Emission spectrographic technique for the quantitative determination of trace elements in granitic rocks

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Abstract. An emission spectrographic technique was developed to estimate 16 trace elements in some samples of Egyptian granite. The detection limits were: 0.1 ppm for Pb, Ba, Mo, Cu, Cr, Yb and Ni, 0.3 ppm for Sn, Ga and Be, 1 ppm for Co, Sc and V, 3 ppm for Bi and Y and 10 ppm for La. The relative deviation of the two-thirds limits ranges between ± 1.5 and ± 24.7 .

Keywords. Emission spectrography; granitic rocks; trace elements.

1. Introduction

Crystalline rocks, including igneous and metamorphic types, constitute more than 95 % of the earth's crust. Granites are the most common igneous rocks. Many valuable ore deposits are genetically related to granitic rocks. Therefore, the determination of trace elements in granite is essential for both genetic and economic reasons. The technique of spectrographic analysis of granites has drawn the attention of a great number of authors (Ahrens and Taylor 1961; Sighinolfi 1966; Peter 1969; Fleischer 1972; Gokun 1975; Watson and Russell 1978). Granites are coarse-grained acid igneous rocks which are mainly composed of alkali feldspars, acid plagioclases, mica and some other accessory minerals. Granites contain high SiO_2 content (usually above 65 %) and are therefore considered acidic and responsible for the dense silica bands in spectrographic analysis. Besides, the increased ratio of alkalis perceptibly lowers the arc temperature. These factors give rise to a dense background and low sensitivity of the analysed elements.

The aim of the present work is to develop a specific technique by which arcing conditions of granite are improved and sensitivities of the elements increased.

2. Experimental

The emission spectrographic technique was developed to determine 16 trace elements in some samples of Egyptian granite using a Zeiss Jena grating spectrograph. Graphite was used as a buffering material while CdF_2 was added as a carrier. The current intensity was 1.4 A, time was 50 sec and Pd was used as the internal standard for most elements.

The optimum conditions of spectrographic analysis of granite can be achieved by studying some factors. These are discussed in this paper.

2.1 Electrode type

For practical reasons, only rod-type graphite electrodes were experimented. Four forms of each of the sample and counter electrodes were alternatively tested. These forms are similar to the Ringsdroff types (RW0006, RW0021, RW0068, RW0070, RW0083, RW0028 and RW0067) with tip angles 20° and 30° . The best forms that gave good burning conditions and high line intensities are those similar to the sample form RW0021 and counter form RW0028. The electrodes (electrode gap: 3.5 mm) were shaped from JMC specpure graphite rods. These are shown in figure 1 and are given the

Figure 1. Electrode shape.

symbols 1, 2, 3 and 4 for sample electrodes (anode) and A, B, C and D for counter electrodes (cathode) respectively.

2.2 Current intensity

According to Bowmans (1966) the intensities of the spectral lines are influenced by the arc current. It is important to obtain the best current intensity to have a smooth burning arc and a stable arc spot.

The dependence of the current densities of the test lines: Ba: 455·404 nm, Ti: 337·280 nm, Cr: 425·434 nm, Zr: 339·198 nm, Zn: 328·233 nm, V: 437·924 nm, Pb: 283·307 nm, Mo: 317·035 nm, Be: 213·042 nm, Yb: 328·937 nm and Y: 332·788 nm on the arc current from 6 to 15 A is represented graphically in figure 2. It is clear that the line densities increase gradually with current intensity. Moreover some of the rare earth elements such as Y and Yb did not appear except at a high current intensity (12 A). The best practical current intensity was 14 A.

2.3 Buffers and carriers

A wide range of additives was used. They include graphite powder, alkali and alkaline earth carbonates and halides, oxides of Mg, Zn, Zr and Ga as well as heavy metal halides (Rasmy 1983) in varying ratios. It was observed that the best buffer and carrier are graphite powder and cadmium fluoride respectively. The ideal mixing ratio of sample, graphite and CdF_2 is 2:2:1. Figure 3 shows a moving plate study at 10 sec intervals for three cases, from which the following can be concluded:

- (a) When the sample is arced alone, the distillation period exceeds 160 sec till the non-volatile elements, e.g. Y, attain their peaks.
- (b) When a mixture of equal amounts of the sample and graphite powder is arced, the distillation period is rather shortened and arcing is improved. However, some elements like Y and Mo exhibit double peaks.
- (c) When the ideal mixture of the sample, graphite and CdF_2 is arced, the distillation period is greatly shortened. Each element exhibits one peak and all peaks appear during the first 50 seconds of arcing. Besides, densities of spectral lines of the elements are perceptibly increased. It seems that the most suitable exposure time is 50 sec, by which time a reasonable background intensity is developed.

2.4 Sample preparation

Samples of granite, each about 2 kg, were crushed by hammering. Small representative samples were prepared by quartering method and ground to about 200 mesh using an agate mortar. Contamination was always avoided.

2.5 Synthetic standards

A matrix was prepared, the composition of which is close to the average composition of granite given by Wedepohl (1969). The small content of Mn, Ti and P oxides was excluded as P_2O_5 was not provided as a specpure chemical while Mn and Ti are later added as a part of the trace elements to be analysed. After thorough mixing of the matrix components, they were sintered in a platinum dish at 1200°C for 6 hr, cooled and ground to 200 mesh. The final composition of the matrix was expected to be:

Figure 2. Current effect.

72.91 % SiO_2 , 14.02 % Al_2O_3 , 2.56 % Fe_2O_3 , 0.53 % MgO , 1.35 % CaO , 3.12 % Na_2O and 5.52 % K_2O .

