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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

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Abstract. The content of trace elements in arsenic and antimony minerals from the Allchar mine, Macedonia, was determined by electrothermal atomic absorption spectrometry (ETAAS) and k_0-instrumental neutron activation analysis (k_0-INAA) after removal of arsenic and antimony. Their direct determination by ETAAS or k_0-INAA in arsenic (realgar and orpiment) and antimony (stibnite) minerals is limited by strong matrix interferences from As and Sb. Successful elimination of both elements was realized by the extraction of their iodide complexes into toluene. It was found that the optimal conditions were triple extraction of arsenic into toluene from $6\,\mathrm{mol \cdot L^{-1}}$ HCl with addition of KI. Triple extraction of antimony was most successful in the system $4.5\,\mathrm{mol \cdot L^{-1}}$ H_2SO_4 and KI into toluene. In both cases, trace elements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were then detected in the aqueous phase by ETAAS. The proposed procedures with ETAAS were checked by the method of standard additions and Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn determined in realgar, orpiment and stibnite. Using k_0-INAA the trace elements Ba, Ce, Co, Cr, Cs, Fe, Hg, Sc, Tb, Th, U and Zn in realgar and orpiment were determined before and after As and Sb removal from the same aliquot of sample. The removal of both elements with KI into toluene was higher than 99.8% and no losses of trace elements were observed.

Key words: Trace elements; realgar; orpiment; stibnite; atomic absorption spectrometry; k_0-instrumental neutron activation analysis; radiochemical separation.

Within the framework of the LOREX project [1, 2], it is 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). Thus, in 1976 Freedman et al. [1] proposed applying the reaction between ^{205}Tl (present in thallium minerals from the Allchar mine) and solar neutrinos producing ^{205}Pb to study the neutrino flux from the sun. The aim of this experiment is to determine the content of ^{205}Pb accumulated in thallium minerals, which is generated by this nuclear reaction. Because of the low cross-section of the $^{205}\mathrm{Tl}(\nu, e^-)^{205}\mathrm{Pb}$ reaction, a high concentration of Tl atoms is necessary to produce measurable amounts of ^{205}Pb. For this purpose, lorandite from the Allchar mine was suggested

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as a target. The fact that we are dealing with a natural target, which after its formation has been exposed to many uncontrolled and unknown factors for not exactly known intervals of time, leads to a number of problems. One of these is to know the quality of the minerals used as the target. Therefore, it is important to accurately determine the concentration of lead in thallium minerals, and also the concentration of all major and trace elements associated with the ^{205}Tl target in realgar, orpiment and stibnite present in the Allchar deposit. This is important because these minerals, providing that they are co-genetic, can be used as monitors for determining the contribution of background reactions originating from natural radioactivity.

Determination of trace elements in realgar, orpiment and stibnite from the Allchar mine was previously performed by atomic absorption spectrometry, AAS [3–19]. It has been explained in previous papers [6–8, 10–16, 18, 19] that the application of flame (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) to trace element analysis of arsenic and antimony minerals is limited because of matrix interferences. The arsenic and antimony decrease the absorbance of some of the trace elements determined by ETAAS, and therefore different extraction [7, 11–13, 15, 18] or precipitation [8, 19] methods were applied to remove As and Sb.

Palme et al. [20], Frantz et al. [21] and Jaćimović et al. [22] determined some trace elements in these minerals by instrumental neutron activation analysis. They reported that the high concentration of As (>50%) and the resulting high background produced by ^{76}As activity after irradiation by thermal neutrons, especially in realgar and orpiment, makes the determination of medium-lived radionuclides present at micro-levels impossible. A similar problem occurred with X-ray fluorescence spectrometry [23] due to the problem of matrix and interelement interference and background effects. Trace elements in arsenic and antimony minerals were also analyzed by mass spectrometry [21, 24–27] and neutron induced autoradiography [28]. It was found that the presence of high amounts of As, Sb, Tl and S interfere in mass spectrometric determination. Therefore, ion exchange separation [21] or extraction [24] were introduced for the separation of trace elements from the mineral matrix.

