

Determination of Niobium and Tantalum in Geological Materials by Atomic Emission Spectroscopy with Inductively Coupled Plasma

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A method using atomic emission spectroscopy with inductively coupled plasma has been developed for determination of low Nb and Ta contents in geological materials. The sample decomposition and the stabilization of Nb and Ta in the gained solution, as well as the separation-preconcentration procedure are described. The study of interferences, among which the Fe influence is the most significant, is performed and appropriate correction proposed. The reliability of the described procedure is checked by the analysis of certified reference materials and in the case of Ta also by instrumental neutron activation analysis.

Different methods ensuring a given level of attained basic analytical parameters have been used for the determination of Nb and Ta in geological materials. In recent time X-ray fluorescence spectrometry (XRFS) can be listed as dominant technique used for the determination of low Nb contents [1, 2] and instrumental neutron activation analysis (INAA) for the determination of Ta [3, 4].

In smaller extent mass spectrometry with inductively coupled plasma (MS-ICP) has been used for the determination of the element in question [5]. It is necessary to emphasize that for some purposes (e.g. geochemical prospecting) the prices of analytical results obtained by the above-mentioned methods are rather high. According to the published data, among the financially less pretentious procedures, spectrophotometric determinations with different reagents [6–8], extractions [9, 10], micelles [11] and mainly methods based on atomic emission spectrometry with excitation in inductively coupled plasma (AES-ICP) [12] are the most common.

The mean contents of Nb and Ta in different types of rocks are as follows: ultrabasic rocks — 1 ppm of Nb and 0.018 ppm of Ta, basic rocks — 20 ppm of Nb and 0.48 ppm of Ta, granitoid rocks — 20 ppm of Nb and 3.5 ppm of Ta [13, 14].

Owing to the introduced low level of Nb and Ta occurrence in different types of geological materials [15], as compared with the detection limit obtained for these elements by AES-ICP, in the majority of cases reliable results can be gained only after a convenient separation-preconcentration procedure.

Apart from the mentioned purpose, separation-preconcentration procedures are used also in order to lower or eliminate spectral interferences of concomitants, mainly of Fe, W, U, Zr on the most sen-

sitive Nb and Ta spectral lines. Despite of the fact that several examples, procedures, and rules for the correction of spectral interferences have been described, they can be used in general only for a given type of real samples having a defined macrocomposition what in the case of geological materials can often be very complicated [16–19].

In spite of the possibility to eliminate or to decrease existing spectral interferences by the use of appropriate procedures, present accompanying elements elevate the background level and consequently cause a deterioration of detection limits. The application of an appropriate separation-preconcentration procedure therefore not only diminishes the influence of possible spectral interferences, but simultaneously improves the detection limit even without necessity of a powerful preconcentration.

At the determination of Nb and Ta in geological materials special care has to be given to the sample decomposition. Minerals containing Nb and Ta belong to chemically resistant materials and their decomposition is performed preferably by fusion. Taking into account that solutions obtained after the fusion of samples show relatively high salt contents influencing negatively the reliability of AES-ICP determinations, it is more advantageous to decompose geological materials by acid mixture and to use fusion only for the decomposition of the insoluble rest.

EXPERIMENTAL

Stock solutions of niobium and tantalum (100 $\mu\text{g cm}^{-3}$) were prepared as follows: 5 cm^3 of HF is added in a platinum dish to 0.1 g Nb or Ta. Aqueous so-

lution of HNO_3 (volume ratio = 1 : 1) is admixed drop by drop till a full dissolution of the metal. The solution with 2 cm^3 of concentrated H_2SO_4 is evaporated two times to SO_3 fumes. The residue is diluted with 1 % solution of tartaric acid to 1 dm^3 .

For determination of low Nb and Ta contents spectrometer Plasmakon S 35 (Kontron, FRG), sequential, with grating 2 400 lines mm^{-1} , concentric glass nebulizer (type B, Meinhard), Ar/Ar plasma with parameters: power 1.7 kW; flow rate of cooling gas 14.5 $\text{dm}^3 \text{min}^{-1}$, of plasma gas 0.9 $\text{dm}^3 \text{min}^{-1}$, of carrier gas 0.8 $\text{dm}^3 \text{min}^{-1}$, sample uptake rate 1.5 $\text{cm}^3 \text{min}^{-1}$, controlled by peristaltic pump; integration time 5 s was used.

