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RELIABILITY OF SPECTROCHEMICAL DETERMINATION OF TRACE ELEMENTS IN CARBONATE STANDARD REFERENCE MATERIALS

(Tabs. 3)

Abstracts: In the paper the authors present the results of long-term observation of spectrochemical determination reliability of trace elements in carbonate rocks standard reference materials ZGI-KH (limestone), GFS-401 (limestone), IU-EA-LLL 1 (limestone), NBS-1b (argillaceous limestone), NBS-88a (dolomitic limestone), GFS-400 (dolomite), IU-EA-ADT (dolomite) and MK (magnesite). Determinations of individual elements in examined standard reference materials were performed in the course of routine analyses of geological materials in the period from 1973 up to 1983 using different synthetic calibration standards and spectrochemical additives with reference elements prepared during the above-mentioned period too. The obtained analytical data have been statistically evaluated and compared with values gained by other authors. On the basis of present study a high temporal stability of results obtained in our laboratory has been established.

Резюме: В статье авторы приводят результаты многолетнего исследования точности спектрохимического определения микроэлементов в стандартных образцах состава карбонатных горных пород ZGI-KH (известняк), GFS-401 (известняк), IU-EA-LLL 1 (известняк), NBS-1b (мергелистый известняк), NBS-88a (доломитовый известняк), GFS-400 (доломит), IU-EA-ADT (доломит) и МК (магнезит). Определения отдельных элементов в исследованных стандартных образцах состава были выполнены в течении нормальных анализов геологических материалов в периоде с 1973 г. до 1983 г. применяя разные синтетические градуировочные стандарты и спектрохимические примеси с элементами сравнения также подготовленными в вышеприведенном периоде. Приобретенные аналитические данные были статистически обработаны и сравнены со значениями достигнутыми другими авторами. На основе настоящего исследования была определена высокая временная стабильность результатов приобретенных в нашей лаборатории.

Introduction

Verification of accuracy of results, i. e. their agreement with true value, which in majority of cases is unknown, can be, as a rule, carried out by two ways. Primarily, the given material is analysed by two or more independent methods. Since this approach is cumbersome, the standard reference materials have been used increasingly for the verification of reliability of analytical results lately.

For a long time we have been paying an attention to determination of trace elements in geological materials in our laboratory, whereby we have been using

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various existing standard reference materials to a great extent. The results of long-term observation of spectrochemical analysis reliability of trace elements in standard reference materials of silicate rocks have been already published (Medveď—Plško, 1982). In the present work a survey of results obtained when analysing the standard reference materials of carbonate rocks is given.

Table 1

Working conditions

Spectrograph	PGS 2, simple transition $m = 1$
Spectral ranges	from 210 up to 390 nm ($\alpha = 5.65$) and from 330 up to 500 nm ($\alpha = 7.86$)
Illumination	three-lens with intermediate stop
Intermediate diaphragm	3.2 mm
Slit width	0.020 mm
Electrode material	graphite, Elektrokarbon Topoľčany
Sample bearing electrode	SU 219
Counter electrode	SG 359
Ratio of dilution sample: graphite: Li_2CO_3	3 : 6 : 1
Electrode gap	3 mm
Emulsion	ORWO WU 3
Developer	ORWO R 09 (dil. 1 : 20)
Excitation	D. C. arc, anodic polarization of sample bearing electrode
Voltage	220 V
Current	6 A
Exposure time	120 s

Experimental part

Spectrochemical procedures worked out in our Institute in co-operation with J. Jarkovský (1969), E. Martiny (1969), J. Kubová and E. Plško (1979) have been used for determination of trace elements in standard reference materials and, at the same time, we have come out mainly from the works of Weber (1964), Matherny (1965), Ingamells—Suhr (1967), Nová (1969), Thompson—Bankston—Pasley (1970) and others.

During the analyses of trace elements in carbonate rocks several unfavourable effects occur, viz.:

1. matrix-effect — caused by variability of macrocomponents, mainly Ca, Mg and Si;
2. intense decomposition during the arcing;
3. difference of the structure of synthetic matrix and natural samples.

Problem of matrix-effect has been solved by classification of analysed standard reference materials in the certain groups corresponding to a given type of geological materials, e. g. limestones, dolomites and magnesites, then by dilution of these samples with spectrochemical additives — graphite powder and lithium carbonate.

