

U.S. GEOLOGICAL SURVEY CIRCULAR 948



Analytical Methods Used in Geochemical Exploration, 1984



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By Richard M. O'Leary and Allen L. Meier

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ANALYTICAL METHODS USED IN GEOCHEMICAL EXPLORATION, 1984

By Richard M. O'Leary and Allen L. Meier

INTRODUCTION

Geochemical exploration involves the measurement of the concentration of an element or group of elements in naturally occurring materials. We use these measurements to recognize abnormal elemental patterns (geochemical anomalies) that may be related to mineralization. The analytical method used to differentiate between background and anomalous concentrations must have adequate sensitivity, accuracy, and precision. Most often the relative elemental concentration and not necessarily the absolute concentration is sufficient to allow recognition of geochemical anomalies. Thus, semiquantitative methods that are rapid, precise, sensitive, and easily applied to a variety of naturally occurring materials are most useful in geochemical exploration.

The USGS (U.S. Geological Survey) uses a variety of analytical methods for geochemical exploration. These include arc and inductively coupled plasma emission spectrometry, atomic absorption spectrometry, X-ray fluorescence spectrometry, colorimetry, ion chromatography, ultraviolet fluorimetry, and specific ion electrodes. Arc emission spectrography has proven to be one of the most useful analytical techniques. Thirty or more elements can be determined simultaneously in each sample with little sample preparation other than pulverizing. The technique lacks sensitivity for some of the more useful elements, and a highly trained analyst must interpret the photographic spectra. Therefore, the other analytical methods are used in place of or to complement the spectrographic technique. In this report, we present some of these methods found to be most useful for this purpose.

The purpose of this report is to bring together

previously published analytical methods currently being used by the Branch of Exploration Geochemistry of the USGS for geochemical exploration, to make them more available to interested persons within and outside the USGS. We present these methods in "cookbook" style and have incorporated slight changes in procedure made since the original publication to provide procedures more easily followed by nontechnical as well as technical persons. Read the original publications if a more comprehensive description of the method is desired.

Statistical data obtained by replicate analysis of six GXR (geochemical exploration reference) samples define the expected precision of each method (Allcott and Lakin, 1975).

<i>Sample</i>	<i>Description</i>
GXR-1	Jasperoid
GXR-2	Soil
GXR-3	Fe-Mn-W-rich hot spring deposit
GXR-4	Porphyry copper mill heads
GXR-5	B-horizon soil
GXR-6	B-horizon soil

These reference materials may be used as quality-control check samples. Observed values for these reference materials are given to indicate the sensitivity and range expected for each method.

In selecting an analytical method, it is useful to know the expected abundance of the element of interest and the sensitivity of methods available. Table 1 gives the average abundance or range of trace elements in the Earth's crust, various rocks, soil, and river water (Levinson, 1974), and table 2 gives the average abundance of major elements in the Earth's crust, basalt, and granite (Taylor, 1964). Both tables include a comparison

TABLE 1.—Average abundance or range of trace elements in the Earth's crust, various rocks, soil, and river water, and limits of determination for six-step semiquantitative emission spectrography and analytical methods of this compilation

[Average abundance data from Levinson (1974). All values in ppm, except river water in ppb. Leaders (—), no data available]

Element	Average abundance or range									Limits of determination	
	Earth's crust	Ultra-mafic	Basalt	Grano-diorite	Granite	Shale	Lime-stone	Soil	River water	Emission spectrography	Other analytical methods
Ag	0.07	0.06	0.1	0.07	0.04	0.05	1	0.1	0.3	0.5	0.05 ^a
As	1.8	1	2	2	1.5	15	2.5	1-50	2	200	1 ^b
Au	.004	.005	.004	.004	.004	.004	.005	--	.002	10	.5 ^f , .002 ^c
B	10	5	5	20	15	100	10	2-100	10	10	--
Ba	425	2	250	500	600	700	100	100-3,000	10	20	--
Be	2.8	--	.5	2	5	3	1	6	--	1	--
Bi	.17	.02	.15	--	.1	.18	--	--	--	10	1 ^a
Br	2.5	1	3.6	--	2.9	4	6.2	--	20	--	--
Cd	.2	--	.2	.2	.2	.2	.1	1	--	20	.5 ^a
Ce	60	8	35	40	46	50	10	--	.06	--	--
Cl	130	85	60	--	165	180	150	--	7,800	--	--
Co	25	150	50	10	1	20	4	1-40	.2	5	5 ^a
Cr	100	2,000	200	20	4	100	10	5-1,000	1	10	--
Cs	3	--	1	2	5	5	--	6	.02	--	--
Cu	55	10	100	30	10	50	15	2-100	7	5	1 ^a , 1 ^b , 5 ^f
Dy	3	.59	3	3.2	.5	5	.4	--	.05	--	--
Er	2.8	.36	1.69	4.8	.2	2	.5	--	.05	--	--
Eu	1.2	.16	1.27	1.2	--	1	--	--	.07	--	--
F	625	100	400	--	735	740	330	--	100	--	100 ^d
Ga	15	1	12	18	18	20	.06	15	.09	--	--
Gd	5.4	.65	4.7	7.4	2	6	.6	--	.04	--	--
Ge	1.5	1	1.5	1	1.5	1.5	.1	1	--	--	--
Hf	3	.5	2	2	4	3	.5	--	--	--	--
Hg	.08	--	.08	.08	.08	.5	.05	.03	.007	--	.01 ^c
Ho	1.2	.14	.64	1.6	.07	1	.1	--	.01	--	--
I	.5	.5	.5	--	.5	2.2	1.2	--	7	--	--
In	.1	.01	.1	.1	.1	.1	.02	--	--	--	.2 ^f
Ir	.0004	--	--	--	--	--	--	--	--	--	--
La	30	3.3	10.5	36	25	20	6	--	.2	20	--
Li	20	--	10	25	30	60	20	5-200	3	--	5 ^f

Lu	.50	.064	.20	--	.01	.5	--	--	.008	--	--
Mn	950	1,300	2,200	1,200	500	850	1,100	850	7	10	--
Mo	1.5	.3	1	1	2	3	1	2	1	5	1 ^f
Nb	20	15	20	20	20	20	--	--	--	20	--
Nd	28	3.4	17.8	26	18	24	3	--	.2	--	--
Ni	75	2,000	150	20	.5	70	12	5-500	.3	5	5 ^a
Os	.0004	--	--	--	--	--	--	--	--	--	--
Pb	12.5	.1	5	15	20	20	8	2-200	3	10	5 ^f , 1 ^a
Pd	.004	.02	.02	--	.002	--	--	--	--	--	--
Pr	8.2	1.02	3.9	8.5	4.6	6	1	--	.03	--	--
Pt	.002	.02	.02	--	.008	--	--	--	--	--	--
Rb	90	--	30	120	150	140	5	20-500	1	--	--
Re	.0005	--	.0005	--	.0005	--	--	--	--	--	--
Rh	.0004	--	--	--	--	--	--	--	--	--	--
Ru	.0004	--	--	--	--	--	--	--	--	--	--
Sb	.2	.1	.2	.2	.2	1	--	5	1	100	1 ^f
Sc	16	10	38	10	5	15	5	--	.004	5	--
Se	.05	--	.05	--	.5	.6	.08	.2	.2	--	.05 ^c
Sm	6	.57	4.2	6.8	3	6	.8	--	.03	--	--
Sn	2	.5	1	2	3	4	4	10	--	10	2 ^f
Sr	375	1	465	450	285	300	500	50-1,000	50	100	--
Ta	2	1	.5	2	3.5	2	--	--	--	--	--
Tb	.9	.088	.63	1.3	.05	1	--	--	.008	--	--
Te	.001	.001	.001	.001	.001	.01	--	--	--	--	.1 ^f , .004 ^c
Th	10	.003	2.2	10	17	12	2	13	.1	100	--
Ti	5,700	3,000	9,000	8,000	2,300	4,600	400	5,000	3	20	--
Tl	.45	.05	.1	.5	.75	.3	--	.1	--	--	.2 ^f
Tm	.48	.053	.21	.5	--	.2	.1	--	.009	--	--
U	2.7	.001	.6	3	4.8	4	2	1	.4	--	.05 ^e
V	135	50	250	100	20	130	15	20-500	.9	10	--
W	1.5	.5	1	2	2	2	.5	--	.03	50	1 ^b
Y	30	--	25	30	40	25	15	--	.7	10	--
Yb	3	.43	1.11	3.6	.06	3	.1	--	.05	--	--
Zn	70	50	100	60	40	100	25	10-300	20	200	1 ^a , 1 ^b , 5 ^f
Zr	165	50	150	140	180	160	20	300	--	10	--

^aOrganic extraction by atomic absorption.

^bColorimetry.

^cFlameless atomic absorption.

^dSpecific ion electrode.

^eFluorimetry.

^fAqueous extraction by atomic absorption.

TABLE 2.—Average abundance of major elements in the Earth's crust, basalt, and granite, and limits of determination for six-step semiquantitative emission spectrography and analytical methods of this compilation

[Average abundance data from Taylor (1964). All values in percent. Leaders (—), no data available]

Element	Average abundance			Limits of determination	
	Earth's crust	Basalt	Granite	Emission spectrography	Other analytical methods
Al	8.23	8.76	7.70	—	—
Ca	4.15	6.72	1.58	0.05	0.05
Fe	5.63	8.56	2.70	.05	—
K	2.09	.83	3.34	—	.1
Mg	2.33	4.5	.16	.02	.001
Na	2.36	1.94	2.77	—	.1
Si	28.15	24.0	32.3	—	—

of the limits of determination of the analytical methods of this compilation and those of a commonly used semiquantitative emission spectrographic technique (Grimes and Marranzino, 1968).

References to other analytical methods, sample preparation and treatment, comparison of methods, separations before analysis, special analysis, and basic information and discussion of chemical methodology published since 1963 by members of our group in the USGS that may be of interest to those involved in analysis of geologic materials are given in the "Selected references" section.

Any use of trade names in this report is for descriptive purposes only and does not imply endorsement by the USGS.

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- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, in Elliott, I. L., and Fletcher, W. K. eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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- Taylor, S. R., 1964, Abundance of chemical elements in the continental crust—A new table: *Geochimica et Cosmochimica Acta*, v. 28, p. 1273-1284.

ANTIMONY, ATOMIC ABSORPTION METHOD

The method described here, excepting minor changes, was developed by Welsch and Chao (1975).

SUMMARY

Traces of antimony in rock, soil, and stream-sediment samples are determined using an atomic absorption method. A dried mixture of the sample and ammonium iodide is heated to volatilize antimony tri-iodide, which condenses on the walls of the test tube. The condensate is put into solution with 10 percent hydrochloric acid, which fails to attack most interfering ions remaining in the sample. When a sample of extremely high iron content is analyzed, ascorbic acid keeps the iron in the reduced form and thus prevents its extraction.

The antimony tri-iodide is extracted by trioctylphosphine oxide and methyl isobutyl ketone solution in the presence of an excess of potassium iodide. The extract is aspirated into an atomic absorption spectrophotometer for estimation. Fifty samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Ammonium iodide: Pulverize to the consistency of extra-fine granulated sugar with a mortar and pestle and store in a desiccator.

Hydrochloric acid, 10 percent: Dilute 100 mL concentrated hydrochloric acid to 1 L with water.

Iodide reagent: Dissolve 30 g potassium iodide and 5 g ascorbic acid in 100 mL of 10 percent hydrochloric acid (prepare daily).

TOPO-MIBK reagent: Dissolve 4 g TOPO (trioctylphosphine oxide) in 100 mL MIBK (methyl isobutyl ketone).

APPARATUS

Atomic absorption spectrophotometer

Centrifuge

Electric oven

Horizontal shaking machine

Pyropot (Pyroco Products, Margat, Queensland, Australia 4019): Heating device accommodating 10 test tubes, provides a controlled heat source for the iodide fusion. When the test tubes are inserted into the holders, only the bottom 3-4 cm is exposed to the desired temperature, thereby leaving the upper portions of the tubes cool enough to allow condensation of antimony tri-iodide vapors.

Test tube, disposable screw-cap, 16×150-mm

Vortex mixer

Water bath

STANDARDS

Stock antimony solution, 1,000 µg/mL: Dissolve 1.370 g potassium antimony tartrate in 500 mL of 6 M hydrochloric acid.

Dilute antimony solution, 100 µg/mL: Combine 10 mL of 1,000 µg/mL stock antimony solution with 5 mL concentrated hydrochloric acid and dilute to 100 mL with water.

Standard antimony solutions in TOPO-MIBK, 0, 10, and 50 µg/mL: Add 0.0, 1.0, and 5.0 mL of 100 µg/mL dilute antimony solution to three 25×200-mm screw-cap test tubes containing 1 g potassium iodide and 1.5 g ascorbic acid. Bring the total volume to 50 mL with 10 percent hydrochloric acid and mix to dissolve. Add 10 mL TOPO-MIBK reagent and shake for 1 minute.

PROCEDURE

1. Weigh 0.5 g sample into a 16×150-mm disposable screw-cap test tube.
2. Add 2 g powdered ammonium iodide, mix thoroughly, and dry overnight at 110°C in an electric oven.
3. Allow to cool and then heat the sample for 10 minutes in the Pyropot, which has been preheated to 350°C.
4. After sample has cooled, add 7 mL of 10 percent hydrochloric acid and 3 mL iodide reagent, and place in a boiling water bath for 15 minutes.
5. Mix the sample well while hot, then cool in a cold water bath.

6. When cool, add 2 mL TOPO-MIBK reagent, cap, shake for 1 minute, and centrifuge.
7. Determine the antimony content by aspirating the organic layer into an atomic absorption spectrophotometer.

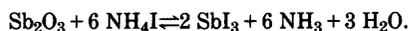
STANDARDIZATION OF INSTRUMENT

The following operating conditions are for a Perkin-Elmer model 603 atomic absorption spectrophotometer.

Grating	ultraviolet
Wavelength	218.4
Slit	0.2 nm
Lamp current	use current recommended on lamp
Source lamp	antimony (hollow cathode lamp)
Background correction	on
Integration time	1 second
Burner	Boiling
Flame condition	oxidizing (lean blue)
10 µg/mL	0.310 absorbance units
50 µg/mL	1.240 absorbance units
Lower limit of determination	0.5 ppm

DISCUSSION

The reaction of antimony present in the sample as Sb_2O_3 with ammonium iodide is as follows:



Any excess of water would tend to reverse the reaction because water is a product of the reaction, therefore, the sample and ammonium iodide mixture must be as dry as possible for maximum efficiency. The temperature and duration of heating in the Pyropot are critical and must be controlled to obtain reproducible results.

Interferences are minimized in three ways. (1) Heating at 350°C isolates the antimony from the sample matrix. The released antimony is dissolved by the 10 percent hydrochloric acid solution, whereas potential interfering ions are only slightly dissolved. (2) Ascorbic acid in the iodide reagent reduces iron (III) to iron (II), which is not extracted by the TOPO-MIBK, thus iron interference is eliminated. (3) The extraction of antimony into TOPO-MIBK further separates the antimony from other potential interferences.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin,

1975), in replicas of five, by the described procedure.

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	89-113	101	8.7
II	36-38	37.2	2.94
III	17-19	17.8	4.7
IV	6-7	6.4	8.6
V	1	1	0
VI	2-3	2.6	21

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, in Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
- Welsch, E. P., and Chao, T. T., 1975, Determination of trace amounts of antimony in geological materials by atomic absorption spectrometry: *Analytica Chimica Acta*, v. 76, p. 65-69.

ARSENIC, CONFINED-SPOT METHOD

The method described here, excepting minor changes, was developed by Almond (1953), and described by Ward and others (1963).

SUMMARY

Arsenic is determined in rock, soil, and stream-sediment samples by a confined-spot method using a modified Gutzeit apparatus. The sample is partly dissolved by molten potassium hydroxide in a test tube. The melt is dissolved with 30 percent hydrochloric acid and the arsenic is reduced by the addition of stannous chloride. Through the action of metallic zinc in the acid solution, arsenic III is reduced to arsine, and the evolved arsine gas is reacted with mercuric chloride paper to form a yellow- to orange-colored spot. The colored spot is compared against colored standards for estimation of arsenic content. Small amounts of hydrogen sulfide evolved with the arsine are removed by reaction with lead acetate on glass wool through which the gases are passed. The black lead sulfide formed by the reaction serves as an indicator for the need of renewing the lead acetate-coated glass wool. Samples with a high sulfide content must be treated with hydrogen peroxide because all hydrogen sulfide will not be

removed by the lead acetate. About 60 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Hydrochloric acid, 30 percent: Dilute 300 mL concentrated hydrochloric acid to 1 L with water.

Hydrogen peroxide, 8 percent: Dilute 8.0 mL hydrogen peroxide, 50 percent strength, to 50 mL with water (prepare daily).

Lead acetate-coated glass wool: Dissolve 15 g lead acetate $[\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}]$ in 100 mL water and 3 mL glacial acetic acid. Saturate as much glass wool as can be conveniently covered with this solution for 15 minutes, remove, and allow to dry. Fill the lower section of the modified gutzeit apparatus with this dried glass wool. Store excess glass wool in stoppered bottle.

Mercuric chloride paper: Dissolve about 25 g mercuric chloride (HgCl_2) in 100 mL ethyl alcohol. Place some filter paper (Black Ribbon, S and S No. 589) in the solution for 1 hour. Remove, and allow the paper to dry in the air. Cut into 1/2-inch squares and store in a box.

Potassium hydroxide, pellets.

Stannous chloride, 10 percent: Dissolve 10 g stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 100 mL concentrated hydrochloric acid.

Zinc, mossy or shot.

