MULTIELEMENT ANALYSIS OF ROCKS AND SEDIMENTS BY WET DIGESTION AND ATOMIC ABSORPTION SPECTROSCOPY

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ABSTRACT

A relatively rapid, accurate, and precise method for the determination of seventeen elements (Fe, Mn, Al, Ti, Mg, Na, K, Ca, Cu, Zn, Pb, Cr, Ni, Co, Cd, Li, and Sr) in rocks and sediments, from as little as 250 mg of sample is presented. The method employs a wet digestion in Teflon (R) beakers using a combination of HF, $HClO_4$, and HNO_3 acids. Quantitation is carried out by atomic absorption spectrophotometry using mixed salt standards and matrix modifiers. Comparison of data generated by this procedure, with data for U.S. Geological Survey Standard Rocks, and National Bureau of Standards' sediments, as well as through interlaboratory comparisons on natural sediment samples, indicate that precise and accurate results can be obtained.

INTRODUCTION

The chemical analysis of rocks and sediments is performed for a variety of environmental and petrological purposes. For example, chemical data are used in the identification of various rock types; also sediments contain significantly higher concentrations of many metals than are found in the overlying water, as such, they must be analyzed for potential pollutant contributions to the environment. The importance of these types of data is well established and has been going on for decades. Silicate dissolution usually involves either a fusion, with subsequent dissolution of the bead, or a wet digestion employing mineral acids. Fusions tend to be limited to major element analyses due to the relatively high dilution factors involved; a desire to quantitate a number of trace (heavy) metals dictates the use of a wet digestion procedure. Various wet digestion procedures have been used with rocks and sediments and have been amply described in the literature (1-7). The application of atomic absorption spectroscopy for the analysis of the digestate has also been amply described (1-7). The digestion technique described herein represents a modification of the procedures outlined by Johnson and Maxwell (5) and Langmyhr and Paus (6). Table 1 specifies the upper and lower concentration limits; samples containing analyte concentrations greater than the upper limit may be analyzed after appropriate dilution.

SUMMARY OF METHOD

Rocks or sediment samples are dried, ground, and homogenized. An aliquot is digested with a combination of nitric, hydrofluoric, and perchloric acids, in Teflon (R) beakers, 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 after the addition, in certain cases, of appropriate matrix modifiers. Additional interferences are removed or compensated for through the use of mixed-salt standards and background correction. Further information about the principles of the method can be found in Walsh (8), Johnson and Maxwell (5) and Pinta (7).

INTERFERENCES

Numerous interelement interferences, both positive and negative, exist for this procedure and have been amply documented elsewhere (1,5,7,8). Interferences are elimated and/or compensated for through the removal of silica by the digestion procedure, dilution, the addition of cesium chloride (CsCl), the use of mixed-salt standards, and the use of a deuterium source background corrector.

Table 1.--Upper and lower concentration limits of the method

Constituent	**Lower Limit**		**Upper Limit**	
	Sample (mg/kg)	**Solution (mg/kg)**	**Sample (mg/kg)**	**Solution (mg/kg)**
Aluminum	20,000	20	150,000	150
Cadmium	.5	.005	10	.1
Calcium	1,000	.1	50,000	5
Chromium	3	.03	400	4
Cobalt	3	.03	600	6
Copper	1	.01	400	4
Iron	5,000	5	100,000	100
Lead	3	.03	1,000	10
Lithium	2	.02	200	2
Magnesium	1,000	1	20,000	20
Manganese	100	.1	4,000	4
Nickel	3	.03	600	6
Potassium	1,000	.1	35,000	3.5
Sodium	1,000	.1	25,000	2.5
Strontium	5	.025	1,000	5
Titanium	1,000	1	20,000	20
Zinc	1	.01	160	1.6

APPARATUS

A Varian Model AA-975(1) double beam atomic absorption spectrophotometer with microprocessor control and digital display, used in conjunction with a Varian Model PSC-55(1) autosampler was employed in this study. Instrumental parameters are listed in table 2.

Teflon (R) beakers, 100 mL capacity, thick wall, capable of withstanding temperatures up to 260°C.

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

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

REAGENTS

Aluminum standard solution, 1.00 mL = 1.00 mg Al: Dissolve 1.000g aluminum metal in 20 mL HCl (sp gr 1.19) with a trace of mercury salt to catalyze the reaction, and dilute to 1000 mL with demineralized water.

