GEOLOGICKÝ ZBORNÍK — GEOLOGICA CARPATHICA, 37, 2, BRATISLAVA, APRIL 1986, Pp. 167—174

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THE STUDY OF RELIABILITY OF SPECTROCHEMICAL TRACE ELEMENTS DETERMINATION IN METAMORPHIC SILICATE ROCKS

(Tabs. 5)

Abstract: The reliability of trace elements determination in black shales and other metamorphic silicate rocks by three described spectrochemical procedures was investigated. The obtained analytical results were statistically treated. A high correlation between the results of the methods in question, as well as the values of regression coefficients do not bear out the presence of significant systematic errors. It proves that the used methods give reliable results of trace element contents in the investigated geological materials.

Резюме: В статье авторы изучают точность результатов спектрохимического определения следов в черных сланцах и других метаморфических силикатовых породах, полученных при помощи трех разных спектрохимических методов. Полученные результаты анализов были статистически оценены. На основе этого исследования была обнаружена высокая корреляция отдельных элементов, а также значения регрессивных коэффициентов не отмечают наличие значительных систематических ошибок. Из вышеприведенного вытекает, что все разработанные методы предоставляют достоверные результаты определения следов в исследованных геологических материалах.

Introduction

In the study of genetic problems of the appearance of pyrite and antimonite ores in the Pezinok—Pernek crystallinic area in Malé Karpaty Mts., which is built up mainly by crushed milonitised rocks among which black shales play a considerable role (Cambel, 1965), the attention was paid to a comprehensive study of the last rocks because of the presence of elevated contents of some trace elements (Cambel — Khun, 1979).

For the determination of trace elements in the black shales, as well as in other metamorphic silicate rocks three different spectrochemical procedures were proposed and applied.

The reliability i. e. the precision and the accuracy of the obtained analytical results represents the main basic parameter characterizing the applicability of the given analytical procedure.

The precision of analytical results is generally characterized by the standard deviation. It can be estimated using either the results of repeated measurements on one sample, or parallel results performed on different real samples (Plško, 1973). The lated procedure gives a better characterisation of the whole concentration range in question.

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The accuracy of analytical results i. e. their agreement with the true value can be estimated only by the comparison of results gained by different procedures respectively by analysing standard reference materials, having certified contents of elements.

In the case of spectrochemical determination of trace elements in geological materials, the reliability of results can be ensured by the dilution of sample with spectrochemical additives (Holdt, 1962), by the appropriate excitation conditions (Plško, 1964), by the heat treatment of samples (Medveď — Plško, 1979; Medveď — Plško, 1980) or by appropriate corrections for the calculation of concentrations (Holdt, 1964; Plško, 1965).

The aim of this work is to evaluate the reliability of analytical results obtained by the following spectrochemical procedures.

Experimental part

Three different spectrochemical procedures elaborated on the basis of methods published by Ahrens (1954), Fuchs et al. (1966), Blackburn et al. (1971), Hofmeyr (1972), Medveď et al. (1974), Medveď — Plško (1980) and others, were used for the determination of trace elements in metamorphic silicate rocks, mainly in black shales and in the standard reference material ZGI[1] TB (clay slate).

The working conditions of the applied methods are listed in the Tab. 1.

The applied spectrochemical methods enable to determine 15 trace elements (B, Ba, Co, Cr, Cu, Ga, Mn, Ni, Pb, Sc, Sr, Ti, V, Y, Zr) in the said geological materials in concentration range 3 to 7000 ppm.

Ge, Pd and Eu added in the form of spectral pure compounds (Johnson — Matthey) as GeO_2, $(NH_4)_2\ PdCl_4$ and Eu_2O_3 in the 0.1 % concentration to the graphite powder served as internal reference elements.

The wavelengths of the analytical and reference elements are listed in the Tab. 2.

In order to stabilize the excitation conditions, as well as to diminish the influence of variable chemical composition, the samples were diluted by the following spectrochemical additives:

Method I (Geological Institute, Slovak Academy of Sciences): Graphite powder and NaCl in the relation 4 : 3 : 1.

Methods II (Geological Institute, Komenský University) and

Methods III (Chemical Institute B. Kidrič) with graphite powder and Li_2CO_3 in the relation 3 : 6 : 1.