APPARATUS

Burner

Heating block; drilled to accommodate 25-mm test tubes

Modified Gutzeit apparatus (fig. 1): To assemble the apparatus, insert the unflanged end of the glass pipe into the rubber stopper. Place a square of mercuric chloride paper on the flanged end. Attach a second glass pipe by clamping the flanged ends together with a joint clamp. Insert the rubber stopper into the test tube when the solution is prepared for arsine evolution. The apparatus is conveniently held upright by a funnel rack. For efficient operation in mass-production determinations, 24 units of the apparatus are required. Additional test tubes are required for fusion of the samples. Only two to four fusions may be made in each test tube before it must be discarded. When the black lead sulfide

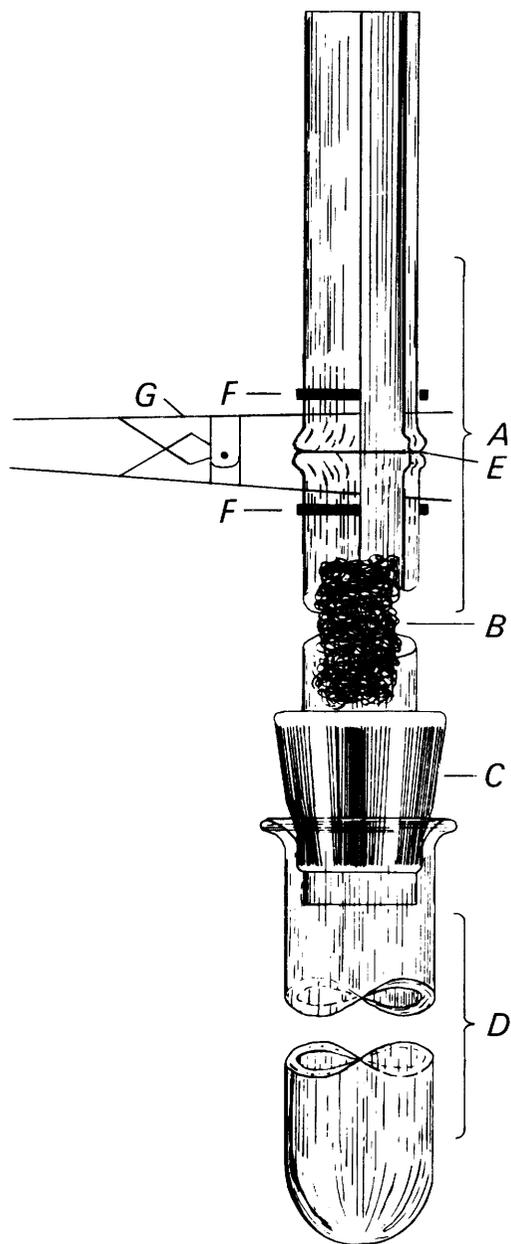


FIGURE 1.—Modified Gutzeit apparatus. A, two sections of glass pipe, 0.5-inch O.D.; B, glass wool coated with lead acetate; C, no. 4 rubber stopper with center hole 0.5 inch in diameter; D, test tube with rim, 25×150-mm; E, mercuric chloride paper; F, surgical tubing 0.2×0.5-inch O.D.; G, joint clamp.

formed by the reaction has discolored the lower half of the glass wool, the glass wool should be removed from the apparatus and replaced by fresh glass wool.

Test tubes, 25×150-mm; with rim
Vortex mixer

STANDARDS

Stock arsenic solution, 1,000 $\mu\text{g}/\text{mL}$: Dissolve 0.13 g arsenic trioxide in 2 mL of 1 M sodium hydroxide, dilute with water to about 50 mL, make slightly acid by adding 3 mL of 1 M hydrochloric acid, and dilute to 100 mL.

Dilute arsenic solution, 100 $\mu\text{g}/\text{mL}$: Dilute 10 mL of 1,000 $\mu\text{g}/\text{mL}$ stock arsenic solution to 100 mL with water.

Standard arsenic solution, 10 $\mu\text{g}/\text{mL}$: Dilute 10 mL of 100 $\mu\text{g}/\text{mL}$ dilute arsenic solution to 100 mL with water.

Arsenic color-spot standards, 1, 2, 4, 8, 12, and 16 μg : Add 0.1, 0.2, 0.4, 0.8, 1.2, and 1.6 mL of 10 $\mu\text{g}/\text{mL}$ standard arsenic solution, respectively, to six 25×150-mm test tubes. Prepare standards in triplicate. Add 10 mL of 30 percent hydrochloric acid and proceed with step 6 of procedure. Select the average (mid-color) spot of each spot standard representing the μg of arsenic being considered. This will give corresponding 10-, 20-, 40-, 80-, 120-, and 160-ppm color-spot standards. Store color standards between pages of a book and expose to light as little as possible. Standards should be prepared weekly or more often if needed.

PROCEDURE

1. Weigh 0.1 g sample into a 25×150-mm test tube.
2. Add 8 pellets (about 0.8 g) of potassium hydroxide.
3. Heat the tube containing sample and potassium hydroxide over a burner for about 20 seconds or until the potassium hydroxide is melted. Avoid continued heating of the tube after the flux has melted because potassium hydroxide attacks glass. Remove the tube from the flame and rotate the tube so that the melt will cool in a thin film on the side of the tube.
4. When the tube is cool, add 10 mL of 30 percent (v/v) hydrochloric acid to the contents and let stand until the melt disintegrates (approximately 30 minutes).
5. Mix on a vortex mixer.
6. Add 0.5 mL of 10 percent stannous chloride and mix on a vortex mixer. If a yellow color is present, add additional 10 percent stannous chloride until the yellow disappears.

This solution should not be left standing because any silica present will form a gel.

7. Add 2-4 g zinc (mossy or shot), and immediately attach the test tube to the rubber stopper on the modified Gutzeit apparatus.
8. After 30 minutes, remove the disk of mercuric chloride paper and compare as soon as possible with the arsenic color-spot standards.
9. For samples with more than 160 ppm, it will be necessary to weigh and fuse the sample again. Add 10 mL of 30 percent (v/v) hydrochloric acid, then transfer a suitable aliquot to another 25×150-mm test tube containing 10 mL of the 30 percent (v/v) hydrochloric acid and proceed to step 6 of procedure.

SULFIDE PROCEDURE

Sulfides can often be recognized in the sample or will form a cloudy, grey precipitate in the acid and give off hydrogen sulfide fumes. If high sulfide concentrations are taken through step 8 of the procedure, the glass wool will turn black. Use this sulfide procedure to prevent interference from high sulfide content.

1. Add 0.3 mL of 8 percent hydrogen peroxide to a fused sample containing 10 mL of 30 percent hydrochloric acid. Mix using a vortex mixer.
2. Place in heating block and heat gently to not more than 65°C until bubbling has nearly ceased.
3. Mix using a vortex mixer, cool, and proceed to step 6 of the previous procedure. If the sample still blackens the glass wool, reprepare sample and add 0.5 mL instead of 0.3 mL of 8 percent hydrogen peroxide.

DISCUSSION

Many of the heavy metals in amounts of 50 mg or more interfere with the arsenic test, but their presence in soils in such high concentrations is most unlikely even in mineralized areas. Lower readings may result from arsenic that remains behind instead of being swept out of the test tube, and by arsine adsorption on the lead acetate. Although variation in the rate of hydrogen evolution causes errors in the readings of the conventional "strip test", they are much less serious for the confined spot method described. The difference in arsenic content of soil in a mineralized area and

that of soil in an unmineralized area is normally so great that there is little danger that the prospector will be misled by the small differences resulting from the errors implicit in this method. Leaks in the apparatus that allow arsine to escape without coming in contact with the mercuric chloride will cause lower values, but this can be avoided by proper assemblage.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

[L(), detected, but below limit of determination, or below value shown]

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	200-320	264	20.33
II	10	10	0
III	2,400-3,200	2,960	12.09
IV	80-120	96	27.16
V	L(10)	L(10)	0
VI	200-240	208	12.88

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- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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ARSENIC, SPECTROPHOTOMETRIC METHOD

The method described here was adapted by Welsch (1979) from Kopp (1973) and Marshall (1978).

SUMMARY

Geologic materials are decomposed by a mixture of aqua regia and hydrofluoric acid. Arsenic is reduced to the trivalent state with potassium iodide. Interferences are minimized by the addition of

iron II and stannous chloride. Arsine, produced by the addition of zinc shot, is bubbled through a chloroform solution of silver diethyldithiocarbamate and ephedrine. The resultant red complex is used to determine trace amounts of arsenic by visible spectrophotometry. About 40 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

AgDDC reagent (silver diethyldithiocarbamate): Dissolve 3.4 g silver nitrate and 4.5 g NaDDC (sodium diethyldithiocarbamate) in separate beakers containing 200 mL water. Chill to 8°C or below. Combine the solutions while mixing vigorously. Vacuum filter and wash the resulting precipitate of AgDDC with two 100-mL portions of cold water. Dry the precipitate in a desiccator. Yield is about 4.5 g AgDDC.

AgDDC-ephedrine solution: Dissolve 0.41 g of 1-ephedrine (formula weight 165.2, available from Aldrich Chemical Co., Milwaukee, Wis.) and 0.625 g AgDDC reagent in 250 mL chloroform.

Hydrochloric acid, concentrated.

Hydrochloric acid, 1 M: Dilute 83 mL concentrated hydrochloric acid to 1 L with water.

Hydrofluoric acid, 48 percent.

Iron solution, 1 percent: Dissolve 7 g ferrous ammonium sulfate hexahydrate ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) and 0.1 g ascorbic acid in 100 mL water.

Nitric acid, concentrated.

Potassium iodide, 40 percent: Dissolve 40 g potassium iodide in 100 mL water.

Stannous chloride, 20 percent: Dissolve 20 g stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 100 mL concentrated hydrochloric acid.

Zinc, shot.

APPARATUS

Arsine generation assembly (fig. 2)

Centrifuge

Hot plate

Spectrophotometer

Teflon beaker, 50-mL

Teflon policeman

Test tubes, 12×75-mm

Test tubes, 16×150-mm

Test tubes, 25×150-mm

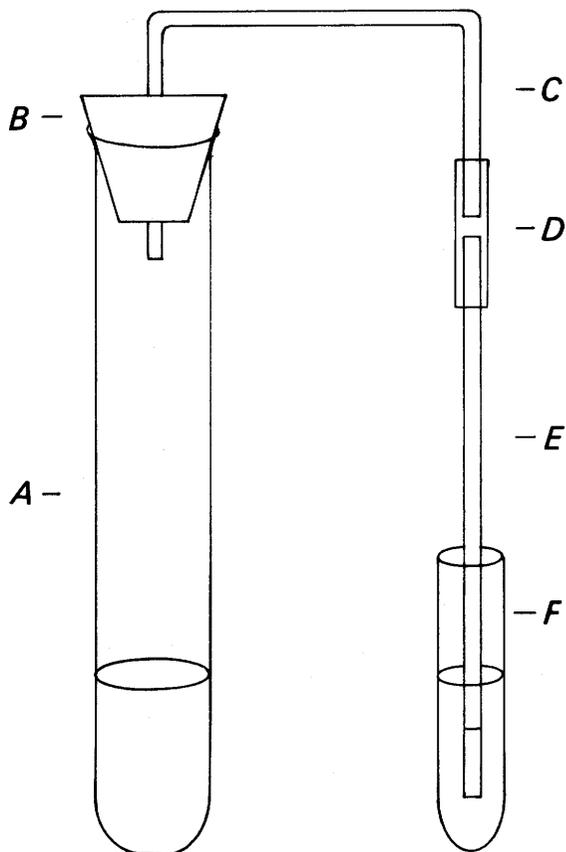


FIGURE 2.—Arsine generation assembly. A, test tube, 25×150-mm with rim; B, no. 4 rubber stopper with center hole 5 mm diameter; C, glass tubing, 5-mm O.D.; D, tygon tubing, 5-mm I.D.; E, gas dispersion tube B porosity fritted glass tip, 5-mm O.D.×10-mm, available from Ace Glass Inc., Vineland, N. J.; F, test tube, 12×75-mm.

STANDARDS

Stock arsenic solution, 1,000 μg/mL: Dissolve 1.300 g arsenic trioxide in 20 mL of 1 M sodium hydroxide, add 500 mL water and 30 mL of 1 M hydrochloric acid, and dilute to 1 L with water.

Stock arsenic solution, 100 μg/mL: Dilute 10 mL of 1,000 μg/mL stock arsenic solution to 100 mL with water.

Stock arsenic solution, 10 μg/mL: Dilute 10 mL of 100 μg/mL stock arsenic solution to 100 mL with water.

Arsenic working standards: Pipette (in triplicate) 0, 0.1, and 0.5 mL of 10 μg/mL stock arsenic solution and 0.1, 0.25, and 0.5 mL of 100 μg/mL stock arsenic solution, respectively, into six

25×150-mm tubes and add 10 mL of 1 M hydrochloric acid to each tube, then proceed to step 9 of the procedure.

PROCEDURE

1. Weigh 1.0 g sample into a 50-mL Teflon beaker.
2. Add 2 mL concentrated nitric acid, 6 mL concentrated hydrochloric acid, and 15 mL of 48 percent hydrofluoric acid.
3. Place beaker on a hot plate set at 110°C and evaporate to dryness.
4. Add 5 mL of 1 M hydrochloric acid and warm to about 50°C.
5. Loosen the residue with the aid of a Teflon policeman and transfer to a 16×150-mm tube.
6. Rinse the beaker with another 5 mL of 1 M hydrochloric acid and transfer to the 16×150-mm tube.
7. Mix the contents of the tube and centrifuge.
8. Transfer a 5-mL aliquot from the 16×150-mm tube into a 25×150-mm tube.
9. Add 5 mL of 1 M hydrochloric acid, 1 mL of 1 percent iron solution, 1 mL of 40 percent potassium iodide solution, and 1 mL of 20 percent stannous chloride solution to the 25×150-mm tubes containing samples and arsenic working standards.
10. Mix the contents of the tubes and let stand for 15 minutes.
11. Add 3 mL AgDDC-ephedrine solution to a 12×75-mm tube for each sample and standard.
12. Add four pieces of zinc shot to the 25×150-mm tube and immediately connect it to the arsine generation assembly as shown in figure 2.
13. Allow the resulting hydrogen and arsine to bubble through the AgDDC-ephedrine solution for 30 minutes.
14. Estimate the arsenic in the AgDDC-ephedrine solution by comparing the absorbance at 540 nm for sample and standards using a spectrophotometer.

STANDARDIZATION OF INSTRUMENT

The absorbances at a wavelength of 540 nm for the standard solutions are used to construct a calibration curve. Arsenic in the samples is estimated

by comparing the absorbance of the sample to the calibration curve. The following absorbance values have been obtained using a Bausch and Lomb model spectronic 100 spectrophotometer.

[Lower limit of determination, 1 ppm]

Standard (μg)	Absorbance units	Corresponding sample concentration (ppm)
1.0	0.044	2.0
5.0	.220	10.0
10.0	.456	20.0
25.0	1.100	50.0
50.0	2.204	100.0

DISCUSSION

The digestion with aqua regia and hydrofluoric acid, in addition to rendering arsenic soluble, destroys organic material, dispels sulfur compounds, subdues frothing, and destroys nitrate ions that interfere with the evolution of arsine. Iron solution is added to insure a uniform rate of hydrogen evolution from sample to sample. The addition of potassium iodide and stannous chloride reduces arsenic to the trivalent state and minimizes interferences from copper, cobalt, nickel, chromium, and molybdenum. As much as 2,000 μg of these elements may be present without seriously affecting the recovery of arsenic. Antimony, tellurium, mercury, and selenium also interfere; however, they are not normally present in concentrations that cause significant interference. The AgDDC reagent must be prepared as needed, otherwise it is difficult to dissolve and precipitates when the hydrogen is bubbled through it. The dispersion tubes should be rinsed with acetone after each use and should be cleaned in hot dichromate cleaning solution weekly. Samples that give absorbance readings higher than that of the highest standard may be rerun using a smaller aliquot of the sample solution to generate the arsine.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	360-490	432	12
II	18-21	19	7
III	3,600-4,400	4,020	7
IV	110-130	123	7
V	9-12	11	13
VI	350-370	362	2

REFERENCES CITED

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BISMUTH, CADMIUM, COPPER, LEAD, SILVER, AND ZINC, ORGANIC EXTRACTION METHOD

The method described here, excepting minor changes, was developed by Viets (1978).

SUMMARY

Interferences commonly encountered in the determination of bismuth, cadmium, copper, lead, silver, and zinc at crustal abundance levels are effectively eliminated using a rapid, sensitive, organic extraction method. A potassium chlorate-hydrochloric acid digestion solubilizes the metals not tightly bound in the silicate lattice of rock, soil, and stream-sediment samples. The six metals are selectively extracted into an organic phase of 10 percent tricapyrylmethylammonium chloride-methyl isobutyl ketone in the presence of ascorbic acid and potassium iodide.

Metals in the organic extract are determined by flame atomic absorption spectrometry to the 0.05 ppm level for cadmium and silver and to the 1.0 ppm level for bismuth, copper, lead, and zinc. About 40 samples can be analyzed per day for the six metals. If only selected metals are determined, more samples can be analyzed.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free, unless otherwise indicated.

Acetone, technical grade.

Aliquat 336-MIBK, 10 percent v/v: Pour 300 mL Aliquat 336 (tricapyrylmethylammonium chloride) [obtainable from General Mills Chemical Division, Minneapolis, Minn.] into a clean 1-L graduated cylinder, dilute to 1 L with MIBK (methyl isobutyl ketone), and swirl to dissolve the Aliquat 336. Pour into a brown glass bottle, add additional 2,000 mL of MIBK, and shake. This solution is stable for at least 1 month.

Ascorbic acid-potassium iodide solution, 20 percent-10 percent w/v: Weigh 200 g ascorbic acid (U.S.P. food grade or metal-free equivalent) and 100 g potassium iodide into a brown glass bottle, add 1 L distilled water, and shake until dissolved (prepare weekly). Some potassium iodide has been found to contain cadmium and silver. However, if samples, standards, and blanks are prepared using the same bottle of reagent, small amounts of contaminants will not be a problem.

Hydrochloric acid, concentrated.

Potassium chlorate.

APPARATUS

Atomic absorption spectrophotometer

Boiling chips

Centrifuge; 16-mm capacity head

Heating block; drilled to accommodate 16-mm test tubes

Horizontal shaking machine

Powder funnel

Scoop, 1-g plastic or aluminum

Silicone rubber or polyethylene stoppers for 16-mm test tubes

Test tubes, disposable, 16×150-mm

STANDARDS

Stock bismuth, cadmium, copper, lead, silver, and zinc solutions, 1,000 µg/mL: Accurately weigh the following amounts of pure metal oxides into separate 100-mL class-A volumetric flasks.

bismuth—0.1115 g bismuth oxide (Bi_2O_3)

cadmium—0.1142 g cadmium oxide (CdO)

copper—0.1252 g copper oxide (CuO)

lead—0.1077 g lead oxide (PbO)

silver—0.1074 g silver oxide (Ag_2O)

zinc—0.1245 g zinc oxide (ZnO)

Add two 1-g scoops of potassium chlorate and 10 mL concentrated hydrochloric acid to all six flasks and allow to react for 1 hour. Place the flasks in a boiling water bath for 2 hours or until the solutions become colorless and the oxides are completely dissolved. The copper solution will be yellow but the other five standards should be nearly colorless, indicating that all yellow reaction products have been volatilized. For silver it may be necessary to add about 80 mL of 10 N hydrochloric acid and heat on the water bath for several more hours to effect solution. Once dissolved, allow standards to cool and dilute to 100 mL with 10 N hydrochloric acid.

