

GEOME 2

Manuscript received: December 15, 2002

Accepted: March 20, 2003

Geologica Macedonica, Vol. 17, p. 73–82 (2003)

ISSN 0352 – 1206

UDC: 553.497 : 543.422

Original scientific paper

DETERMINATION OF TRACE ELEMENTS IN ARSENIC AND ANTIMONY MINERALS BY ATOMIC ABSORPTION SPECTROMETRY WITH PREVIOUS MATRIX MODIFICATION

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Abstract: The application of direct electrothermal atomic absorption spectrometry (ETAAS) in the analysis of arsenic (realgar and orpiment) and antimony (stibnite) minerals is limited due to strong matrix interferences on the atomization of trace analytes. Therefore the trace elements determination is possible only after matrix separation. Methods based on matrix separation by reduction or precipitation of arsenic and antimony as a matrix element is suggested. In the present paper, matrix separation by precipitation is studied in order to propose optimal methods for the determination of Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb and Zn in realgar, orpiment and stibnite. The removing of arsenic and antimony can be successfully performed by its reduction with sodium tetrahydridoborate(III) (NaBH_4) in the presence of HCl or HNO_3 . The conditions for this method (mass of NaBH_4 , concentration of acids, temperature) were optimized. During this procedure investigate elements are not reduced and can be determined from the solution by ETAAS or by flame atomic absorption spectrometry (for Fe, Mn and Zn). Applying this method, the investigated elements were determined in realgar, orpiment and stibnite minerals from Allchar mine, Macedonia.

Key words: Trace elements; realgar; orpiment; stibnite; determination; atomic absorption spectrometry

INTRODUCTION

The most occurred minerals in Allchar location, Republic of Macedonia, are arsenic minerals realgar (As_4S_4) and orpiment (As_2S_3) and antimony mineral stibnite (Sb_2S_3). It is very important to follow the content of lead in these minerals because of using them as monitors for determining the contribution of background reactions, which originate from natural radioactivity, on condition that they are genetically formed at the same period as the lorandite (Freedman *et al.*, 1976). The examinations on the other element contents will help for obtaining important knowledge for geochemistry on the mine and explanation on the background radiation of the location (Palme *et al.*, 1988). This is very important in the investigation in the LOREX Project which used the mineral lorandite (TlAsS_2) present in this deposit, as solar neutrino detector measuring the content of ^{205}Pb isotope produced by the nuclear reaction between solar neutrino and ^{205}Tl accumulated in lorandite (Freedman *et al.*, 1976, Pavićević, 1994).

Atomic absorption spectrometry (AAS) is one of the most used technique for trace elements de-

termination in geological samples (Stafilov, 2000). However, the application of flame (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) in trace elements analysis of minerals is limited because of matrix interferences, especially because of high content of main constituent elements in the minerals. Therefore, determination of trace elements is easier after their separation from the matrix. There are a number of paper concerning of trace elements determinations in geological samples by ETAAS (Stafilov, 2002). In some of presented papers (Sedykh *et al.*, 1980a; Sedykh *et al.*, 1980b; Tominaga and Umezaki, 1982; Zelentsova and Yudelevich, 1983; Kuroda *et al.*, 1986; Stafilov *et al.*, 1990a; Lazaru and Stafilov, 1993, 1994, 2000) direct determination was suggested. In our previous investigations we have showed that in ETAAS determinations arsenic (Stafilov *et al.*, 1990a, 1990c; Lazaru and Stafilov, 1993, 1994, 2000) and antimony (Stafilov *et al.*, 1990c) decrease the absorbance of some of the investigated elements. Similar results were obtained by Zelentsova and Yudelevich (1983).