Sample Dissolution and Preconcentration-Separation Procedure

0.5–1.0 g of sample is treated in a platinum dish ca. for 2 h with 5 cm^3 of 40 % HF. (Rock samples containing greater amounts of organic compounds are before weighing ignited in electric oven for 1–1.5 h at 600 °C.) Another 10 cm^3 of HF and 1 cm^3 of 65 % HNO_3 , and 1 cm^3 of 70 % HClO_4 are added and evaporated to dense fumes of HClO_4 (not to dryness). After cooling 5 cm^3 of 40 % HF are added and the content is evaporated to dryness. 1 cm^3 of 70 % HClO_4 and 10 cm^3 of H_3BO_3 (saturated solution) are then added to the residue and again evaporated to dryness. The obtained residue is moistened with 1 cm^3 of 37 % HCl, 20 cm^3 of 1 % tartaric acid are added and digestion to full dissolution is performed. If insoluble residue is present it is separated by filtration and washed. The filter is burned, ignited and obtained ashes are fused with NaBO_2 . The fusion is dissolved in 5 cm^3 of 1 % tartaric acid, added to the main solution and adjusted with 1 % tartaric acid to 100 cm^3 .

To the aliquot part of the sample solution (50 cm^3) prepared according to the above described acid decomposition including the fusion of the insoluble rest, H_2SO_4 is added to pH = 4.5–5.0. The solution is diluted by 100–150 cm^3 of redistilled water and 2 g of tartaric acid are added. The sample solution is cooled to 4–10 °C and precipitated with 6–10 cm^3 of freshly prepared 6 % aqueous solution of cupferron. The precipitate is filtered and washed on the filter with chilled (4–10 °C) diluted cupferron containing H_2SO_4 (500 cm^3 of concentrated H_2SO_4 + 500 cm^3 of water + 0.15 g of cupferron).

The filter with the precipitate is dried and 0.1 g of powdered oxalic acid is added (to prevent a vigorous thermal decomposition of cupferronates and consequently Nb and Ta losses). After the ignition at 900–1000 °C to constant mass the solid is treated with a mixture of 5 cm^3 of 40 % HF with 0.5 cm^3 of

98 % H_2SO_4 and the content is evaporated to dryness, moistened with 1 cm^3 of 37 % HCl and 5 cm^3 of redistilled water. 30 % H_2O_2 is thoroughly added dropwise till a full dissolution. The solution is brought to the final volume of 100 cm^3 with redistilled water.

RESULTS AND DISCUSSION

At the choice of spectral lines suitable for the determination of low Nb and Ta contents by AES-ICP we used data published on the properties of sensitive lines of these elements ensuring the best detection limit with special attention to possible spectral interferences of accompanying elements [20–25].

At optimized experimental conditions we investigated the influence of three most important plasma parameters: observation height, carrier gas flow rate, and plasma power on the detection limit obtained for two most sensitive spectral lines of Nb and Ta.

We found out that maximal net intensities were obtained at lower viewing heights despite of the "hard" character of the investigated spectral lines (Fig. 1).

On the contrary, the net intensity depends significantly (especially for Ta – see Fig. 2) on the plasma power which corresponds with theoretical expectation for "hard" lines [26]. Apart from the net intensity I_{net} Fig. 2 shows also the dependence of the signal to background ratio (SBR) and of the signal to noise ratio (SNR) on the plasma power; these relations being important as concerns the attainable detection limit. For the final determination we have taken the optimal plasma power for Ta, i.e. 1.7 kW because we needed the best possible detection limit, namely for this element owing to its lower occurrence in geological materials (by ca. one order of magnitude) as compared with Nb, as well as owing to worse detection limits for Ta (Table 1).

As regards the investigations performed in dependence on carrier gas flow rate (Fig. 3), on the basis of the same considerations as in the previous case 0.8 $\text{dm}^3 \text{min}^{-1}$ carrier gas flow rate, optimum for Ta determination, was taken for both elements.