For biological materials, Byrne and co-workers [29–32] studied the toluene extraction of the trace elements As and Sb as iodides from sulphuric acid – potassium iodide media. The aim of the present study was to find optimum conditions for arsenic and antimony removal by extraction of their iodides into toluene from matrix solutions, and to determine trace elements in the residue of arsenic and antimony minerals (realgar, orpiment and stibnite) by ETAAS and k_0-INAA.

Experimental

Methods

Atomic absorption spectrometry.

Instrumentation

A Varian SpectrAA 640Z Zeeman atomic absorption spectrophotometer equipped with a Varian PSD-100 Autosampler and Varian SpectrAA 220 atomic absorption spectrophotometer was used for FAAS. The instrumental parameters for trace element determination by FAAS (As, Sb, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and ETAAS (Co, Cd, Ni, Cu, Cr and Pb) were those described in the producer's manual.

Reagents and Samples

All reagents and standards were of analytical grade (Merck, Germany). Stock solutions of all elements investigated were prepared by dissolution of high-purity salts or metals. The mass concentrations of elements in these solutions were $1000\,\mathrm{mg \cdot L^{-1}}$, from which diluted solutions were prepared. The solution of potassium iodide was prepared by dissolving 85 g KI in a 100 mL volumetric flask. After dissolution the flask was filled up to mark.

Mineral specimens of realgar, orpiment and stibnite were taken from the Allchar mine, Crven Dol locality, adit No. 21 [33, 34]. Mineral specimens were carefully selected from ore samples using a microscope, and then ground to a powder.

Procedures

Realgar and orpiment. In a 100 mL glass beaker, 0.1 g of powdered sample of realgar or orpiment was dissolved in 10 mL concentrated HNO_3 and 1 mL of H_2O_2 (30%). The solution was evaporated almost to dryness. The residue was dissolved in 10 mL concentrated HCl with a minimum of boiling and transferred to a separatory funnel, adding 10 mL of redistilled water. The extraction of As was performed by adding 1 mL of KI solution ($0.85\,\mathrm{g \cdot mL^{-1}}$) and 10 mL of toluene and by shaking the mixture for 5 min. The extraction was repeated twice with 10 mL toluene. The water phase was transferred to a 25 mL volumetric flask and filled to the mark. From this solution determination of trace elements was performed. Iron, manganese and zinc were analyzed by flame atomic absorption spectrometry (FAAS) and the other elements by ETAAS.

Stibnite. In a 100 mL glass beaker, 0.1 g of powdered sample was dissolved in 10 mL of conc. HCl, 1 mL of conc. HNO_3 and 1 mL of H_2O_2. The solution was evaporated almost to dryness, and the residue was then dissolved in 5 mL concentrated H_2SO_4 with a minimum of boiling and transferred to a separatory funnel, adding 15 mL of redistilled water. The extraction of Sb was performed by adding 0.5 mL of KI solution ($0.85\,\mathrm{g \cdot mL^{-1}}$) and 10 mL of toluene and by shaking the mixture for 5 min. The extraction of Sb was repeated twice with 10 mL toluene. The water phase was transferred to a 25 mL volumetric flask and filled to the mark. From this solution determination of trace elements was performed.

Radiochemical Separation and Detection by k_0-Instrumental Neutron Activation Analysis

Samples were irradiated in the TRIGA Mark II reactor of the Jožef Stefan Institute 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-530 disc of 6 mm diameter and 0.2 mm thickness were stacked together and fixed in the polyethylene ampoule in sandwich form and irradiated at a thermal neutron fluence rate of $1.1 \cdot 10^{12}\,\mathrm{n\,cm^{-2}\,s^{-1}}$ for 20 h in the carousel facility of the TRIGA reactor. 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.

The k_0-INAA method requires an absolutely calibrated detector [35]. For peak area evaluation, the HYPERMET-PC [36, 37] program was used. For elemental concentrations and effective solid angle calculations, a software packet called KAYZERO/SOLCOI® program [38] was used.

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 boiled again and evaporated to 0.5 mL (no HNO_3 should remain).

