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APPLICATION OF k_0-METHOD OF NEUTRON ACTIVATION ANALYSIS FOR DETERMINATION OF TRACE ELEMENTS IN VARIOUS MINERAL SAMPLES[♦] (A REVIEW)

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A review on the determination of various trace elements in different types of arsenic (orpiment, As_2S_3; realgar, As_4S_4; lorandite, $TlAsS_2$), antimony (stibnite, Sb_2S_3), copper (brochantite, $Cu_4SO_4(OH)_6$; chalcanthite, $CuSO_4\cdot 5H_2O$; chalcopyrite, $CuFeS_2$; covellite, CuS; native copper, Cu) and iron based geological materials (hematite, Fe_2O_3; pyrite, FeS_2; chalcopyrite, $CuFeS_2$) using k_0-method of neutron activation analysis (k_0-NAA) in both forms: instrumental (k_0-INAA) and radiochemical (k_0-RNAA) is presented. In order to avoid interferences from the matrix element in each mineral (As, Sb, Cu and Fe), various procedures were applied for its removal. Elimination of the matrix element enabled investigation from 35 to 47 trace elements in the samples using short (up to few minutes) and long (up to 20 hours) irradiations in typical irradiation channels of TRIGA reactor. The minerals were collected from various localities within the territory of the Republic of Macedonia, except covellite, which was obtained from Bor, Serbia.

Keywords: k_0-NAA; minerals; trace elements; matrix interferences; arsenic; antimony; copper; iron

ПРИМЕНА НА k_0-МЕТОД НА НЕУТРОНСКА АКТИВАЦИОНА АНАЛИЗА ЗА ОПРЕДЕЛУВАЊЕ ТРАГИ ОД ЕЛЕМЕНТИ ВО РАЗЛИЧНИ ПРИМЕРОЦИ МИНЕРАЛИ: (ПРЕГЛЕД)

Даден е преглед на примена на инструменталната (k_0-INAA) и радиохемиската k_0-неутронска активациона анализа (k_0-RNAA) за определување различни елементи во траги во минерали на арсен (аурипигмент, As_2S_3; реалгар, As_4S_4; лорандит, $TlAsS_2$), на антимон (стибнит, Sb_2S_3), на бакар (брошантит, $Cu_4SO_4(OH)_6$; халкантит, $CuSO_4\cdot 5H_2O$; халкопирит, $CuFeS_2$; ковелин, CuS; самороден бакар, Cu) и на геолошки материјали со основен хемиски состав на железо (хематит, Fe_2O_3; пирит, FeS_2; халкопирит, $CuFeS_2$). Во елиминацијата на влијанието на матричните елементи (As, Sb, Cu и Fe), применети се различни постапки за нивно отстранување. Елиминацијата на матричниот елемент овозможува определување на 35 до 47 елементи во траги во примероците применувајќи кратко време на озрачување (до неколку минути) и подолго време на озрачување (до 20 часа) во карактеристични канали за озрачување во реакторот TRIGA. Примероците од минерали се колекционирани од различни локалитети од територијата на Република Македонија, освен ковелитот кој потекнува од Бор, Србија.

Клучни зборови: k_0-NAA; минерали; елементи во траги; матрични интерференции; арсен; антимон; бакар; железо

[♦] Dedicated to Academician Gligor Jovanovski on the occasion of his 70th birthday.

1. INTRODUCTION

Although minerals are naturally-occurring inorganic substances with a definite chemical composition (and physical properties), they contain traces of other elements that can change some of their characteristics. In addition, a variety of minerals are quite easily interchangeable, making possible one mineral to grade into another [1]. Therefore, there are many reasons to analyze trace elements in minerals. Some involve determination of mineral purity and presence of very rare and/or important elements that could be extracted (or used) in order to obtain important information for the geology of mines and mineral localities. In this review we will focus on arsenic, antimony, copper and iron based minerals and geological materials.

In the framework of the LORandite EXperiment (LOREX) project [2], it was very important to determine the content of lead in lorandite ($TlAsS_2$) and in the most frequently occurring minerals of the Allchar mine, Republic of Macedonia (realgar, As_4S_4; orpiment, As_2S_3 and stibnite, Sb_2S_3). The importance lies in the fact that minerals, provided as co-genetic, can be used as monitors to determine the contribution of background reactions originating from natural radioactivity. The results of this work can be found in Jaćimović *et al.* [2] and Stafilov *et al.* [3], where k_0-INAA was directly applied for determination of major and trace elements in the powder form whereas k_0-RNAA was used after As and Sb removal from the minerals.

The purity of iron minerals is of great importance due to their utilization in iron and steel production. It should be stressed that the presence of some trace elements could influence to improve (i.e. Co, Mo, REE) or deteriorate (As, Cr, Sb, Zn) the quality of iron and steel products. Furthermore, the necessity to eliminate some of the latter elements (present in the iron raw material) leads to increase of the costs for steel manufacturing. A number of studies have been undertaken concerning the determination of elements in similar geological samples directly from the dissolved sample by atomic absorption spectrometry (AAS) [4], and atomic emission spectrometry with inductively coupled plasma (AES-ICP) [4–7], or after the separation and concentration of the elements of interest [6, 8–16]. Instrumental methods (instrumental neutron activation analysis – INAA, X-ray fluorescence spectrometry – XRF, particle induced X-ray emission – PIXE) are rarely used to determine trace elements due to matrix and inter-element interferences and background effects [2, 17–21].

Iron as the matrix element has nuclear characteristics (cross-section, abundance, resonance integral) such as that the induced radionuclide ^{59}Fe ($t_{1/2}$ = 44.5 d, with mean gamma energies in the spectrum E_γ = 1099.3 keV and E_γ = 1291.6 keV). Additionally, it is moderately activated and interferes on the determination of many trace elements by INAA. In order to avoid interferences from iron on the determination of elements present in trace levels, a radiochemical separation was developed. Determination of the investigated elements in the aqueous phase was undertaken by k_0-instrumental neutron activation analysis (k_0-INAA) and k_0-radiochemical neutron activation analysis (k_0-RNAA) after the iron was extracted by isoamyl acetate (IAA) and diisopropyl ether (DIPE) from hydrochloric acid solution. The distribution of 35 elements in extraction systems (with intermediate/medium and long half-life radionuclides) present in the studied minerals was investigated. On the other hand, to avoid the interferences of iron matrix element, a liquid-liquid extraction with DIPE in hydrochloric acid and determination of trace elements in the inorganic phase was carried out prior to irradiation. The k_0-INAA was applied for simulations measurements of 39 elements in four iron based geological reference materials [JSS 804-1 (hematite), JSS 802-2 (limonite), SU-1 and SU-1a (iron-nickel-copper-cobalt ores)] [22].