Table 1. Optimization of Observation Height

Element	λ	EP + IP	h	D.L.	s_r
	nm	V	mm	mg dm^{-3}	%
Ta	240.063	13.81	10	0.028	1.24
Ta	268.517	13.01	12	0.030	1.32
Nb	309.418	11.40	10	0.004	1.28
Nb	316.340	11.18	12	0.008	1.50

EP – excitation potential, IP – ionization potential, h – observation height, s_r – relative standard deviation estimated from ten repeated measurements, D.L. – detection limit based on 3s.

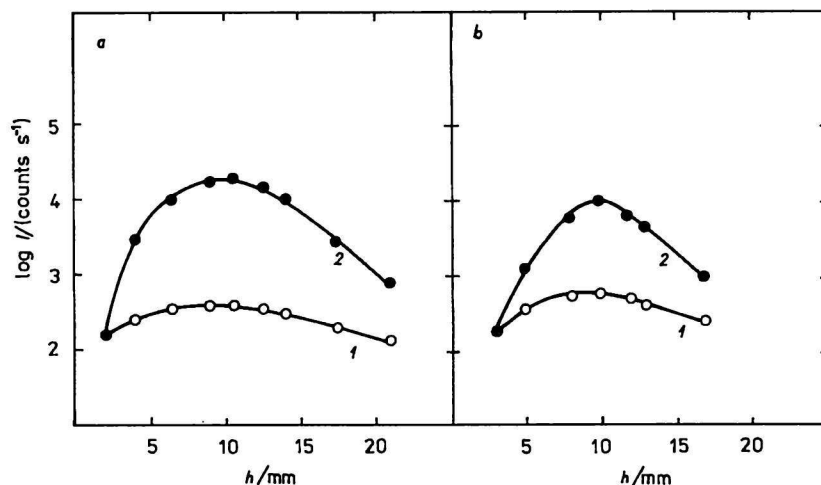


Fig. 1. Dependence of the signal intensity of 1. background and 2. peaks on the observation height for a) Nb and b) Ta.

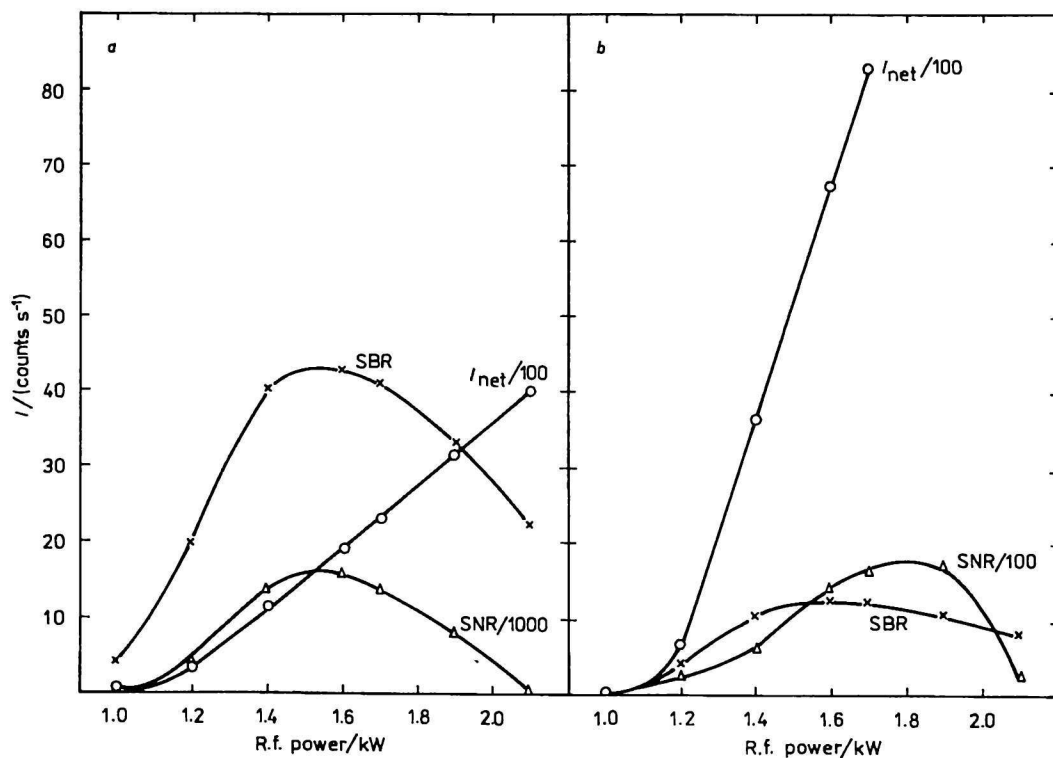


Fig. 2. Plasma power optimization for the determination of a) Nb and b) Ta. SBR – signal to background ratio, SNR – signal to noise ratio, I_{net} – net intensity.

