

Determination of Trace Elements in Some Arsenic Minerals by Atomic Emission Spectrometry With Inductively Coupled Plasma After Matrix Removal

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ABSTRACT: Various trace elements content in two arsenic minerals were investigated using atomic emission spectrometry with inductively coupled plasma (ICP-AES). Both, realgar (As_4S_4) and orpiment (As_2S_3) belonged to the sulfide group of minerals. The studied minerals originate from Allchar mine, Crven Dol locality, Republic of Macedonia. To avoid the interference of arsenic as matrix element, a liquid-liquid extraction of its iodide complex into toluene in hydrochloric solution was applied. The extraction method was optimized. Operating parameters, such as the amount of As present and number of extractions were determined. The removal of arsenic was performed by KI with 4 steps of extraction with toluene for 5 min shaking time each, was higher than 99%. After the phase separation, determination of different trace elements in the aqueous phase was undertaken. The proposed procedure was verified by the method of standard additions and by its applications to the minerals. The results of the trace elements determination shown that satisfactory recoveries were obtained.

Keywords: Realgar, orpiment, trace elements, inductively coupled plasma atomic emission spectrometry

INTRODUCTION

Minerals are naturally-occurring inorganic substances with a definite chemical composition and physical properties, but they always contain traces of other elements that can change some of their characteristics. The knowledge about the presence of trace elements in the mineral sample helps to establish the conditions in which these minerals have been formed. Also, a variety of minerals are quite easily interchangeable, making it possible for one mineral to grade into another. Therefore, there are many reasons to analyze trace elements in minerals. Some involve the determination of mineral purity and the presence of very rare or important elements that could be extracted, or used in order to obtain important information about the geology of the mines and mineral localities [1].

Most arsenic in nature is found in minerals associated with sulfur. Because arsenic is produced from the ore deposits, it is very important to follow the content of trace elements in its minerals samples. The presence of arsenic minerals in the Republic of Macedonia [1] is

mainly due to the well known Allchar mine which is quite unusual and attractive locality situated in the depth of the mountain Kozuf [2, 3]. The Allchar locality is very rich in mineral composition of 45 different minerals were the realgar (As_4S_4) and orpiment (As_2S_3) are the most present minerals, beside stibnite (Sb_2S_3) and thallium-arsenic mineral loradnidte (TlAsS_2) [2-7]. In the framework of the LOREX project [8], it is very important to determine the quality of the minerals used as the target for neutrino detection as lorandite (TlAsS_2) and in the most frequently occurring minerals in Allchar mine (realgar and orpiment). Therefore, it is important to determine accurately the concentration of all major and trace elements associated with the realgar and orpiment from this deposit.

Determination of trace elements in realgar and orpiment from the Allchar mine has been previously performed by flame and electrothermal atomic absorption spectrometry, FAAS, ETAAS [1, 5, 9-16]. It was explained in previous papers that the application of FAAS and ETAAS to trace element analysis of minerals is limited because of matrix interferences. Neutron activation analysis

was also applied for the analysis of minerals [3, 6, 17]. 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 in X-ray fluorescence spectrometry [18] due to the problem of matrix and interelement interference and background effects. Trace elements in arsenic minerals were also analyzed by mass spectrometry [3, 19] and neutron induced autoradiography [20].

The application of atomic emission spectrometry with inductively coupled plasma (ICP-AES) to some trace element analysis of arsenic minerals is also limited because of matrix interferences [21-24]. In this work the method for determination of different trace elements in arsenic minerals (realgar and orpiment) was proposed by ICP-AES in the liquid phase after the removal of As by liquid-liquid extraction of iodide complex into toluene in HCl media.

EXPERIMENTAL

Samples and Reagents

Both realgar (As_4S_4) and orpiment (As_2S_3) mineral samples were collected from the Allchar mine, Crven Dol locality, Republic of Macedonia. Mineral specimens were carefully hand-picked under an optical microscope from the mineral samples and ground to powder. For this study all reagents and standards were of analytical grade (Merck, Germany). Redistilled water was used for preparation of all solutions. Standard solutions of elements were prepared by dilution of 1000 mg l⁻¹ solutions (11355-ICP multi Element Standard). The solution of potassium iodide was prepared by dissolving of 85 g KI in 100 mL volumetric flask.

Instrumentation

The samples analyses were performed by ICP-AES, Varian 715-ES. Total contents of 18 elements were analyzed in the liquid phase after the removal of arsenic from the minerals by liquid-liquid extraction of iodide complex into toluene in HCl media: Ag, Al, Ba, Ca, Cd, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn. The proposed procedure was verified by the method of standard additions and it was found that the recovery for

the investigated elements ranges for ICP-AES around 100%. The optimal instrumental conditions were given in our previously published paper [25].

