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СОДРЖИНА

Виолета Стојанова, Гоше Петров

Корелација на стратиграфска фораминиферна распространетост
во овчеполскиот и тиквешкиот палеогенски басен во Република Македонија 1–8

Орце Спасовски, Војо Мирчовски

Нови податоци за хидротермалните промени во наоѓалиштето Плавица
(Источна Македонија) 9–16

Тодор Серафимовски, Тадеј Доленец, Горан Тасев, Настја Роган, Матеј Доленец

Состав на главните минерили од порфирското бакарно наоѓалиште Бучим,
Република Македонија 17–26

Блажо Боев, Тена Шијакова-Иванова, Лидија Робева-Чуковска, Иван Боев

Минералошки испитувања на примероци од археолошкиот локалитет „Стоби“
со примена на рендгенска дифракција 27–41

Милена Тасеска, Петре Макрески, Векослава Стибиль, Радојко Јакимовик,

Трајче Стafilov

Определување на елементи во траги во хематитен референтен материјал JSS-804-1
со примена на k_0 -INNA 43–48

Војо Мирчовски, Орце Спасовски, Владо Мирчовски

Загадување и заштита на подземните води во алувијалните седименти на реката
Брегалница во регионот на Делчево, во зависност од нивните хидрогоеолошки
карактеристики 49–57

Упатства за авторите 59–61

Geologica Macedonica	Год.	стр.	Штип
Geologica Macedonica	Vol.	22	Štip

pp. 1–62 2008

TABLE OF CONTENTS

Violeta Stojanova, Goša Petrov

- Correlation of stratigraphic distribution of the foraminifers in the Ovče Pole and Tikveš
Paleogene basin, the Republic of Macedonia 1–8

Orce Spasovski, Vojo Mirčovski

- New data on the hydrothermal alterations in the Plavica deposit (Eastern Macedonia) 9–16

Todor Serafimovski, Tadej Dolenec, Goran Tasev, Nastja Rogan, Matej Dolenec

- The composition of major minerals from the Buchim porphyry copper deposit,
Republic of Macedonia 17–26

Blažo Boev, Tena Šijakova-Ivanova, Lidija Robeva-Čukovska, Ivan Boev

- Mineral researches of the examples of the archeological locality “Stobi” using
the method of the x-ray diffraction 27–41

Milena Taseska, Petre Makreski, Vekoslava Stibilj, Radojko Jaćimović, Trajče Stafilov

- Determination of trace elements in hematite’s iron reference material, JSS-804-1 using
 k_0 -INAA 43–48

Vojo Mirčovski, Orce Spasovski, Vlado Mirčovski

- Contamination and protection of ground waters in the alluvial sediments
of the Bregalnica River in the Delčevo region, depending on their hydrogeological
characteristics 49–57

- Instructions to authors** 59–61

DETERMINATION OF TRACE ELEMENTS IN HEMATITE'S IRON REFERENCE MATERIAL JSS-804-1 USING k_0 -INAA

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A b s t r a c t: Different trace elements in hematite's iron ore reference material (JSS-804-1) were investigated using k_0 -instrumental neutron activation analysis (k_0 -INAA). To avoid the interference of iron as matrix elements, a method for its separation was applied. Namely, a liquid-liquid extraction procedure by diisopropyl ether (DIPE) in hydrochloric acid solution and determination of trace elements in the aqueous phase was undertaken. The k_0 -INAA method was applied to determine the content of the investigated elements thus making it possible to follow the distribution of 39 elements (with intermediate/medium and long half-lived radionuclides) in the studied referent material. An important advantage of the proposed method is the possibility to determine the content of several trace elements after Fe separation. Additionally, the elimination of the matrix element also lowered the detection limit for some trace elements compared to their corresponding values determined by k_0 -INAA and certified values for some elements.

Key words: k_0 -INAA; k_0 -RNAA; trace elements; reference material; hematite

INTRODUCTION

For the calibration of different types of instruments, as well as for method validation in the analysis of major and trace elements, iron ore reference materials are used as very important materials in the analytical chemistry of quality control of raw and final products in mining and metallurgy. However, there are many iron reference materials without certified values for the content of many trace elements present that could be very important in validating methods used for process control in the iron and steel production industry. Therefore it is very important to extend the list of certified elements in these types of reference materials.

