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April, 1992

Linden Grove Area Soil Geochemistry Analysis

The Linden Grove area soil survey is a westward expansion of the 1971 and 1991 USGS soil geochemistry study areas near and around Lake Vermilion in western St. Louis and eastern Itasca counties. The primary objective is to sample B horizon soil samples and outcrop samples in the proposed area over or adjacent to greenstone units for geochemical analysis. 792 samples were collected in portions of 13 7.5 minute USGS quadrangles (see tables 1 & 2) covering approximately 450 square miles. Henry Alminas (USGS) supervised the overall project with fieldwork being done by Dale Cartwright (DNR) and Pat Geiselman (DNR) and analysis by J.B. McHugh (USGS).

FIELD METHODS

The first 600 samples were collected in August and September of 1991 with some fill-in sampling in June of 1992. The Geologic map of Minnesota, Hibbing sheet, 1970 and the Bedrock Geologic Map of the Cook-Side Lake Area, St. Louis and Itasca Counties, Minnesota, 1991 were used to locate greenstone units. Preliminary sample sites were identified on 7.5 minute quads. If any of these sites could not be reached, adjustments were made in the field. Sample sites were located along roads and trails and spaced approximately 1/2 mile apart.

Sample collection was done with one truck and a two man crew. Sites were located in the field using an odometer and topographic maps. Samples were taken off the road, usually at the tree line of the ditch, in an undisturbed place. Land ownership was determined from plat maps, and samples were taken on private land when permission was obtained. A B-horizon soil sample was taken at each sample site. The site was cleared of roots and topsoil with a grub axe. An area about 2 feet square was disturbed. The B-horizon was then sampled with an impact post hole digger. In rocky areas, a crow bar was used to pry apart boulders. Two 5"x10" sample bags were filled at each site. One sample went to the USGS, Denver for analysis and the other was archived at the Drill Core Library in Hibbing. Notes on location, color, texture, drainage, and moisture were taken at each site.

SAMPLE PREPARATION

The soil samples were air-dried in the original cloth sample bag. Extremely clay-rich samples were disaggregated in a jaw crusher, using a wide jaw setting. All of the soils were then sieved through an 80-mesh (177 µm opening) sieve, and a 84 g (3 oz) container of the fine fraction was saved for analysis.

Outcrop samples were crushed in a jaw crusher and ground in a vertical grinder to approximately 105 µm.

ANALYTICAL METHODS

See attached excerpts from USGS Open-File Report 90-668 for analytical methods and quality control procedures of 40-element ICP analysis, partial extraction analysis and gold determinations.

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Quality assurance manual for the Branch of Geochemistry, U.S. Geological Survey

by

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Open-File Report 90-668

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1990

[redacted]

Elemental analysis of geological material by inductively coupled plasma-atomic emission spectrometry

By Paul Briggs

Code: E010 Accepted: Provisional

Principle

Forty major and trace elements are determined in geologic materials by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Lichte and others, 1987; Crock and others, 1983). The sample is decomposed using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acid at low temperature. The digestion is taken to dryness, the residue treated with aqua regia, and the solution brought to 10 g with dilute nitric acid. The solution is nebulized into the ICP-AES plasma discharge for determination of the elements.

Aqueous rock standards and multi-element standard solutions are used to calculate the calibration curves for each determined element. Two standard samples, two reagent blanks, and two duplicate unknowns are processed with each lot of samples for quality control purposes.

Interferences

ICP-AES interferences may result from spectral line overlap, background shifts, and matrix effects. Spectral line interferences are resolved by applying mathematical correction factors determined by using single-element standards (Thompson and Walsh, 1983; Thermo, Jarrell, and Ash, 1979). Background shift corrections are made by measuring and subtracting emission in the vicinity of the analytical line. Matrix effects can generally be negated by proper matching of standard and sample matrices.