Table 2

Measured spectral lines, precision of determination and concentration range of trace elements in ppm

Element	λ nm	Limestones		Dolomites		Magnesites	
		s_{rp}[1]	ΔC[2]	s_{rp}	ΔC	s_{rp}	ΔC
Ag	328.06	0.080	1–300	0.091	1–300	0.034	1–300
B	249.77	0.122	10–1000	0.105	10–1000	0.076	10–1000
Ba	233.52		100–3000				
	455.40	0.117	3–1000	0.142	3–1000	0.130	3–1000
Co	345.35	0.076	1–1000	0.078	3–1000	0.084	1–1000
Cr	425.43	0.112	1–1000	0.128	1–1000	0.121	1–1000
Cu	324.75	0.097	1–300	0.110	3–300	0.116	1–300
Mn	260.56	0.101	10–3000	0.121	10–3000	0.110	10–3000
Ni	341.47	0.073	3–1000	0.081	1–1000	0.076	1–1000
Pb	283.30	0.085	3–300	0.132	3–300	0.142	3–300
Sr	460.73	0.109	10–1000	0.114	3–1000	0.101	3–1000
Ti	308.80	0.035	10–1000	0.145	10–1000	0.160	10–1000
V	318.39	0.035	3–1000	0.092	3–1000	0.100	3–1000
Eu[3]	459.40						
Ge[3]	265.11						
Pd[3]	311.40						
	342.12						

Explanations: [1]s_{rp} – relative standard deviation of analytical determination of elements; [2]ΔC – concentration range, in which the individual elements can be determined by the given spectrochemical procedures; [3]Eu, Ge, Pd – reference elements.

Table 3

Trace element contents in standard reference materials of carbonate rocks in ppm

Index	Ag	B	Ba	Co	Cr	Cu	Mn	Ni	Pb	Sr	Ti	V
$n = 11$[1]	Limestone ZGI-KH (time interval September 1973 — September 1983)											
C_o[2]	—	35	49	4	19	10	710	20	7	490	780	25
a_p[3]	<1	36.5	53.5	5.2	17.1	9.1	670	18.8	7.5	506	753	23.8
s[4]	—	6.3	6.2	1.0	2.6	2.0	78.9	3.8	1.3	46.2	83.8	3.9
g_p[5]	<1	36	53.2	5.1	16.9	8.9	665	18.4	7.4	504	749	23.5
s_r[6]	—	0.079	0.049	0.089	0.075	0.097	0.053	0.089	0.078	0.039	0.048	0.081
$n = 6$	Limestone GFS-401 (time interval July 1974 — September 1983)											
C_o	<1	22	1074	3	<2	7.2	112	4.8	<2	138	113	10
a_p	<1	20.2	1146	2.8	4.5	3.8	97.6	4.7	<3	116	82.6	7.5
s	—	5.1	95.9	0.5	0.4	0.6	10.5	0.7	—	12.1	34.1	2.6
g_p	<1	19.8	1143	2.7	4.6	3.8	97.1	4.7	<3	116	75.8	7.1
s_r	—	0.098	0.038	0.103	0.038	0.072	0.048	0.066	—	0.044	0.213	0.177
$n = 11$	Limestone IU-EA-LLL 1 (time interval March 1979 — September 1983)											
C_o	—	—	6?	3?	8?	2?	23	20?	6	196	21	8?
a_p	<1	<10	41.7	3.2	2.6	2.3	21.1	3.6	5.5	171	25.2	10.5
s	—	—	2.2	0.5	0.4	0.4	4.9	1.8	1.6	8.9	5.2	3.2
g_p	<1	<10	41.6	3.1	2.3	2.3	20.6	3.1	5.2	171	24.7	10.1
s_r	—	—	0.024	0.067	0.062	0.075	0.091	0.235	0.145	0.022	0.093	0.126
$n = 5$	Argillaceous limestone NBS-1b (time interval July 1974 — August 1983)											
C_o	<1	44	124	4.3	3.7	5.7	1348	12	<2	1280	232	<10
a_p	<1	24.9	80	5.1	4.9	5.3	1343	12.5	4.8	1120	232	33
s	—	2.7	23.0	0.3	0.9	1.2	94.0	1.6	1.7	194.8	15.5	5.5
g_p	<1	24.8	77.7	5.1	4.8	5.2	1340	12.4	4.5	1105	281	32.6
s_r	—	0.047	0.127	0.029	0.084	0.093	0.030	0.055	0.160	0.079	0.025	0.074

