Spectrochemical behaviour of scandium and yttrium in silicate rocks

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Dedicated to Corresponding Member M. Zikmund, in honour of his 60th birthday

The spectrochemical determination of the investigated elements in silicate rocks is normally performed in one procedure together with the determination of other microelements. The most intensive spectral lines of Sc and Y, which are of ionic character, are compared with atomic lines of the internal reference element (Pd).

In the present work a procedure enabling the treatment of scatter diagrams obtained using results of parallel determinations of contents of the above elements and further elements giving atomic spectral lines in a set of granitoid and basic rock samples is described.

On the basis of the obtained results the sense of some parameters of scatter diagrams is cleared in relation to the attained precision of the determination and in regard to the character of the measured spectral lines, as well as to the changes in the composition of the matrix.

Спектрохимическое определение скандия и иттрия в силикатных породах обычно проводится совместно с определением других микроэлементов. Наиболее интенсивные линии Sc и Y ионного характера и они сравниваются с атомными линиями элемента внутреннего сравнения (Pd).

В настоящей работе описывается ход обработки диаграмм рассеяния полученных из параллельных определений указанных и других элементов, которые дают атомные спектральные линии в серии образцов гранитных и основных пород.

На основании обнаруженных результатов объясняется значение некоторых параметров диаграмм рассеяния в отношении к достигнутой точности определения, характеру измеряемых спектральных линий и изменениям состава матрицы.

As concerns the occurrence in the nature, scandium and yttrium are typical representatives which do not form more significant accumulations in spite of the

fact that according to their abundance they belong to the first half of all elements. The knowledge of scandium and yttrium contents in geological materials, mainly in rocks, is of extreme interest for the solution of some genetic problems. The spectra of Sc and Y are comparatively poor in lines, but they contain some intensive lines [1] enabling a relatively good detection power sufficient for direct spectrochemical determination of these elements in geological materials [2]. The mentioned spectrochemical properties make it normally possible to determine these two elements in silicate rocks spectrochemically in one procedure together with other currently analyzed microelements without application of any special techniques.

Regarding to the mentioned claims and owing to the relative simplicity, different spectrochemical procedures for the determination of scandium and yttrium in silicate rocks have already been described [2—6].

From the point of view of their volatility, both the elements are not very volatile and evaporate practically simultaneously [1]. Lanthanides are recommended as internal reference elements [7]; lanthanum [1] and zirconium [2] have also been used. Palladium has been used with good results as internal reference element, too [4]. It evaporates simultaneously with Sc and Y as proved [8] by using evaporation relation curves [9, 10]. Apart from these properties which are available for the choice of palladium as internal reference element for the determination of scandium and yttrium, the following problem must be taken into account: The most intensive spectral lines of Sc and Y ensuring the necessary detection limit are of ionic character [11], whereas normally used palladium reference lines (311.4 and 342.1 nm) correspond to the radiation of its atoms. This situation makes impossible to apply the calculations [12] describing the homology of such pairs of spectral lines and their analytical use is normally discouraged. Despite this situation no comprehensive study pointing directly to the spectrochemical behaviour of scandium and yttrium has been performed yet.

Experimental

For the presented evaluation of the spectrochemical determination of scandium and yttrium in silicate rocks we chose two following kinds of samples: 50 granites and 50 basic rocks. In the experimental technique we started from the procedures described for granites [6] and for basic rocks [5].

In comparison with the given conditions we obtained better results after the change of analytical spectral lines.

In the cited papers the line from visible region of the spectrum Sc II 424.68 having the ionization potential 3.23 eV was used and europium was used as internal reference element. In the present work we replaced it by the line Sc II 335.37 with the ionization potential 4.01 eV. Palladium line Pd I 342.12 was used as reference. The original line ensured a better detection limit which, however, was not necessary for the analysis of rock samples. On the

other hand, the necessity of separate taking of visible spectrum, as well as the use of another reference element was disadvantageous.

For the determination of yttrium we replaced the Y II 371.02 line (3.52 eV) by the line 332.79 (4.14 eV) to which the same palladium line Pd I 342.12 was used as reference. The original line lay in the longwave ultraviolet region where cyanogen bands could interfere and special calibration of the photographic emulsion was necessary.

For the statistical evaluation also the intensities of Pd I 311.40 line and the lines V I 318.54 and Ni I 341.47 were measured.

Statistical procedure

For the statistical evaluation of the homology of analytical spectral line pairs the parameters of their scatter diagrams [12—14] have often been used [15]. They are normally calculated from the results obtained from many times repeated takings of spectra of the same, sometimes only randomly chosen sample. The whole procedure is long and laborious.

A procedure enabling the construction of scatter diagrams from the results of normally made parallel measurements on different current samples of one kind of analyzed material was therefore suggested [16] as addition to the statistical treatment of such results [17]. In the present work we describe the full procedure for the calculation of parameters of the scatter diagrams on the basis of results of parallel measurements. The achievement and full evaluation of these data is so accessible also in laboratories where there is no time and funds to make repeated measurements on one sample but many parallel analytical results of different current samples are available.

In order to use the results of parallel measurements performed on different samples the differences of Y values between the first and the second measurement of the same spectral line in one sample are formed

$$\delta_a = Y_{1a} - Y_{2a} \qquad (1)$$

The distribution of δ values can be described with a high degree of accordance by the laws of normal gaussian distribution as it can be seen in case of Sc in basic rocks (Fig. 1).

