Spectrochemical determination of low tungsten contents in silicate rocks

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At the multielemental spectrochemical analysis of silicate rocks apart from tungsten up to 20 trace elements are determined. At these compromise conditions tungsten can be determined only over 30 ppm or even 100 ppm. In the present work the monoelemental spectrochemical procedure for determination of W in silicate rocks in mass fractions over 0.3 ppm is described. The sample is mixed with the mixture of $PbCl_2$ and $AgNO_3$ excited in A.C. arc. The accuracy of the obtained results was checked by means of standard reference materials.

При многоэлементном спектрохимическом анализе силикатных пород кроме W определяется до 20-ти других элементов в следах. При этих условиях можно W определить только при его значениях выше 0,003 % (масс.) или даже 0,010 % (масс.). В данной работе описан спектрохимический метод, позволяющий только определение W в силикатных породах при массовых долях, начиная с 0,00003 % (масс.). Образец смешивают с смесью $PbCl_2$ и $AgNO_3$ и возбуждают в дуге переменного тока. Правильность результатов была проверена с помощью стандартных референтных материалов.

Apart from the deposit occurrence of tungsten this element is found in the nature also in the scattered form of accessoric minerals in silicate rocks. The analytical determination of low tungsten contents in geological materials is connected with difficulties and it has not yet been solved satisfactorily.

At the spectrochemical determination of low tungsten contents the role is played not only by the fact that its spectrum is extremely line rich and consequently the intensity of the lines is comparatively low, but physical properties of some tungsten compounds, such as their melting and boiling points have unfavourable influence, too. The metallic tungsten belongs to the at least volatile elements at all. Its carbide created at normal spectrochemical analyses performed using carbon electrodes or mixtures of the sample with graphite powder has the same properties so that the evaporation of this element lasts relatively long time. Since many other compounds of tungsten, mainly its halogenides evaporate relatively easily, several procedures

using different carriers and spectrochemical additives supporting the formation of easily volatile tungsten compounds were proposed.

The problem of spectrochemical tungsten determination was treated rather early. *Nedler* [1] published the determination of W, Sn, and Mo in slags and ores and *Raikhbaum* [2] the determination of W in ores and minerals.

At the multielemental quantitative spectrochemical analysis of silicate rocks up to 20 trace elements inclusive W are determined simultaneously. At these procedures compromise experimental conditions are applied so that W can be according to our experience determined only over 30 ppm resp. 100 ppm and even with a relatively high error.

Among the multielemental determinations the work by *Rusanov* [3] enabling simultaneous determination of 13 elements in silicate rocks can be mentioned. The sample is mixed with powdered quartz containing 30 % Na_2CO_3. No reference element is used and the detection limit for W is 10 ppm.

The clark value of tungsten in the Earth crust is according to *Voitkevich et al.* [4] approximately about 1.3 ppm. It is therefore necessary to have analytical methods enabling reliable determination of tungsten mass fraction in the vicinity of this value, which has according to recent experience been possible only by monoelemental methods optimized only for this element.

Among the spectrochemical additives proposed for the tungsten determination by different authors in the majority are halogenides, *viz.* chlorides. The thermochemical reactions of W were studied by *Schroll* [5], *Rautschke* [6], *Kántor et al.* [7].

Pavlenko [8] determined tungsten in igneous rocks from 5 ppm by the addition of AgCl. The further method using AgCl as carrier, described by *Janda* [9] has the detection limit 0.1 ppm. The sample, AgCl and PbO as flux is evaporated from crucible electrode by the use of double arc of 30 A. *Kupčo et al.* [10] used the mixture of AgCl and $PbCl_2$ with sample and obtained the detection limit of 1—3 ppm. *Ivanova* [11] determined W, Mo, Sn in rocks by mixing the sample with $CuCl_2$ or with polytetrafluoroethylene. *Špačková* [12] used for the determination of W and Mo in silicates spectrochemical additive composed of the mixture of LiF with ZnS.

A similar problem to the choice of an appropriate spectrochemical additive is the choice of the reference element having similar properties with tungsten. The use of different elements has been described. *Raikhbaum* [2] used Co; *Nedler* [1] Na; *Janda* [9] and *Kupčo* [10] used Ag; several authors worked with background in the vicinity of the measured line; *Plško* [13] valuated records of spectrum without any reference element, *etc.*

As already mentioned the spectrum of tungsten is composed of a great number of weak lines. For analytical purposes the most intensive tungsten lines from the visible range of spectrum, *viz.* λ (W I) = 400.875 nm and λ (W I) = 429.461 nm are

commonly used. In the ultraviolet range the most frequently used lines are as follows: λ (W I) = 294.698 nm; λ (W I) = 294.439 nm, and λ (W I) = 289.645 nm. The ultraviolet lines can, however, be interfered by the Nb, Fe, Cr, Ce, Mo, V and in the visible spectrum possible coincidences with Ti and Fe lines must be taken into account.