Copper minerals are common and modern civilization is heavily dependent on copper and its products. Copper ores can be found in large deposits, relatively close to the surface, and are amenable to relatively low cost bulk mining methods. The combination of its physical properties, abundance, and low cost make it a valuable commodity. Native copper is a relatively rare mineral, and this element is mostly found either in minerals associated with sulfur or in their oxidized products. Thus, Cu nuclides interfere with the determination of many mineral trace elements. In order to avoid the copper interferences, it is necessary to eliminate the matrix element and to separate trace elements before their determination by INAA. In addition, the necessity to avoid the interferences from As and Sb matrix elements in determination of trace elements in the corresponding minerals by NAA is of particular importance.

Therefore, the data regarding the nuclear characteristics of Cu, As and Sb lead to possible interferences with the remaining elements in such mineral systems. Thus, the copper radionuclides ^{64}Cu ($t_{1/2}$ = 12.7 h with mean gamma ray energies E_γ = 511.0 keV and E_γ=1345.9 keV) and ^{66}Cu ($t_{1/2}$ = 5.12 min with gamma ray energy E_γ = 1039.2 keV) dominate the gamma spectrum [2] in the case when INAA is applied to copper matrix samples. Similar situation arise for As and Sb minerals where induced radionuclides ^{76}As ($t_{1/2}$ = 26.24 h, with mean gamma energies in the spectrum E_γ = 559.1 keV and E_γ = 657.1 keV) and ^{124}Sb ($t_{1/2}$ = 60.20 d, with mean gamma energies in the spectrum E_γ = 602.7 keV and E_γ = 1691.0 keV), respectively, lead to interfering effects [2].

In this work, a review of the application of k_0-INAA method for direct and simultaneous determination of trace elements in both powdered minerals and dissolved samples after removal of the matrix component is presented.

2. EXPERIMENTAL

2.1. *Samples*

The mineral samples of lorandite, realgar (As_4S_4), orpiment (As_2S_3) and stibnite (Sb_2S_3), were taken from the Allchar mine. Pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and hematite (Fe_2O_3) were collected from Bučim, Sasa and Damjan mines, respectively. The brochantite ($Cu_4SO_4(OH)_6$) specimen originated from the Sasa mine, whereas chalcanthite ($CuSO_4 \cdot 5H_2O$) specimen and native copper were collected from Bučim. The crystals of mineral specimens (around 300 mg) were carefully hand-picked under an optical microscope from the ore samples and ground to powder. All localities are within the territory of the Republic of Macedonia except Bor locality (Serbia) where the covellite sample was excavated.

2.2. *k_0-instrumental neutron activation analysis (k_0-INAA)*

For k_0-INAA purposes, the samples in powder form were irradiated in the TRIGA Mark II reactor of the Jožef Stefan Institute (JSI) in Ljubljana, Slovenia. About 100 mg of sample was sealed into a pure polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). A sample and a standard Al-Au(0.1%) IRMM-530R [23] disc of 6 mm diameter and 0.2 mm thickness were stacked together and fixed in the polyethylene ampoule in sandwich form and irradiated. Depending on the purpose of the analysis, typically two irradiations were performed: short irradiation (up to few minutes) in the pneumatic tube (PT) at a thermal neutron flux of $3.5 \cdot 10^{12}$ cm^{-2} s^{-1} to determine elements via their corresponding short half-life radionuclides and second irradiation (up to 20 hours) at a thermal neutron flux of $1.1 \cdot 10^{12}$ cm^{-2} s^{-1} in the carousel facility (CF) of the TRIGA reactor to determine elements via their corresponding medium/long half-life radionuclides.

After irradiation and appropriate cooling time, the samples were measured on an absolutely calibrated detector [24, 25]. For peak area evaluation, the HYPERMET-PC [26, 27] and HyperLab [28] programs were used. For elemental concentrations and effective solid angle calculations a software packet called KAYZERO/SOLCOI$^{®}$ [29] and Kayzero for Windows (KayWin$^{®}$) [30] software were used, which are based on the k_0-standardization method of NAA. The KayWin software is frequently updated and use the recommended nuclear data library (k_0 database) [31], which can be found in the form of an Excel file (http://www.kayzero. com/ k0naa/k0naa/News/News.html) dated 2012-03-14.

2.3. *Sample digestion and extraction*

2.3.1. *Arsenic and antimony removal*

About 100 mg of sample was irradiated and after irradiation the samples were cooled for 8 days to allow the high activity of the induced radionuclide ^{76}As ($t_{1/2}$ = 26.24 h) decay and then measured on an HPGe detector.

After gamma measurement, the sample (orpiment and realgar) was dissolved in 4 ml 65 % HNO_3, heated and boiled for 10 min. Then, 30 % H_2O_2 was added dropwise several times, the solution was reboiled and evaporated to 0.5 ml (no HNO_3 should remain).

For As and Sb removal the method described by Byrne and collaborators [32–35] with slight modifications was used. For realgar 5 ml 9.0 mol l^{-1} H_2SO_4, diluted to 8 ml and 2 ml of 5 mol l^{-1} KI were added. Arsenic extraction with 10 ml toluene was repeated 8 or 9 times and the organic phases were discarded. The aqueous phase was then measured three times on a calibrated coaxial HPGe detector (Ortec, USA) after 8, 25 and 40 days cooling time. Antimony was removed according to the same procedure beside the stibnite was dissolved in aqua regia.

2.3.2. *Fe removal after irradiation*

Duplicate irradiated mineral samples (~100 mg) of hematite (Fe_2O_3) and chalcopyrite ($CuFeS_2$) were quantitatively transferred to a flask with cover and slowly dissolved on a hot plate by adding two 3 ml portions of freshly prepared aqua regia. The complete digestion of the irradiated pyrite (FeS_2) sample was achieved by adding 3 ml conc. HCl and 3 ml conc. HNO_3. After evaporation to total dryness, 1 ml of 2 mol l^{-1} HNO_3 was added and enough HCl to prepare a 7.7 mol l^{-1} HCl solution (total volume 5 ml). Then, the gamma activity of the dissolved samples was measured on HPGe detector and in order to remove Fe as the matrix element, extraction using 4 ml of DIPE was performed and the procedure was repeated 5 times (shaking time for each extraction was 30 s). Then, after the Fe was removed the gamma activity of the radionuclides in the water phase was measured on an HPGe detector. More details for the procedure can be found in Ref. [36].