Combined standard solutions: Prepare three combined standards in 10 N hydrochloric acid from the individual 1,000 $\mu\text{g}/\text{mL}$ stock solution to contain the following amounts of the six metals.

Metal	Std. 1 ($\mu\text{g}/\text{mL}$)	Std. 2 ($\mu\text{g}/\text{mL}$)	Std. 3 ($\mu\text{g}/\text{mL}$)
Bismuth	20.0	50.0	100
Cadmium	2.00	5.00	10.0
Copper	20.0	50.0	100
Lead	20.0	50.0	100
Silver	2.00	5.00	10.00
Zinc	20.0	50.0	100

Standard solutions in Aliquat 336-MIBK: Add 1.0 mL each of Std. 1, Std. 2, and Std. 3 to three 16 \times 150-mm test tubes containing boiling chips. Add 1 g potassium chlorate and slowly add 3 mL concentrated hydrochloric acid and then treat as a normal sample continuing at step 4 of the procedure section. Also prepare a blank with each set of standards. If all six metals are to be determined, two sets of standards should be prepared for every 50 samples.

Working organic blank: Shake 300 mL of 10 percent Aliquat 336-MIBK solution with 100 mL of 3 N hydrochloric acid in a 500-mL reagent bottle.

PROCEDURE

1. Weigh 1.00 g sample into a 16 \times 150-mm disposable test tube containing a clean boiling chip. Include a tube with no sample as a blank with each set of samples.

2. Add approximately 1 g potassium chlorate using a scoop and mix thoroughly.
3. Slowly add four 1-mL portions of concentrated hydrochloric acid, allowing ample time for the reaction to subside between additions. Mix the contents of the tubes after the first and last addition of acid. Samples containing appreciable amounts of carbonate or organic materials may require a powder funnel to contain the foaming digestion solution. The residue in the funnel is rinsed into the tube after step 4 with the ascorbic acid-potassium iodide solution.
4. After 30 minutes or longer, place the tubes in a heating block and bring to a moderate boil for 2 minutes or until all yellow fumes have evolved and the blank is colorless.
5. Allow samples to cool, add 8 mL ascorbic acid-potassium iodide solution, and mix thoroughly.
6. Accurately add 5.0 mL of the Aliquat 336-MIBK solution to the tube, which is then capped with a silicone rubber or polyethylene stopper and shaken on a horizontal shaker for 5 minutes.
7. Centrifuge samples to separate all the organic phase. Estimate the metal content of the organic phase by flame atomic absorption spectrometry. If the metal content of a sample exceeds that of the standards, make a one-in-ten dilution using the Aliquat 336-MIBK solution. If necessary, make further dilutions until the sample's metal content is below that of the highest standard.

STANDARDIZATION OF INSTRUMENT

The working organic blank is aspirated between samples and used to zero the instrument. If the reagent blanks read a higher absorbance than the working organic blank, they are used for zeroing the instrument as they will "blank out" any reagent contamination. The working organic blank should be used between samples to purge the burner system of the previous samples and maintain the burner's thermal stability.

Typical absorbance values are given in the following table to check instrument performance for mid-range (Std. 2) and upper standards (Std. 3). Std. 1 should be within the linear range of most instruments, whereas Std. 2 and Std. 3 will require curve correction. Copper may be run with

the burner perpendicular or parallel to light path. Zinc must be run with the burner perpendicular for proper calibration, as Std. 1 will not be in the linear range if the burner is parallel.

The following operating conditions are for a Perkin-Elmer model 603 atomic absorption spectrophotometer.

These conditions are the same for all six metals:

Grating ultraviolet
 Source lamp hollow cathode lamp
 Integration time 1 second
 Flame conditions oxidizing (lean blue)

These conditions differ:

[Star (*), burner parallel to light path; dagger (†), burner perpendicular to light path]

	Bismuth	Cadmium	Copper
Wavelength (nm)	223.0	228.8	324.7
Slit (nm)	0.2	0.7	0.7
Lamp current (mA) . . .	8	8	8
Burner (cm)	10*	10*	10†
Background correction .	yes	no	no
X µg/mL=Y absorbance units	10=0.280 20=0.540	1=0.440 2=0.680	10=0.105 20=0.200
Lower limit of determination	1.0	0.05	1.0

	Lead	Silver	Zinc
Wavelength (nm)	383.3	328.1	213.9
Slit (nm)	0.7	0.7	0.7
Lamp current (mA) . . .	8	12	8
Burner (cm)	10*	10*	10†
Background correction .	no	no	no
X µg/mL=Y absorbance units	10=0.215 20=0.380	2=0.230 2=0.440	10=0.290 20=0.520
Lower limit of determination	1.0	0.05	1.0

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

N(), not detected at limit of determination, or at value shown. Data were recorded in multiples of lower reporting limits, rounded down, and reported at two significant digits]

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
Bismuth			
I	1,600-1,800	1,700	4.1
II	N(1)	N(1)	0
III	N(1)	N(1)	0
IV	20-22	21.2	3.9
V	N(1)	N(1)	0
VI	N(1)	N(1)	0
Cadmium			
I	2.4-2.7	2.56	4.4
II	3.5-3.9	3.76	4.5
III	0.35-0.40	0.37	7.5
IV	0.35-0.40	0.36	6.2
V	0.10-0.15	0.14	15.9
VI	0.10-0.10	0.10	0
Copper			
I	1,000-1,100	1,080	4.1
II	68-72	70.4	2.4
III	10-12	11	6.4
IV	6,800-7,000	6,880	1.2
V	360-390	370	3.3
VI	55-60	58	4.7
Lead			
I	570-590	580	1.2
II	610-660	630	3.4
III	11-13	12	5.9
IV	43-44	43.4	1.3
V	14-16	15	2.2
VI	79-84	81.2	2.7
Silver			
I	32-34	32.8	2.6
II	17-19	17.8	4.7
III	0.10	0.10	0
IV	3.6-3.8	3.7	1.9
V	0.70-0.80	0.76	5.5
VI	0.25-0.30	0.29	7.7
Zinc			
I	610-630	622	1.3
II	420-450	432	3.0
III	180-200	188	4.4
IV	68-72	70.8	2.5
V	36-40	37.6	4.5
VI	78-88	82.6	4.8

DISCUSSION

The potassium chlorate-hydrochloric acid digestion dissolves most metals not bound or occluded in insoluble silicates, desirable for most geochemical exploration purposes. However, a hydrofluoric acid digestion may be used to obtain a "total" digestion (Viets, 1978).

Because the Aliquat 336-MIBK solution is sticky, disposable test tubes are used to avoid tedious clean up. Stoppers and glassware, however, may be easily cleaned with acetone or other water-miscible organics such as ethanol or methanol.

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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CALCIUM, LITHIUM, MAGNESIUM, POTASSIUM, AND SODIUM, ATOMIC ABSORPTION METHOD

The method described here was developed by Meier (1980).

SUMMARY

Calcium, lithium, magnesium, potassium, and sodium are determined by atomic absorption spectrophotometry in rock, soil, and stream-sediment samples. The sample is decomposed by heating in hydrofluoric acid. The residue formed upon decomposition is dissolved by hydrochloric acid with the addition of boric acid solution to complex fluorides that may lead to incomplete dissolution of calcium, lithium, and magnesium. Lanthanum chloride is added to mask interference in the determination of calcium and magnesium.

The following concentration ranges can be determined using the method: calcium, 0.1 to 50 percent; lithium, 5 to 2,500 ppm; magnesium, 0.1 to 5.0 percent; potassium, 0.005 to 6.0 percent; sodium, 0.005 to 3.0 percent. The sensitivity of atomic absorption for these elements allows considerable latitude in sample dilution to adjust the concentration of the element of interest to a level suitable for measurement. About 50 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Boric acid solution: Dissolve 50 g boric acid in 1 L water. Warm to aid dissolution.

Hydrochloric acid, 6 N: Dilute 500 mL concentrated hydrochloric acid to 1 L with water.

Hydrofluoric acid, 48 percent.

Lanthanum chloride solution, 10 percent lanthanum: Weigh 58.7 g lanthanum oxide into a 1-L beaker and wet with water. Cautiously, add 100 mL concentrated hydrochloric acid in small portions. When the oxide is completely dissolved, slowly dilute to 500 mL with water while stirring to avoid overheating.

Lanthanum chloride solution, 1.1 percent lanthanum: Dilute 110 mL of the lanthanum chloride solution (10 percent lanthanum) to 1 L with water.

APPARATUS

Atomic absorption spectrophotometer

Hot plate

Teflon beaker, 50-mL; molded of TFE Teflon

Volumetric flask, 100-mL

STANDARDS

Stock calcium solution, 1,000 $\mu\text{g}/\text{mL}$: Dissolve 2.497 g dried calcium carbonate (overnight at 100°C) in a mixture of 50 mL water and 10 mL of 6 N hydrochloric acid. Dilute to 1 L with water.

Stock calcium solution, 100 $\mu\text{g}/\text{mL}$: Dilute 10 mL of 1,000 $\mu\text{g}/\text{mL}$ stock calcium solution to 100 mL with water.

Calcium working standard solution, 0, 2, 5, 10, 50, and 100 $\mu\text{g}/\text{mL}$: Pipette 0, 2, 5, and 10 mL of 100 $\mu\text{g}/\text{mL}$ stock calcium solution and 5 and 10 mL of 1,000 $\mu\text{g}/\text{mL}$ stock calcium solution into separate 100-mL volumetric flasks containing 10 mL lanthanum chloride solution (10 percent lanthanum), and dilute to 100 mL with water.

Stock lithium solution, 1,000 $\mu\text{g}/\text{mL}$: Dissolve 9.935 g lithium nitrate in water and dilute to 1 L with water.

Stock lithium solution, 100 $\mu\text{g}/\text{mL}$: Dilute 10 mL of 1,000 $\mu\text{g}/\text{mL}$ stock lithium solution to 100 mL with water.

Lithium working standard solution, 0, 1, 3, and 5 $\mu\text{g/mL}$: Pipette 0, 1, 3, and 5 mL of 100 $\mu\text{g/mL}$ stock lithium solution into separate 100-mL volumetric flasks containing 5 mL of 6 N hydrochloric acid and 5 mL boric acid solution, and dilute to 100 mL with water.

Stock magnesium solution, 1,000 $\mu\text{g/mL}$: Dissolve 1.000 g pure metallic magnesium in a minimum amount of 6 N hydrochloric acid (about 15 mL) and dilute to 1 L with water.

Stock magnesium solution, 100 $\mu\text{g/mL}$: Dilute 10 mL of 1,000 $\mu\text{g/mL}$ stock magnesium solution to 100 mL with water.

Stock magnesium solution, 10 $\mu\text{g/mL}$: Dilute 10 mL of 100 $\mu\text{g/mL}$ stock magnesium solution to 100 mL with water.

Magnesium working standard solution, 0, 0.2, 0.5, 1.0, 5.0, and 10.0 $\mu\text{g/mL}$: Pipette 0, 2, 5, and 10 mL of 10 $\mu\text{g/mL}$ stock magnesium solution and 5 and 10 mL of 100 $\mu\text{g/mL}$ stock magnesium solution into separate 100-mL volumetric flasks containing 10 mL lanthanum chloride solution (10 percent lanthanum), and dilute to 100 mL with water.

Stock potassium solution, 1,000 $\mu\text{g/mL}$: Dissolve 1.907 g potassium chloride in water and dilute to 1 L with water.

Stock potassium solution, 100 $\mu\text{g/mL}$: Dilute 10 mL of 1,000 $\mu\text{g/mL}$ stock potassium solution to 100 mL with water.

Potassium working standard solution, 0, 2, 6, 12, 20, 60, and 120 $\mu\text{g/mL}$: Pipette 0, 2, 6, and 12 mL of 100 $\mu\text{g/mL}$ stock potassium solution and 2, 6, and 12 mL of 1,000 $\mu\text{g/mL}$ stock potassium solution into separate 100-mL volumetric flasks containing 5 mL of 6 N hydrochloric acid and 5 mL boric acid solution, and dilute to 100 mL with water.

Stock sodium solution, 1,000 $\mu\text{g/mL}$: Dissolve 2.542 g sodium chloride in water and dilute to 1 L with water.

Stock sodium solution, 100 $\mu\text{g/mL}$: Dilute 10 mL of 1,000 $\mu\text{g/mL}$ stock sodium solution to 100 mL with water.

Sodium working standard solution, 0, 1, 3, 6, 10, 30, and 60 $\mu\text{g/mL}$: Pipette 0, 1, 3, 6, and 10 mL of 100 $\mu\text{g/mL}$ stock sodium solution and 3.0 and 6.0 mL of 1,000 $\mu\text{g/mL}$ stock sodium solution into separate 100-mL volumetric flasks containing 5 mL of 6 N hydrochloric acid and 5 mL boric acid solution, and dilute to 100 mL with water.

PROCEDURE

1. Weigh 0.20 g sample into a 50-mL Teflon beaker.
2. Add 15 mL of 48 percent hydrofluoric acid to the beaker.
3. Place the beaker on a hot plate set at high (about 250°C) and heat until all of the acid has been boiled off and all fumes have subsided.
4. Add 5 mL of 6 N hydrochloric acid and heat until acid begins to boil.
5. Add 5 mL boric acid solution and heat until the solution comes to a slight boil.
6. Remove the beaker from the hot plate and transfer quantitatively, with water, to a 100-mL volumetric flask. Dilute to volume with water. Mix well by shaking.
7. Dilute a 1-mL aliquot of the solution to 10 mL with lanthanum chloride solution (1.1 percent lanthanum).
8. Lithium, potassium, and sodium concentrations are estimated by using the dilution in step 6 of the procedure. Calcium and magnesium concentrations are estimated by using the dilution with lanthanum chloride added in step 7 of the procedure. Estimations are performed on an atomic absorption spectrophotometer.

STANDARDIZATION OF INSTRUMENT

The following operating conditions are for a Perkin-Elmer model 603 atomic absorption spectrophotometer.

These conditions are the same for all five elements:

Lamp current	10 mA
Integration time	3 seconds
Burner	10 cm
Fuel	acetylene
Oxidant	air
Flame condition	oxidizing (lean blue)

These conditions differ:

	Calcium	Lithium	Magnesium
Grating	visible	visible	ultraviolet
Wavelength (nm)	211	335	285
Slit (nm)	4	3	4
Source lamp	calcium	lithium	magnesium
Filter	out	in	out

	Potassium	Sodium
Grating	visible	visible
Wavelength (nm)	383	295
Slit (nm)	3	4
Source lamp	potassium	sodium
Filter	in	out

By using the instrument parameters described in the preceding, the instrument is calibrated to read sample concentration directly by using the following standards and settings with burners parallel or perpendicular to source beam.

Element, and burner orientation	Standard ($\mu\text{g/mL}$)	Absorbance units	Set concentration (percent, lithium in ppm)
Calcium			
Parallel	2.00	0.190	1.0
	5.00	.424	2.5
	10.00	.835	5.0
Perpendicular	50.0	.146	25.0
	100.0	.292	50.0
Lithium			
Parallel	1.00	.170	500
	3.00	.488	1,500
	5.00	.766	2,500
Magnesium			
Parallel	.5	.410	.25
	1.0	.753	.50
Perpendicular	5.0	.149	2.50
	10.0	.291	5.00
Potassium			
Parallel	2.0	.242	.100
	6.0	.585	.300
	12.0	.946	.600
Perpendicular	20.0	.105	1.00
	60.0	.311	3.00
	120.0	.543	6.00
Sodium			
Parallel	1.0	.285	.05
	3.0	.709	.150
	6.0	1.062	.300
Perpendicular	10.0	.114	.50
	30.0	.302	1.50
	60.0	.509	3.00

DISCUSSION

The procedure as presented is useful for decomposition and dissolution of geologic material for the determination of calcium, lithium, magnesium, potassium, and sodium by atomic absorption spectrophotometry. The sample weight used can be decreased or increased to accommodate lower or

higher concentrations of the elements of interest. Hydrofluoric acid effectively removes silicon as the volatile tetrafluoride and renders most mineral components soluble in hydrochloric acid and boric acid. If organic material is present in the sample, a black residue will be observed. However, this residue has little effect on the solubility of the elements of interest. The 6 N hydrochloric acid and boric acid solution can be conveniently added to the Teflon beakers without removing them from the hot plate. The hydrochloric acid and boric acid solution additions should come to a slight boil but should not be allowed to boil excessively as the acid concentration of the final solution can affect the estimation. The final dilution can be increased or decreased to accommodate the range of concentrations expected in the sample. The dilution for the determination of calcium and magnesium can also be increased or decreased to accommodate the range of concentration expected in the sample, but should contain 0.1 percent lanthanum in the final solution.

INTERFERENCES

Calcium: Phosphate, sulfate, silicate, and aluminum can interfere with the estimation of calcium, but are masked by the addition of lanthanum chloride. Boric acid solution is added to dissolve slightly soluble or complex fluorides of calcium that form in the decomposition with hydrofluoric acid.

Lithium: Brown and others (1970) reported the following elements to interfere with the estimation of lithium when concentrations were in excess of: sodium, 1,000 $\mu\text{g/mL}$; potassium, 100 $\mu\text{g/mL}$; magnesium, 200 $\mu\text{g/mL}$; calcium, 200 $\mu\text{g/mL}$; chloride, 1,000 $\mu\text{g/mL}$; sulfate, 2,000 $\mu\text{g/mL}$; nitrate, 100 $\mu\text{g/mL}$; and strontium, 5 $\mu\text{g/mL}$. Boric acid solution is added to dissolve slightly soluble or complex fluorides of lithium that form in the decomposition with hydrofluoric acid.

Magnesium: Silicate and aluminum can interfere with the estimation of magnesium but are masked by the addition of lanthanum chloride. Boric acid solution is added to dissolve slightly soluble or complex fluorides of magnesium that form in the decomposition with hydrofluoric acid.

Potassium: Interferences are not common to potassium determination.

