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**A NEW SPECTROGRAPHIC PROCEDURE
OF THE DETERMINATION OF SODIUM AND POTASSIUM
IN SILICATE MINERALS**

A b s t r a c t. A new spectrographic method of the determination of sodium and potassium in silicate minerals has been proposed. It does not require dissolution of the solid sample, is quite rapid and simple and may be applied to the determination of both alkali metals in the concentration range 0.1–10.0 per cent.

INTRODUCTION

The determination of alkali metals in rocks and minerals calls for rapid and simple methods of analysis. These conditions are met by emission spectroscopy with $d-c$ arc excitation of samples and photographic recording of spectra (Rusanow 1954, Ahrens and Taylor 1961).

In elaboration of the analytical procedure we chose two standard "IGEM" rock samples as objects of our study, namely myaskite "MIW-I" (hornblende nepheline syenite) and granodiorite "Rizhik". The chemical composition of the specimens of both rocks assayed are set up in Table 1. These data were averaged over the results obtained by various methods in an interlaboratory assay (Chitrow, Kortman 1969). They are referred to in this paper as the expected values.

In order to determine sodium and potassium in silicate minerals the direct excitation in a smooth $d-c$ arc of powdered samples from graphite electrode craters has been applied. The resulting spectra are recorded on photographic plates sensitive in the UV region (Schweder 1969). In this region are situated analytical Na and K lines which are suitable for the evaluation of higher concentrations of both elements (Borowik 1953, Dennen and Fowler 1955). Lithium and rubidium were chosen as internal standards for sodium and potassium respectively (Canney 1952).

As the response function to be maximized in the optimization process of the analytical procedure the difference ΔS between intensities of an analytical line and reference (a line of the internal standard or background) was assumed. The

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Chemical composition of investigated rock specimens (wt. %)

Table 1

Component	Granodiorite	Myaskite	Component	Granodiorite	Myaskite
SiO ₂	64.00	57.96	K ₂ O	3.93	6.13
Al ₂ O ₃	15.40	21.69	(K 3.24)	(K 5.08)	
Fe ₂ O ₃	2.09	1.46	TiO ₂	0.54	0.41
FeO	2.86	1.48	MnO	0.158	0.118
MgO	1.39	0.38	P ₂ O ₅	0.230	0.063
CaO	4.03	1.17	CO ₂	0.16	0.06
Na ₂ O	3.25	8.55	S (total)	0.022	0.016
	(Na 2.40)	(Na 6.34)	F	0.070	0.083

decision variables were: current, exposure time, composition of the diluting mixture and electrode shape.

EXPERIMENTAL

Preparation of analytical and standard samples

The weighed samples of finely ground rocks (myaskite and granodiorite) were diluted in the ratio 1:399 with a mixture composed of graphite powder, caesium chloride, rubidium chloride and lithium nitrate. The percentage content of the components in the diluting mixture is presented in Table 2. After dilution the sample was ground in an agate mortar for 20 min. The resulting preparation was used to fill up electrode craters. Average mass of the preparation used for one excitation amounted to 10 mg.

The standards were prepared with graphite powder as matrix. In order to diminish interelement effects a mixture of 70% SiO₂, 25% Al₂O₃, 4% CaO, 1% MgO, named "synthetic mineral", was added to each standard. The components of the synthetic mineral were mixed and ground in an agate mortar, calcinated at 400°C for ca. 4 h and then once more ground in an agate mortar. The synthetic mineral was diluted in exactly the same way as analytical samples with the same diluting mixture (see Table 2).

To the weighed portions of the resulting mixture measured volumes of the standard NaCl and KCl solutions were instilled in order to obtain solid standards of 0.006, 0.009, 0.012 and 0.015 per cent content of sodium and potassium. The standard NaCl and KCl solutions were prepared by the dissolution in distilled water of weighed portions of the calcinated salts. As the graphite powder is not wettable by water, each portion of the mixture used for the preparation of standards

Table 2
Dilution parameters

Dilution mixture	4% CsCl, 0.1% LiNO ₃ , 0.05% RbCl, 95.85% graphite powder SU-601 (Topolčany)
Dilution ratio of analytical samples and of the "synthetic mineral" in the standards	1:399

was wetted by several drops of acetone prior to the instillation of NaCl and KCl solutions. Then, after drying at 100°C, the standard preparations were carefully ground in an agate mortar for 20 min. They were subsequently used to fill up electrode craters.

All the reagents used were spec. pure and the vessels made of quartz. Only water bidistilled from quartz apparatus was used.

The spectrographic analysis

In order to exclude possible coincidences of analytical lines with spectral lines of other elements (e.g. zinc) a spectrograph of high dispersion was used equipped with the standard grating of 651 lines per 1 mm. The reciprocal linear dispersion of the grating amounted to 7.4 Å/mm.