To overcome interferences, it was suggested on addition of different matrix modifier (Komarek *et al.*; 1980; Kuroda *et al.*, 1986). In the case of arsenic matrices, different methods for trace elements separation were applied: extraction (Stafilov and Todorovski, 1987, 1988, 1990; Stafilov *et al.*, 1994; Lazaru and Stafilov, 2000), precipitation (Stafilov *et al.*, 1990c) or evaporation of arsenic in the form of sesquioxide (Shelpakova, 1991). Continuing our work on trace elements determination in arsenic and antimony minerals (Stafilov and Todorovski, 1987, 1990; Lazaru and Stafilov, 1993, 1994, 1998, 2000; Stafilov *et al.*, 1988, 1990a, 1990b, 1990c, 1993, 1994, 1995, Lazaru *et al.*, 1999, 2002; Zendelovska and Stafilov, 2001), in

this paper the method of separation of different trace elements (Cd, Co, Cu, Cr, Pb, Ni, Fe, Mn and Zn) from arsenic (realgar, As_4S_4 and orpiment, As_2S_3) and antimony (stibnite, Sb_2S_3) minerals is suggested. The elimination of arsenic and antimony from the matrix solution is performed by their reduction by sodium tetrahydridoborate(III) ($NaBH_4$) in the presence of HCl or HNO_3 to elementary form and elimination as a precipitate. Investigated elements don't precipitate and stay in the solution and can be analyze applying FAAS or ETAAS. Optimization of important parameters which influence on this process (mass of $NaBH_4$, concentration of acids, temperature) were determined.

EXPERIMENTAL

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 FAAS and ETAAS determination are given in Tables 1 and 2.

Table 1

Instrumental parameters for determination by FAAS

Parameter	As	Sb	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Wavelength, nm	193.7	217.6	228.8	240.7	357.5	324.8	248.3	279.5	232.0	283.3	213.9
Spectral slit, nm	0.5	0.2	0.3	0.2	0.7	0.7	0.2	0.7	0.2	0.7	0.7
Lamp current, mA	10	10	20	30	25	15	30	20	4	10	15
Gas mixture	Acetylene/air										

Table 2

Instrumental parameters for trace elements determination by ETAAS

Parameter	Co	Cd	Ni	Cu	Cr	Pb
Wavelength, nm	242.5	228.8	232.0	327.4	357.9	283.3
Spectral slit, nm	0.2	0.5	0.2	0.5	0.2	0.5
Lamp current, mA	7.0	4.0	4.0	4.0	7.0	5.0
Calibration mode	Absorbance, peak height					
Background correction	Zeeman					
DRY						
Temperature, °C	120	120	120	120	120	120
Ramp time, s	45	45	45	45	45	45
Hold time, s	10	10	10	10	10	10
PYROLYSIS						
Temperature, °C	750	250	800	800	1000	400
Ramp time, s	5	5	5	5	5	5
Hold time, s	3	3	3	3	3	3
ATOMIZATION						
Temperature, °C	2300	1800	2400	2300	2600	2100
Ramp time, s	1	1	1	1	1	1
Hold time, s	2	2	2	2	2	2
CLAENING						
Temperature, °C	2400	1900	2500	2400	2600	2100
Ramp time, s	1	1	1	1	1	1
Hold time, s	2	2	2	2	2	2
Gas	Argon					

Reagents and samples

All reagents and standards were of analytical grade. Stock solutions of all investigated elements were prepared by dissolving of high-purity salts or metals. The mass concentrations of elements in these solutions were $1000 \text{ mg}\cdot\text{l}^{-1}$, from which all diluted solutions, were prepared. The solution of sodium tetrahydridoborate(III) was prepared by dissolving 1.25 g NaBH_4 in volumetric flask of 25 ml in the mixture of 3 ml 25 % NH_4OH and 10–15 ml redistilled water. After dissolution 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 (Janković, 1988; Boev *et al.*, 1993a). Mineral specimens were carefully selected from ore samples using microscope, and then grinded to powder.