Sodium: Interferences are not common to sodium determination, but contamination from reagents,

the environment, and apparatus can be a problem.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

GXR sample	Range (percent, lithium in ppm)	Mean	Percent relative standard deviation
Calcium			
I	0.88-0.92	0.90	2.0
II	0.94-1.0	0.98	2.3
III	11-12	11	4.8
IV	0.98-1.1	1.1	5.4
V	0.88-1.0	0.90	8.2
VI	0.44-0.47	0.45	3.6
Lithium			
I	6-8	7	10.1
II	62-68	64	3.6
III	134-138	135	1.3
IV	11-12	11	4.0
V	45-48	47	3.2
VI	38-39	38	1.4
Magnesium			
I	0.23-0.25	0.24	3.5
II	0.82-0.87	0.84	2.1
III	0.78-0.86	0.82	4.0
IV	1.4-1.7	1.6	7.8
V	1.0-1.2	1.1	8.2
VI	0.58-0.64	0.62	4.0
Potassium			
I	0.03-0.04	0.03	3.2
II	1.2-1.3	1.3	2.1
III	0.61-0.64	0.62	1.9
IV	3.7-3.9	3.8	1.8
V	0.69-0.73	0.71	2.5
VI	1.5-1.6	1.5	1.7
Sodium			
I	0.039-0.041	0.040	1.8
II	0.50-0.53	0.51	2.8
III	0.69-0.71	0.70	1.4
IV	0.46-0.48	0.47	1.5
V	0.63-0.68	0.66	2.5
VI	0.09-0.10	0.10	1.8

REFERENCES CITED

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COBALT, COPPER, LEAD, NICKEL, AND ZINC, ATOMIC ABSORPTION METHOD

The method described here, excepting minor changes, was developed by Ward and others (1969).

SUMMARY

Cobalt, copper, lead, nickel, and zinc are determined in samples of rock, soil, stream sediment, and heavy-mineral concentrates by atomic absorption spectrophotometry. The sample is treated with hot concentrated nitric acid, which solubilizes all adsorbed ions and most common sulfides and oxides of these elements. Although this method is not a quantitative analysis, as silicates are only sparingly attacked on surface exposures, secondary dispersions and economic sulfide minerals are readily detected. The acid solution is diluted and aspirated into an atomic absorption spectrophotometer. About 70 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Nitric acid, concentrated.

Nitric acid, 8N: Dilute 500 mL concentrated nitric acid to 1 L with water.

APPARATUS

Atomic absorption spectrophotometer

Boiling granules, metal-free

Centrifuge

Hotplate; fitted with aluminum heating block drilled to hold 16-mm test tubes

Test tubes, disposable, 16×150-mm

STANDARDS

Stock cobalt, copper, lead, nickel, and zinc solutions, 1,000 $\mu\text{g}/\text{mL}$: Dissolve the indicated weight of the dried metal or metal salt in a 500-mL volumetric flask with 8 N nitric acid.

cobalt—1.970 g cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$)

copper—1.964 g clear-copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

lead—0.800 g lead nitrate ($\text{Pb}(\text{NO}_3)_2$)

nickel—2.48 g nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)

zinc—0.500 g zinc metal

Dilute copper, lead, and zinc combined solution, 100 $\mu\text{g}/\text{mL}$: Combine 10 mL of each 1,000 $\mu\text{g}/\text{mL}$ stock copper, lead, and zinc solution and dilute to 100 mL with 8 N nitric acid.

Standard copper, lead, and zinc combined solution, 20, 10, and 5 $\mu\text{g}/\text{mL}$: Dilute 20, 10, and 5 mL of 100 $\mu\text{g}/\text{mL}$ dilute copper, lead, and zinc solution to 100 mL with 8 N nitric acid.

Dilute cobalt and nickel combined solution, 100 $\mu\text{g}/\text{mL}$: Combine 10 mL of each 1,000 $\mu\text{g}/\text{mL}$ stock cobalt and nickel solution and dilute to 100 mL with 8 N nitric acid.

Standard cobalt and nickel combined solution, 20, 10, and 5 $\mu\text{g}/\text{mL}$: Dilute 20, 10, and 5 mL of 100 $\mu\text{g}/\text{mL}$ dilute cobalt and nickel solution to 100 mL with 8 N nitric acid.

PROCEDURE

1. Weigh 1.0 g sample into a 16×150-mm disposable test tube containing a metal-free boiling granule. (Samples being analyzed for nickel should be roasted for 1 hour at 450°C.)
2. Carefully add 5 mL concentrated nitric acid and place tube in the heating block on a hot plate and boil for 30 minutes.
3. Dilute the sample to 10 mL with water and bring back to boil.
4. Remove tube from block, cool, and centrifuge.
5. Estimate the metal content by atomizing the solution in an atomic absorption spectrophotometer.

STANDARDIZATION OF INSTRUMENT

The following operating conditions are for a Perkin-Elmer model 603 atomic absorption spectrophotometer.

These conditions are the same for all five metals:

Grating ultraviolet
Lamp current use current recommended on lamp
Source lamp hollow cathode lamp
Integration time 1 second
Burner 10 cm (perpendicular to source beam)
Flame condition oxidizing (lean blue)
Lower limit of determination 5.0 ppm

These conditions differ:

	Cobalt	Copper	Lead
Wavelength (nm)	240.7	324.8	283.3
Slit (nm)2	.7	.7
5 $\mu\text{g}/\text{mL}$ (absorbance units)152	.279	.043
10 $\mu\text{g}/\text{mL}$ (absorbance units)288	.523	.085
	Nickel	Zinc	
Wavelength (nm)	232.0	213.9	
Slit (nm)2	.7	
5 $\mu\text{g}/\text{mL}$ (absorbance units)157	.075	
10 $\mu\text{g}/\text{mL}$ (absorbance units)287	.144	

DISCUSSION

Copper is often used to check instrument performance because it is one of the easiest of all metals to determine by atomic absorption spectrophotometry and is free from interferences.

The determination of lead is generally free of interferences, but is affected by molecular absorption of the dissolved calcium in carbonates.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
Cobalt			
I	21–22	21.2	2.11
II	13	13	0
III	36–38	36.6	2.44
IV	21–22	21.6	2.54
V	38–39	38.6	1.42
VI	22–23	22.4	3.99

Copper			
I	1,051-1,075	1,064	1.12
II	78-79	78.2	.57
III	13	13	0
IV	6,480-6,740	6,624	1.56
V	349-357	351	1.07
VI	62-64	63.2	1.32
Lead			
I	613-647	623	2.14
II	676-717	694	2.27
III	42-44	43	1.64
IV	52-56	53.8	2.76
V	23-24	23.2	1.93
VI	95-99	96.4	1.74
Nickel			
I	33-34	33.8	1.32
II	19	19	0
III	45-48	46	2.66
IV	44-46	45	2.22
V	77-80	78.2	1.67
VI	26-28	27	3.7
Zinc			
I	711-745	724	1.92
II	513-551	533	3.23
III	170-190	182	4.60
IV	80-82	80.6	1.11
V	45-47	45.8	1.83
VI	105-109	107.4	1.69

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
- Ward, F. N., Nakagawa, H. M., Harms, T. F., and VanSickle, G. H., 1969, Atomic absorption methods useful in geochemical exploration: U.S. Geological Survey Bulletin 1289, 45 p.

COPPER, ACID-EXTRACTABLE METHOD

The method described here, excepting minor changes, was developed by Canney and Hawkins (1958).

SUMMARY

The amount of copper that is extracted from a soil or sediment by cold hydrochloric acid is estimated by comparing the intensity of the color of

the copper-2, 2'-biquinoline complex in an isoamyl alcohol extract against colored standards. Although the ambient temperature extraction yields only about 10-30 percent of the total copper in most samples, it has been found that the geochemical pattern of analytical data revealed by its use is often more significant than the geochemical pattern of total copper; and because the method is rapid and requires only simple, portable items of equipment, it is ideally suited for use under rough field conditions—at the sample site if desired. The method has a limiting sensitivity of about 1 ppm, which means that a positive test can usually be obtained on most samples. The method is not recommended for use on samples containing appreciable quantities of decaying organic material because soluble organic matter may dissolve in the organic solvent to yield a yellow solution that masks the pink or purple color of the copper-biquinoline complex. Much data can be collected in a short time because a single determination requires about 2 minutes.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Biquinoline reagent solution, 0.02 percent: Add 0.2 g of 2, 2'-biquinoline to about 900 mL isoamyl alcohol in a beaker. Warm on a steam bath in a well-ventilated area away from open flame until the biquinoline is dissolved. Allow the solution to cool and dilute to 1 L with isoamyl alcohol. The solution should be colorless. If it is yellow, pink, or purple, the reagent is impure and should not be used. The biquinoline reagent is stable.

Buffer solution: Dissolve 400 g sodium acetate trihydrate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$), 100 g sodium tartrate ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$), and 20 g hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) in 1 L metal-free water. If necessary, adjust the pH of this solution to between 6 and 7 with hydrochloric acid or sodium hydroxide solutions. To check for copper contamination, place 10 mL of buffer in a culture tube, add 1 mL of the biquinoline reagent, cap, and shake for 2 minutes. Absence of a pink coloration in the organic layer indicates that the solution is satisfactory for use. If contaminated, the buffer may be cleaned as follows. Dissolve 0.005 g dithizone

(diphenylthiocarbazon) in 500 mL carbon tetrachloride. Shake the mixture intermittently over a period of about 1 hour to effect solution. Transfer the contaminated buffer solution and 50 mL of the dithizone solution to a large separatory funnel, shake, allow the carbon tetrachloride phase to collect in the bottom of the funnel, and discard. Continue this process with additional 50-mL increments until the discarded organic phase is green. Some dithizone is dissolved in the buffer solution, imparting to it a yellow color. This is removed by successive extractions with 50-mL portion of chloroform. Chloroform dissolved in the buffer solution is removed by shaking the buffer solution with 100 mL carbon tetrachloride and discarding the organic phase.

Hydrochloric acid, 6M: Dilute 500 mL concentrated hydrochloric acid to 1 L with water.

APPARATUS

Centrifuge

Culture tube, 22×175-mm

Illuminator or white card

Scoop, 0.2-g

Stopper, polyethylene

STANDARDS

Stock copper solution, 100 µg/mL: Dissolve 0.2 g copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 500 mL of 0.1 M hydrochloric acid.

Dilute copper solution, 10 µg/mL: Dilute 10 mL of 100 µg/mL stock copper solution to 100 mL with 0.1 M hydrochloric acid.

Dilute copper solution, 1 µg/mL: Dilute 10 mL of 10 µg/mL dilute copper solution to 100 mL with 0.1 M hydrochloric acid.

Standard copper solutions, 0, 1, 5, 10, 20, and 50 ppm: Add 0.0, 0.2, and 1.0 mL of 1.0 µg/mL dilute copper solution and 0.2, 0.4, and 1.0 mL of 10 µg/mL dilute copper solution to six 22×175-mm culture tubes, respectively. Add 1 mL of 6 M hydrochloric acid to each tube and proceed with step 3 of the following procedure. These are equivalent to 0, 1, 5, 10, 20, and 50 ppm copper contents in an 0.2-g sample. Mid-point concentrations may be estimated giving reporting intervals of 0, 1, 3, 5, 7, 10, 15, 20, 35, and 50 ppm. One set of standards should remain stable for several months provided the tubes are kept tightly capped to prevent evaporation of

the isoamyl alcohol, and stored in a dark place to prevent sunlight from fading the standards.

PROCEDURE

1. Place an 0.2-g scoop of the fine fraction of a soil or stream-sediment sample in a 22×175-mm culture tube.
2. Add about 1 mL of 6 M hydrochloric acid and slosh the sample in the acid for about 30 seconds.
3. Immediately add 10 mL buffer solution and 2 mL biquinoline reagent. Cap the tube with a polyethylene stopper, and shake the tube vigorously for about 30 seconds.
4. Allow the organic layer to separate, centrifuge if necessary.
5. Estimate the copper concentration by comparing the color of the upper layer with that of the standards, using an illuminator when in the laboratory or a white card when in the field. Tip the tube 45° if film on glass obscures color.

DISCUSSION

The acid-extractable copper test is specific for copper, no other metal will react with 2, 2'-biquinoline. Copper must be in the form of Cu^+ to react in this test. If the reducing agent in the buffer deteriorates, low values will result. A standard sample should be analyzed at the start of each day as a check on the reagents and standards, and to insure comparable results from day to day.

The complex formed with the biquinoline reagent is not a strong complex. Ions that form strong complexes with copper (for example, the ammonium ion) will prevent the copper-biquinoline complex from forming and therefore should not be present during the test.

Coarse organic matter in some samples may interfere by accumulating at the water-alcohol interface. If this happens, the debris can usually be removed from the interface and dispersed throughout the buffer by manually or mechanically centrifuging the tube. Sometimes samples with appreciable organic material will give a yellow color, but this does not normally completely mask the pink or purple color given by copper.

The sample size can be increased if the amounts of acid and buffer are increased proportionately to achieve a lower limit of determination. Con-

versely, the upper limit of the method can be extended by decreasing the sample size or by increasing the volume of biquinoline reagent. In either case, appropriate factors are required for conversion from micrograms of copper in the standards to parts per million in the sample.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

[N.A., method not applicable to this sample medium]

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	N.A.	N.A.	N.A.
II	15-20	18.0	15.2
III	1-3	1.4	63.9
IV	N.A.	N.A.	N.A.
V	150-200	190	11.8
VI	10-15	11	20.3

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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FLUORINE, ION-SELECTIVE ELECTRODE METHOD

The method described here, excepting minor changes, was developed by Hopkins (1977).

SUMMARY

Fluorine is determined in rock, soil, and stream-sediment samples by an ion-selective electrode method. Samples are fused with a sodium carbonate-potassium carbonate-potassium nitrate flux and the fused sample is dissolved with citric acid. Sodium citrate buffer, which also serves as an ionic strength adjustor, is then added to this solution prior to determining the fluorine concentration by standard-additions technique. About 50 samples can be analyzed per day.

REAGENTS

All reagents should be of reagent grade and all water should be metal free.

Citric acid, 1 M: Dissolve 210.15 g citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) in 1 L water.

Sodium carbonate-potassium carbonate-potassium nitrate flux: Separately grind anhydrous sodium carbonate (Na_2CO_3) and anhydrous potassium carbonate (K_2CO_3) (previously oven dried at 100°C overnight) and potassium nitrate to pass an 80-mesh sieve, and prepare a 4:4:2 mixture, by weight.

Sodium citrate buffer, 1 M: Dissolve 294 g sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) in 800 mL water and adjust the pH to 6.0 with 6 N hydrochloric acid. Dilute this solution to 1 L.

APPARATUS

Beaker, 100-mL, graduated polypropylene
Magnetic stirrer (with stirring mechanism extended from motor to prevent heating of sample solution)

Orion reference electrode; model 90-01-00

Orion specific ion electrode; model 94-09A

Orion specific ion meter; model 407

Pyropot (Pyroco Products, Margat, Queensland, Australia 4019): Heating device accommodating 10 test tubes, provides a controlled heat source for the fusion.

Stirring bar, Teflon-coated magnetic

Test tube, disposable, 25×150-mm

STANDARDS

Stock fluorine solution, 10,000 µg/mL: Dissolve 2.21 g sodium fluoride (previously dried at 110°C overnight) in 100 mL water.

Standard fluorine solution, 1,000 µg/mL: Dilute 10 mL of 10,000 µg/mL stock fluorine solution to 100 mL with water (prepare monthly).

Standard fluorine solution, 100 µg/mL: Dilute 10 mL of 1,000 µg/mL standard fluorine solution to 100 mL with water (prepare monthly).

Standard fluorine solution, 10 µg/mL: Dilute 10 mL of 100 µg/mL standard fluorine solution to 100 mL with water (prepare monthly).

Store all fluoride standards in polyethylene bottles.

PROCEDURE

1. Weigh 0.05 g sample and mix with 2 g sodium carbonate-potassium carbonate-potassium nitrate flux in a disposable, 25×150-mm test tube.
2. Fuse at 700°C for 10 minutes in a Pyropot. Remove fused sample and roll it on heat-resistant surface.
3. Allow test tube to cool and add 15 mL of 1 M citric acid.
4. Allow the mixture to digest until carbon dioxide evolution is no longer detected (15 minutes).
5. Transfer to a 100-mL polypropylene beaker containing 25 mL sodium citrate buffer.
6. Rinse the test tube with water, and add the rinse to the beaker.
7. Dilute the sample solution to 100 mL with water and add a Teflon-coated magnetic stirring bar.

STANDARDIZATION OF INSTRUMENT

1. Add 1 mL of 1,000- or 100-μg/mL sodium fluoride working standard to a 100-mL polypropylene beaker containing 15 mL of 1 M citric acid and 2 g of the sodium carbonate-potassium carbonate-potassium nitrate flux.
2. Then add 25 mL of 1 M sodium citrate buffer solution, dilute to 100 mL with water, and add a Teflon-coated magnetic stirring bar.
3. Place the electrodes of the specific ion meter in the solution while it is gently stirred on a magnetic stirrer.
4. Turn the meter's calibration control for a center-scale reading, and then add 1 mL of the 1,000- or 100-μg/mL sodium fluoride working standard that was used initially.
5. Adjust the temperature control to give a reading of 1 on the known-addition scale.
6. Move the slope control until the sample temperature is read on the temperature scale. The percent of theoretical slope can be read on the slope scale.
7. The instrument is now calibrated and ready to determine fluorine content.

ESTIMATION

1. Using a calibrated specific ion meter for estimation, rinse electrodes with water, blot them with absorbent tissue, and place them

in the sample solution, which is gently being stirred.

2. Turn the meter calibration control knob until the needle points to midscale.
3. Pipette an appropriate aliquot (approximately the same total μg fluorine as the sample) from one of the working sodium fluoride standard solutions.
4. Allow approximately 5 minutes before taking a reading if the standard addition totals less than 100 μg fluorine. Allow 3 minutes for 100- to 500-μg additions and 1-3 minutes for higher additions.
5. Calculate the fluorine concentration in the sample by using the following formula:

$$\text{fluorine ppm} = \frac{(\mu\text{g/mL fluorine in standard})(\text{mL standard added})(\text{meter reading})}{\text{g of sample}}$$

6. Reagent blanks are run with the samples to determine an average value of fluoride contamination. The average blank value is subtracted from the sample readings.
7. If the sample is estimated to contain 100,000 ppm or more fluorine, the solution containing citric acid and fused sample should be diluted to 100 mL with water. A suitable aliquot should be added to 25 mL of sodium citrate buffer, diluted to 100 mL, and estimated.

DISCUSSION

The fluoride-selective electrode responds to and develops a potential to the activity of free, unbound, uncomplexed fluoride ions in solution. The potential difference forms between the faces of a single lanthanum fluoride crystal, which separates an internal filling solution from the sample solution. The measured potential, E , is given by the simplified Nernst equation:

$$E = \frac{RT}{E_e - 2.303 F \log_{10} a_{F^-}}, \quad (1)$$

where E_e is a constant potential characteristic of the electrode, R is the gas constant, F is the Faraday constant, T is the absolute temperature, and a_{F^-} is the activity of fluoride ions in solution. The relationship between the free fluoride ion concentration and the free fluoride ion activity is:

$$a_{F^-} = \gamma f C_t, \quad (2)$$

where γ is the activity coefficient of the fluoride ion, f is the fraction of the total fluoride ion concentration that is free, and C_t is the total concentration of fluoride ion in all its forms—free, complexed, or bound.

