ANALYSIS OF ROCKS AND SEDIMENTS FOR ARSENIC, ANTIMONY, AND SELENIUM, BY WET DIGESTION AND HYDRIDE GENERATION ATOMIC ABSORPTION

By Kent A. Elrick and Arthur J. Horowitz

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Donald P. Hodel, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information
write to:

District Chief
U.S. Geological Survey, WRD
6481 Peachtree Industrial Boulevard
Suite B
Doraville, Georgia 30360

Copies of this report can be
purchased from:

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ABSTRACT

A relatively rapid, accurate, and precise method is presented for the determination of arsenic, antimony, and selenium in rocks and sediments. The method requires only 250 mg of sample and employs a wet digestion in Teflon[1/] breakers using a combination of hydrofluoric, perchloric, and nitric acids. Quantitation is carried out by atomic absorption spectroscopy coupled with hydride generation. Comparison of data generated by this procedure with data for U.S. Geological Survey Rock Standards and National Bureau of Standards Sediments, as well as through interlaboratory comparisons on natural sediment samples, indicates that precise and accurate results can be obtained.

[1/] The use of brand names in this report is for identification purposes only, and does not constitute an endorsment by the U.S. Geological Survey.

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INTRODUCTION

The chemical analysis of rocks and sediments is performed for a wide variety of environmental and petrological purposes. For example, sediments may contain significantly higher concentrations of metals than are found in the overlying water, and as such, they may be analyzed for chemical contributions to the environment or to locate ore bodies. The importance of this type of data is well established and this type of analysis is well established and has been been used for decades. Various wet digestion procedures have been used for the determination of hydride forming elements and have been amply described in the literature (Thompson and Thomerson, 1974; Aslin, 1976; Chapman and Dale, 1979; Johnson and Maxwell, 1981; Crock and Lichte, 1982; and Narasaki and Ikeda, 1984). The application of atomic absorption coupled with hydride generation as a means of analysis has also been amply described in the above references. The digestion technique described herein represents a modification of the procedures outlined by Horowitz and Elrick (1985) and Crock and Lichte (1982). The upper and lower concentration limits within which the method may be used are listed below. Samples containing greater than the upper limit may be analyzed after appropriate dilution.

Upper and lower concentration limits of the method

Element	Lower limit		Upper limit	
	Sample (mg/kg)	Solution (mg/L)	Sample (mg/kg)	Solution (mg/L)
Antimony	0.1	0.001	5.0	0.050
Arsenic	.1	.001	5.0	.050
Selenium	.1	.001	5.0	.050

SUMMARY OF METHOD

Rock and(or) sediment samples are dried, ground, and homogenized. An aliquot is digested with a combination of nitric, perchloric, and hydroflulorit acids in Teflon breakers and heated on a hot plate at 200°C. The resulting salts are dissolved in hydrochloric acid and deionized water. The solutions are analyzed by atomic absorption spectroscopy coupled with hydride generation after the addition, for arsenic and antimony, of a reductant and stabilizer. Interferences are removed and(or) compensated for through the use of hydride generation, mixed salt standards, and background correction. Further information about the principles of the method can be found in Chapman and Dale (1979) and Thompson and Thomerson (1974).

INTERFERENCES

Several interelement interferences, primarily negative, exist and have been documented elsewhere (Crock and Lichte, 1982; Narasaki and others, 1984). Interferences are eliminated or compensated for through the digestion procedure, dilution, the addition of a hydroxylaine hydrochloride/oxalic acid solution, the use of mixed salt standards, and a deuterium source background corrector.

APPARATUS

A Varian Model AA-975 atomic absorption spectrophotometer with microprocessor control and digital display and a Varian Model VGA-76 hydride generator with a flame-heated quartz cell, used in conjunction with a Varian Model PSC-55 autosampler, were used in this study. Instrumental conditions are listed in table 1.

Table 1.--Instrumental settings used for this method

Parameters	Antimony	Arsenic	Selenium
Wavelength (nm)	217.6	193.7	196.0
Slit width (nm)	.2	.2	1.0
Lamp current (ma)	10	7	10
Flame type	air/acet	air/acet	air/acet
Oxident (L/min)	11.0	11.0	11.0
Fuel (L/min)	1.5	1.5	1.5
Integration time (s)	3.0	3.0	3.0
Background corrector	off	off	on
Autosampler settings			
Rinse rate	1	1	1
Rinse time(s)	25	25	25
Delay time(s)	40	40	40
Multiples	3	3	3
Reslope rate	10	10	10
Hydride generator			
Acid line (mL/min)	1	1	1
Reductant line (mL/min)	1	1	1
Sample line (mL/min)	7.5-8	7.5-8	7.5-8

Teflon breakers, 100 mL capacity, thick wall, capable of withstanding temperatures up to 260°C;

Perchloric-acid hood, with appropriate washdown facility and gas or electrical outlets.

