MAJOR ELEMENT ANALYSIS
OF ROCKS AND SEDIMENTS BY
ATOMIC ABSORPTION SPECTROSCOPY

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ABSTRACT

A relatively rapid, accurate, and precise method for the determination of major elements (Si, Al, Fe, Mg, Mn, Na, K, and Ca) in rocks and sediments is presented. The method employs a fusion with a combination of lithium metaborate and tetraborate followed by dissolution in boiling distilled water acidified with nitric acid. 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 on sediment samples quantitated by Inductively Coupled Plasma (ICP) 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 is 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 their generation has been going on for decades. Silicate decomposition usually involves either a fusion with acid or alkaline compounds and subsequent dissolution of the bead, or a wet digestion employing mineral acids. A desire to quantitate silica precluded most of the wet digestion techniques, thus, a fusion method was selected, in order to decompose the samples. Various fusion fluxes, and sample to flux ratios have been used with silicates and have been amply described in the literature (1-4). The application of atomic absorption spectroscopy for the analysis of the dissolved bead has also been well described (1,4).

The fusion method described herein represents a modification of the procedures outlined by Shapiro(2) and Johnson and Maxwell(4). 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

Rock or sediment samples are dried, ground, and homogenized. An aliquot is fused with a mixture of lithium metaborate and lithium tetraborate, in a muffle furnace at 1000°C. The resulting bead is dissolved in acidified, boiling, deionized water, and the solutions are analyzed by atomic absorption spectroscopy after the addition of appropriate matrix modifiers. Additional interferences are removed or compensated for through the use of mixed-salt standards. Further information about the principles of the method can be found in Shapiro(2) and Johnson and Maxwell(4).

INTERFERENCES

Numerous interelement interferences, both positive and negative, exist for this procedure and have been amply documented elsewhere (1, 2, 4). Interferences are eliminated or compensated for through the use of cesium chloride (CsCl), orthoboric acid (H_3BO_3), lithium metaborate ($LiBO_2$), lithium tetraborate ($Li_2B_4O_7$), and the use of mixed salt standards prepared in the fusion matrix.

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
Calcium	1,000	.1	50,000	5
Iron	5,000	5	100,000	100
Magnesium	1,000	1	20,000	20
Manganese	100	.1	4,000	4
Potassium	1,000	.1	35,000	3.5
Silica	40,000	40	150,000	150
Sodium	1,000	.1	25,000	2.5

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.

Graphite crucibles, drill point, with a 7.5 mL capacity and a 1 in. OD, 0.75 in. ID, and a total depth of 1.375 in.

Magnetic stirrer, a multiplace unit speeds sample dissolution.

Muffle furnace, capable of reaching a temperature of at least 1000°C.

REAGENTS

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

Flux mixture: Thoroughly mix 1 part reagent-grade powdered anhydrous lithium metaborate, $LiBO_2$, and 2 parts anhydrous lithium tetraborate, $Li_2B_4O_7$. Store in tightly closed bottle.(2)

Lithium metaborate, $LiBO_2$: at least five ninths purity (10 ppm impurities).(2)

Lithium tetraborate, Li_2BO_4: at least five ninths purity (10 ppm impurities).(2)

Mixed salt standard stock solution: 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

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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.

(2) It is possible to purchase pre-mixed fusion fluxes from several suppliers, and provided they are of sufficient purity, have been found satisfactory.

Table 2.--Instrumental operating conditions used in the method

Parameters	Aluminum	Calcium	Iron	Magnesium	Manganese	Potassium	Silica	Sodium
Wavelength (nm)	309.3	422.7	372.0	202.6	279.5	766.5	251.6	589.0
Slit (nm)	.5	.5	2	1.0	.2	1.0	.2	1.0
Lamp Current (ma)	10	4	5	4	5	5	20	5
Flame Type (a,b)	N-A	N-A	N-A	N-A	N-A	A-A	N-A	A-A
Oxident (L/min)(c)	12.8	12.0	11.0	11.0	11.0	14.0	11.0	16.2
Fuel (L)/min)(c)	7.00	6.50	7.00	7.00	4.70	3.10	7.00	2.20
Integration Time (s)	5	5	5	5	5	3	5	3
Background Correction	off	off	off	off	off	off	off	off

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

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

(0.040g), potassium chloride (0.668g), ammonium hexafluorosilicate (18.987g), sodium chloride (0.636g), and ammonium titanyl oxalate (1.227g), and dilute to 1000 mL with standard diluent solution. 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), silica (3000 mg/L), sodium (250 mg/L), and titanium (200 mg/L). Store in a plastic or teflon$^{(R)}$ bottle.