A number of studies have been carried out concerning the determination of trace elements in iron ore materials directly from dissolved samples by atomic absorption spectrometry (AAS) and atomic emission spectrometry with inductively coupled plasma (AES-ICP), (Schrön et al., 1983; Castillo et al., 1988; Barros , 1989; Stafilov, 2000; Makreski et al., 2004) or after the separation and concentration of the elements of interest (Viets, 1984; Eidecker & Jackwerth, 1988; Stafilov et al., 1993; Kabil et al., 1996; Lazar & Stafilov, 1998;

Zendelovska & Stafilov, 2001; Stafilov & Zendelovska, 2002). Radioanalytical instrumental methods (instrumental neutron activation analysis – INAA, x-ray fluorescence spectrometry – XRF, and particle (proton) induced x-ray emission – PIXE) are rarely used to determine trace elements due to matrix and inter-element interferences and background effects (Palme et al., 1988; Suzuki & Hirai, 1995; Tomura & Tomuro, 1999; Jaćimović et al., 2002; Tomuro & Tomura, 2002; Nečemer et al., 2003; Taseska et al., 2006; Jaćimović et al., 2008; Makreski et al., 2008).

Iron as the matrix of the investigated materials has such nuclear characteristics (cross-section, abundance, resonance integral) that the induced radionuclide ^{59}Fe ($T_{1/2} = 44.5$ d, with mean gamma energies at $E_\gamma = 1099.3$ keV and $E_\gamma = 1291.6$ keV) is moderately activated and interferes with the determination of many trace elements by INAA (Tomura & Tomuro, 1999; De Soete et al., 1972). In this work a method is presented for simultaneous measurement of 39 elements in hematite's iron reference material JSS 804-1 using k_0 -INAA after the extraction of Fe by diisopropyl ether (DIPE).

EXPERIMENTAL

Sample

JSS 804-1 (Iscor Hematite), iron-based reference material was supplied by the Iron and Steel Institute of Japan.

Extraction of iron from matrix

The powder sample of JSS 804-1 (~100 mg) was dissolved on a hot plate by successively adding freshly prepared aqua regia. After evaporation to dryness, 1 mL of 2 mol L⁻¹ HNO₃, 0.8 mL of redistilled water and 3.2 mL conc. HCl were introduced (7.7 mol L⁻¹ HCl solution). Iron was removed by extraction with 4 mL of DIPE (5 times, 30 s each). The organic layer was removed using a Pasteur pipette. After the phase separation, the aqueous part was evaporated almost to dryness and transferred in a polyethylene ampoule with 2 mL of 2 mol L⁻¹ HNO₃ and irradiated in the carousel facility (CF) of the TRIGA Mark II reactor of the Jožef Štefan Institute in Ljubljana, Slovenia. In the same way, two blank samples were prepared and

irradiated together with the aqueous phase of the reference material.

k₀-Instrumental neutron activation analysis

The iron reference material was analyzed by k₀-INAA as follows: Powder (0.1 g) was sealed into a pure polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). Sample and standard (Al-0.1%Au IRMM-530 disc of 6 mm in diameter and 0.2 mm high) were stacked together and fixed in the polyethylene ampoule in sandwich form and irradiated for 20 hours in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor at a thermal neutron flux of 1.1·10¹² cm⁻² s⁻¹ (Jaćimović et al., 2008).

Trace elements in aqueous phase were analyzed by k₀-INAA (Fig. 1) in four repetitions. The aqueous phase (3–4 g) was transferred in a pure polyethylene ampoule and irradiated for 18 hours at the CF at a thermal flux of 1.1·10¹² n cm⁻² s⁻¹ for intermediate/medium and long lived isotopes.