Continuation of Tab. 3

Index	Ag	B	Ba	Co	Cr	Cu	Mn	Ni	Pb	Sr	Ti	V
n = 5	Dolomitic limestone NBS-88a (time interval April 1979 — August 1983)											
C_o	<1	<1.5	24	2.9	<2	5.9	218	<2	<2	26	65	<10
a_p	<1	<10	12	<3	1.8	4.1	222	2.2	<3	36	67.2	7.7
s	—	<10	2.9	—	0.7	0.7	28.8	0.7	—	6.6	31.5	0.4
g_p	<1	—	11.7	<3	1.7	4	221	2.2	<3	35.5	62.8	7.7
s_r	—	1.3	0.106	—	0.157	0.070	0.056	0.117	—	0.078	0.167	0.022
n = 5	Dolomitic limestone NBS-88a (time interval April 1979 — August 1983)											
C_o	<1	1.3	34	3.1	<2	3	51	2	3	550	12.5	<10
a_p	<1	<10	38.7	<3	2.7	3.6	50.2	2	4	574	26.4	7.4
s	—	—	28.9	—	0.7	0.8	4.3	0.6	1.3	125.8	17.7	2.5
g_p	<1	<10	31.9	<3	2.6	3.6	50	2	3.8	564	21.8	7
s_r	—	—	0.291	—	0.111	0.091	0.035	0.132	0.180	0.086	0.302	0.188
n = 9	Dolomite IU-EA-ADT (time interval April 1979 — August 1983)											
C_o	—	—	50?	5?	10?	1?	155	12?	159	132	21	10?
a_p	<1	<10	57	<3	1.9	3.4	142	3.1	159	125	22.4	11.5
s	—	—	12.9	—	0.4	1.0	17.6	0.6	9.4	11.6	1.0	3.4
g_p	<1	<10	56	<3	1.9	3.2	140	3.1	159	125	22	10.7
s_r	—	—	0.094	—	0.082	0.140	0.052	0.077	0.026	0.045	0.020	0.210
n = 8	Magnesite MK (time August 1983)											
C_o	0.5	37.8	17	1.3	6.5	2.5	1239	4.9	1.5	6.2	113.9	9.2
a_p	0.5	30.8	14.1	1.4	5.8	2.4	1157	5.1	7.8	8	100	8.5
s	0.1	1.0	0.8	0.4	0.8	0.4	120	0.4	3.0	2.2	20.6	0.8
g_p	0.5	30.8	14.1	1.4	5.8	2.4	1151	5.1	7.3	7.8	98	8.5
s_r	0.085	0.014	0.036	0.125	0.060	0.031	0.048	0.036	0.138	0.119	0.096	0.040

Explanations: [1]n — number of analytical data; [2]C_o — recommended value; [3]a_p — arithmetical mean; [4]s — standard deviation; [5]g_p — geometrical mean; [6]s_r — relative standard deviation.

Intense decomposition of carbonate samples during the arcing has been subdued partly by addition of the above-mentioned spectrochemical additives, partly by selection of suitable electrode shapes.

Errors resulting from difference of the structure of synthetic matrices prepared for the standardization, and of the natural samples have been in our case removed by preparation of synthetic limestone, dolomite and magnesite matrices little differing structurally from the natural samples.

The working conditions under which the spectra of carbonate rocks standard reference materials have been taken are listed in Tab. 1.

Results and discussion

Precision of determination expressed by relative standard deviation (s_{rp}) of individual elements has been calculated for each procedure from the results of parallel measurements performed on 40 samples of corresponding types of carbonate rocks and standard reference materials with changing content of element in question. Results of calculation of relative standard deviation for one taking are given in Tab. 2 for individual elements in corresponding rocks. Besides the results the wavelengths of the used analytical and reference lines, as well as the concentration range Δ C, in which the elements can be determined by the described spectrochemical procedures, are listed in Tab. 2. The lower limit of the range Δ C represents practically attainable limit of determination. All data on contents are given in ppm.

Accuracy of analytical results of carbonate rocks standard reference materials has been checked by the comparison of obtained results with recommended ones presented by Ingamells–Suhr (1967), Thompson–Bankston–Pasley (1970), Grassman (1972), Schindler (1972), Flanagan (1973), Schroll (1983) and others.

Statistically treated data on trace element contents in standard reference materials – limestones ZGI[1]-KH, GFS[2]-401, IU-EA-LLL 1[3], NBS[4]-1b; dolomites NBS[4]-88a, GFS[2]-400, IU-EA-ADT[3] and magnesite MK[5] obtained during the period of about 10 years in our Institute as well as recommended values of element contents presented by the above-mentioned authors are listed in Tab. 3. Evaluating the obtained results, in majority of samples a good agreement with recommended values has been reached.