The similar procedure was carried out using IAA for iron extraction [14] whereas 8 mol l^{-1} HCl concentration was found as optimal medium for Fe removal using DIPE solvent.

It is worth mentioning that digestion, extraction and measurements were conducted in the same glass flask keeping all the necessary conditions unchanged during all procedure steps. All used reagents and standards were of analytical grade.

2.3.3. *Extraction of Fe from the matrix before irradiation*

A powdered sample (~100 mg) of the iron based geological reference materials, JSS 804-1 and JSS 820-2 was dissolved in a glass beaker on a hot plate by adding several 4 ml portions of freshly prepared aqua regia. A complete digestion of SU-1 and SU-1a samples (iron-nickel-copper-cobalt ores) in a teflon beaker was achieved by adding a total of 20 ml aqua regia and 0.5 ml of conc. HF. After evaporation to dryness, 1 ml of 2 mol l^{-1} HNO_3, 0.8 ml of redistilled water and 3.2 ml concentrated HCl were introduced (7.7 mol l^{-1} HCl solution). The used chemicals were suprapur grade. Iron was removed by five extractions successive with 4 ml of DIPE (shaking time of 30 s each). The organic layer was removed using a Pasteur pipette. After phase separation, the aqueous layer was evaporated to near dryness and transferred to a polyethylene ampoule using 2 ml of 2 mol l^{-1} HNO_3 and sealed. An identical procedure was followed for preparation of blank samples. Each reference material was analyzed in two or four replicates [22].

2.3.4. *Copper removal*

The powdered copper mineral samples of 0.1 g were dissolved in 10 ml redistilled water in a 250 ml glass beaker. Afterwards, 2 ml of conc. H_2SO_4, 1 ml conc. HNO_3 and redistilled water up to 100 ml were added before electrolysis. The sample of native Cu (0.1 g) was dissolved in 2 ml of conc. HNO_3 by heating on a hot plate. The solution was evaporated to dryness and the residue re-dissolved in 2 ml of conc. H_2SO_4, 1 ml conc. HNO_3 and made up with redistilled water to 100 ml before electrolysis.

A Pt-electrode was employed for copper removal by electrolysis for 45 min at 2 V and 3–4 A [15]. Afterwards, the solution was evaporated on a hot plate at 80 ºC to about 2 ml, transferred to a polyethylene ampoule by adding 2 ml redistilled water and irradiated twice in the 250 kW TRIGA Mark II reactor. The first (short) irradiation was undertaken in the pneumatic tube (PT) to determine elements via their corresponding short half-life radionuclides. After an appropriate cooling time, long irradiation of the same solution in the carousel facility (CF) for determination of elements via medium and long lived radionuclides using k_0-INAA was applied.

2.4. *QA/QC of the k_0-NAA*

For QA/QC purposes of the k_0-NAA, different certified reference materials (CRMs) or reference materials (RMs) were used: BCR-320 River Sediment and BCR-320R Channel Sediment delivered by EU, JRC, Institute for Reference Materials and Measurements (IRMM); JSS 804-1 (Iscor Hematite), JSS 805-1 (MBR Hematite), JSS 820-2 (Robe River Limonite) and JSS 850-4 (Marcona Pellet) delivered by the Nippon Sample Plant Co., Ltd.; and SU-1 and SU-1a (iron-nickel-copper-cobalt ores) delivered by Canadian Center for Mineral and Energy Technology. Data for the certified reference materials obtained by the applied methods are in the frame of the certified values and the comparison of the obtained and certified values are given in our previous papers – BCR CRMs [2, 25, 37, 38], JSS RMs [16, 22, 39, 40], SU-1 and SU1a [22, 41]. Unfortunately, all of above reference materials are certified or recommended for relatively small number of elements.

3. RESULTS AND DISCUSSION

In order to avoid matrix interferences, it is necessary to eliminate major elements and to separate trace elements before their determination by INAA. Thus, various trace elements in different types arsenic (orpiment, As_2S_3; realgar, As_4S_4; lorandite, $TlAsS_2$), antimony (stibnite, Sb_2S_3), copper (brochantite, $Cu_4SO_4(OH)_6$; chalcanthite, $CuSO_4·5H_2O$; chalcopyrite, $CuFeS_2$; covellite, CuS; native copper, Cu) and iron based geological materials (hematite, Fe_2O_3; pyrite, FeS_2) were investigated using k_0-NAA in both forms: instrumental (k_0-INAA) and radiochemical (k_0-RNAA). In order to avoid interferences from the matrix element (As, Sb, Cu and Fe) in particular mineral, the various procedures were applied using k_0-methods for determination of elemental concentrations. Thus, from 35 to 47 trace elements were investigated in studied materials using short (up to few minutes) and long (up to 20 hours) irradiations in typical irradiation channels of TRIGA reactor. Some results from the studies are presented in Tables 1–4.

Using k_0-INAA, the trace elements Ba, Ce, Co, Cr, Cs, Fe, Hg, Sc, Tb, Th, U and Zn in realgar, orpiment and stibnite were determined before and after As and Sb removal. The removal of both elements with KI in toluene was higher than 99.8% and no losses of trace elements were observed (Table 1) [3]. The obtained results indicate that extraction method was appropriate for removing As and Sb and allowed determination of more trace elements after matrix removal. Additionally, the limits of detection after As or Sb removal for all trace elements were significantly lower. Obviously, the removal of As and Sb with KI in toluene was successful and allowed analysis of the following trace elements (Co, Cr, Cs, Fe, Sc, Tb, Th and Zn) which did not coextract with arsenic or antimony [3].