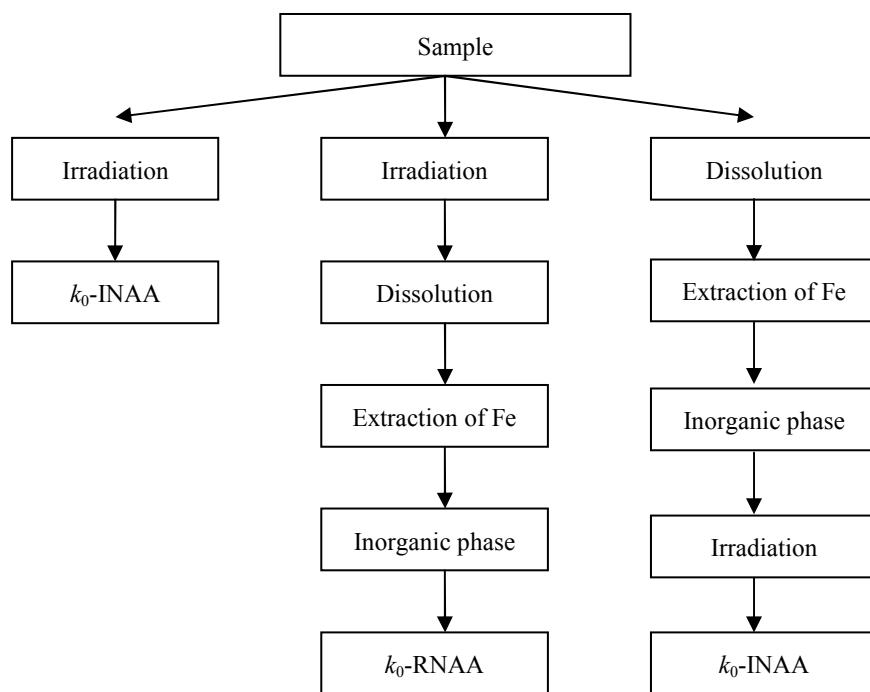


Fig. 1. Scheme of the separation and determination of the element contents of iron reference material using k₀-INAA and k₀-RNAA

After long irradiation, the samples were transferred in clean polyethylene ampoules and measured after 3, 8–10 and 30–35 days cooling time on an absolutely calibrated HPGe detector.

The HyperLab (HyperLab 2002 System, 2002) program was used for peak area evaluation, whereas for determination of f (thermal to epithermal flux ratio) and α (epithermal flux deviation

from the ideal 1/E distribution), the "Cd-ratio" method for multimonitor was applied (Jaćimović et al., 2003). The values $f = 28.6$ and $\alpha = -0.001$ were used to calculate the element concentrations. The elemental concentrations and effective solid angle calculations were carried out on the software package Kayzero for Windows (User's Manual Kayzero for Windows Version 2, 2005).

RESULTS AND DISCUSSION

A comparison between the results obtained in the inorganic phase after iron extraction with DIPE and in the powdered sample by k_0 -INAA for the reference material JSS-804-1 is presented in Table 1. It is evident that after extraction, iron was practically removed (98.5%). The results of the analysis of the extracted sample show that 18 elements remained in the acidified solution (As, Ba, Ce, Co, Cr, Cs, Eu, K, La, Nd, Sc, Sm, Sr, Tb, Th, U, W and Yb), i.e. they are not removed by DIPE. As can be seen, the rare-earth elements (REE) e.g. Ce, Eu, La, Nd, Sm, Tb and Yb fit into this group (the ratio between k_0 -INAA in the powdered sample and after iron extraction is near 1). The limit of detection (LOD) for numerous elements (Ag, Rb, Se, Sn, Ta, Te, Zn and Zr) was much lower after iron extraction compared to the corresponding values obtained by k_0 -INAA measurements in powdered sample which means that they could be analyzed in the inorganic phase after iron removal. This could be explained by either their low content in the iron materials or the presence of ^{59}Fe ($T_{1/2} = 44.5$ d) in the gamma spectrum. Comparing the results obtained in the powdered sample and inorganic phase after iron extraction, it could be concluded that Br, Mo and Sb are also extracted by DIPE (Tables 1).

It should be pointed out that these results and the previously published results for the same refer-

ence material obtained by radioanalytical procedure (Jaćimović et al., 2008) are in good agreement (see Table 1). The samples were irradiated firstly and then digested and iron was extracted by DIPE and the trace elements were determined in aqueous phase by k_0 -radiochemical instrumental neutron activation analysis, k_0 -RNAA (Fig. 1). Using k_0 -RNAA the contents of the elements in blank sample are negligible, but it is not the case when we did first extraction and then irradiation. The contents of elements in blank samples are presented in Table 1. So, we should emphasize that the proposed method could eliminate the necessity of using the irradiated samples and radioanalytical laboratory for majority of investigated elements. The disadvantage of this procedure is that some elements like As, Au, Ba, Hf, K, Na, Zn and Zr are introduced into the sample during iron extraction with DIPE especially when dealing with relatively small element quantities.

