GEOLOGICKÝ ZBORNÍK — GEOLOGICA CARPATHICA 31, 1—2, BRATISLAVA, JUNE 1980, PP 177—184

JÁN MEDVEĎ, EDUARD PLŠKO*

SPECTROCHEMICAL DETERMINATION OF MICROELEMENTS IN WEATHERED MATERIALS ON SILICATE ROCKS

(Tab. 6)

Abstract: In the present paper is described a fast, simple and reliable method for the determination of 8 microelements (B, V, Mo, Cu, Ni, Co, Sr, Ba) interesting from the geochemical point of view in weathered materials (coils) in silicate rocks. The determination limit and the precision of the method are given. The accuracy of the results is checked by the use of standard reference materials.

Резюме: В статье описан быстрый простый и достоверный метод для определения 8 микроэлементов (B, V, Mo, Cu, Ni, Co, Sr, Ba), интересный с геохимической точки зрения в выветренных материалах (почвах) на кремнистых породах. Граница определения и точность метода описаны. Правильность результатов проверена применением стандартных сравнительных материалов.

Introduction

The analysis of weathered materials (soils) has in comparison with other geological samples some different specific features. Apart from the electrical parameters the evaporation of these materials as well as the exitation of their spectra is significantly influenced by chemical and physical properties of the analysed samples.

The disturbing effect of matrix can be supressed or even eliminated by the dilution of both the samples and the synthetic calibration standards by spectrochemical additives (G. Holdt, 1962; O. Filo et al., 1967), by the choice of appropriate excitation conditions (E. Plško), 1964), or by mathematical corrections applied to the calculation of concentrations (E. Plško, 1965). As spectrochemical additives different salts of alcali metals (J. Beintema — J. Kroonen, 1955; T. F. Borovik-Romanova, 1956; J. Medveď — J. Jarkovský, 1971) and of alkali earth metals (O. Filo et al., 1967; T. F. Borovik-Romanova, 1956) have been commonly used.

Another specific feature of the soil analysis is the presence of water which can be in weathered materials bound in different kinds (R. Šály — A. Mihálik, 1970). To remove it, heating of samples up to 110 °C is used. This statement can not be considered as absolute; there are several data (W. A. Deer — R. A. Howie, 1962) showing that not all water can be removed at the given temperature. In some cases part of „interlayer" water is retained even at the temperatures of 250—300 °C and its release can overlap the release of OH groups from the lattice of clay mineral. Appart from the mechanical mixtures and simpler organomineral compounds, there exists also a great variety of organic complexes with clay minerals, as described by R. Calvet (1963).

---

* RNDr. Ján Medveď, CSc., Geological Institute, Slovak Academy of Sciences, Zadunajská 15, 811 00 Bratislava; Prof. Ing. Eduard Plško, DrSc., Geological Institute, Faculty of Natural Sciences, Comenius University, Zadunajská 15, 811 00 Bratislava.

The presence of water and organic components causes sputtering of the sample during the arcing which can lead to the lowering of the final analytical precision. The phenomenon can be removed by ignition of the samples at 500—700 °C (T. F. Borovik-Romanova, 1956; J. Medveď — E. Plško, 1977).

In regard to the actuality of solved problems a lot of papers have already been published on spectrochemical analysis of miroelements in weathered materials, in spite of the mentioned experimental difficulties.

As first, the papers by R. L. Mitchell (1940, 1946, 1948, 1951, 1964), R. L. Mitchell and R. O. Scott (1967), R. O. Scott et al. (1971 and J. Gliński (1973) have to be cited.

J. Connor, N. R. Shimp and I. C. F. Tudrow (1957) determined spectrochemically microelements in soil profiles whereas L. Lappi and O. Mäkitie (1955) used for the determination of trace elements in soils the method described by L. H. Ahrens (1954).