The method for determination of major and trace elements in iron oxide (hematite, Fe_2O_3) and sulfide (pyrite, FeS_2 and chalcopyrite, $CuFeS_2$) minerals using the k_0-method of neutron activation analysis in both forms: instrumental (k_0-INAA) and radiochemical (k_0-RNAA) was developed on the basis of radiochemical separation extraction of iron by isoamyl acetate (IAA) and diisopropyl ether (DIPE) from hydrochloric acid solution. Determination of the investigated elements in the aqueous phase was performed by k_0-RNAA after the extraction. The distribution of 35 elements in extraction systems (with intermediate/medium and long half-lived radionuclides) present in the studied minerals was investigated. The results for hematite (Fe_2O_3) are presented in Table 2, where results are compared with k_0-INAA in powder and k_0-RNAA obtained after Fe removal from the mineral by DIPE and IAA [36].

It could be concluded that the major and trace elements content in three iron minerals using the k_0-INAA could be determined before and after quantitative removal of Fe by liquid-liquid extraction [36]. It was found that Au, Se, Te, Mo and Sb show similar behaviour in hydrochloric acid solution to Fe, and they could be removed with high efficiency. The ratio between k_0-RNAA and k_0-INAA results for the REE was near 1, leading to conclusion that both organic solvents are not selective for this group of elements (Fig. 1).

Table 1

Content of macro and trace elements (and corresponding limits of detection) in realgar (As_4S_4) and orpiment (As_2S_3) determined by k_0-NAA (in mg kg^{-1}) [3]

El.	Found in realgar		Found after As removal in realgar			Found in orpiment		Found after As removal in orpiment		
	Content	LOD*	Content	Ratio#	LOD*	Content	LOD*	Content	Ratio#	LOD*
As	447000	100	246	0.0006	0.2	461000	100	217	0.0005	0.4
Ba		20	16.8		6					
Ca	8820	6000	1525	0.17	600		10000	891		600
Ce	1.63	0.3	1.04	0.64	0.4					
Co	11.3	0.04	9.95	0.88	0.03		0.5	0.036		0.02
Cr	2.48	0.5	3.53	1.42	0.5	2.0	1	0.62	0.31	0.3
Cs	1.03	0.05	0.92	0.89	0.06		0.05	0.054		0.01
Fe	47750	40	42580	0.89	30		400	51.8		15
Hg	0.80	0.1			0.2	16.0	1			0.1
La		2	0.71		0.01					
Na		1000	19.4		8					
Nd						103	50			1
Sb	9.39	0.08	6.64	0.71	0.07	2890	0.5	5.14	0.002	0.02
Sc	0.21	0.005	0.181	0.86	0.005		0.04	0.0069		0.001
Sm		0.5	0.105		0.005					
Sr	19.5	15			15					
Tb	0.049	0.02	0.066	1.35	0.02					
Th	0.082	0.03	0.1	1.22	0.04					
Tm	0.41	0.1			0.1	4.4	0.7			0.1
U		2	2.02		0.06		2			0.06
Yb		0.5	0.168		0.02					
Zn	55.1	2	51.1	0.93	2					

*Limit of detection;

Ratio between the determined element content after (determined by k_0-RNAA) and before the As removal (determined by k_0-INAA).

Table 2

Results obtained by k_0-INAA and k_0-RNAA in the aqueous phase for hematite (Fe_2O_3) from Damjan mine (all values are in mg kg^{-1}) [36]

El.	k_0-INAA		k_0-RNAA								
	Powder		Dissolved sample[#]			Fe removal with DIPE			Fe removal with IAA[#]		
	Content	Unc.[$]	Content	Unc.[$]	Ratio[##]	Content	Unc.[$]	Ratio[##]	Content	Unc.[$]	Ratio[##]
Ag	< 0.4		< 7			0.26	0.04	*	0.50	0.06	*
As	33.3	1.2	30.2	1.6	0.91	23.2	1.0	0.70	19.6	1.01	0.59
Ba	89.5	8.9	< 91			77.5	3.8	0.87	79.5	4.67	0.89
Br	8.02	0.32	< 1.1			< 0.20			< 0.28		
Ce	11.9	0.5	12.3	2.3	1.04	10.4	0.4	0.87	10.8	0.60	0.91
Co	3.64	0.13	3.49	0.41	0.96	3.06	0.11	0.84	3.20	0.16	0.88
Cr	29.3	2.1	28.6	4.7	0.98	24.8	1.1	0.85	25.7	1.85	0.88
Cs	0.41	0.04	< 1.5			0.39	0.02	0.95	0.40	0.02	0.96
Eu	0.47	0.07	< 0.35			0.43	0.02	0.93	0.49	0.03	1.04
Fe	603051	21122	590692	29393	0.98	713	27	0.0012	1353	76	0.0022
K	728	182	< 1661			479	86	0.66	< 703		
La	16.1	0.6	15.4	0.8	0.96	13.4	0.5	0.83	15.6	0.78	0.97
Mo	7.38	0.55	5.37	1.38	0.73	0.78	0.23	0.11	< 0.5		
Na	37.4	3.0	38.1	5.9	1.02	28.9	1.4	0.77	39.4	4.42	1.05
Nd	10.1	2.1	< 9.7			8.83	0.75	0.88	8.97	0.76	0.89
Rb	< 6.9		< 38			2.44	0.32	*	2.60	0.29	*
Sb	8.02	0.29	7.30	0.39	0.91	0.49	0.02	0.06	0.58	0.03	0.07
Sc	0.58	0.02	0.57	0.05	0.98	0.50	0.02	0.85	0.54	0.03	0.93
Sm	1.95	0.08	1.79	0.10	0.92	1.63	0.07	0.84	1.84	0.10	0.94
Sr	117	27	< 657			56.1	8.2	0.48	56.4	6.00	0.48
Tb	0.34	0.02	< 0.43			0.29	0.01	0.88	0.30	0.02	0.88
Th	0.12	0.02	< 0.9			0.08	0.01	0.67	0.042	0.01	0.34
U	1.87	0.08	1.63	0.16	0.87	1.50	0.07	0.80	1.29	0.09	0.69
W	8.64	0.47	7.67	0.75	0.89	4.07	0.16	0.47	< 0.5		
Yb	0.30	0.03	0.39	0.12	1.27	0.32	0.01	1.04	0.30	0.02	1.00
Zn	22.0	1.7	< 21			18.3	0.7	0.83	16.1	1.15	0.73
Zr	< 165		< 972			17.7	2.7	*	14.4	3.89	*

[$] Combined standard uncertainty of the method.

[#] Two independent measurements.

[##] Ratio between the determined element content after (determined by k_0-RNAA) and before the Fe removal (determined by k_0-INAA).

