

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Analytical Methods for the Analysis of Stream Sediments
and Rocks from Wilderness Study Areas

by

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Open-File Report 87-84

1987

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ABSTRACT

The analysis of rock and stream sediment samples is required for the mineral potential assessment of federally owned lands. The large number of samples that must be analyzed in a timely fashion and the sample diversity demand highly productive and flexible analytical procedures. Such procedures are put forth in this report. The primary approach used to analyze wilderness samples is the determination of major and minor elements by a semi-quantitative emission spectrographic method. The samples are also analyzed for selected elements that lack sufficient sensitivity by the emission spectrometric method. These supplemental methods include a flame atomic absorption spectrometric (A.A.S.) method for the determination of gold, an automated, continuous-flow, cold-vapor A.A.S. method for mercury, an inductively coupled argon plasma-atomic emission spectroscopic (ICAP-AES) method for arsenic, antimony, bismuth, cadmium, and zinc following a hydrochloric acid-hydrogen peroxide digestion, and an ion selective electrode determination of fluoride.

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INTRODUCTION

Federal mineral assessments are required to be conducted on the lands affected as part of the wilderness land review process. The former Branch of Analytical Chemistry, Denver, Colorado, of the U.S. Geological Survey now part of the Branch of Geochemistry initiated modified procedures to allow for the timely analysis of rock and stream sediment samples generated by the geologists of the U.S. Geological Survey for the assessment of these Wilderness Study areas. Thirty-one elements are determined by a semi-quantitative emission spectrographic analysis (Myers and others, 1961). This data is then augmented using other techniques where the emission analysis has less than adequate detection (Au, Hg, As, Sb, Bi, Cd, Zn and F). These specialized techniques are described in this open file report. The elements under consideration are important in the mineral assessment of wilderness lands due to their importance as a mineral commodity (such as Au) or an important pathfinder element (such as As, Hg, or Sb) for other ore deposits.

Although methods have been published for similar supplemental analytical requirements (O'Leary and Meier, 1986), different procedures were used by the Branch of Analytical Chemistry. For the semiquantitative emission spectrographic analysis, only slight modifications of a method used for over 25 years, including instrumentation, standard makeup, and trained personnel, were incorporated. Instead of using the extraction procedure given in O'Leary and Viets (1986), a digestion compatible with existing inductively coupled argon plasma-atomic emission spectrographic (ICAP-AES) equipment was developed. This allows for the simultaneous determination of As, Bi, Cd, Sb, and Zn by eliminating the organic extraction not compatible with the available ICAP-AES equipment. An automated Hg detection system was developed for these studies. The digestion procedure given is satisfactory for most geological samples.

SAMPLE PREPARATION

Stream Sediments

Stream sediment samples are air dried in an oven with forced air at room temperature and then sieved through 80 mesh stainless steel (SS) sieves. The portion of the sediment passing through the sieve is ground to pass through 100 mesh SS sieves using a ceramic-lined "shatterbox." This portion is used for all the subsequent analyses.

Rocks

Rock samples are crushed in a jaw-crusher to pea size, coarse ground in a BICO vertical grinder with ceramic plates, and fine ground to pass completely through a 100 mesh sieve using a ceramic-lined "shatterbox."

To minimize cross-contamination, a pure quartz sand is processed through both the vertical grinder and shatterbox between samples.

LABORATORY METHODS

Semi-quantitative emission spectrography

The semi-quantitative emission spectrographic procedure used for these studies is a modification of existing procedures (Myers and others, 1961). A 10.0 mg sample is mixed with 20 mg pure graphite and transferred to the cavity of an electrode. The samples are then arced to completion and the elemental concentrations which are recorded on photographic plates are estimated by visual comparison of the line intensities to those of arced mixed pure-element oxide standards.

Apparatus

- Lower Electrodes: #3170 ultra pure carbon (Ultra Carbon Corp., Bay City, MI).
- Upper Electrodes: 38 mm lengths of 3.2 mm x 300 mm, U-2 grade graphite rods (Ultra Carbon Corp., Bay City, MI).
- Photographic Plate: Eastman Kodak (Rochester, NY) type III-0, 50 x 250 mm and 100 x 250 mm with the same emulsion lot number. Unused plates are stored at -15°C to retard emulsion fogging.
- Spectrograph: Jarrel-Ash Model 70-15e, 21 ft Wadsworth mounted spectrograph (Boston, MA). The grating has 15,000 lines per inch and a reciprocal linear dispersion of 0.524 nm per mm in the first order. The wavelength region is 225.0 nm to 475.0 nm in the first order. Light intensity is controlled by neutral density filters. A spherical quartz lens having a focal length of 270 mm is used to focus a 12X image of the electrodes onto the collimating mirror.
- Comparator: An Applied Research Laboratories (Glendale, CA) ARL projection comparator microphotometer, (split viewing screen) on magnification.

Reagents

- Graphite: #2-200, Ultra Carbon Corp., Bay City, MI.

Procedure

1. A 10.0 mg sample is mixed thoroughly with 20 mg pure carbon in a weighing pan with a tooth pick and transferred to the cavity of the lower electrode. This mixture is tamped firmly with a glass rod.
2. Samples are arced to completion for 101 seconds with a 4 mm electrode gap manually maintained throughout the length of exposure. The excitation source is a direct current arc operated at 15 amperes and 300 volts.

3. The standards are weighed and arced under identical conditions as the samples. A new set of standards is arced for each different plate emulsion used.
4. The plates are developed, rinsed, and acid-fixed according to the manufacturer's suggestions.
5. A visual comparison of the line intensities is made between samples and standards to estimate the elemental concentration. For a detailed discussion of this method refer to Myers and others (1961).

Discussion

An estimate of the concentration of an element is thus based on the line intensity for the unknown as falling between two adjacent standard reference spectral lines or matching a single standard reference spectral line.

Calcium, Fe, Mg, and Ti are reported as percent and all the other elements in parts per million (ppm). Results are identified with geometric brackets whose boundaries are 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, but are reported arbitrarily as mid-points of these brackets: 1, 0.7, 0.5, 0.3, 0.20, 0.15, 0.1. The concentration of the standards used for matching and bracketing the unknown and symbols used in reporting are given in table 1. The precision of a reported value is approximately plus or minus one bracket at 68%, or two brackets at the 95% confidence level. Both upper and lower limits are given in table 2.

Table 1.--Visual comparator analysis (magnification 2x) symbols and reporting values used in semi-quantitative emission spectrography

Concentration of Reference standard in Percent	Visual Determination of Result in Percent	
	Matching	Bracketing
10	G	7
4.64	5	3
2.15	2	1.5
1	1	0.7
0.464	0.5	0.3
.	.	.
.	.	.
.	.	.
.	.	.
0.001	0.001	0.0007
0.000464	0.0005	0.0003
0.000215	0.0002	0.00015

Symbols used in reporting results.

G = Greater than 10%, or greater than value shown

* = Usual limits of determination do not apply due to use of dilution techniques

- = Not looked for

H = Interference

N = Not detected, at limit of detection or at value shown

L = Detected, but below limit of detection or below value shown

Table 2.--Limits of determination for the semi-quantative spectrographic analysis of rocks and stream sediments based on a 10-mg sample

Elements	Lower determination limit	Upper determination limit
Percent		
Iron (Fe)	0.05	20
Magnesium (Mg)	0.02	10
Calcium (Ca)	0.05	20
Titanium (Ti)	0.002	1
Parts per million		
Manganese (Mn)	10	5,000
Silver (Ag)	0.5	5,000
Arsenic (As)	700	10,000
Gold (Au)	15	500
Boron (B)	10	2,000
Barium (Ba)	20	5,000
Beryllium (Be)	1	1,000
Bismuth (Bi)	10	1,000
Cadmium (Cd)	30	500
Cobalt (Co)	5	2,000
Chromium (Cr)	10	5,000
Copper (Cu)	5	20,000
Lanthanum (La)	30	1,000
Molybdenum (Mo)	5	2,000
Niobium (Nb)	20	2,000
Nickel (Ni)	5	5,000
Lead (Pb)	10	20,000
Antimony (Sb)	100	10,000
Scandium (Sc)	5	100
Tin (Sn)	10	1,000
Strontium (Sr)	100	5,000
Vanadium (V)	10	10,000
Tungsten (W)	50	10,000
Yttrium (Y)	10	2,000
Zinc (Zn)	200	10,000
Zirconium (Zr)	10	1,000
Thorium (Th)	200	2,000

The order here is that used in the report.