In order to stabilize Nb and Ta in sample solutions, tartaric acid as complexing agent was added. A growth of the tartaric acid content leads, however, to lower net intensity values at practically unchanged background intensities. The determined intensity drop caused by the addition of tartaric acid to analyzed solutions is presented in Table 2.

At tartaric acid contents higher than 20 cm^3 ($c = 1 \text{ mol dm}^{-3}$) in 100 cm^3 of the analyzed solutions, clogging of injector by carbon generation occurred. For all determinations the content of 1 M tartaric acid in

calibration and sample solutions was set to 10 cm^3 in 100 cm^3 .

Table 2. Influence of Tartaric Acid on the Intensity of Ta Spectral Line (1 mg of Ta in 100 cm^3)

Addition of 1 M tartaric acid		$I_{\text{net rel}}$
V/cm^3		
0		1.00
10		0.90
15		0.88
20		0.88
25		0.88

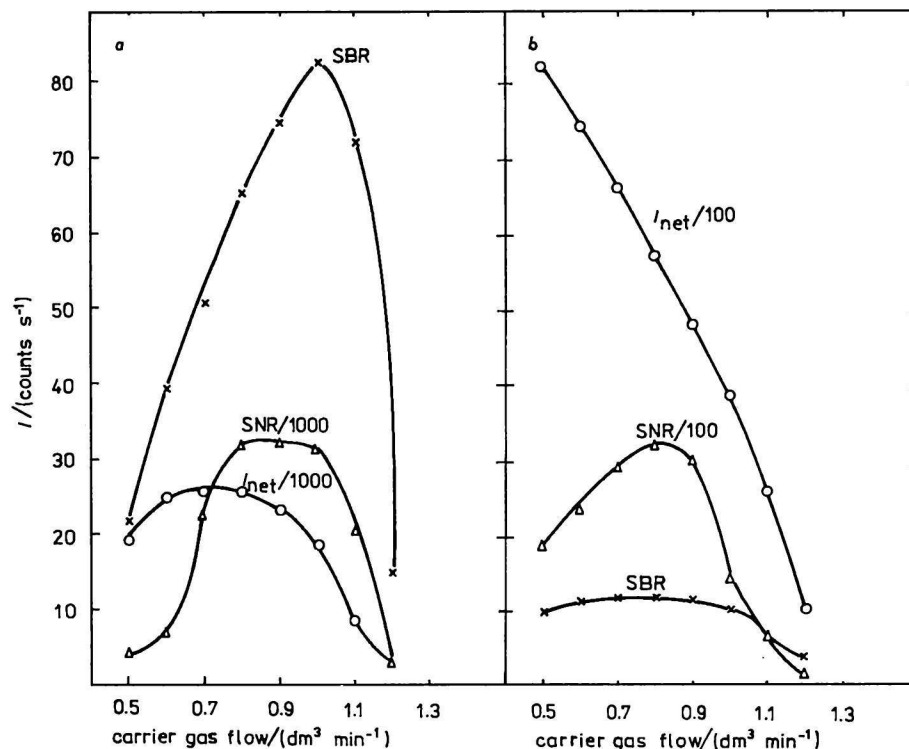


Fig. 3. Carrier gas flow rate optimization for the determination of a) Nb and b) Ta. Denotation as in Fig. 2.

Possible spectral interferences occurring at the used spectral lines of Nb and Ta were investigated on spectral scans of corresponding model solutions. These solutions contained Nb, Ta, and possible interfering elements (Fe, Ti, V, W) in the amount of substance ratio 10 : 1 : x , where $x = 10$ and 100 and for Fe also $x = 1000$. The results have shown that the most serious problems are caused namely at the Ta determination in the presence of Fe, as it can be seen in Fig. 4.