In some cases the analytical results, mainly of Ti and Ba are loaded by a considerable error, though the results are accurate. On the other hand, different values of e. g. Ba, Cr and Ni from recommended ones are acquired in some standard reference materials. On the basis of this fact, it can be stated, that the recommended values of these elements in examined standard reference materials are not yet enough reliable. It can be documented on an example of

[1] ZGI – Zentrales Geologisches Institut, Berlin, GDR.

[2] GFS – G. Frederick Smith Chemical Company, Columbus, Ohio, USA.

[3] IU-EA-LLL 1 and IU-EA-ADT – Geotechnisches Institut, Vienna, Austria.

[4] NBS – National Bureau of Standards, Washington D. C., USA.

[5] MK – Ustav nerostných surovin (Institute of Mineral Raw Materials), Kutná Hora, CSSR.

Austrian standard reference materials of limestone IU-EA-LLL 1 and dolomite IU-EA-ADT, in which these values have been indicated as questionable by the author S c h r o l l (1983) himself.

In conclusion it can be stated that the spectrochemical methods worked out in our laboratory provide long-term reliable results, which may be fully applied to determination and verification of composition even of further standard reference materials used for verification of accuracy of analytical procedures serving for chemical characterization of trace elements in geological materials of a similar type.

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REFERENCES

FLANAGAN, F. J., 1973: 1972 values for international geochemical reference samples. Geochim. cosmochim. Acta (London), 37, pp. 1189—1200.,

GRASSMAN, H., 1972: Die Standardgesteinsproben des ZGI, 6. Mitteilung: Neue Auswertung der Analysen auf Hauptkomponenten der Proben Granit GM, Basalt BM, Tonschifer TB, Kalkstein KH und erste Auswertung der Proben Anhydrit AN und Schwarzschiefe TS. Z. angew. Geol. (Berlin), 18, pp. 278—284.

INGAMELLS, C. O. — SUHR, N. H., 1967: Chemical and spectrochemical analysis of standard carbonate rocks. Geochim. cosmochim. Acta (London), 31, pp. 1347—1350.

MATHERNY, M., 1965: Emissionsspektrochemische Untersuchungen von Sintermagnesiten. Z. anal. Chem. (München), 209, pp. 293—298.

MEDVEĎ, J. — JARKOVSKÝ, J., 1969: Quantitative spektrochemische Methode zur Bestimmung von Mikroelementen in Karbonatgesteinen. Sympózium o metódach stanovenia nízkych koncentrácií prvkov v nerastných surovinách. Smolenice 1969, Vyd. Univ. Kom. (Bratislava), pp. 129—149.

MEDVEĎ, J. — MARTINY, E., 1969: Beitrag zu der Bestimmung von Sr in Karbonaten mit Hilfe der emissionsspektrochemischen Methode und der Atom-Absorptions--Spektroskopie. Sympózium o metódach stanovenia nízkych koncentrácií prvkov v nerastných surovinách. Smolenice 1969. Vyd. Univ. Kom. (Bratislava), pp. 151—161.

MEDVEĎ, J. — KUBOVÁ, J. — PLŠKO, E., 1979: Spectrochemical determination of trace elements in magnesites. Geol. Zbor. Geol. carpath. (Bratislava), 30, 2, pp. 253—259.

MEDVEĎ, J. — PLŠKO, E., 1982: The reliability of data on microelement contents in standard reference materials based on spectrochemical determination performed in long time interval. Geol. Zbor. Geol. carpath. (Bratislava), 33, 3, pp. 363—375.

NOVÁ, A., 1969: Spektrochemische Bestimmung von Mikroelementen in Kalziten und Dolomiten. Sympózium o metódach stanovenia nízkych koncentrácií prvkov v nerastných surovinách. Smolenice 1969, Vyd. Univ. Kom. (Bratislava), pp. 119—127.

SCHINDLER, R., 1972: Die Standardgesteinsproben des ZGI, 5. Mitteilung: Stand der Spurenelementanalyse der Gesteine GM, TB, BM und KH. Z. Angew. Geol. (Berlin), 18, pp. 221—228.

SCHROLL, E., 1983: Bericht über Limestone Lafatsch IU-EA-LLL 1 und Dolomit Topla IU-EA-ADT. Geotechnisches Institut (GTI) Wien.

THOMPSON, G. — BANKSTON, D. C. — PASLEY, S. M., 1970: Trace element data for reference carbonate rocks. Chem. Geol. Amsterdam), 6, pp. 165—170.

WEBER, J. N., 1964: Trace element composition of dolostones and dolomites and its bearing on the dolomite problem. Geochim. cosmochim. Acta (London), 28, pp. 1817—1826.

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