For As removal, the method described by Byrne and collaborators [29–32] with slight modifications was used. For realgar, 5 mL 9.0 M H_2SO_4 diluted to 8 mL and 2 mL of 5 M 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), with a 40% relative efficiency connected to a Canberra S100 multichannel analyser, after 8, 25 and 40 days cooling time. Measurements were performed at such distances that the dead time was kept at <10% and random coincidences were negligible. The relevant nuclear data of radionuclides used in the determination by k_0-INAA up to 21 elements in realgar and 12 elements in orpiment are given elsewhere [22].

Results and Discussion

Atomic Absorption Spectrometry

Investigations of the interference of matrix elements in the minerals studied (As and Sb) on the determination of Fe, Mn, and Zn by FAAS and on the determination of Cd, Co, Cr, Cu, Ni, Pb by ETAAS have been presented in a previously published paper [19]. It was found that during direct determination of the investigated trace elements, the absorbances of arsenic and antimony decrease. Elimination of As and Sb was performed by reduction to the elemental state by sodium tetrahydridoborate(III), precipitation and filtration [19]. The disadvantage of the mentioned methods is the likely co-precipitation of trace elements. Hence, a method which removes the matrix in soluble form, such as iodide extraction, is favourable.

In this study, the removal of arsenic and antimony using the KI-toluene system was applied. It was known that traces of arsenic and antimony could be extracted as iodides from acidic solutions with toluene in high recovery (100%) [29–32, 39, 40]. Optimization of experimental conditions for extraction of major amounts of As and Sb was performed by the determination of the optimal mass of KI, the concentration of HCl and H_2SO_4 and the number of extractions.

Optimization of the Condition for Arsenic and Antimony Extraction Using Potassium Iodide

During dissolution of the investigated minerals, nitric acid and H_2O_2 were added, which means that As and Sb were in the five oxidation state forms. KI reduces As(V) to As(III) and Sb(V) to Sb(III) and they are probably extracted as AsI_3 and SbI_4^- [31]. Taking into account that the mass fraction of As and Sb in the investigated minerals is 61–72%, the concentration of KI required when 0.1 g of mineral mass is taken was investigated. The most suitable mass of KI was established by measuring the extraction recovery of As (50 mg) and Sb (70 mg) upon varying the mass of KI in a model solution of various concentrations of H_2SO_4 and HCl. The solutions contained $50\,\mu g \cdot mL^{-1}$ of the following elements: Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. It was found that the optimum mass of KI was 0.83 g (5 mmol) for As in $5–6\,mol \cdot L^{-1}$ H_2SO_4, and for Sb it was $4.5\,mol \cdot L^{-1}$ H_2SO_4.

However, in the case of arsenic, hydrochloric acid was taken for further investigation because the presence of H_2SO_4 decreased the AAS signal for the trace elements Cd, Co, Cu, Pb, Ni and Zn (at the level of $50\,\mu g \cdot mL^{-1}$) after removal of As (50 mg). For the above elements the recovery varied from 91.0% for Pb to 97.6% for Cd. The copper concentration was 30% lower in the presence of both acids. Byrne and Gorenc [29], using ^{64}Cu tracer, found that Cu is non-extractable by KI in toluene, but forms an insoluble iodide at the interface between the water and toluene. After triple extraction of antimony, the recovery of Co and Ni in the water phase was 95.6% and 91.6%, respectively. After five-fold extraction of Sb, we observed losses for both elements (82.6% and 83.7% recovery, respectively).

To verify the method, some samples of realgar, orpiment and stibnite minerals (taken from the Allchar mine) were prepared with standard additions of Co, Cr, Cu, Ni and Pb and treated using the proposed

Table 1. Content of Cd, Co, Cr, Cu, Ni and Pb in realgar, orpiment and stibnite determined by standard addition method (after As or Sb removal)