Scope

The ICP-AES analysis of major, minor, and trace elements has found wide application in geochemical studies. The method is routinely applied to the elemental analysis of rock, soil, and sediment samples for studies in petrogenesis, mineral deposits formation and exploration, and for investigations in environmental geochemistry. The lower limits of analyte concentration for which this method is useful are shown in table 18. Two hundred samples may be analyzed in a day; assuming the digestion is completed.

Apparatus

ICP-AES, 63-channel Jarrell-Ash ICP-AES polychromator, Model 1160 Plasma Atomcomp.
30-mL Teflon vessel (Savillex)
Hotplate with 50-position aluminum heating block
Acid dispensers (Labindustries)
Repeating pipet (Eppendorf)
60-mL square bottomed bottles with caps (Nalgene)

Reagents

Hydrochloric acid, concentrated reagent grade, 37% HCl
Nitric acid, concentrated reagent grade, 70% HNO_3
Hydrofluoric acid, concentrated reagent grade, 48% HF
Perchloric acid, concentrated double distilled, 70% $HClO_4$,
G. Frederick Smith Co.
Aqua regia: 3 parts HCl per 1 part HNO_3
Demineralized (DM) water
Lutetium internal standard: 500 µg/mL, Lu as Lu_2O_3 in 5% (v/v) HCl

Safety precautions

All laboratory personnel must wear safety glasses, rubber gloves, and lab coats when working in the laboratory. All sample digestions must be performed in the perchloric acid hood; the latter is cleaned after use. See the MSDS for precautions, effects of overexposure, first-aid treatment, etc. for reagents used in this procedure. Adequately vent the RF generator and plasma chimney to exhaust the heat buildup. Use extreme caution handling the ICP-AES due to the potential lethal voltage associated with the instrument. Have the ICP serviced by trained personnel.

Procedure

A. Digestion of samples and rock standards

1. Select appropriate number of teflon vessels to contain samples, duplicate samples, standards, and blanks.
2. Weigh 0.200 g sample into Teflon vessel.
3. Add 100 µL of 500 µg/mL stock lutetium internal standard to each vessel with repeating Eppendorf pipet.
4. Rinse sample from side walls of Teflon vessel with 2 to 3 mL amount of DM water.
5. Slowly add 3 mL conc HCl.
6. Add 2 mL conc HNO_3, allow any reaction to subside.
7. Add 1 mL conc $HClO_4$ and 2 mL conc HF. Place sample on aluminum heat block at a controlled temperature of 110°C.
8. Evaporate sample to dryness on hot plate, usually overnight.
9. Remove from hotplate, add 1 mL conc $HClO_4$ and add water to the Teflon vessel until halffull.
10. Return to hot plate, evaporate to dryness. This step takes 4 to 8 hours. The temperature of hot plate should be increased to 150°C.
11. Remove vessel with dried sample from hot plate and cool.
12. Add 1 mL aqua regia to each sample with repeating Eppendorf pipet.
13. Transfer contents of each Teflon vessel to a 60-mL square-bottomed bottle, having first placed each bottle on top loading balance and tared to zero. Rinse the vessel with 1% HNO_3, pour into bottle and bring to final 10.0 g weight. Cap and label bottle.
14. Place capped bottles in drying oven set at 95°C for 1 hour.
15. Analyze sample solution by ICP-AES.

B. ICP-AES treatment of calibrating rock standards and multi-element solutions

Calibration curves are performed at the start of each day's run (see table 15 for operating conditions). The calibrating solutions include a reagent blank, U.S. Geological Survey reference rock BHVO-1, Canadian Certified Reference Materials Project rock sample SY-3, and four multi-element solutions to calibrate the elements not covered by the two rock standards. Determine the 40-element spectral array by direct intensity measurements at the wavelengths (see table 16). There is a direct correlation between the intensity of the emmitted light and the concentration. The actual calibration process involves nebulizing the standard solution, equilibrating the spray chamber with that solution for 20 seconds, start the calibration process by integrating that solution signal for 32 seconds, nebulize a rinse solution and repeat this process until all calibrating solutions are run. The dedicated computer that operates the instrument performs the iterations of taking the electronic signals and transforming that information to concentration readings to set the calibration curves.

