

## *Quantitative Spectrochemical Analysis of Minor Elements in Silicates with Double Internal Standards*

By Hiroshi HAMAGUCHI, Rokuro KURODA and Ryokichi NEGISHI

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The spectrochemical procedures for determining a number of traces of elements in silicate rocks involve some difficult problems. The fact that many of the geochemical studies on the minor elements in the lithosphere have been carried out with a semiquantitative scheme, may be, in part, attributed to the troublesome problems associated with the accurate simultaneous determination of minor elements in silicate rocks. The main difficulty arises from the different rates of volatilization of the elements from the electrode cavity into the arc column.

Ahrens<sup>1)</sup> divided the minor elements into two groups, i. e. volatile and involatile group. For the elements of the volatile group which complete their distillation before or at the same time that the alkali metals complete theirs, Ahrens suggested a general arcing procedure with or without an internal standard. In the former case indium has been chosen as the internal standard for its volatility, satisfactory excitation properties and its extremely low concentration in most silicates. For the involatile group that includes all elements which emit their maximum line intensity after

the main phase of alkali metal distillation has subsided, one part of the sample was buffered with two parts of carbon powder containing palladium as the internal standard and the mixture was completely distilled with 7 amp. d. c. carbon arc. Shaw<sup>2)</sup> employed the total energy method for determining about 19 minor elements in silicate rocks. He also divided the subject elements into two groups according to the volatility difference of the elements, as was done in the case of Ahrens.

These schemes of quantitative spectrochemical analysis are rather tedious and even without the internal standard two arcing procedures are needed. The selection of suitable internal standards, buffer and excitation conditions may eliminate the necessity of separate arcing for volatile and involatile group. An attempt was made to determine the minor elements differing much in the volatilization rates, i. e. lead, gallium, tin, chromium, vanadium, cobalt, nickel and scandium in silicates in a single arcing procedure by using double internal standards. As a result a method was established without serious loss of precision and with reasonably high sensitivities.

1) L. H. Ahrens, "Quantitative Spectrochemical Analysis of Silicates," Pergamon Press, London (1954), p. 74.

2) D. M. Shaw, *Bull. Geol. Soc. Amer.*, **65**, 1151 (1954).

### Experimental and Results

**Equipment and Procedure.**—To establish the procedure the densitometric and the logarithmic sector method were used. Although the logarithmic sector method is rather obsolete, some special advantages are obtained by this method. The intensity ratio of subject to internal standard lines is generally independent of conditions of exposure,

slit width, development and plate calibration. The time required for the analysis is shortened by a factor of 2 or 3, compared with the densitometric method. No expensive densitometer is necessary.

Equipment and excitation conditions are listed in Table I for both calibrating methods.

**Standard, Internal Standard and Buffer.**—As the object for analysis is naturally occurring silicates, the general chemical composition and physical

TABLE I. EQUIPMENT AND EXCITATION CONDITIONS

Subject	Densitometric method	Logarithmic sector method
Spectrograph	Shimadzu-QL170 Littrow type quartz spectrograph	Hilger E <sub>2</sub> , medium type quartz spectrograph
Power source	Continuous a. c. arc supplied from the Pfeilsticker type intermittent a. c. arc source unit with radiofrequency spark.	D. c. arc supplied from commercial unit with full wave rectification with radio frequency initiating spark.
Power	8 A	5 A
Working voltage	210 V.	100 V.
Preburn	None	None
Exposure	60 sec.	40 sec.
Arc gap	3 mm.	3 mm.
Electrodes	Upper: 1/4 in. diameter graphite rod (National Carbon Co., "Special Grade") The end is a 30° cone. Lower: 1/4 in diameter rod containing an axial crater 1/16 in. diameter, 1/6 in. deep. (National Carbon Co. "Special Grade")	Upper (cathode): 5 mm. diameter graphite rod. (Shimadzu Manufacturing Co.) The end is a ca. 60° cone. Lower (anode): 5 mm. diameter graphite rod containing an axial crater 3 mm. diameter, 2 mm. deep (Shimadzu Manufacturing Co.)
Spectral region	2650 to 4000 Å	ca 2300 to 4500 Å
Sector	Five step sector: Step ratio 1:2	Logarithmic sector
Slit width	30 microns	20 microns
Densitometer	Rigaku Denki Co. Ltd. MD-2 type.	None

