Multielement Analysis of Rocks and Sediments by Wet Digestion and Atomic Absorption Spectroscopy*

Table 1. *Upper and Lower Concentration Limits of the Method*

Constituent	Lower limit Sample (mg/kg)	Solution (mg/kg)	Upper limit Sample (mg/kg)	Solution (mg/kg)
Aluminium	20,000	20	150,000	150
Cadmium	0.5	0.005	10	0.1
Calcium	1,000	0.1	50,000	5
Chromium	3	0.03	400	4
Cobalt	3	0.03	600	6
Copper	1	0.01	400	4
Iron	5,000	5	100,000	100
Lead	3	0.03	1,000	10
Lithium	2	0.02	200	2
Magnesium	1,000	1	20,000	20
Manganese	100	0.1	4,000	4
Nickel	3	0.03	600	6
Potassium	1,000	0.1	35,000	3.5
Sodium	1,000	0.1	25,000	2.5
Strontium	5	0.025	1,000	5
Titanium	1,000	1	20,000	20
Zinc	1	0.01	160	1.6

Summary

Interferences

Numerous interelement interferences, both positive and negative, exist for this procedure and have been amply documented elsewhere [1,5,7,8]. Interferences are eliminated 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 background correction.

Apparatus

An Agilent Model AA-975* double beam atomic absorption spectrophotometer with microprocessor control and digital display, used in conjunction with a Varian Model PSC-55* autosampler was employed in this study. Instrumental parameters are listed in Table 2.

Teflon 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

Aluminium standard solution, 1.00 mL = 1.00 mg Al: Dissolve 1.000 g aluminium 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 4 g CsCl of at least 99.999% purity 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: Dissolved 1.000 g iron metal in 20 mL HCl (1 + 1) and dilute to 1000 mL with demineralized water.

Mixed salt standard stock solution 1 (minors):

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 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 bottle.

Mixed salt standard stock solution 1A (minors):
Take 100 mL of mixed salt standard stock solution 1, 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 bottle. Solution is stable for 3 months.

Mixed salt standard solution 2 (majors):
Dissolve by appropriate means the following compounds or elements: aluminium 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 (0.668 g), sodium chloride (0.636 g), and ammonium titanyl oxalate (1.227 g); add 20 mL HCl (sp gr 1.19) and dilute to 1000 mL with demineralized water.

This solution will contain the following concentrations: aluminium (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 bottle.

Working standard solution 1:
Take respectively, a 10 mL, 5 mL and 1 mL aliquot of mixed-salt standard stock solution 1A, add to each 4 mL HCl (sp gr 1.19), 20 mL of mixed-salt standard stock solution 2, and dilute to 200 mL in volumetric glassware with demineralized water. Store in plastic or Teflon bottles. Prepare fresh for each analysis. 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

Working standard solution 2:
Take respectively, a 10 mL, 6 mL, and 2 mL aliquot of mixed-salt standard stock solution 2, 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. Store in plastic or Teflon bottles. Prepare fresh for each analysis. 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

Working standard solution 3:
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. Store in plastic or Teflon bottles. Prepare fresh for each analysis. 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

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 2.542 g 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 6.135 g 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 aluminium 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 100 g, split it down to less than 100 g 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 beaker; weigh out appropriate standard materials as well, and use several empty beakers for blanks*.

Place the hot plate in a perchloric acid hood, turn on the hood and hot plate, 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**.

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 hot plate 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*. 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**, 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**, 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 10,000X.

Set up the atomic absorption spectrophotometer according to the specifications outlined in Table II, 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***.

Set up the atomic absorption spectrophotometer as outlined in Table II, 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****.

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.

*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.

**The CsCl acts as an ionization suppressant.

***The additional dilution is required to eliminate interferences due to density differences [1], and the CsCl acts as an ionization suppressant.

****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.

*This procedure can be used with sample weights of between 0.2500 and 1.0000 g, 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 $HClO_4$.

**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.

Table 2.   Instrumental Settings Used for the Method

Parameters	Al	Ca	Fe	Mg	Mn	K	Na	Ti	Cu	Zn	Pb	Ni	Co	Cr	Cd	Li	Sr
Wavelength (nm)	309.3	422.7	372.0	202.6	279.5	766.5	589.0	364.3	324.7	213.9	217.0	232.0	240.7	357.9	228.8	670.8	460.7
Slit (nm)	0.5	0.5	0.2	1.0	0.2	1.0	1.0	0.5	0.5	1.0	1.0	0.2	0.2	0.2	0.5	1.0	0.5
Lamp current (mA)	10	4	5	4	5	5	5	20	4	5	5	4	7	7	4	5	10
Flame type (a,b)	N-A	N-A	A-A	N - A	A-A	A-A	A-A	N-A	A - A	A-A	A-A	A-A	A-A	N-A	A-A	A-A	N-A
Oxidant (L/min)c	12.8	12.0	12.5	11.0	14.0	14.0	16.2	11.0	11.0	11.0	11.5	11.0	11.0	11.0	11.0	11.5	12.0
Fuel (L/min) c	7.00	6.50	2.00	7.00	2.10	3.10	2.20	7.20	2.20	2.20	2.20	2.20	2.20	6.50	2.20	2.20	5.50
Integration time (s)	5	3	3	5	3	3	3	5	3	3	3	3	3	5	3	3	5
Background corr.	off	off	off	off	off	off	off	off	on	on	on	on	on	off	on	off	off

*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

Calculations and Reporting Limits

Determine the concentration of each constituent in the 100X solutions (Cd, Cr, Co, Cu, Pb, Ni and Zn) while aspirating each sample and record the results (average of three 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.

Determine the concentration of each constituent in the 200X solutions (Li and Sr) 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) while aspirating each sample and record the results (average of three 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) while aspirating each sample and record the results (average of three 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: aluminium (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 hundredth of a percent. The reporting limits for each minor constituent are as follows: 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 US 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 procedure 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 in Table 5. Quantitation by the outside laboratory for all elements but Ti, came from an $HF/HClO_4/HNO_3$ digestion with subsequent quantitation by flame or furnace AA. Ti was determined by ICP-AES 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, 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.

Table 4.   Comparison of Major Element Concentrations Determined by Fusion and by This Method

	Fe[1] F[2] W D[3]	Mn[1]	Mg[1]	Al[1]	Ca[1]	Na[1]	K[1]

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 RM 94	a[1]	4	23	12	23	<0.5	4	10	9	43	4500
	b[2]	6	23	15	20	0.03	6	10	8	ND3	4600
Patuxent River at Hog Point	a[1]	20	111	22	56	0.8	26	32	40	60	4700
	b[2]	20	110	25	59	0.5	27	33	41	50	4900
Doane Lake Outlet	a[1]	33	127	29	58	<0.5	34	25	16	300	6600
	b[2]	35	130	32	56	0.14	29	28	17	290	6600
Mississippi River at Venice	a[1]	28	120	32	76	0.9	37	16	38	100	4800
	b[2]	30	120	32	77	0.5	36	16	39	90	4900
Ned Wilson Lake	a[1]	28	113	38	90	0.9	66	20	36	210	4900
	b[2]	30	110	37	90	0.4	55	20	37	190	4700
Yaharra River	a[1]	13	28	23	28	0.5	11	18	6	107	1900
	b[2]	12	27	22	30	0.1	13	16	7	94	1900

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