Gold by Flame Atomic Absorption Spectrophotometry

A high temperature ash of a sample is digested using hydrobromic acid and bromine. The Au in the digested sample is extracted with methyl isobutyl ketone (MIBK) and washed with dilute hydrobromic acid to remove a possible Fe interference. The MIBK layer is then analyzed for Au using standard flame atomic absorption. The procedure is a modification of that given by Thompson and others (1968). This digestion will dissolve Au in most samples, but if the Au is occluded in a silicate material, the Au value determined may be low due to an incomplete digestion.

Apparatus

Hotplate:	Standard laboratory, with a 30 x60 cm heating surface.
Shaker:	Oscillatory, horizontal, set at 180 cycles/min.
Centrifuge:	Capable of holding 25 x 200 mm culture tubes and centrifuging at 2000 RPM.
Culture tubes:	Pyrex glass, 25 x 200 mm with teflon-lined caps.
Muffle furnace:	large capacity, 800°C maximum temperature required.
Aluminum block:	30 cm x 60 cm x 7.5 cm drilled to hold fifty 25 x 200 mm culture tubes.
Ashing dishes:	Coors 60196 porcelain evaporating dishes.
Digesting beaker:	Low form, 150 mL Griffin, Pyrex glass.
Pipettes:	Disposable, polypropylene, 5 mL bulb.

Reagents

Bromine: Liquid, ACS reagent grade

HBr: concentrated (47-49%), ACS reagent grade

0.1 M HBR: Dilute 23 mL concentrated HBr to 2.0 L using demineralized water.

MIBK: methyl isobutyl ketone, reagent grade.

Digesting solution: Dissolve 10 mL of liquid bromine in 2 L concentrated HBr.

Procedure

1. Weigh 10.00 g of -100 mesh sample into a porcelain evaporating dish. Ash the sample at 800°C for 2-3 hr in a muffle furnace, ramping the temperature slowly over a 4 hr period. This ashing step eliminates sulfide sulfur and organic carbon. If sulfur and carbon in these forms are not eliminated, there will be insufficient bromine to insure complete dissolution of the Au.

2. Transfer the ash to a glass 150 mL beaker and slowly add 20 mL of the digesting solution. If the sample contains carbonate material, there will be foaming. Let the slurry set for about 1 hr before proceeding with the heating step. Slowly heat to boiling on a hotplate, remove the beaker from the hotplate, and cool.
3. Use water to transfer the slurry from the beaker to a 25 mm x 200 mm pyrex culture tube bringing the volume to about 40 mL.
4. Place culture tube in the aluminum heat block on a preheated hotplate set at 75° C. Bring samples to boiling, remove from the hotplate and cool. The samples at this point may be left overnight if capped.
5. Adjust the volume to about 40 mL with demineralized water and add 10 mL MIBK. If the MIBK layer does not separate, add more water.
6. Cap the culture tube and shake on the shaker for 15 minutes at 180 cycles/min.
7. Centrifuge the culture tube at about 2000 RPM for about 3 min to separate the organic and aqueous phases.
8. Transfer the upper MIBK layer with a disposable polypropylene 5.0 mL pipette into a clean 25 mm x 200 mm culture tube and add 25 mL 0.1 M HBr solution, cap, and manually shake for about 10 seconds.
9. Aspirate the MIBK layer into the atomic absorption spectrophotometer using standard instrumental conditions recommended by the manufacturer for an organic solvent to estimate the Au content. Use Au standards made from serial dilutions of an aqueous Au standard solution taken through the procedure corresponding to 0.5, 2.0, 5.0 ppm Au in the final solution.

Discussion

There are several limitations to this method for the analysis of geological materials for gold. Since this is not a total digestion, Au may be occluded by a non-reactive phase, such as quartz, resulting in lower results. This occlusion problem can be minimized by grinding the sample to less than 100 mesh. A second potential problem in some samples is elevated Sb concentrations (usually greater than 0.1%). This high Sb content will result in poor separation of the aqueous and organic layers. One remedy is the addition of 1.0 g tartaric acid which improves the phase separation. If the phase separation is not achieved, the sample must be analyzed using standard fire assay procedures (e.g., Haffty and others, 1977). Also, if the sample is high in Mn (usually greater than 1.0%), the aqueous phase will be colorless after the first shaking. Other elements may also cause this colorless solution, such as high As or Sb. If this occurs, add more of the digesting solution and repeat the shaking. Any excess bromine from the digestion must be eliminated by heating the sample to near boiling. This is especially critical when the sample contains elevated Mn concentrations (Campbell, 1981). Excess bromine could brominate the MIBK and cause it to be heavier than the aqueous phase.

Using a 10.00 g sample size and extracting it with 10 mL of MIBK, a detection/reporting limit of 0.1 ppm Au in sample is observed. This corresponds to approximately 1% absorption. For routine samples, approximately 25 samples/person can be prepared.

Analysis of standard geological reference materials is part of the quality control procedure. Currently two standards from the Canada Centre for Mineral and Energy Technology are routinely analyzed as quality control checks. The two standards used are GTS-1, Au tailings standard reference material certified at 0.35 ppm Au (Steger and Bowman, 1984) and MA-1, Au ore standard reference material certified at 17.9 ppm Au (Faye and others, 1975). Routinely two samples of each standard are used: 10.00 g of GTS-1 and 1.00 g of MA-1. For GTS-1, 0.3-0.4 ppm Au range is acceptable and for MA-1 15-20 ppm Au is acceptable. If the Au values are not within the acceptable range for the standards, the whole sample set is rejected and redigested. Due to the smaller sample size and the problems with analyzing a geologic material for a trace element which occurs as a major constituent of a trace phase (Clifton and others 1969; Harris, 1982), a larger range of Au content for MA-1 is expected and is observed. Also, sample replicates are prepared with each batch of samples. Every tenth sample, when there is sufficient sample material, is prepared and analyzed in duplicate. The duplicate digestion values must agree within $\pm 20\%$ of each other or the sample set is rejected and redigested. If either reagent blank carried through out the procedure shows detectable Au at ≥ 0.1 ppm, the whole sample set is redone due to possible contamination.

Mercury by automated, continuous-Flow, Cold Vapor
Atomic Absorption Spectrophotometry

The method developed for the determination of mercury in Wilderness Study samples is a modification of the continuous-flow method as given by Koirtyohann and Khalil (1976). The sample is digested in a closed teflon vessel with nitric acid and sodium dichromate. This digestion is very effective at dissolving Hg in the sample and stabilizing it in solution (Feldman, 1974). The sample digest is transferred to a glass test tube, placed on a carousel of an autosampler and introduced to the continuous-flow system. The sample is mixed with air, a complexing-reducing solution of hydroxylamine hydrochloride-sodium chloride and finally stannous chloride is added. The sample stream passes into a phase separator where the liquid goes to waste and the Hg vapor passes into an absorption cell positioned in the light path of an atomic absorption spectrometer. The absorption signal is recorded on a strip chart recorder where the peak heights are measured and compared to standard Hg solution peak heights for calculation.

Apparatus

Autosampler:	Technicon (Tarrytown, NY) autosampler AAI, modified by replacing sampling probe with a glass tube (3 mm x 100 mm).
Pump:	Gilson Medical Electronic (Middleton, Wisconsin) Model Minipulse 2, eight channel, variable speed peristaltic pump equipped with standard tygon pump tubing.
Hot Plate:	Standard laboratory with a 30 x 60 cm heating surface.
Heat Lamps:	General Electric Chill Chaser Deluxe Infrared Heatlamp. Position around the flow-through cell and the phase separator.
Aluminum heating block:	2.5 cm thick x 25 cm wide x 50 cm long, with 34 mm holes drilled through in a five by ten matrix.
Digestion vessel:	Thick walled, 30 mL teflon bottles, #0201T from Savillex Corp., Minnetonka, MN.
Special glassware:	See figures 1 and 2 for the phase separator and flow through cell used in this method. These have been described by Skougstad and others (1978). Mixing coils are available from Technicon, Inc., Tarrytown, New York.