Apart from the cited papers further papers by (G. Kupčo, 1959; B. Cambel — G. Kupčo, 1965; L. H. Ahrens — S. R. Taylor, 1962; J. Medveď — E. Plško — J. Cubínek, 1974) served as starting point for the elaboration of the suggested method too.

Experimental part

The basic experimental conditions chosen on the basis of our previous experiences in the spectrochemical analysis of microelements in rocks (J. Medveď et al., 1974; J. Medveď — E. Plško, 1977) as well as on the basis of some preliminary experiments are listed in the Tab. 1.

The blackening of spectral lines was transformed to intensities by using of emulsion calibration curves plotted for regions of 250, 300, 350 and 450 nm by means of preliminary curves (E. Plško, 1969).

In order to remove the bound water all samples were ignited for 3 hours at 700 °C. The loss of ignition was determined and used for the calculation of concentration in natural untreated samples from the determined values.

For to ensure as equal experimental conditions as possible the synthetic calibration standards were ignited too.

As already mentioned the weathered materials show a pronounced variability in their chemical macrocomposition. In order to suppress the unwanted effect of matrix we studied the influence of Li_2CO_3 and NaCl used as spectrochemical additives on the unification of the evaporation. Apart from the spectrochemical additives also graphite powder containing admixed compounds of reference elements was added to the sample.

Spectra with photographic plate moving stepwise each 10 s were taken and evaporation relation curves were constructed (E. Plško, 1964, 1976). On the basis of the evaluation of these curves the addition of NaCl ensures a uniform evaporation in a longer time of arcing for more analysed elements as well as suppresses better the continuous background than the addition of Li_2CO_3. A mixture of sample to graphite powder and to NaCl in the relation of 4 : 3 : 1 was found as appropriate in spite of fact that a significant influence of matrix composition has still been observed. As the matter of fact a further dilution of the sample by the additive would lead to a greater

Table 1

Basic experimental 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
Carrier electrode	SU—308
Counter electrode	SG—359
Gap lenght	4 mm
Relation—sample: graphite:NaCl	4 : 3 : 1
Photographic material	ORWO WU — 3
Developer	ORWO R—09 (1 : 20) 5 min. 20 °C
Exitation	D.C. arc, anodic polarization of the analytical electrode
Voltage	220 V
Current	6 A
Exposure time	90 s

Table 2

Composition of used matrices

Component	Content in %	
	A	B
SiO_2	65.70	48.06
Al_2O_3	14.57	13.70
Fe_2O_3	2.62	10.13
MgO	0.74	6.04
$CaCO_3$	3.36	17.86
Na_2CO_3	6.74	3.36
K_2CO_3	6.28	0.86

Explanations: A — Weathered materials on granite, gneiss and phylite, B — Weathered materials on amphibolite.

lowering of the discharge temperature and thus to the spoiling of the limit of determination for some elements. We therefore continued by the imitation of the macrocomposition of samples by the marcocompositions of synthetic calibration standards.

According to the chemical macrocomposition the weathered materials on silicate rocks can be divided roughly in two groups. The first group contains the weathered materials on granites, gneiss or phyllite and be analysed by using synthetic calibration standards imitating in macrocomposition the standard reference material G-2 (U. S. G. S.). The second group is formed by weathered materials on amphibolite. The samples from this group are analysed by using synthetic calibration standards with a matrix imitating the macrocomposition of the standard reference material W-1 (U. S. G. S.).

Table 3

Wavelengths of used spectral lines

Element	Analytical lines (in nm)	Element	Reference lines (in nm)
B I	249.77	Ge I	265.11
Ba II	455.40	Eu I	459.40
Co I	345.35	Pd I	342.12
Cu I	324.75	Ge I	265.11
Mo I	317.03	Pd I	311.40
Ni I	341.47	Pd I	342.12
Sr I	460.73	Eu I	459.40
V I	318.39	Pd I	311.40