C. ICP-AES treatment of interelement interferences.

The ICP-AES system makes 219 interelement corrections. The correction factors are based on a granitic type rock. The following is a list of the elements which produce the largest number of interferences: Al, Ce, Cu, Fe, Mn, Ti, U, and V. Interference factors for these elements, except Ce and Cu, are updated with each day's run. By applying a mathematical interelement correction, spectral interferences can be corrected. For instance, if 1,000 ppm of element A gives an interference signal on channel B equivalent to 10 ppm of element B, then a simple correction can be made when analysing for element B in the presence of element A (see Thompson and Walsh, 1983). These interelement interference factors are applied when calculating the element concentration (see **Calculation.**)

D. ICP-AES treatment of sample analysis

Once the instrument is calibrated, the interferring elements are updated, sample solutions are run. The actual analysis process is the same as the calibration, i.e., nebulization of sample solution, equilibration, integration, and rinse for each sample, blank, and rock standard.

E. Treatment of results

After sample analysis, the results are reviewed for precision and accuracy. The following is the sequence that is followed:

1. Check the low-voltage channel for bad sample burns, if one is found, that sample needs reanalysis.
2. Check the Lu channel for intensity counts (all readings should be within ±2000 counts), if not, those samples are redigested and reanalyzed.
3. Check duplicate sample analyses for precision, if elements are not within ±5% of each other, redigest and reanalyze samples.
4. Refere to the reagent blank analysis and determine which elements need to be subtracted from the sample analysis.

5. Determine which elements need to be normalized by comparing in-house reference values from your analysis to recommended in-house reference values.
6. Determine if further interelement corrections need to be made.

Once these determinations are made, use the ICP-AES computer and make the corrections. New sample analysis is ready to transfer to sample control for final reporting.

Table 15. Operating conditions for determination of forty elements by ICP-AES

Power	1250 W
Argon flow rate	18 L/min coolant 0.50 L/min, sample
Sample pump rate to nebulizer	0.70 mL/min
Observation height	14.5 mm above load coil
Reciprocal linear dispersion	0.54 mm/mm
Nebulizer	Modified Babington
Optics	1:3 magnification at entrance slit
Slits	25 μm x 33 mm, entrance 50 μm x 33 mm, exit

[illegible] Extraction

Organometallic halide extraction applied to the analysis of geologic materials for 10 elements by inductively coupled plasma-atomic emission spectrometry

By Jerry Motooka

Code: E020 Accepted: Provisional

Principle

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) has been applied to practically all types of materials. A widely used extraction technique (Aliquat/MIBK) (Viets, 1978) has been modified and adapted for use with ICP-AES for the analysis of geologic materials. A hydrochloric acid--hydrogen peroxide digestion (O'Leary and Viets, 1986) solubilizes metals not tightly bound in the silicate lattice of rocks, soils, and stream sediments. The metals are extracted by a 10% aliquat 336-diisobutylketone (Motooka, 1988) solution as organic halides. The separated organic phase is pneumatically aspirated into a multichannel ICP instrument where the concentrations of the extracted metals (Ag, As, Au, B, Cd, Cu, Mo, Pb, Sb, Zn) are determined simultaneously.

Interferences

Organic solvent extraction provides preconcentration of the analyte species and when combined with ICP-AES virtually eliminates the need for complex interference corrections. There are, however, some spectral interferences that must be considered, particularly where very high concentrations of iron and extracted metals (Cu, Mo, and Pb) are encountered. Correction coefficients are determined and computer calculations made to compensate for these interferences.

Scope

ICP-AES offers the capability of generating high quality analytical data in a relatively short period of time, approximately 100 samples can be analyzed in an 8-hour day. The technique is especially useful in geochemistry and in the environmental sciences where the need to determine trace metals at or near their crustal abundance level is of great importance. This method is applicable to practically all types of geologic materials, including ashed plants. The lower limits of determination are well below 1 ppm (see table 20) and the upper limits extend beyond four orders of magnitude.

