DETERMINATION OF LEAD IN ANTIMONITE BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

T. Stafilov, V. Jordanovska, S. Aleksovska

Institute of Chemistry, Faculty of Science, University
"Cyril and Methodius", POB 162 91000 Skopje

In this paper a method for lead determination in antimonite by electrothermal atomic absorption spectrometry (ETAAS) is presented. The antimonite samples are from "Alshar" mine near Kavadarci, SR Macedonia.

Because of the very low concentration of lead in this mineral and the antimony interferences, it was necessary to separate the lead from the matrix. For this purpose, after the dissolution of antimonite, lead was extracted with sodium diethyldithiocarbamate in carbon tetrachloride. By adjusting pH in the range from 10.5 to 12.5, antimony was not coextracted with lead.

With this method, it is possible to determine lead in antimonite up to 0.1 $\mu g \cdot g^{-1}$.

INTRODUCTION

According to the investigation for using the thallium minerals from "Alshar" mine, near Kavadarci, SR Macedonia, as solar neutrino detectors, it is necessary to determine the content of ^{205}Pb which is produced in the nuclear reaction between the solar neutrino and ^{205}Tl, and is accumulated in the mineral lorandite [1]. But, because of the possibility

of presence of lead in the other minerals and materials, it is necessary exactly determination of the lead content in the minerals, ores and rocks from "Alshar".

Until recently, there are little data about the content of lead in the minerals from this mine. There are some data from Todt who has determined the content of lead in lorandite, orpiment and realgar by mass spectrometry [2].

Continuing our investigations about using electrothermal atomic absorption spectrometry (ETAAS) for lead determination in minerals from "Alshar" [3,4], in this paper a method for lead determination in antimonite (Sb_2S_3) is presented.

There are many data about the determination of lead by ETAAS in variety of geological materials [5,6] and also, there are number of papers for lead determination in different types of sulfidic minerals and ores [7,8]. Usually, an acid digestion is used for sample dissolution, but this, however, produces solutions that contain different ions of elements dissolved from the sample matrix. Interelemental interferences are a common source of errors in atomic absorption spectrometry. Therefore, different methods for lead separation from the matrix, before its determination by ETAAS were developed. For this purpose, several methods based on extraction [9, 10], ionic exchange [11, 12], and by precipitation [13] are described. For lead separation from antimony, in this work, an extraction method was chosen,. For this purpose, lead was extracted with sodium diethyldithiocarbamate in CCl_4.

EXPERIMENTAL

INSTRUMENTATION

A Perkin-Elmer Model 703 atomic absorption spectrophotometer equipped with a deuterium background corrector, HGA-400 graphite furnace and a Model 056 strip hart recorder was used.

A lead electrodeless discharge lamp was used as a source. Background corrector was applied throughout the course of analysis.

Operation conditions for lead determination are given in Table I.

REAGENTS AND SAMPLES

The mineral samples are from "Alshar" mine, near Kavadarci, SR Macedonia.

All reagents and standards were of analytical grade. Stock solution of lead was prepared by dissolving $Pb(NO_3)_2$ in distilled water. The mass concentration of lead was 1000 $mg \cdot dm^{-3}$, and from this solution the other dilute solutions were prepared.

PROCEDURE

About 1 g of powdered mineral antimonite (Sb_2S_3) was transferred to a glass beaker and 20 cm^3 conc. HCl and 1 cm^3 conc. HNO_3 were added. The mixture was heated and mixed, until it was totally dissolved. When the reaction mixture was cool, it was filtered through a filter paper, and 5 cm^3 50% ammonium citrate were added. Than the pH value was adjusted to about 11.5 (10.5 -12.5) with 20% NaOH. After that, 5 cm^3 5% KCN were added and the mixture was transferred to a separating funnel. 5 cm^3 0.2% sodium diethyldithiocarbamate were added and the mixture was shaken for a minute. After 10 min. 5 cm^3 CCl_4 were added. The mixture was shaken 1-2 min. and after 10 min. the organic layer was filtered off and from this solution a volume of 20 mm^3 was introduced in the graphite furnace with Eppendorff pipette, and lead was determined by ETAAS.

Table I

Instrumental parameters for lead determination by ETAAS

Atomic absorption spectrophotometer

Wavelength	383.3 nm
Spectral slit	0.7 nm
Lamp power	10 W
Calibration mode	Absorbance, peak height
Background correction	Deuterium arc lamp

Graphite furnace

DRYING	
Temperature	120 °C
Time	30 s
Ramp time	2 s
CHARRING	
Temperature	550 °C
Time	20 °C
Ramp time	1 s
ATOMIZING	
Temperature	2100 °C
Time	5 s
Ramp time	0 s
CLEANING	
Temperature	2700 °C
Time	1 s
GAS	Argon

RESULTS AND DISCUSSION

There are no data about the antimony interferences on lead
determination by ETAAS, so our first step in this work was

to investigate the matrix interferences. For this purpose, series of samples with constant mass of lead and varying masses of antimony were prepared and lead was determined by ETAAS. The mass ratios of Pb and Sb varied from 1:0 to 1:300000 . The measurements were performed in 2 mol dm^{-3} HCl solutions. The results of the lead determination by ETAAS in these samples are given in Table II.