The difference of logarithms of spectral line intensities corresponding to the logarithm of their relation does not depend on their absolute intensity values and according to the *Lomakin* and *Scheibe*'s equation [18, 19] also on the absolute concentration value. It only depends on the reproducibility of the procedure. The results obtained with different samples having different concentration of the element in question can be therefore used for the estimation of the precision [17]. Owing to the gaussian distribution of the δ value corresponding to the difference of elements belonging to two similar even non gaussian distributions [23], equations for normal distribution can be applied for its statistical description. The distribution
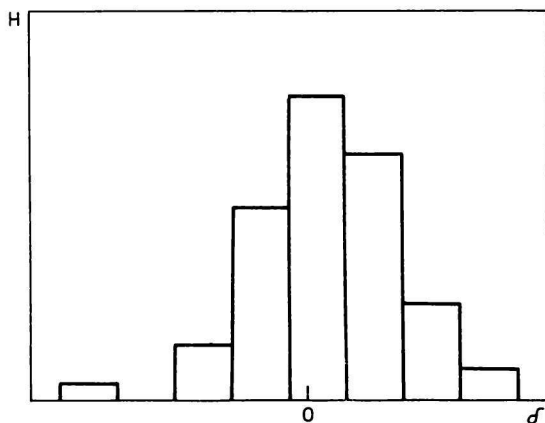
Fig. 1. Distribution of δ values.

of simple Y values need not be of gaussian character [20—22] and the parameters of "classical" scatter diagrams calculated using the equations for the normal distribution can therefore be loaded by systematical errors.

From two δ values obtained for different spectral lines $\Delta\delta$ values corresponding to ΔY values can be calculated, where

$$\Delta\delta = \delta_a - \delta_r \tag{2}$$

The corresponding standard deviations for δ values (as well as for the $\Delta\delta$ value) can be estimated using the equation [17]

$$s = \sqrt{\frac{\sum_{i=1}^{n} \delta_i^2}{2n}} \tag{3}$$

The calculation of standard deviation is comparatively simple and included in software of practically any computer, and even many pocket calculators. Not so easy is the calculation of the covariance $s_{a,r}$ performed according to the equation

$$s_{a,r} = \frac{1}{2n} \sum_{i=1}^{n} (\delta_a \delta_r)_i \tag{4}$$

Special programs are necessary for its solution. To calculate the covariance we used the following equation

$$s^2 = s_a^2 + s_r^2 - 2s_{a,r} \tag{5}$$

containing apart from the wanted covariance only already easily estimated standard deviations. The other parameters of the scatter diagrams were calculated as usual [23].

Table 1

Results of statistical treatment

Spectral lines	Procedure	Granitoid rocks			Basic rocks		
		r	ω	$s_{\Delta Y}$	r	ω	$s_{\Delta Y}$
Sc II 335.37/Pd I 342.12	a	0.5977	1.4889	0.0244	0.9269	0.6660	0.0286
	b	0.5982	1.4858		0.9124	0.6600	
Y II 332.79/Pd I 342.12	a	0.5953	1.9815	0.0287	0.8420	0.5711	0.0373
	b	0.5970	1.9785		0.8416	0.5711	
V I 318.54/Pd I 311.40	a	0.9050	1.4096	0.0187	0.8450	0.9771	0.0283
	b	0.9006	1.4124		0.8452	0.9768	
Ni I 341.47/Pd I 342.12	a	0.7210	1.6394	0.0232	0.9418	0.9859	0.0217
	b	0.7209	1.6369		0.9417	0.9863	
Pd I 311.40/Pd I 342.12	a	0.8312	1.3436	0.0166	0.9496	0.7918	0.0222
	b	0.8319	1.3423		0.9503	0.7923	

a) Proposed procedure; b) original procedure.

Results and discussion

The obtained results of the most important statistical parameters for different line pairs measured in granitic, as well as basic rock matrix are gathered in Table 1.

The values of the correlation coefficients (r) and orthogonal regression coefficients (ω) were calculated using the covariances obtained by the proposed procedure from eqn (5) as well as by the original procedure. The equality of the results proves the good applicability of the proposed simpler procedure.

In Table 1 there are results for mixed ion—atom line pairs for the case of the Sc and Y determination compared with the results for atom—atom line pairs for V and Ni determination and the pair Pd I/Pd I in which case no differences in evaporation can be manifest.

As it can be seen the correlation coefficient depends more on the composition of the matrix than on the type of the line pair. The same can be observed also for the value of the orthogonal regression coefficient.

The most important role among the presented parameters is played by the standard deviation of the $\Delta\delta$ value which is in direct connection with the error of the precision.

As it can be expected, the best precision is obtained for the pair formed from the lines of the same element that is palladium. The precision obtained for the Sc and Y determination performed using ion lines combined with atomic lines of palladium is against the expected behaviour in general significantly the same as the precision of the vanadium and nickel determination performed using atomic line pairs. There are also no significant differences in the precision as a function of the matrix composition despite the mentioned differences of parameters of corresponding scatter diagrams. These results are in accordance with our earlier statements [16, 24] that the parameters of scatter diagrams for the valuation of analytical applicability of the investigated spectral line pair are to be used with extreme care.

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