No.	m_{M}(added)/μg*	w_{M}(calculated)/μg · g^{-1}**	w_{M}(found)/μg · g^{-1}	R (%)	Limit of detection (μg · g^{-1})
Cd					
Stibnite					
1	–	–	2.94	–	0.03
2	50	3.44	3.23	93.89	
3	100	3.94	3.66	92.89	
Co					
Realgar					
1	–	–	0.46	–	0.15
2	100	1.46	1.30	89.04	
3	200	2.46	2.29	93.08	
Orpiment					
1	–	–	0.27	–	0.15
2	100	1.27	1.22	96.06	
3	200	2.27	2.15	94.71	
Stibnite					
1	–	–	8.78	–	0.12
2	100	9.28	9.28	100	
3	200	9.78	9.78	100	
Cr					
Realgar					
1	–	–	1.77	–	0.13
2	100	2.27	2.11	92.95	
3	200	3.77	3.49	92.55	
Orpiment					
1	–	–	1.43	–	0.13
2	100	2.43	2.38	97.94	
3	200	3.43	3.30	96.2	
Stibnite					
1	–	–	3.08	–	0.19
2	100	4.08	3.68	90.19	
3	200	5.08	4.80	94.48	
Cu					
Realgar					
1	–	–	0.31	–	0.21
2	50	0.81	0.61	76.50	
3	100	1.31	1.07	81.61	
Orpiment					
1	–	–	0.82	–	0.21
2	50	1.32	1.06	81.50	
3	100	1.82	1.16	63.73	
Stibnite					
1	–	–	0.93	–	0.20
2	50	1.43	1.01	76.4	
3	100	1.93	1.36	70.46	
Ni					
Realgar					
1	–	–	1.47	–	0.32

(*continued*)

Table 1 (*continued*)

2	100	2.47	2.41	97.57	
3	200	3.47	3.30	95.10	
Orpiment					
1	–	–	1.00	–	0.32
2	100	2.00	1.85	92.00	
3	200	3.00	2.90	96.66	
Stibnite					
1	–	–	8.67	–	0.30
2	100	9.17	9.10	99.2	
3	200	9.47	9.36	96.7	
Pb					
Realgar					
1	–	–	1.87	–	0.24
2	100	2.87	2.70	94.00	
3	200	3.87	3.63	93.79	
Orpiment					
1	–	–	0.37	–	0.24
2	100	1.37	1.25	91.24	
3	200	2.37	2.30	97.00	
Stibnite					
1	–	–	1.62	–	0.29
2	100	2.12	1.90	89.6	
3	200	2.62	2.25	95.8	

* m_M Mass of investigated element (M).
** w_M Mass fraction of investigated element (M).

Table 2. Content of Fe, Mn and Zn and limit of detection in realgar, orpiment and stibnite mineral samples (after As or Sb removal (in $\mu g \cdot g^{-1}$))

Mineral	Fe		Mn		Zn	
	Content	Limit of detection	Content	Limit of detection	Content	Limit of detection
Realgar	1383.3	2.45	1845.0	2.92	95.0	0.05
Orpiment	226.0	2.45	38.7	2.92	62.2	0.05
Stibnite	10.2	2.60	13.9	2.78	9.25	0.06

extraction procedure. The results given in Table 1 show that satisfactory recoveries were obtained. Also, linearity of recovery is evident and other elements did not interfere with any particular analyte. Because of the higher content of Fe, Mn and Zn, these elements were determined by FAAS (Table 2). Tables 1 and 2 also give the limit of detection of the investigated elements (calculated as 3 SD of the blank).

Determination of Trace Elements by k_0-INAA

It was known that the trace element contents in realgar and orpiment were relatively inhomogeneous [14, 15, 18–22, 28]. K_0-INAA gave us the possibility to determine elements before and after As and Sb removal from the same aliquot of sample (see Tables 3 and 4). After the first gamma measurement of the sample, dissolution, removal of As and Sb, and a second gamma measurement were performed in the same glass flask. The majority of As was removed, in realgar from 44.7 down to 0.024% and in orpiment from 46.1 down to 0.0217%. Sb in realgar was present in traces, so its removal was not as significant (from 9.39 to 6.64 $\mu g \cdot g^{-1}$), and we assumed that equilibrium was obtained between the two phases. This result agrees well with the data reported by Byrne and Gorenc [29]. In their experiments about 0.5% of Sb remained in the water phase. In orpiment, Sb was removed from

Table 3. Content of macro and trace elements and limit of detection in realgar determined by k_0-INAA (in $\mu g \cdot g^{-1}$)

