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SPECTROCHEMICAL DETERMINATION OF TRACE ELEMENTS IN MAGNESITES

(Tab. 1—4, Fig. 1)

Introduction

Abstract: A spectrochemical method enabling the determination of 11 trace elements in magnesites is described. The method supplies sufficiently precise and accurate analytical results having corresponding limit of determination. It ensures reliable and fast determinations for the purposes of geochemical study.

Резюме: В предлагаемой работе описывается спектрохимический метод которым можно определить 11 микроэлементов в магнезитах. Этот метод дает возможность вполне правильно получить точные данные аналитических данных с требуемой границей обнаружения, что возможно быстро и выгодно использовать для определения микроэлементов в магнезитах для целей дальнейшего геохимического изучения.

The problem of spectrochemical analysis of magnesites has been solved in the literature only partly. J. Polaček (1959), M. Matherny (1965) and M. Matherny et al. (1965) described the determination of macrocomponents. The data concerning the spectrochemical determination of trace elements in magnesites have not been found in the accessible literature sources. Therefore we used as starting points the papers by J. E. Hawley and G. Mac Donald (1956), P. Hahn-Weinheimer (1961), E. I. Andreev et al. (1964), J. N. Weber (1964), C. O. Ingamells and N. H. Suhr (1967), A. Nova (1969), J. Medveď and J. Jarkovský (1969) and J. Medveď and E. Martiny (1969). The mentioned papers are dedicated to the determination of trace elements in limestones and dolomites which belong to the same group of carbonates as magnesite.

At the spectrochemical analysis of trace elements an elevated matrix—effect has been observed due to the variability of their macrocomponents Ca, Mg, Fe, Al and Si. This effect was studied among the other by O. Filo et al. (1967) and D. Kupkova (1965, 1967).

A further problem is represented by the fact, that a vehement decomposition of carbonates occurs during the arcing. Some authors solved this problem by the solution of the carbonate matrix in the hydrochloric acid (L. L. Anderson — B. C. Aschenbrenner 1954), or by the transformation of the carbonates to oxides by their burning (J. Poláček 1959). Other authors diluted the carbonates by different spectrochemical additives (P. Hahn-Weinheimer 1961, M. Matherny et al. 1965, J. Medveď — J. Jarkovský 1969), resp. they used special shapes of analytical and counter

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electrodes (A. Nová 1969, K. Flórián et al. 1969, J. Medveď – J. Jarkovský 1969).

To suppress the possible errors caused by the differences in the composition of calibration standards and the composition of analysed samples we used a synthetic matrix which structure is practically identical with the natural samples.

From the geochemical point of view the determination of following microelements is of importance: B, Ba, Co, Cr, Cu, Mn, Ni, Pb, Sr, Ti, V.

The accuracy of the obtained results was checked on 10 samples as well as on the Czechoslovak analytical standard 6–02–001: "Magnesite O II" by atomic absorption spectrometry and/or spectrophotometry.

The precision of the methode was estimated by the standard deviation calculated from the results obtained with 50 samples of magnesites.

Experimental part

The spectrally pure $MgCO_3$ necessary for the preparation of calibration standards is commercially not available. It was therefore synthetized in the Laboratory of experimental mineralogy and geochemistry of the Geological Institute of Comenius University. The synthesis was carried out according the following reactions:

$$MgO + 2HCl \rightleftharpoons MgCl_2 + H_2O \quad (1)$$

$$MgCl_2 + 2NH_4OH \rightleftharpoons Mg(OH)_2 + 2NH_4Cl \quad (2)$$

$$Mg(OH)_2 + CO_2 \rightleftharpoons MgCO_3 + H_2O \quad (3)$$

The specpure MgO (Johnson-Mathey) was used. The HCl and NH_4OH were purified by destillation using silica vessels.

The reaction (1) represents a common solution. The reactions (2) and (3) were carried out in closed teflon vessels at the temperature of 200 °C in a thermobox in the duration of 7 days. The CO_2 was preliminary saturated into the NH_4OH up to the neutral reaction. The solution was then added in such an excess (related to the stoichiometry) that the pH > 9 remained. The purity of the synthetized $MgCO_3$ was proved by qualitative spectrochemical analysis.