The success of standard additions depends on making the addition in such a way that γ and f remain constant. The fluoride ion concentration can then be substituted for the activity in equation (1) and a linear relationship between the logarithm of the fluoride ion concentration and the measured potential is obtained. The activity coefficient, γ , remains constant if a large amount of noninterfering salt is added to maintain a high constant ionic strength. The fraction of the total concentration of fluoride ions that is free, f , is held constant by adding a large excess of a reagent, such as sodium citrate, which releases fluoride ions from any complexes formed with Al^{3+} , Fe^{3+} , Si^{4+} , and Be^{2+} ions. Sodium citrate buffer solution also provides enough noninterfering ions to maintain a high constant ionic strength background in the method described. The buffer adjusts the pH between 5 and 6 to dissociate any HF formed when the pH is less than 5 and to prevent hydroxide ion interference at pH values above 7. Citric acid dissolution of the fused sample gives additional sodium, potassium, and citrate ions for ionic strength and decomplexing.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	1,025–1,075	1,053	1.83
II	238–276	257	5.51
III	89,950–96,850	93,370	2.72
IV	2,305–2,365	2,333	.98
V	142–159	153	4.62
VI	151–161	156	2.50

REFERENCES CITED

Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, in Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659–681.

Hopkins, D. M., 1977, An improved ion-selective electrode method for the rapid determination of fluorine in rocks and soils: *U.S. Geological Survey Journal of Research*, v. 5, no. 5, p. 589–593.

GOLD, FLAME ATOMIC ABSORPTION METHOD

The method described here, excepting minor changes, was developed by Thompson and others (1968) and described by Ward and others (1969).

SUMMARY

Gold is determined in samples of rock, soil, stream sediment, and heavy-mineral concentrates by atomic absorption spectrophotometry. The sample is treated with a hydrobromic acid-0.5 percent bromine solution. The gold-bromide complex that is formed is extracted from the acid solution with MIBK (methyl isobutyl ketone). The interference due to iron is removed by washing the organic solvent with dilute hydrobromic acid. The MIBK is atomized in an atomic absorption spectrophotometer for estimation of gold content. About 50 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Hydrobromic acid-0.5 percent bromine solution: Add 5 mL bromine per liter of concentrated hydrobromic acid.

Hydrobromic acid 0.1 N, equilibrated: Dilute 12 mL concentrated hydrobromic acid to 1 L with water. Add an excess of MIBK, shake thoroughly, allow phases to separate, and discard MIBK layer.

MIBK (methyl isobutyl ketone), 4-methyl-2-pentanone.

APPARATUS

Atomic-absorption spectrophotometer
Centrifuge
Culture tubes, 25×150-mm, screw-cap
Horizontal shaking machine
Hot plate
Muffle furnace
Porcelain evaporating dish, 60-mm diameter

STANDARDS

Stock gold solution, 1,000 $\mu\text{g/mL}$: Dissolve exactly 1.000 g gold in 100 mL hydrobromic acid-0.5 percent bromine solution. Heat gently to expel

excess bromine. Cool and dilute to 1 L with concentrated hydrobromic acid.

Dilute gold solution, 100 $\mu\text{g}/\text{mL}$: Dilute 10 mL of 1,000 $\mu\text{g}/\text{mL}$ stock gold solution to 100 mL with concentrated hydrobromic acid.

Standard gold solution in MIBK, 0.5, 1.0, and 2.0 $\mu\text{g}/\text{mL}$: Add 1.0, 2.0, and 4.0 mL of 100 $\mu\text{g}/\text{mL}$ dilute gold solution to three 200-mL volumetric flasks containing 200 mL MIBK. Shake vigorously. Transfer contents to three 500-mL reagent bottles containing 100 mL equilibrated 0.1 N hydrobromic acid and shake.

PROCEDURE

1. Weigh 10 g sample into a porcelain evaporating dish.
2. Ignite sample at 700°C in a muffle furnace for 1 hour or until sulfides and organic matter are completely oxidized.
3. Transfer sample to a 25×150-mm screw-cap culture tube containing 10 mL hydrobromic acid-0.5 percent bromine solution.
4. Mix sample thoroughly and gently heat on a hot plate or in a water bath.
5. When cool, add 10 mL MIBK and 10 mL water, cap, and shake in a horizontal shaking machine for 3 minutes.
6. Centrifuge until layers separate and transfer the MIBK layer to a 25×150-mm culture tube containing 40 mL equilibrated 0.1 N hydrobromic acid. Cap, shake for 2 minutes, and allow phases to separate.
7. Estimate the gold content by atomizing the organic layer into an atomic absorption spectrophotometer.

STANDARDIZATION OF INSTRUMENT

The following operating conditions are for a Perkin-Elmer model 603 atomic absorption spectrophotometer.

Grating	ultraviolet
Wavelength	242.8 nm
Slit	0.7 nm
Lamp current	10 mA
Source	gold (hollow cathode lamp)
Integration time	1 second
Burner	Boling (three slot)
Flame condition	oxidizing (lean blue)
1 $\mu\text{g}/\text{mL}$	0.084 absorbance units
2 $\mu\text{g}/\text{mL}$	0.165 absorbance units
Lower limit of determination	0.05 $\mu\text{g}/\text{mL}$

DISCUSSION

Care must be taken when adding a sample containing carbonate materials to the hydrobromic acid-0.5 percent bromine solution. Rapid effervescence may cause loss of sample from the culture tube. Add sample slowly, mix, and add extra hydrobromic acid-0.5 percent bromine solution to insure a high acid concentration. For samples that contain little organic materials or sulfides, it is not necessary to include the ignition step before the digestion.

Lakin and Nakagawa (1965) stated that any gold minerals completely enclosed in insoluble particles such as quartz would not be brought into solution and that the resulting gold values would be low. The sample must be ground to a powder to insure reasonable attack on the gold. However, if the sample is ground too fine, it is difficult to get a separation of the ketone layer. Fine grinding may also result in loss of gold by plating onto the grinding equipment. Thus, a compromise must be reached. We have found, when a 10-g split of sample is used, that good reproducibility can be generally obtained if the sample is ground to pass a 100-mesh screen but is mostly held on a 150-mesh screen.

The only interference in the estimation is caused by the presence of an excessive amount of iron coextracted into the MIBK. The iron is presumed to interfere by causing light scattering. The iron is removed by washing the MIBK extract with the 0.1 N hydrobromic acid solution; the gold remains quantitatively in the ketone.

The solubility of MIBK in hydrobromic acid increases with increasing concentration of the latter; if the decrease in volume of the ketone is appreciable during extraction, additional ketone is added to correct for apparent loss. To avoid MIBK loss in the wash procedure, equilibrated 0.1 N hydrobromic acid (MIBK-saturated 0.1 N hydrobromic acid) is used. It has been observed, using radioactive gold as a tracer, that all the gold was in the separated ketone and none was in the solubilized ketone.

If a detection level at or below the crustal abundance of gold is desired, refer to the flameless atomic absorption method for gold.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin,

1975), in replicas of five, by the described procedure.

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	2.6-3.5	3.0	9.3
II	0.02-0.14	0.07	42.5
III	Less than 0.05 limit of determination		
IV	0.28-0.40	0.35	11.9
V	Less than 0.05 limit of determination		
VI	0.04-0.07	0.06	19.5

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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GOLD, FLAMELESS ATOMIC ABSORPTION METHOD

The method described here was developed by Meier (1980).

SUMMARY

Gold is determined in rock, soil, and stream-sediment samples by flameless atomic absorption spectrophotometry and a graphite furnace atomizer. A solution of hydrobromic acid and bromine is used to dissolve the gold. MIBK (methyl isobutyl ketone) is used to extract the gold from the acid solution to eliminate interference. Gold can be determined by the method as described in the concentration range of 0.002 to 0.05 ppm. About 50 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Hydrobromic acid-0.5 percent bromine solution: Dissolve 5 mL bromine in 1 L concentrated hydrobromic acid.

Hydrobromic acid, 0.1 N, MIBK-saturated: Dilute 23 mL concentrated hydrobromic acid to 2 L with water. Add an excess of MIBK (approximately 50 mL), shake thoroughly, allow phases to separate, and discard MIBK layer.

MIBK (methyl isobutyl ketone), 4-methyl-2-pentanone.

APPARATUS

Atomic absorption spectrophotometer; equipped with graphite furnace

Centrifuge

Evaporating dish, porcelain; size 0000

Horizontal shaking machine

Hot plate

Metal rack; to accommodate 25-mm diameter tubes

Muffle furnace

Pipette, automatic, 5-mL

Test tubes, 25×150-mm, screw-cap

Vortex mixer

STANDARDS

Stock gold solution, 1,000 µg/mL: Dissolve exactly 1.000 g gold in 100 mL hydrobromic acid-0.5 percent bromine solution. Heat the solution gently to expel excess bromine. Cool and dilute to 1,000 mL with concentrated hydrobromic acid.

Stock gold solution, 100 µg/mL: Dilute 10 mL of 1,000 µg/mL stock gold solution to 100 mL with concentrated hydrobromic acid.

Stock gold solution, 10 µg/mL: Dilute 10 mL of 100 µg/mL stock gold solution to 100 mL with concentrated hydrobromic acid.

Stock gold solution, 1 µg/mL: Dilute 10 mL of 10 µg/mL stock gold solution to 100 mL with concentrated hydrobromic acid.

Dilute gold solutions, 0.002, 0.005, 0.01, 0.02, and 0.05 µg/mL: Dilute 0.2, 0.5, 1.0, 2.0, and 5.0 mL of 1 µg/mL stock gold solution to 100 mL with concentrated hydrobromic acid.

Standard gold solutions in MIBK, 0.002, 0.005, 0.01, 0.02, and 0.05 µg/mL: Transfer 10.0 mL of each of the dilute gold solutions (0.002, 0.005, 0.01, 0.02, and 0.05 µg/mL) and a blank solution to a series of six 25×150-mm screw-cap tubes. Add 10.0 mL MIBK and 10 mL water to each

tube and shake for 5 minutes. Transfer the MIBK layer, with an automatic pipette, to another tube containing 40 mL MIBK-saturated 0.1 N hydrobromic acid. Shake the tubes for 2 minutes and use the MIBK layer for calibration of the atomic absorption spectrophotometer.

PROCEDURE

1. Transfer 10 g pulverized sample to an 0000 porcelain evaporating dish.
2. Roast the sample in a muffle furnace at 700°C for 1 hour.
3. After the sample is cool, transfer to a 25×150-mm, screw-cap test tube containing 10 mL hydrobromic acid-0.5 percent bromine solution.
4. Mix sample and acid thoroughly using a vortex mixer.
5. Heat the tubes by placing them in a metal rack on a hot plate set at its maximum setting until the acid begins to boil at the bottom of the tube. Remove the tubes from the hot plate when the tubes begin to bump the rack and chatter, and allow them to cool.
6. Add 10 mL water and 10 mL MIBK to each tube.
7. Cap the tubes and shake on a horizontal shaking machine for 5 minutes.
8. Centrifuge the samples to separate the MIBK layer from the acid layer.
9. Using a 5-mL automatic pipette, transfer the MIBK layer to another 25×150-mm screw-cap tube containing 40 mL MIBK-saturated 0.1 N hydrobromic acid.
10. Cap the tubes and shake on the shaking machine for 2 minutes.
11. Allow the phases to separate, and estimate the gold in the MIBK layer using an atomic absorption spectrophotometer equipped with a graphite furnace.

STANDARDIZATION OF INSTRUMENT

A 20- μ L aliquot of the MIBK layer is pipetted into the graphite furnace using either a micro-pipette or an automatic sampler. The peak absorbance observed is compared with absorbance values for standards prepared and atomized using the same conditions to determine the gold concentration of the sample. The following operating conditions are for a Perkin-Elmer model 360 atomic ab-

sorption spectrophotometer equipped with a Perkin-Elmer model HGA 2200 graphite furnace.

Wavelength	242.8 nm
Slit	0.7 nm, alternate (alternate setting reduces slit height for furnace use)
Mode	absorbance (readout is in unexpanded absorbance units)
Signal	peak (peak height is measured and is displayed on readout)
Lamp current	10 mA
Source lamp	gold (hollow cathode lamp)
Purge gas	nitrogen
Purge gas flow	20 divisions on flow meter (approximately 35 cc/minute)
Flow time	normal, 3 seconds (internal gas flow through the graphite tube is reduced to approximately 35 cc/minute during the first 3 seconds of atomization)
Drying time	20 seconds
Ramp drying time	15 seconds
Drying temperature	120°C
Charring time	20 seconds
Charring temperature	500°C
Atomizing time	8 seconds
Atomizing temperature	2,700°C
Graphite tube	pyrolytic coated

Using the preceding instrument parameters, the following absorbance readings were observed for five replicate analyses of the gold working standard solutions.

[Lower limit of determination, 0.002 ppm]

Gold concentration (μ g/mL)	Mean absorbance	Standard deviation	Percent relative standard deviation
0.000	0.000	0.000	0.0
.002	.018	.003	16.7
.005	.055	.003	5.5
.010	.120	.002	1.7
.020	.250	.002	.8
.050	.630	.003	.5

DISCUSSION

Roasting of geologic material that contains sulfides or organic carbon is necessary to remove these materials which consume a large amount of bromine. Excess bromine is essential to ensure dissolution of gold. Although metallic gold and gold-bearing minerals are soluble in acid solutions of bromine even at room temperature (Thompson and others, 1968), observations of gold particles in some samples showed that the reaction was

slow or incomplete in the hydrobromic acid-0.5 percent bromine solution unless the solution was heated. The heating step ensures a more rapid and complete dissolution of gold.

Gold is efficiently extracted by MIBK from hydrobromic acid solutions over a wide range of acid concentrations (Morrison and Freiser, 1957). Iron, a source of interference in the estimation of gold, is also extracted into MIBK. Iron is removed from the MIBK extract by washing with 0.1 N hydrobromic acid, the gold remains quantitatively in the MIBK (Thompson and others, 1968). The 0.1 N hydrobromic acid used for washing is saturated with MIBK to prevent loss of volume of the MIBK extract due to its solubility in acid solutions. Standard solutions are carried through the same extraction and washing to closely match standards to samples.

The calibration curve for gold in the extract by flameless atomic absorption is linear to about 0.05 $\mu\text{g/mL}$ under the conditions described. Samples with concentrations greater than 0.05 ppm must be diluted or analyzed by conventional flame atomic absorption. Ramp drying provides the best precision, although step drying produces reasonable precision. Sensitivity is reduced if greater flow rates are used. Sensitivity also decreases as the graphite tube deteriorates with use; however, the decrease is small over several hundred atomizations. The graphite tube should be changed when sensitivity decreases significantly if maximum sensitivity is to be maintained. No background absorption was observed on standards or samples used in this study, so the use of background correction is unnecessary.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	2.86-3.14	2.98	4.3
II	0.020-0.026	0.022	11.4
III	0.002-0.003	0.003	21.1
IV	0.317-0.372	0.353	6.0
V	0.005-0.008	0.007	17.3
VI	0.061-0.066	0.063	3.7

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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HEAVY METALS, AMMONIUM CITRATE-EXTRACTABLE METHOD

The method described here, excepting minor changes, was developed by Bloom (1955) and described by Ward and others (1963).

SUMMARY

An aqueous ammonium citrate solution is used at ambient temperature to extract heavy metals from a sample of soil or sediment, and a xylene or toluene solution of dithizone is used to estimate the concentration of heavy-metal ions. Although this method measures only a small fraction of the total metal content of a sample, geochemical dispersion patterns related to base-metal deposits are sometimes revealed more clearly than by using the total metal content.

The method is extremely rapid; a determination can be made in less than 1 minute. As only a few simple items of equipment are needed, the method is well adapted to field use because samples can be analyzed as rapidly as they are collected. Thus, a geologist's efficiency in finding and outlining economically important dispersion patterns of heavy metals is increased. The method has been widely used in geochemical prospecting.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Ammonium citrate solution: Dissolve 50 g ammonium citrate $((\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7)$ and 8 g hydroxylamine hydrochloride $(\text{NH}_2\text{OH}\cdot\text{HCl})$ in 1 L water. Adjust the pH of the solution to 8.5 by adding metal-free ammonium hydroxide. This

final adjustment of the pH should be made carefully because the rate of extraction of the metal dithizonates is dependent on pH. If the color of 1 mL of 0.0015 dithizone does not remain green when shaken for 30 seconds with 5 mL of the ammonium citrate solution, clean the ammonium citrate buffer solution as follows. Heavy metals are removed from the ammonium citrate solution by shaking the solution with 15-mL portions of 0.01 percent dithizone solution using a separatory funnel until the organic layer remains green. Extract the dissolved dithizone by shaking the aqueous solution with 25-mL portions of chloroform until the latter is colorless. Then wash twice with carbon tetrachloride to remove dissolved chloroform.

Dithizone solution, 0.1 percent in chloroform: Dissolve 0.1 g dithizone (diphenylthiocarbazone) in 100 mL reagent-grade chloroform approximately 2 hours before using. Store the solution in a glass-stoppered Pyrex bottle that has been wrapped with paper or aluminum foil, and keep it cool.

Dithizone solution, 0.0015 percent in xylene: Dilute 1.5 mL of 0.1 percent dithizone solution to 100 mL with xylene. This solution can be conveniently dispersed in the field from an aluminum-foil-wrapped polyethylene wash bottle. As this dilute solution is less stable than the 0.1 percent dithizone solution, only about 100 mL should be made up at one time, and care should be taken in the field to keep the container away from direct sunlight.

Xylene: Occasionally a manufacturer's best grade of xylene may be unsatisfactory, as indicated when fresh dithizone solutions rapidly take on yellow hues caused by oxidation of dithizone. Such xylene can sometimes be made satisfactory for use by distillation or by shaking it with small amounts of concentrated sulfuric acid, and freezing out water remaining after the acid wash.

APPARATUS

Graduated cylinders, glass-stoppered, 25-mL
Scoop, 0.2-g

PROCEDURE

1. Weigh or scoop 0.2 g of the fine fraction of a soil or sediment sample into a 25-mL glass-stoppered cylinder and add 5 mL ammonium citrate solution and 1 mL of 0.0015 percent dithizone solution.