Cesium chloride solution, 4 g/L: Dissolve 4g CsCl of at least 5/9ths purity (10 ppm impurities) in demineralized water and dilute to 1 L.

Hydrochloric acid, concentrated, (sp gr 1.19).

Hydrochloric acid, dilute (1 + 1): Add 250 mL concentrated hydrochloric acid (sp gr 1.19) to 250 mL demineralized water. Store in a plastic bottle.

Hydrochloric acid, dilute, (2 + 98): Add 10 mL concentrated hydrochloric acid (sp gr 1.19) to 490 mL demineralized water. Store in a plastic bottle.

Hydrofluoric acid, concentrated (48-51%), (sp gr 1.17).

Iron standard solution, 1.00 mL = 1.00 mg Fe: Dissolve 1.000g iron metal in 20 mL HCl (1 + 1)) and dilute to 1000 mL with demineralized water.

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

Table 2--Instrumental settings used for the method

Parameters	Al	Ca	Fe	Mg	Mn	K	Na	Ti	Cu	Zn
Wavelength (nm)	309.3	422.7	372.0	202.6	279.5	766.5	589.0	364.3	324.7	213.9
Slit (nm)	.5	.5	.2	1.0	.2	1.0	1.0	.5	0.5	1.0
Lamp Current (ma)	10	4	5	4	5	5	5	20	4	5
Flame Type (a,b)	N-A	N-A	A-A	N-A	A-A	A-A	A-A	N-A	A-A	A-A
Oxident (L/min)c	12.8	12.0	12.5	11.0	14.0	14.0	16.2	11.0	11.0	11.0
Fuel (L/min)c	7.00	6.50	2.00	7.00	2.10	3.10	2.20	7.20	2.20	2.20
Integration Time(s)	5	3	3	5	3	3	3	5	3	3
Background Correction	off	off	off	off	off	off	off	off	on	on

*All determinations carried out with a fixed-rate nebulizer, approximate uptake of 5-6 mL/minute

a. N-A - nitrous oxide/acetylene
b. A-A - air/acetylene
c. Readings on automatic gas control

Mixed salt standard stock solution I (minors): Dissolve by appropriate means, the following compounds or elements: cadmium metal (0.200g), chromium metal (0.800g), cobalt metal (1.200g), copper metal (0.800g), lead metal (2.000g), lithium carbonate (2.130g), manganese metal (2.000g), nickel metal (1.200g), strontium carbonate (1.685g), and zinc metal (0.320g), add 20 mL HCl (sp gr 1.19), and dilute to 1000 mL with demineralized water. This solution will contain the following concentrations: cadmium (200 mg/L), chromium (800 mg/L), cobalt (1200 mg/L), copper (800 mg/L), lead (2000 mg/L), lithium (400 mg/L), manganese (2000 mg/L), nickel (1200 mg/L), strontium (1000 mg/L), and zinc (320 mg/L). Store in a plastic or Teflon (R) bottle.

Mixed salt standard solution IA (minors): Take 100 mL of mixed salt standard stock solution I, add 20 mL HCl (sp gr 1.19), and dilute to 1000 mL. This solution will contain the following concentrations: cadmium (20 mg/L), chromium (80 mg/L), cobalt (120 mg/L), copper (80 mg/L), lead (200 mg/L), lithium (40 mg/L), manganese (200 mg/L), nickel (120 mg/L), strontium (100 mg/L), and zinc (32 mg/L). Store in a plastic or Teflon (R) bottle. Solution is stable for 3 months.

Mixed salt standard solution II (majors): Dissolve by appropriate means, the following compounds or elements: aluminum metal (1.500g), calcium carbonate (1.249g) iron metal (1.000g), magnesium metal (0.200g), manganese metal (0.040g), sodium chloride (0.636g), and ammonium titanyl oxalate (1.227g), add 20 mL HCl (sp gr 1.19), and dilute to 1000 mL with demineralized water.

This solution will contain the following concentrations: aluminum (1500 mg/L), calcium (500 mg/L), iron (1000 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 a plastic or Teflon $^{(R)}$ bottle.

