

DETERMINATION OF TRACE ELEMENTS IN CHALCOPYRITE (CuFeS_2) BY k_0 -INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS AFTER MATRIX ELEMENTS REMOVAL

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A method for trace elements determination in chalcopyrite, CuFeS_2 , by k_0 -instrumental neutron activation analysis (k_0 -INAA) was proposed. To avoid the interference of iron and copper as matrix elements, methods for their separation were applied. The copper interferences were eliminated by applying an electrolytic separation method. To eliminate iron interferences, a liquid-liquid extraction procedure by diisopropyl ether (DIPE) in hydrochloric acid solution and determination of trace elements in the aqueous phase were undertaken. The k_0 -INAA method was applied to determine the content of the investigated elements, making it possible to follow the distribution of even fifty elements (with intermediate/medium and long half-lived radionuclides) in the studied mineral. The important advantage of the proposed method is the possibility to determine the content of several trace elements after Fe and Cu separation. Additionally, the elimination of the matrix elements lowered the limit of detection for some trace elements in the water phase compared to their corresponding values determined by k_0 -INAA in the powder sample.

Key words: chalcopyrite; trace elements; neutron activation analysis; k_0 -INAA

ОПРЕДЕЛУВАЊЕ НА ЕЛЕМЕНТИ ВО ТРАГИ ВО ХАЛКОПИРИТ (CuFeS_2) СО k_0 -ИНСТРУМЕНТАЛНА НЕУТРОНСКА АКТИВАЦИОНА АНАЛИЗА ПО ОТСТРАНУВАЊЕ НА МАТРИЧНИТЕ ЕЛЕМЕНТИ

Предложен е метод за определување на елементи во траги во халкопирит, CuFeS_2 , со примена на k_0 -инструментална неутронска активациона анализа (k_0 -INAA). За да се избегне влијанието на железото и бакарот како матрични елементи, применет е метод за нивно сепарирање. Интерференциите од бакарот се елиминирани така што е применета негова електролитичка сепарација. Железото е елиминирано со примена на течно-течна екстракција со диизопропилетер (DIPE) од раствор на хлороводородна киселина, а потоа е извршено определување на елементите во траги во водната фаза. За определување на содржината на испитуваните елементи применет е методот на k_0 -INAA со што е овозможено следење на дистрибуцијата на речиси педесет елементи (преку соодветни радионуклиди со среден и долг полупериод на распаѓање) во испитуваниот минерал. Посебно важна предност на предложениот метод е дополнителната можност за определување на содржината на некои елементи во траги по сепарирањето на Fe и на Cu. Дополнителна предност е и фактот што елиминацијата на матричните елементи доведува до намалување на границата на детекција на некои од елементите во траги во водната фаза споредено со соодветните вредности добиени со k_0 -INAA во прашкаст примерок.

Клучни зборови: халкопирит; елементи во траги, неутронска активациона анализа; k_0 -INAA

INTRODUCTION

Chalcopyrite (CuFeS_2) is a copper and iron containing sulphide mineral that crystallizes in the

tetragonal system. Chalcopyrite is often confused with pyrite, although the latter belongs to a cubic crystal system. Furthermore, chalcopyrite is often massive, rarely crystalline, and less brittle. It is

also a darker yellow in colour, with a greenish tinge and diagnostic greasy lustre. When exposed to air, chalcopyrite oxidises to a variety of oxides, hydroxides and sulphates. It is often contaminated by a variety of other trace elements such as Co, Ni, Mn, Zn and Sn as substitutes for Cu and/or Fe, as well as Se, Fe and As as substitutes for S. In addition, trace amounts of Ag, Au, Pt, Pd, Pb, V, Cr, In, Al and Sb have also been reported.

There is a limited number of studies concerning the determination of elements in copper and iron based geological samples by various methods, such as atomic absorption spectrometry (AAS) [1–10], atomic emission spectrometry with inductively coupled plasma (ICP-AES) [9, 11] or laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS) [12]. Nuclear and nuclear-related techniques (INAA, XRF, PIXE) are rarely used to determine trace elements due to matrix and inter-element interferences and background effects [13–19].

In our previous work [20] it was found that the presence of copper as a matrix element in chalcopyrite interfered on the most of the trace element determination by the k_0 -instrumental neutron activation analysis (k_0 -NAA) even after Fe removal. Therefore, it was concluded that it is necessary to eliminate both copper and iron matrix elements in order to increase the number of the determined present trace elements in the samples.