The elimination of interferences was performed by the use of correction procedure [27—29] based on the following consideration: At the peak wavelength of the analytical line the intensity of the interfering spectral line is determined. The intensity measured at the wavelength where the opposite wing of the interfering spectral line (or of another adjacent spectral line of the interfering element) shows the same intensity as it does at the peak wavelength of the analytical spectral line, is subtracted from the gross intensity measured at the peak wavelength of the analytical line. The procedure enables so a simple simultaneous background and interference correction. The correction can be used at the ratios Fe : Ta up to 1000 : 1. At higher Fe contents separation-preconcentration procedures essentially lowering the concentration of Fe have to be performed. The essential part of Fe and Al from the decomposed samples was removed before preconcentration procedure with cupferron by hydrolysis in HF medium.

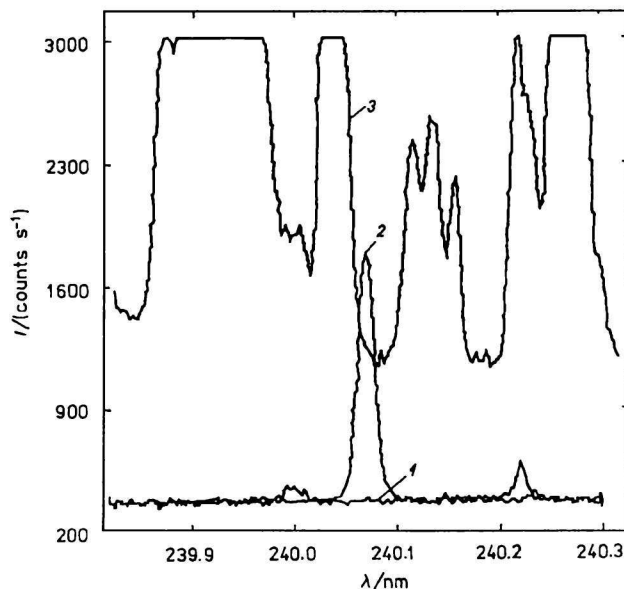


Fig. 4. Spectrum of the Ta and Fe model solution: 1. blank, 2. 1 ppm Ta, 3. 1000 ppm Fe.

Table 3. Comparison of Results for Granite Samples

Sample	Method	Nb		Ta	
		\bar{w} /ppm	s_r /%	\bar{w} /ppm	s_r /%
1	AES-ICP	37.82	5.8	16.65	4.5
	INAA			16.5	
2	AES-ICP	9.0	8.5	1.49	9.2
	INAA			1.43	

\bar{w} – average content from ten times repeated analysis, s_r – relative standard deviation ($n = 10$).

The reliability of results gained by the described AES-ICP analytical method was checked for Ta determination on real samples, two granite ones analyzed by INAA and for both investigated elements by the analysis of attested reference materials.

The sample 1 contains according to the INAA results 16.5 ppm of Ta, *i.e.* a content which should be determined with sufficient reliability by the described AES-ICP method without any preconcentration-separation step. The sample was ten times decomposed and the content of Nb and Ta was determined using the correction on Fe. Comparison of the results obtained by both the methods, as well as the standard deviation of the AES-ICP procedure containing also the error of decomposition is presented in Table 3.

Since the content of Ta in sample 2 is by order of magnitude smaller than in the previous case, the use of separation-preconcentration step was necessary.

The reliability of results was verified also by analyzing attested reference materials. The results are listed in Table 4.

Table 4. Analysis of Certified Reference Materials

Material	Value	$\rho(\text{Nb})/(\mu\text{g dm}^{-3})$	$\rho(\text{Ta})/(\mu\text{g dm}^{-3})$
NIM L [*]	Experimental	1000	20.1
(lujavrit)	Recommended	960	22.0
NIM G [*]	Experimental	50.6	4.6
(granite)	Recommended	53.0	4.5

* Certified reference materials MINTEK South Africa.