Hot plate, gas or electric, capable of reaching at least 250°.

REAGENTS

Antimony standard solution, 1.00 mL = 1.00 mg Sb: Dissolve 1.0000 g Sb metal in 10 mL HNO_3 (sp gr 1.41) plus 5 mL HCl (sp gr 1.19). Dilute 1,000 mL with dilute (1+1) HCl[2].

Arsenic standard solution, 1.00 mL = 1.00 mg As: Dissolve 1.3203 g As_2O_3 in a minimum of oncentrated HCl (sp gr 1.19). Dilute to 1,000 mL with dilute (1+1) HCl[2].

Selenium standard solution, 1.00 mL = 1.00 mg Se: Dissolve 1.0000 g Se metal in 5 mL HNO_3 (sp gr 1.41). Dilute to 1,000 mL with dilute (1+1) HCl[2].

Hydrochloric acid, concentrated (sp gr 1.19)

Hydrochloric acid, dilute (1+1): Add 500 mL concentrated HCl to 500 mL demineralized water. Store in glass or plastic bottle.

Hydrochloric acid, concentrated (48-51 percent, sp gr 1.17).

Hydroxylamine hydrochloride solution (stabilizer): Dissolve 200 g hydroxylamine hydrochloride in 800 g of a saturated solution of oxalic acid.

[2] Commercially prepared atomic absorption standards are available for these elements and may be used.

Mixed element primary standard, 1.00 mL - 0.050 mg As, Sb, Se: Pipet 10 mL of each element standard solution into a 200 mL volumetric flask. Add 100 mL concentrated HCl (sp gr 1.19) and dilute to volume with demineralized water. Store in glass or plastic bottle.

Mixed salt-standard solution I (for matrix matching): Dissolve by appropriate means, the following compounds or elements: cadmium metal (0.200 g), chromium metal (0.800 g), cobalt metal (1.200 g), copper metal (0.800 g), lead metal (2.000 g), lithium carbonate (2.130 g), manganese metal (2.000 g), nickel metal (1.200 g), strontium carbonate (1.685 g), and zinc metal (0.320 g). Add 20 mL concentrated HCl (sp gr 1.19) and dilute to 1,000 mL with demineralized water. This solution will contain the following concentrations: cadmium (200 mg/L), chromium (800 mg/L), cobalt (1,200 mg/L), copper (800 mg/L), lead (2,000 mg/L), lithium (400 mg/L), manganese (2,000 mg/L, nickel (1,200 mg/L), strontium (1,000 mg/L), and zinc (320 mg/L). Store in a plastic or Teflon bottle.

Mixed salt solution II: Dissolve by appropriate means the following compounds or elements: aliminium metal (1.500 g), calcium carbonate (1.249 g), iron metal (1.000 g), magnesium metal (0.200 g), manganese metal (0.040 g), potassium chloride (0.688 g), sodium chloride (0.636 g), ammonium titanyl oxalate (1.227 g). Add 20 mL oncentrated HCl (sp gr 1.19) and dilute to 1,000 mL with demineralized water. This solution will contain the following concentrations: aluminium (1,500 mg/L,) calcium (500 mg/L), iron

(1,000 mg/L, magnesium (200 mg/L), manganese (40 mg/L), potassium (350 mg/L), sodium (250 mg/L), and titanium (200 mg/L). Store in plastic or Teflon bottle.

Nitric acid, concentrated (sp gr 1.41).

Oxalic acid solution, saturated: Dissolve approximately 150 g oxalic acid in demineralized water using mild heating. Cool until crystallization stops.

Perchloric acid, concentrated (70-72 percent, sp gr 1.67)

Potassium iodide, 10 percent w/v: Dissolve 100 g potassium iodide in demineralized water and dilute to one liter. Store in plastic bottle.

Sodium borohydride solution, (0.6 percent w/v): Dissolve 3.0 g sodium borohydride and 2.5 g sodium hydroxide in demineralized water and dilute to 500 mL.