In this work we propose elimination of copper interferences in chalcopyrite mineral by applying an electrolytic separation and then separation of the chloride complex of iron by rapid extraction into diisopropyl ether. The k_0 -method of instrumental neutron activation analysis (k_0 -INAA) is used for determination of trace elements in water phase.

EXPERIMENTAL

Samples

Chalcopyrite specimen (CuFeS_2) was collected from Bučim (active mine close to Radoviš, Republic of Macedonia). The single crystals of the mineral were carefully hand-picked under an optical microscope from the ore and were ground to a powder.

Sample preparation for k_0 -INAA

Powdered sample (0.1 g) was dissolved in 6 ml of conc. HCl, 2 ml conc. HNO_3 and few drops of conc. H_2O_2 in 250 ml glass beaker. The solution

was evaporated to dryness and the residue dissolved in 2 ml of conc. H_2SO_4 and 1 ml conc. HNO_3 followed by addition of 100 ml redistilled water. The Pt-electrode was employed for copper electrolysis for 45 min at 2 V and 3–4 A [10]. After Cu electrolysis, the electrolytic solution was evaporated almost to dryness, transferred into 25 ml glass flask, and HCl was added in order to obtain a concentration of 7.8 mol l^{-1} [20]. Then, the triplicate extraction was carried out using 10 ml volume of diisopropyl ether (DIPE) and the two phase liquid system was shaken for 1 min. After the phase separation, the aqueous part was evaporated to 2 ml and transferred into polyethylene ampoule. The flask was washed with 2 ml of redistilled water and transferred to a polyethylene ampoule.

k_0 -Instrumental neutron activation analysis (k_0 -INAA)

The mineral was analyzed by k_0 -INAA as follows: Powder (0.1 g) was sealed into a pure polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). The 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 a sandwich form and irradiated for 18 hours in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor of the Jožef Stefan Institute in Ljubljana, Slovenia, at a thermal neutron flux of $1.1 \cdot 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$.

Trace elements in water phase were also analyzed by k_0 -INAA. Firstly, the water phase (3–4 g), transferred in a pure polyethylene ampoule, was irradiated for 1 minute in the pneumatic tube (PT) at a thermal neutron flux of $3.5 \cdot 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for short lived isotopes. After appropriate cooling time, it was additionally irradiated for 17 hours at the CF at a thermal flux of $1.1 \cdot 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for long lived isotopes. In both cases standard (Al–0.1 % Au IRMM–530 disc) was stacked in the centre of polyethylene ampoule and co-irradiated with the sample.

After the short and long irradiations, the samples were measured on an absolutely calibrated HPGe detector [21] with 45 % relative efficiency and energy resolution (FWHM) of 1.8 keV at 1332.5 keV gamma line of ^{60}Co . For peak evaluation, the HyperLab program was used [22]. The elemental concentration and effective solid angle calculations were undertaken using a software program KAYZERO/SOLCOI[®] [23]. The radionuclides used in the determination up to 50 elements

in the powder sample and water phase of chalcopyrite from Bučim and their relevant nuclear data are presented in Table 1.

RESULTS AND DISCUSSION

It should be emphasized that the purity of copper minerals is very important because of their utilization in copper production. The presence of some trace elements could deteriorate the quality of copper products. Furthermore, the necessity to eliminate some of the latter elements (present in the copper raw material) leads to increase of the costs for copper manufacturing. Therefore, the knowledge of the presence of trace elements in copper minerals is very important and the proposed method makes possible the determination up to 50 such elements.

The results of the elemental composition of the chalcopyrite (powder mineral sample) obtained by *k₀*-INAA with their 1 σ uncertainty (considering net peak area, nuclear data for a particular nuclide, neutron flux parameters, full-energy peak detection efficiency, etc.) are given in Table 2. Due to the relatively favourable nuclear characteristics of copper and iron (cross-section, abundance, resonance integral), forty three elements were simultaneously determined. The contents of nineteen elements were under the limit of detection. The obtained data for Cu content is 7.8 % lower compared to the theoretical value (34.62 %) whereas the presence of Fe was found to be higher by

4.9 % (theoretical value 30.43 %). The difference can be explained due to measurement uncertainty of the *k₀*-INAA and presence of other elements. The concentration of Ag, As, Co, Se and Sn is higher compared to the other determined trace elements.