Experimental

At the elaboration of the spectrochemical procedure for the determination of low tungsten contents experimental work was focused on the checking of the literature citations and recommended procedures with the use of our instrumental facilities.

In the first period it was looked for the most convenient spectrochemical additive with the objective to obtain a reliably measurable spectral line at the W mass fraction of 1 ppm. Following spectrochemical additives were studied: Cu, AgCl, Cu + AgCl, $CuCl_2$, Cu_2Cl_2, LiF + ZnS, teflon, $PbCl_2$, AgCl + $PbCl_2$, and $PbCl_2$ + $AgNO_3$. The samples mixed with the additives were arced from the crater of carbon electrodes in both the D.C. and A.C. arc. In the case of the mixture with copper powder the samples were arced also from copper electrodes in order to fully avoid the influence of the carbon; no reproducible results were, however, obtained by this procedure.

The mixture of $PbCl_2$ with AgCl was found as the most convenient spectrochemical additive, but problems with the preparation of AgCl and its homogenization with the sample arose. The mixture of $AgNO_3$ with $PbCl_2$ in the mass ratio 2:1 mixed with the sample in the mass ratio 3:4 was therefore used.

Different shapes of electrodes were examined. The graphite electrodes with the crater diameter 4.5 mm and crater depth 5 mm were found as the most convenient. Further improvement of the detectability was achieved by the filling of two similar electrodes and their use as sample bearing and counter electrodes, so that two times greater mass of sample was evaporated into the arc plasma.

Because of the higher intensity of spectral lines obtained in A.C. arc the further work was performed with this excitation source. The exposure time was determined from the intensity—time curve.

Following internal reference elements were examined: V, Eu, Co, Cu, Nb, and Ag. Nb was found as the most appropriate not only as regards the run of evaporation relation curves [14—16] but also due to some well measurable spectral lines occurring in the investigated spectral range. The evaporation relation curve for W and Nb is shown in Fig. 1.

We worked in the visible region using the most intensive spectral line λ (W I) = 400.875 nm. As observed the analytical spectral line was in the case of taking the spectrum using the single pass through the spectrograph interfered by the line λ (Ti I) = 400.893 nm. It cannot be therefore used for the analysis of silicate rocks which practically always contain measurable interfering concentrations of titanium. On the other hand, the use of other W spectral lines was disadvantageous as concerns the detection limit. We therefore took the spectra using the double pass enabling the significant resolution of the Ti line from the W line as it can be seen on the record presented in Fig. 2.

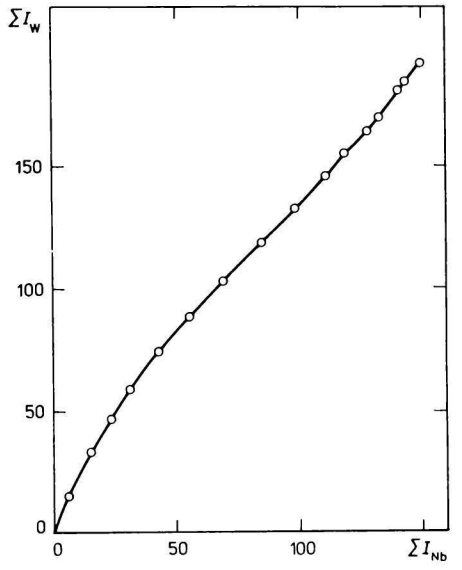

Fig. 1. Evaporation relation curve for W and Nb.

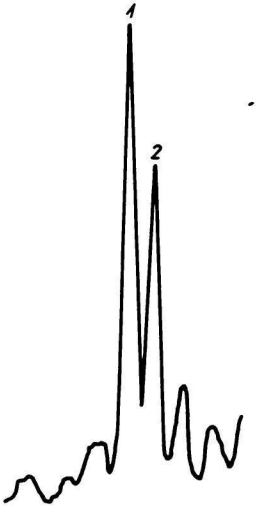

Fig. 2. Record of W and Ti spectrum. *1.* λ (W I) = 400.875 nm; *2.* λ (Ti I) = 400.893 nm.

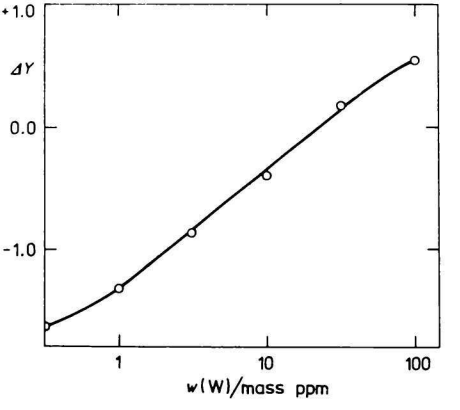

Fig. 3. Analytical calibration curve for W.