The considerable amount (4%) of caesium chloride was added both to analytical samples and standards in order to eliminate mutual interactions of sodium and potassium and to lower arc temperature. Relatively low arc temperature resulted in the reduction of intensity of cyanogen bands in the vicinity of analytical Na and K lines. It also resulted in the reduction of evaporation rate of other elements characterized by high excitation potentials. In order to diminish interactions due to other matrix elements appropriate quantities of a mixture called "synthetic mineral" were added to each standard.

Table 3
Summary of spectral analysis conditions

Apparatus	
Spectrograph	PGS-2, Carl Zeiss, Jena
Universal generator	UBI-1, Carl Zeiss, Jena
Microphotometer	MD-100, Carl Zeiss, Jena
Excitation	
Discharge	dc arc, 4A
Sample electrode	SU-305, Topolčany; anode
Counter electrode	SU-202, Topolčany
Analytical gap	2 mm
Exposure time	for sodium 164 s for potassium 41 s powder, ca. 10 mg
Spectrography	
Slit width	0.020 mm
Analysis wavelengths (nm)	{Na: 330.24 K: 404.40
Wavelength of internal standards (nm)	{Li: 323.26 Rb: 421.55
Photographic plate	blau hart WU-2, ORWO Wolfen
Plate development	as recommended by the manufacturer
Quantitation	
Densitometry	analytical lines read on the S scale
ΔS conversion to concentration	via calibration equation

Each standard and each analytical sample was distributed over 5 electrode craters in order to obtain spectra from 5 independent excitations. The spectra of analytical samples and corresponding standards were always recorded together on the same photographic plate. Optical density measurements were always replicated three times for each spectral line and background. The conditions of the spectrographic analysis are presented in Table 3.

Results and discussion

Using least squares method the following calibration equations were formulated basing on data obtained for the standards:

$$\Delta \hat{S}_{\text{Na-Li}} = 226.51 + 90.85 \log c_{\text{Na}} \quad [1]$$

$$\Delta \hat{S}_{\text{Na-B}} = 253.80 + 83.88 \log c_{\text{Na}} \quad [2]$$

$$\Delta \hat{S}_{\text{K-Rb}} = 146.43 + 87.68 \log c_{\text{K}} \quad [3]$$

$$\Delta \hat{S}_{\text{K-B}} = 198.84 + 79.52 \log c_{\text{K}} \quad [4]$$

Eq. 1 and 3 correspond to data obtained with lithium and rubidium as internal standards respectively. Eq. 2 and 4 correspond to data obtained with background as reference.

With the use of these equations the concentrations of sodium and potassium in both minerals under study were evaluated. The results of the determinations

Table 4
Results of spectrographic determinations (%)

Granodiorite										
Sodium					Potassium					
Internal standard: Li					Internal standard: Rb					
2.42	2.20	2.36	2.32	2.58		3.16	3.41	3.24	3.32	3.16
$\bar{x} = 2.36$	$s = 0.15$				$\bar{x} = 3.26$	$s = 0.19$				
Background as reference										
2.43	2.42	2.43	2.20	2.51		3.12	3.58	3.48	3.20	3.38
$\bar{x} = 2.36$	$s = 0.25$				$\bar{x} = 3.35$	$s = 0.21$				
Myaskite										
Internal standard: Li					Internal standard: Rb					
6.50	6.20	6.04	6.50	6.20		4.80	5.33	4.80	5.33	5.20
$\bar{x} = 6.29$	$s = 0.15$				$\bar{x} = 5.09$	$s = 0.19$				
Background as reference										
6.54	6.04	6.04	6.91	6.37		4.52	4.93	4.65	4.65	5.08
$\bar{x} = 6.38$	$s = 0.25$				$\bar{x} = 4.77$	$s = 0.21$				

are presented in Table 4. They are in good agreement with the expected (certified) values (see Table 5).

It should be stressed, that the proposed procedure makes use of the synthetic standards in contrast to common practice to use minerals analyzed by other (mostly chemical) methods as standards.

The proposed procedure makes full use of fractional distillation of sodium and potassium from the nonvolatile matrix. Using deep electrode craters filled up only to the half by the powdered sample and a large addition of caesium chloride as the spectral buffer lowering arc temperature, a selective evaporation of sodium and potassium has been achieved. The fractional distillation was also made more effective by excitation of the sample from anode and by low arc current. Low arc current in a large measure contributed to suppression of cyanogen bands which enabled to use rubidium as internal standard in the determination of potassium.