The Cu and Fe removal was made in parallel (Table 2). It can be seen that Cu was practically eliminated by electrolysis (>98 %). The efficiency of Fe removal from solution using DIPE was nearly 100 %. The removal of the both matrix elements enabled the determination of the following 14 elements (Al, Ba, Ca, Cs, Dy, Hf, K, Mn, Mo, Nd, Rb, Ta, Th and Zr). Fig. 1 shows the differences in the gamma spectra between the powder sample and water phase of chalcopyrite from Bučim after similar irradiation in the CF of TRIGA reactor and 9 days cooling time. Additional advantage of the proposed method is that it lowers the limit of detection for numerous elements (Cd, Eu, Hg, Ir, Pd and Sr) compared to their corresponding values obtained by *k₀*-INAA measurement. On the other hand, the content of Pt was found to be higher after removal of Cu and Fe, when compared to its content in the mineral, due to the use of Pt electrodes for electrolysis. The inconsistency for Cr data can be explained by high interferences from the ⁵⁴Fe(*n,α*)⁵¹Cr reaction and blank subtraction of Cr in the SPRONK ampoule for the results obtained in the powder sample. The enrichment of Na, Sb, U and Zn most likely originates from impurities in the chemicals used for dissolution, electrolysis and extraction with DIPE.

Table 1

Relevant nuclear data for the nuclides used in k₀-INAA

Elem.	Nuclide	Half-life	E _γ , keV	k ₀	Q ₀
Ag	^{110m} Ag	249.8 d	657.8; 884.7; 937.5	3.50E-2; 2.69E-2; 1.27E-2	16.7
Al	²⁸ Al #	2.241 min	1778.9	1.75E-2	0.71
As	⁷⁶ As	26.24 h	559.1	4.83E-2	13.6
Au	¹⁹⁸ Au	2.695 d	411.8	≡ 1	15.7
Ba	¹³¹ Ba	11.50 d	216.1; 373.2; 496.3	2.75E-5; 1.92E-5; 6.48E-5	24.8
Br	⁸² Br	35.30 h	554.3; 698.4; 776.5	2.38E-2; 9.38E-3; 2.76E-2	19.3
Ca	⁴⁷ Ca	4.536 d	1297.1	9.54E-7	1.3
	⁴⁷ Sc	3.349 d	159.4	8.57E-7	1.3
Cd	¹¹⁵ Cd	53.46 h	527.9	4.77E-4	32.4
	^{115m} In	4.486 h	336.2	7.73E-4	32.4
Ce	¹⁴¹ Ce	32.51 d	145.4	3.66E-3	0.83
Co	⁶⁰ Co	5.271 y	1173.2; 1332.5	1.32; 5.93E-1	2.0
Cr	⁵¹ Cr	27.70 d	320.1	2.62E-3	0.53