Apparatus

Applied Research Laboratories Model 3580 ICP spectrometer.
Standard equipment for acid digestions done in water bath. See procedure for test tubes, etc.

Reagents

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

Aliquat 336-DIBK (diisobutylketone) 10% (v/v): Pour 200 mL Aliquat 336 (tricaprylmethylammonium chloride, obtainable from Henkel Chemicals, Minneapolis, Minn.) into a clean 1-L stoppered, graduated cylinder, dilute to 1 L with DIBK, shake to dissolve the Aliquat 336, and pour into brown glass bottle. This solution is stable for at least 1 month.

Ascorbic acid-potassium iodine solution, 30% - 15% (w/v): Weigh 300 g ascorbic acid (U.S.P. Food grade or metal-free equivalent) and 150 g potassium iodide into a brown glass bottle, add 1 L water, stir, and warm over low heat until dissolved. Prepare fresh weekly. Note: Some potassium iodide has been found to contain cadmium and silver contaminants. However, if samples, standards, and blanks are prepared using the same bottle of reagents, small amounts of contaminants will not affect the accuracy of the results.

Hydrochloric acid, HCl

Hydrogen peroxide, H_2O_2, 30%

Safety precautions

All work with open or uncapped reagents must be done in a chemical hood. Protective clothing, including laboratory coats or aprons, gloves, and eyeware must be worn. A good ventilating system should be employed over samples when analysis is performed even though MSDS indicates health hazard for DIBK is only slight. See the MSDS for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

1. Weigh 1.0 g of sample into a 25x150-mm disposable test tube (see below).
2. Add 5.0 mL of concentrated hydrochloric acid followed by 1.0 mL of 30% hydrogen peroxide dispensed in ½-mL portions, 15 minutes apart. Mix sample well after each addition of the hydrogen peroxide.
3. Allow samples to stand for 1 hour, mixing once after 30 minutes, and then place samples in boiling water bath for 20 minutes.
4. After sample is cool, add 4.0 mL of the ascorbic acid-potassium iodide solution, mix, and let stand for 20 minutes.
5. Accurately add 3.0 mL of 10% Aliquat 336 DIBK solution to each tube. Cap and shake for 5 minutes.
6. Centrifuge the samples to separate the organic layer from the acid layer.
7. Transfer the organic layer to a 13x100-mm disposable test tube. This tube is specific for the Gilson carousel-type auto sampler.
8. Place tubes in carousel and analyze.

Standardization of equipment

The following table lists the standard operating conditions using an Applied Research Laboratories Model 3580 ICP spectrometer.

Table 19. Operating conditions for determination of the elements by ICP-AES

Nebulizer	Meinhard concentric glass, TR-30-C1
Torch configuration	Standard, three concentric-tube
Coil	Three turn, water cooled
Power	1400 W
Gas	Argon Coolant, 16 L/min Plasma, 1 L/min Carrier, 1.5 L/min
Observation height	16 mm above coil
Integration time	2 periods, 5 sec each
Sample introduction rate	1.0 to 1.5 mL/min

Table 20. Suggested wavelength and lower limit of determination for 10 elements by ICP-AES

Element	ICP Wavelength (nm)	Lower limits of determination (μg/g)
Ag	328.0	0.045
As	193.7	0.600
Au	242.8	0.150
Bi	223.0	0.600
Cd	226.5	0.050
Cu	324.7	0.050
Mo	202.0	0.090
Pb	220.3	0.600
Sb	217.5	0.600
Zn	213.8	0.050

Assignment of uncertainty

Table 21 is a tabulation of data obtained in the original experimental phase with lower limits higher than indicated in previous wavelength table.