Working standard solution I: Take respectively, a 10 mL, 5 mL and 1 mL aliquot of mixed-salt standard stock solution IA, add to each, 4 mL HCl (sp gr 1.19), 20 mL of mixed salt standard stock solution II, and dilute to 200 mL in volumetric glassware with demineralized water. Concentrations are as follows:

	Standard 1 (mg/L)	**Standard 2 (mg/L)**	**Standard 3 (mg/L)**
Volume (mL)	10	5	1
Cd	1	0.5	0.1
Cr	4	2	0.4
Co	6	3	0.6
Cu	4	2	0.4
Pb	10	5	1
Li	2	1	0.2
Ni	6	3	0.6
Sr	5	2.5	0.5
Zn	1.6	0.8	0.16

Store in plastic or Teflon $^{(R)}$ bottles. Prepare fresh for each analysis.

Working standard solution II: Take respectively, a 10 mL, 6 mL, and 2 mL aliquot of mixed salt standard stock solution II, add 2 mL HCl (sp gr 1.19), and 10 mL of the CsCl solution, and dilute to 100 mL in volumetric glassware with demineralized water. Concentrations are as follows:

	Standard 4 (mg/L)	**Standard 5 (mg/L)**	**Standard 6 (mg/L)**
Volume (mL)	10	6	2
Al	150	90	30
Fe	100	60	20
Mg	20	12	4
Mn	4	2.4	0.8

Store in plastic or Teflon (R) bottles. Prepare fresh for each analysis.

Working Standard solution III: Take a 10 mL aliquot of standards 4, 5, and 6, add 2 mL HCl (sp gr 1.19), and 10 mL of the CsCl solution, and dilute to 100 mL in volumetric glassware with demineralized water. Concentrations are as follows:

	Standard 7 (mg/L)	**Standard 8 (mg/L)**	**Standard 9 (mg/L)**
Volume (mL)	10(Standard 4)	10(Standard 5)	10(Standard 6)
Ca	5.0	3.0	1.0
K	3.5	2.1	0.7
Na	2.5	1.5	0.5

Store in plastic or Teflon (R) bottles. Prepare fresh for each analysis.

Nitric acid, concentrated (sp gr 1.41).

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

Sodium standard solution, 1.00 mL = 1.00 mg Na: Dissolve 2.542g NaCl in demineralized water, add 20 mL HCl (sp gr 1.19), and dilute to 1000 mL with demineralized water.

Titanium standard solution, 1.00 mL = 1.00 mg Ti: Dissolve 6.135g of ammonium titanyl oxalate in demineralized water, and dilute to 1000 mL with demineralized water.

Titanium working standard solutions: Take respectively, a 2 mL, 1 mL, and 0.5 mL aliquot of the titanium standard solution, add to each, 10 mL of the aluminum standard solution, 5 mL of the iron standard solution, 3.5 mL of the sodium standard solution, 10 mL of the CsCl solution, and 2 mL HCl (sp gr 1.19) and dilute to 100 mL in volumetric glassware with demineralized water. The standards contain, respectively, 20,10, and 5 mg/L titanium.

PROCEDURE

Immediately before each use, clean all glassware by rinsing, first with dilute HCl (1+1), and then with demineralized water. Dry the sample by an appropriate procedure such as freeze-drying, or in an oven at 105°C. If the sample is greater than 100g, split it down to less than 100g by use of a non-metallic sample splitter (riffle sampler) or by coning 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 (R) beaker; weigh out appropriate standard materials as well, and use several empty beakers for blanks. (2)

Place the hot plate in a perchloric acid hood, turn on the hood and hotplate, and adjust the hot plate to produce a surface temperature of 200°C. To each beaker, add 6 mL HNO_3 (sp gr 1.41), and place it on the hot plate for approximately 30 minutes.(3)

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(2) This procedure can be used with sample weights of between 0.2500 and 1.0000g, with appropriate adjustments 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 $HClO_4$.

(3) 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, otherwise a violent explosion could occur.

Remove the beakers from the hot plate and wait 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 until the evolution of white perchloric fumes and the solutions have reached incipient dryness; however, do not bake the residues. Remove the beakers from the hot plate, wait 5 minutes, and repeat the process again. Remove the beakers from the hot plate, wait 5 minutes, and add 2 mL $HClO_4$ (sp gr 1.67) and return the beakers to the hot plate. Continue heating until the evolution of white perchloric fumes and the solution reaches incipient dryness; however, do not bake the residues. Remove the beakers from the hot plate, lower the hot plate temperature to 100°C, and add 2 mL dilute HCl (1+1) and swirl the beaker; add 10 mL demineralized water and return to the hotplate until the residues dissolve.