* Obtained result due to lower limit of detection.

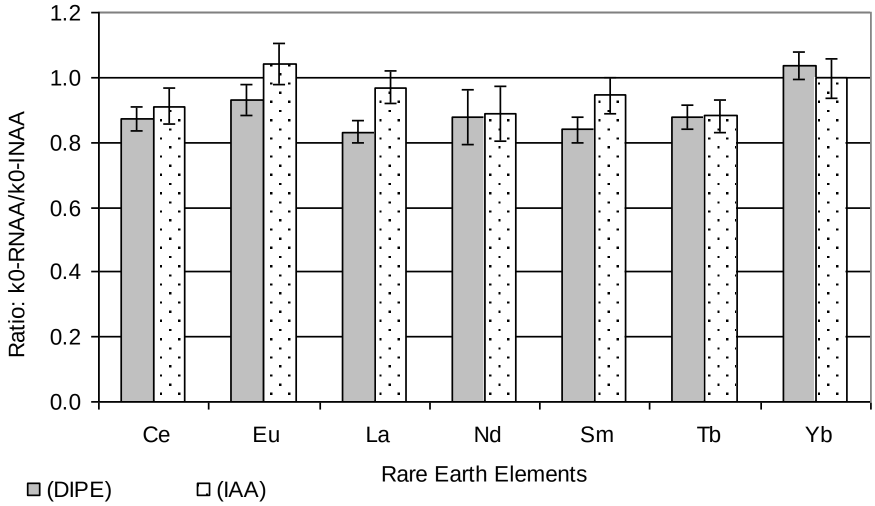

Fig. 1. Ratio between k_0-RNAA (extraction into DIPE and IAA) and k_0-INAA for REE in hematite [36]

In addition, a high recovery of another 12 elements (Ag, Ba, Cd, Co, Cr, Cs, Hg, In, Na, Nd, Sc and Zn) in the aqueous phase after Fe removal with DIPE was also found. Moreover, after the extraction of Fe, the limits of detection for several elements (Ag, Ba, Ca, Ce, U, W) became lower compared to the corresponding values in the k_0-INAA.

Results obtained by k_0-INAA and k_0-RNAA in the dissolved, inorganic and organic phases for JSS 804-1 are presented in Table 3.

Table 3

Results obtained by k_0-INAA and by k_0-RNAA in the dissolved, inorganic and organic phases for JSS 804-1. Certified values for some elements are also given (all values are in mg kg^{-1} with a coverage factor k=1) [39]

El.	k_0-INAA		k_0-RNAA									JSS 804-1	
	Powder		Dissolved#			Inorganic#			Organic#				
	Content	Unc.*	Content	Unc.*	Ratio**	Content	Unc.*	Ratio**	Content	Unc.*	Ratio**	Certified	Unc.*
Ag	< 0.6		< 6.9			< 0.3			< 0.4				
As	24.6	0.9	22.9	1.0	0.929	20.3	0.7	0.824	2.82	0.12	0.114	20.0	4.0
Au	< 0.003		< 0.013			< 0.001			< 0.002				
Ba	1717	7	143	17	0.835	147	6	0.862	< 14				
Br	1.25	0.06	< 0.7			< 0.1			< 0.5				
Ca	< 1097		< 5225			450	67		< 707			277	10
Cd	< 3.2		< 11.2			< 0.5			< 1.8				
Ce	21.6	0.8	24.0	1.0	1.111	24.1	0.9	1.115	< 0.5				
Co	3.89	0.14	2.93	0.22	0.754	3.55	0.13	0.912	< 0.09				
Cr	37.9	1.5	37.8	1.7	0.998	42.0	1.5	1.108	< 1.1			40.0	2.0
Cs	0.29	0.03	< 1.4			0.40	0.02	1.362	< 0.2				
Cu	< 305		< 1185			< 283			< 855			< 10	
Eu	0.32	0.04	< 0.3			0.35	0.02	1.112	< 0.02				
Fe	671751	23513	385420	13540	0.574	5734	201	0.009	538943	18891	0.802	662610	340
Ga	< 3.2		< 493			< 18			< 122				
Hf	0.29	0.04	< 0.8			0.30	0.01	1.037	< 0.1				
Hg	< 2.3		< 2.6			< 0.1			< 0.4				
K	1282	57	< 28016			< 2123			< 5148				
La	10.3	0.4	11.3	0.4	1.098	11.8	0.4	1.143	0.087	0.005	0.008		
Mo	2.97	0.21	< 5.1			0.56	0.04	0.187	1.46	0.12	0.492		
Na	154	5	199	24	1.290	156	6	1.015	6.08	1.52	0.039		
Nd	8.0	0.9	< 6.8			11.1	0.4	1.382	< 1.0				
Rb	< 7.1		< 35.0			4.5	0.2		< 5.4				
Re	< 0.03		< 0.1			< 0.005			< 0.015				
Sb	1.28	0.05	0.93	0.05	0.723	0.18	0.01	0.138	0.91	0.03	0.713		
Sc	3.36	0.12	3.13	0.11	0.932	3.29	0.12	0.981	< 0.02				
Se	< 0.7		< 5.7			< 0.3			< 0.7				
Sm	1.45	0.05	1.57	0.06	1.083	1.52	0.05	1.048	0.011	0.001	0.008		
Sn	< 44.8		< 211			< 8.9			< 28.4			< 10	
Sr	113.1	10.7	< 506			121.7	4.9	1.076	< 70.8				
Ta	< 0.03		< 0.3			0.11	0.01		< 0.1				
Tb	0.16	0.01	< 0.3			0.16	0.01	0.991	< 0.05				
Te	< 2.4		< 11.3			< 0.4			< 1.6				
Th	0.97	0.04	0.89	0.07	0.924	0.66	0.02	0.681	0.26	0.01	0.266		
U	0.61	0.03	0.50	0.05	0.821	0.57	0.02	0.929	< 0.06				
W	69.9	2.5	62.03.1		0.886	57.5	2.0	0.822	6.08	0.25	0.087		
Yb	0.81	0.03	0.73	0.05	0.895	0.81	0.03	0.998	< 0.06				
Zn	< 6.8		< 61.3			2.60.2			< 9.3				
Zr	< 108		< 798			< 19.0			< 122				

* Combined standard uncertainty of the method.