Because of the variable content of differently bound water (1—15 %) and organogene material, the samples were ignited the Methods I and III for 2 hours at 950 °C and the lost on ignition was considered at the calculation of the trace elements concentrations.

The exposure time of 90 s was determined on the basis of evaporation relation curves (Plško, 1964), which procedure enabled also to check the optimisation of the dilution of samples by spectrochemical additives and the choice of reference elements.

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[1] ZGI — Zentrales geologisches Institut, Berlin, GDR.

Table 1

Working conditions

	Method I.[1]	Method II.[2]	Method III.[3]
Spectrograph	PGS-2, C. Zeiss, Jena, m = 1	PGS-2, C. Zeiss, Jena, m = 1	Jarrell Ash, Mark IV, m = 1
Spectral range	210—390 nm and 330—500 nm	210—390 nm and 330—500 nm	220—360 nm
Slit width	0.020 nm	0.016 nm	0.020 nm
Provenience of electrodes	Elektrokarbon Topoľčany	Elektrokarbon Topoľčany	Ringsdorf — Werke
Sample bearing electrode	SU 308	SU 308	RW 003
Counter electrode	SG — 359	SG — 359	RW 001
Electrode gap	3 mm	3 mm	3 mm
Excitation	D. C. arc. anodic polarization 220 V/6 A	D. C. arc. anodic polarization 220 V/6 A	D. C. arc. anodic polarization 220 V/10 A
Atmosphere	Air	Air	Ar: O_2 = 4:1; 51/min.
Exposure time	90 s	90 s	90 s
Photographic material	ORWO WU-3	ORWO WU-3	Ilford
Developer	ORWO R 09 (dil. 1:20) 5 min. 20 °C	ORWO R 09 (dil. 1:20) 5 min. 20 °C	ID-2, 3.5 min. 20 °C
Dilution of samples	Sample: graphite: NaCl = = 4:3:1	Sample: graphite: Li_2CO_3 = 3:6:1	Sample: graphite: Li_2CO_3 = 3:6:1
Ignition of samples	950 °C, 2 hours	—	950 °C, 2 hours
Microphotometer	MD-100, C. Zeiss, Jena	Schnellphotometer II, C. Zeiss, Jena	Jarrel Ash

Explanations:
[1] Method I. — Geological Institute Slovak Academy of Sciences, Bratislava; [2] Method II. — Geological Institute, Komenský University, Bratislava; [3] Method III. — Chemical Institut "Boris Kidrič", Ljubljana.

Table 2

Measured spectral lines and the precision of trace elements determination

Element	λ[1] nm	Method I.	Method II.	Method III.
		Srp[2]	Srp	Srp
Ba	233.52	0.0897	0.0411	0.0354
B	249.77	0.0650	0.654	0.1087
Mn	259.37	0.0746	—	—
Pb	283.30	0.802	0.0416	0.1904
Ga	294.36	0.0609	0.0704	0.1116
Cu	324.75	0.0389	0.2172	—
	327.40	—	—	0.0951
Ti	308.80	0.0687	0.0437	—
V	318.39	0.0621	0.0778	0.0634
Ni	341.47	0.0303	0.0785	—
	305.08	—	—	0.0680
Zr	343.82	0.0941	0.2506	—
	339.20	—	—	0.1279
Co	345.35	0.0352	0.1042	—
	340.51	—	—	0.2572
Y	371.00	0.0573	0.0270	—
Sc	424.68	0.0859	—	—
Cr	425.43	0.0387	0.1998	—
	284.32	—	—	0.1514
Sr	460.73	0.0284	0.0517	—
	346.44	—	—	0.0613
Ge[3]	265.12	— Method I., II., III.		
Pd[3]	311.40	— Method I., II., III.		
	342.12	— Method I., II.		
Eu[3]	459.40	— Method I., II.		

Explanations: [1]λ – wavelengths of spectral lines in nm; [2]S_{rp} – relative standard deviation; [3]Ge, Pd, Eu – internal reference elements.