Reagents

25% (W/V) Sodium dichromate solution: Dissolve 500 g reagent grade $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ in sufficient demineralized water to bring the volume to 2.0 L.

Nitric acid wash: Dilute 40 mL "Baker instra-analyzed" grade HNO_3 , (16M) to 4.0 L with demineralized water.

Stannous Chloride Solution: Dissolve 100.0 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Baker, Suitable for Hg Determination grade) in 100 mL concentrated (12M) "Baker instra-analyzed" grade HCl . Let the solution stand for 20 to 30 minutes until the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ totally dissolves. Dilute to 1.0 L with demineralized water. This solution is stable for about one week with refrigeration.

Complexing-Reducing Solution: Dissolve 30.0 g hydroxylamine hydrochloride and 30.0 g NaCl in about 500 mL demineralized water. Add very slowly 100.0 mL concentrated (18M) H_2SO_4 , "Baker instra-analyzed" grade. When the solution is cool, dilute to 1.0 L with demineralized water.

Procedure

1. Weigh 0.100 g of sample into a clean, thick walled, 30 mL teflon vessel. The threads of the vessel should be wrapped previously with teflon tape, to insure a tight seal when capped.
2. Add 2.0 mL 16M HNO_3 and 0.50 mL of the sodium dichromate solution to the sample. Swirl gently to wet the entire sample.
3. Cap the vessel and place in the aluminum heating block for 3 hours at 110°C. Remove from the heating block and allow to cool completely. (Overnight cooling is acceptable).
4. Uncap and rinse lid with demineralized water into the vessel. Transfer entire contents into an empty, tared 16 mm x 100 mm disposable flint glass test tube. Bring contents to mass of 12.00 g with demineralized water.
5. If the sample is thought to be mineralized or if the sample has more than 10 ppm Se, transfer the vessel contents to a 100 mL volumetric flask. Add 20 mL 16M HNO_3 and 2.0 mL 25% sodium dichromate solution and dilute to volume with demineralized water. Use an aliquot of this solution for analysis. If the sample contains elevated Se concentrations (>500 ppm), use a three point method of standard additions (unspiked sample and two samples spiked with different Hg contents) to establish the Hg content.
6. Prepare duplicate standards (usually GXR-3) and duplicate samples for each job. Replicates totalling at least 5% of the samples are routinely analyzed. Aqueous standards of 5, 10, 20 ppb Hg are used for the calibration curve with each day's analysis. These are prepared from a serial dilution of a 10/ μg Hg/mL standard with the final solution being 3M HNO_3 and 0.5% sodium dichromate (20 mL 16 M HNO_3 and 2 mL of the sodium dichromate solution for a 100 mL volumetric flask).
7. Measure the Hg content by measuring the peak height generated using the automated continuous flow manifold in figure 3. The operating conditions for the AA spectrometer are given in table 3. The system is calibrated with aqueous standards.

Table 3.--Instrument settings used for a Instrumentation Laboratories 457 A. A. Spectrometer and a Perkin-Elmer 056 Recorder

Lamp	Hg hollow cathode, 6 ma
Slit	0.7 nm
Photo multiplier High voltage	900
Wavelength	253.7 nm, no background correction
Recorder	50 mv full scale response (2x), 5 mm/min

Figure 1.--The flow-through cell used for the determination of mercury. The two 16 mm end windows of this cell are quartz and the remainder of the cell is pyrex glass.