The composition of the synthetic magnesite matrix used for the preparation of calibration standards was put equal to the concentration of macroelements in the above mentionned Czechoslovak analytical standard of magnesite: SiO_2 – 1,64 %, Al_2O_3 – 0,21 %; Fe_2O_3 – 4,22 %; CaO – 3,56 % (added as $CaCO_3$).

The analysed trace elements were admixed to the synthetic magnesite matrix in descending concentrations (by the factor $\sqrt{10}$) since 10 000 g/t to 3,16 g/t. The trace elements were used in the form of their oxides.

The mentioned matrix–effect due to the changes in the macrocomposition of magnesites was suppressed by the appropriate dilution by graphite powder and Li_2CO_3. The relation of the sample to the graphite powder and Li_2CO_3 at which the matrix–effect is practically eliminated for the matrices $MgCO_3$, $CaCO_3$ and $FeCO_3$ was determined by using the so called vanadium indices (G. Holdt 1962). The vanadium indices were calculated from the following spectral lines intensities: V II 310,23 nm and V I 318,51 nm.

The corresponding relation – sample: graphite powder: Li_2CO_3 equals to 3 : 6 : 1 (J. Medveď – J. Jarkovský 1969).

Different shapes of electrodes were studied. As the best the shape of the electrodes represented in the Fig. 1 was found. The advantage of the used electrodes is that no sputtering of the sample, as well as no climbing of the discharge on the counter electrode occurs (J. Medveď – E. Martiny 1969).

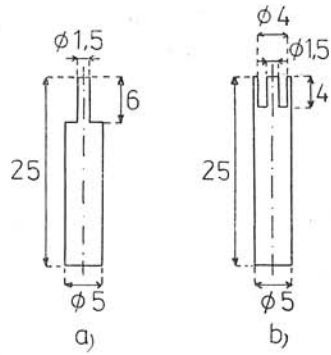

Fig. 1. The shape of the electrodes. *Explanations:* a – Counter-electrode, b – Carrier electrode.

The optimal exposure time of 120 s was determined from the evaporation relation curves (E. Plško 1964) used also for the choice of appropriate internal reference elements (Ge, Pd, Eu).

The full working conditions are listed in the Tab. 1.

The transformation of the blackening of spectral lines to the intensity values was carried out by the use of emulsion calibration curves plotted at 250; 300; 350 and 450 nm. The emulsion calibration curves were constructed by using

Table 1

Working conditions

Spectrograph	PGS-2, m = 1
Spectral range	210–390 nm and 330–500 nm
Illumination	3 lenses
Intermediate diaphragm	3,2 mm
Electrodes – material	graphite SU, Elektrokarbon Topoľčany
Shape	see Fig. 1.
Gap length	4 mm
Relation-sample: graphite: Li_2CO_3	3 : 6 : 1
Photographic material	ORWO WU-3
Developer	ORWO R-09 (1 : 20) 5 min. 20 °C
Excitation	DC arc, anodic polarization of the analytical electrode
Voltage	220 V
Current	6 A
Exposure time	120 s

preliminary curves (E. Plško 1964). If necessary, the background correction was applied.

The spectra of each synthetic calibration standard were taken three times whereas the spectra of each sample were repeated two times. The final result represents the geometrical mean of the experimental results.

Discussion

The standard deviation characterizing the precision of the determination was calculated from the results of parallel measurements performed on 50 samples of natural magnesites by the procedure described by E. Plško (1973) and J. Medveď, E. Plško and J. Cubínek (1974). The wavelengths of the measured spectral lines are listed together with the values of the relative standard deviations for one measurement in the Tab. 2. Practical analyses are normally repeated so that a better precision by the factor of 0,707 is obtained. Apart from the wavelengths and relative standard deviations, the table 3 contains also the concentration ranges in which the described method can be used.