The composition of the synthetic matrix used for the preparation of calibration standards was simulated according to the average composition of metamorphic rocks given in the Tab. 3. The matrices were homogenised for 2 hours, ignited at 950 °C and afterwards again homogenised. The calibration standards

Table 3

The composition of the synthetic matrices

Components	Content in %	
	Method I. and III.	Method II.
SiO_2	60.30	62.00
Al_2O_3	20.55	22.00
Fe_2O_3	6.92	8.65
MgO	3.00	3.50
CaO	4.00	0.90
Na_2O	1.31	0.15
K_2O	3.85	2.80

Table 4

The comparison of the used spectrochemical procedures

Element	Method I. III.		Method II. III.	
	r[1]	w_{ort}[2]	r	w_{ort}
B	0.956	0.690	0.820	0.873
Ba	0.964	1.261		
Co	0.941	1.059	0.928	1.509
Cr	0.935	1.109	0.984	0.795
Cu	0.996	0.959	0.993	0.918
Ga	0.943	0.854		
Ni	0.999	1.017	0.876	0.494
Pb	0.859	0.714		
Sr	0.965	0.905	0.945	0.636
V	0.925	1.691	0.946	1.237
Zr	0.945	0.734	0.643	0.635

Explanations: [1]r — correlation coefficient; [2]w_{ort} — orthogonal regression coefficient.

were prepared by the addition of known concentrations of the analysed elements in the form of appropriate spectral pure compounds, mainly oxides.

The blackening of the measured spectral lines was transformed to intensity values by the use of emulsion calibration curves constructed by the use of preliminary curves (Plško, 1969). The spectra of the synthetic calibration stan-

Table 5

The contents of trace elements in the certified reference material ZGI – TB (clay slate) in ppm (time period: Apr. 1977 – March 1982)

Element	a_p[1]	s[2]	g_p[3]	s_r[4]	C_0[5]	n[6] = 48
Ba	829	35	829	0.043	725	
B	94	10	93	0.117	92	
Mn	415	17.7	414	0.044	420	
Pb	7.8	0.6	7.8	0.075	7	
Ga	26	2.2	26	0.090	25	
Cu	44.6	3.4	44.6	0.083	50	
Ti	5354	194	5351	0.037	5580	
V	102	9.3	101	0.096	106	
Ni	42.6	3	42.5	0.071	40	
Zr	176	42	171	0.308	175	
Co	12.5	1	12.5	0.080	13	
Y	38.5	3	38.4	0.081	39	
Sc	13.4	1.7	13.3	0.137	13.4	
Cr	90.4	9.3	90	0.109	80	
Sr	167	5	167	0.031	155	

Explanations: [1]a_p – arithmetical mean; [2]s – standard deviation; [3]g_p – geometrical mean; [4]s_r – relative standard deviation; [5]C_0 – recommended value, Flanagan (1973); [6]n – number of analytical data.

dards, as well as of the standard reference material ZGI-TB were taken three times, the spectra of samples two times.

Owing to the logarithmic-normal distribution of spectrochemical results (Ahrens, 1962; Plško – Kubová, 1978) the average of the results was expressed by the geometrical mean of the obtained results.

Results and discussion

Samples of black shales, as well as of other metamorphic silicate rocks from the Western Carpathians were analysed for to evaluate the parameters of the described spectrochemical procedures.

The relative standard deviations listed in the Tab. 2 were estimated from the results of the repeated takings of spectra.

In order to describe the reliability of the results obtained by the described procedures, correlation and regression coefficients mutually between two methods were calculated. The corresponding numerical values are presented in the Tab. 4. The obtained correlation coefficients for the determination of all elements by all combinations of the used methods are practically equal to one, what proves a very high correlation of the results. The values of orthogonal regression coefficients are in the majority of cases also not far from one and their occasional deviations do not corroborate the presence of significant systematic error for the range adjacent to their mean contents (Plško, 1984). It can therefore be concluded that the presented analytical methods furnish reliable results for the trace element contents in the studied geological materials.

Apart from that, the Method I was used for the determination of trace elements in the certified reference material ZGI-TB (clay slate). The results of repeated analyses performed in a greater time period are presented in the Tab. 5 and compared with the recommended values published by Flanagan (1973). These results also witness for a broad applicability of the described procedures as it has already been proved by the geochemical conclusions on black shales (Cambel — Khun, 1979; Cambel — Khun, 1983) achieved on the basis of analytical results obtained by the described spectrochemical methods.

Translated by E. Chmulíková

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Manuscript received, January 31, 1985.