Table II

Influence of antimony on lead determination by ETAAS

Sample No	Mass ratios m_{Pb} : m_{Sb}	Lead Absorbance
1.	1 : 0	0.180
2.	1 : 500	0.180
3.	1 : 1000	0.180
4.	1 : 5000	0.180
5.	1 : 10000	0.172
6.	1 : 50000	0.160
7.	1 : 100000	0.155
8.	1 : 200000	0.151
9.	1 : 300000	0.145

As it can be seen from the Table II, antimony interfere on the determination of lead by ETAAS with decreasing the Pb absorbance, when the mass ratio is up to 1:10000. Therefore, it was necessary to separate the lead from the matrix, before its determination by ETAAS. Also, the concentration of lead in antimony from "Kishar" is very low, so it was necessary to concentrate the content of lead.

For these purposes a method based on extraction was used. The literature data [14], showed that when lead was extracted with sodium diethyldithiocarbamate in carbon tetrachloride, in alkaline medium, antimony was not coextracted with lead. Bode [15], found that by adding ammonium citrate and

KCN. the extraction of lead with sodium diethyldithiocarbamate is the most effective in the pH range from 10.5 to 12.5.

To verify this method, series of samples with known concentrations of lead, with antimony were prepared and treated as it was described above. The mass concentrations of antimony in these samples were the same as in the 1 g of antimonite (Sb_2S_3). The results of lead determination by ETAAS in these samples, are in agreement with that samples with the same concentrations of lead without antimony, so it can be concluded that antimony was not coextracted with lead.

Since, this method gives a possibility for determination of very low concentration of lead by ETAAS, some antimonite samples were dissolved and treated by the same method and lead was determined by ETAAS. Also, some samples of antimonite with standard addition of lead were prepared and treated in the same manner. The results of lead determination by ETAAS in these samples are given in Table III.

From these results it can be concluded that lead concentrations in antimonite from "Alshar" is from 0.3 $\mu g \cdot g^{-1}$ to 2.5 $\mu g \cdot g^{-1}$.

A calibration curve was constructed by similar treatment of samples containing from 0 to 20 ng lead. The overall standard deviation was calculated as 0.046 $\mu g \cdot g^{-1}$ and applying the 2σ detection limit rule a detection limit on the order of 0.1 $\mu g \cdot g^{-1}$ is obtained.

Table III

The results of lead determination in antimonite from "Alshar"

Sample No	Pb added $\mu g \cdot g^{-1}$	Pb calc. $\mu g \cdot g^{-1}$	Pb found $\mu g \cdot g^{-1}$	Deviation %
1	-	-	0.69	
1'	2	2.69	2.31	18.50
2	-	-	2.47	
2'	2.5	4.97	4.92	2.80
3	-	-	0.38	
3'	2	2.38	2.19	9.50
4	-	-	0.59	

REFERENCES

1. M. K. Pavićević, *Nucl. Instr. Meth. Phys. Res.*, A271, 287 (1988).

2. W. Todt, *Nucl. Instr. Meth. Phys. Res.*, A271, 251 (1988).

3. T. Stafilov, V. Jordanovska, S. Aleksovska, *Bull. Chem. Technol. Macedonia*, 8, 93 (1990).

4. T. Stafilov, V. Jordanovska, S. Aleksovska, *Bull. Chem. Technol. Macedonia*, 9, (1990) (in press).

5. J. Korkisch, H. Gross, *Talanta*, 21, 1025 (1974).

6. R. F. Sanzolone, T. T. Chao, *Anal. Chim. Acta*, 86, 163 (1976).

7. I. Rubeška, *Anal. Chim. Acta*, 40, 187 (1968).

8. I. Rubeška, M. Mikšovsky, *Collect. Czech. Chem. Commun.*, 39, 3485 (1974).

9. R. P. Mitcham, *Analyst*, 105, 43 (1980).

10. J. Arnarez, F. Palacios, J. C. Vidal, At. Apsorpt. Newsl., 3, 192 (1932).

11. J. Korkisch, A. Sorio, *Talanta*, 22, 273 (1975).

12. A. H. Victor, F. W. E. Strelow, *Talanta*, 28, 207 (1981).

13. V. Hudnik, S. Gomišček, B. Gorenc, *Anal. Chim. Acta*, 98, 39 (1978).

14. R. Keil, *Z. Anal. Chem.*, 229, 117 (1967).

15. H. Bode, *Z. Anal. Chem.*, 143, 182 (1954).

POVZETEK

Izdelali smo metodo za določanje svinca v antimonitu z elektrotermično atomsko absorpcijsko spektrometrijo in jo uporabili za analize vzorcev rudnika "Alšar" v Makedoniji. Zaradi nizke koncentracije svinca v tem mineralu in interference antimona smo za separacijo svinca uporabili ekstrakcijo dietilditiokarbamatnega kelata v CCl_4. Optimalno ločitev smo dosegli pri pH 10,5 - 12,5. Meja zaznavnosti pri tej metodi znaša $0,1 \, \mu g/g$.