TABLE II. INTERNAL STANDARDS AND ANALYSIS LINES

	Element	Wavelength	Excitation potential, eV.	Analysis range, p.p.m.
Volatile group	Sb (internal standard)	2877.915	5.3	
	Ga	2943.637	4.3	10~300 (L) 10~300 (D)
	Pb	2833.069	4.4	30~500 (L) 10~1000 (D)
	Sn	3175.019	4.3	10~3900 (D)
Involatile group	Pd (internal standard)	3242.703	4.6	
		3481.152	4.8	
	Sc	3613.836	10.1	
	Cr	3593.488	3.4	5~500 (D)
	V	3183.982	3.9	10~400 (L) 10~1000 (D)
	Ni	3414.765	3.6	5~300 (L) 5~500 (D)
	Co	3453.505	4.0	5~300 (D) 5~1000 (L)

L: Logarithmic sector method

D: Densitometric method

properties of the standards should approximate as closely as possible those of the unknown ones. Thus, a potash feldspar was used as a base material of the standards for nickel, chromium, cobalt and scandium. It was also possible to use a serpentinite and two specimens of granite as the base materials for lead, gallium, tin and vanadium. Since traces of gallium were apparent on the granite-base material, the granite was analyzed for gallium fluorometrically (Sandell)<sup>3)</sup> and a correction was made for the residual impurity of gallium.

For the simultaneous determination of elements with the arc excitation, it is essential to volatilize all elements in approximately the same rate from the electrode cavity. The addition of carbon causes the elements of widely different volatilities to evaporate simultaneously. Though it would be possible to suppress considerably the selective volatilization with the addition of a large amount of carbon, some loss of sensitivities will result in general. In the present work 1:1 ratio of carbon to each of standard and sample was selected to maintain the highest sensitivities for most elements. In the presence of such a small amount of carbon buffer the choice of internal standard is highly critical. Consequently, two internal standards were used to assure the similarity in volatilization rates for the selected pairs of subject and internal standard elements; antimony(III) oxide for the elements of volatile group i. e., lead, tin and gallium, and palladium black for the elements of involatile group i. e., nickel, cobalt, chromium, vanadium (and scandium). The carbon powder as the buffer was previously well mixed with antimony(III) oxide and palladium black to give the concentrations 0.80 per cent for antimony(III) oxide and 0.04 per cent for palladium. Selected internal standard

and analysis lines are listed in Table II with their excitation potentials and analysis ranges.

**Procedure for Constructing Working Curves.**—To one part of the final standard one part of the carbon powder prepared as described in the previous section is added and the mixtures are excited according to the analytical conditions listed in Table I. The spectrograms are recorded on Fuji Process Hard plate. The plate is developed for 3 min. in Fuji FD 31 developer, placed in a 3% acetic acid stop bath for 30 sec., and fixed in Fuji Fixer for 5 min. After washing for 20 min. with running water, the plate is air-dried.

In the case of the densitometric method, the intensity ratios of analysis pairs were obtained by a self-calibrating method. The working curves are

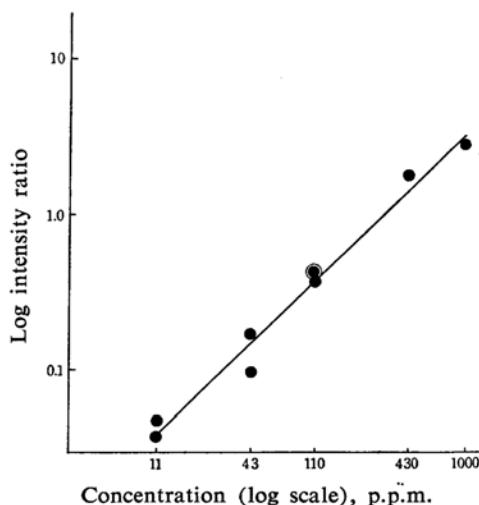


Fig. 2. Working curve for vanadium (Densitometric method).