Elem.	Nuclide	Half-life	E_{γ} , keV	k_0	Q_0
Cs	¹³⁴ Cs	2.065 y	604.7; 795.8	4.76E-1; 4.15E-1	12.7
Cu	⁶⁴ Cu	12.70 h	1345.9	4.98E-4	1.14
	⁶⁶ Cu #	5.12 min	1039.2	1.86E-3	1.06
Dy	¹⁶⁵ Dy #	2.334 h	94.7	3.57E-1	0.19
Eu	¹⁵⁴ Eu	8.593 y	1274.4	7.77E-1	5.66
Fe	⁵⁹ Fe	44.50 d	1099.3; 1291.6	7.77E-5; 5.93E-5	0.975
Ga	⁷² Ga	14.10 h	834.0	5.23E-2	6.69
Hf	¹⁸¹ Hf	42.39 d	133.0; 345.9; 482.2	2.37E-2; 7.93E-3; 4.56E-2	2.52
Hg	²⁰³ Hg	46.61 d	279.2	1.10E-2	0.88
I	¹²⁸ I #	24.99 min	442.9	1.12E-2	24.8
In	^{114m} In	49.51 d	190.3; 558.4; 725.2	1.06E-3; 2.86E-4; 2.90E-4	24.2
Ir	¹⁹⁴ Ir	19.28 h	328.4	1.03E-1	12.0
K	⁴² K	12.36 h	1524.7	9.46E-4	0.97
La	¹⁴⁰ La	40.272 h	328.8; 815.8; 1596.2	2.87E-2; 3.32E-2; 1.34E-1	1.24
Mg	²⁷ Mg #	9.462 min	843.8; 1014.4	2.53E-4; 9.80E-5	0.64
Mn	⁵⁶ Mn #	2.579 h	846.8; 1810.7	4.96E-1; 1.35E-1	1.053
Mo	^{99m} Tc	6.01 h*	140.5	5.27E-4	53.1
Na	²⁴ Na	14.96 h	1368.6; 2754.0	4.68E-2; 4.62E-2	0.59
Nd	¹⁴⁷ Nd	10.98 d	91.1; 531.0	1.02E-3; 4.56E-4	2.00
Pd	^{109m} Ag	807.6 min	88.0	1.58E-3	25.0
Pr	¹⁴² Pr	19.12 h	1575.6	6.12E-3	1.51
Pt	¹⁹⁹ Au	75.336 h	158.4	1.03E-3	17.0
Rb	⁸⁶ Rb	18.63 d	1077.0	7.65E-4	14.8
	¹²² Sb	2.724 d	564.2	4.31E-2	33.0
Sb	¹²⁴ Sb	60.20 d	602.7; 1691.0	2.96E-2; 1.41E-2	28.8
	⁴⁶ Sc	83.83 d	889.3; 1120.5	1.22; 1.22	0.43
Se	⁷⁵ Se	119.80 d	136.0; 264.7	6.76E-3; 7.11E-3	10.8
Sm	¹⁵³ Sm	46.50 h	103.2	2.31E-1	14.4
Sn	^{113m} In	1.658 h**	391.7	5.99E-5	48.4
Sr	⁸⁵ Sr	64.84 d	514.0	9.15E-5	13.2
Ta	¹⁸² Ta	114.4 d	1189.0; 1221.4; 1231.0	3.88E-2; 6.45E-2; 2.72E-2	33.3
Tb	¹⁶⁰ Tb	72.3 d	298.6; 879.4; 1178.0	8.25E-2; 9.42E-2; 4.71E-2	17.9
Te	¹³¹ I	8.021 d	284.3; 364.5	6.62E-5; 8.67E-4	1.8
Th	²³³ Pa	26.97 d***	312.2;	2.52E-2;	11.5
Ti	⁵¹ Ti #	5.76 min	320.1	3.74E-4	0.67
U	²³⁹ Np	2.357 d****	106.1; 277.6	6.52E-3; 3.40E-3	103.4
V	⁵² V #	3.75 min	1434.1	1.96E-1	0.55
W	¹⁸⁷ W	23.72 h	479.6; 685.7	2.97E-2; 3.71E-2	13.7
Yb	¹⁷⁵ Yb	4.185 d	282.5; 396.3	1.46E-2; 3.12E-2	0.46
Zn	⁶⁵ Zn	244.3 d	1115.5	5.72E-3	1.908
Zr	⁹⁵ Zr	64.02 d	756.7	1.10E-4	5.306

- * parent half-life: 65.94 h
** parent half-life: 115.1 d
*** parent half-life: 22.3 min
**** parent half-life: 23.45 min
nuclide used for the element determination via short irradiation
1 y = 365.2422 d (http://www-nds.iaea.org/xgamma_standards/)
 E_{γ} , keV γ -energy in keV
 k_0 composite nuclear constant [23]
 $Q_0 = I_0/\sigma_0$ resonance integral to 2200 m s⁻¹ cross-section ratio [23]

Table 2

Results obtained by k₀-INAA for chalcopyrite (CuFeS₂) from Bučim in powder sample and water phase after Fe and Cu separation. All results are in mg kg⁻¹