Procedure

The powdered sample of realgar and orpiment (~100 mg) was dissolved on a hot plate by adding 2 aliquots of 10 mL concentrated HNO_3 followed by 3 mL H_2O_2 (30%). After evaporation almost to dryness, the residue was dissolved in 10 mL concentrated HCl and transferred to a separatory funnel with 10 mL redistilled water. The extraction of arsenic was carried out with 1 mL KI solution (0.85 g mL⁻¹) and 10 mL of toluene by shaking the mixture 4 times, 5 min each. After the phase separation, to concentrate the investigated elements, the inorganic layer was evaporated and the residue dissolved in 10 mL of 2 mol l⁻¹ HNO_3 . This solution was used for determination of trace elements by ICP-AES. An identical procedure was followed for the preparation of the blank samples that were prepared at the same time as the aqueous phase of the minerals.

RESULTS AND DISCUSSION

The major problem in ICP-AES is very strong spectral interferences from matrix elements (arsenic in the case of the investigated minerals) [21-24]. These facts pointed out to the necessity of trace elements separation from the matrix before the determination by ICP-AES. After dissolution of the mineral samples, the method of arsenic separation by simple and rapid liquid-liquid extraction of iodide complexes of arsenic by toluene was applied, which effectively eliminates potential interference of arsenic. Similar method was applied in trace elements separation in arsenic minerals and their determination by NAA [7]. This method was modified by changing of some of the important parameters (digestion of minerals, optimal mass of As, number and times of extractions etc.). To check whether trace elements were extracted together with the matrix element, the procedure with model solutions of arsenic oxide into HCl with equal concentration of examined elements was undertaken.

Also it was found that arsenic tends to decrease the ratios between the intensity of element in the presence of large amounts of arsenic and the

intensity of the element in the absence of arsenic (I/I_0) for most of the investigated trace elements (Figs. 1 and 2). Due to the increasing the mass of arsenic, I/I_0 of Ag, Al, Ba, Ca, Mg, Na, P and Zn

decreases below 60%, for Cd, Cu, Mn and V the ratio I/I_0 decreases to about 80% and I/I_0 of Cr, Fe, Li, Ni, Pb and Sr remains between 90 and 100%. (Figs. 1 and 2)