Element	Found in mineral		Found after As removal		
	Content	Limit of detection	Content	R (%)	Limit of detection
As	447000	100	246	0.06	0.2
Ba		20	16.8	–	6
Ca	8820	6000	1525	17	600
Ce	1.63	0.3	1.04	64	0.4
Co	11.3	0.04	9.95	88	0.03
Cr	2.48	0.5	3.53	142	0.5
Cs	1.03	0.05	0.92	89	0.06
Fe	47750	40	42580	89	30
Hg	0.80	0.1		–	0.2
La		2	0.71	–	0.01
Na		1000	19.4	–	8
Sb	9.39	0.08	6.64	71	0.07
Sc	0.21	0.005	0.181	86	0.005
Sm		0.5	0.105	–	0.005
Sr	19.5	15		–	15
Tb	0.049	0.02	0.066	135	0.02
Th	0.082	0.03	0.1	122	0.04
Tm	0.41	0.1		–	0.1
U		2	2.02	–	0.06
Yb		0.5	0.168	–	0.02
Zn	55.1	2	51.1	93	2

Table 4. Content of macro and trace elements and limit of detection in orpiment determined by k_0-INAA (in $\mu g \cdot g^{-1}$)

Element	Found in mineral		Found after As removal		
	Content	Limit of detection	Content	R (%)	Limit of detection
As	461000	100	217	0.05	0.4
Ca		10000	891	–	600
Co		0.5	0.036	–	0.02
Cr	2.0	1	0.62	31	0.3
Cs		0.05	0.054	–	0.01
Fe		400	51.8	–	15
Hg	16.0	1		–	0.1
Nd	103	50		–	1
Sb	2890	0.5	5.14	0.2	0.02
Sc		0.04	0.0069	–	0.001
Tm	4.4	0.7		–	0.1
U		2		–	0.06

2890 down to 5.14 $\mu g \cdot g^{-1}$. So it is evident that with this procedure we can remove both elements from the $mg \cdot g^{-1}$ to the $\mu g \cdot g^{-1}$ level. The ratio of trace element contents before and after matrix removal is near 1. It is evident that negligible losses were obtained, except for volatile elements (e.g. Hg). From the results we could conclude that the extraction method was appropriate for removing As and Sb and allowed the determination of many more trace elements after removal of the matrix interference. Tables 3 and 4 show that the limit of detection after As or Sb removal in all cases was significantly lower. On the other hand, we could not measure some of the elements (Cu, Cd, Mn, Ni and Pb) due to their nuclear characteristics (half-life or insufficient neutron activation).

The removal of As and Sb with KI in toluene was successful, amounting to more than 99% from matrix solutions. Co, Cr, Cs, Fe, Sc, Tb, Th and Zn were determined in the aqueous solution and did not coextract with arsenic or antimony.

The values obtained for the content of trace elements obtained using neutron activation analysis [20–22], mass spectrometry [21, 24, 27] and AAS [7–11, 13, 15, 16] are compared in Table 5. Differences in the content of some elements are due to inhomogeneity of the mineral samples and the

Table 5. The content of trace elements in realgar, orpiment and stibnite from Allchar mine obtained by different methods (given in $\mu g \cdot g^{-1}$)*, Zn for Orpiment messing authors and method used: 2.8; Palme at al., INAA [20]