2. Shake the cylinder vigorously for 30 seconds.
3. Allow the organic and aqueous phases to separate, and observe the color of the xylene (upper) layer. If it is green, green-blue, or blue, record as 0, 0.5, or 1 mL, respectively.
4. If the color is blue-purple to red, add 0.0015 percent dithizone solution in 1-mL increments and shake for a few seconds after each addition until a blue color is obtained.
5. Record the volume of dithizone solution used and convert to parts per million using the standardization chart.

STANDARDIZATION CHART

Chart was prepared by titrating a series of solutions that contain known amounts of zinc.

Volume in mL of 0.0015 percent dithizone solution added to reach blue endpoint	Heavy-metal content (ppm)
0	0
1.0	1
1.5	2
2.0	3
2.5	4
3.0	5
4.0	7
5.0	9
6.0	11
7.0	14
8.0	17
9.0	20
10.0	22
11.0	25
12.0	27
13.0	30
14.0	32
15.0	35
16.0	38
17.0	40
18.0	40
19.0	45
20.0	45

DISCUSSION

To ensure comparable results in day-to-day use of this method, the frequent determination of a standard sample whose exchangeable-metal content is known is highly recommended.

In areas where the exchangeable-metal content of most samples is unusually high, the strength

of the work solution can be advantageously increased to 0.003 percent, or the sample size reduced.

The 0.1 percent dithizone solution may be prepared in either xylene or chloroform. Chloroform was chosen because of its more rapid dissolution of dithizone. If desired, other lighter-than-water solvents may be used; toluene is widely used.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

[N.A., method not applicable to this sample medium. For sample GXR II, an 0.04-g sample was titrated with 0.003 percent dithizone solution]

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	N.A.	N.A.	N.A.
II	200-250	218	9.4
III	17-22	19.2	11.3
IV	N.A.	N.A.	N.A.
V	14-20	17.0	12.5
VI	1-2	1.4	39.1

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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INDIUM AND THALLIUM, ATOMIC ABSORPTION METHOD

The method described here, excepting minor changes, was developed by Hubert and Lakin (1972).

SUMMARY

Rock, soil, and stream-sediment samples are decomposed by hydrofluoric acid, and indium and thallium are determined by atomic absorption spectrophotometry. Organic-rich samples are ashed over a Meeker burner before the hydro-

fluoric-acid attack. The hydrofluoric acid is evaporated to dryness and the sample residue is dissolved in a solution of bromine in hydrobromic acid, heated to dispel the excess bromine, and diluted with water. The cool solution is then shaken with methyl isobutyl ketone to extract indium and thallium. Interference of iron is minimized by extracting the ketone with 1.5 N hydrobromic acid. Indium and thallium are measured in the samples at concentrations of 0.2 ppm or more by atomic absorption spectrophotometry using an air-acetylene flame. Fifty samples can be analyzed per day for the two elements.

Special digestion procedures for iron and manganese oxides, sulfides, organic materials, and a more drastic attack using perchloric, nitric, and hydrofluoric acids are described by Hubert and Lakin (1972).

REAGENTS

All chemicals should be of reagent grade, and all water should be metal free.

Bromine.

Hydrobromic acid, 1.5 N: Dilute 172 mL concentrated hydrobromic acid to 1 L with water.

Hydrobromic acid-1 percent bromine solution: Dissolve 10 mL liquid bromine in 1 L concentrated hydrobromic acid.

Hydrofluoric acid, 48 percent.

MIBK (methyl isobutyl ketone), 4-methyl-2-pentanone.

Potassium hydroxide, pellets.

Sodium bromate.

APPARATUS

Atomic absorption spectrophotometer

Centrifuge

Horizontal shaking machine

Hot plate

Meeker burner

Porcelain evaporating dish, 105-mm diameter

Teflon beakers, 100-mL capacity

Test tubes, 25×150-mm screw-cap

STANDARDS

Stock indium and (or) thallium solutions, 1,000 µg/mL: Dissolve 1.00 g pure indium and (or) 1.00 g pure thallium in 200 mL hydrobromic acid-1 percent bromine solution; add concentrated hydrobromic acid to make 1 L.

Dilute indium and (or) thallium solutions, 100 µg/mL: Dilute 10 mL of 1,000 µg/mL stock indium and (or) thallium solutions to 100 mL with concentrated hydrobromic acid.

Standard indium and (or) thallium solutions in MIBK, 0, 0.1, 0.2, 1.0, and 2.0 µg/mL: Add 0, 0.1, 0.2, 1.0, and 2.0 mL of 100 µg/mL dilute indium and (or) thallium solutions to 100 mL of 1.5 N hydrobromic acid. Add 100 mL MIBK and shake for 1 minute to partition metals into organic phase.

PROCEDURE

1. Place 2 g pulverized rock or soil sample in a 100-mL Teflon beaker. (If the sample is organic rich, place 2 g in a porcelain evaporating dish and ash over a meeker burner. Then place the ashed sample in a 100-mL Teflon beaker.)
2. Wet the sample with water and add 15 mL of 48-percent hydrofluoric acid.
3. Allow the solution to stand overnight, and then evaporate on a hot plate to dryness.
4. Let the Teflon beaker cool, add 10 mL water, warm the beaker to effect solution, and add two potassium hydroxide pellets.
5. Evaporate the resulting solution to dryness, cool the beaker, and add 25 mL hydrobromic acid-1 percent bromine solution.
6. Let the beaker stand for 30 minutes and then warm to effect solution.
7. Once the sample is in solution, add about 0.1 g sodium bromate.
8. Place the Teflon beaker on a hot plate and boil gently until the volume of the solution is reduced to approximately 15 mL, and then allow to cool.
9. Transfer the entire contents (sample and acid) of the beaker to a 25×150-mm screw-cap test tube, wash the beaker with approximately 15 mL water, and add to test tube.
10. Add 10 mL MIBK, cap, and shake the tube using the horizontal shaking machine for 5 minutes.
11. Centrifuge the tube until the two layers separate.
12. Transfer all of the MIBK layer to another screw-cap test tube containing 30 mL of 1.5 N hydrobromic acid.

13. Shake the tube using the horizontal shaking machine for 5 minutes and then centrifuge to separate the two layers.
14. The indium and thallium remaining in the MIBK phase are ready for determination by atomic absorption spectrophotometry.

STANDARDIZATION OF INSTRUMENT

The following operating conditions are for a Perkin-Elmer model 603 atomic absorption spectrophotometer.

	Indium	Thallium
Grating	ultraviolet	ultraviolet
Wavelength (nm)	304.0	276.8
Slit (nm)	0.7	0.7
Lamp current	use current recommended on lamp	
Source lamp	indium (hollow cathode lamp)	thallium (hollow cathode lamp)
Integration time (seconds)	1	1
Burner	three-slot	three-slot
Flame condition	oxidizing (lean blue)	oxidizing (lean blue)
0.1 µg/mL (absorbance units)	0.004	0.003
0.2 µg/mL (absorbance units)	0.008	0.006
1.0 µg/mL (absorbance units)	0.036	0.028
Lower limit of determination (µg/mL)	0.2	0.2

DISCUSSION

A radioactive isotope of thallium was used to determine that thallium bromide can be extracted from a hydrobromic acid solution with MIBK. If the normality of the hydrobromic acid used in the extraction is between 0.5 and 6.0 N, the percentage extraction into MIBK is at least 98. Because there is no suitable radioisotope for indium for study of extraction methods, the amount of indium in both phases of the extraction was determined by atomic absorption. At a concentration of 0.5 N hydrobromic acid, approximately 75 percent of the indium bromide is extracted into MIBK, and with a 1 N to 4 N hydrobromic acid solution (and increasing concentrations) the extraction of indium is greater than 98 percent.

If enough iron is present in the sample to color the MIBK layer brown, it will interfere with the indium determination, possibly by a process called "light scattering", as described by Billings (1965). Most of the iron is normally extracted from the MIBK in the 1.5 N hydrobromic acid wash step.

If the MIBK layer remains brown in color from iron, it must be washed a second time with 1.5 N hydrobromic acid.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

[N(), not detected at limit of determination, or at value shown; L(), detected, but below limit of determination, or below value shown. Data were recorded in multiples of lower reporting limits, rounded down, and reported at two significant digits]

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
Indium			
I	0.9-1.3	1.08	13.73
II	0.2-0.4	0.34	26.3
III	N(0.2)	N(0.2)	0
IV	L(0.2)-0.2	L(0.2)	0
V	0.5-0.7	0.56	23.96
VI	L(0.2)	L(0.2)	0
Thallium			
I	0.4-0.6	0.5	14.14
II	1.4-1.7	1.54	7.4
III	4.0-4.7	4.34	5.78
IV	3.4-3.6	3.48	2.4
V	0.9-1.1	1.04	8.6
VI	2.6-2.8	2.7	3.7

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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MOLYBDENUM, ATOMIC ABSORPTION METHOD

The method described here was modified from a procedure described by Rao (1971).

SUMMARY

Rock, soil, and stream-sediment samples are decomposed by fusion with potassium pyrosulfate. Molybdenum is converted to phosphomolybdate with phosphoric acid and hydrogen peroxide, and extracted into a solution of methyl isobutyl ketone and 3 percent tricaprylylmethylammonium chloride. Molybdenum in the extract is determined by atomic absorption spectrophotometry using a nitrous oxide-acetylene flame. Molybdenum concentrations of 1.0 ppm or more can be determined by this method. Approximately 50 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Aliquat 336-MIBK solution, 3 percent: Dilute 30 mL Aliquat 336 (tricaprylylmethylammonium chloride), available from General Mills Inc., Minneapolis, Minn., to 1 L with MIBK (methyl isobutyl ketone).

Phosphoric acid-hydrogen peroxide solution: Add 200 mL phosphoric acid to 134 mL hydrogen peroxide and dilute to 2 L with distilled water. This solution should be prepared weekly. The hydrogen peroxide should be checked by shaking 0.1 mL hydrogen peroxide with 10 mL water to which 0.2 g ferrous ammonium sulfate has been added. A rust brown color should appear, if not the hydrogen peroxide has decomposed and should not be used.

Potassium pyrosulfate: Molybdenum contamination is common in reagent potassium pyrosulfate. Each bottle of reagent should be tested to insure low molybdenum contamination prior to use. Reagent-grade potassium pyrosulfate, marketed by Mallinckrodt Inc., St. Louis, Mo., has proven to be the most molybdenum free.

APPARATUS

- Atomic-absorption spectrophotometer
- Centrifuge
- Horizontal shaking machine
- Meeker burner
- Polyethylene or silicone rubber stoppers; to fit 16-mm tubes
- Test tube, 16×150-mm disposable
- Test tube, 25×200-mm screw-cap
- Vortex mixer
- Water bath

STANDARDS

Stock molybdenum solution, 1,000 $\mu\text{g/mL}$: Fuse 0.3751 g molybdenum trioxide (MoO_3) with 3.0 g potassium pyrosulfate over a burner. Cool and dissolve the melt in approximately 20 mL phosphoric acid-hydrogen peroxide solution. Bring the volume to 250 mL with additional phosphoric acid-hydrogen peroxide solution.

Stock molybdenum solution, 100 $\mu\text{g/mL}$: Dilute 10 mL of 1,000 $\mu\text{g/mL}$ stock molybdenum solution to 100 mL with phosphoric acid-hydrogen peroxide solution.

Stock molybdenum solution, 10 $\mu\text{g/mL}$: Dilute 10 mL of 100 $\mu\text{g/mL}$ stock molybdenum solution to 100 mL with phosphoric acid-hydrogen peroxide solution.

Stock molybdenum solution, 1 $\mu\text{g/mL}$: Dilute 10 mL of 10 $\mu\text{g/mL}$ stock molybdenum solution to 100 mL with phosphoric acid-hydrogen peroxide solution.

Organic working standard solutions, 0, 0.25, 0.5, 1.0, 2.5, and 5.0 $\mu\text{g/mL}$: Pipette 0, 5, and 10 mL of 1 $\mu\text{g/mL}$ stock molybdenum solution and 2, 5, and 10 mL of 10 $\mu\text{g/mL}$ stock molybdenum solution into six 25 \times 200-mm screw-cap test tubes. Bring the volume of each tube to 50 mL with phosphoric acid-hydrogen peroxide solution and add 20 mL Aliquat 336-MIBK solution. Cap and shake the tubes for 45 seconds. These standards should be prepared daily and are equivalent to 0, 5, 10, 20, 50, and 100 ppm in the sample.

PROCEDURE

1. Weigh 0.2 g sample into a 16 \times 150-mm disposable test tube.
2. Add 1.5 g potassium pyrosulfate to each tube containing the sample and to three tubes containing no sample to be used as blanks.
3. Mix sample and potassium pyrosulfate thoroughly with a vortex mixer.
4. Heat the sample and potassium pyrosulfate over a Meeker burner until a uniform melt is achieved.
5. Cool the tubes in a horizontal position while rotating them to deposit the melt uniformly on the sides of the tubes.
6. Add 10 mL phosphoric acid-hydrogen peroxide solution.
7. Heat the tubes in a boiling water bath until

the melt is dissolved. Vortex mixing aids in breaking up the melt.

8. Allow the tubes to cool and add 4 mL Aliquat 336-MIBK solution.
9. Cap the tubes with polyethylene stoppers and shake on a horizontal shaking machine for 45 seconds.
10. Centrifuge to separate the organic layer.
11. Determine the molybdenum in the organic layer, within the same day, by atomic absorption using a nitrous oxide-acetylene flame.

STANDARDIZATION OF INSTRUMENT

The following operating conditions are for a Perkin-Elmer model 603 atomic-absorption spectrophotometer.

Grating	ultraviolet
Wavelength	313.3 nm
Slit	0.7 nm
Lamp current	15 mA
Source lamp	molybdenum (hollow cathode lamp)
Integration time	1 second
Burner	5 cm, nitrous oxide
Fuel	acetylene
Oxidant	nitrous oxide
Flame condition	rich, but not yellow

INSTRUMENT CALIBRATION

Using the preceding instrument parameters, the instrument is calibrated to read sample concentration directly by using the following standards and settings.

[Lower limit of determination, 1 ppm]

Standard ($\mu\text{g/mL}$)	Absorbance units	Set concentration (ppm)
0.25	0.013	5
.5	.026	10
1.0	.054	20
2.5	.135	50
5.0	.270	100

DISCUSSION

Molybdenum is rendered soluble by fusion with potassium pyrosulfate. Blanks of potassium pyrosulfate are run with samples to determine an average blank value of the pyrosulfate used. The average blank is subtracted from sample readings.

The phosphoric acid-hydrogen peroxide solution dissolves the melt and oxidizes molybdenum to hexavalent state forming molybdenum (VI) phosphomolybdate. It is this species that is extracted into the Aliquat 336-MIBK solution. Iron and other elements that might possibly interfere in the estimation are not extracted.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	14-15	14	1.4
II	0.8-1.1	1.0	17.5
III	not detected		
IV	310-330	310	2.7
V	23-25	24	3.8
VI	1.7-2.1	1.8	9.8

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
- Rao, P. D., 1971, Determination of molybdenum in geological materials: *Atomic Absorption Newsletter*, v. 10, no. 5, p. 118-119.

SELENIUM, FLAMELESS ATOMIC ABSORPTION METHOD

The method described here, excepting minor changes, was developed by Sanzalone and Chao (1981).

SUMMARY

Selenium is determined in geological material by flameless atomic absorption spectrophotometry and a carbon-rod atomizer. The sample is decomposed by a mixture of nitric, perchloric, and hydrofluoric acids. Selenium is reduced to Se^{+4} by heating with hydrochloric acid. Selenium is then extracted into toluene from a hydrochloric and hydrobromic acid solution that contains iron.

Selenium is determined directly in the toluene extract using a nickel solution as a matrix modifier for samples that contain from 0.2 to 200 ppm selenium. For samples that contain less than 0.2 ppm and have a concentration range of 0.05 to 100 ppm, a back-extraction of the selenium into dilute hydrochloric acid is used. The only observed interferences are from arsenic in concentrations greater than 1,000 ppm and from nitric acid if it is not removed in the sample digestion procedure. About 30 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Hydrobromic acid, concentrated.

Hydrochloric acid, concentrated.

Hydrochloric acid, 3.0 M: Dilute 250 mL concentrated hydrochloric acid to 1 L with water.

Hydrochloric acid-nickel solution, 0.01 M: Dissolve 4.95 g nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 50 mL water, add 0.83 mL concentrated hydrochloric acid, and dilute to 1 L with water.

Hydrofluoric acid, 48 percent.

Iron solution, 10 percent (w/v) in 1 M hydrochloric acid: Dissolve 10 g Specpure iron powder in 53 mL concentrated hydrochloric acid while heating on a hot plate. After dissolution, add 5 mL of 50 percent hydrogen peroxide to oxidize the iron. Heat to remove residual peroxide and dilute to 100 mL with water.

Nickel solution, 0.1 percent (w/v): Dissolve 0.49 g nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 100 mL water.

Nitric acid, concentrated.

Perchloric acid (HClO_4), 70 percent.

Toluene.

APPARATUS

Aluminum heating block; drilled to accommodate 25-mm test tubes

Atomic absorption spectrophotometer; equipped with a carbon rod atomizer

Centrifuge

Horizontal shaking machine

Hot plate

Teflon beakers, 50-mL

Test tubes, 16×150-mm disposable

Test tubes, 25×150-mm screw-cap

STANDARDS

Stock selenium solution, 1,000 $\mu\text{g}/\text{mL}$: Dissolve 2.190 g anhydrous sodium selenite (Na_2SeO_3) in 50 mL water, add 10 mL concentrated hydrochloric acid, and dilute to 1 L with water.

Stock selenium solution, 100 $\mu\text{g}/\text{mL}$: Dilute 10 mL of 1,000 $\mu\text{g}/\text{mL}$ stock selenium solution to 100 mL with 0.1 M hydrochloric acid.

Stock selenium solution, 10 $\mu\text{g}/\text{mL}$: Dilute 10 mL of 100 $\mu\text{g}/\text{mL}$ stock selenium solution to 100 mL with 0.1 M hydrochloric acid.

Stock selenium solution, 1 $\mu\text{g}/\text{mL}$: Dilute 10 mL of 10 $\mu\text{g}/\text{mL}$ stock selenium solution to 100 mL with 0.1 M hydrochloric acid.

Selenium working standards, 0, 0.025, 0.1, 0.5, 1.0, 3.0, 5.0, and 10 μg : Pipette 0 mL, 0.25 mL, and 1.0 mL of 0.1 $\mu\text{g}/\text{mL}$ stock selenium solution; 0.5 mL and 1.0 mL of 1.0 $\mu\text{g}/\text{mL}$ stock selenium solution; and 0.3 mL, 0.5 mL, and 1.0 mL of 10 $\mu\text{g}/\text{mL}$ stock selenium solution into eight 25 \times 150-mm test tubes, respectively, containing 5 mL of 3 M hydrochloric acid. These are to be carried through the procedure with the samples starting at step 8.