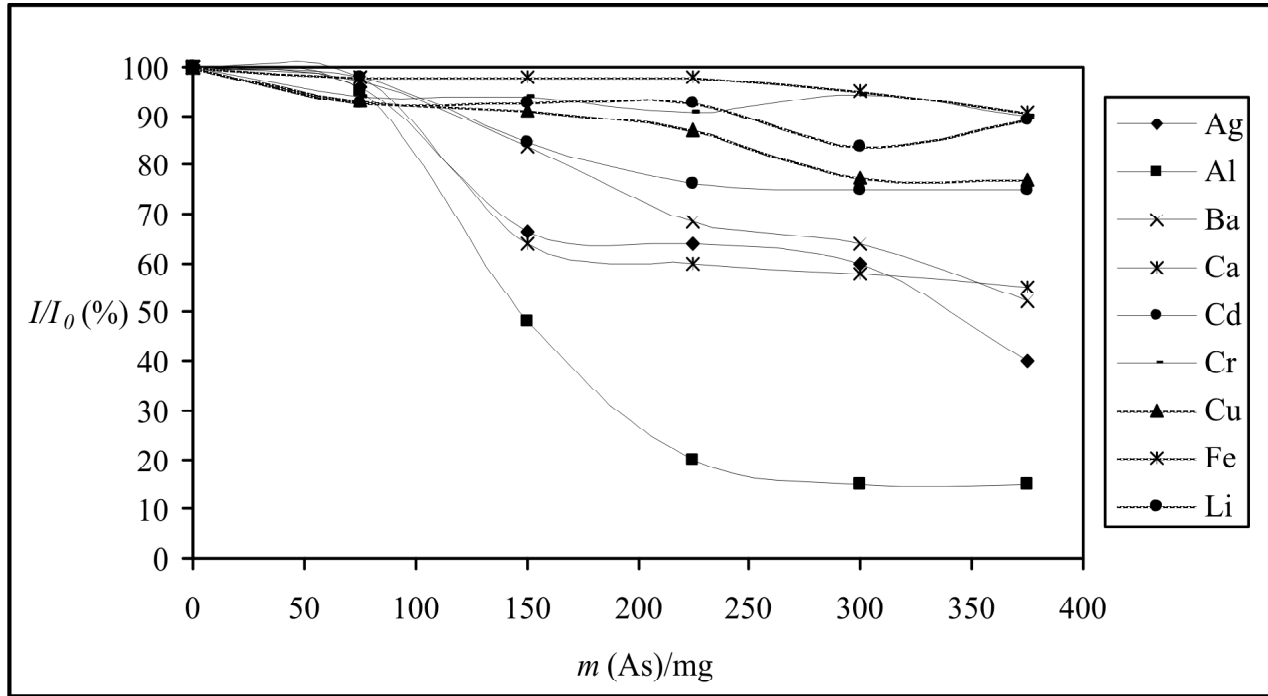


Figure 1: Matrix interferences on I/I_0 of Ag, Al, Ba, Ca, Cd, Cr, Cu, Fe and Li

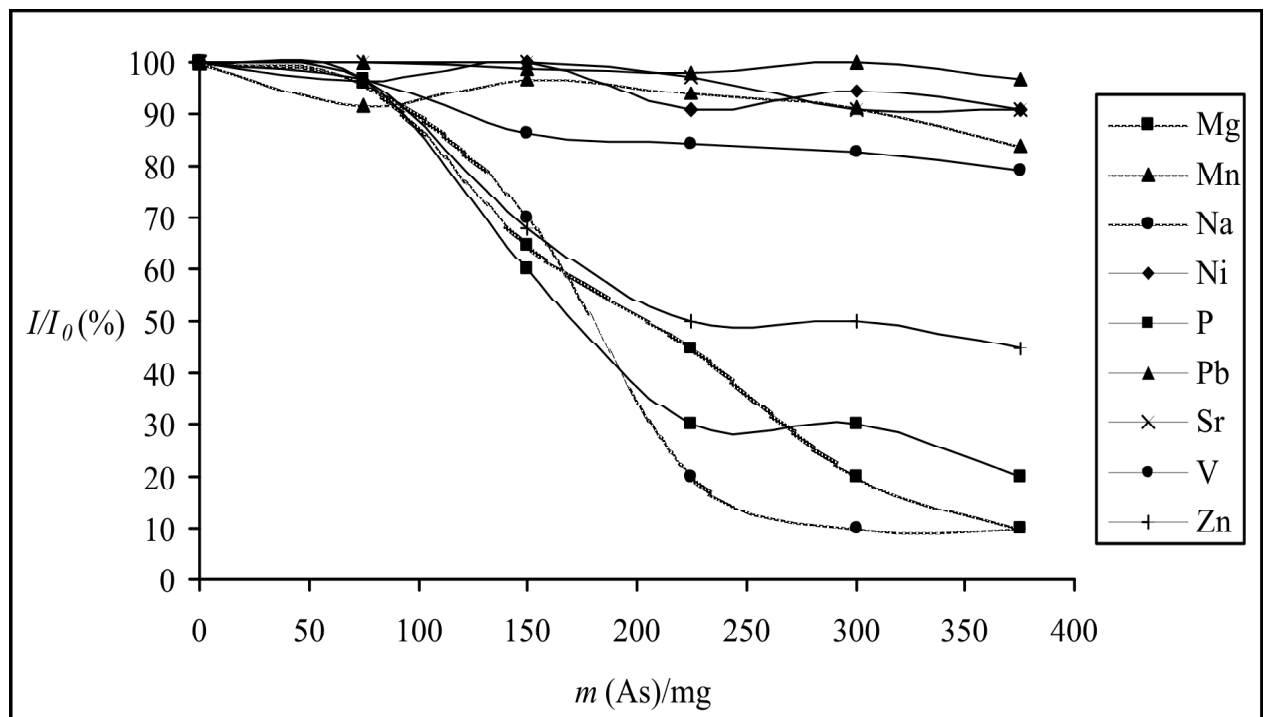


Figure 2: Matrix interferences on I/I_0 of Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn

The extraction method was additionally optimized. Operating parameters such as the amount of As present and number and time of extractions were determined (Fig. 3). As can be seen that the quantitative extraction (coefficient of distribution, K_D) of arsenic was achieved over

99 % when the mass of arsenic is 75 mg and four-step extraction of iodide complex into toluene was optimal in this procedure. The proposed method enables measurement of 18 elements (Ag, Al, Ba, Ca, Cd, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) in the studied samples.

