

MICROANALYSIS OF ZEOLITES

ANNA G. LOSCHI GHITTONI*

ELIO PASSAGLIA*

RIASSUNTO.—Viene descritto un metodo per la determinazione degli elementi alcalino e alcalino terrosi, del ferro e manganese su piccole quantità di materiale (10 mg o meno) mediante spettrofotometro ad assorbimento atomico. Il metodo è valido per i silicati poveri in ferro e magnesio (zeoliti, feldspati e feldspatoidi). I risultati delle determinazioni su 4 rocce standard (3 graniti e una tonalite) e su 2 zeoliti, rispettivamente ricche in Ba e Sr, sono confrontati con i rispettivi dati della letteratura.

SUMMARY.—A method for the determination of the alkalies, alkaline earths, iron and manganese on very small amounts of material (10 mg even 5 mg) by atomic absorption spectrophotometer is described. The method is suitable for the silicate minerals poor in Fe and Mg (zeolites, feldspars and feldspathoids). The results of the determinations on four standard rocks (3 granites and 1 tonalite) and on two zeolites, respectively rich in Ba and Sr, are compared with the data of literature.

INTRODUCTION

There is in literature a rich bibliography about the procedures on the determination of the most common elements of a silicate rock by atomic absorption spectroscopy [ALLAN (1962); TRENT and SLAVIN (1964); SLAVIN (1965); FARRAR (1966); ALTHAUS (1966); SIGHINOLFI (1969); etc.].

The need of making analyses on small amounts of natural zeolites, has led us to set up a microanalytical method to determine the following cations: Na, K, Ca, Mg, Sr, Ba, Fe, Mn. This method is suitable for the silicate minerals poor in Fe and Mg like zeolites, feldspars and feldspathoids.

Considering both the average cation content of a zeolite or an acid rock and the average value in ppm of the optimum working range for each cation, Table 1 shows clearly that the minimum amount of material that we need for the determination appears to be about 5 mg. As the cation content of the sample can go remarkably down the average values reported in Table 1, appears advisable, when possible, to use 10 mg of material.

* Istituto di Mineralogia e Petrologia dell'Università di Modena, Italy.

TABLE 1

Element	Average concentration of element in the solu- tion to be examined	Average concentration of element in the mi- nerals to be analyzed	μg of mineral required to get in 1ml the concentration given in the first column
	ppm	percent	μg
Na	6	4	150
K	6	4	150
Mg	0.5	0.1	500
Ca	7	4	175
Sr	7	1	700
Ba	7	1	700
Fe	10	1	1,000
Mn	8	0.1	800
			Sum... 4.175 μg $\sim$ 5 mg

STANDARD ROCK SAMPLES AND OVERALL ANALYTICAL PROCEDURES

The following standards have been analyzed:

GH granite.

GA acid granite (Centre de Recherches Petrographiques et Geochimiques de l'Université, Nancy).

GR granite.

T1 Msusule tonalite (Geological Survey of Tanganika, Dodoma).

Harmotome (zeolite) from Andreasberg, Germany.

Chabazite (zeolite) from Vallerano, Roma, Italy.

The granites and the tonalite have been used as standards for the determination of: Na, K, Ca, Mg, Fe, Mn; the Harmotome from Andreasberg for the Ba determination and the Chabazite from Vallerano for the Sr determination.

The standard stock solutions were obtained by dissolving stoichiometric quantities of chlorides or carbonates of the various elements in distilled deionized water, as hinted by the Perkin-Elmer Analytical methods book.

A Perkin-Elmer mod. 303 spectrophotometer was used and the standard instrumental settings and the special adjustments for the various elements are those reported in Table 2.

TABLE 2

Instrument settings and adjustments

Element	Wavelength	Slit	Lamp current	Pressure of fuel (acetylene)	Pressure of Oxider	Optimum working range (ppm)	Burner
Na	VIS 295	4	10 mA	6	5	0.5—10	b
K	VIS 383	4	700 mA	9	9	0.5—10	a
Mg	VIS 211	5	20 mA	9	8.5	0.2— 2	a
Ca	UV 285	4	20 mA	9	8.5	1.0—15	a
Sr	VIS 230	4	20 mA	9	8.5	0.5— 8	a
Ba	VIS 277	3	25 mA	>15	7	0.5— 8	c
Mn	UV 279	4	20 mA	9	9	0.5— 8	a
Fe	UV 248	4	30 mA	9	9	0.5—20	a

a) 10 cm long acetylene — air burner head.

b) 5 cm long acetylene — air burner head.

c) Acetylene-nitrous oxide burner head.

All the acids used are Suprapur Merck products.

The drawings for the various dilutions have been made by Marburg-Eppendorf micropipettes.

EXPERIMENTAL PROCEDURES

Weigh with a microanalytical balance about 10 mg of material in a 10 ml platinum crucible. Wet with deionized water and add; 0.5 ml of HF (concentrated), 0.3 ml of HNO_3 (1:1) and 0.3 ml of HClO_4 (1:3). After leaving for 12h on a water bath, dry almost completely by an ironclad plate; then add 0.1 ml of HClO_4 (1:3) and dry again; at last add 0.3 ml of HCl (concentrated) and deionized water. When the solution is clear, transfer it to a 10 ml volumetric flask and fill to the mark.