Element	Realgar	Orpiment	Stibnite
Ba	<20; Jaćimović et al., INAA [22] 16.8; This work, INAA	<20; Jaćimović et al., INAA [22]	
Ce	2.07 ± 0.17; Jaćimović et al., INAA [22] 1.63; This work, INAA	<0.6; Jaćimović et al., INAA [22]	
Cd	<100; Jaćimović et al., INAA [22] 1.54; Angelov&Stafilov, AAS [19]	<100; Jaćimović et al., INAA [22] 0.45; Angelov&Stafilov, AAS [19]	2.9; Angelov&Stafilov, AAS [19] 2.94; This work, AAS
Co	<0.08; Palme et al., INAA [20] <4.0; Frantz et al., INAA [21] 13.9 ± 0.56; Jaćimović et al., INAA [22] <1; Boev et al., MS [27] 0.10–0.80; Lazaru&Stafilov, AAS [15] 0.08; Angelov&Stafilov, AAS [19] 0.46; This work, AAS 11.3; This work, INAA	<0.41; Palme et al., INAA [20] <7; Frantz et al., INAA [21] 0.100 ± 0.017; Jaćimović et al., INAA [22] 0.086–1.16; Lazaru&Stafilov, AAS [15] 0.05; Angelov&Stafilov, AAS [19] 0.27; This work, AAS 0.036; This work, INAA	<10; Boev et al., MS [27] 5.90; Angelov&Stafilov, AAS [19] 8.78; This work, AAS
Cr	<20; Palme et al., INAA [20] 69.8; Frantz et al., INAA [21] 2.64 ± 0.14; Jaćimović et al., INAA [22] <1; Lazaru&Stafilov, AAS [10] 1.60; Angelov&Stafilov, AAS [19] 1.77; This work, AAS 2.48; This work, INAA	<100; Palme et al., INAA [20] <1–32.6; Lazaru&Stafilov, AAS [10] 0.42 ± 0.04; Lazaru&Stafilov, AAS [15] 1.19; Angelov&Stafilov, AAS [19] 1.43; This work, AAS 2.0; This work, INAA	<10; Boev et al., MS [27] 4; Lazaru&Stafilov, AAS [10] 3.95; Angelov&Stafilov, AAS [19]
Cs	1.5; Frantz et al., INAA [21] 1.27 ± 0.05; Jaćimović et al., INAA [22] <3; Boev et al., MS [27] 0.92; This work, INAA	0.037 ± 0.008; Jaćimović et al., INAA [22] <0.7; Boev et al., MS [27] 0.054; This work, INAA	
Cu	<300; Palme et al., INAA [20] <2; Boev et al., MS [27] <1; Lazaru&Stafilov, AAS [10] 0.46; Lazaru&Stafilov, AAS [13] $0.31^{\$}$; This work, AAS	<1200; Palme et al., INAA [20] <4; Boev et al., MS [27] <1–4.7; Lazaru&Stafilov, AAS [10] 0.55; Lazaru&Stafilov, AAS [13] $0.82^{\$}$; This work, AAS	<10; Boev et al., MS [27] 1.8; Lazaru&Stafilov, AAS [10] 0.75; Lazaru&Stafilov, AAS [13] $0.93^{\$}$; This work, AAS
Fe	<20; Palme et al., INAA [20] 57500 ± 2300; Jaćimović et al., INAA [22] 365–1410; Lazaru&Stafilov, AAS [10] 14058; Angelov&Stafilov, AAS [19] 13838.3; This work, AAS 42580; This work, INAA	<200; Palme et al., INAA [20] 169 ± 12; Jaćimović et al., INAA [22] <800; Boev et al., MS [27] 96–620; Lazaru&Stafilov, AAS [10] 226.7; Angelov&Stafilov, AAS [19] 226.0; This work, AAS 51.8; This work, INAA	1000; Boev et al., MS [27] 9.25; Angelov&Stafilov, AAS [19] <10.2; This work, AAS
Hg	<0.5; Palme et al., INAA [20] <1; Frantz et al., INAA [21] 0.99 ± 0.06; Jaćimović et al., INAA [22] 0.8; This work, INAA	<1; Palme et al., INAA [20] 3.52 ± 0.14; Jaćimović et al., INAA [22] 16.0; This work, INAA	
Mn	<4; Frantz et al., INAA [21] <90; Boev et al., MS [27] 70.4–955; Lazaru&Stafilov, AAS [10] 1780; Angelov&Stafilov, AAS [19] 226.0; This work, AAS	100; Palme et al., INAA [20] <8; Frantz et al., INAA [21] 5.0–28.3; Lazaru&Stafilov, AAS [10] 31.8; Angelov&Stafilov, AAS [19] <20; Boev et al., MS [27] 38.7; This work, AAS	50; Boev et al., MS [27] 11.5; Angelov&Stafilov, AAS [19] 13.9; This work, AAS
Ni	<1–41.0; Lazaru&Stafilov, AAS [10] 0.75–1.76; Lazaru&Stafilov, AAS [15] 1.30; Angelov&Stafilov, AAS [19] <10; Palme et al., INAA [20] 1.47; This work, AAS	<1–7.4; Lazaru&Stafilov, AAS [10] 1.29–4.86; Lazaru&Stafilov, AAS [15] 0.73; Angelov&Stafilov, AAS [19] <30; Palme et al., INAA [20] 1.0; This work, AAS	<200; Boev et al., MS [27] 9.6; Lazaru&Stafilov, AAS [10] 8.21; Angelov&Stafilov, AAS [19] 8.67; This work, AAS
Pb	0.01–2.02; Frantz et al., INAA [21] 1.1–5; Ljubićić et al., INAA [25] 0.38; Todt, MS [24] 0.8; Boev et al., MS [27]	0.07–11.6; Frantz et al., INAA [21] 11.6; Todt, MS [24] <2; Boev et al., MS [27] 5.3–9.4; Stafilov, AAS [7]	<10; Boev et al., MS [27] 0.38–2.47; Stafilov et al., AAS [8] 0.65; Angelov&Stafilov, AAS [19] 1.62; This work, AAS