$$\frac{V\ 3183.982}{Pd\ 3242.703}$$

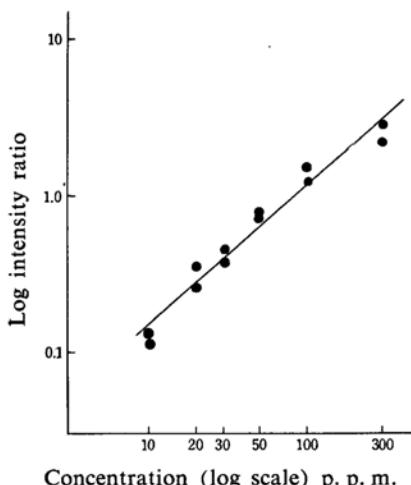


Fig. 1. Working curve for gallium (Densitometric method).

$$\frac{Ga\ 2943.637}{Sb\ 2877.915}$$

3) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd. Ed., Interscience Publishers, Inc., New York (1950), p. 326.

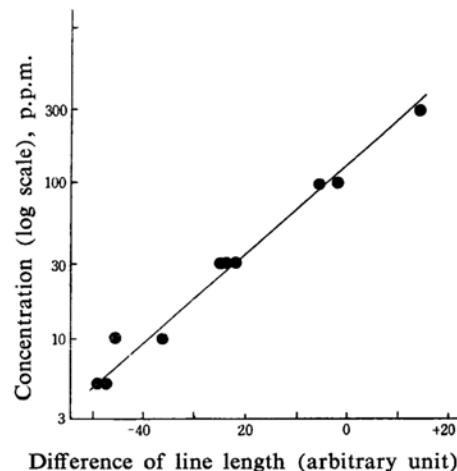


Fig. 3. Working curve for cobalt (Logarithmic method).

$$\frac{Co\ 3453.505}{Pd\ 3481.152}$$

TABLE III. PRECISION DATA  
D: Densitometric method, L: Logarithmic sector method

Sample	Subject element	Sx*		Mean p.p.m.		Confidence limit, 68%		Concentration range previously reported p.p.m.	Recommended value by Ahrens (1954) p.p.m.	Analysis line pair	
		D	L	D	L	D	L			D	L
W-1	Ga	0.038	0.124	13.6	18.4	14.8 ~12.5	24 ~13	11~20	14.5	Ga 2943.637	Ga 2943.637
W-1	Co	0.075	0.080	55	53	65 ~46	63 ~44	20~55	36	Sb 2877.915	Sb 2877.915
Potash-feldspar	Pd	0.040	0.039	177	164	194 ~161	180 ~150	6~7	—	Co 3453.505	Co 3453.505
W-1	V	0.047	0.042	236	160	263 ~212	176 ~145	170~340	240	Pd 3481.152	Pb 3481.152
Biotite-gneiss	Sn	0.088	0.084	48	—	59 ~39	—	—	—	Pb 2833.069	Pb 2833.069
W-1	Cr	0.059	—	139	—	159 ~121	—	100~150	130	Sb 2877.915	Sb 2877.915
W-1	Ni	0.042	0.110	59	84	65 ~54	106 ~65	47~150	90	V 3183.982	V 3183.982
W-1	Sc	0.119	—	280	—	368 ~213	—	15~51	37	Pd 3242.703	Pd 3481.152
										Sc 3613.836	Sc 3613.836
										Pd 3242.703	Pd 3481.152

\* Sx is the standard deviation of log concentration of a sample for its single analysis.

prepared by plotting the logarithm of the intensity ratios against the logarithm of the concentrations of the elements. Typical results are shown in Figs. 1 and 2.

In the case of the logarithmic sector method, the ratio of intensities between two lines is measured by their difference in lengths. The working curves are obtained in the same manner as by the densitometric method. A typical working curve is shown in Fig. 3.

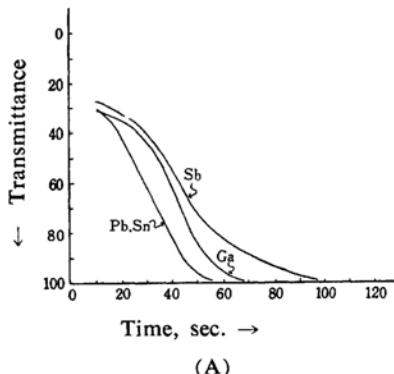
The procedure for sample analysis is almost the same as that for the standards.