Table 4

Standard deviation of $\triangle Y$ — values

Element	B	Cu	V	Ni	Co	Sr	Ba
Ignited	0.0061	0.0137	0.0526	0.0146	0.0094	0.0102	0.0117
Not ignited	0.0622	0.0206	0.0537	0.0210	0.0132	0.0227	0.0621

Table 5

Relative standard deviations and concentration ranges

Element	S_r	$\triangle C_i$ (in $g.t^{-1}$)	$\triangle C$ (in $g.t^{-1}$)
B	0.108	<10 — 105	10 — 1000
Ba	0.049	272 — >3000	10 — 3000
Co	0.060	13 — 149	3 — 1000
Cu	0.064	7 — 132	3 — 300
Mo	0.096	<1 — 2.7	1 — 300
Ni	0.063	14 — 179	3 — 1000
Sr	0.037	40 — 837	10 — 1500
V	0.088	33 — 427	3 — 1000

The composition of the proposed matrices is given in the Tab. 2.

The calibration standards were prepared by the admixture and thorough homogenization of the analysed elements in appropriate compounds (mainly oxides) to the matrix in concentrations from 0,0001 % up to 1 % growing by the factor $\sqrt{0.1}$.

The linear run of the evaporation relation curves was decisive for the use of 90 s exposition time and also for the selection of optimal reference elements. They were added to the graphite powder in following form and concentration: 0,1 % Ge (as GeO_2), 0,1 % Pd (as $(NH_4)_2PdCl_4$) and 0,1 % Eu (as Eu_2O_3).

The wave-lengths of analytical spectral lines and spectral lines of corresponding reference elements are listed in the Tab. 3.

The spectra of all samples were taken two times and the spectra of all calibration standards three times.

Table 6

Comparison of obtained results with recommended values

SRM U.S.G.S.	Citation	Content in g.t^{-1}							
		B	Mo	Cu	V	Ni	Co	Sr	Ba
W-1	1	17.6	<1	126	300	76	44	200	186
	2a	17.4	0.7	106	248	91	45	182	184
AGV-1	1	<10	2.3	81	135	11.5	13.8	630	1120
	2b	5	3.7	64	121	17.8	15.5	657	1410
	3b	3.8—13.8	1.7—5.5	52—83	70—171	11—27	10—30	348—1050	1047—2700
BCR-1	1	<10	3.7	25	470	13.5	34	400	790
	2b	5	3.9	22	384	15	35.5	345	790
	3b	2.3—12	1.2—6.6	7—33	120—700	8—30	29—60	244—525	480—1230
G — 2	1	<10	1.7	10.7	33	3.5	4.5	460	2100
	2b	2	1.2	10.7	37	6.4	4.9	463	1950
	3b	—	0.9—1.9	6—17	26—60	2—14	2—21	235—680	1500—3000

Explanations: 1 — This paper, 2a — W. H. Blackburn et al. (1971) — Recommended values
2b — F. J. Flanagan (1969) — Recommended values,
3b — F. J. Flanagan (1969) — Range of analytical results.

The analytical calibration curves were plotted in coordinates ΔY against logarithm of the concentration value.

Results and discussion

The ignition of the analysed samples extends the duration of the proposed method in comparison with the methods which do not involve this step. The negative influence of the said operation on one of the economic parameters of the analysis (E. Plško, 1977) is however highly compensated by the improvement of the reliability of the obtained results. The standard deviation of ΔY values characterizing the error of precision estimated from parallel results of one ignited as well as not ignited samples are presented for the analysed elements in the Tab. 4.

As it can be seen from Tab. 4 the ignition of samples leads to more precise results. The accuracy of results obtained with ignited samples is also improved as it follows from a better matching of their macrocomposition with the macrocomposition of the used synthetic calibration standards, whereas the variable content of water in not ignited samples can cause additional systematic errors.

The precision of the determination of concentration can be well characterized by the relative standard deviation (S_r) calculated from parallel results obtained on 35 different samples.