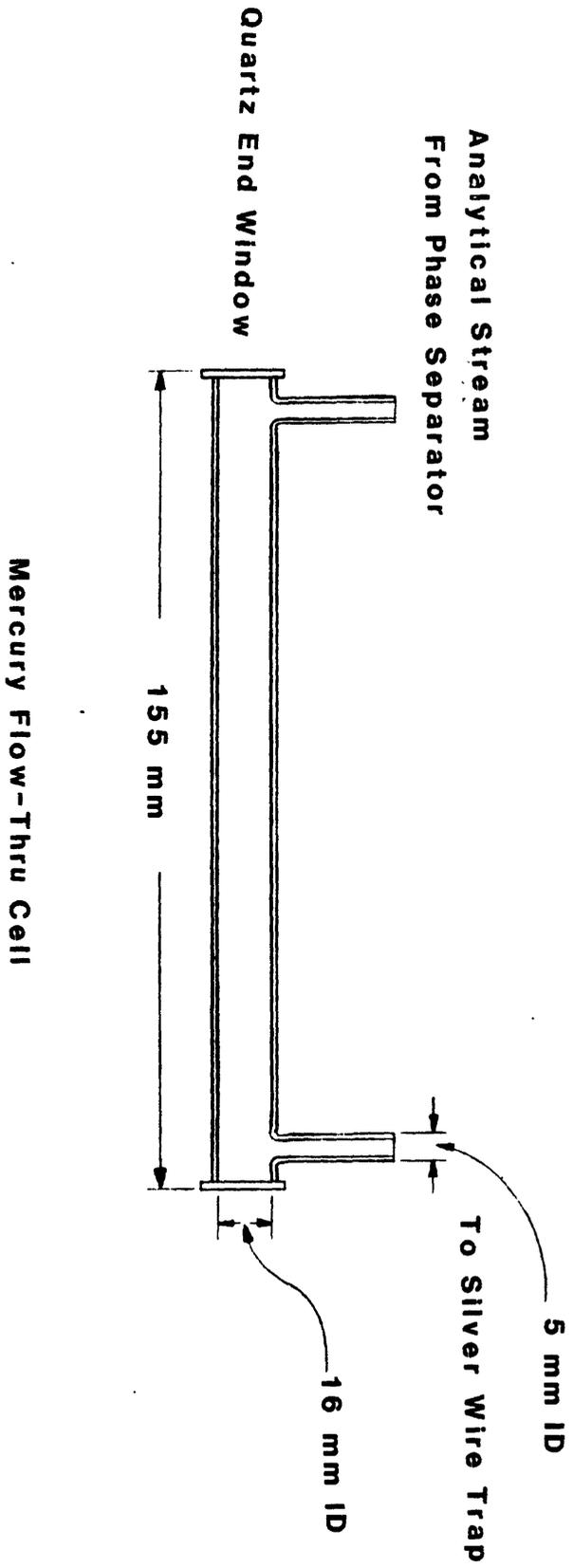
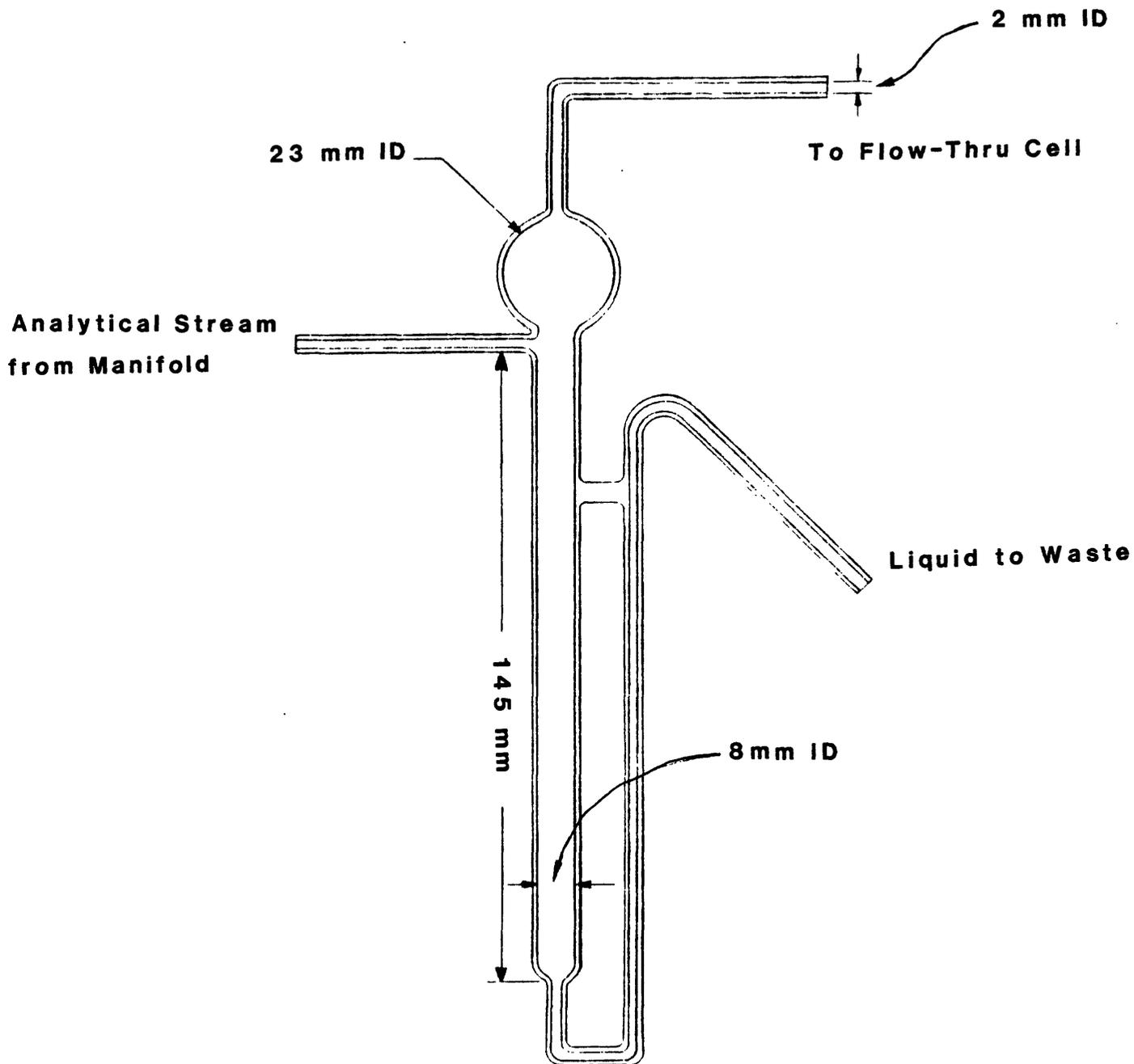
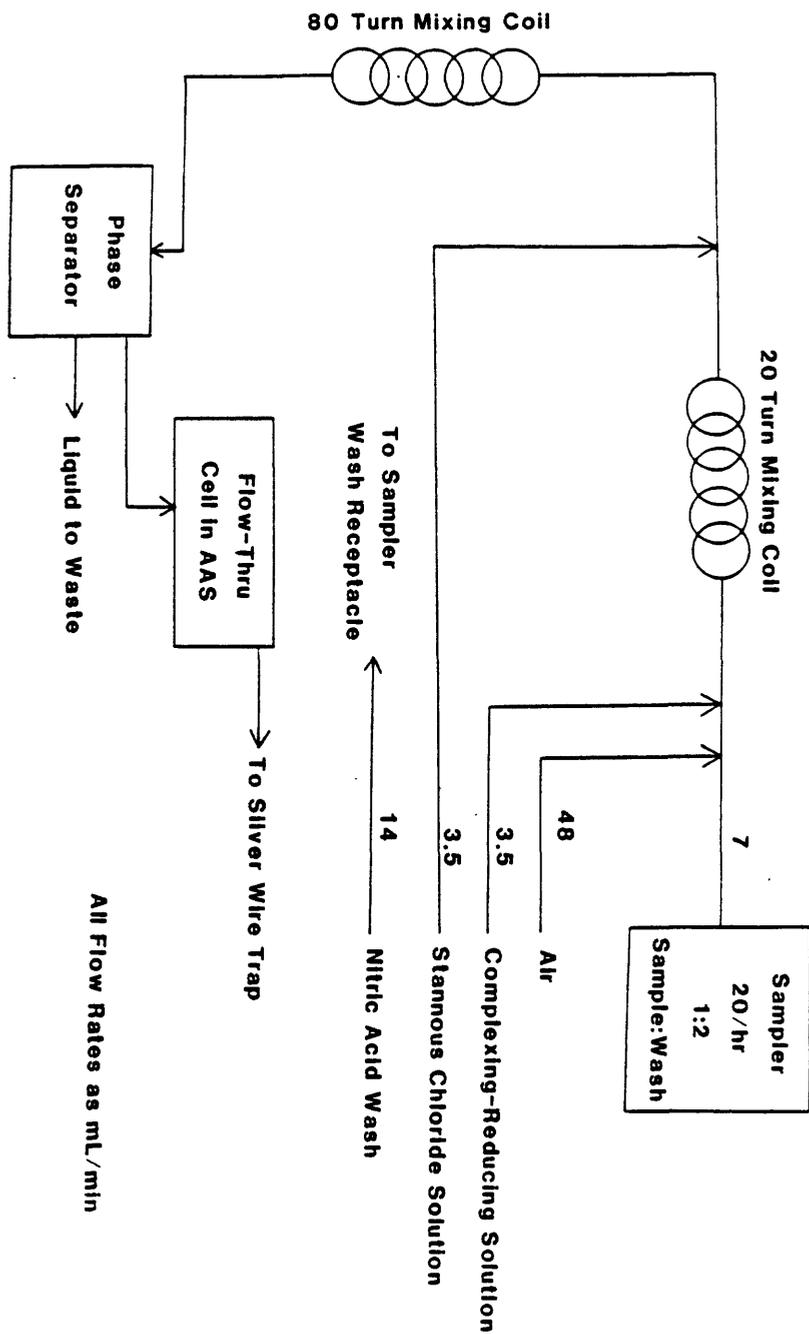


Figure 2.--Phase separator used in the determination of mercury. The whole separator is made from Pyrex glass.



Mercury Phase Separator

Figure 3.--Manifold used for the automated generation of mercury vapor.



Discussion

Short term precision of the method was determined by analyzing sixteen 10 µg Hg/L solutions and was found to be 1.2% RSD and less than 5% RSD for U.S.G.S. standard reference shale SGR-1 containing 0.17 ppm Hg. The sensitivity of the method was determined using a 0.21 µg Hg/L producing a signal of 0.0044 absorbance (1% absorption). The method has an in-sample detection limit of 0.02 ppm Hg using the described digestion procedure and operating conditions.

If a sample of elevated Hg content (over 10 ppm Hg) is run through the system, the system must be taken apart, all tygon tubing replaced, and all the glass wear soaked in 4 M HNO₃ overnight. The system then is reassembled and only reagents taken through the manifold until a zero, stable baseline is achieved. This may take up to 8 hours, depending on the sample's mercury content.

The phase separator and the absorption cell should be warmed to 35-40° C using infrared heat lamps. This helps minimize sample carry over allowing the baseline to be reached between samples. The heating also prevents excess condensation of water in the absorption cell.

Table 4 shows the elements tested that do not interfere with the determination of mercury using the given manifold system at the concentration shown. Elements that significantly reduce the observed mercury signal include Ag, Au, Pt, Te, and Se. With the given digestion and normal occurrences of these elements in geological materials, only Se poses a significant problem. The interference due to Se on Hg is shown in figure 4. For most geological materials there is no Se problem; but when Se is present at elevated levels (≥ 10 ppm Se), dilute the sample digest or use the method of standard additions.