Procedures

Realgar and orpiment. In the glass beaker of 100 ml, 0.1 g of powdered samples of realgar or orpiment were 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 2 ml concentrated HCl with a minimum of boiling and 13 ml of redistilled water were added. The reduction of As was performed by adding of 1.8 ml (slowly by dropping) of sodium tetrahydridoborate (NaBH_4) solution (1.26 mg of NaBH_4 for 1 mg As(V)) and HCl so the solution have concentration of $1 \text{ mol}\cdot\text{l}^{-1}$ HCl . The precipitate of elemental form of arsenic was filtered and the solution was transferred into a volumetric flask of 25 ml. From this solution determination of investigated trace element was performed. Iron, manganese and zinc were analyzed by flame atomic absorption spectrometry (FAAS) and the other elements by ETAAS.

Stibnite. In the glass beaker of 100 ml, 0.1 g of powdered sample was dissolved in 10 cm^3 of conc. HCl , 1 cm^3 of conc. HNO_3 and 1 cm^3 of H_2O_2 . The solution was evaporated almost to dryness and the residue was then dissolved in 2 cm^3 concentrated HCl with a minimum of boiling and 13 ml of redistilled water were added. The following procedure is the same as for realgar and orpiment.

RESULTS AND DISCUSSION

Investigation of arsenic and antimony interferences on trace elements absorbance

As it was mentioned in the Introduction, the major problem, which must be confronted in AAS, mostly in ETAAS, besides the choice of appropriate instrumental parameters, regards the study and control of the matrix effects. The interference of matrix element of the mineral studied (As and Sb) on the Fe, Mn, and Zn determination by FAAS and on the Cd, Co, Cr, Cu, Ni, Pb determination by ETAAS, was investigated. Series of solutions with the same concentration of these elements and different concentration of interfering elements were prepared so that the concentrations of these elements were similar to the concentrations in the sample solutions. Results show that the interfering element tends to decrease the absorbance of investigated elements in ETAAS measurements (Figs. 1 and 2). As it can be seen, during direct determination of investigated trace elements arsenic and antimony decrease their absorbance. To eliminate these interferences it is necessary to separate trace

elements from arsenic and antimony matrix. In this study, elimination of As and Sb was performed by reduction in elemental state, precipitation and filtration. Reduction of As and Sb from the mineral solutions was performed by sodium tetrahydridoborate(III).

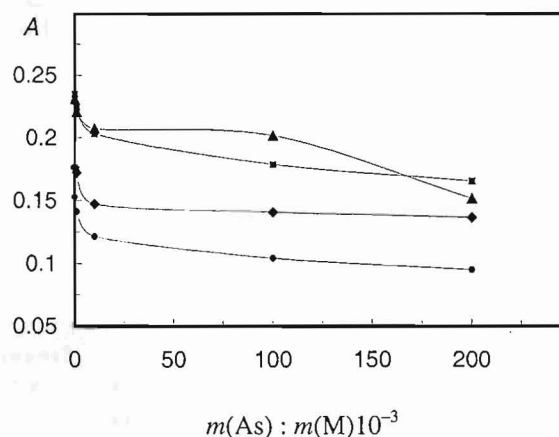


Fig. 1. Influence of arsenic on the absorbance of Co (◆), Ni (●), Pb (▲) and Cd (■) in ETAAS determination

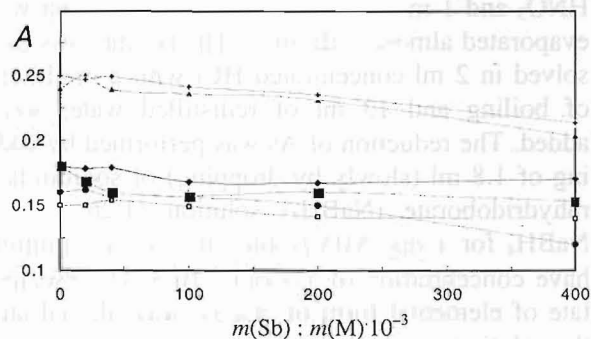
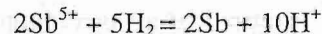
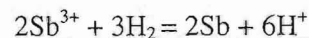
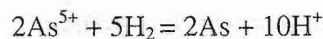
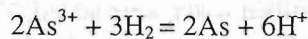
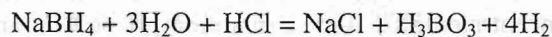