The data obtained by k_0 -INAA for the content of the elements in the studied iron reference material is in agreement with certified values given in the last column of Table 1. Taking into account that the JSS 804-1 standard gives certified values for only 4 elements, the results obtained provide useful additional information on the content of the other elements in the standard.

CONCLUSIONS

The proposed method enabled the measurement of 39 elements in the studied sample. The ratios between the k_0 -INAA values obtained before and after iron extraction were near 1 for 18 elements (As, Ba, Ce, Co, Cr, Cs, Eu, K, La, Nd, Sc, Sm, Sr, Tb, Th, U, W and Yb) including REE. This shows that DIPE is not selective for these elements. Also, after Fe extraction, the limit of detection for many elements was lowered. Taking into account that certified values in the studied iron ore

reference standard are given only for few elements, the obtained results provide important information on the content of many other elements.

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Table 1

Results obtained by k_0 -INAA in the powdered sample and in the aqueous phase after iron extraction with DIPE for the reference material JSS-804-1. All results are in mg kg⁻¹

El.	k_0 -INAA ^{\$} (Powder)	k_0 -RNAA ^{\$} (Inorganic)	R [#]	k_0 -INAA ^{\$\$} (Inorganic)	n	k_0 -INAA ^{**} (Inorganic-Blank)	n	JSS 804-1
	Cont. \pm Unc.*	Cont. \pm Unc.*		Cont. \pm Unc.*		Cont. \pm Unc.*		
Ag	<0.6	<0.3		0.22 \pm 0.01	2	0.050 \pm 0.003	1	
As	24.6 \pm 0.9	20.3 \pm 0.7	0.824	25.0 \pm 1.9	4	1.013	1.96 \pm 0.09	2 20 \pm 4
Au	<0.003	<0.001		0.008 \pm 0.009	2		0.019 \pm 0.020	2
Ba	171 \pm 7	147 \pm 6	0.862	179 \pm 7	4	1.046	14.2 \pm 0.7	2
Br	1.25 \pm 0.06	<0.1		0.26 \pm 0.20	2	0.206	0.065 \pm 0.004	2
Ca	<1097	450 \pm 67		<245	4		71.8 \pm 23.6	2 277 \pm 10
Cd	<3.2	<0.5		<1.7	4		<0.2	2
Ce	21.6 \pm 0.8	24.1 \pm 0.9	1.115	21.8 \pm 1.2	4	1.009	0.91 \pm 0.03	2
Co	3.89 \pm 0.14	3.55 \pm 0.13	0.912	4.17 \pm 1.10	4	1.071	0.0089 \pm 0.0004	2
Cr	37.9 \pm 1.5	42.0 \pm 1.5	1.108	30.7 \pm 5.8	4	0.810	0.598 \pm 0.038	2 40 \pm 2
Cs	0.29 \pm 0.03	0.40 \pm 0.02	1.362	0.41 \pm 0.02	4	1.426	0.021 \pm 0.001	2
Cu	<305	<283		<2837	4		<500	2 <10
Eu	0.32 \pm 0.04	0.35 \pm 0.02	1.112	0.30 \pm 0.02	4	0.954	0.0068 \pm 0.0002	2
Fe	671751 \pm 23513	5734 \pm 201	0.009	9980 \pm 5573	4	0.015	3.62 \pm 1.48	2 662610 \pm 340
Ga	<3.2	<18		<9.4	4		<1.7	2
Hf	0.29 \pm 0.04	0.30 \pm 0.01	1.037	1.28 \pm 0.21	4	4.384	0.485 \pm 0.017	2
Hg	<2.3	<0.1		0.19 \pm 0.01	2		<0.016	2
K	1282 \pm 57	<2123		1941 \pm 370	4	1.515	469 \pm 16	2
La	10.3 \pm 0.4	11.8 \pm 0.4	1.143	9.42 \pm 0.94	4	0.916	0.49 \pm 0.04	2
Mo	2.97 \pm 0.21	0.56 \pm 0.04	0.187	1.64 \pm 0.61	4	0.552	0.34 \pm 0.01	2
Na	154 \pm 5	156 \pm 6	1.015	4524 \pm 1358	4	29.35	2255 \pm 82	2
Nd	8.0 \pm 0.9	11.1 \pm 0.4	1.382	8.54 \pm 0.62	4	1.066	0.38 \pm 0.03	2
Rb	<7.1	4.5 \pm 0.2		4.65 \pm 0.52	4		0.33 \pm 0.03	2
Re	<0.03	<0.005		<0.04	4		<0.02	2
Sb	1.28 \pm 0.05	0.18 \pm 0.01	0.138	0.53 \pm 0.06	2	0.411	0.030 \pm 0.006	2
Sc	3.36 \pm 0.12	3.29 \pm 0.12	0.981	2.81 \pm 0.13	4	0.837	0.018 \pm 0.001	2
Se	<0.7	<0.3		1.08 \pm 0.06	1		<0.05	2
Sm	1.45 \pm 0.05	1.52 \pm 0.05	1.048	1.40 \pm 0.13	4	0.970	0.080 \pm 0.007	2
Sn	<44.8	<8.9		12.9 \pm 2.2	1		<2.5	2 <10
Sr	113.1 \pm 10.7	121.7 \pm 4.9	1.076	107.9 \pm 18.8	4	0.953	<1.7	2
Ta	<0.03	0.11 \pm 0.01		0.12 \pm 0.06	3		0.0035 \pm 0.0002	2
Tb	0.16 \pm 0.01	0.16 \pm 0.01	0.991	0.17 \pm 0.02	4	1.024	0.0083 \pm 0.0005	2
Te	<2.4	<0.4		<0.88	4		<0.08	2
Th	0.97 \pm 0.4	0.66 \pm 0.02	0.681	1.37 \pm 0.15	4	1.419	0.26 \pm 0.01	2
U	0.61 \pm 0.03	0.57 \pm 0.02	0.929	0.72 \pm 0.06	4	1.184	0.072 \pm 0.003	2
W	69.9 \pm 2.5	57.5 \pm 2.0	0.822	77.3 \pm 18.1	4	1.105	<0.3	2
Yb	0.81 \pm 0.03	0.81 \pm 0.03	0.998	0.72 \pm 0.11	4	0.889	0.030 \pm 0.001	2
Zn	<6.8	2.6 \pm 0.2		3.08 \pm 3.13	4		2.35 \pm 0.31	2
Zr	<108	<19.0		52.9 \pm 18.2	4		22.5 \pm 0.8	2