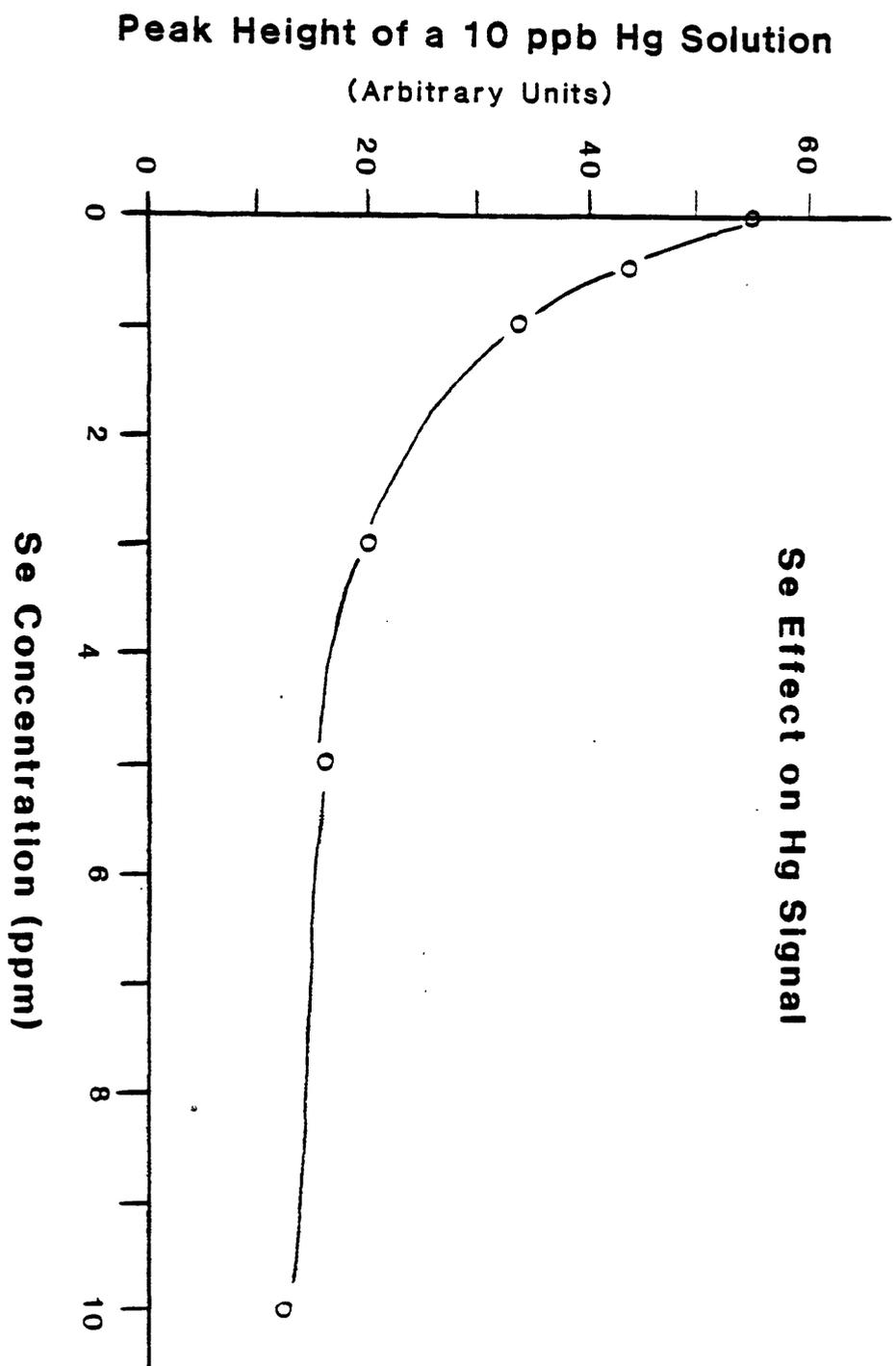
Glass tubes must be used to preserve the mercury in solution (Feldman, 1974). The solutions stored in these tubes are stable for at least 24 hours. The solutions stored in the teflon vessels are stable for over 48 hours. A constant 12.00 g weight was chosen to provide sufficient liquid to do the analysis. A different volume may be required if a different autosampler or manifold system is to be used. Constant weight is chosen because it is operationally easier to bring all samples to a constant weight in disposable glassware than to constant volume in a volumetric flask. A silver trap is shown in the manifold in figure 3. This is a quartz tube (20 mm x 150 mm), necked and dimpled at both ends after about 5 g of 36 gauge silver wire has been positioned inside. This trap will minimize the amount of Hg vapor vented into the laboratory.

Table 4.--Elements investigated showing no interference on the determination of mercury* by cold vapor AAS

<u>Element</u>	<u>Maximum Concentration tested (ppm)</u>
Zn	1,000
Pb	1,000
Cu	500
Cd	50
Bi	50
Co	100
Mn	1,000
U	100
Mo	100
V	100
Ni	100
Ag	3.5
Fe	500
As	30
Sb	10

*A solution of 10 $\mu\text{g Hg/L}$, 3.0 M HNO_3 and 0.2% (W/V) $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

Figure 4.--The Se effect on a 10µg Hg/L solution.



Hydrochloric Acid-Hydrogen Peroxide Extractable Metals

This method was developed as a fast, sensitive and precise method for the determination of extractable As, Bi, Cd, Sb and Zn in geological samples used for the evaluation of Wilderness areas. This method was developed to augment the information found in the semi-quantitative emission spectrographic procedure where the detection limits are poor for these important pathfinder elements. Most minerals containing these elements will be sulfides and will be dissolved by the hot HCl/H₂O₂ digestion. These metals will also be dissolved if they are associated with clays, oxide phases or carbonates. Metals bound within the lattice of silicate minerals will be only very slightly attacked. This problem is remedied in part by using samples less than 100 mesh.

The inductively coupled argon plasma-atomic emission spectrometry (ICAP-AES) is used to determine the extracted metals and offers speed, sensitivity, and wide dynamic range. The primary limitation of the technique is spectral interferences. For most rocks and stream sediments the expected interferences are quite small. The limits of detection are as listed in table 5. Mineralized samples may have higher limits of detection due to spectral interferences and larger dilution factors. A detailed description of the ICAP-AES analytical wavelengths for the elements and the operating conditions is given in Crock and others (1983).

Apparatus

Polychrometer: 63 channel Jarrell-Ash ICAP-AES polychrometer, Model 1160
Plasma Atomcomp

Digestion Station: Aluminum frame insulated with styrofoam to hold a 72 position, 12 mm test tube rack, heated with a Master heat gun. Preheat to 104° C.

Mixer: Standard vortex test tube mixer.

Test Tube: Disposable, polypropylene, 6.0 ml, 12 x 76 mm (A. Paigger & Col, Chicago, Illinois.)

Autosampler: Gilson autosampler, Model 212 B (Middletown, Wisconsin)

Reagents

HCl: concentrated (36%) reagent grade.

H₂O₂: 30% reagent grade. This must be stored in a refrigerator.

Lu internal standard: A 500 µg Lu/mL stock solution is made from an appropriate amount of 99.999% Lu₂O₃, available from Spex Industries, Edison, NJ, and is dissolved in 50 mL of concentrated HCl. This solution is brought to a 1.00 L volume with demineralized water.

Calibration Standards: Single element solutions of 20 ppm each As, Bi, Cd, Sb and Zn are prepared from commercially available 1000 µg/mL stock solutions.

Procedure

1. Weigh 0.150 g of sample into a disposable polypropylene test tube and add 30 μ L of 500 μ g/mL Lu internal standard.
2. Add 1 drop of HCl and note any samples that bubble, then add 3.0 mL HCl acid slowly to the samples. If the samples bubble, do a replicate digestion in a 50 mL pyrex beaker and then transfer the solution to the polypropylene test tube for analysis.
3. Add 0.1 ml 30% H_2O_2 and mix with a vortex mixer.
4. Let stand for 10 minutes, then add an additional 0.1 ml H_2O_2 and mix with the vortex mixer.
5. Let stand 30 minutes, then heat at 104° C on the hot air digestion station for twenty minutes. Cool and cap the tube until analyzed.
6. Allow residue to settle overnight or centrifuge if samples are to be run on the same day.
7. Determine As, Bi, Cd, Sb, and Zn by ICAP-AES on this solution directly.

Discussion

The extraction method was optimized using the standard reference materials GXR-1, GXR-2, GXR-3, GXR-4, GXR-5, GXR-6 (Allcott and Lakin, 1975). The extraction response was tested for the parameters of time, temperature, and concentration of hydrochloric acid. Figure 5 shows the reaction was complete after 20 minutes. Figure 6 shows the response of extraction efficiency versus temperatures indicating that temperature is the most important parameter to control. As can be seen in figure 7, the extraction requires a minimum acid to sample ratio of 3:1. While higher acid to sample ratios yield only slightly better extraction efficiency, a ratio of 20:1 was chosen because a subsequent dilution step was eliminated.

A typical sample set for the extractable metals consists of the samples, a minimum of two sample duplicates, two reagent blanks and the six GXR standards all digested as a batch. Table 6 lists the threshold values for each element in the GXR standards. If the analyzed values for the GXR standards does not meet the threshold values the entire sample set is redone. Replicate analyses of samples must agree within 10% of each other or the sample set is redone. Approximately 80 samples per person day can be prepared. Table 7 summarizes the accuracy and precesion of this procedure.