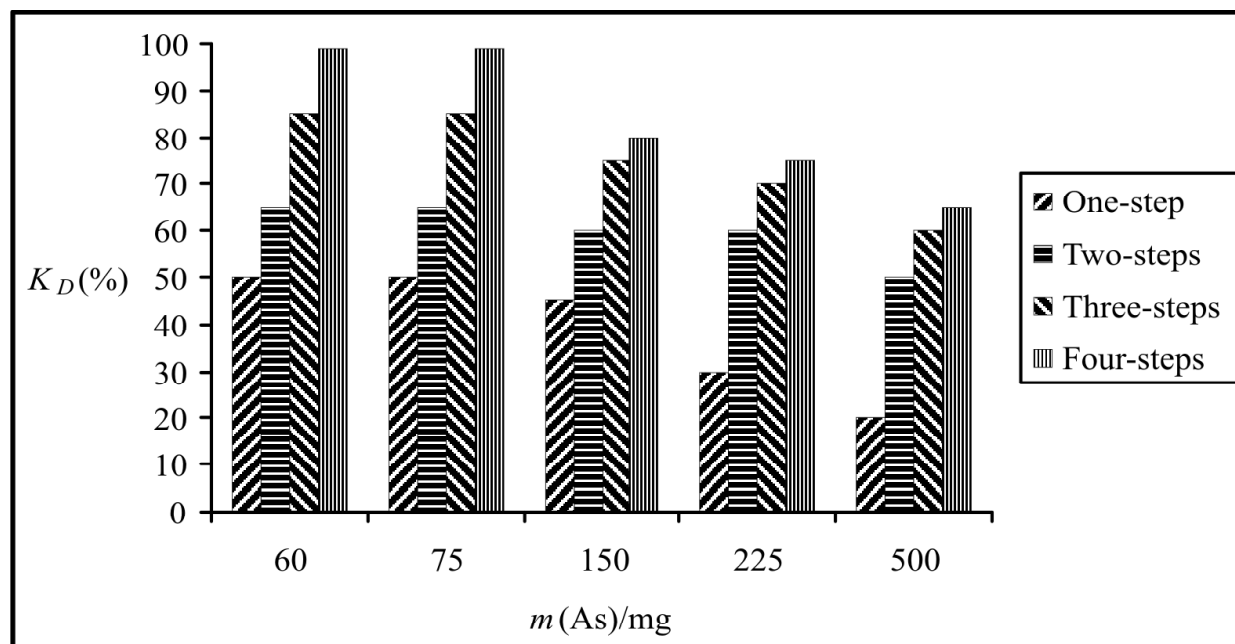


Figure 3: Influence of number of extraction on the distribution coefficient, K_D

The method was verified by the method of standard additions for the investigated elements and minerals. An exact amount of standard solutions with a known concentration of investigated elements was added to mineral samples. The results of the calculated and the obtained results as well as the recoveries of the investigated elements are presented in Tables 1 and 2 for realgar and orpiment, respectively.

The proposed method enables measurement of 18 elements (Ag, Al, Ba, Ca, Cd, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) in the studied samples.

The obtained results for trace elements by ICP-AES in both, realgar and orpiment, from Allchar mine from Crven Dol locality, shown that the iron content is much higher in comparison with other elements. It is initiated by the presence of large amount of iron mineral pyrite, the most common of the sulfide minerals and the high value of iron in minerals is due to the possible contamination from it [3, 26]. Also, it can be seen from the obtained results that both, realgar and orpiment

are rich with magnesium and calcium due to the vast deposits of dolomite [carbonate mineral composed of calcium magnesium carbonate, $CaMg(CO_3)_2$] in Allchar mine [3].

It can be seen from the results presented in Table 1 that the contents of Ag, Cr, Li and Sr are very low in realgar with average values of 1.38; 0.13; 0.36; 1.07 $\mu g g^{-1}$, respectively. Slightly higher results were obtain for Ba (2.47 $\mu g g^{-1}$), Cd (3.99 $\mu g g^{-1}$), Cu (3.90 $\mu g g^{-1}$), Ni (5.43 $\mu g g^{-1}$), Pb (4.24 $\mu g g^{-1}$) and V (3.04 $\mu g g^{-1}$) and Al, Mn, Na, P and Zn ranging between 101 $\mu g g^{-1}$ (for Al) and 593 $\mu g g^{-1}$ (for Mn).

In Table 2 it can be seen that the content of Cd is under the limit of detection in orpiment and it is lower than 0.01 $\mu g g^{-1}$. Also the obtain results for Cr, Li and Sr trace elements are very low and they are range between 0.88 $\mu g g^{-1}$ (for Li) and 1.50 $\mu g g^{-1}$ (for Sr). Slightly higher results were obtain for Ag, Ba, Cu, Ni, Pb and V and they are equal to 2.50; 2.67; 6.56; 2.50; 4.35 and 2.06 $\mu g g^{-1}$ respectively. Al, Mn, Na, P and Zn are range between 22.3 $\mu g g^{-1}$ (for Mn) and 289 $\mu g g^{-1}$ (for Na).