Working standard solution I: Take respectively a 200 uL, 100 uL, and 8 uL aliquot of mixed element primary standard. Add to each, 1 mL mixed salt standard solution I, 20 mL mixed salt standard solution II, 100 mL concentrated HCl (sp gr 1.19), and dilute to 200 mL in volumetric glassware with demineralized water. Store in plastic or Teflon bottles and prepare fresh for each analysis concentrations are as follows:

	Standard 1 (μg/L)	Standard 2 (μg/L)	Standard 3 (μg/L)
Volume (μL)	200	100	8
Sb	50	25	2
Se	50	25	2

Working standard solution II: Take respectively a 200 uL, 100 uL, and 8 uL aliquot of mixed element primary standard. Add to each 100 mL concentrated HCl (sp gr 1.19), and dilute to 200 mL in volumetric glassware with demineralized water. Store in plastic or Teflon bottles and prepare fresh for each analysis. Concentrations are as follows:

	Standard 4 (μg/L)	Standard 5 (μg/L)	Standard 6 (μg/L)
Volume (μL)	200	100	8
As	50	25	2

PROCEDURE

Immediately before each use, clean all glassware by rinsing first with dilute HCl (1+1) and then with demineralized water. Dry the sediment by freeze-drying or air-drying at room temperature. If the sediment sample is greater than 100 g, split it down to less than 100 g by the use of a nonmetalic sample splitter (riffle sampler) or by coneing and quartering. Grind the sample with a mixer mill or an agate mortar and pestle until all material is finer than 100 mesh. Weigh and transfer 0.5000 g of finely ground sample to a 100 mL Teflon breaker. Weigh out appropriate reference standard materials as well, and use several empty breakers for blanks[3/].

[3/] This procedure can be used with sample weights between 0.2500 and 1.000 g, with appropriate adjustment to the final solution volumes and acid strengths. Larger sample weights may be used, but will almost certainly require a triple digestion with HF and $HClO_4$.

Place the hot plate in a perchloric acid hood, and adjust the hot plate to produce a surface temperature of 200°C. Add 6 mL of concentrated nitric acid (sp gr 1.41) to each beaker and place the beakers on the hot plate. Continue heating until the residue is nearly dry, approximately 30 minutes. If sample is still evolving brown fumes of NO_X at this point, repeat this step. THIS STEP IS DESIGNED TO OXIDIZE ORGANIC MATTER IN THE SAMPLE. IT IS IMPERATIVE THAT THIS STEP BE CARRIED OUT PRIOR TO THE ADDITION OF PERCHLORIC ACID. FAILURE TO DO SO COULD RESULT IN A VIOLENT EXPLOSION!

Remove the beakers from the hot plate and allow to cool for 5 minutes. Add 6 mL HF (sp gr 1.17) and 2 mL $HClO_4$ (sp gr 1.67), and return the beakers to the hot plate. Continue heating the beakers until the evolution of dense white perchloric fumes occurs and the solution has reached incipient dryness. Do not bake the residues. Remove the beakers from the hot plate, cool for 5 minutes, and repeat this step.

Remove the beakers from the hot plate, cool for 5 minutes, add 2 mL $HClO_4$ (sp gr 1.67), and return the beakers to the hot plate. Continue heating until the solution has reached incipient dryness. Do not bake the residues.

Remove the beakers from the hot plate, and lower the temperature of the hot plate to 100°C. Add 25 mL concentrated HCl (sp gr 1.19) to each beaker and swirl; return the beaker to the hot plate until the residues dissolve.

Cool the solutions, and pour each into a 50 mL volumetric flask. Rinse the beaker several times with demineralized water and dilute to the mark with demineralized water. Pour the solution into an acid rinsed plastic bottle for storage. This solution represents a dilution factor of 100X[4/].

[4/] If a sample contained a large amount of organic matter, it is not unusual to have black "flecks" in the final solution. These can be ignored if they are allowed to settle prior to pumping into the hydride generator.

Set up the atomic absorption spectrometer and hydride generator according to the specifications outlined in table 1, using demineralized water for the sample line, and allow the quartz cell to come to thermal equilibrium (about 5 min). Run the high standard and blank alternately until stable readings are obtained for each. Analyze the 100X solutions for selenium, using working standards 1, 2, and 3. Dilute the samples, if required.

Transfer 20 mL aliquots of each sample, working standards 1, 2, and 3 for Sb, and working standards 4, 5, and 6 for As, into test tubes. Add 2 mL of the potassium iodide solution and heat on a dry bath at 90°C for 1 hour. Cool and add 2 mL of the hydroxylamine hydrochloride/oxalic acid solution and mix thoroughly with a vortex mixer[5].

Set up the atomic absorption spectrometer and hydride generator according to the specifications outlined in table 1, using demineralized water for the sample line, and allow the quartz cell to come to thermal equilibrium (about 5 min.). run the high standard and blank alternately until stable readings are obtained for each. Analyze the reduced stabilized solutions for antimony using working standards 1, 2, and 3, and for arsenic using working standards 4, 5, and 6. Dilute the samples, if required.