Correction for interelement spectral overlaps and background changes are done automatically by mathematical algorhythms designed by Jarrell Ash and are determined by the matrix standards and the interference elements. One potentially important interfering element is tungsten. There are important spectral over-lap interferences on Cd and Sb when W is present in concentrations greater than 1%. These high W samples are not common and therefore W is not commonly a problem. This W interference is noted in table 7 with the analysis of GXR-3 where W is present at $1.08 \pm 0.06\%$ (Gladney and others, 1979).

Figure 5.--The effect of heating time on the extraction of arsenic and zinc from GXR-1 at 70° C.

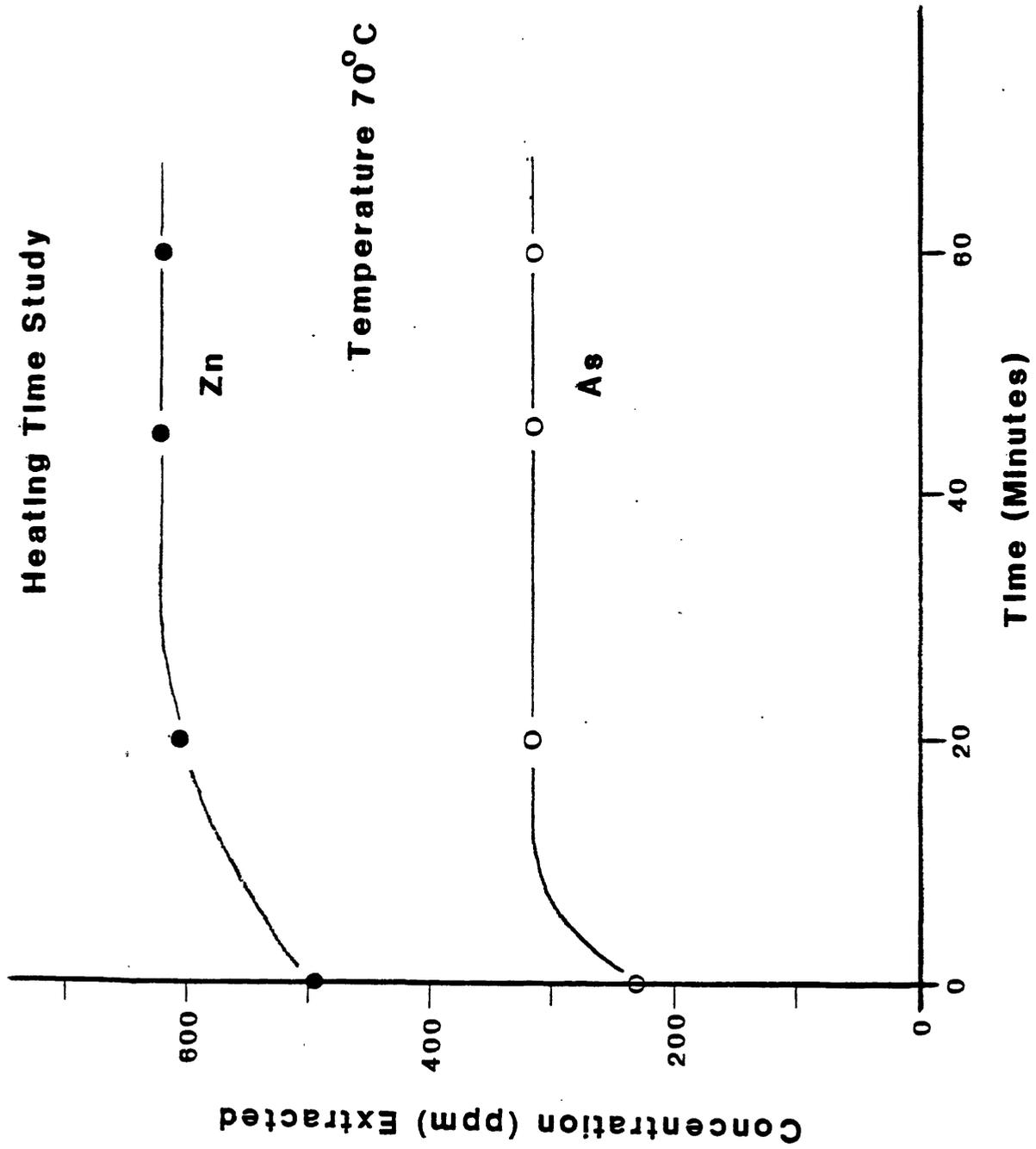


Figure 6.--The effect of extraction temperature on the extraction of arsenic from GXR-1.

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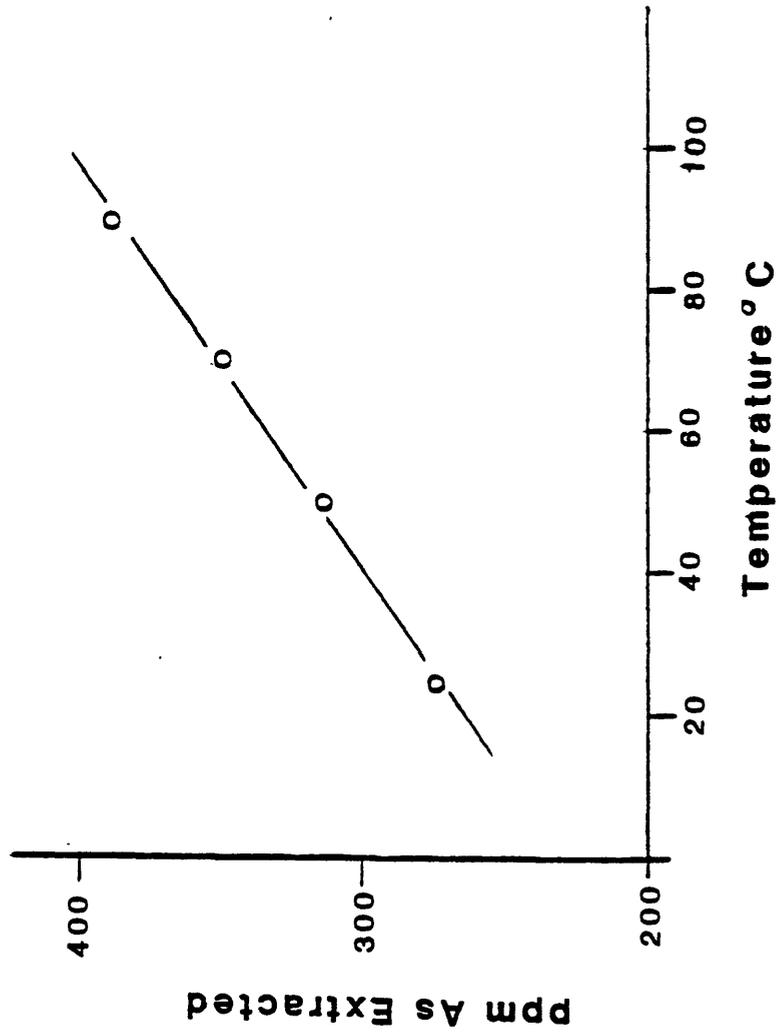


Figure 7.--The effect of HCl to sample size ratio on the extraction of arsenic from GXR-1.