Working standard solutions: take respectively, a 10 mL, 6 mL, and 2 mL aliquot of the mixed salt standard stock solution and dilute to 100 mL in volumetric glassware with standard diluent solution. Concentrations are listed in Table 3

Nitric acid, HNO_3: concentrated (sp gr 1.41).

Nitric acid, dilute (1 + 1): Add 250 mL concentrated nitric acid (sp gr 1.41) to 250 mL demineralized water. Store in a plastic bottle.

Orthoboric acid solution, 50g/L: Dissolve 50g H_3BO_3 of at least five ninths purity (10 ppm impurities) in demineralized water and dilute to 1L. Heat may be required to complete dissolution. Prepare fresh as required because orthoboric acid may precipitate within 12 to 18 h.

Standard diluent solution: Dissolve 6 g of flux mixture in 500 mL of demineralized water, add 12.5 mL nitric acid (sp gr 1.41), and dilute to 1L with demineralized water. Store in a plastic bottle.

PROCEDURE

Immediately before each use, clean all glassware by rinsing, first with dilute nitric acid (1 + 1), and then with demineralized water.

Dry the sediment sample by an appropriate procedure such as freeze-drying, or in an oven at 105°C. If the sediment sample is greater than 100g, split it down to less than 100g by use of a non-metallic sample splitter (riffle sampler) or by

Table 3.--Concentrations of Working Standards

	Standard 1	**Standard 2**	**Standard 3**
Volume of Stock Solution	10 mL	6 mL	2 mL
Constituent	(mg/L)	(mg/L)	(mg/L)
Fe	100	60	20
Mg	20	12	4
Si	300	180	60
Al	150	90	30
Ti	20	12	4
Ca	50	30	10
Na	25	15	5
K	35	21	7
Mn	4	2	1

coning and quartering. Grind the sediment or rock sample with a mixer mill or an agate mortar and pestle until all material is finer than 100 mesh.

Transfer approximately 1.2g of flux mixture to a waxed or plastic coated weighing paper (6 in. x 6 in.). Weigh and transfer 0.2000g of ground sample to the flux mixture and mix by rolling successive corners of the paper about 30 times. Carefully transfer the combined sample and flux to a graphite crucible, and tamp down. Weigh appropriate standard materials and treat as unknowns. Also, carry several blanks through the procedure by using only flux and treat as unknowns. Fuse the mixtures in a muffle furnace, pre-heated to 1000°C, for 30 minutes.(3) Remove the crucibles from the furnace and allow to cool; dislodge the beads by gentle tapping or with a spatula.(4) Place the bead in an acid-washed 250 mL plastic bottle and add a 3/4 to 1 in. stirring bar. Add approximately 50 mL boiling demineralized water using a plastic graduate, place the bottle on a magnetic stirrer, and mix. Add 5 mL dilute nitric acid (1 + 1) to each bottle and stir rapidly for about 60 minutes. Cap the bottle lightly, during the stirring, to prevent both contamination and possible spattering. Immediately after 60 minutes, remove the bottles from the stirrers, and add about 100 mL demineralized water to prevent the polymerization of silica.(5)

Pour each solution into a 200 mL volumetric flask, using a funnel in order to retain the stirring bar. Rinse the bottle and cap and bring to the mark with

(3) When crucibles, samples, and crucible racks are placed in the muffle furnace, the temperature may drop as much as 200°C. Time is still measured from the time of insertion in the furnace.

(4) The beads can be dissolved immediately after cooling, or can be stored in plastic vials for dissolution at a later time.