** Ratio between the determined element content after (determined by k_0-RNAA) and before the Fe removal (determined by k_0-INAA).

Two independent measurements.

Table 4

Results obtained by k_0-NAA in powdered and dissolved samples of chalcanthite ($CuSO_4{\cdot}5H_2O$) from Bučim (results are given in mg kg^{-1}) [42]

El.	Powder		Electrolysis						
			Aliquot 1		Aliquot 2		Average		
	Content	Unc.**	Content	Unc.**	Content	Unc.**	Content	Unc.**	Ratio[#]
Ag	<0.4		<0.4		<1		<1		
Al			7484	264	7473	263	7479	373	
As	2.78	0.23	1.79	0.07	4.76	0.18	3.28	0.18	1.18
Au	0.0062	0.0004	0.019	0.001	0.019	0.001	0.019	0.001	3.06
Ba	<15		<43		<37		<43		
Br	0.76	0.16	0.79	0.05	<0.28		0.79	0.05	1.04
Ca	1698	340	2131	341	2807	421	2469	541	1.45
Cd	< 3		<8		<6		<8		
Ce	19.2	0.7	23.8	1.1	17.7	0.7	20.8	1.3	1.08
Cl			<112		<36		<112		
Co	238	8	265	9	266	9	266	13	1.12
Cr	7.45	0.44	7.21	1.15	45.0*	1.7	7.21	1.15	0.97
Cs	0.24	0.02	<0.31		<0.23		<0.31		
Cu	207919	8127	1766	85	2451	98	2109	132	0.010
Dy			12.6	0.5	13.3	0.5	13.0	0.7	
Eu	1.65	0.07	1.56	0.08	1.71	0.09	1.64	0.12	0.99
Fe	1944	70	1191	55	1005	41	1098	68	0.56
Ga	<26		<1		<1		<1		
Hf	0.087	0.014	0.60	0.04	<0.2		0.60	0.04	6.90
Hg	<0.21		<1.6		<6.0		<6.0		
K	<2187		437	21	315	17	376	27	
La	3.70	0.24	3.41	0.28	2.80	0.21	3.11	0.35	0.84
Mg			3884	528	4939	365	4412	683	
Mn			742	26	735	26	739	37	
Mo	<2		<0.9		<5		<5.4		
Na	616	23	390	14	436	15	413	21	0.67
Nd	27.4	1	33.2	2.0	26.1	1.7	29.7	2.6	1.08
Pt			20.9	1.4	10.5	1.3			
Rb	4.35	1.03	<7.2		<7.0		<7.2		
Re			0.58	0.06	<0.16		0.58	0.06	
Sb	0.144	0.026	0.23	0.02	36.0*	1.3	0.23	0.02	1.60
Sc	0.43	0.02	0.25	0.01	0.23	0.01	0.24	0.01	0.56
Se	2.15	0.12	6.67*	0.61	46.0*	1.7			
Sm	11.3	0.5	11.2	0.4	10.9	0.4	11.1	0.6	0.98
Sn	<31		<197		<160		<197		
Sr	<38		<122		<102		<122		
Ta	<0.02		<0.15		<0.15		<0.15		
Tb	2.38	0.08	2.40	0.09	2.39	0.08	2.40	0.12	1.01
Te	<1.4		<3.6		<2.6				
Th	3.61	0.13	4.16	0.20	3.65	0.13	3.91	0.23	1.08
Ti			<1041		<592		<1041		
U	23.3	0.9	30.5	1.1	22.1	0.8	26.3	1.3	1.13
V			<3.8		9.35	0.52	9.35	0.52	
W	<1.1		<0.3		<0.2		<0.3		
Yb	9.84	0.35	10.3	0.6	10.1	0.4	10.2	0.7	1.04
Zn	59.9	2.4	130*	5	334*	12			
Zr	<45		<37		<256		<256		

** Combined standard uncertainty of the method.

[#] Ratio between the determined element content after (determined by k_0-RNAA) and before the Cu removal (determined by k_0-INAA).

* Not used for calculation of average value.

Good agreement was found between obtained and certified values in all steps of RNAA procedure for Fe removal (dissolved, inorganic and organic phase) [39] and after iron extraction we witness much lower limit of detection (LOD) for numerous elements (Ag, Au, Ca, Cs, Cd, Hg, Rb, Re, Se, Sn, Te and Zr) compared to the corresponding values obtained by k_0-INAA measurements [39]. Depending on the type of the reference material and the concentration levels, it was found that REE, as well as additional 16 elements (Ag, As, Ba, Ca, Co, Cr, Cs, Hf, Na, Rb, Sc, Sr, Th, U, W and Zn), could be analyzed in the inorganic phase after iron removal. The data obtained by k_0-INAA measurement for the content of the elements in the studied iron reference materials are in agreement with the certified values. Taking into account that the number of certified values for the JSS standards is given for a maximum of 7 elements, the obtained results provide useful additional information on the content of the other elements in the standards.

In the case of copper minerals the interferences of Cu were eliminated by removing Cu with electrolysis [37, 42]. Results obtained by k_0-INAA before and after quantitative removal of copper in powdered and dissolved samples of chalcanthite ($CuSO_4 \cdot 5H_2O$) from Bučim mine are presented in Table 4. The main advantage of the proposed method is the possibility to determine the content of several elements (Al, Dy, K, Mg, Mn, Pt, Re and V) via their short lived nuclides after the electrolysis of Cu as a result of the elimination of interferences from the matrix element. However, the results showed that electrolysis was not an appropriate method for determination of some trace elements (As, Na, Sb, Pt and Zn) at low concentration level due to contamination from the Pt-electrode or inadequate purification of the glassware used, adsorption/desorption on glassware (e.g. Na, Sb, Se), or losses during evaporation of the solution (heated to about 80 ºC) to ~ 2 ml (e.g. Se) [42].

The trace element contents in two copper minerals (brochantite, $Cu_4SO_4(OH)_6$ and native copper, Cu) were determined using k_0-NAA before and after quantitative removal of copper with electrolysis [37]. The advantage of using the combination of k_0-NAA for the powdered mineral and after electrolysis is the possibility of simultaneous study of the distribution of many elements (up to 47 elements) from a complex mineral matrix.