Cool the beakers, and pour each solution into a 50 mL volumetric flask. Rinse the beaker several times with demineralized water and bring to the mark with demineralized water.(4) Pour the solution into an acid-rinsed plastic bottle for storage. This solution represents a dilution factor of 100X. Remove a 5 mL aliquot from the 100X solution, add 1 mL HCl (sp gr 1.19), and 5 mL CsCl solution(5), place in a 50 mL volumetric flask, and bring to the mark with demineralized water. Pour the solution into an acid rinsed plastic bottle for storage. This solution represents a dilution factor of 1000X. Finally, remove a 5 mL aliquot from the 1000X solution, add 1 mL HCl (sp gr 1.19), and 5 mL CsCl solution(5), place in a 50 mL volumetric flask, and bring to the mark with demineralized water. Pour the solution into an acid rinsed plastic

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(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 allowed to settle prior to aspiration into the AAS.

(5) The CsCl acts as an ionization suppressant.

bottle for storage. This solution represents a dilution factor of 10,000X.

Set up the atomic absorption spectrophotometer according to the specifications outlined in table 2 and analyze the 100X solutions for Cd, Cr, Co, Cu, Pb, Ni, and Zn using standards 1, 2, and 3. Dilute samples further if required.

Transfer 5 mL aliquots of each sample and standard to an appropriate container, add 5 mL dilute HCl (2 + 98), and 1 mL CsCl solution, and analyze the solutions for Li and Sr using the conditions listed in table 2.(6)

Set up the atomic absorption spectrophotometer as outlined in table 2 and analyze the 1000x solutions for Fe, Mn, Mg, and Al using standards 4, 5, and 6. Dilute further if required. Also analyze the 1000X solutions for Ti using the Ti working standards (7)

Set up the atomic absorption spectrophotometer as outlined in table 2 and analyze the 10,000X solutions for Ca, K, and Na using standards 7, 8, and 9. Dilute samples further if required.

CALCULATIONS AND REPORTING LIMITS

Determine the concentration of each constituent in the 100X solutions (Cd, Cr, Co, Cu, Pb, Ni, and Zn) from the digital display while aspirating each sample and record the results (average of 3 readings once the system has stabilized). The actual concentration of each constituent in the sample, can be obtained by multiplying the concentration in each sample solution by 100, if no further dilutions are made.

(6) The additional dilution is required to eliminate interferences due to density differences (1), and the CsCl acts as an ionization suppressant.

(7) Titanium determinations by atomic absorption are subject to severe interferences and sensitivity is heavily dependent on flame stoichiometry (6,8). Adjust the nitrous oxide flame so that it is nearly luminous (increase the fuel flow until the reducing red cone turns orange-yellow, then reduce the fuel flow until the flame just becomes red again). The CsCl acts as an ionization suppressant.

Determine the concentration of each constituent in the 200X solutions (Li and Sr) from the digital display while aspirating each sample and record the results (average of 3 readings once the system has stabilized). The actual concentration of each constituent in the sample, can be obtained by multiplying the concentration in each sample solution by 200, if no further dilutions are made.

Determine the concentration of each constituent in the 1000X solutions (Fe, Mn, Mg, Al, and Ti) from the digital display while aspirating each sample and record the results (average of 3 readings once the system has stabilized). The actual concentration of each constituent in the sample, can be obtained by multiplying the concentration in each sample solution by 1000, if no further dilutions are made.

Determine the concentration of each constituent in the 10,000X solutions (Na, K, and Ca) from the digital display while aspirating each sample and record the results (average of 3 readings once the system has stabilized). The actual concentration of each constituent in the sample, can be obtained by multiplying the concentration in each sample solution by 10,000, if no further dilutions are made.

