Determination of Silver in Sulfide Minerals by ETAAS

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INTRODUCTION

It is known that the mineral lorandite ($TlAsS_2$) from the Alshar deposit (Republic of Macedonia) could be used as a solar neutrino detector (1). The aim of this study was to determine the Pb concentration in the thallium minerals from Alshar, particularly in lorandite, which is produced in the nuclear reaction between solar neutrinos and ^{205}Tl (present in lorandite):

$$^{205}Tl + \nu \longrightarrow\, ^{205}Pb + e^-$$
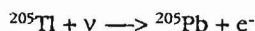
Therefore, it is necessary to be able to exactly determine the lead concentration in thallium and non-thallium minerals (2-5), marcasite (FeS_2), or in dolomite [$CaMg(CO_3)_2$]. The results provide the necessary data on the purity of the minerals, which is important for different geochemical investigations and also helps to explain the background radiation of the Alshar locality. In continuing our previous work on the determination of these elements (6-10), we now suggest a new method for the determination of silver in the above-mentioned minerals using electrothermal atomic absorption spectrometry (ETAAS).

With the first investigations in the 1960's, flame AAS was used for the determination of silver in geological samples (11-12). The influence of the matrix in the determination of silver was reported only when the potential interfering element was present in high concentrations. Tyndall (11) proposed a method for the direct determination of silver from copper ore samples with a low Pb concentration. Spitzer and Tesik (12) concluded that the presence of high amounts of iron influences the determination

ABSTRACT

A method for the determination of silver in sulfide minerals (realgar, orpiment, lorandite, marcasite, and stibnite) as well as dolomite by electrothermal atomic absorption spectrometry is discussed. After dissolution of the samples, silver was extracted by diphenyl thiocarbamate in hydrochloric acid media using methyl isobutyl ketone, butyl acetate, or toluene as the solvent. The procedure was verified by the method of standard additions and with standard reference samples. The standard deviation (SD) for 0.5 ng/Ag was 0.01 ng. The relative standard deviation ranged from 3–5%. The detection limit, calculated as three SDs of the blank, was found to be 0.001 µg/g.

of silver by FAAS. Some authors (13-14) suggested the direct determination of silver in solutions. To remove the potential interferences in the determination of silver in different geological samples with FAAS, extraction was suggested using the compounds methyl isobutyl ketone (MIBK) (15-16), diethyldithiocarbamate (17), or other organic compounds (18-23).

Different approaches are described for the determination of silver by ETAAS. Brooks et al. (24), Persiani and Durking (25), and Hamalainen et al. (26) suggested the direct determination of silver in solutions of copper ore samples. The direct determination of silver in solid geological samples using the graphite furnace was suggested by other authors (27-29). Some authors proposed the separation of silver from the matrix (32-35).

The interference of various elements in the determination of silver by ETAAS in geological samples was investigated by a small number of authors (34-35). Fishkova and Vilenkin (34) established that only iron interferes at concentrations higher than 100 mg.dm^{-3}.

Because of the differences in results reported in the literature for the determination of silver at low concentrations in complex matrices using FAAS or ETAAS, we performed a complete investigation as to the interference of all elements in arsenic-antimony-thallium ores and some sulfide minerals. The extraction of silver by diphenyl thiocarbamate in hydrochloric acid media and different solvents (MIBK, butyl acetate, and toluene) is described here.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer® Model Zeeman 3030 atomic absorption spectrometer, equipped with a Perkin-Elmer HGA-600 graphite furnace and a Perkin-Elmer AS-60 autosampler, was used. The light source was a silver hollow cathode lamp (Perkin-Elmer Model Intensitron®). Pyrolytically coated graphite tubes with platforms were used. The instrumental parameters are given in Table I.

Reagents and Standards

All reagents and standards were of analytical grade. The stock solution of silver was prepared by dissolving $AgNO_3$ with deionized water. The concentration of silver

TABLE I
Instrumental Parameters for the Determination of Silver by ETAAS

Wavelength	328.1 nm
Spectral slit with	0.7 nm
Calibration mode	Peak area
Lamp current	10 mA
Background correction	Zeeman corrector
Matrix modifier	$NH_4H_2PO_4$
Aliquot injected into HGA	20 µL

Dry

Temperature	110°C
Ramp time	20 s
Hold time	30 s

Char

I.	Temperature	400°C
	Ramp time	10 s
	Hold time	10 s
II.	Temperature	600°C
	Ramp time	10 s
	Hold time	10 s

Atomization

Temperature	1800°C
Ramp time	0 s
Hold time	3 s
Flow mode	Gas stop

Cleaning

Temperature	2650°C
Ramp time	1 s
Hold time	3 s
Gas	Argon

in this solution was 1000 mg.dm^{-3}, from which all diluted solutions were prepared. Ore and mineral samples were taken from the Alshar Mine, Republic of Macedonia.