Fig. 2. Influence of antimony on the absorbance of Cd (+), Co (◆), Cr (●), Cu (■), Ni (□), Pb (▲) in ETAAS determination

Optimization of the condition for arsenic and antimony reduction and elimination by sodium tetrahydridoborate(III)

In this work the elimination of arsenic and antimony was performed by their precipitation into elemental As and Sb using NaBH_4 :



As it can be seen from the reactions, the reduction of As and Sb has two phases: obtaining of hydrogen and the reduction of As and Sb from three or five-oxidant state into elemental As or Sb. From these reactions it can be seen also that the stoichiometric ratio of As(III) or Sb(III) and NaBH_4 is 2:3, and for As(V) or Sb(V) this ratio is 2:5. The optimal mass of NaBH_4 was established by measuring the reduction grade of As and Sb by changing the mass of NaBH_4 . Experiments were performed both for As(III) and Sb(III) and for As(V) and Sb(V) on room temperature and on temperature of water bath (about 70 °C). Mass of NaBH_4 , which was taken during these experiments, was 0.9; 1; 1.2; 1.6 and 2 times higher than calculated stoichiometric ratio. For three-oxidant state forms nitric acid was taken and for five valent form hydrochloric acid. The obtained recoveries for As, Sb and the investigated elements are given in Tables 3 and 4.

Table 3

Dependence of recovery (R, %) of As, Co, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn from mass of NaBH_4 in the presence of As

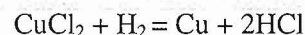
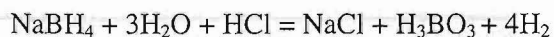
$m(\text{NaBH}_4)/m\text{NaBH}_4\text{calculated}$	As	Co	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
As(III)										
Room temperature										
0.9	35.4	98.0	98.1	100	79.5	92.9	95.60	98.0	98.0	100
1.0	19.0	98.0	96.1	100	84.6	91.7	95.60	98.1	98.0	100
1.2	6.8	100	96.1	100	93.5	91.8	95.60	100	97.7	100
1.6	1.4	96.5	95.3	95.6	92.1	87.5	92.50	98.2	95.0	96.5
2.0	1.4	89.8	91.0	81.0	89.0	85.1	89.90	93.8	94.3	89.6
Temperature of 70 °C										
0.9	36.7	96.6	95.0	100	86.1	93.6	100	100	100	100
1.0	24.5	94.3	94.5	100	85.4	92.6	98.00	100	100	100
1.2	9.5	96.0	94.5	95.5	83.0	87.5	97.21	100	100	95.5
1.6	3.7	91.0	90.1	95.5	72.9	87.5	94.15	95.0	96.1	95.5
2.0	1.4	85.4	87.7	94.7	70.0	85.1	90.12	93.8	90.2	91.1
As(V)										
Room temperature										
0.9	34.9	69.4	94.8	100	10.1	92.9	100.0	98.5	98.6	100
1.0	14.8	100.0	94.8	100	10.1	91.8	93.6	97.6	98.6	100
1.2	8.7	100.0	91.9	100	6.9	93.5	95.4	90.3	81.5	100
1.5	1.8	100.0	89.7	100	6.0	93.0	95.4	87.3	81.5	100
2.0	1.7	76.7	79.3	95.9	4.5	80.0	91.3	75.6	71.0	93.5
Temperature of 70 °C										
0.9	41.5	74.7	98.2	100	98.3	93.8	100.0	100	100	100
1.0	22.7	100.0	96.3	100	93.4	92.8	95.5	97.6	100	100
1.2	10.8	100.0	97.4	100	91.5	89.9	97.2	95.4	100	100
1.5	9.8	100.0	95.9	100	79.7	75.0	97.2	94.2	100	100
2.0	4.6	100.0	94.2	100	68.4	88.1	93.6	94.2	100	96.94