The reporting limits for each major constituent are as follows: aluminum (nearest 1000 mg/kg), calcium (nearest 1000 mg/kg), iron (nearest 1000 mg/kg), magnesium (nearest 1000 mg/kg), manganese (nearest 100 mg/kg), potassium (nearest 1000 mg/kg), sodium (nearest 1000 mg/kg), and titanium (nearest 1000 mg/kg). As 10,000 mg/kg equals 1%, Al, Ca, Fe, Mg, K, Na, and Ti should be reported to the nearest tenth of a percent; Mn should be reported to the nearest hundreth of a percent. The reporting limits for each minor constituent are as follow: cadmium (nearest 0.1 mg/kg to 10, above 10, nearest mg/kg), chromium (nearest 1 mg/kg), cobalt (nearest 1 mg/kg), copper (nearest 1 mg/kg), lead (nearest 1 mg/kg), lithium (nearest 1 mg/kg), nickel (nearest 1 mg/kg), strontium (nearest 1 mg/kg) and zinc (nearest 1 mg/kg).

PRECISION AND ACCURACY

The precision and accuracy of this method was determined by replicate analyses (actual separate digestions and subsequent quantitation) on 2 National Bureau of Standards' Standard Reference Materials, and 6 U.S. Geological Survey Rock Standards. The results are presented in table 3. As can be seen from the data, the method is capable of generating both precise and accurate analytical results.

DISCUSSION AND CONCLUSIONS

In order to further evaluate the precision and accuracy of this method, 17 natural freshwater and marine sediment samples were dried, digested, and analyzed. The samples came from different geological settings and water bodies (Appalachicola River, Florida; Patuxent River, Maryland; Doane Lake, Swan Island and Columbia Slough, Oregon; Mississippi River, Louisiana; Ned Wilson Lake, Colorado; Yaharra and Nemadji Rivers, Wisconsin; Lake Bruin, Louisiana; and George's Bank from the North Atlantic Outer Continental Shelf). The results for the major element analyses were compared with the results obtained from a fusion digestion with subsequent atomic absorption quantitation (table 4). The results from the two sets of analyses are remarkably consistent.

As an additional check for the minor elements, 6 of the samples, already dried and ground, were sent to another laboratory for dissolution and subsequent quantitation. The results of the two sets of analyses are presented (table 5). Quantitation by the outside laboratory for all elements but Ti, came from an $HF/HClO_4/HNO_3$ digestion with subsequent quantition by flame or flameless

Table 3—Comparison of reported concentration with those found by the method

Element	No. of Det's	NBS River Sediment	NBS Estuarine Sediment	W-2	G-2	BCR-1	MAG-1	SGR-1	SCO-1
Cu^1 rpt^3		109 ± 19	18 ± 3	106 ± 5	10 ± 2	16 ± 3	33 ± 3	65 ± 3	30 ± 3
fnd^4	6	106 ± 2	18 ± 1	105 ± 2	10 + 2	16 ± 1	31 ± 1	62 ± 2	29 ± 2
Zn^1 rpt		1720 ± 170	138 ± 6	80 ± 3	88 ± 4	127 ± 4	132 ± 7	88 ± 6	110 ± 6
fnd	6	1705 ± 5	134 ± 3	80 ± 3	85 ± 1	130 ± 2	130 ± 3	85 ± 1	106 ± 2
Pb^1 rpt		714 ± 28	28.2 ±1.8	14 ± 2	29 ± 2	14 ± 2	25 ± 2	40 ± 3	28 ± 3
fnd	6	708 ± 7	28 ± 3	14± 1	29 ± 2	13 ± 1	25 ± 1	41 ± 1	29 ± 2
Ni^1 rpd		45.8± 2.9	32 ± 3	67 ± 3	3 ± 1	10 ± 2	52 ± 3	31 ± 3	28 ± 3
fnd	6	43 ± 2	30 ± 1	66 ± 2	3 ± 1	9 ± 1	51 ± 1	31 ± 2	27 ± 1
Co^1 rpt		10.1± .6	10.5± 1.3	43 ± 2	5 ± 1	39 ± 2	19 ± 2	11 ± 2	11 ± 2
fnd	6	9 + 1	12 ± 1	44 ± 2	6 ± 1	40 ± 2	22 ± 1	13 ± 1	12 ± 1
Cd^1 rpt		10.2± 1.5	.36 ± .7	1	1	1	1	1	1
fnd	6	10 ± .4	.4 ± .08	.5	.5	.5	.5	.5	.5
Li^1 rpt		-	49	10 ± 1	34 ± 2	14 ± 2	75 ± 1	130 ± 5	44 ± 2
fnd	6	-	47 ± 1	8 ± 1	34 ± 1	14 ± 1	73 ± 1	132 ± 5	45 ± 2
Cr^1 rpt		-	76 ± 3	92 ± 4	8 ± 1	14 ± 2	103 ± 3	31 ± 2	65 ± 2
fnd	6	-	75 ± 2	91 ± 3	8 ± 1	13 ± 1	102 ± 3	31 ± 1	65 ± 3
Sr^1 rpt		-	-	192 ± 3	480	330	150	430	175
fnd	6	-	-	208 +14	475 ± 14	341 ± 8	144 ± 10	430 ± 13	163 ± 6