The results of the calculation performed after E. Plško (1973) are in the Tab. 5. In the same table the concentration range ΔC_i corresponding to the contents of elements in question in analysed samples and the concentration range ΔC in which the elements can be reliably determined are also presented. All values are given in $g \cdot t^{-1}$.

The values of the presented relative standard deviation characterize the error of precision of one measurement related to different samples covering the whole concentration range. In practical laboratory work spectra of all samples are taken two times so that the standard deviation of the mean value is lower by the factor 0.707.

There are no available standard reference materials for weathered materials. To check the accuracy of the described method we therefore analysed U.S.G.S. standard reference materials W-1 (diabase), AGV-1 (andesite) and BCR-1 (basalt) according to the procedure for weathered materials on amphibolite and G-2 according to the procedure for weathered materials on granite, gneiss or phyllite.

The obtained results with the recommended values (F. Flanagan, 1969; W. H. Blackburn et al., 1971) as well as with the ranges of analytical results quoted in the first cited paper are listed in the Tab. 6.

The contents of analysed microelements obtained by the procedure described in the present paper fit with the recommended values and all the contents lie in the range of analytical results quoted in the literature.

On the basis of the performed evaluation it is possible to state that the parameters of the proposed spectrochemical method fully correspond to the claims of geochemical study of microelements in weathered materials or soils.

Translated by E. Chmulíková

REFERENCES

AHRENS, L. H., 1954: Quantitative spetrochemical analysis of silicates. Pergamon Press Oxford, 121 p.

AHRENS, L. H., — TAYLOR, S. R., 1961: Spectrochemical analysis. 2 nd Ed. Addison—Wesley, Reading, Mass. London, 454 p.

BEINTEMA, J. — KROONEN, J., 1955: Eine allgemeine Methode zur spektrochemischen Analyse von nichtleitenden Stoffen. Microchim. Acta (Wien), p. 345—350.

BLACKBURN, W. H. — GRISWOLD, T. B. — DENNEN, W. H., 1971: Spectrochemical determination of trace elements in the U.S.G.S. silicate rock standards. Chem. geol. (Amsterdam), 7 .p. 143—147.

BOROVIK-ROMANOVA, T. F., 1956: Spektraľno-analitičeskoje opredelenije ščeločnych i ščeločnozemeľnych elementov v vodach, rastenijach, počvach i porodach. Izd. AN SSSR (Moskva), 183 p.

CALVET, R., 1963: Mise au point bibliographique: les complexes organiques des argiles. Annales agronomiques. (Paris), 14, p. 31—117.

CAMBEL, B. — KUPČO, G., 1965: Petrochemie und Geochemie der metamorphen Hornblendegesteine aus der Kleinkarpatenregion Nauka o zemi, Geologica, Vyd. SAV Bratislava. 1, 104 p.

CONNOR, J. — SHIP, N. R. — TUDROW, I. C. F., 1957: A spectrographic study of the distribution of microelements in some grey wood soils, Soil Sci. (Amsterdam), 83, p. 65—73.

DEER, W. A. — HOWIE, R. A. — ZUSSMAN, J., 1962: Rock-forming minerals 3, Sheet silicates. Longmans London, 165 p.

FILO, O. — MATHERNY, M. — RYBÁROVÁ, Ž., 1967: Die Matrix-effekte bei der spektralen Anregung von Pulvermaterialen. Proc. 14, CSI. (Debrecen), K4, p. 955—969.

FLANAGAN, F. J., 1969: U.S. Geological Survey standards — II. First complication of data for the new U.S.G.S. rocks. Geochim. Cosmochim. Acta (Oxford), 33, p. 81—120.

GLIŇSKIJ, J., 1973: Applicability of the Spectral Emission Analysis in Studies Connected with the Protection of the Natural Agricultural Environment. 17., CSI. (Firenze), p. 688—692.

HOLDT, G., 1962: A study of the influence of buffers on the accuracy and sensitivity of spectrochemical results. Apl. Spectr. (Baltimore), 16, p. 96—102.