(5) The solutions may contain small amounts of graphite from the crucibles which can be ignored. However, if the solutions are cloudy, this indicates a very high concentration of silica in the original sample and that it has polymerized. Such solutions must be discarded, and a new fusion performed using a smaller quantity of sample.

demineralized water. Pour the solution back into the plastic bottle for storage. Add 10 mL CsCl and 20 mL H_3BO_3 solution to each bottle.(6) Prepare the mixed salt working standards and to each 100 mL, add 5 mL CsCl solution, and 10 mL H_3BO_3 solution.(6)

Set up the atomic absorption spectrophotometer according to the specifications outlined in Table 2 and analyze the solutions for Fe, Mn, Mg, Si, and Al. Dilute samples if required, using the standard diluent solution and add appropriate quantities of CsCl and H_3BO_3 solutions.(7)

Transfer 10.0 mL aliquots of each sample and working standard solution to 100 mL volumetric flasks and dilute to 100 mL. Transfer solutions to plastic bottles and add 5 mL CsCl and 10 mL H_3BO_3 solutions to each.(6)

Set up the atomic absorption spectrophotometer according to the specifications outlined in Table 2 and analyze the solutions for Ca, K, and Na. Dilute samples if required, using the standard diluent solution and add appropriate amounts of CsCl and H_3BO_3 solutions.(6)

CALCULATIONS AND REPORTING LIMITS

Determine the concentration of each constituent (Fe, Mn, Mg, Si, and Al) in each sample solution 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 dilutions are made.

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(6) CsCl acts as an ionization suppressant and the H_3BO_3 stabilizes the silica.

(7) Although the mixed salt standard contains up to 300 mg/L Si, samples containing more than 150 mg/L Si should be diluted prior to quantitation. This is because there is a significant suppression of Si above this concentration. The high Si level in the standard is needed for matrix matching.

Determine the concentration of each constituent (Ca, K, and Na) in each sample solution 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 dilutions are made. The reporting limits for each constituent are as follows: aluminum (nearest 1000 mg/kg), calcium (nearest 1000 mg/kg), iron (nearest 1000 mg/kg), magnes-ium (nearest 1000 mg/kg), manganese (nearest 100 mg/kg), potassium (nearest 1000 mg/kg), silica (nearest 1000 mg/kg), and sodium (nearest 1000 mg/kg). As 10,000 mg/kg equals 1%, all but Mn should be reported to the nearest tenth of a percent, Mn should be reported to the nearest hundreth of a percent.

PRECISION

The precision of this method was determined by replicate analyses (actual separate fusions and subsequent quantitation) of 11 U.S. Geological Survey rock standards. The results are presented in Table 4, and are summarized below for the minimum and maximum concentrations in these standards.

	Minimum Concentration			**Maximum Concentration**		
Element	**n[1]**	**Mean[2]**	**RSD[3]**	**n[1]**	**Mean[2]**	**RSD[3]**
Aluminum	5	3.5	3	10	8.5	1
Calcium	5	.7	11	10	7.8	3
Iron	5	1.2	3	10	9.3	1
Magnesium	10	.5	2	5	4.3	3
Manganese	10	.02	20	5	.16	12
Potassiun	10	.5	10	10	3.7	3
Silica	5	13.2	2	10	32.4	1
Sodium	5	.7	9	10	3.1	3

[1] number of replicate determinations

[2] mean in weight percent

[3] relative standard deviation in percent

Table 4.--Determination of major elements in U.S. Geological Survey rock standards (concentrations in weight percent)