Table 1
The Content of Trace Elements in Realgar from Allchar Mine

$w^{*(calc.)}/\mu\text{g g}^{-1}$	w (found)/ $\mu\text{g g}^{-1}$	$R(\%)$	$w^{*(calc.)}/\mu\text{g g}^{-1}$	w (found)/ $\mu\text{g g}^{-1}$	$R(\%)$
Ag			Mg		
-	1.38	-	-	1074	-
10.12	10.05	99.3	1083	1069	98.7
18.18	18.08	99.4	1091	1063	97.4
Al			Mn		
-	101	-	-	593	-
109	119	109	602	567	94.3
118	119	101	610	565	92.6
Ba			Na		
-	2.47	-	-	272	-
10.82	10.34	95.6	280	263	93.7
19.15	17.80	93.0	289	320	110
Ca			Ni		
-	2917	-	-	5.43	-
2925	2957	101	14.17	14.30	101
2934	3007	103	22.24	22.01	98.9
Cd			P		
-	3.99	-	-	280	-
12.73	12.34	96.9	289	288	99.9
20.80	19.22	92.4	297	312	105
Cr			Pb		
-	0.13	-	-	4,24	-
8.87	8.33	93.9	12,59	12,54	99.6
16.81	15.18	90.3	20,92	20,47	97.8
Cu			Sr		
-	3.90	-	-	1.07	-
12.25	12.12	98.9	9.42	9.10	96.6
20.58	19.98	97.1	17.75	17.02	95.9
Fe			V		
-	57481	-	-	3.04	-
57489	57007	99.2	11.39	11.00	96.6
57497	57269	99.6	19.85	18.28	92.1
Li			Zn		
-	0.36	-	-	151	-
8.71	7.99	91.7	159	159	99.7
17.04	15.73	92.3	168	164	97.9

*Calculated content of Ag, Al, Cd, Cr, Mn, Ni, P and Zn that corresponds to the first standard addition of $8.74 \mu\text{g g}^{-1}$, calculated content of Ag, Ca, Cd, Cr, Fe, Mg, Ni, V and Zn that corresponds to the second standard addition of $16.81 \mu\text{g g}^{-1}$, calculated content of Ba, Ca, Cu, Fe, Li, Mg, Na, Pb, Sr and V that corresponds to the first standard addition of $8.35 \mu\text{g g}^{-1}$, calculated content of Al, Ba, Cu, Li, Mn, Na, P, Pb and Sr that corresponds to the second standard addition of $16.68 \mu\text{g g}^{-1}$

Table 2
The Content of Trace Elements in Orpiment from Allehar Mine

$w^{*(calc.)}/\mu\text{g g}^{-1}$	w (found)/ $\mu\text{g g}^{-1}$	$R(\%)$	$w^{*(calc.)}/\mu\text{g g}^{-1}$	w (found)/ $\mu\text{g g}^{-1}$	$R(\%)$
Ag			Mg		
-	2.50	-	-	4932	-
11.54	10.42	90.27	4941	5426	110
21.60	21.95	101.6	4951	5204	105
Al			Mn		
-	154	-	-	22.3	-
163	178	109.1	31.4	34.3	109
172	165	96.00	40.4	40.9	101
Ba			Na		
-	2.67	-	-	289	-
11.65	10.90	93.61	298	281	94.43
21.77	20.90	95.99	308	341	111
Ca			Ni		
-	8295	-	-	2.50	-
8304	7948	95.71	11.47	11.10	96.74
8314	9090	109.3	21.60	20.21	93.57
Cd			P		
-	<0.01	-	-	41.16	-
8.98	8.20	91.35	50.14	52.32	104
19.10	18.11	94.81	60.26	57.56	95.51
Cr			Pb		
-	0.93	-	-	4.35	-
9.91	9.09	91.75	13.39	14.35	107
20.03	18.23	90.99	23.45	25.10	107
Cu			Sr		
-	6.56	-	-	1.50	-
15.54	16.52	106.3	10.48	10.01	95.55
25.67	23.72	92.42	20.60	19.11	92.76
Fe			V		
-	745	-	-	2.06	-
754	799	106	11.03	9.99	90.54
763	824	108	21.16	19.32	91.31
Li			Zn		
-	0.88	-	-	77.17	-
9.86	8.99	91.17	86.21	80.3	93.15
19.99	18.11	90.61	96.27	99.12	103

*Calculated content of Ag, Al, Ca, Mg, Mn, Na, Pb and Zn corresponds to the first standard addition of $9.04 \mu\text{g g}^{-1}$, calculated content of Ag, Ba, Ca, Cd, Cr, Cu, Li, Mg, Na, Ni, P, Pb, Sr, V and Zn corresponds to the second standard addition of $19.10 \mu\text{g g}^{-1}$, calculated content of Ba, Cd, Cr, Cu, Fe, Li, Ni, P, Sr and V corresponds to the first standard addition of $8.98 \mu\text{g g}^{-1}$, calculated content of Al, Fe and Mn corresponds to the second standard addition of $18.07 \mu\text{g g}^{-1}$

In addition, to express how much variation or dispersion exists from the average (mean), standard deviation (σ) of 10 measurements were performed (Table 3). A relatively low standard deviation indicates that the obtained results tend to be very close to the mean.