Procedure

(a) Realgar and orpiment. 0.1–0.5 g of powdered sample of realgar or orpiment was dissolved in 10 cm^3 concentrated HNO_3. A few drops of H_2O_2 were added and the solution evaporated to near dryness. The residue was dissolved in a solution of 1 mol.dm^{-3} HCl. After dissolution of the mineral samples, the solution was filtered and transferred into a separatory funnel. Then, 1.5 cm^3 diphenyl thiocarbamate (1% in acetone) was added, the solution brought to 20 cm^3 volume with 1 mol.dm^{-3} HCl, and then 5 cm^3 MIBK, butyl acetate, or toluene was added. The mixture was shaken for five minutes and silver was determined by ETAAS in the organic layer, using aliquots of 20 mm^3 for introduction into the graphite furnace.

(b) Stibnite and dolomite: 0.1–0.5 g powdered mineral sample was dissolved in 10 cm^3 concentrated HCl and 1 mL concentrated H_2O_2. Then the same procedure was followed as described for realgar and orpiment.

(c) Marcasite: 0.1–0.5 g powdered mineral sample was dissolved in 5 cm^3 concentrated HCl, 5 cm^3 concentrated HNO_3, and a few drops of H_2O_2. The solution was evaporated to dryness, and then the same procedure was followed as described for realgar and orpiment, but with toluene or butyl acetate as the solvent.

(d) Lorandite: 0.1–0.2 g powdered mineral sample was dissolved in 15 cm^3 concentrated HCl, 5 cm^3 concentrated HNO_3, and a few drops of H_2O_2. The solution was evaporated to dryness and then the same procedure was followed as described for realgar and orpiment, but using butyl acetate as the solvent.

RESULTS AND DISCUSSION

The interference of the following matrix elements present in ores and minerals was studied: As, Sb, Fe, Al, Tl, Ca, and Mg. Solutions with the same concentration of silver but with various concentrations of the interfering elements were prepared so that the concentrations of these elements were similar to the concentrations in the sample solutions. Figure 1 shows that the interfering elements tend to decrease the integrated absorbance of silver at high concentrations. In order to avoid these interferences and because of the very low concentration of silver in the samples investigated, it is necessary to separate and concentrate the silver in the samples. For this reason, an extraction method is proposed.

In the literature, authors describe the analysis of different types of samples using diphenyl thiocarbamate for the extraction of silver but using different conditions and procedures than we propose in this work. For instance, Shaburova et al. (36) used diphenyl thiocarbamate for silver extraction from bromide with chloroform as the solvent. Bashov and Sokolova (19) proposed the extraction of silver in different silicate ore samples with diphenyl thiocarbamate in butyl acetate. In both procedures, FAAS was used. Aruscavage and Campbell (37) suggested the extraction of silver with diphenyl thiocarbamate from silicate samples with butyl acetate, but from a 20% tartaric acid solution.

To check whether As, Ca, Mg, Sb, Fe, and Tl coextract with Ag, solutions with the same silver concentration but with different interfering element concentrations were prepared. Silver was extracted using the proposed method with MIBK, butyl acetate, or toluene as the solvent. After extraction, silver was determined in the organic phase by neutron activation analysis, and Tl, Fe, Sb, Ca, and Mg were determined by FAAS after evaporation and dissolution of the residue. Only 0.3–0.4% of the total As was found to be extracted together with the silver and 0.005–0.01% of the remaining elements. With such depletion factors, further interferences are not
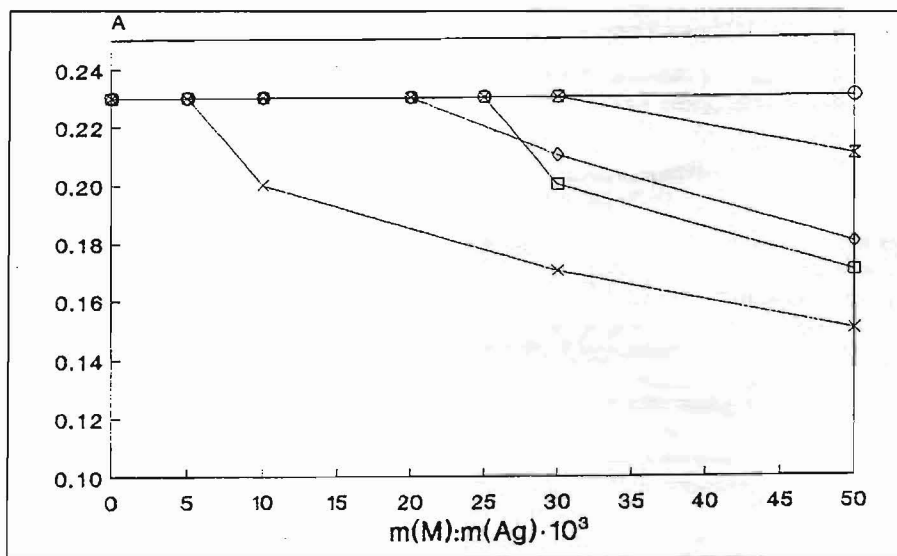
Fig. 1. *Influence on silver absorbance from different matrix elements: Ca and Mg (○), Fe (⊠), Al (◇), Tl and Sb (□), and As (×).*