Table 4

Dependence of recovery (R, %) of Sb, Co, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn from mass of NaBH₄ in the presence of Sb

$m(\text{NaBH}_4)/m_{\text{NaBH}_4(\text{calculated})}$	Sb	Co	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Sb(III)										
Room temperature										
0.9	3.8	100	100	100	41.3	100	93.0	100	90.0	100
1.0	1.9	100	98.6	100	36.0	100	95.0	100	100	94.5
1.2	1.5	100	98.6	96.0	34.6	100	94.0	100	100	89.1
1.5	1.1	100	100	92.0	25.3	100	97.0	96.6	70.0	83.5
2.0	0.7	100	100	92.0	25.3	100	94.0	93.3	90.0	70.2
Temperature of 70 °C										
0.9	5.4	100	98.6	92.0	70.6	93.3	92.0	93.3	100	87.2
1.0	4.6	100	98.6	92.0	72.0	93.3	93.0	90.6	90.0	86.0
1.2	4.2	96.0	98.6	92.0	68.0	96.5	93.0	90.6	90.0	83.0
1.5	3.9	96.0	98.0	92.0	62.6	97.7	93.0	90.6	80.0	78.3
2.0	3.1	94.0	98.0	92.0	62.4	88.8	91.0	90.6	78.0	76.5
Sb(V)										
Room temperature										
0.9	38.0	100	100	100	92.2	89.2	97.4	100	100	100
1.0	33.9	100	96.0	100	89.7	84.6	97.4	100	100	97.0
1.2	30.0	100	100	100	82.3	97.5	97.4	100	100	97.0
1.5	27.7	100	100	95.8	60.3	90.1	98.7	97.0	100	96.0
2.0	20.3	100	94.6	95.8	60.3	84.3	98.7	97.0	100	91.0
Temperature of 70 °C										
0.9	40.0	94.1	79.0	100	86.7	87.2	97.4	97.0	95.0	94.0
1.0	37.9	94.1	83.5	100	88.2	89.6	97.4	94.0	95.0	94.0
1.2	34.7	94.1	100	100	88.2	89.7	97.4	94.0	100	92.0
1.5	29.0	88.2	98.0	97.0	86.7	77.5	93.5	87.0	100	92.0
2.0	26.3	76.5	83.3	97.0	72.5	61.5	88.3	86.0	95.0	91.0

As it can be seen from the results given in Tables 3 and 4, better results on the reduction of As and Sb are obtained on room temperature. The reduction rate for As is from 64.64 % (0.9 from stoichiometric ratio with NaBH₄) up to 98.66 % (2 times higher than stoichiometric ratio). As optimal mass of NaBH₄ for the reduction of As was taken 1,2 times higher mass than calculated. It can be also seen that except Cu, the other investigated elements don't precipitate with NaBH₄ and stay in the solution and can be directly analyzed. In the case of copper, by the increasing of mass of NaBH₄ the recovery of copper decreases because in the presence of HCl copper precipitates by NaBH₄:



Keeping mass of NaBH₄ constant and changing the concentration of acids, optimal concentrations of HCl (for As(III) and Sb(III) and Sb(V) and HNO₃ (for As(V)) were determined. The concentration range for HCl and HNO₃ for As was from 0.25 to 2.0 mol·l⁻¹, and for Sb from 1.5 to 3.5 mol·l⁻¹. The results are given in Tables 5 and 6. Experiments were performed both on room temperature and on water bath temperature. For optimal concentration for arsenic was taken 2 mol·l⁻¹ of HCl and HNO₃, and 3 mol·l⁻¹ of HCl for Sb.