Table 3
Average of Content of Trace Elements (in $\mu\text{g g}^{-1}$) in Realgar and Orpiment and Standard Deviation (σ) of 10 measurements

Element	<i>Realgar</i>	<i>Orpiment</i>
	Average $\pm \sigma$	Average $\pm \sigma$
Ag	1.38 \pm 0.11	2.50 \pm 0.18
Al	101 \pm 7.07	154 \pm 10.8
Ba	2.47 \pm 0.17	2.67 \pm 0.19
Ca	2917 \pm 224	8295 \pm 565
Cd	3.99 \pm 0.28	<0.01
Cr	0.13 \pm 0.01	0.93 \pm 0.01
Cu	3.90 \pm 0.29	6.56 \pm 0.46
Fe	57481 \pm 4004	745 \pm 52
Li	0.36 \pm 0.02	0.88 \pm 0.02
Mg	1074 \pm 74.2	4932 \pm 323
Mn	593 \pm 40.9	22.3 \pm 1.54
Na	272 \pm 20.4	289 \pm 21.2
Ni	5.43 \pm 0.80	2.50 \pm 0.19
P	280 \pm 22.1	41.16 \pm 3.01
Pb	4.24 \pm 0.65	4.35 \pm 0.68
Sr	1.07 \pm 0.10	1.50 \pm 0.11
V	3.04 \pm 0.21	2.06 \pm 0.19
Zn	151 \pm 10.5	77.17 \pm 5.53

It is important to point out that after the matrix removal, several elements could be analysed due to the elimination of the interferences arising from the matrix element. As additional advantage of the proposed method it should be mentioned that for

the first time the content of Ag, Al, Li, Mg, Mn, Na, P and V in both, realgar and orpiment, was determined by ICP-AES.

The values obtained for the content of trace elements using different techniques as neutron activation analysis [3, 6, 7, 17], mass spectrometry [3, 19, 27] and atomic absorption spectrometry [1, 4, 5, 12-14, 16, 28] are compared in Table 4. It can be seen that the obtained values for the analyzed elements in this work are within the previously obtained contents by another techniques. Differences in the content of some elements are due to inhomogeneity of the mineral samples and the variety of methods used with different limits of detection.

CONCLUSION

It was shown that some trace elements could be determined by atomic emission spectrometry with inductively coupled plasma in different arsenic minerals. The studied minerals realgar (As_4S_4) and orpiment (As_2S_3) were originating from Allchar mine, Crven Dol locality, Republic of Macedonia. To avoid the interference of arsenic as matrix element, a liquid-liquid extraction of its iodide complex into toluene in hydrochloric solution was applied. The extraction method was optimized. It was confirmed that toluene is selective for arsenic. The proposed method enables measurement of 18 elements (Ag, Al, Ba, Ca, Cd, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) in the studied samples. The proposed procedure was verified by the method of standard additions and by its applications to the minerals.

Table 4
The Content of Some Trace Elements in Realgar and Orpiment from Allchar Mine Obtained by Different Methods (given in $\mu\text{g g}^{-1}$)

<i>Element</i>	<i>Realgar</i>	<i>Orpiment</i>
Ba	<20; Jacimovic et al., INAA [6] 16.8; Stafilov et al., INAA [7] 2.47; This work, ICP-AES	<20; Jacimovic et al., INAA [6] 2.67; This work, ICP-AES
Cd	<100; Jacimovic et al., INAA [6] 1.54; Angelov&Stafilov, AAS [29] 3.99; This work, ICP-AES	<100; Jacimovic et al., INAA [6] 0.45; Angelov & Stafilov, AAS [29] <0.01; This work, ICP-AES
Cr	<20; Palme et al., INAA [17] 69.8; Frantz et al., INAA [3] 2.64 \pm 0.14; Jacimovic et al., INAA [6] <1; Lazaru&Stafilov, AAS [4] 1.60; Angelov&Stafilov, AAS [29] 1.77; Stafilov et al., AAS [7] 2.48; Stafilov et al., INAA[7] 0.13; This work, ICP-AES	<100; Palme et al., INAA [17] <1-32.6; Lazaru&Stafilov, AAS [4] 0.42 \pm 0.04; Lazaru&Stafilov, AAS [16] 1.19; Angelov&Stafilov, AAS [29] 1.43; Stafilov et al., AAS [7] 2.0; Stafilov et al., INAA[7] 0.93; This work, ICP-AES