PROCEDURE

1. Weigh 0.5 g sample into a 50-mL Teflon beaker.
2. Moisten with 1 to 2 mL water.
3. Add 10 mL each of concentrated nitric, 70 percent perchloric, and 48 percent hydrofluoric acids.
4. Heat the beaker on a hot plate preset at 150°C under a perchloric-acid fume hood.
5. Gradually raise the temperature of the hot plate to 220°C over a 1.5-hour period.
6. Remove the beaker from the hot plate when the volume has been reduced to between 1 and 2 mL.
7. Transfer the contents of the beaker into a 25 \times 150-mm screw-cap tube using two 2.5-mL portions of 3 M hydrochloric acid.
8. Heat the tubes containing sample and standards in an aluminum heating block preset at 100°C for 5 minutes.
9. Cool tubes to room temperature, add 10 μL iron solution to each, and mix.
10. Add 10 mL concentrated hydrobromic acid and mix.
11. Proceed with extraction A if samples contain more than 0.2 ppm selenium or proceed

with extraction B if samples contain less than 0.2 ppm selenium.

Extraction procedure A (for samples containing 0.2 ppm or more selenium):

1. Add 2 mL toluene and shake the tubes on a horizontal shaking machine for 5 minutes.
2. Centrifuge the tubes.
3. Pipette 1 mL of the toluene extract into a 16 \times 150-mm disposable tube and cap.
4. Carefully remove the remaining toluene layer with a pipette and discard.
5. Add another 2 mL toluene to the 25 \times 150-mm tubes containing samples and standards and shake the tubes for 5 minutes.
6. Pipette 1 mL of the toluene extract into the 16 \times 150-mm tube containing the first extract and mix.
7. Transfer the organic extract into the automatic sample dispenser of the atomic absorption spectrophotometer for selenium determination using the carbon-rod atomizer.

Extraction procedure B (for samples containing less than 0.2 ppm selenium):

1. Add 2 mL toluene and shake the tube on a horizontal shaking machine for 5 minutes.
2. Centrifuge the tubes.
3. Transfer the entire toluene layer into a 16 \times 150-mm screw-cap tube.
4. Add another 2 mL toluene to the 25 \times 150-mm tubes containing samples and standards and shake the tubes for 5 minutes.
5. Centrifuge the tubes.
6. Transfer the entire toluene layer into the 16 \times 150-mm tube containing the first extract.
7. Pipette 1 mL of the 0.01 M hydrochloric acid-nickel solution into the 16 \times 150-mm tube containing the combined extracts.
8. Shake the tube for 5 minutes and centrifuge.
9. Transfer the aqueous back-extract, with a pipette, into the automatic sample dispenser of the atomic absorption spectrophotometer for selenium determination using the carbon-rod atomizer.

STANDARDIZATION OF INSTRUMENT

Five μL of the nickel solution is pipetted manually into the carbon-rod atomizer just prior to the injection of a 2- or 5- μL aliquot of the toluene extract by the automatic sample dispenser from extraction procedure A. Two or ten μL of the

aqueous back-extract from extraction procedure B is injected by the automatic sample dispenser without the addition of nickel solution. The peak absorbance observed is compared with absorbance values for standards using the same conditions. The following operating conditions are used for a Varian model AA-6 atomic absorption spectrophotometer equipped with a model 63 carbon-rod atomizer and a model 53 automatic sample dispenser.

Wavelength	196.0 nm
Slit	1.0 nm
Background correction	on
Source lamp	selenium (electrodeless discharge lamp)
Lamp current	8 W
Readout mode	peak height
Purge gas	nitrogen
Purge gas-flow setting	8.0
Drying voltage setting	6.0 (90°C) for toluene, 6.5 (100°C) for aqueous
Drying time	25 seconds for toluene, 30 seconds for aqueous
Ashing voltage setting	6.0 (400°C)
Ashing time	10 seconds
Atomizing voltage setting	8.5 (2,500°C)
Atomizing time	2 seconds

Using the preceding instrument parameters, the following absorbance values for standards have been observed and correspond to the indicated selenium concentration in samples.

Toluene from extraction procedure A
[Lower limit of determination, 0.2 ppm]

2- μ L aliquot			5- μ L aliquot		
Selenium (μ g)	Absorbance units	Sample (ppm Se)	Selenium (μ g)	Absorbance units	Sample (ppm Se)
3.0	0.085	6.0	0.1	0.010	0.2
5.0	.190	10.0	1.0	.100	2.0
7.5	.317	15.0	3.0	.290	6.0
10.0	.450	20.0	5.0	.440	10.0

Aqueous back-extract from extraction procedure B
[Lower limit of determination, 0.05 ppm]

2- μ L aliquot			10- μ L aliquot		
Selenium (μ g)	Absorbance units	Sample (ppm Se)	Selenium (μ g)	Absorbance units	Sample (ppm Se)
1.0	0.086	2.0	0.025	0.009	0.05
3.0	.253	6.0	.1	.036	.2
5.0	.420	10.0	.5	.172	1.0
			1.0	.352	2.0

DISCUSSION

The use of hydrofluoric acid in the sample digestion is necessary to decompose selenium occluded in or coated by siliceous materials. The digest should not be taken to dryness, as a loss of selenium is possible through volatilization.

The procedure may be interrupted after the sample is transferred with 3 M hydrochloric acid into 25×150-mm tubes. However, once the sample is heated with the hydrochloric acid, the procedure should be completed within the same day. The sample is heated with hydrochloric acid to insure that the selenium is in the +4 oxidation state, this is the only valence that will be extracted by toluene from the hydrochloric acid-hydrobromic acid solution. Iron is added before extraction to exert a synergistic effect on the extraction of selenium. The iron must be added before hydrobromic acid is added or the extraction of selenium will be incomplete. Two extractions are necessary to achieve 95 percent or more extraction efficiency.

Selenium is effectively back-extracted into 0.01 to 0.1 M hydrochloric acid. The selenium present may thereby be concentrated into a smaller volume, allowing a lower concentration to be determined.

The addition of nickel solution along with selenium to the carbon-rod atomizer greatly enhances the absorbance signals of selenium. This effect may be due to the formation of a stable nickel selenide compound, which reduces the loss of selenium during the ashing stage and increases the efficiency of the atomization. A similar enhancement of absorbance is obtained for the aqueous back-extracted selenium when the nickel is present in the 0.01 M hydrochloric acid solution.

The sensitivity (1 percent absorption) of the carbon rod for selenium in either toluene or aqueous solution has been determined to be 6×10^{-12} g. When using the selenium standards in toluene, a linear relationship exists between absorbance and μ g selenium: 0.1 to 5 μ g selenium using 5- μ L aliquots and 3 to 10 μ g selenium using 2- μ L aliquots. These selenium amounts correspond to 0.2 to 20 ppm in the actual sample. For selenium values greater than 20 ppm and as much as 200 ppm, a one-to-ten dilution of the organic layer may be made. For values higher than 200 ppm, a sample size smaller than 0.50 g should be used. To determine selenium values lower than 0.2 ppm, a back-extraction of the selenium into an aqueous

nickel-0.01 M hydrochloric acid solution is necessary. A linear relationship exists between absorbance and μg selenium in the aqueous back-extracted standards: 0.025 to 1 μg selenium using 10- μL aliquots and 0.25 to 5 μg selenium using 2- μL aliquots. These selenium amounts correspond to 0.05 to 10 ppm in the actual sample.

Nitric acid prevents the extraction of selenium into toluene. Therefore, it must be removed by evaporation during digestion. Arsenic apparently hinders the extraction of selenium into toluene if its concentration is 1,000 ppm or greater in the sample. Samples with greater than 1,000 ppm arsenic may be analyzed by using a smaller sample size to reduce the apparent arsenic concentration. Other major and trace elements commonly encountered in geologic samples do not cause interference.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

[GXR III determined by back-extraction procedure]

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	18.0-20.7	3.0	6.1
II	0.54-0.62	0.07	6.4
III	0.17-0.20	0.19	6.1
IV	5.95-6.50	6.28	4.1
V	0.96-1.08	1.03	5.9
VI	0.86-0.97	0.91	4.7

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, in Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
- Sanzolone, R. F., and Chao, T. T., 1981, Determination of submicrogram amounts of selenium in geological materials by electrothermal atomic-absorption spectrophotometry after solvent extraction: *The Analyst*, v.106, p. 647-652.

TELLURIUM, FLAME AND FLAMELESS ATOMIC ABSORPTION METHODS

The method described here, excepting minor changes, was developed by Chao and others (1978).

SUMMARY

Tellurium in rock, soil, and stream-sediment samples is determined by flame atomic absorption in the 0.1 to 20 ppm range and by flameless atomic absorption in the 0.004 to 0.2 ppm range. Decomposition is accomplished by heating with hydrobromic acid and bromine. Tellurium is extracted into MIBK (methyl isobutyl ketone) after the addition of ascorbic acid to reduce iron (III). The MIBK extract is washed with 0.5 M hydrobromic acid before flameless atomic absorption determination. About 20 samples can be analyzed per day by the flameless method, and about 40 by the flame method.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Ascorbic acid.

Bromine.

Hydrobromic acid-2 percent bromine solution: Pipette 20 mL bromine into a 1-L volumetric flask and bring to 1L with concentrated hydrobromic acid.

Hydrobromic acid, 0.5 M: Dilute 60 mL concentrated hydrobromic acid to 1 L with water.

Hydrobromic acid, 3 M: Dilute 360 mL concentrated hydrobromic acid to 1 L with water.

Iron solution, 10 percent (w/v) in 3 M hydrobromic acid: Dissolve 10 g of Specpure iron powder in concentrated hydrobromic acid, add 1 mL bromine, and evaporate to dryness. Add 34.2 mL concentrated hydrobromic acid to the residue, heat gently to effect dissolution, and dilute to 100 mL with water.

MIBK (methyl isobutyl ketone).

APPARATUS

Atomic-absorption spectrophotometer; with graphite atomizer
Centrifuge

Horizontal shaking machine

Hot plate; with aluminum heating block for 25-mm tubes

Separatory funnel, 60-mL

Shaker, separatory-funnel

Test tubes, 25×150-mm screw-cap

Vile, capped

Vortex mixer

STANDARDS

Stock tellurium solution, 100 µg/mL: Dissolve 0.125 g Specpure tellurium dioxide in 1 L of 3 M hydrobromic acid.

Stock tellurium solution, 10 µg/mL: Dilute 10 mL of 100 µg/mL stock tellurium solution to 100 mL with 3 M hydrobromic acid.

Stock tellurium solution, 1 µg/mL: Dilute 10 mL of 10 µg/mL stock tellurium solution to 100 mL with 3 M hydrobromic acid.

Stock tellurium solution, 0.1 µg/mL: Dilute 10 mL of 1.0 µg/mL stock tellurium solution to 100 mL with 3 M hydrobromic acid (prepare daily).

Standard tellurium solutions in MIBK for flame atomic absorption, 0, 0.25, 1, 5, 10, 20, and 50 µg: Add 0, 0.25, 1.0, and 5.0 mL of 1 µg/mL stock tellurium solution and 1.0, 2.0, and 5.0 mL of 10 µg/mL stock tellurium solution to seven 25×150-mm tubes, respectively, and dilute to 43 mL with 3 M hydrobromic acid. Add 0.5 mL of the iron solution and 1 g ascorbic acid to each standard and mix. Add 3 mL MIBK, cap, and shake for 2 minutes on a horizontal shaking machine. Centrifuge to separate the phases and use to calibrate the atomic absorption spectrophotometer.

Standard tellurium solution in MIBK for flameless atomic absorption, 0, 0.01, 0.025, 0.05, 0.1, 0.25, and 0.5 µg: Add 0, 0.1, 0.25, 0.5, 1.0, 2.5, and 5.0 mL of the 0.1 µg/mL stock tellurium solution to seven 25×150-mm tubes, respectively, and dilute to 43 mL with 3M hydrobromic acid. Add 0.5 mL of the iron solution and 1 g ascorbic acid to each standard and mix. Add 3 mL of MIBK, cap, and shake for 2 minutes on a shaker. Centrifuge to separate the phases and use to calibrate the atomic absorption spectrophotometer. The standards for flameless determination are also carried through the procedure for flameless determination.

PROCEDURE

For flame and flameless determinations:

1. Weigh 2.5 g pulverized sample into a 25×150-mm screw-cap test tube.
2. Add 15 mL hydrobromic acid-2 percent bromine solution in small portions to prevent vigorous reactions that may be caused by carbonated and organic matter. If sample contains visible sulfides, add an additional 2 mL bromine.
3. Allow the acid to react with the sample for 1 hour with occasional vortex mixing.
4. Heat the tube in an aluminum heating block on a hot plate set at 135°-140°C for 30 minutes to expel excess bromine. Sample containing sulfide must be heated longer.
5. Add 28 mL water and mix. Solution is approximately 3 M hydrobromic acid.
6. Centrifuge and decant the liquid phase into another 25×150-mm tube containing approximately 1 g ascorbic acid.
7. Mix to dissolve ascorbic acid. The solution should have a light-yellow color. If the color does not appear, add additional ascorbic acid.
8. Add 3 mL of MIBK, cap, and shake the tube for 2 minutes on a horizontal shaking machine.
9. Centrifuge to separate the phases and determine tellurium in the organic phase by flame atomic absorption, or use the contents of the tube in the following procedure for flameless determination.

For flameless determination:

1. For samples containing less than 0.1 ppm tellurium, transfer the contents of the tube in step 8 of the previous procedure to a 60-mL separatory funnel.
2. Drain and discard the aqueous layer.
3. Add 2 mL of 0.5 M hydrobromic acid and shake for exactly 5 minutes on a separatory-funnel shaker.
4. Allow the layers to separate completely, drain and discard the aqueous layer.
5. Transfer the organic extract to a capped vial to be used for the flameless atomic absorption tellurium determination.

STANDARDIZATION OF INSTRUMENT

The following operating conditions are for a Varian model AA-6 atomic absorption spectrophotometer and a Varian model 63 carbon-rod atomizer.

[Leaders(—), not used]

	Flame	Flameless
Background correction	on	on
Source lamp	Tellurium (electrodeless discharge lamp)	
Lamp current (W)	8	8
Wavelength (nm)	214.3	214.3
Slit (nm)	0.5	0.5
Readout mode	—	peak height
Burner	air-acetylene	—
Fuel flow meter setting	acetylene=0.2	—
Oxidant flow meter setting	air=4	—
Flame conditions	oxidizing (lean blue)	—
Purge gas and flow meter	—	nitrogen 7.5
Dry voltage setting	—	5.5=100°C
Dry time (seconds)	—	35
Ash voltage setting	—	6.5=500°C
Ash time (seconds)	—	15
Atomize voltage setting	—	Ramp 8=2,100°C
Atomize time (seconds)	—	5

INSTRUMENT CALIBRATION

Using the preceding instrument parameters, a calibration curve of absorbance versus concentration for the standards is constructed.

[Lower limits of detection: flame, 0.1 ppm; flameless, 0.004 ppb]

Flame			Flameless		
Standard (μg)	Absorbance units	Sample concentration (ppm)	Standard (μg)	Absorbance units	Sample concentration (ppm)
0.25	0.006	0.1	0.01	0.002	4
1.0	.023	.4	.025	.005	10
5.0	.122	2.0	.05	.010	20
10.0	.240	4.0	.1	.020	40
20.0	.439	8.0	.25	.050	100
50.0	.728	20.0	.5	.100	200

DISCUSSION

The hydrobromic acid-bromine digestion is adequate to dissolve tellurium in most geologic samples. However, if tellurium minerals are occluded in, or protected by, silicates or siliceous materials, decomposition involving hydrofluoric acid may be beneficial. The optimum sample weight is 2.5 g; larger samples tend to reduce the efficiency of the digestion.

Tellurium can be extracted from 2 to 4 M hydrobromic acid into MIBK in the presence of ascorbic acid. Iron suppresses the extraction. However, once 0.05 g iron (corresponding to 2 percent iron dissolved from the sample in the digestion) is present in the sample solution, additional amounts of iron do not further suppress the extraction of tellurium into MIBK, provided that sufficient ascorbic acid is added to reduce the iron. The amount of ascorbic acid added is not critical as long as it is sufficient to reduce the iron present. Add 0.5 mL of 10 percent iron solution to all the standards along with 1 g ascorbic acid to compensate for the variable amounts of iron encountered in diverse sample types.

The procedure may be interrupted after decanting the sample solution from the digestion tube following centrifugation. The solution is stable and can be saved for future analysis. Once ascorbic acid has been added, the extraction of tellurium into MIBK should proceed without delay and the analysis should be completed on the same day.

Iron causes suppression of absorbance readings in both flame and flameless determinations of tellurium. Ascorbic acid removes this interference in the flame procedure. The tolerance to iron is much less with the carbon-rod atomizer, and ascorbic acid alone is not sufficient to prevent suppression of the absorbance. Washing the organic extract with 0.5 M hydrobromic acid is necessary to remove the residual iron and maintain the absorbance readings constant at iron concentrations greater than 0.05 g in the sample solutions. Without washing, the absorbance decreases with increasing concentrations of iron in the original sample solution and the sensitivity of the flameless procedure is greatly reduced. Absorbance readings obtained after washing are linearly related to concentrations of tellurium, with an absorbance of 0.10 corresponding to 0.50 g tellurium in standards (200 ppb in samples).

For both flame and flameless procedures, the tolerance to the presence of iron is remarkable, amounting to 1 g iron in the sample solution, or 40 percent iron in the sample; this is equivalent to 57 percent Fe₂O₃. The use of background correction is necessary to eliminate interference due to molecular absorption and (or) light scattering in the flame procedure.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

[GXR I, II, and IV, flame atomization; GXR III and VI, flameless atomization]

GXR sample	Range (ppm, GXR III and VI in ppb)	Mean	Percent relative standard deviation
I	8.4-9.0	8.7	1.2
II	0.85-0.90	0.88	1.4
III	7-10	9	15.6
IV	0.96-1.0	1.0	2.6
V	not determined		
VI	15-16	16	2.8

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, in Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
- Chao, T. T., Sanzolone, R. F., and Hubert, A. E., 1978, Flame and flameless atomic-absorption determination of tellurium in geological materials: *Analytica Chimica Acta*, v. 96, p. 251-257.

TIN, ATOMIC ABSORPTION METHOD

The method described here, excepting minor changes, was developed by Welsch and Chao (1976).