Table 5

Dependence of recovery (R, %) of As, Co, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn from the concentration of HCl in the presence of As

c(HCl)/mol·l ⁻¹	As	Co	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
As(III)										
Room temperature										
0.25	43.6	42.4	22.4	35.3	30.1	20.7	26.6	16.2	40.7	100
0.5	37.2	100	82.9	100	28.5	83.1	82.7	75.6	100	100
1.0	17.5	100	92.1	100	27.5	88.3	91.1	82.1	100	100
1.5	6.2	100	97.1	100	25.4	100.0	91.9	85.4	100	100
2.0	2.8	100	94.1	100	21.8	100.0	95.3	91.0	100	44.2
Temperature of 70 °C										
0.5	43.6	49.0	20.9	40.1	48.1	21.0	26.6	15.3	42.3	100
1.0	29.9	100	82.9	100	39.7	83.1	90.8	69.1	100	100
1.2	14.3	100	91.7	100	30.6	90.3	94.5	72.8	100	96.6
1.5	13.8	100	92.7	100	27.8	100	96.1	85.4	100	98.3
2.0	13.6	100	91.7	100	24.5	100	89.1	88.8	100	98.0
As(V)										
Room temperature										
0.25	42.0	91.8	60.1	85.1	90.0	66.6	87.5	100.0	98.2	100.0
0.5	33.5	85.6	89.7	97.8	92.3	83.3	91.7	98.0	95.1	100.0
1.0	18.0	93.0	94.8	100.0	94.5	91.8	93.5	97.6	93.5	100.0
1.5	6.5	93.6	94.8	92.9	94.5	95.8	91.7	95.5	90.2	93.2
2.0	4.0	85.6	94.8	87.7	95.0	45.8	93.3	94.2	90.2	95.4
Temperature of 70 °C										
0.25	42.9	95.0	65.8	93.4	92.0	91.6	87.5	100.0	98.2	100.0
0.5	21.0	96.8	97.0	100.0	93.5	91.8	96.6	99.9	96.2	100.0
1.0	11.0	98.0	97.3	100.0	96.0	91.8	97.0	100.0	95.5	100.0
1.5	9.5	95.2	98.2	96.3	96.8	95.8	96.6	98.7	96.8	98.8
2.0	8.7	95.2	97.9	94.2	97.5	95.8	95.8	99.3	93.7	98.8

Table 6

Dependence of recovery (R, %) of Sb, Co, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn from the concentration of HCl, for Sb(III)

c(HCl)/mol·l ⁻¹	Sb	Co	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Room temperature										
1.5	2.6	100.0	100	96.0	58.6	100.0	93.0	90.0	90.0	98.6
2.0	3.5	100.0	98.6	96.0	50.6	100.0	93.0	93.5	100.0	98.6
2.5	5.4	100.0	98.0	96.0	61.3	100.0	94.0	98.6	100.0	100
3.0	5.0	100.0	97.0	96.0	64.3	100.0	93.0	96.6	90.0	99.3
3.5	6.6	100.0	96.0	92.0	68.0	100.0	91.0	96.6	90.0	95.6
Temperature of 70 °C										
1.5	5.4	100.0	98.0	84.0	76.0	100.0	92.0	96.6	90.0	87.1
2.0	5.4	100.0	98.0	84.0	78.6	100.0	92.0	96.6	100.0	86.0
2.5	6.2	100.0	98.0	84.0	90.6	100.0	92.0	93.0	100.0	83.7
3.0	6.6	100.0	95.7	84.0	78.6	100.0	89.0	93.0	100.0	75.6
3.5	7.0	100.0	95.7	82.0	88.0	100.0	88.0	93.0	100.0	76.3

To verify the method, some samples of realgar and orpiment minerals with standard addition of Cd, Co, Cr, Ni and Pb, were prepared and treated by using the proposed procedure. The results given in Table 7 show that satisfactory recovery results were obtained (from 92.6 to 99.5). Because of higher content of Fe, Mn and Zn, these elements were determined by FAAS directly from the obtained solutions (Table 8).