Fe[2]	rpt		11.3 ± 1.2	3.35 ± .1	7.6 ± .2	1.9	9.4	4.8	2.2	3.6
	fnd	5	10.8 ± .2	3.2 ± .05	7.5 ± .1	1.8 ± 0	9.4 ± .2	4.6 ± .05	2.1 ± .07	3.6 ± 0.1
Mn[2]	rpt		.08 ± .01	.04 ± .002	.13 ± .01	.02	.14	.08	.02	.04
	fnd	5	.07 ± .005	.04 ± 0	.13 ± 0	.02 ± .005	.14 ± 0	.08 ± .004	0.2 ± 0	.04 ±0
Mg[2]	rpt		.074 ± .02	1.09 ± .08	3.8 ± .1	.45	2.1	1.8	2.7	1.6
	fnd	5	.7± 0	1.1 ± .05	3.8 ± .15	.44 ± .01	2.0 ± .04	1.7 ± .04	2.6 ± .05	1.5 ± .05
Al[2]	rpt		2.26 ± .04	6.25 ± .2	8.2 ± .1	8.2	7.3	8.7	3.5	7.2
	fnd	5	2.4 ± .04	6.3 ± .15	8.2 ± .11	8.3 ± .11	7.2 ± .18	8.7 ± .25	3.4 ± .08	7.2 ± .15
Ti[2]	rpt		-	.51	.67 ± .2	.3	1.4	.4	.2	.4
	fnd	5		.46 ± .03	.68 ± .02	.3 ± .02	1.4 ± .06	.4 ± .-2	.2 ± .01	.4 ± .03
Ca[2]	rpt		2.9	.83 ± .03	7.8 ± .1	1.4	5.0	1.0	6.4	1.9
	fnd	5	2.8 + .09	.74 ± .05	7.7 ± .08	1.3 ± .04	4.9 ± .08	.9 ± 0	6.3 ± .08	1.8 ± .04
Na[2]	rpt		.54 ± .01	2.0	1.6 ± .01	3.0	2.5	2.8	2.2	.7
	fnd	5	.56 ± .09	2.0 ± .09	1.6 ± .04	2.9 ± .1	2.5 ± .05	2.8 ± .05	2.2 ± .09	.7 ± .07
K[2]	rpt	5	1.26 ± .05	1.4	.5 ± .1	3.7	1.4	3.0	1.3	2.2
	fnd	5	1.26 ± .05	1.5 ± .05	.6 ± .05	3.6 ± .07	1.4 ± 0	2.9 ± .05	1.3 ± .04	2.2 ± 0

[1] concentration in mg/kg

[2] concentration in weight percent

[3] rept: reported

[4] fnd: found

Table 4—Comparison of major element concentrations determined by fusion and by this method