Table 21. Tabulation of data for ten elements by ICP-AES and AA

Element	$\bar{X}$ ICP/DIBK	s	% RSD	$\bar{X}$ AA/MIBK	Element	$\bar{X}$ ICP/DIBK	s	% RSD	$\bar{X}$ AA/MIBK
GXR-1 (jasperoid)					GXR-2 (soil)				
Ag	31	0.50	1.6	32	Ag	17	0.19	1.1	18
As	440	5.3	1.2	468	As	15	0.47	3.1	16
Au	3.1	0.05	1.7	2.98	Au	N*(0.25)	--	---	0.022
Bi	1600	24	1.5	1640	Bi	N(1.0)	--	---	<1.0
Cd	2.6	0.05	2.1	2.89	Cd	3.6	0.05	1.3	3.85
Cu	1100	14	1.2	1250	Cu	74	0.74	1.0	71
Mo	19	0.23	1.2	20	Mo	0.95	0.02	2.5	1.1
Pb	720	10	1.4	780	Pb	650	8.5	1.3	712
Sb	96	1.3	1.4	105	Sb	38	0.46	1.2	39.6
Zn	770	20	2.6	714	Zn	500	5.5	1.1	518
GXR-5 (soil)					GXR-6 (soil)				
Ag	0.67	0.02	2.4	0.72	Ag	0.31	0.004	1.2	0.32
As	5.9	0.24	4.0	8.4	As	280	2.2	0.8	308
Au	N(0.25)	--	---	0.007	Au	N(0.25)	--	---	0.063
Bi	N(1.0)	--	---	<1.0	Bi	N(1.0)	--	---	<1.0
Cd	0.12	0.004	2.9	0.13	Cd	0.13	0.004	3.4	0.11
Cu	320	2.6	0.8	330	Cu	66	0.26	0.4	64
Mo	31	0.25	0.8	30	Mo	2.2	0.02	1.1	2.3
Pb	13	2.2	1.7	14	Pb	100	0.90	0.9	95
Sb	N(1.5)	--	---	<1.0	Sb	2.7	0.07	2.6	1.98
Zn	41	0.90	2.2	41.6	Zn	120	1.1	0.9	105

All results are in ppm, and ICP results are rounded to two significant figures.

*Not detected at values shown, ICP/DIBK results are a mean value of ten replicate digestions; AA/MIBK results are latest recommended values from O'Leary and Viets, 1986.

Bibliography

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[redacted]

Determination of gold, tellurium, and thallium, in rock, stream-sediment, and soil samples by flame, and gold by graphite furnace, atomic absorption spectrophotometry following dissolution by HF, aqua regia, and $HBr-Br_2$

By Richard M. O'Leary and T.T. Chao

Code: A050, A060, A070, A080 Accepted: Provisional

Principle

Gold, tellurium, and thallium in rock, stream-sediment, and soil samples are determined by the flame atomic absorption method (Hubert and Chao, 1985). The sample is decomposed with hydrofluoric acid, aqua regia, and hydrobromic acid-bromine solution. Gold, thallium, and tellurium are separated and concentrated from the sample digest by a two-step MIBK (methyl isobutyl ketone) extraction at two concentrations of hydrobromic acid. Gold and thallium are first extracted from 0.1M hydrobromic acid medium, then tellurium is extracted from 3M hydrobromic acid in the presence of ascorbic acid to eliminate iron interference. The elements are then determined by flame atomic absorption spectrophotometry (AAS). Gold can also be determined by graphite furnace AAS.

Interference

This method is not applicable for the determination of gold in a carbonaceous matrix (e.g. non-oxidized Carlin-type material) or soils and stream sediments rich in organics (>5%), due to a low recovery of gold in the presence of carbon. When determining gold in these types of materials, use the alternate atomic absorption gold method (10 g sample with dissolution by $HBr-Br_2$) in which the samples are roasted at 700°C to oxidize and remove the carbon. Iron is the major interfering element in the determination of the three analytes in geologic materials. Prior removal of iron by solvent extraction, reduction of iron by ascorbic acid, stripping the co-extracted iron, and selective extraction of the analyte may be used to eliminate the iron interference. Because iron is practically unextracted into MIBK at low concentrations of hydrobromic acid (Denaro, 1955), gold and thallium can be separated from iron by MIBK extraction from a sample solution adjusted to 0.1M hydrobromic acid concentration. It is for this reason that the procedure uses the two-step extraction to isolate gold and thallium first for determination. Tellurium can be extracted into MIBK from 3M hydrobromic acid, but an appreciable amount of iron is also extracted (Denaro, 1955), and interferes in tellurium determination (Chao and others, 1978; Zhou and others, 1984). Addition of ascorbic acid to reduce (Zhou and others, 1985) iron removes the interference completely. Therefore, the extraction of tellurium after addition of ascorbic acid constitutes the second phase of the two-step solvent-extraction procedure.