Table 7
Content of Co, Cd, Cr, Ni and Pb in realgar, orpiment and stibnite determined by standard addition method

No.	$m_M(\text{added})$ μg	$\gamma_M(\text{calculated})$ $\mu\text{g g}^{-1}$	$\gamma_M(\text{found})$ $\mu\text{g g}^{-1}$	R %
Co				
Realgar				
1	–	–	0.08	–
2	100	1.08	1.00	92.6
3	200	2.08	1.96	94.2
Orpiment				
1	–	–	0.05	–
2	100	1.05	0.98	93.8
3	200	2.05	1.98	93.6
Stibnite				
1	–	–	5.90	–
2	50	6.42	5.94	92.5
3	100	6.94	6.45	92.9
Cd				
Realgar				
1	–	–	1.54	–
2	50	2.04	1.99	97.5
3	100	2.54	2.50	98.4
Orpiment				
1	–	–	0.45	–
2	50	0.95	0.89	93.6
3	100	1.45	1.38	95.2
Stibnite				
1	–	–	2.94	–
2	50	3.44	3.23	93.9
3	100	3.94	3.66	92.9
Cr				
Realgar				
1	–	–	1.60	–
2	50	2.1	2.01	95.8
3	100	2.6	2.57	99.0

No.	$m_M(\text{added})$ μg	$\gamma_M(\text{calculated})$ $\mu\text{g g}^{-1}$	$\gamma_M(\text{found})$ $\mu\text{g g}^{-1}$	R %
Orpiment				
1	–	–	1.19	–
2	50	1.69	1.65	97.6
3	100	2.19	2.18	99.5
Stibnite				
1	–	–	3.95	–
2	50	4.45	4.34	97.5
3	100	4.95	4.70	94.4
Pb				
Realgar				
1	–	–	1.14	–
2	50	1.64	1.63	98.8
3	100	2.14	2.09	96.1
Orpiment				
1	–	–	0.21	–
2	50	0.71	0.67	94.7
3	100	1.21	1.19	98.8
Stibnite				
1	–	–	0.65	–
2	50	1.15	1.07	93.0
3	100	1.65	1.52	92.1
Ni				
Realgar				
1	–	–	1.30	–
2	50	1.80	1.74	96.7
3	100	2.30	2.20	95.6
Orpiment				
1	–	–	0.73	–
2	50	1.03	0.99	96.1
3	100	1.53	1.46	95.4
Stibnite				
1	–	–	8.21	–
2	50	8.71	8.26	94.8
3	100	9.21	8.63	93.7

Table 8
Content of Fe, Mn and Zn in realgar, orpiment and stibnite mineral samples (in $\mu\text{g g}^{-1}$)

Mineral	Fe	Mn	Zn
Realgar	14058	1780	92.5
Orpiment	226.7	31.8	54.9
Stibnite	9.25	11.5	8.86

Using these methods, investigated elements were determined in various samples of the realgar, orpiment and stibnite from Allchar mine (Table 9). The obtained values for their content are in agreement with those obtained for the same minerals (Table 9) by us and by the others authors using

neutron activation analysis (Palme *et al.*, 1988; Frantz *et al.*, 1994; Lazaru *et al.*, 2002), mass spectrometry (Todth, 1988; Boev *et al.*, 1993b; Frantz *et al.*, 1994) or AAS (Lazaru and Stafilov, 1993; 2000; Stafilov *et al.*, 1990).