The calibration standards were prepared from reagents of spectral grade purity of the composition corresponding in the macrocomponents to the standard reference material G-2 (U.S.G.S.) to which WO_3 was added in mass fraction from 0.1 mass ppm to 1 mass % W. The spectra were taken under the experimental conditions listed in Table 1.

Table 1

Experimental conditions

Spectrograph	PGS-2 (Zeiss, Jena)
Grating	652 number of grooves/mm; 1st order, double pass
Slit width	0.020 mm
Imaging	3 lenses with intermediate stop 5 mm
Electrodes	SU 305, Elektrokarbon, Topoľčany
Electrode gap	8 mm
Excitation	A.C. arc, 12 A
Photographic emulsion	ORWO, WU-3
Developing	ORWO R 09; 1:20; 5 min; 20 °C
Additives	$m[w(AgNO_3):w(PbCl_2)=2:1]:m(\text{sample})=3:4$

We measured as analytical spectral line the line $\lambda(\text{W I})=400.875$ nm, as well as the background in its neighbourhood and the internal reference spectral line $\lambda(\text{Nb I})=410.092$ nm. The measured blackenings were transformed to the logarithms of intensities using emulsion calibration curve constructed at $\lambda=405$ nm by means of the preliminary curve [17]. In the case of the W line background correction was performed. The analytical calibration curve was plotted in the coordinates ΔY *vs.* $\log(w/\text{mass ppm})$ (Fig. 3). As it can be seen the run of the analytical calibration curve is practically linear at mass fractions higher than 0.3 mass ppm.

Conclusion

The described method enables the tungsten determination in the mass fractions range between 0.3 mass ppm and 1 mass %.

The error of the precision of the described method is characterized by the relative standard deviation of one measurement equal to 7 %. This value was estimated by the method described by *Plško* [18] from the parallel results obtained on natural samples.

The accuracy of the method was checked by the use of four international standard reference materials. The results are presented in Table 2. The deviation of

Table 2

Checking of the accuracy of the results

Standard reference material	Recommended value *w*/mass ppm	This paper *w*/mass ppm
Scarn	8.5—11.5	16.2
Granite	22—25	24
Feldspar slate	15	15
Quartzite	23	23

the experimentally found value of the tungsten mass fraction from its recommended value in the case of scarn can be explained by the differences in the mineral and chemical composition of this material as compared with the composition of the granitic matrix G-2 which served as the basis at the elaboration of the method and so by their different spectrochemical behaviour. In the case of the other three types of standard reference materials having similar composition of the matrix, very good agreement of the results was achieved.

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References

1. Nedler, V. V., *Zavod. Lab.*, No. 11 (1938); cited in Mandeľshtam, S. L., *Vvedenie v spektraľnyi analiz*, p. 260. Gos. izd. tekhn.-teor. literatury, Moscow—Leningrad, 1946.
2. Raikhbaum, Ya. D., *Zavod. Lab.*, No. 6 (1939); cited in Mandeľshtam, S. L., *Vvedenie v spektraľnyi analiz*, p. 260. Gos. izd. tekhn.-teor. literatury, Moscow—Leningrad, 1946.
3. Rusanov, A. K., *Osnovy kolichestvennogo spektraľnogo analiza rud i mineralov*, p. 360. Nedra, Moscow, 1971.
4. Voitkevich, G. V., Miroshnikov, A. E., Povarennykh, A. S., and Prokhorov, V. G., *Kratkii spravochnik po geokhimii*, p. 278. Nedra, Moscow, 1970.
5. Schroll, E., *Proc. XIVth Colloquium Spectrosc. Internat.*, p. 397. Debrecen, 1967.
6. Rautschke, R., *Spectrochim. Acta 23B*, 55 (1967).
7. Kántor, T., Hanák–Juhai, E., and Pungor, E., *Spectrochim. Acta 35B*, 401 (1980).
8. Pavlenko, L. L., *Zh. Anal. Khim. 15*, 463 (1960).
9. Janda, I., *Mikrochim. Acta II1976*, 473.
10. Kupčo, G., Klinčeková, M., and Ďuriš, M., unpublished results.
11. Ivanova, G. F., *Zh. Anal. Khim. 20*, 82 (1965).
12. Špačková, A., *Collect. Czech. Chem. Commun. 30*, 1255 (1965).
13. Plško, E., *Chem. Anal.* (Warsaw) *22*, 603 (1977).
14. Plško, E., *Chem. Zvesti 18*, 830 (1964).
15. Plško, E. and Kubová, J., *Chem. Zvesti 27*, 781 (1973).
16. Plško, E., *Pure Appl. Chem. 48*, 69 (1976).
17. Plško, E., *Chem. Zvesti 23*, 150 (1969).
18. Plško, E., *Kem. Közlem. 39*, 351 (1973).

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