Element	Powder sample		Water phase				Average	Unc.#	Ratio*
	Cont.	Unc.	Cont.	Unc.	Cont.	Unc.			
Ag	79.6	2.8	5.94	0.21	1.33	0.05	3.63		0.05
Al			3874	137	3164	112	3519	176	
As	140	5	84.3	3.0	68.4	2.4	76.4	3.8	0.54
Au	15.5	0.5	0.037	0.001	0.021	0.001	0.029		0.002
Ba	< 21		17.9	1.9	23.2	1.2	20.6	2.4	
Br	1.44	0.10	0.48	0.03	0.61	0.03	0.55	0.04	0.38
Ca	< 1939		490	98	529	69	510	122	
Cd	< 5		< 2		< 1				
Ce	6.75	0.33	5.16	0.20	6.04	0.22	5.60	0.30	0.83
Co	63.7	2.2	36.7	1.3	31.0	1.1	33.9	1.7	0.53
Cr	1.25	0.20	2.73	0.13	3.80	0.14	3.27	0.20	2.61
Cs	< 0.1		0.14	0.01	0.13	0.01	0.13	0.02	
Cu	319087	11942	9045	325	2519	96	5782		0.02
Dy			0.32	0.03	0.39	0.03	0.35	0.04	
Eu	0.080	0.005	0.066	0.005	0.065	0.004	0.066	0.006	0.82
Fe	319173	11172	263	12	305	11	284	16	0.001
Ga	< 43		< 5		< 4				
Hf	< 0.1		2.02	0.07	1.47	0.05	1.75	0.09	
Hg	< 7		< 0.11		< 0.05				
I			< 3		< 2				
In	5.98	0.33	3.81	0.13	3.37	0.12	3.59	0.18	0.60
Ir	< 6.1		< 2		< 1				
K	< 1956		1327	80	1333	72	1330	108	
La	3.31	0.14	2.35	0.12	3.07	0.13	2.71	0.18	0.82
Mg			< 846		< 945				
Mn			45.7	1.6	41.5	1.5	43.6	2.2	
Mo	< 2.7		1.87	0.16	1.18	0.09	1.53	0.17	
Na	81.5	4.3	7247	254	5954	209	6601	327	81
Nd	< 2.7		1.20	0.26	2.47	0.19	1.84		
Pd	< 1733		< 75		< 56				
Pr	< 22		< 21		< 19				
Pt	< 2.5		4.66	0.26	2.39	0.14	3.52		
Rb	< 6.5		1.38	0.22	1.27	0.15	1.33	0.26	
Sb	0.22	0.01	0.73	0.03	0.30	0.01	0.51		2.34
Sc	0.37	0.01	0.22	0.01	0.22	0.01	0.22	0.01	0.61
Se	49.3	1.7	< 1		< 1				
Sm	0.80	0.04	0.56	0.02	0.65	0.02	0.61	0.03	0.75
Sn	37.3	7.5	38.0	4.6	38.9	3.1	38.4	5.5	1.03
Sr	< 62		< 31		< 17				
Ta	< 0.1		0.057	0.007	< 0.017		0.057	0.007	
Tb	0.100	0.007	0.067	0.004	0.085	0.003	0.076	0.006	0.76
Te	8.15	0.46	2.68	0.18	2.40	0.12	2.54	0.21	0.31
Th	< 0.1		0.78	0.03	0.75	0.03	0.77	0.04	
Ti			< 455		< 352				
U	0.29	0.03	0.59	0.03	0.54	0.02	0.57	0.03	1.95
V			1.48	0.24	1.77	0.21	1.63	0.32	
W	20.5	0.9	19.6	0.7	15.9	0.6	17.8	0.9	0.87
Yb	0.14	0.01	0.167	0.008	0.180	0.007	0.174	0.011	1.23
Zn	195	7	262	9	276	10	269	13	1.38
Zr	< 102		85.4	5.0	69.0	3.5	77.2	6.0	

Combined uncertainty from two measurements; * Water phase/Powder sample; < under limit of detection