KUPČO, G., 1959: Stanovenie stopových prvkov v horninách. Acta geol. geogr. Univ. Com. (Bratislava), 6, p. 352—360.

LAPPI, L. — MÄKITIE, O., 1955: Spectrochemical determination of the Trace Elements in Soil. Acta Agr. Scand. (Helsinki), 5, p. 69—73.

MEDVEĎ, J. — JARKOVSKÝ, J., 1971: Quantitative spektrochemische Methode zur Bestimmung von Mikroelementen in Karbonat-gesteinen. Sympózium o metódach stanovenia nízkych koncentrácií prvkov v nerastných surovinách, Smolenice 1969, Vyd. Univ. Kom. (Bratislava), p. 129—149.

MEDVEĎ, J. — PLŠKO, E., 1977: Spektrochemische spurenbestimmung in ultrabasischen Gesteinen. Sympózium o petrogenéze a geochémii geologických procesov, Bratislava, p. 297—303.

MEDVEĎ, J. — PLŠKO, E. — CUBÍNEK, J., 1974: Studium der Zuverlässigkeit von Mikroelementen in Silikatgesteinen. Acta geol. geogr. Univ. Com. Geologica (Bratislava), 27, p. 183—194.

MITCHELL, R. L., 1940: The spectrographic determination of trace elements in soil. I. The catode layer arc. J. Soc. Chem. Ind. (Philadelphia), 59, p. 210—218.

MITCHELL, R. L., 1946: Applications of spectrographic analysis to soil investigations. Analyst (Cambridge), 5, p. 361—366.

MITCHEL, R. L., 1948: The spectrographic analysis of soils, plants and related materials. Pergamon Press (Oxford), 114 p.

MITCHEL, R. L., 1951: The spectrographic analysis of trace elements in rocks, minerals and soils. Microchim. Acta (Wien), 36—37, p. 1042—1049.

MITCHEL, R. L., 1964: The Spectrochemical Analysis of Soils, Plants and Related Materials, Commonwealth Bureau of Soils, Tech. Commun. (Harpenden), 44A, 225 p.

MITCHELL, R. L. — SCOTT, R. O. — URE, A. M., 1967: A display microphotometer for use in the analysis of soils and related materials. 13, CSI. (Ottawa), p. 324—338.

PLŠKO. E.. 1964: Sledovanie odparovania nevodivých materiálov z uhlíkových elektród

pri spektrálnej analýze. Chem. zvesti (Bratislava), 18, p. 830—836.
PLŠKO, E., 1965: Korekcia vplyvu binárnej matrix pri spektrochemickej analýze. Chem. zvesti (Bratislava), 19, p. 544—550.
PLŠKO, E., 1969: Bedeutung der Vorkurve bei der Transformation der Schwärzung auf die Intensität der Spektrallinien. Chem. zvesti (Bratislava), 23, p. 150—158.
ULŠKO, E., 1973: Színkepelemzési modszerek statistikus parametereinek meghatározása üzemi minták alapján. MTA, Kémisi közlemények. (Budapest), 39, p. 351—361.
PLŠKO, E., 1976: Les propriétés spectrochimiques de certaines sources lumineuses. Pure appl. Chem. (Oxford), 48, p. 69—75.
PLŠKO, E., 1977: A gazdaságossági paraméterek szerepe a színképelemzésben. MTA, Kémiai Közlemények. (Budapest), 48, p. 316—320.
SCOTT, R. O. — MITCHELL, R. L. — PURVES, D. — VOSS, R. C., 1971: Spectrochemical Methods for the Analysis of Soils, Plants and other Agricultural Materials. CCDSW Bull. (Aberdeen), 2, 87 p.
ŠÁLY, R. — MIHÁLIK, A., 1970: Ílové nerasty v lesných pôdach na Slovensku. Náuka o Zemi. Geol. Zbor. — Geol. Carpath. (Bratislava), p. 109.

Review by J. JARKOVSKÝ Manuscript received September 10, 1979