This work confirmed the results obtained in our previous work, that the content of some trace elements (Na, K, Rb, Cs, Sb, Pt and Zn) was higher after Cu removal in chalcopyrite ($CuFeS_2$) [43] and chalcantite ($CuSO_4 \cdot 5H_2O$) [42]. This means that using electrolytic solutions for determination of these elements (lower than 100 mg kg^{-1}) with other spectrometric methods probably results in systematically higher results. Additionally, spectrometric methods (AAS, ETAAS, AES-ICP) are not appropriate to determine volatile elements (Br, Cr, Se) because their losses during Cu removal cannot be determined.

Additional data of our studies on the determination of trace elements in iron and copper-based materials can be found in the Ref. [16, 22, 36–47].

On the basis of our results it could be concluded that the main advantage of the k_0-NAA (in form of k_0-INAA or k_0-RNAA) is that no sample contamination and no blank subtraction is needed (blank is negligible). This allows following traceability chain of the element contents in the minerals from powder to organic or watering phase, as it is partly demonstrated in this paper.

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REFERENCES

[1] G. Jovanovski, B. Boev, P. Makreski, *Minerals from the Republic of Macedonia with an Introduction to Mineralogy*, Macedonian Academy of Sciences and Arts, Skopje, 2012.

[2] R. Jaćimović, A. Lazaru, D. Mihajlović, R. Ilić, T. Stafilov, Determination of major and trace elements in some minerals by k_0-instrumental neutron activation analysis, *J. Radioanal. Nucl. Chem.*, **253**, 427–434 (2002).

[3] T. Safilov, N. Angelov, R. Jaćimović, V. Stibilj, Determination of trace elements in arsenic and antimony minerals by atomic absorption spectrometry and k_0-instrumental neutron activation analysis after removal of As and Sb, *Microchim. Acta*, **149**, 229–237 (2005).

[4] T. Stafilov, Determination of trace elements in minerals by electrothermal atomic absorption spectrometry, *Spectrochim. Acta*, Part B, **55**, 893–906 (2000).

[5] J. R. Castillo, M. J. Mir, M. L. Martinez, T. Gomez, Study of the composition of siliceous material by AAS, *At. Spectrosc.*, **9**, 9–12 (1988).

[6] J. S. Barros, Determination of antimony, arsenic, bismuth, cadmium, cobalt and silver in complex sulphide minerals by flame atomic absorption spectrometry, *Analyst*, **114**, 369–373 (1989).

[7] P. Makreski, G. Jovanovski, B. Kaitner, T. Stafilov, B. Boev, D. Cibrev, Minerals from Macedonia. X. Separa-

tion and identification of some oxide minerals by FT IR spectroscopy, AAS, AES-ICP and powder XRD, *Neues Jb. Miner. Abh*., **180**, 215–243 (2004).

[8] J. G. Viets, M. R. O'Leary, R. J. Clark, Determination of arsenic, antimony, bismuth, cadmium, copper, lead, molybdenum, silver and zinc in geological materials by atomic-absorption spectrometry, *Analyst*, **109**, 1589-1592 (1984).

[9] E. Eidecker, E. Jackwerth, Multielement preconcentration from iron and iron compounds, *Fresenius J. Anal. Chem.*, **331**, 401–407 (1988).

[10] T. Stafilov, A. Lazaru, E. Pernicka, Determination of thallium in some sulfide minerals by Zeeman electrothermal atomic absorption spectrometry, *Acta Chim. Slov*., **40**, 37–46 (1993).

[11] M. A. Kabil, A. G. El-Kourashy, M. A. El-Hagrasy, Flame atomic absorption spectrometric investigation and determination of cobalt and copper using ethanolamine and triethanolamine as chemical modifiers, *J. Anal. At. Spectrom*., **11**, 379–387 (1996).

[12] A. Lazaru, T. Stafilov, Determination of copper in sulfide minerals by Zeeman electrothermal atomic absorption spectrometry, *Fresenius J. Anal. Chem*., **360**, 726–728 (1998).

[13] D. Zendelovska, T. Stafilov, Extraction separation and electrothermal atomic absorption spectrometric determination of thallium in some sulfide minerals, *Anal. Sci*., **17**, 425–428 (2001).

[14] T. Stafilov, D. Zendelovska, Determination of trace elements in iron minerals by atomic absorption spectrometry, *Turkish J. Chem*., **26**, 271–280 (2002).

[15] M. Taseska, T. Stafilov, P. Makreski, G. Jovanovski, Determination of trace elements in some copper minerals by atomic absorption spectrometry, *Ovidius Univ. Ann. Chem*., **16**, 43–46 (2005).

[16] M. Taseska, T. Stafilov, P. Makreski, R. Jaćimović, V. Stibilj, G. Jovanovski, Liquid-liquid extraction and determination of trace elements in iron minerals by atomic absorption spectroscopy, *Geol. Maced*., **20**, 33–38 (2006).

[17] H. Palme, M. K. Pavićević, B. Spettel, Major and trace elements in some minerals and ore from Crven Dol, Allchar, *Nucl. Instr. Meth. Phys. Res. A*, **271**, 314–319 (1988).

[18] E. Frantz, H. Palme, W. Todt, A. El Goresy, K. Pavićević, Geochemistry of Tl-As minerals and host rocks at Allchar (Macedonia), *Neues Jb. Miner. Abh*., **167**, 359–399 (1994).

[19] M. Nečemer, P. Kump, M. Rajčevič, R. Jaćimović, B. Budič, M. Ponikvar, Determination of sulfur and chlorine in fodder by X-ray fluorescence spectral analysis and comparison with other analytical methods, *Spectrochim. Acta*, Part B, **58**, 1367–1373 (2003).

[20] M. A. B. C. Menezes, H. E. L. Palmieri, L. V. Leonel, H. A. Nalini Jr., R. Jaćimović, Iron Quadrangle, Brazil: Elemental concentration determined by k_0-instrumental neutron activation analysis. Part I. Soil samples, *J. Radioanal. Nucl. Chem*., **270**, 111–116 (2006).

[21] K. Tomura, H. Tomuro, Determination of trace manganese in high-purity iron by instrumental neutron activation analysis using a thermal column, *J. Radioanal. Nucl. Chem*., **247**, 147–153 (1999).

[22] M. Taseska, P. Makreski, V. Stibilj, R. Jaćimović, T. Stafilov, Is extraction of Fe from iron based reference materials an appropriate method for determination of trace elements?, *Radiochim. Acta*, **100**, 57 (2012).