SUMMARY

Traces of tin in rock, soil, and stream-sediment samples are determined using an atomic absorption method. A dried mixture of the sample and ammonium iodide is heated to volatilize tin tetraiodide, which condenses on the walls of the test tube. The condensate is put into solution with 5 percent hydrochloric acid, extracted into trioctylphosphine oxide-methyl isobutyl ketone, and aspirated into a nitrous oxide-acetylene flame of an

atomic absorption spectrophotometer. About 50 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Ammonium iodide: Granular (pulverize to a consistency of extra-fine granulated sugar with a mortar and pestle and store in a desiccator).

Ascorbic acid solution: Dissolve 10 g ascorbic acid in 100 mL of 5 percent hydrochloric acid (prepare daily).

Hydrochloric acid, 5 percent: Dilute 50 mL concentrated hydrochloric acid to 1 L with water.

Hydrofluoric acid, 49 percent.

Nitric acid, concentrated.

TOPO (trioctylphosphine oxide)-MIBK (methyl isobutyl ketone) reagent: Dissolve 4 g TOPO in 100 mL MIBK.

APPARATUS

Atomic-absorption spectrophotometer; with nitrous oxide burner

Centrifuge

Electric oven

Evaporating dish, porcelain; size 0000

Glass rod

Horizontal shaking machine

Hot plate

Muffle furnace

Pyropot (Pyroco Products, Margat, Queensland, Australia 4019): Heating device accommodating 10 test tubes, provides a controlled heat source for the iodide fusion. When the test tubes are inserted into the holders, only the bottom 3-4 cm is exposed to the desired temperature, thereby leaving the upper portions of the tubes cool enough to allow condensation of tin vapors.

Separatory funnel, 125-mL

Teflon beakers, 100-mL

Test tubes, 16×150-mm screw-cap, disposable

Test tubes, 25×200-mm screw-cap

Vortex mixer

Water bath

STANDARDS

Stock tin solution, 1,000 µg/mL: Dissolve 1.000 g reagent-grade tin metal in 1 L of 6 M hydrochloric acid.

Dilute tin solution, 100 µg/mL: Dilute 10 mL of

1,000 µg/mL stock tin solution to 100 mL with 5 percent hydrochloric acid. This solution is stable for at least 2 weeks.

Standard tin solution in TOPO-MIBK, 0, 20, and 50 µg/mL: Add 0, 2, and 5 mL of 100 µg/mL dilute tin solution to three 125-mL separatory funnels each containing 3 g of ascorbic acid. Dilute to a total volume of 90 mL with 5 percent hydrochloric acid and add 10 mL TOPO-MIBK reagent solution. Shake for 30 seconds, drain aqueous portion, and transfer organic portion to 16×150-mm test tube.

PROCEDURE

Procedure for non-silicate-bound tin:

1. Weigh 1.0 g sample into a 25×200-mm screw-cap test tube containing 4 g of dry granular ammonium iodide and mix thoroughly.
2. Dry overnight in an electric oven at 105°C.
3. Allow tube to cool to room temperature and heat the sample for 15 minutes in a preheated Pyropot set at 500°C.
4. After sample has cooled, add 12 mL of 5 percent hydrochloric acid and 6 mL ascorbic acid solution.
5. Heat the mixture in boiling water bath for 15 minutes.
6. Mix while hot on a vortex mixer until the sample is finely dispersed.
7. When thoroughly cooled, add 2 mL TOPO-MIBK reagent, cap, and shake for 30 seconds.
8. Decant the liquid into a 16×150-mm test tube, cap, centrifuge, and aspirate into an atomic-absorption spectrophotometer.

Procedure for silicate-bound tin:

1. Weigh 1 g sample into a 0000 porcelain evaporating dish and roast for 1 hour at 700°C in muffle furnace.
2. Transfer to a 100-mL Teflon beaker and add 5 mL concentrated nitric acid and 20 mL of 49 percent hydrofluoric acid.
3. Heat to dryness and transfer residue to a 25×200-mm test tube.
4. Reduce the residue to fine powder with aid of a vortex mixer and a glass rod. Proceed from step 1 of the preceding procedure.

STANDARDIZATION OF INSTRUMENT

The following operating conditions are for a Perkin-Elmer model 603 atomic absorption spectrophotometer.

Grating	ultraviolet
Wavelength	286.3 nm
Slit	0.7 nm
Lamp current	use current recommended on lamp
Source	tin (hollow cathode lamp)
Integration time	1 second
Burner	Varian nitrous oxide-acetylene
Flame condition	nitrous oxide-acetylene flame, reducing (rich, red)
20 µg/mL	0.154 absorbance units
50 µg/mL	0.390 absorbance units
Lower limit of determination	2 ppm

DISCUSSION

The reaction of cassiterite with ammonium iodide is as follows:



As water is a product of the reaction, obviously the sample-ammonium iodide mixture must be as dry as possible for maximum efficiency. Any excess of water would tend to reverse the reaction. The temperature and duration of heating in the Pyropot are critical and must be controlled to obtain reproducible results.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	42-46	43.4	3.7
II	0.7-1.1	0.88	19
III	0.7-1.2	1.02	19
IV	3.5-3.7	3.54	2.5
V	0.6-0.7	0.64	8.6
VI	0.8-1.4	1.14	21

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, in Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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TUNGSTEN, VISIBLE SPECTROPHOTOMETRIC METHOD

The method described here, excepting minor changes, was developed by Welsch (1983).

SUMMARY

Tungsten is determined in rock, soil, and stream-sediment samples by visible spectrophotometry. The sample is decomposed by nitric acid and hydrofluoric acid and dissolved in concentrated hydrochloric acid. A clear aliquot of the solution is treated with stannous chloride to inhibit interferences, particularly from molybdenum. The blue tungsten dithiol complex is developed at 85°C within a half-hour period. The complex is extracted into 5 mL heptane and the concentration is determined by measuring the absorption at 630 nm with a spectrophotometer. About 50 samples can be analyzed per day.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Dithiol, 1.5 percent solution: Acidify 1.5 g zinc dithiol (toluene-3, 4-dithiol, zinc derivative) with 2 mL concentrated hydrochloric acid and dissolve in 100 mL ethanol, preferably by immersion in a sonic bath, for 10 minutes or until a clear pink solution is obtained (prepare daily).

Heptane.

Hydrochloric acid, concentrated.

Hydrofluoric acid, 49 percent.

Nitric acid, concentrated.

Potassium ferricyanide, 10 percent (w/v): Dissolve 10 g potassium ferricyanide ($K_3Fe(CN)_6$) in 100 mL water.

Stannous chloride, 30 percent solution: Dissolve 30 g stannous chloride ($SnCl_2 \cdot 2H_2O$) in 100 mL concentrated hydrochloric acid.

APPARATUS

Boiling chips

Centrifuge

Cuvettes, 12-mm; matched to within 0.002 absorbance unit

Heating block; drilled to accommodate 16-mm test tubes

Hot plate

Spatula, Teflon

Spectrophotometer

Teflon beakers, 50-mL

Test tubes, 16×150-mm, disposable

STANDARDS

Stock tungsten solution, 1,000 $\mu\text{g/mL}$: Dissolve 0.897 g sodium tungstate, dihydrate ($Na_2WO_4 \cdot 2H_2O$) in 500 mL water.

Dilute tungsten solution, 100 $\mu\text{g/mL}$: Dilute 10 mL of 1,000 $\mu\text{g/mL}$ stock tungsten solution to 100 mL with water.

Dilute tungsten solution, 10 $\mu\text{g/mL}$: Dilute 10 mL of 100 $\mu\text{g/mL}$ dilute tungsten solution to 100 mL with water.

Standard tungsten solution in heptane, 1, 10, and 50 μg : Add 0.1 mL of 10 $\mu\text{g/mL}$ and 100 $\mu\text{g/mL}$ dilute tungsten solutions and 0.50 mL of 100 $\mu\text{g/mL}$ dilute tungsten solution to three 16×150-mm test tubes, each containing a boiling chip, 1 mL water, 4 mL concentrated hydrochloric acid, and 5 mL of 30 percent stannous chloride solution. Prepare standards in triplicate and continue through the procedure starting at step 5. These solutions correspond to samples containing 2, 20, and 100 ppm tungsten.

PROCEDURE

1. Weigh 1 g sample into a 50-mL Teflon beaker, add 5 mL concentrated nitric acid and 15 mL of 49 percent hydrofluoric acid, place on a hot plate, and heat at 125°C to dryness.
2. Add 2 mL water and warm to effect solution, transfer to a 16×150-mm test tube with a total of 8 mL concentrated hydrochloric acid, and mix well. (If copper is in excess of 1,000 ppm in the sample, the sample should now be treated with 1 mL of 10 percent potassium ferricyanide. Mix, wait 10 minutes, and proceed to step 3.)

3. Centrifuge and transfer a 5-mL aliquot to a second 16×150-mm test tube.
4. Add 5 mL of 30 percent stannous chloride solution and a boiling chip, and mix solution.
5. Place tube in a heating block set at 85°C for 10 minutes, then add 1 mL of 1.5 percent dithiol solution, mix, and continue to heat for 30 minutes. (Dithiol solution should be injected down the center of the tube rather than the sides to avoid the formation of excessive amounts of tin dithiol.)
6. Add 5 mL heptane to the cooled sample, cap, and shake for 1 minute.
7. Allow the layers to separate, transfer 3 mL of the organic phase to matched cuvettes, and read absorbance on the spectrophotometer at 630 nm. Samples containing greater than 100 ppm tungsten should be reprocessed from step 3 using a smaller aliquot.

STANDARDIZATION OF INSTRUMENT

The following operating conditions are for a Bausch and Lomb spectronic 100 spectrophotometer.

Wavelength 630 nm
 Mode absorbance

The following absorbance readings were observed from the corresponding standards.

Standards (µg)	Absorbance units
1	0.020
10	0.220

Find the mean absorbance value for each standard concentration and plot the absorbance values versus the concentration on linear graph paper.

DISCUSSION

The digestion of the sample cannot be hurried as temperature above 125°C will result in the evolution of tungsten halides. The additional 2 mL of water helps to loosen the digested material prior to transfer with hydrochloric acid.

Stannous chloride prevents formation of green molybdenum dithiol and eliminates a number of interfering elements that would otherwise compete with the tungsten for dithiol bonding sites.

Matched cuvettes differing by no more than 0.002 absorbance units are required for accurate results at the limits of determination.

No interference from lead, chromium, cobalt, nickel, manganese, molybdenum, and vanadium has been observed. However, copper and bismuth at 1,000-ppm concentrations cause a severe suppression of the absorbance reading of approximately 50 percent. The addition of potassium ferricyanide will reduce or eliminate this problem for samples with copper concentrations of 1,000 ppm and greater.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	160-180	172	4.9
II	1.4-1.6	1.5	5.5
III	12,500-14,000	12,900	5.0
IV	30-32	30.9	2.9
V	1.8-2.1	1.9	6.9
VI	2.1-2.4	2.3	5.6

REFERENCES CITED

- Allcott, G. H., and Lakin, H. W., 1975, The homogeneity of six geochemical exploration reference samples, *in* Elliott, I. L., and Fletcher, W. K., eds., *Geochemical exploration 1974*: Amsterdam, Elsevier, p. 659-681.
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URANIUM, ULTRAVIOLET FLUORESCENCE METHOD

The method described here, excepting minor changes, was developed by Centanni and others (1956).

SUMMARY

Uranium is determined in rock, soil, and stream-sediment samples by ultraviolet fluorescence. The sample is decomposed by means of the volatile nature of nitric, hydrofluoric, and hydrochloric acids or a partial leach by a hot nitric acid

digestion. Uranium is taken up in dilute nitric acid, and a salting agent (aluminum nitrate) is added that also complexes fluoride, phosphate, and sulfate ions that otherwise seriously hinder the extraction of uranium. The uranyl nitrate is extracted by ethyl acetate, which separates uranium from its quencher elements. A carbonate fluoride phosphor is obtained by fusing the extracted uranyl nitrate with sodium and potassium carbonate and sodium fluoride. The phosphor is introduced to a ultraviolet fluorometer and estimated for uranium content. About 20 to 40 samples can be analyzed per man day depending on digestion chosen.

REAGENTS

All chemicals should be of reagent grade and all water should be metal free.

Aluminum nitrate solution: Dissolve 1,000 g aluminum nitrate, 9-hydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in 500 mL of H_2O by heating solution.

Ethyl acetate.

Hydrochloric acid, concentrated.

Hydrochloric acid, 6 N: Dilute 500 mL concentrated hydrochloric acid to 1 L with water.

Hydrofluoric acid, 48 percent.

Nitric acid, concentrated.

Nitric acid, 15 percent(v/v): Dilute 150 mL concentrated nitric acid to 1 L with water.

Sodium carbonate-potassium carbonate-sodium fluoride flux: Oven dry anhydrous sodium carbonate, potassium carbonate, and sodium fluoride at 105°C overnight. Separately grind sodium carbonate and potassium carbonate to pass an 80-mesh sieve and prepare a 5:5:1 mixture, by weight.

APPARATUS

Beakers, Teflon, 50-ml

Boiling chip

Centrifuge

Fisher burner, or automatic fusion rotary burner

Heating block; drilled to accommodate 25×150 -mm culture tubes

Horizontal shaking machine

Hot plate

Platinum crucibles; 10×35 -mm inside diameter

Quartz glass triangle

Teflon stirring rod

Test tubes, 25×150 -mm, screw-cap

Ultraviolet fluorimeter

STANDARDS

Stock uranium solution, 1,000 $\mu\text{g}/\text{mL}$: Dissolve exactly 0.211 g uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 100 mL of 4N nitric acid. Prepare 100, 10, and 1 $\mu\text{g}/\text{mL}$ standard uranium solutions by successive 10-fold dilutions of 1,000 $\mu\text{g}/\text{mL}$ stock uranium solution with 4N nitric acid.

Standard uranium phosphor: Pipette 0.2 mL of the 1 $\mu\text{g}/\text{mL}$ standard uranium solution into a 25×150 -mm culture tube containing 6 mL of 15 percent nitric acid and 10 mL aluminum nitrate and proceed from step 8 of procedure A. The standard phosphor contains 0.1 μg uranium. A blank phosphor is prepared in the same manner, but with no uranium added.

PROCEDURE

- A. Digestion with hydrochloric, hydrofluoric, and nitric acids:
 1. Weigh 0.5 g sample into a Teflon beaker and add 5 mL concentrated nitric acid and 20 mL hydrofluoric acid.
 2. Place on a hot plate at moderate heat and evaporate to dryness. Alternately heat overnight on warm-to-touch hot plate.
 3. Add 3 mL concentrated hydrochloric acid and evaporate to dryness.
 4. Add 3 mL concentrated nitric acid and evaporate to dryness. Rinse the sides with water and evaporate to dryness if needed.
 5. Add 10 mL aluminum nitrate solution to a 25×150 -mm screw-cap test tube.
 6. Add 3 mL of 15 percent (v/v) nitric acid to the Teflon beaker and warm slightly. Break up residue with Teflon stirring rod if necessary. Transfer to the 25×150 -mm test tube containing the aluminum nitrate solution.
 7. Add 3 mL of the 15 percent (v/v) nitric acid to beaker, warm slightly, and transfer to the test tube.
 8. After mixture has cooled, add 10 mL of ethyl acetate, cap, shake for 2 minutes, and then centrifuge to obtain a clean layer separation.
 9. Pipette 5-mL aliquot of organic layer and transfer to a clean, dry platinum crucible.

10. Ignite the ethyl acetate to evaporate the organic solvent.
11. Place the crucible over a Fisher burner to red heat for 10-20 seconds.
12. After cooling, add 2.0 g sodium carbonate-potassium carbonate-sodium fluoride flux and place the platinum crucible on a quartz-covered triangle that is mounted over a Fisher burner. The height should be adjusted so that most of the flux melts within the first 45-60 seconds. Heat over burner for a total of 3 minutes. If an automatic fusion rotary burner is available, consult the operation manual for set-up conditions that best approximate these conditions.
13. Cool the crucible and measure the fluorescence with an ultraviolet fluorimeter.
14. Clean the platinum crucibles in hot 6 N hydrochloric acid.

B. Hot nitric acid digestion:

1. Weigh 0.5 g sample into a 25×150-mm screw-cap culture tube.
2. Add three boiling chips and 5 mL concentrated nitric acid.
3. Nestle each tube into a sand-filled heating block and boil moderately to dryness.
4. Add 6 mL of 15 percent (v/v) nitric acid and boil for 5 minutes in heating block. Remove tube and add 10 mL of the aluminum nitrate solution.
5. Allow tubes to cool and proceed to step 8 of procedure A.

STANDARDIZATION OF INSTRUMENT

The estimation of uranium content is made with an ultraviolet fluorimeter using the manufacturer's operating procedure. The instrument is standardized by setting the 0.1 µg standard phosphor to read 50 divisions. Readings are taken for the blank phosphor and the sample. Uranium concentration in the sample is calculated using the following formula:

$$\text{Sample uranium concentration ppm} = \frac{0.4 \times (\text{sample reading} - \text{blank reading})}{50 - \text{blank reading}}$$

DISCUSSION

The digestion with hydrochloric, hydrofluoric, and nitric acids is effective for decomposing and releasing most silicate-bound uranium. Refractory minerals usually require fusion with fluxes, such as mixtures of sodium carbonate and sodium borate.

The hot nitric acid digestion is a partial extraction because silicates are only sparingly attacked on surface exposures; however, the secondary dispersions are readily detected.

Care must be taken when heating Teflon beakers. Teflon loses strength at 320°C and complete depolymerization occurs at 400°-450°C.

The aluminum nitrate solution, a salting out agent, also prevents the interference from anions. Uranium is separated from quenchers, elements that reduce the fluorescence, by extraction into ethyl acetate.

High blank readings can originate from several of the following sources: contamination in the flux reagents or in the aluminum nitrate solution, or improperly cleaned platinum dishes.

REFERENCE SAMPLES

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedures.

PROCEDURE A. Hydrochloric, hydrofluoric, and nitric acids digestion			
GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	23-29	26	8.16
II	1.9-2.7	2.2	12.9
III	1.6-2.4	2.1	19.6
IV	3.0-5.6	4.4	23.7
V	1.4-2.0	1.6	15.1
VI	0.89-1.4	1.1	20.5

PROCEDURE B. Hot nitric acid digestion			
GXR sample	Range (ppm)	Mean (ppm)	Percent relative standard deviation
I	23-26	24.2	6.9
II	1.2-1.7	1.5	14.2
III	1.7-2.4	2.0	13.8
IV	3.7-5.1	4.3	12.5
V	1.6-1.9	1.6	10.1
VI	0.72-0.84	0.75	8.74

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