Scope

Gold, tellurium, and thallium can be determined in rocks, stream sediments, and soils with a lower limit of determination of .05 ppm for each element by flame atomic absorption spectrophotometry. The upper limit of determination can be extended beyond 20 ppm by dilution of an aliquot from the MIBK layer. The lower limit of determination for gold by graphite furnace is 0.002 ppm, concentrations greater than 0.05 ppm are determined by flame. Approximately 25 samples can be analyzed per person-day.

Apparatus

Atomic-absorption spectrophotometer equipped with a flame and graphite furnace atomizers
Beakers, Teflon, 100-mL
Centrifuge
Horizontal shaking machine
Hot plate, oscillating
Scoop, calibrated to deliver 2-g ascorbic acid
Vacuum system
Test tubes, 25x150-mm, disposable

Reagents

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

Ascorbic acid, $C_6H_8O_6$
Hydrobromic acid, HBr, concentrated (48%)
Hydrobromic acid-10% bromine solution: Dilute 10 mL of bromine (Br_2) to 100 mL with hydrobromic acid
Hydrochloric acid, HCl concentrated (37%)
Hydrofluoric acid, HF concentrated (49%)
Iron solution, 4% in 3M hydrobromic acid: Dissolve 4 g of pure iron (Fe) powder in concentrated hydrobromic acid, add 1 mL of bromine, and evaporate to dryness. Add 34 mL of concentrated hydrobromic acid, heat to dissolve the residue, and dilute to 100 mL with water.
MIBK (methyl isobutyl ketone), 4-methyl-2-pentanone
Nitric acid, HNO_3 concentrated (70%)
Gold (Au), tellurium (Te), and thallium (Tl) individual stock solutions, 1,000 µg/mL: Individually dissolve 1.000 g of pure gold, thallium, and 1.250 g of tellurium dioxide (TeO_2) in 20 mL of hydrobromic acid-10% bromine solution, heat gently to expel excess of bromine, and make up to volume in 1,000-mL volumetric flask with concentrated hydrobromic acid. The solution has a hydrobromic acid concentration of approximately 9M.
Combined Au and Tl standard solutions: Prepare five combined standards from the individual 1,000-ug/mL stock solutions and concentrated hydrobromic acid to contain the following volumes in six 250-mL volumetric flasks. Make up to volume with water.

Solution	Blank (mL)	S_1 (mL)	S_2 (mL)	S_3 (mL)	S_4 (mL)	S_5 (mL)
Au	0.0	1.0	2.0	5.0	10.0	20.0
Tl	0.0	1.0	2.0	5.0	10.0	20.0
HBr	55	53	51	45	35	15

Te standard solutions: Prepare five combined standards from the individual 1,000-ug/mL stock solution, concentrated hydrobromic acid, and 4% Fe solution to contain the following volumes in six 250-mL volumetric flasks. Make up to volume with water.

Solution	Blank (mL)	S_1 (mL)	S_2 (mL)	S_3 (mL)	S_4 (mL)	S_5 (mL)
Te	0.0	1.0	2.0	5.0	10.0	20.0
HBr	75	74	73	70	65	55
4% Fe	25	25	25	25	25	25

Gold and thallium working standards in MIBK for flame AAS: Add 1.0 mL each of Blank, S_1, S_2, S_3, S_4, S_5 to six 25x150-mm test tubes. Add 19 mL of water and 4 mL of MIBK, stopper, shake for 5 minutes, and centrifuge. The concentration of Au and Tl in the MIBK working standard corresponds to 0.0, 1.0, 2.0, 5.0, 10.0, and 20.0 ppm of the metal based on a 4-g sample.