Table 5
Comparison of analytical results with the expected values

Rock	Sodium (%)		Potassium (%)	
	Spectrography	Expected value	Spectrography	Expected value
Granodiorite	2.36	2.40	3.26	3.24
Myaskite	6.29	6.34	5.09	5.08

The results of determinations obtained with use of internal standards appear to be somewhat better than those obtained with background as reference. Precision of the proposed procedure is comparable with that of other methods recommended previously. This procedure may be used for the determination of sodium and potassium in silicate minerals in the concentration range 0.1 – ca. 10%. The most important advantage over other classical and instrumental methods (e.g. flame-photometry) is that it renders dissolution of analytical sample not necessary. After dilution with the mixture of the composition presented in table 2 the sample may be excited directly from the crater of a graphite electrode. According to the proposed method the sample is diluted with the same mixture (see Table 2) for the determination of both elements Na and K. Moreover, the application of internal standards proved to be not necessary (see Table 4). Accordingly, as compared with other methods, the analytical procedure recommended in this paper is much less time consuming and more simple.

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NOWA SPEKTROGRAFICZNA METODA OZNACZANIA SODU I POTASU W MINERAŁACH KRZEMIANOWYCH

Streszczenie

Opracowano nową spektrograficzną metodę oznaczania sodu i potasu w minerałach krzemianowych. Procedura analityczna jest następująca:

Sposzkowaną próbkę rozcierającą się w stosunku 1:399 proszkiem grafitowym z dodatkiem chlorku cezu jako buforu spektralnego oraz azotanu litu i chlorku rubidu jako wzorców wewnętrznych dla oznaczania odpowiednio sodu i potasu. Po wymieszaniu, rozcierającą próbkę umieszcza się w kraterze elektrody grafitowej i wzbudza w wygładzonym łuku prądu stałego o natężeniu 2 A. Po zarejestrowaniu widma, jako linie analityczne dla sodu i potasu wykorzystuje się odpowiednie linie 330,24 nm (Na) i 404,40 nm (K), a jako linie wzorców wewnętrznych odpowiednio linie 323,26 nm (Li) i 421,55 nm (Rb).

Kalibrację metody oznaczania przeprowadza się na podstawie serii wzorców. Stosuje się syntetyczne wzorce proszkowe powstałe przez rozcierczenie tzw. „minerału syntetycznego” (mieszanina o składzie 70% SiO_2 , 25% Al_2O_3 , 4% CaO , 1% MgO) tą samą co próbki analityczne mieszaniną rozcierającą oraz wprowadzenie odpowiednich ilości sodu i potasu w postaci roztworów chlorków tych metali. Po wysuszeniu i roztarciu w moździerzu agatowym, wzorce te służą do sporządzania wykresów kalibracyjnych w układzie współrzędnych: różnica zaczerń linii analitycznej i linii wzorca wewnętrznego – logarytm dziesiętny stężenia oznaczanego metalu we wzorcu.

Proponowaną metodę zastosowano z bardzo dobrym skutkiem do oznaczania sodu i potasu w nefelinowym sjenicie hornblendowym „Mjaskit” oraz granodiorcie „Rizyk” (wzorce IGEM, ZSRR). Metoda ta jest szybka i dokładna oraz nie wymaga rozpuszczenia próbki.

Андрей РОКОШ, Павел СТРЫХАРСКИ

НОВЫЙ СПЕКТРОГРАФИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ КАЛИЯ И НАТРИЯ В СИЛИКАТНЫХ МИНЕРАЛАХ

Резюме

Разработан спектрографический метод определения натрия и калия в силикатных минералах. Ход анализа следующий:

Измельченный образец разбавляется в пропорции 1:399 порошком гра-

фита с примесью хлорида цезия в качестве спектрального буфера, а также нитрата лития и хлорида рубидия как внутренних эталонов для определения соответственно натрия и калия. После смешивания разбавленный образец помещается в углубление графитового электрода и возбуждается в слаженной дуге постоянного тока силой 2 А. После записи спектра, в качестве аналитических линий для натрия и калия используются соответственно линии 330,24 нм (Na) и 404,40 нм (K), а как линии внутренних эталонов соответственно линии 323,26 нм (Li) и 421,55 нм (Rb).

Калибровку метода определения проводится на основе серии эталонов. Применяются искусственные порошковые эталоны, полученные путем разбавления так называемого „синтетического минерала” (смесь состава 70% SiO_2 , 25% Al_2O_3 , 4% CaO и 1% MgO) той же самой разбавляющей смесью, что для анализируемых образцов, а также введением соответствующих количеств натрия и калия в виде растворов хлоридов этих металлов. После просушки и растирания в агатовой ступке, эти эталоны служат для составления калибровочных графиков в системе координат: разница зачертнения аналитической линии и линии внутреннего эталона — десятичный логарифм концентрации определяемого металла в эталоне.

Предлагаемый метод с очень хорошим результатом применялся для определения натрия и калия в рогообманковом нефелиновом сиените „Миаскит”, а также в гранодиорите „Рижик” (эталоны ИГЭМ, СССР). Это скорый и точный метод, не требующий растворения образца.