expected in the determination of silver. Very good results were obtained for the extraction of silver with diphenyl thiocarbamate from acid solutions in the recovery values with MIBK, butyl acetate, or toluene was used as the solvent in the presence of As, Sb, Ca, and Mg (realgar, orpiment, stibnite, and dolomite). When Fe is present in the sample (marcasite) it is not possible to extract silver in MIBK because iron coextracts with silver. Extraction of silver from a Tl-matrix (lorandite) is possible only with butyl acetate.

Tables II and III show that satisfactory results were obtained for the determination of silver in mineral samples from the Alshar Mine with and without standard addition.

TABLE II
Determination of Ag in Orpiment and Realgar by Method of Standard Additions (in µg/g), Determined by ETAAS

Mineral/ solvent	Ag added (µg/g)	Ag calc. (µg/g)	Ag found (µg/g)	Recovery (%)
Orpiment				
Butyl acetate				
1	-	-	0.18	-
2	0.25	0.43	0.42	97.4
3	0.50	0.68	0.65	101.5
Toluene				
1	-	-	0.03	-
2	0.25	0.28	0.29	103.5
MIBK				
1	-	-	0.02	-
2	0.25	0.27	0.26	96.3
3	0.50	0.52	0.54	103.8
Realgar				
Butyl acetate				
1	-	-	0.10	-
2	0.25	0.35	0.35	100.0
3	0.50	0.60	0.57	95.0
Toluene				
1	-	-	0.01	-
2	0.25	0.26	0.25	96.2
MIBK				
1	-	-	0.02	-
2	0.25	0.27	0.27	100.0
3	0.50	0.52	0.54	103.8

TABLE III
Determination of Ag in Dolomite, Marcasite, Stibnite, and Lorandite by Method of Standard Additions (in µg/g), Determined by ETAAS

Mineral/ solvent	Ag added (µg/g)	Ag calc. (µg/g)	Ag found (µg/g)	Recovery (%)
Dolomite				
Butyl acetate				
1	-	-	0.05	-
2	0.25	0.30	0.29	96.7
Toluene				
1	-	-	0.16	-
2	0.25	0.41	0.42	102.4
MIBK				
1	-	-	0.25	-
2	0.25	0.50	0.51	101.0
3	0.50	0.75	0.72	95.4
Marcasite				
Toluene				
1	-	-	0.09	-
2	0.25	0.34	0.34	100.0
3	0.50	0.59	0.61	103.0
Stibnite				
Toluene				
1	-	-	0.07	-
2	0.25	0.32	0.34	106.2
Lorandite				
Butyl acetate				
1	-	-	0.01	-
2	0.25	0.26	0.27	103.8

The determination of silver was also performed for three standard reference sulfide ore samples (SU-1, SU-1a and UM-1) and one standard reference copper concentrate (NR-3). The results of measured and certified silver values for SU-1 (38), SU-1a (39), and the two standard samples are given in Table IV. As can be seen, the concentrations for silver using the proposed method are very similar to those provided for the certified samples.

TABLE IV
Determination of Ag in Standard Sulfide Ore Samples

Sample	Certified Value (µg/g)	Value found (µg/g)
SU-1	4.2	4.3
SU-1a	4.3±0.3	4.5
UM-1	–	0.05
NR-3	1260.0	1257.7

A calibration curve (for organic solution containing up to 1 ng/Ag) was prepared using the proposed extraction procedure for standard silver solutions. The standard deviation (SD) for 0.5 ng/Ag was 0.01 ng and the relative standard deviation for this method ranged from 3.0-4.5%. The detection limit of the method, calculated as 3 SD of the blank, was found to be 0.01 ng/g. The sensitivity was 4×10^{-12}/1% absorption for silver.

CONCLUSION

The results of our investigation show that diphenyl thiocarbamate can be successfully used for the extraction of silver in MIBK, butyl acetate, or toluene from As (realgar and orpiment), Pb (stibnite), and Fe (marcasite) sulfide minerals, as well as from dolomite. Silver was determined using Zeeman ETAAS with the extraction being performed in HCl media (1 mol.dm^{-3}).

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