The following procedure was elaborated and applied for the description of the matrix–effect: 5 % graphite powder, than 5 % Al_2O_3 and 5 % Fe_2O_3, 5 % $CaCO_3$ and 5 % SiO_2 were added to the analytical standard 6–02–001 "Magnesite O II". Five samples with the same concentration of trace elements, but with different composition of the matrix were prepared on this way. Parallel spectra of these 5 samples were taken and the concentration of 5 choosen elements was evaluated. Corresponding relative standard deviations were

Table 2

Spectral lines and obtained parameters. *Explanations:* Ge[1], Pd[1], Eu[1] – Internal reference elements.

Element	Wavelength nm	Relative standard deviation	Concentration range g. t^{-1}
B I	249,77	0,076	10–1000
Mn II	260,56	0,110	10–3000
Pb I	283,30	0,142	10– 300
Cu I	324,75	0,116	3– 300
Ge[1] I	265,11		
Ti II	308,80	0,160	10–3000
V I	318,54	0,100	3–1000
Ni I	341,47	0,076	10–3000
Co I	345,35	0,084	10–1000
Pd[1] I	342,12		
Cr I	425,43	0,121	3–1000
Ba II	455,40	0,130	3–1000
Sr I	460,73	0,101	10–1000
Eu[1] I	459,40		

Table 3

Data for the F-test

Element	$s_{r\lambda}$ (mixture)	$s_{r\lambda}$ (0 II)	F exp
Mn	0,142	0,079	3,2
Ti	0,172	0,197	< 1
Cu	0,115	0,083	1,9
Ni	0,114	0,132	< 1
V	0,155	0,100	2,4

calculated from the obtained 10 results. These standard deviations were compared by using the Snedecor's F-test with the standard deviations calculated from the results obtained by the 10 times repeated taking of spectra of the original analytical standard of the magnesite. The corresponding F-values are in the Tab. 3.

The tabulated F-value corresponding to the given degree of freedom (9) is equal to 3,18 for the probability level of 0,05 and 5,35 for the probability level of 0,01 (C. J. Brookes et al. 1966). As it follows from the comparison with the experimentally determined F-values, the differences between relative standard deviations estimated on the basis of repeated measurements of the analytical standard magnesite O II and the standard deviations obtained using the samples with the changed matrix are caused only by random errors. In the case of manganese is the F exp something higher than the F_{95}, it however cannot be accepted as significant for the rejection of the zero hypothesis so it can be concluded, that even the absolute 5 % changes in the concentration of macroelements do not influence significantly the obtained results.

The accuracy of the determination of the trace elements in magnesites by using the described spectrochemical method was checked also by atomic

Table 4

Comparison of the results. *Explanations:* OS — Optical spectroscopy; AAS — Atomic absorption spectrometry; SP — Spectrophotometry.

Samples	Mn (g. t^{-1})			Cu (g. t^{-1})			Sr (g. t^{-1})		Ti (g. t^{-1})	
	OS	AAS	SP	OS	AAS	SP	OS	AAS	OS	SP
M-608	1410	1450	1471	6,3	7	—	10	10,4	288	138
M-609	1800	1820	1549	5,3	6,5	—	17,4	16,2	309	234
M-614	1120	1180	1084	5	6,4	—	174	206	955	920
M-615	1260	1140	1239	5	6,2	—	10	9,5	52	53
M-617	2630	2170	2169	4,8	6,3	—	19,5	20,6	10	5
M-622	1230	1220	1162	5	6,5	—	33	28	10	6
M-648	1110	1250	1008	6,8	7,9	—	10	4,1	174	257
M-653	955	1220	929	6,5	8	—	10	3,5	117	100
M-670	1320	1290	1162	8,5	9,5	—	26,3	22,3	55	54
M-676	1450	1290	1239	8	9,5	—	10	5	145	125
O II	2340	2282	2272	67	67,7	69,3	21	26,4	25,3	26,3

absorption spectrometry (AAS) and/or spectrophotomery (SP). The corresponding results are in Tab. 4.

According to the presented results the deseribed simple method is suitable for reliable spectrochemical determination of geochemically important trace elements in magnesites.

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