From this solution we determine the various elements as follows:

Sodium and Potassium

Transfer 2 ml of solution to a 25 ml volumetric flask, add 3 ml of a 1% Cs_2O solution and fill to the mark. With this procedure the optimum determination range is from 0.5 to 10% of Na_2O and K_2O .

Calcium, Magnesium and Strontium

Transfer 2 ml of solution to a 25 ml volumetric flask, add 4 ml of a 5% lantantum solution and fill to the mark. This procedure allows the determination of CaO in the range from 1 to 15%, that of MgO from 0.2 to 2% and that of SrO from 0.5 to 15%.

Barium

Transfer 2 ml of solution to a 25 ml volumetric flask, add 4 ml of a 1% K₂O solution and fill to the mark. With this procedure the optimum determination range is from 0.5 to 8% of BaO.

Iron and manganese

As the content in iron and manganese of zeolites and acid rocks is very small these are directly determined on the starting solution.

In this way the optimum determination range for Fe₂O₃ is from 0.1 to 2% and for MnO from 0.05 to 0.8%.

The above mentioned dilutions are of course only indicative and therefore the most suitable dilutions for determining the various cations will be chosen by the analyst according to the presumable cation content of the analyzed material.

ANALYTICAL RESULTS AND PRECISION AND ACCURACY CHECKS

The results of the analyses on the six standards examined and reported in Table 3, are the average of 5 determinations made on different solutions carried out at long intervals, sometimes months.

TABLE 3
Analytical results and standard deviation σ

Standard		Na ₂ O	K ₂ O	MgO	CaO	SrO	BaO	Total Fe as Fe ₂ O ₃	MnO
GH	σ	0.16	0.05		0.04			0.05	0.005
	this work	3.85	4.89	n.d.	0.72			1.38	0.05
	a)	3.83	4.78	0.07	0.68			1.30	0.05
GA	σ	0.15	0.12	0.07	0.06			0.14	0.005
	this work	3.62	4.10	0.95	2.51			2.78	0.085
	a)	3.57	4.03	0.99	2.48			2.77	0.09
GR	σ	0.14	0.10	0.07	0.11			0.09	0.005
	this work	3.79	4.61	2.31	2.41			4.02	0.06
	a)	3.80	4.50	2.40	2.50			4.05	0.06
Tl	σ	0.10	0.05	0.10	0.10			0.12	0.005
	this work	4.35	1.24	1.82	4.96			5.79	0.10
	b)	4.37	1.26	1.83	5.22			5.95	0.10
Chabazite Vallerano	σ					0.08			
	this work					3.92			
	c)					3.78			
Harmotome Andreasberg	σ						0.60		
	this work						20.14		
	d)						20.16		

- a) ROUBAULT, DE LA ROCHE et GOVINDARAJU (1966).
- b) SIGHINOLFI (1969).
- c) PASSAGLIA (1970).
- d) RINALDI [(personal communication): average value from the wet chemical analysis (20.18) and from the X-ray fluorescence analysis (20.14)].

In the same Table, there are the calculated standard deviation σ and the comparison with the values reported in literature.

In the GH standard the content in Mg has not been determined, since it is too low to be determined with this method. From the data of Table 2 we can observe that the method allows a good determination of all the elements and that the determinations made in different times never shift from the average value more than 3%.

CONCLUSIONS

The procedure above described is suitable for the analysis of silicates with a low content in Fe and Mg (zeolites, feldspars, feldspathoids) when we can get little material: if one can have at his disposal only a Perkin-Elmer mod 303 spectrophotometer an analysis with an amount of material less than that here advised is so far impossible.

If we consider the amounts of material needed for this analysis (10 mg or even only 5 mg), that required for the complete analysis can be restricted to only 20 mg when we dispose of TGA apparatus and X-ray fluorescence. In fact with the last one the Si/Al ratio on 20 mg of sample can be determined indestructively; these 20 mg of sample can be used further, a part for the H₂O determination with TGA and the other one for the cation determination with the method here described. To check the reliability of the analysis, remember that in the framework silicates the Al content can also be calculated from the content in alkalies in alkaline earths.

REFERENCES

- ALLAN, J. E. (1962): *A review of recent work in atomic absorption spectroscopy*. Spectrochim. Acta, 18, 605-612.
- ALTHAUS, E. (1966): *Die Atom-Absorption-Spektralphotometrie ein neues Hilfsmittel zur Mineralanalyse*. Neues Jahrb. Mineral., Monatsh, 9, 259-280.
- FARRAR, B. (1966): *Determination of calcium in ore and magnesium in rock samples*. Atomic Absorption Newsletter, 5 (3).
- PASSAGLIA, E. (1970): *The crystal chemistry of chabazites*. Amer. Mineral., 55, 1278-1301.
- ROUBAULT, M.; ROCHE, H. de la et GOVINDARAJU, K. (1966): *Rapport sur quatre roches etalons geochemique: granits GR, GA, GH et basalte BR*. Sci. Terre, 11, 105-121.
- SIGHINOLFI, G. P. (1969): *Determination of some major and trace elements in new standard rock samples by atomic absorption spectroscopic routine analysis*. Atti Soc. Tosc. Sci. Nat., 76, 312-325.
- SLAVIN, W. (1965): *An atomic absorption bibliography for 1964 and index to references*. Atomic Absorption Newsletter, 4 (2), 194-211.
- TRENT, D. and SLAVIN, W. (1964): *Determination of the major metals in granitic and diabasic rocks by atomic absorption spectrophotometry*. Atomic Absorption Newsletter, 3 (19).