(*continued*)

Table 5 (*continued*)

Element	Realgar	Orpiment	Stibnite
	4.8; Stafilov, AAS [7] 0.29–3.16; Lazaru&Stafilov, AAS [15] 1.14; Angelov&Stafilov, AAS [19] 1.87; This work, AAS	1.65–3.73; Lazaru&Stafilov, AAS [15] 0.21; Angelov&Stafilov, AAS [19] 0.37; This work, AAS	
Sc	0.064; Palme et al., INAA [20] <0.04; Frantz et al., INAA [21] 0.263 ± 0.011; Jaćimović et al., INAA [22] 0.21; This work, INAA	0.32; Palme et al., INAA [20] <2; Frantz et al., INAA [21] 0.0056 ± 0.0007; Jaćimović et al., INAA [22] 0.0069; This work, INAA	
Tb	0.0577 ± 0.0035; Jaćimović et al., INAA [22] 0.066; This work, INAA	<0.02; Jaćimović et al., INAA [22] 0.0069; This work, INAA	
Th	<0.06; Palme et al., INAA [20] 0.0017–0.009; Frantz et al., INAA [21] 0.080 ± 0.010; Jaćimović et al., INAA [22] <13; Ljubićić et al., INAA [25] 1.19; Todt, MS [24] <13; Anovski et al., MS [26] 0.1; This work, INAA	<0.1; Palme et al., INAA [20] 0.0056–2.64; Frantz et al., INAA [21] <0.06; Jaćimović et al., INAA [22] 2.64; Todt, MS [24] <0.1; Anovski et al., MS [26]	
Zn	<30; Frantz et al., INAA [21] 66.5 ± 2.7; Jaćimović et al., INAA [22] 92.5; Angelov&Stafilov, AAS [19] 95.0; This work, AAS 55.1; This work, INAA	<0.7; Jaćimović et al., INAA [22] 54.9; Angelov&Stafilov, AAS [19] 2.8 [20] 62.2; This work, AAS <20; This work, INAA	<30; Boev et al., MS [27] 8.86; Angelov&Stafilov, AAS [19] 9.25; This work, AAS
U	<2.2; Palme et al., INAA [20] 0.017–0.28; Frantz et al., INAA [21] <2; Jaćimović et al., INAA [22] 5 ± 1; Ljubićić et al., INAA [25] 0.74; Todt, MS [24] 13.2 ± 0.9; Anovski et al., MS [26] 0.024 ± 0.007 and 0.043 ± 0.013; Lazaru et al., NIA [28] 2.02; This work, INAA	<2.7; Palme et al., INAA [20] 0.01–0.092; Frantz et al., INAA [21] <2; Jaćimović et al., INAA [22] 0.084; Todt, MS [24] <0.1; Anovski et al., MS [26] 0.03 ± 0.01 and 0.07 ± 0.02; Lazaru et al., NIA [28] <0.06; This work, INAA	0.7 ± 0.2; Lazaru et al., NIA [28]

* *INAA* Instrumental Neutron Activation Analysis, *MS* Mass Spectrometry, *AAS* Atomic Absorption Spectrometry, *NIA* Neutron induced autoradiography.

$ Data is at least 30% lower (see Table 1).

variety of methods used with different limits of detection.

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