Element	Realgar	Orpiment
Cu	<300; Palme et al., INAA [17] <2; Boev et al., MS [27] <1; Lazaru&Stafilov, AAS [4] 0.46; Lazaru&Stafilov, AAS [5] 0.31; Stafilov et al., AAS [7] 3.90; This work, ICP-AES	<1200; Palme et al., INAA [17] <4; Boev et al., MS [27] <1-4.7; Lazaru & Stafilov, AAS [4] 0.55; Lazaru & Stafilov, AAS [5] 0.82; Stafilov et al., AAS[7] 6.56; This work, ICP-AES
Fe	<20; Palme et al., INAA [17] 57500±2300; Jacimovic et al., INAA [6] 365-1410; Lazaru & Stafilov, AAS [4] 14058; Angelov & Stafilov, AAS [29] 13838.3; Stafilov et al., AAS[7] 42580; Stafilov et al., INAA [7] 57481; This work, ICP-AES	<200; Palme et al., INAA [17] 169±12; Jacimovic et al., INAA [6] <800; Boev et al., MS [27] 96-620; Lazaru & Stafilov, AAS [4] 226.7; Angelov & Stafilov, AAS [29] 226.0; Stafilov et al., AAS [7] 51.8; Stafilov et al., INAA [7] 745; This work, ICP-AES
Mn	<4; Frantz et al., INAA [3] <90; Boev et al., MS [27] 70.4-955; Lazaru & Stafilov, AAS [4] 1780; Angelov & Stafilov, AAS[29] 226; Stafilov et al., AAS [7] 593; This work, ICP-AES	100; Palme et al., INAA [17] <8; Frantz et al., INAA [3] 5.0-28.3; Lazaru & Stafilov, AAS [4] 31.8; Angelov & Stafilov, AAS [29] <20; Boev et al., MS [27] 38.7; Stafilov et al., AAS [7] 22.3; This work, ICP-AES
Ni	<1-41.0; Lazaru & Stafilov, AAS [4] 0.75-1.76; Lazaru & Stafilov, AAS [16] 1.30; Angelov & Stafilov, AAS [29] <10; Palme et al., INAA [17] 1.47; Stafilov et al., AAS [7] 5.43; This work, ICP-AES	<1-7.4; Lazaru & Stafilov, AAS [4] 1.29-4.86; Lazaru & Stafilov, AAS [16] 0.73; Angelov & Stafilov, AAS [29] <30; Palme et al., INAA [17] 1.0; Stafilov et al., AAS [7] 2.50; This work, ICP-AES
Pb	0.01-2.02; Frantz et al., INAA [3] 1.1-5; Ljubicic et al., INAA [30] 0.38; Todt, MS [19] 0.8; Boev et al., MS [27] 4.8; Stafilov, AAS [12] 0.29-3.16; Lazaru&Stafilov, AAS [16] 1.14; Angelov&Stafilov, AAS [29] 1.87; Stafilov et al., AAS [7] 4.24; This work, ICP-AES	0.07-11.6; Frantz et al., INAA [3] 11.6; Todt, MS [19] <2; Boev et al., MS [27] 5.3-9.4; Stafilov, AAS [12] 1.65-3.73; Lazaru & Stafilov, AAS [16] 0.21; Angelov & Stafilov, AAS [29] 0.37; Stafilov et al., AAS [7] 4.35; This work, ICP-AES
Zn	<30; Frantz et al., INAA [3] 66.5±2.7, Jacimovic et al., INAA[6] 92.5; Angelov&Stafilov, AAS [29] 95.0; Stafilov et al., AAS [7] 55.1; Stafilov et al., INAA [7] 151; This work, ICP-AES	<0.7; Jacimovic et al., INAA [6] 54.9; Angelov & Stafilov, AAS [29] 2.8 Palme et al., INAA [17] 62.2; Stafilov et al., AAS [7] <20; Stafilov et al., INAA [7] 77.17;This work, ICP-AES

References

- [1] Stafilov T, Determination of trace elements in minerals by electrothermal atomic absorption spectrometry, *Spectrochim. Acta Part B*, 55, **2000**, 893–906.
- [2] Rieck B, Allchar, Macedonia, Mineral. Record., 24 **1993**, 437–448.
- [3] Frantz E, Palme H, Todt W, El Goresy A and Pavlaevia MK, Geochemistry of Tl-As minerals and basement rocks at Allchar, Republic Macedonia, *N. Jb. Miner. Abh.*, 167, **1994**, 359-399.
- [4] Lazaru A and Stafilov T, Determination of Fe, Mn, Cu, Cr and Ni in sulfide minerals from Alshar by atomic absorption spectrometry, *Geologica Macedonica*, 7, **1993**, 73–80.
- [5] Lazaru A and Stafilov T, Determination of copper in sulfide minerals by Zeeman electrothermal atomic absorption spectrometry, *Fresenius' J. Anal. Chem.*, 360, **1998**, 726–728.
- [6] Jačimoviæ R, Lazaru A, Mihajlović D, Ilić R and Stafilov T, Determination of major and trace elements in some minerals by k0-instrumental neutron activation analysis, *J. Radioanal. Nucl. Chem.*, 253, **2002**, 427–434.
- [7] Stafilov T, Angelov N, Jačimović R and Stibilj V, Determination of trace elements in arsenic and antimony minerals by atomic absorption spectrometry and k0-instrumental neutron activation analysis after As and Sb removal, *Microchim. Acta*, 149, **2005**, 229–237.
- [8] Pavičević MK, The “LOREX”-Project, solar neutrino detection with the mineral lorandite. *N. Jb. Miner. Abh.*, 167, **1994**, 205.