Tellurium and working standards in MIBK: Add 1.0 mL each of Blank, S_1, S_2, S_3, S_4, and S_5 to six 25x150-mm test tubes. Add 19 mL of 3M hydrobromic acid, 2 g of ascorbic acid, and mix to reduce iron and make the solution light yellow. Add 4 mL of MIBK, stopper, shake for 5 minutes, and centrifuge. The concentration of Te in the MIBK working standard corresponds to 0.0, 1.0, 2.0, 5.0, 10.0, and 20.0 ppm of the metal (based on a 4-g sample).

Dilute gold solution for graphite furnace AAS, 1 µg/mL: Prepare by serial dilution of the 1000 µg/mL stock solution.

Standard gold solution in MIBK for graphite furnace AAS, 0.025 and 0.050 µg/mL: Add 0.25 mL and 0.50 mL of 1 µg/mL dilute gold solution to two 25x150-mm disposable test tubes containing 10 mL of MIBK and 40 mL of equilibrated .1N HBr. Cap and shake vigorously for 2 minutes.

Safety precautions

All work with open or uncapped reagents must be done in a chemical hood. Protective clothing, safety glasses, and gloves must be worn. See the MSDS for further information concerning first-aid treatment and disposal procedures for chemical products used in this section.

Procedure

1. Weigh 4.0-g sample into a 100-mL Teflon beaker.
2. Wet sample with 2 mL of water.
3. Add 5 mL of concentrated nitric acid, 15 mL of concentrated hydrochloric acid, and 20 mL of concentrated hydrofluoric acid.
4. Place on an oscillating hot plate and evaporate to dryness at 100 to 110°C.
5. Add 5 mL of concentrated hydrobromic acid and evaporate to dryness at the same temperature as above. (Complete dryness is very necessary to insure good separation of the metals in the two-step solvent extraction.)
6. Add 0.22 mL of the hydrobromic acid-10% bromine solution and 5 mL of water.

7. Warm to dissolve residue, wash sample solution into a 25x150-mm disposable tube with water, and make up to 20 mL volume.
8. Add 4 mL of MIBK, cap, and shake for 5 minutes.
9. Centrifuge to separate the MIBK phase.
10. Determine the Au and Tl content of the MIBK layer. When graphite furnace gold is requested, care must be taken to avoid contamination of the graphite furnace by samples containing high concentrations (>0.1 ppm) of gold. All samples must be first analyzed by flame. Only samples with concentrations less than 0.05 ppm gold should be analyzed by graphite furnace. Both flame values ≥0.05 ppm and graphite furnace values should be reported. Recalibrate the flame AAS or reslope the graphite furnace AAS after every 10 samples.
    [Continue procedure for the determination of Te]
11. Remove and discard the remaining MIBK layer using the vacuum system.
12. Add 10 mL of concentrated hydrobromic acid and mix.
13. Add 2 g or more of ascorbic acid and mix to reduce the iron and decolorize the solution from brown to light yellow.
14. Extract with 4 mL of MIBK as above and use organic solution for the determination of Te.

Standardization of Instrument

Table 8 lists the operating conditions for a Perkin-Elmer 5000 atomic absorption spectrophotometer for determining Au, Tl, and Te by this method.

Table 8. Operating conditions for determination of gold, thallium, and tellurium by flame AAS

	Au	Tl	Te
Grating..................	UV	UV	UV
Source lamp...............	Hollow cathrode lamp	EDL	EDL
Integration time..........	1 second	1 second	1 second
Flame conditions..........	oxidizing (lean blue)		
Wavelength, nm............	242.8	276.8	214.3
Slit, nm..................	0.7	0.7	0.2
Lamp current, mA..........	Use current as recommended on lamp		
Burner....................	Boling (3-slot)	Boling (3-slot)	Boling (3-slot)
Background correction.....	No	No	Yes
S_1 = X absorbance units...	0.090	0.045	0.063
S_2 = X absorbance units...	0.170	0.090	0.126
Lower determination limit, µg/g (ppm)..............	0.05	0.05	0.05

Calibration for gold, tellurium, and thallium, by flame AAS

Standard	µg	Instrument setting (ppm)
S_1	4	1.0
S_2	8	2.0
S_3	20	5.0
S_4	40	10
S_5	80	20

The following operating conditions, table 9, are for a Perkin-Elmer 5000 equipped with a graphite furnace with Zeeman background correction.