**Precision.**—The precision of the methods was evaluated from the working curve data and from the standard diabase W-1 (U. S. Geological Survey) analysis, following the treatment of the statistical method described by Shaw and Bankier<sup>4)</sup>. The results are listed in Table III. As tin and lead were not detected in the standard diabase W-1, a gneiss and a potash feldspar were analyzed instead of the standard W-1.

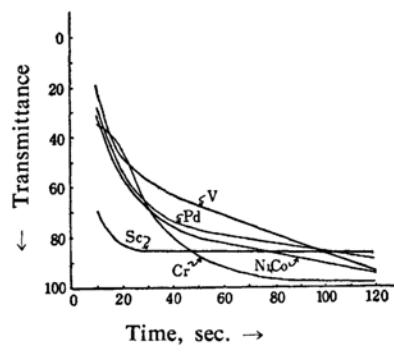
### Discussion

The procedure presented could be extended to cover further species of minor elements except for extremely involatile elements, e.g., rare earth elements.

To check the accuracy of the methods, the ranges previously reported and the recommended values concerning the contents of minor elements in the standard diabase W-1 are also listed in Table III. Satisfactory agreement is observed with the recommended values by Ahrens except for cobalt, nickel and scandium.



(A)



(B)

Fig. 4. Volatilization curves for the elements of volatile and involatile groups.

A: Volatile group

B: Involatile group

4) D. M. Shaw and J. D. Bankier, *Geochim. et Cosmochim. Acta*, 5, 111 (1954).

Smales<sup>5)</sup> has found the values 54, 52, 50, 46, 46, 45 p. p. m. Co for the W-1 with the radio-activation method of analysis which may be regarded at present as the most reliable tool for the trace analysis. The present figure for cobalt agrees rather well with the values obtained by Smales. The nickel content of the W-1 was also obtained by Smales, who gave the values of 78, 78, 76, 73, 71, 63, p. p. m. Ni. The recommended value for nickel might be somewhat higher. The present figure for scandium is remarkably high and probably in error. The cause may be attributed to the matrix effect depending on the difference in chemical composition between the potash feldspar used as a base material for the standards and the analyzed diabase W-1. The analysis line Sc II 3613.836 is an ionic line having high excitation potential (10.1 eV.) and its intensity may be largely suppressed in the low temperature arc prevailing in the excitation of the alkali-rich feldspar. The low temperature arc also accelerates the selective volatilization of scandium remarkably, as illustrated in Fig. 4. For other elements the matrix effect may not be remarkable, as judged from the comparison of given data with the recommended value by Ahrens in Table III. The matrix effect on scandium can be completely eliminated by the addition of a large amount of carbon buffer, at least three times the weight of each standard and sample, as pointed out previously by Hamaguchi and coworkers<sup>6)</sup>. The requirement for the establishment of highly sensitive methods obliges us to compromise with a 1:1 weight ratio of each standard or sample to the carbon buffer. Under this circumstance the

volatilization trends of the subject and the selected internal standard elements are illustrated in Fig. 4. Reasonably parallel volatilization trends are found for the pairs of the subject element and its internal standard. However, the volatilization curve for scandium differs significantly from that for palladium, as described previously.

Using the medium type spectrograph, available analysis lines are limited because of the rather complex spectrum of silicate rocks. Especially, highly sensitive analysis of tin is practically impossible owing to the coincidence of its sensitive lines with interfering lines. The entire coverage of concentration range of chromium encountered in silicate rocks is also impossible even with the utilization of several spectral lines. Thus the establishment of procedure for chromium and tin with the medium type spectrograph was not attempted.

### Summary

Two internal standards have been used in the spectrographic analysis of silicates, antimony(III) oxide for volatile elements and palladium black for the involatile group. The former was used as the standard for the determination of gallium, lead and tin, and the latter for the determination of nickel, cobalt, chromium, vanadium and scandium. A medium spectrograph is not suitable for the determination of chromium or tin, and scandium did not volatilize in a manner parallel to the palladium but it was possible to obtain reasonable results for the other elements.

Department of Chemistry  
Faculty of Science  
Tokyo University of Education  
Koishikawa, Tokyo

5) A. A. Smales, *ibid.*, 8, 300 (1955).

6) H. Hamaguchi, K. Tomura and R. Kuroda, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, 79, 504 (1958).