CONCLUSION

Determination of low Nb and Ta contents in different types of geological materials cannot be performed using only one recommended AES-ICP procedure. For samples of this kind showing a great variability of their macrocomposition, special attention has to be paid not only to the choice of appropriate decomposition and stabilization of Nb and Ta in the solution, but also to a comprehensive study of spectral interferences and possibilities of their correction or elimination which can be different for any type of material. The presented work represents a contribution to the solution of the mentioned complex problem.

REFERENCES

1. Stork, A. L., Smith, D. K., and Gill, J. B., *Geostand. Newsl.* 11, 107 (1987).
2. Vivit, D. V. and King, B. S. W., *Geostand. Newsl.* 12, 363 (1988).
3. Potts, P. J., *A Handbook of Silicate Rocks*. Blackie, Glasgow, 1987.
4. Potts, P. J., Williams Thorpe, O., Isaacs, M. C., and Rogers, N. W., *Geostand. Newsl.* 9, 173 (1985).
5. Hall, G. E. M. and Pelchat, J. C., *J. Anal. At. Spectrom.* 5, 339 (1990).
6. Sandell, E. B. and Onishi, H., *Chemical Analysis, Traces of Metals: General Aspects*, Vol. 3, Part I. Wiley—Interscience, New York, 1978.
7. Liu, Y., Zhou, F., Hu, Z., Jia, X., and Wu, Z., *Huaxue Shiji* 10, 207 (1988); *Anal. Abstr.* 3B, 170 (1989).
8. Verdizade, N. A. and Amrakov, T. I., *Zh. Anal. Khim.* 44, 671 (1989).
9. Jin, Z., Tang, Z., Huang, B., and Wu, Y., *Lihua Jiannan Huaxue Fence* 25, 289 (1989); *Anal. Abstr.* 11B, 130 (1990).
10. Nakashima, R., Sasaki, S., and Shibata, S., *Anal. Chim. Acta* 70, 265 (1974).
11. Sanz-Medel, A., Garcia Alonso, J. I., and Blanco Gonzales, E., *Anal. Chem.* 57, 1681 (1985).
12. U.S. Geological Survey Bull. 1770 *Methods for Geochemical Analysis*, 1987.
13. Krivan, V., Hausbeck, R., Kriesmer, R., Wilhartitz, P., and Ortner, H. M., *ICP Inform. Newslett.* 15, 770 (1990).
14. Vinogradov, A. P., *Geokhimiya* 7, 555 (1962).
15. Taylor, S. R., *Geochim. Cosmochim. Acta* 29, 1989 (1964).
16. Boumans, P. W. J. M., *Inductively Coupled Plasma Emission Spectroscopy*, Part I, p. 358. Wiley—Interscience, New York, 1987.
17. Piško, E., *Acta Fac. Rerum Nat. Univ. Comenianae (Chimia)* 39, 91 (1991).
18. Thompson, M. and Walsh, J. N., *Handbook of ICP Spectrometry*. Blackie, Glasgow, 1989.
19. Taylor, P. and Schutyser, P., *Spectrochim. Acta* 41, 98 (1986).
20. Wunsch, G. and Wennemer, A., *Fresenius Z. Anal. Chem.* 329, 546 (1987).
21. Meggers, F. W., Corliss, Ch. H., and Scribner, B. F., *NBS Monograph 145, Tables of Spectral-Line Intensities*. U.S. Government Printing Office, Washington, 1975.
22. Harrison, G. R., *Wavelength Tables*, Massachusetts Institute of Technology. Wiley, New York, 1969.
23. Boumans, P. W. J. M., *Line Coincidence Tables for ICP-AES*. Pergamon Press, Oxford, 1980.
24. Wohlers, C. W., *ICP Inform. Newslett.* 10, 593 (1985).
25. Winge, R. K., Fassel, V. A., Peterson, V. J., and Floyd, M. A., *ICP-AES, An Atlas of Spectral Information*. Elsevier, Amsterdam, 1985.
26. Boumans, P. W. J. M., *ICP Inform. Newslett.* 4, 89 (1979).
27. Piško, E., *XXVI. Colloquium Spectroscopicum Internationale; Selected Papers* 7, 113 (1989).
28. Piško, E., *Chem. Anal. (Warsaw)* 35, 237 (1990).
29. Piško, E., *Acta Fac. Rerum Nat. Univ. Comenianae (Chimia)* 38, 31 (1990).

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