Table 9. Operating conditions for determination of gold by graphite furnace AAS; dissolution by HF, aqua regia, and HBr-Br_2

Grating	ultraviolet
Wavelength	242.8 nm
Slit	0.7 nm
Lamp current	10 mA
Source	gold (hollow cathode lamp)
Purge gas	nitrogen
Dry cycle	
Ramp	10 sec
Hold	20 sec
Temp	120°C
Char cycle	
Ramp	1 sec
Hold	15 sec
Temp	500°C
Atomization Cycle	
Ramp	0 sec
Hold	3 sec
Temp	2000°C
REC	-1 sec
Read	-1 sec
Baseline	-6 sec
INT FLOW	0
0.025 µg/mL	0.300 ± 10% absorbance units calibration setting = .025
Clean-up cycle	
Ramp	1 sec
Hold	3 sec
Temp	2500°C

Calibration for gold by graphite furnace AAS

Standard	µg	Instrument setting (ppm)
.025	.25	0.025
.050	.50	0.500

Calculation

When using the recommended sample weight, calibration standards, and instrument settings, the resulting sample reading is the actual element concentration in the sample reported as µg/g (ppm).

Assignment of uncertainty

Tables 10 and 11 are tabulations of statistical data obtained by analyzing the GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975) in six replicas, by the described procedures.

Table 10. Gold, thallium, and tellurium content of GXR samples by flame AAS [N( ), not detected at limit of determination]

Reference samples (description)	Range (ppm)	$\bar{X}$ (ppm)	s	% RSD	Literature value[1] (ppm)
		Gold			
GXR1 (jasperoid)	3.5-.4.0	3.7	0.22	6	3.3
GXR2 (soil)	N(.05)	--	--	--	0.036
GXR3 (Fe-Mn mineral deposit)	N(.05)	--	--	--	--
GXR4 (copper mill head)	.47-.57	.51	0.04	8	0.470
GXR5 (soil)	N(.05)	--	--	--	--
GXR6 (soil)	.10-.13	.11	0.01	9	0.095
		Thallium			
GXR1	.38-.43	.41	0.02	5	--
GXR2	.77-1.1	.95	0.12	13	1.03
GXR3	2.5-3.0	2.8	0.20	7	3.6
GXR4	3.0-3.2	3.1	0.07	2	3.2
GXR5	.24-.27	.25	0.01	4	0.33
GXR6	1.8-2.1	1.9	0.12	6	2.2
		Tellurium			
GXR1	11-13	12.0	0.71	6	13
GXR2	.18-.28	.22	0.04	18	0.690
GXR3	N(.05)	--	--	--	0.009
GXR4	.59-.70	.64	0.05	8	0.970
GXR5	N(.05)	--	--	--	--
GXR6	N(.05)	--	--	--	0.018

[1] Govindaraju, 1989

Table 11. Gold content of GXR samples by graphite furnace AAS; dissolution by HF, aqua regia, and $HBr-Br_2$

Reference samples (description)		Range (ppm)	$\bar{X}$ (ppm)	s	% RSD	Literature value[1] (ppm)
GXR2	(soil)	.020-.021	.021	0.0006	3	0.036
GXR3	(Fe-Mn mineral deposit)	.001-.002	.002	0.0007	35	--
GXR5	(soil)	.004-.005	.005	.0005	10	--
GXR6	(soil)	.065-.077	.071	0.006	8	0.095

[1] Govindaraju, 1989.

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