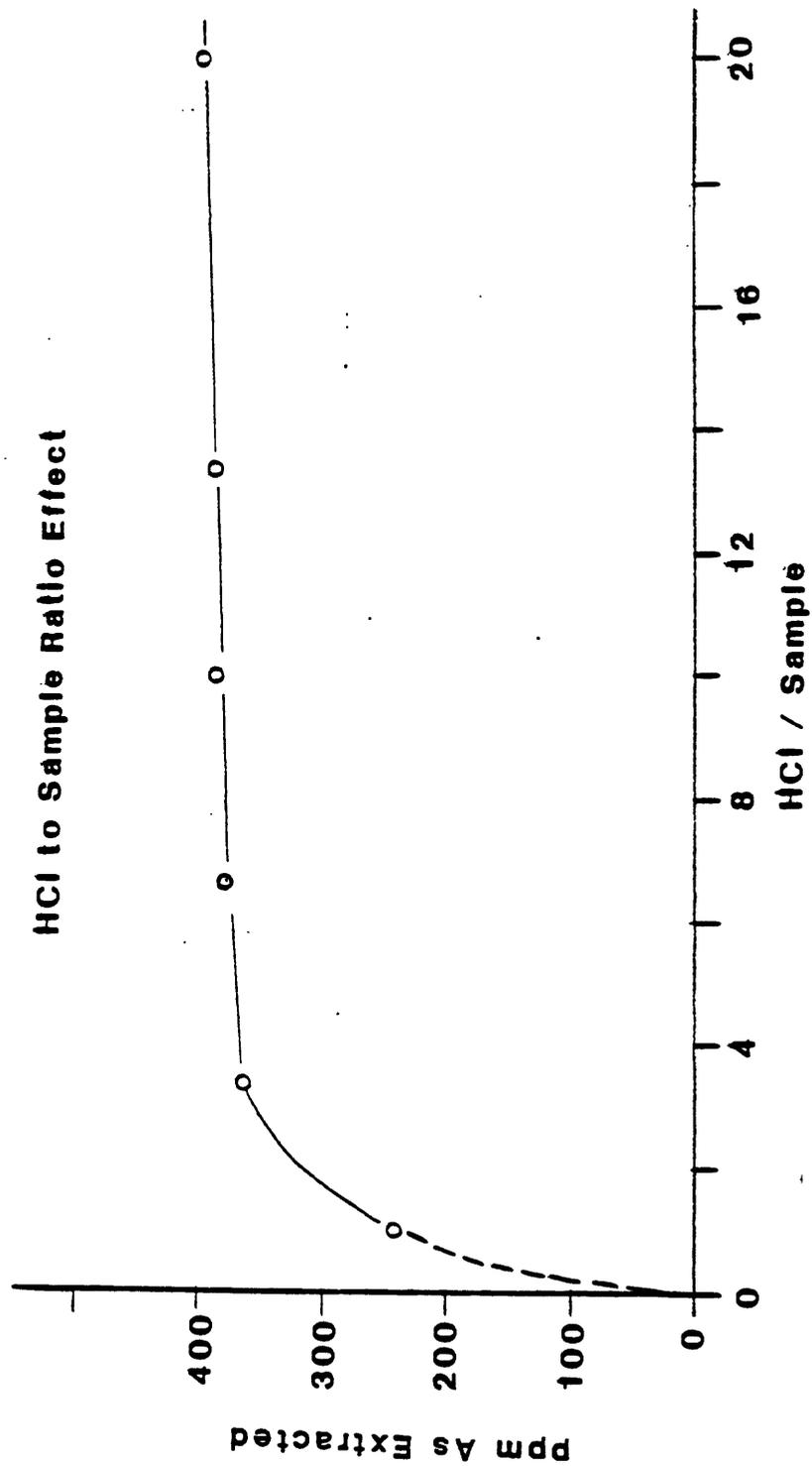


Table 5.--ICAP-AES conditions for the HCl-H₂O₂ digestion

<u>Element</u>	<u>Analytical Wavelength (nm)</u>	<u>Detection limit: In sample (ppm)</u>	<u>Maximum* concentration In sample (ppm)</u>
As	193.7	5.0	20,000
Bi	223.0	2.0	20,000
Cd	226.5	0.1	1,000
Sb	217.5	2.0	20,000
Zn	213.8	2.0	18,000

*Concentrations higher than this value must be diluted.

Table 6.--Standards used in the HCl-H₂O₂ digestion and the minimum acceptable extractable values for element using ICAP-AES detection.

<u>Sample</u>	<u>Description (Allcott and Lakin, 1975)</u>	<u>Threshold Value*</u>				
		<u>As</u>	<u>Bi</u>	<u>Cd</u>	<u>Sb</u>	<u>Zn</u>
GXR-1	Jasperoid	360	1400	3	75	700
GXR-2	Soil, residual	18	<2	3	30	500
GXR-3	Fe-Mn-W rich hot spring deposit	3400	<2	<0.1	H**	100
GXR-4	Unoxidized porphyry copper mill heads	90	15	<0.1	3	70
GXR-5	B-horizon podzol soil	6	<2	<0.1	<2	40
GXR-6	B-horizon soil composite	240	<2	<0.1	1-2	100

*The determined value of these elements in these standards must be at least this value. If the value determined is lower, the whole job is redone. All values as ppm.

**H=Interference. There is a large Mn interference on Sb in this sample.

Table 7.--Comparison of values obtained by this method (ICP-AES) with other published values for the GXR standards

<u>Arsenic (ppm)</u>				
	This method x, RSD%*	O'Leary and Viets (1986) x, RSD%	Published values	
			Gladney and others, (1979)	Sanzalone and others (1979)
GXR-1	396, 3.5	468, 3.2	460 ± 30	332
GXR-2	21, 14	19, 2.9	31 ± 5	18.2
GXR-3	3430, 3.6	4280, 9.7	4000, ± 450	4560
GXR-4	98, 4.3	105, 1.6	98 ± 10	89
GXR-5	6.7, 20	8.4, 6.4	12 ± 3	9.8
GRX-6	247, 4.4	308, 2.7	340 ± 30	330

<u>Bismuth (ppm)</u>				
	This method, x, RSD%*	O'Leary and Viets, (1986) x, RSD%	Ficklin and Ward (1976)	Viets (1978)
				GXR-1
GXR-2	<2.0	<1.	0.36	0.4
GXR-3	<2.0	<1.	----**	<0.2
GXR-4	18.3, 11.9	20, 0	22	21.
GXR-5	<2.0	<1.	0.35	0.4
GXR-6	<2.0	<1.	0.21	0.2

<u>Cadmium (ppm)</u>				
	This Method x, RSD%*	O'Leary and Viets (1986) x, RSD%	Motooka and others (1979)	Viets (1978)
				GXR-1
GXR-2	4.0, 2.8	3.85, 0.9	4.7	3.94
GXR-3	H*	0.37, 4.0	---	0.39
GXR-4	<0.1	0.38, 5.1	0.5	0.34
GXR-5	<0.1	0.13, 6.3	0.22	0.14
GRX-6	<0.1	0.11, 9.8	0.18	0.11

<u>Antimony (ppm)</u>				
	This Method, x, RSD%	O'Leary and Viets (1986) x, RSD%	Gladney and others 1979	Welch and Chao (1975)
				GXR-1
GXR-2	42, 11	39.6, 2.9	48 ± 5	44
GXR-3	H*	36., 2.0	40 ± 3	22
GXR-4	<2.0	3.6, 3.2	4.4 ± 0.8	5.1
GXR-5	<2.0	L (1)	2 ± 1	1.6
GXR-6	<2.0	1.98, 0.7	3.8 ± 0.7	2.8

<u>Zinc ppm)</u>				
	This Method x, RSD%	O'Leary and Viets (1986) x, RSD%	Gladney and others 1979	Viets (1978)
				GXR-1
GXR-2	544, 2.0	518, 0.9	500 ± 60	428
GXR-3	108, 11.9	226, 2.4	220 ± 70	124
GXR-4	70, 1.4	72, 0.9	64 ± 10	59
GXR-5	40.0, 2.1	41.6, 21	50 ± 5	41
GXR-6	105, 2.3	105, 1.2	120 ± 20	78

*H=There is a large W interference on Cd and Sb in this sample.

**--- = No data available.

The x and RSD % are based on 25 determinations over a 6 month period.

Fluoride by Ion Selective Electrode

Twenty-five milligrams of powdered rock sample are fused with 0.5g sodium hydroxide. The fusion cake is dissolved in water and the solution is buffered with ammonium citrate to about pH 6. The fluoride is determined with an ion selective electrode using a calibration curve. Limit of determination is 0.01% in sample.

Apparatus

Digital potentiometer, Orion model 901.

Fluoride ion activity electrode, Orion solid state electrode 94-09.

Reference electrode, Orion single junction 90-01.

Reagents

1000 $\mu\text{g/mL}$ fluoride stock solution prepared from reagent grade sodium fluoride (2.210 g/L).

Sodium hydroxide pellets, reagent grade.