^{\$} – Results from Jaćimović et al., 2008; ^{\$\$} – Results after blank subtraction; * – Total estimated uncertainty of the method; ** – Results in the solution of the blank samples; # – Ratio between k_0 -RNAA and k_0 -INAA in powder sample; ## – Ratio between k_0 -INAA in the aqueous phase and k_0 -INAA in powder sample; n – Number of independent measurements; < – limit of detection (LOD).

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Резиме

**ОПРЕДЕЛУВАЊЕ НА ЕЛЕМЕНТИ ВО ТРАГИ ВО ХЕМАТИТЕН РЕФЕРЕНТЕН МАТЕРИЈАЛ
JSS-804-1 СО ПРИМЕНА НА k_0 -INAA****Милена Тасеска¹, Петре Макрески¹, Векослава Стибиль², Радојко Јакимовиќ², Трајче Страфилов¹**¹Институција за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“, б. фах 162, МК-1001 Скопје, Република Македонија,²Институција Јожеф Штефан,
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Извршено е определување на различни елементи во траги во хематитен железен референтен материјал (JSS-804-1) со примена на k_0 -инструменталната неутронска активациона анализа (k_0 -INAA). За да се избегне влијанието на железото како матричен елемент, воведен е метод за негово сепарирање. Имено, применета е течно-течната екстракција со диизопропилетер (DIPE) во раствор од хлороводородна киселина и потоа определување на елементите во траги во водната фаза. k_0 -INAA е применета за определување на содржината на испитуваните елементи,

при што има можност за следење на дистрибуцијата на 39 елементи (со кратко и долго полувреме на распаѓање на радионуклидите) во испитуваниот референтен материјал. Важна предност на предложениот метод е можноста за определување на содржината на повеќе елементи во траги по отстранувањето на железото. Освен тоа, елиминацијата на матричниот елемент доведува до намалување на границите на детекција за некои елементи во траги споредени со соодветните вредности добиени со k_0 -INAA и со сертифицираните вредности за некои елементи.