demineralized water. Pour this emulsion into 1 liter of boiling water. Let settle overnight.

Reference

Kolthoff, I. M. and Elving, Treatise on Analytical Chemistry, Part II: Vol. 7, p. 404-405.

FLUORESCEIN: DETERMINATION BY FLUOROMETER OR SPECTROPHOTOMETER

Sample preservation - filter through 0.45 μ filter paper, store in the dark.

Stability - light sensitive. Apparent concentration decreases markedly with exposure to light.

Detection limits - fluorometry, 0.02 mg/l; colorimetry, 0.2 mg/l.

Range - fluorometry, 0.02 to 2 mg/l; colorimetry, 0.2-4 mg/l.

Precision - RPD = 2%

Discussion

The concentration of disodium fluorescein can be measured with either fluorometric or spectrophotometric instruments by comparison with known standards. A lower detection limit is possible using fluorometric methods.

Procedure

1. Prepare a series of standards by diluting a fluorescein stock standard. Standards must be prepared from the same manufacturer and lot as the samples. Measure the fluorescence or optical density.
2. Dilute the samples and adjust pH if necessary prior to measuring the fluorescence or optical density. Samples must be neutral or slightly basic.

The following instrument parameters should be used:

Fluorometer (Turner 111):

Primary filter: 2A and 47B

Secondary filter: 2A-12

Spectrophotometer:

493 nm wavelength. Scan across this wavelength when changing manufacturer or lot of disodium fluorescein. Some disodium fluorescein

has been found to have an absorption maximum at a wavelength significantly below 493 nm.

Calculations

$$\text{slope factor} = \frac{\text{standard concentration}}{\text{instrument reading}}$$

sample concentration = slope factor x instrument reading x dilution factor

Reagents

1000 mg/l stock solution. Dissolve 0.1000 g dried disodium fluorescein in demineralized water. Store in bottle in darkness.

References

Evaluation of Some Fluorescent Dyes for Water Tracing: Water Resources Research, vol. 13, no. 1, Feb. 1977, pp. 15-33.

Operating Instructions, Turner Filter Fluorometer, Model 111, 1981, Turner Sequoia.

Merck Index, 9th Edition, Merck and Co., Inc., 1976, pp. 537-538.

RHODAMINE B: DETERMINATION BY FLUOROMETER OR COLORIMETER

Sample preservation - filter through 0.45 μ filter paper.

Stability - may be decomposed by heat.

Detection limits - fluorometry, 0.02 mg/l; colorimetry, 0.1 mg/l

Range - fluorometry, 0.02 to 2 mg/l; colorimetry, 0.1 to 2 mg/l.

Precision - Insufficient data.

Discussion

The concentration of Rhodamine-B can be determined by measuring either absorbance or fluorescence of the sample. For very low concentrations, fluorometry is preferable because of its lower detection limit.

Procedure

1. Prepare a series of standards by diluting stock Rhodamine B solution with demineralized water and determine fluorescence or optical density.
2. Dilute the samples, if necessary, and measure their fluorescence or optical density.

The following instrument parameters should be used:

Fluorometer (Turner Model 111):

Primary filter 1-60

Secondary filter - 23A

Spectrophotometer:

555 nm wavelength

Calculations

$$\text{slope factor} = \frac{\text{standard concentration}}{\text{instrument reading}}$$

$$\text{sample concentration} = \text{slope factor} \times \text{instrument reading} \times \text{dilution factor}$$

Reagents

1000 mg/l Rhodamine-B stock solution: Dissolve 0.1000 g dried Rhodamine-B in demineralized water. Store in a cool location in an opaque bottle. It is preferable that standards and samples contain Rhodamine-B from the same manufacturer and lot.

References

Evaluation of Some Fluorescent Dyes for Water Tracing: Water Resources Research, vol. 13, no. 1, Feb. 1977, pp. 15-33.

Operating Instructions, Turner Filter Fluorometer, Model 111, 1981, Turner Sequoia.