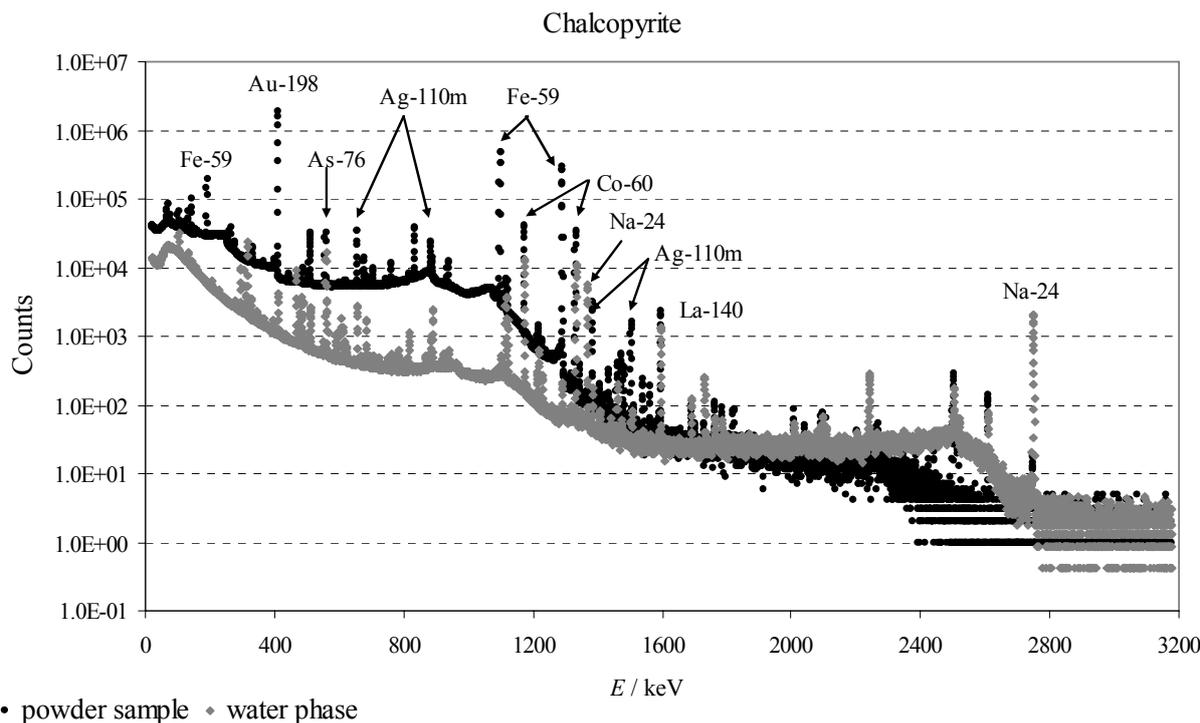


Fig. 1. Gamma spectra of chalcopyrite in powder sample and water phase measured on the same HPGe detector. Spectrum for powder sample was obtained after $t_{\text{irr}} = 18$ h (in the CF), $t_{\text{d}} = 9$ d, $t_{\text{m}} = 31000$ s, while spectrum for water phase was obtained after $t_{\text{irr}} = 17$ h (in the CF), $t_{\text{d}} = 9$ d, $t_{\text{m}} = 31800$ s. The spectrum for water phase was only normalized on the same measurement time and measured distance from the HPGe detector (the same efficiency) as it was in case for powder sample.

For the rare-earth elements (REE) e.g. Ce, La, Nd, Sm, Tb and Yb, it can be seen that the ratio between water phase and powder sample results ranges from 0.75 to 1.23 indicating that these elements, in general, are not eliminated by electrolysis and extraction. The relatively small deviation from 1 is negligible when the uncertainties in determination of the particular element are taken into account. In addition, it can be observed that Ag, As, Au, Br, Co, In, Se and Te were mostly removed during dissolution and electrolysis.

CONCLUSIONS

The trace element content in chalcopyrite was determined using the k_0 -INAA, before and after quantitative removal of copper by electrolysis and iron by the extraction with DIPE. The advantage of using the combination of k_0 -INAA and k_0 -INAA after electrolysis and extraction is in the possibility of simultaneous study of the distribution of many elements (up to 50).

The comparison between the results obtained by k_0 -INAA (measured in the aqueous layer after Cu and Fe elimination) and the k_0 -INAA results for the studied mineral has shown that Cu and Fe were quantitatively removed after the complete dissolution of the mineral samples. The ratio between the k_0 -INAA results in the water phase and powder sample for the content of REE is between 0.75 and 1.23, serving as an indication that these elements mostly remain in the solution. The important advantage of the proposed method is the possibility to determine the content of several elements (Al, Ba, Ca, Cs, Dy, Hf, K, Mn, Mo, Nd, Rb, Ta, Th and Zr) after the removal of the matrix elements. In addition, the limit of detection for some elements (Cd, Eu, Hg, Ir, Pd and Sr) in the dissolved sample is increased compared to that in powder sample.

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