	Fe^1		Mn^1		Mg^1		Al^1		Ca^1		Na^1		K^1	
	F^2	WD^3	F	WD	F	WD	F	WD	F	WD	F	WD	F	WD
Appalachicola River, R.M. 94	1.1	1.1	.04	.04	.06	.07	1.9	2.1	.26	.25	.4	.5	1.0	1.0
Patuxent River at Hog Point	2.8	3.0	.04	.05	.75	.74	5.1	4.9	.5	.4	1.3	1.4	1.6	1.5
Doane Lake Outlet	6.0	6.1	.08	.09	1.0	1.0	8.1	8.0	2.3	2.2	1.9	1.8	1.3	1.2
Mississippi River at Venice	3.7	3.8	.09	.09	1.0	1.1	7.6	7.6	1.0	1.0	.8	.9	2.1	2.2
Ned Wilson Lake	2.8	2.8	.04	.03	1.3	1.3	7.2	7.2	1.0	1.0	.8	.9	1.9	1.9
Yaharra River	1.2	1.3	.07	.06	2.2	2.3	3.3	3.3	4.7	4.6	.3	.5	3.0	3.2
Appalachicola River, R.M. 86	.05	.10	.02	.01	.01	.02	.3	.4	.1	.1	.5	.4	.3	.3
Appalachicola River, Sandbar	.25	.29	.02	.02	.02	.02	.4	.4	.1	.1	.3	.3	.3	.4
Mississippi River at Tarbert	.48	.48	.01	.01	.09	.09	1.5	1.6	.4	.4	1.0	.9	1.0	1.1
George's Bank M8 5-4	.48	.43	.01	.02	.07	.07	.2	.3	.2	.2	.6	.5	.3	.2
Patuxent River at Pt. Patience	2.2	2.3	.05	.06	.5	.6	3.9	4.0	.6	.5	1.2	1.0	1.2	1.2
Patuxent River at St. Leonard's Ck.	3.8	4.1	.08	.10	.8	.9	7.2	7.2	.6	.6	1.2	1.1	1.3	1.5
Columbia Slough	3.5	3.7	.07	.06	1.0	1.0	7.9	8.1	2.6	2.5	2.1	2.2	1.6	1.5
Swan Island	4.9	4.8	.09	.09	1.2	1.2	8.5	8.5	2.6	2.5	2.0	2.1	1.3	1.4
Nemadji River	2.4	2.4	.07	.06	1.1	1.1	4.3	4.3	1.8	1.7	.9	1.0	2.5	2.5
George's Bank M13A	2.4	2.5	.05	.04	.7	.8	4.8	4.9	1.0	.9	1.8	2.0	2.0	1.8
Lake Bruin	3.3	3.2	.10	.09	.7	.8	6.6	6.5	.8	.8	1.0	.9	2.0	1.8

x^1 - all concentrations in weight percent (1% = 10,000 mg/kg)
F^2 - fusion with lithium metaborate/tetraborate followed by AAS quantitation
WD^3 - this method

Table 5—Interlaboratory comparison of minor element data in selected sediment

(concentration in mg/kg)

Sample		Cu	Zn	Pb	Cr	Cd	Ni	Co	Li	Sr	Ti
Appalachicola River	a[1]	4	23	12	23	.5	4	10	9	43	4500
RM 94	b[2]	6	23	15	20	.3	6	10	8	ND[3]	4600
Patuxent River	a[1]	20	111	22	56	.8	26	32	40	60	4700
at Hog Point	b[2]	20	110	25	59	.5	27	33	41	50	4900
Doane Lake Outlet	a[1]	33	127	29	58	.5	34	25	16	300	6600
	b[2]	35	130	32	56	.14	29	28	17	290	6600
Mississipp River	a[1]	28	120	32	76	.9	37	16	38	100	4800
at Venice	b[2]	30	120	32	77	.5	36	16	39	90	4900
Ned Wilson Lake	a[1]	28	113	38	90	.9	66	20	36	210	4900
	b[2]	30	110	37	90	.4	55	20	37	190	4700
Yaharra River	a[1]	13	28	23	28	.5	11	18	6	107	1900
	b[2]	12	27	22	30	.1	13	16	7	94	1900

a[1] - this method
b[2] - USGS Branch of Analytical Services, Reston, VA, determined on a sample digested with $HF/HClO_4/HNO_3$
Cu - digestate extracted with butyl acetate, further extracted with diethyldithiocarbamate in chloroform, dried, brought up in HCl, graphite furnace
Zn - see Cu, quantitation by flame AAS
Pb - see Cu
Cd - see Cu
Cr - digestate diluted 1:10, quantitation by graphite furnace
Ni - see Cr
Co - see Cr
Li - digestate diluted, quantitation by flame AAS
Sr - see Li
Ti - borate fusion, quantitation by ICP
ND[3] - not determined

atomic absorption spectrophotometry. Ti was determined by inductively coupled plasma spectroscopy (ICP) following a borate fusion.

As can be seen from all the comparative data on standards and samples, analytical precision and accuracy, as well as comparability, is quite good (tables 3, and 4, and 5.) All these results indicate that very precise and accurate analyses can be obtained on rocks and sediments by using flame atomic absorption spectroscopy.

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