[23] Certified Reference Material IRMM-530R Al-0.1%Au alloy, EC, JRC, IRMM, Latest revision: May 2007.

[24] B. Smodiš, R. Jaćimović, S. Jovanović, P. Stegnar, P. Vukotić, Efficiency characterisation of HP Ge detectors for use in the k_0-method of neutron activation analysis, *Vestn. Slov. Kem. Druš*., **35**, 397–408 (1988).

[25] F. De Corte, R. van Sluijs, A. Simonits, J. Kučera, B. Smodiš, A. R. Byrne, A. De Wispelaere, D. Bossus, J. Frána, Z. Horák, R. Jaćimović, The validation of Kayzero-assisted NAA in Budapest, Řež, and Ljubljana via the analysis of three BCR certified reference materials, *Fresenius J. Anal. Chem*., **370**, 38–41 (2001).

[26] B. Fazekas, G. Molnár, T. Belgya, L. Dabolczi, A. Simonits, Introducing HYPERMET-PC for automatic analysis of complex gamma-ray spectra, *J. Radioanal. Nucl. Chem*., **215**, 271–277 (1997).

[27] HYPERMET-PC V5.0, User's Manual, Institute of Isotopes, Budapest, Hungary, 1997.

[28] HyperLab 2002 System (2002): Installation and quick start guide, HyperLabs Software, Budapest, Hungary.

[29] KAYZERO/SOLCOI® for Reactor-Neutron activation analysis (NAA) using the k_0-standardization method, DSM Research, Geleen, Netherlands, Dec. 1996.

[30] Kayzero for Windows (KayWin®), User’s Manual for reactor neutron activation analysis (NAA) using the k_0 standardization method, Version 2, November 2005.

[31] R. Jaćimović, F. De Corte, G. Kennedy, P. Vermaercke, Z. Revay, The 2012 recommended k_0 database, *J. Radioanal. Nucl. Chem.*, **300**, 589–592 (2014).

[32] A. R. Byrne, D. Gorenc, The toluene extraction of some elements as iodides from sulphuric acid-potassium iodide media. Application to neutron activation analysis. Part I. Extraction behaviour of As, Au, Bi, Br, Cd, Cu, Ga, Ge, In, Hg, Mo, Pb, Sb, Se, Sn, W and Zn, *Anal. Chim. Acta*, **59**, 81–89 (1972).

[33] A. R. Byrne, The toluene extraction of some elements as iodides from sulphuric acid-potassium iodide media. Application to neutron activation analysis. Part II. Determination of arsenic and antimony in biological materials at submicrogram levels, *Anal. Chim. Acta*, **59**, 91–99 (1972).

[34] A. R. Byrne, A. Vakselj, Rapid neutron activation analysis of arsenic in a wide range of samples by solvent extraction of the iodide. *Croat. Chem. Acta*, **46**, 225–235 (1974).

[35] A. R. Byrne, Low-level simultaneous determination of As and Sb in standard reference materials using radiochemical neutron activation analysis with isotopic ^{77}As and ^{125}Sb tracers. *Fresenius J. Anal. Chem*., **326**, 733–735 (1987).

[36] P. Makreski, R. Jaćimović, V. Stibilj, T. Stafilov, G. Jovanovski, Determination of trace elements in iron minerals by instrumental and radiochemical neutron activation analysis, *Radiochim. Acta*, **96**, 855–861 (2008).

[37] M. Taseska, R. Jaćimović, V. Stibilj, T. Stafilov, P. Makreski, G. Jovanovski, Determination of trace elements in some copper minerals by k_0-neutron activation analysis, *Appl. Radiat. Isot*., **70**, 35–39 (2012).

[38] R. Jaćimović, B. Smodiš, T. Bučar, P. Stegnar, k_0-NAA quality assessment by analysis of different certified reference materials using the KAYZERO/SOLCOI software, *J. Radioanal. Nucl. Chem.*, **257**, 659–663 (2003).

[39] R. Jaćimović, P. Makreski, V. Stibilj, T. Stafilov, Determination of major and trace elements in iron reference materials using k_0-NAA, *J. Radioanal. Nucl. Chem.*, **278**, 795–799 (2008).

[40] M. Taseska, P. Makreski, V. Stibilj, R. Jaćimović, T. Stafilov, Determination of trace elements in hematite's iron reference material JSS-804-1 using k_0-INAA, *Geol. Maced.*, **22**, 43–48 (2008).

[41] P. Makreski, R. Jaćimović, V. Stibilj, T. Stafilov, Determination of major and trace elements in iron-nickel-copper-cobalt ore reference materials using k_0-NAA, *Radiochim Acta,* **97**, 643–649 (2009).

[42] M. Taseska, R. Jaćimović, V. Stibilj, T. Stafilov, P. Makreski, G. Jovanovski, Is removal of copper by electrolysis from copper minerals an appropriate method for determination of trace elements?, *Nucl. Inst. Meth. Phys. Res. A*, **622**, 449–452 (2010).

[43] M. Taseska, P. Makreski, V. Stibilj, R. Jaćimović, T. Stafilov, G. Jovanovski, Determination of trace elements in chalcopyrite ($CuFeS_2$) by k_0-instrumental neutron activation analysis after matrix elements removal, *Maced. J. Chem. Chem. Eng*., **27**, 141–147 (2008).

[44] R. Jaćimović, P. Makreski, V. Stibilj, T. Stafilov, G. Jovanovski, Characterization of some iron minerals from the Republic of Macedonia using instrumental neutron activation analysis, *Geol. Maced*., **19**, 33–38 (2005).

[45] P. Makreski, G. Jovanovski, A. Gajović, T. Biljan, D. Angelovski, R. Jaćimović, Minerals from Macedonia. XVI. Vibrational spectra of some common appearing pyroxenes and pyroxenoids, *J. Mol. Struct.*, **788**, 102–114 (2006).

[46] R. Jaćimović, M. Taseska, V. Stibilj, P. Makreski, T. Stafilov, G. Jovanovski, Element composition of some copper minerals from the Republic of Macedonia, *Geol. Maced*., **21**, 87–91 (2007).

[47] P. Makreski, G. Jovanovski, T. Runčevski, R. Jaćimović, Simple and efficient method for detection of traces of rare earth elements in minerals by Raman spectroscopy instrumentation, *Maced. J. Chem. Chem. Eng*., **30**, 241–250 (2011).