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[5] The addition of potassium iodide serves to reduce the As and Sb to valence states most favorable for hydride generation. The addition of the hydroxalamine hydrochloride/oxalic acid solution (see Crock and Lichte, 1982) was found to give more constant results.

CALCULATIONS AND REPORTING LIMITS

Determine the concentrations of each constituent in the 100X solutions (As, Sb, and Se) from the digital display, printer, or chart recorder, and record the results (average of three readings once the system has stabilized). The actual concentration of each constituent in the sample, in mg/L, is obtained by multiplying the concentration in each solution by 100, if no other dilutions are made. To obtain a concentration in ppm, divide the concentration in each sample solution by 10, if no other dilutions are made.

The reporting limits for the three elements are to the nearest 1 μg/L in solution; that is, to the nearest 100 μg/kg (or 0.1 mg/kg in the sample).

PRECISION AND ACCURACY

The precision and accuracy of this method was detrmined by replicate analyses (actual separate digestions and subsequent quantitation) on two National Bureau of Standards Sediments and eight U.S. Geological Survey Rock Standards. The results are presented in table 2. As can be seen from the data, the method is capable of providing both precise and accurate analytical results.

Table 2.--Comparison of reported concentrations with those found this by method [Concentration in mg/kg].

Standard		Number of analyses	Arsenic	Antimony	Selenium
National Bureau of Standards					
Estuarine	report		11.6±1.3	0.4	0.6
Sediment	found	10	10.8±1.0	.4±.07	.5±.1
River	report		66	51	1.5
Sediment	found	10	74+5	31+2	1.3+.2
U.S. Geological Survey Rock Standards					
W-2	report		1.2	.9	.10
	found	10	.9±.2	.9±.1	.08±.02
G-2	report		.3±.1	.08±.03	--
	found	10	.4±.1	.09±.02	--
SDC	report		.2	.5±.1	.04
	found	10	.4±.1	.5±.08	.04±.01
STM	report		5.	1.7±.06	--
	found	10	4.9±.8	1.7±.2	--
BHVO	report		.6/.2	.2±.005	--
	found	10	.4±.1	.3±.07	--
RGM	report		.2	1.3±.09	--
	found	10	.5±.2	1.3±.01	--
SCO	report		11±3	2.5±.1	.08
	found	10	12.4±1.1	2.6±.2	.7±.1
MAG-1	report		10	.9±.05	1.1
	found	10	9.2±.9	1.0±.1	1.0±.1

DISCUSSION AND CONCLUSIONS

In order to further evaluate the precisison and accuracy of this method, five natural freshwater and marine sediment samples were dried, digested, and analyzed. The samples came from different geological settings and water bodies (Mississippi River, La.; Ned Wilson Lake, Colo.; Patuxent River, Md.; Yaharra River, Wis.; and Georges Bank, from the North Atlantic Outer Continental Shelf). These samples were dried and ground, then sent to another laboratory for dissolution and subsequent quantitation. Results of the two sets of analyses are presented in table 3. Quantitation by the outside laboratory for antimony and selenium came from a mixed acid digestion with subsequent quantitation by graphite furnace for Sb, and by hydride generation for Se. Arsenic was determined by graphite furnace following a sodium hydroxide fusion. Comparative data for standards and samples indicates that analytical precision and accuracy, as well as comparability, is good (tables 2 and 3). All of these results indicate that precise and accurate analyses can be obtained by utilizing this method.

Table 3.--Interlaboratory comparison of data for selected sediment samples [Concentration in mg/kg].

Sample		Arsenic	Antimony	Selenium
Mississippi River at Venice, La.	a[1]	12.8	1.2	0.4
	b[2]	11.5	1.0	.6
Georges Bank M13A	a[1]	9.8	.4	.5
	b[2]	7.7	.2	.7
Ned Wilson Lake, Colo.	a[1]	4.6	.8	.6
	b[2]	5.0	.6	.8
Patuxent River at St. Leonards Creek, Md.	a[1]	13.5	.7	.9
	b[2]	12.4	.3	1.0
Yaharra River, Wisc.	a[1]	2.2	.2	.1
	b[2]	2.2	.1	.1

a[1] - This method.
b[2] - USGS Branch of Analytical Services, Reston, Va.

Sb - digested with $HF/HNO_3/H_2SO_4$, diluted with demineralized water, Fe reduced with ascorbic acid/NaI solution, extracted with toluene, and quantitated by graphite furnice atomic absorption.

As - digested by NaOH fustion/H_2SO_4 dissolution, Fe reduced with absorbic acid/NaI solution, extracted with toluene, quantitated by graphite furnace atomic absorption.

Se - digested with HNO_3HClO_4/HF, quantitated by hydride generation.

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