Standard	n[1]	Iron			Magnesium			Silicon			Aluminum			Calcium			Potassium			Sodium			Manganese		
		R[2]	F[3]		R[2]	F[3]		R[2]	F[3]		R[2]	F[3]		R[2]	F[3]		R	F		R	F		R	F	
W-2	10	7.6	7.5	.1	3.8	3.9	.15	24.6	24.6	.4	8.2	7.9	.1	7.8	7.8	.2	.5	.5	.05	1.6	1.6	.1	.13	.13	.004
G-2	10	1.9	1.8	.07	.45	.45	.1	32.4	32.4	.3	8.2	7.9	.1	1.4	1.3	.1	3.7	3.7	.2	3.0	3.1	.1	.02	.02	.004
BCR-1	10	9.4	9.3	.1	2.1	2.1	.08	25.5	25.2	.2	7.3	7.2	.1	5.0	4.8	.1	1.4	1.4	.1	2.5	2.5	.1	.14	.13	.005
MAG-1	10	4.8	4.6	.2	1.8	1.8	.07	23.8	23.4	.3	8.7	8.5	.1	1.0	.9	.06	3.0	3.0	.06	2.8	2.9	.1	.08	.07	.005
RGM-1	5	1.3	1.2	.04	.17	.17	.01	34.2	33.7	.7	7.3	7.1	.2	.8	.8	.09	3.6	3.7	.05	3.0	3.1	.1	.03	.03	.006
QLO-1	5	3.0	2.9	.05	.6	.6	.06	30.6	30.4	.4	8.6	8.6	.1	2.3	2.1	.2	3.0	3.0	.04	3.1	3.2	.1	.07	.07	0
STM-1	5	3.6	3.6	.09	.06	.06	.01	27.8	27.5	.2	9.8	9.7	.1	.8	.7	.08	3.6	3.6	.08	6.7	6.8	.2	.17	.16	.02
SGR-1	5	2.2	2.1	.1	2.7	2.7	.08	13.2	13.2	.3	3.5	3.5	.1	6.4	6.3	.3	1.3	1.3	.041	2.2	2.3	.1	.02	.02	0
SCo-1	5	3.6	3.5	.09	1.6	1.6	.05	29.4	29.3	.5	7.2	7.0	.2	1.9	1.7	.1	2.2	2.2	.1	.7	.7	.06	.04	.04	0
BHVO-1	5	8.4	8.3	.08	4.3	4.3	.11	23.3	23.8	.6	7.3	7.3	.2	8.2	8.2	.3	.4	.5	.05	1.7	1.7	.05	.13	.13	.006
SDC-1	5	4.8	4.7	.08	1.0	1.0	.07	30.9	30.6	.5	8.5	8.3	.2	1.0	1.1	.1	2.7	2.6	.13	1.5	1.4	.08	.09	.08	.006

n[1] number of determinations
R[2] reported concentrations (4)
F[3] determined concentrations

DISCUSSION AND CONCLUSIONS

In order to further check on the precision and accuracy of this method, six natural freshwater sediment samples were dried and analyzed. The samples came from different geographical areas and water bodies (Appalachicola River, Florida, Patuxent River, Maryland, Doane Lake Outlet, Oregon, Mississippi River, Louisiana, Ned Wilson Lake, Colorado, and Yahara River, Wisconsin). Subsamples of the dried and ground sediment were sent to another laboratory for fusion and subsequent quantitation. The results of the two sets of analyses are presented in Table 5. Quantitation by the outside laboratory was by ICP for all elements except K, which was done by flame atomic absorption spectroscopy.

As can be seen from the data in Table 5, analytical comparability is quite good. These results, along with the precision and accuracy data on U.S. Geological Survey rock standards presented in Table 4, indicate that very precise and accurate results can be obtained on rocks and sediments by using the fusion technique described and flame atomic absorption spectroscopy.

Table 5.--Interlaboratory Comparison of Major Element Concentrations in Selected Sediments
(Concentration in weight percent)

Element	**Appalachicola River (R.M. 94)**		**Patuxent River at Hog Point**		**Doane Lake Outlet**		**Mississippi River at Venice**		**Ned Wilson Lake**		**Yahara River**	
	a[1]	b[2]	a[1]	b[2]	a[1]	b[2]	a[1]	b[2]	a[1]	b[2]	a[1]	b[2]
Si	39.6	41.8	31.0	32.2	26.4	27.3	30.5	29.7	26.5	26.3	28.8	29.5
Al	1.9	2.0	5.1	5.0	8.1	8.0	7.6	7.7	7.2	7.0	3.3	3.3
Fe	1.1	1.2	2.9	3.1	6.0	6.1	3.8	3.9	2.8	2.7	1.2	1.3
Mg	.1	.1	.8	.9	1.0	1.2	1.0	1.1	1.3	1.4	2.2	2.5
Ca	.2	.2	.5	.5	2.3	2.3	1.0	.9	1.0	1.0	4.7	4.7
Na	.4	.2	1.3	1.4	1.9	1.9	.8	.7	.8	.7	.3	.3
K	1.0	1.1	1.5	1.3	1.3	1.2	2.1	1.9	1.9	1.8	3.0	3.0
Mn	.04	.05	.04	.05	.08	.09	.09	.09	.04	.05	.07	.06

a[1]: this method

b[2]: U.S. Geological Survey Branch of Analytical Services, Reston, Va. - determination on fused sample, all quantitation by ICP except K which was done by flame AA.

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