The first standard, containing 3000 ppm of each of the trace ingredients, was prepared from the calculated amount of JMC Spectromel No. 1 mixture containing 1.18 % of 53 different trace elements, to which the corresponding amounts of the oxides of Y, La and Yb are added and finally diluted with the weighed amount of the matrix. From this first standard, other standards containing 1000, 300, 100 . . . down to 0.1 ppm of the trace elements were prepared by successive dilution with the matrix.

2.6 Internal standard

An amount equivalent to 100 ppm palladium, as chloride, was added to each of the samples and standards for internal standardization. The intensities of the less volatile elements (Ahrens and Taylor 1961) are related to that of Pd. No other internal standard could be used for volatile elements including Ga, Pb, Cu and Sn. They were related to their adjacent background.

Figure 3. Time-intensity diagrams of granite standard with about 100 ppm traces showing the effect of buffer and carrier: (A) Standard alone, (B) Standard: Buffer 1/1, (C) Standard: Buffer: CdF_2 2/2/1.

2.7 Slit width adjustments

The slit width of the spectrograph is of great importance when the background effect is considered. The background intensity, due to continuous radiation, increases with slit width. Therefore the slit must be adjusted to give maximum line intensity with reasonable background. The granitic sample was arced using variable values of slit width such as 10, 12, 14 and 16 μ . It is clear from the results obtained (figure 4) that the slit width of 12 μ was most preferable, considering the exposure time of 50 sec and other conditions.

2.8 Calibration and evaluation

Calibration curves were drawn by plotting blackness D of some Fe spectral lines against their log intensities using a six-step diminisher with 100, 40, 16, 10, 6 and 4% transmissions. Four curves were drawn covering the whole wavelength range 282–456 nm (figure 5). The background correction was made using the relation given by Mika and Torok (1974).

Figure 4. Effect of slit width.

Figure 5. Sample of the calibration curves.

Working curves were drawn between log intensity ratio and log concentration (figure 6). The trace elements content of the analyzed granite samples and its implications were discussed in detail by El Bialy *et al* (1984). The analytical lines and detection limits of the analysed elements of our work and that of Gokun (1975) (the best available compatible work) are shown in table 1.

Table 1 shows that the improvements in the minimum detection limit are as follows: 1000 for Pb, Mo, Cu, Yb, Ni, Cr and Ba, 333.33 for Ga and Be, 100 for Co, Sc and V, 33.33 for Y and 16.66 for Sn.

2.9 Precision and accuracy

Precision expressed as the standard deviation S and the relative deviation C at the two-thirds limits is shown in table 2 using data obtained by arcing granite rock standard G_2 , distributed by the U.S. Geological survey, as an unknown sample. The standard deviation S ranges between ± 0.02 and ± 1.9 ppm while the relative deviation C ranges

Figure 6. Samples of working curves for the determination of Pb, Sn, Mo and Ga.

Table 1. Detection limits and wavelength of spectral lines of the analysed elements of the present work compared to that of Gokun (1975)

Element	Wave-length (nm)	Detection limit (ppm)		Element	Wave-length (nm)	Detection limit (ppm)	
		Present work	Gokun (1975)			Present work	Gokun (1975)
Pb	283.307	0.1	100	Ga	294.364	0.3	100
Mo	317.035	0.1	100	Be	313.042	0.3	100
Cu	327.396	0.1	100	Co	345.351	1	N.D.
Yb	328.937	0.1	N.D.	Sc	424.683	1	100
Ni	341.477	0.1	100	V	437.924	1	100
Cr	425.434	0.1	100	Bi	306.772	3	N.D.
Ba	455.404	0.1	100	Y	332.788	3	100
Sn	283.999	0.3	5	La	433.347	10	N.D.

N.D. not detected.

Table 2. Results of analysis of granite rock standard USGS-G₂ together with standard deviations (S) and relative deviation (C)

Element	Flanagan (1973)	Present work	S	C
Be	2.6	3.1	0.70	24.7
Ga	22	18	1.9	11.5
Cu	11.7	10.27	1.58	13.8
Mo	0.36	0.5	0.06	11.5
Y	12	11.1	1.69	15.25
Yb	0.88	0.8	0.15	18.8
Sn	1.5	1.33	0.02	1.5
Cr	7	5.3	0.77	14.5
Sc	3.7	3.22	0.16	5.08

between ± 1.5 and ± 24.7 . As shown in table 2, the present values of trace elements in G₂, are in good agreement with earlier values (Flanagan 1973). This shows that the accuracy of the method is satisfactory. Moreover the reported relative deviation values in table 2 for all the elements are much better than the value of 25% given by Gokun (1975).

References

- Ahrens L H and Taylor S R 1961 *Spectrochemical analysis* (London: Addison-Wesley) 2nd edn
 Bowmans P W J M 1966 *Theory of spectrochemical excitation* (London: Hilger Watts) pp 192
 El Bialy A, Rasmy M N, Guirguis L A and Moussa W 1984 *Bull. Nat. Res. Council (Cairo)* (accepted)
 Flanagan F J 1973 *Geochim. Cosmoch. Acta* **37** 1189
 Fleischer M 1972 *Science* **199** 6
 Gokun V N 1975 *Tr. Akad. Nauk USSR* **35** 105
 Mika J and Torok T 1974 *Analytical emission spectroscopy Fundamentals (Hung)*, Eng. Transl. P A Floyd (London: Butterworth)
 Peter S 1969 *Math. Natur. Wiss. Reihe* **1**, 8, 8 971
 Rasmy M 1983 *Bull. Nat. Res. Council (Cairo)*
 Sighinolfi G P 1966 *Period Minerol Rome* **35**, 3 769
 Watson A F and Russell G U 1978 *Spectrochim. Acta part 2*, **33**, 5 173
 Wedepohl K H (ed.) 1969 *Data of geochemistry* (Berlin: Springer) Vol. 1