1.1 M ammonium citrate (2.5 kg/10 L).

Procedure

1. Weigh 0.025 g of sample into a 45 ml zirconium crucible and add approximately 0.5 g of NaOH (4-5 pellets).
2. Melt NaOH over low heat and swirl crucible to insure mixing, and then fuse for 2 minutes at red heat using a Meker burner.
3. Add 10 ml of deionized water to cooled crucible.
4. After at least partial dissolution of the fusion cake, transfer crucible contents to 100 ml volumetric flask using ammonium citrate solution for rinsing. Dilute sample solution to 100 ml with ammonium citrate solution.
5. Equilibrate fluoride and reference electrodes with continuous stirring in 1 L of ammonium citrate to which 0.5 mL of 100 $\mu\text{g/mL}$ F solution has been added.
6. After stabilization of the electrode potential, record mV reading.
7. Add 0.5 mL of 100 $\mu\text{g/mL}$ F and after 5 minutes record mV reading.
8. Add 2 mL of 100 $\mu\text{g/mL}$ F and after minutes record mV reading.
9. Repeat step 5 twice (see table 8 and figure 8) to establish the calibration curve.
10. Calculate calibration line using least squares, first degree regression for mV vs. $\log [F]$.

11. Place electrodes in about 50 mL of sample solution, with continuous stirring. After 5 minutes record mV reading.
12. Dilute sample, if necessary, so that mV reading falls in range of calibration values.
13. Calculate %F using regression equation obtained from calibration line.

Discussion

Fluorine is a minor constituent of most rocks and is usually present at less than 0.1%. However, it may exceed 1% in a variety of minerals such as apatites, tourmalines, and micas. Many of these fluorine-containing minerals are particularly resistant to different digestion procedures. Alkaline hydroxides are particularly aggressive fluxes for decomposing many of these minerals (Dolezal and others, 1968). Sodium hydroxide has been used to decompose a variety of minerals, rocks, soils, and stream sediments (Hopkins, 1977; Kester and others, 1973; Van Loon, 1968; McQuater and Gurney, 1977). As outlined above, our procedure uses a flux to sample ratio of 20:1 to help ensure complete decomposition of the resistant minerals. The use of the NaOH also helps eliminate the F complexing metals, iron and aluminum, as insoluble hydroxides. Since the extraction solution is not filtered prior to buffering with the citrate, some iron and aluminum hydroxides redissolve; however, the citrate serves as a masking agent and there is no apparent interference with most samples.

Nicholson (1983) reviews the problems associated with the ion selective electrode determination of fluoride in geological materials including practical experimental errors, limitations of the potentiometric sensor, and interfering species. Interference due to hydrogen, aluminum, and iron complexation of fluoride are generally avoided by buffering the solution at about pH 6 and adding citrate as a masking agent. The lanthanum fluoride sensing crystal dissolves slightly in the citrate buffer due to formation of a lanthanum citrate complex. This tends to increase the limit of determination (Durst, 1969).

An example of our fluoride calibration line is shown in Figure 8. The average slope of the calibration line is -55 ± 1 mV/decade [F] ($\pm 1\sigma$).

The majority of published papers describing ion selective electrode techniques for the determination of fluoride in geological materials report precision on the order of 5-10% relative standard deviation. A drift of 1 mV in potential would represent a relative error of about 4% which approximates the best precision that can be attained with an ion selective electrode procedure (Nicholson, 1983). Four U.S.G.S. standards were analyzed in replicate. The results are shown in Table 9. Our results compare favorably with the Abbey's (1983) usable values despite the difference in weight basis (as received versus dry-weight basis). The precision for these replicate measurements was about 8% RSD which is typical of our results for a wide variety of silicate rocks.

Table 8. Typical fluoride determination calibration line data

<u>Cummulative Standard added, mL</u>	<u>Fluoride Concentration, ppm</u>	<u>Typical Relative MV</u>	<u>Equivalent %F in ₁ Sample</u>
0.5	0.05	0	0.02
1.0	0.1	-14.4	0.04
3.0	0.3	-41.0	0.12
5.0	0.5	-54.2	0.20
7.0	0.7	-62.8	0.28

¹ Assumes 0.025 g of sample in 100 ml.

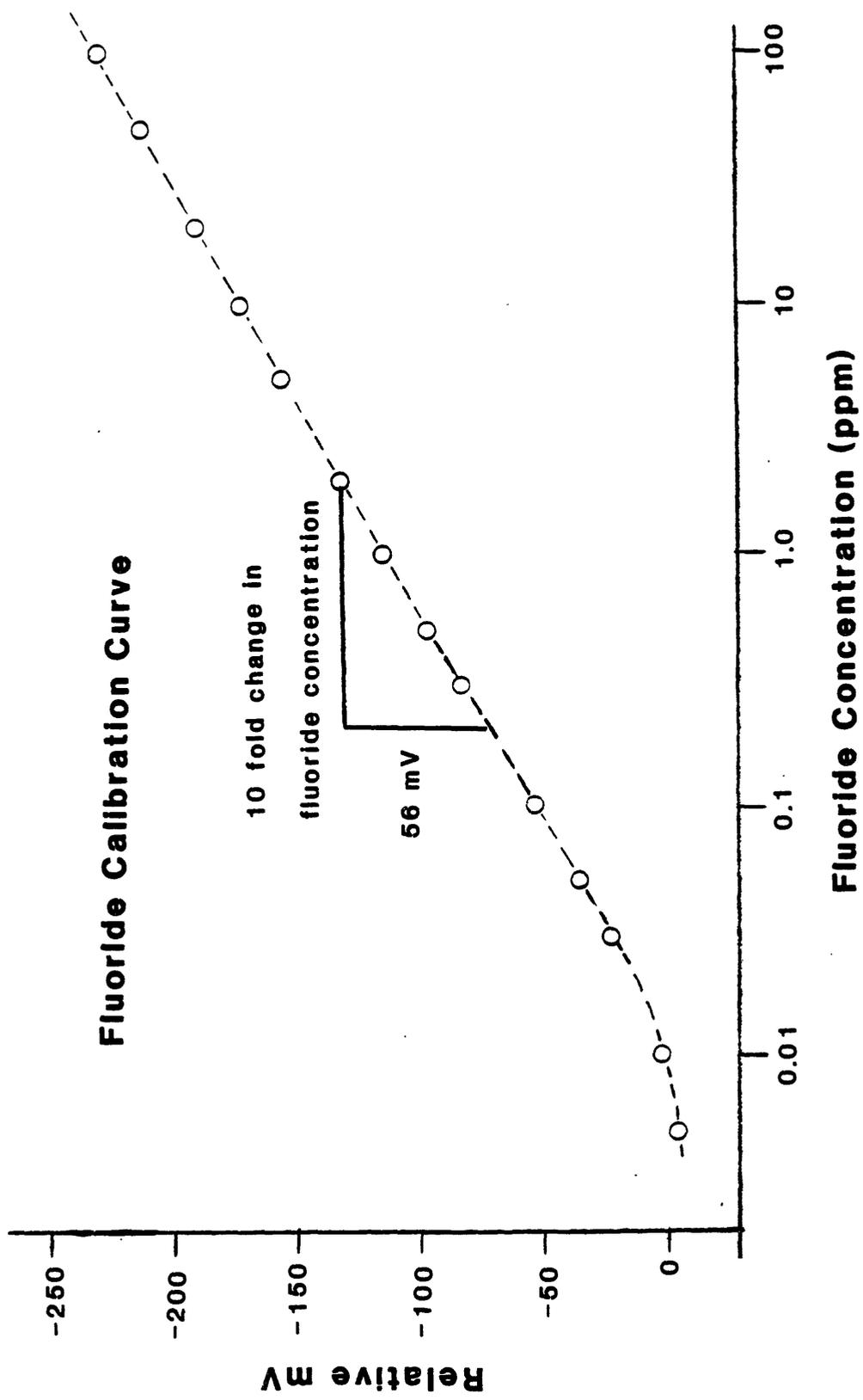
Table 9. Percent F in four U.S.G.S. Rock Standards

<u>Standard</u>	<u>Abbey's Usable Value</u>	<u>This method² Mean, number of determinations</u>	<u>RSD%</u>
BHV0-1 basalt	0.038?	0.037 (5)	8
G-2, granite	0.12	0.12 (13)	8
GSP-1, granodiorite	0.37	0.35 (8)	8
SGR-1, oil shale	0.19?	0.20 (8)	6

¹ Dry-weight basis.

² As-received basis.

Figure 8. A typical fluoride calibration curve, relative mV versus $\log [F^-]$.



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