- [9] Stafilov T and Todorovski T, Determination of gold in arsenic-antimony ore by flameless atomic absorption spectrometry, *At. Spectrosc.*, 8, **1987**, 12–14.
- [10] Stafilov T and Todorovski T, Determination of molybdenum in arsenic-antimony ore by flameless atomic absorption spectrometry, *At. Spectrosc.*, 11, **1990**, 202–204.
- [11] Stafilov T, Todorovski T, Grozdanova B and Spandzeva Lj, Determination of thallium in ore from Allchar by atomic absorption spectrometry, *Nucl. Instr. Meth. Phys. Res.*, A271, **1988**, 321-323.
- [12] Stafilov T, Jordanovska V and Aleksovska S, Determination of lead in arsenic minerals from Alshar by atomic absorption spectrometry, *Bull. Chem. Technol. Macedonia*, 9, **1990**, 159–166.
- [13] Stafilov T, Lazaru A and Pernicka E, Determination of thallium in sulfide minerals by Zeeman electrothermal atomic absorption spectrometry, *Acta Chim. Slov.*, 40, **1993**, 37–46.
- [14] Stafilov T, Aleksovska S and Jordanovska V, Determination of lead in lorandite and marcasite from Allchar by electrothermal atomic absorption spectrometry, *N. Jb. Miner. Abh.*, 167, **1994**, 401–408.
- [15] Stafilov T, Lazaru A and Pernicka E, Determination of silver in sulfide minerals by electrothermal atomic absorption spectrometry, *At. Spectrosc.*, 16, **1995**, 158–161.
- [16] Lazaru A and Stafilov T, Determination of Co, Ni and Pb in arsenic minerals by Zeeman electrothermal atomic absorption spectrometry, *Bull. Chem. Technol. Macedonia*, 19, **2000**, 21–26.
- [17] Palme H, Pavićević MK and Spettel B, Major and trace elements in some minerals and ore from Crven Dol, Allchar, *Nucl. Instr. Meth. Phys. Res.*, A271, **1988**, 314–319.
- [18] Mihajlović D and Stafilov T, Determination of thallium in geological samples by X-Ray fluorescence spectrometry. *X-Ray Spectrometry* 27, **1998**, 397-400.
- [19] Todt W, Isotope dilution measurements of Pb, U and Th concentration in lorandite from Allchar. *Nucl. Instr. Meth. Phys. Res.*, A271, **1988**, 251.
- [20] Lazaru A, Ilic R, Skvarc J, Kristof ES and Stafilov T, Neutron induced autoradiography of some minerals from Allchar mines. *Radiat. Meas.*, 31, **1999**, 677-682.
- [21] Pickford CJ and Brown RM, Comparison of ICP-MS with ICP-ES: detection power and interference effects experienced with complex matrices, *Spectrochim. Acta Part B*, 41, **1986**, 183–187.
- [22] Lambkin DC and Alloway BJ, The problem of arsenic interference in the analysis of soils for cadmium by inductively coupled plasma-optical emission spectrometry, *Sci. Total Environ.*, 256, **2000**, 77-81.
- [23] Chan GCY, Fundamental mechanisms and diagnostic tools for interference effects in inductively coupled plasma – atomic emission spectrometry, Bloomington, Indiana University, Indiana, 2007.
- [24] Waterlot C and Douay F, The problem of arsenic interference in the analysis of Cd to evaluate its extractability in soils contaminated by arsenic, *Talanta*, 80, **2009**, 716-722.
- [25] Balabanova B, Stafilov T, Baèeva K and Šajin R, Biomonitoring of atmospheric pollution with heavy metals in the copper mine vicinity located near Radoviš, Republic of Macedonia, *J. Environ. Sci. Health, Part A*, 12, **2010**, 1504-1518.
- [26] Zendelovska D and Stafilov T, Extraction separation and electrothermal atomic absorption spectrometric determination of thallium in some sulfide minerals, *Anal. Sci.*, 17, **2001**, 425–428.
- [27] Boev B, Serafimovski T and Milosavljevic B, Trace elements in some minerals from Alshar Deposit, *Geologica Macedonica*, 7, **1993**, 41-43.
- [28] Stafilov T, Jordanovska V and Aleksovska S, Matrix interferences in the determination of lead in As-Sb-Tl ores by electrothermal atomic absorption spectrometry, *Bull. Chem. Technol. Macedonia*, 8, **1990**, 93–98.
- [29] Angelov N and Stafilov T, Determination of trace elements in arsenic minerals by atomic absorption spectrometry with previous matrix modification, *Geologica Macedonica*, 17, **2003**, 73–82.
- [30] Ljubicic A, Krcmar M, Kaucic S and Logan B. A., Experimental determination of uranium and thorium in Allchar ore, *Nucl. Instr. Meth. Phys. Res.*, A271 **1988**, 262-263.