Table 9

Measured content levels for Co, Cd, Cr, Ni, Pb, Fe, Mn and Zn in realgar, orpiment and stibnite from Allchar mine (given in $\mu\text{g g}^{-1}$)

Element	Realgar	Orpiment	Stibnite
Co	<0.08 (Palme <i>et al.</i> , 1988) <1 (Boev <i>et al.</i> , 1993) <4.0 (Frantz <i>et al.</i> , 1994) 0.10–0.80 (Lazaru and Stafilov, 2000) 13.9±0.56 (Lazaru <i>et al.</i> , 2002) 0.08*	<0.41 (Palme <i>et al.</i> , 1988) <7 (Frantz <i>et al.</i> , 1994) 0.086–1.16 (Lazaru and Stafilov, 2000) 0.100±0.017 (Lazaru <i>et al.</i> , 2002) 0.05*	<10 (Boev <i>et al.</i> , 1993) 5.90*
Cd	<100 (Lazaru <i>et al.</i> , 2002) 1.54*	<100 (Lazaru <i>et al.</i> , 2002) 0.45*	2.94*
Cr	<20 (Palme <i>et al.</i> , 1988) <1 (Lazaru and Stafilov, 1993) 69.8 (Frantz <i>et al.</i> , 1994) 2.64±0.14 (Lazaru <i>et al.</i> , 2002) 1.60*	<100 (Palme <i>et al.</i> , 1988) <1–32.6 (Lazaru and Stafilov, 1993) 0.42±0.04 (Lazaru <i>et al.</i> , 2002) 1.19*	<10 (Boev <i>et al.</i> , 1993) 4 (Lazaru and Stafilov, 1993) 3.95*
Ni	< 10 (Palme <i>et al.</i> , 1988) <1–41.0 (Lazaru and Stafilov, 1993) 0.75–1.76 (Lazaru and Stafilov, 2000) 1.30*	< 30 (Palme <i>et al.</i> , 1988) <1–7.4 (Lazaru and Stafilov, 1993) 1.29–4.86 (Lazaru and Stafilov, 2000) 0.73*	<200 (Boev <i>et al.</i> , 1993) 9.6 (Lazaru and Stafilov, 1993) 8.21*
Pb	0.38 (Todt, 1988) 0.8 (Boev <i>et al.</i> , 1993) 0.01–0.8 (Frantz <i>et al.</i> , 1994) 5 (Ljubičić <i>et al.</i> , 1988) 0.29–3.16 (Lazaru and Stafilov, 2000) 1.14*	11.6 (Todt, 1988) 2 (Boev <i>et al.</i> , 1993) 0.07–11.6 (Frantz <i>et al.</i> , 1994) 1.65–3.73 (Lazaru and Stafilov, 2000) 0.21*	<10 (Boev <i>et al.</i> , 1993) 0.38–2.47 (Stafilov <i>et al.</i> , 1990) 0.65*
Fe	<20 (Palme <i>et al.</i> , 1988) 365–1410 (Lazaru and Stafilov, 1993) 57500±2300 (Lazaru <i>et al.</i> , 2002) 14058*	<200 (Palme <i>et al.</i> , 1988) <800 (Boev <i>et al.</i> , 1993) 96–620 (Lazaru and Stafilov, 1993) 169±12 (Lazaru <i>et al.</i> , 2002) 226.7*	>1000 (Boev <i>et al.</i> , 1993) 9.25*
Mn	<90 (Boev <i>et al.</i> , 1993) 70.4–955 (Lazaru and Stafilov, 1993) <4 (Frantz <i>et al.</i> , 1994) 1780*	100 (Palme <i>et al.</i> , 1988) <20 (Boev <i>et al.</i> , 1993) 5.0–28.3 (Lazaru and Stafilov, 1993) <8 (Frantz <i>et al.</i> , 1994) 31.8*	<50 (Boev <i>et al.</i> , 1993) 11.5*
Zn	<30 (Frantz <i>et al.</i> , 1994) 66.5±2.7 (Lazaru <i>et al.</i> , 2002) 92.5*	2.8 (Palme <i>et al.</i> , 1988) <0.7 (Lazaru <i>et al.</i> , 2002) 54.9*	<30 (Boev <i>et al.</i> , 1993) 8.86*

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