

DETERMINATION OF LEAD IN ARSENIC MINERALS FROM "ALSHAR" BY ATOMIC ABSORPTION SPECTROMETRY

T. Stafilov, V. Jordanovska and S. Aleksovska

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

In this paper, the method for dissolving of some arsenic sulfide minerala from the Alshar mine, such as realgar and orpiment, and lead determination by atomic absorption spectrometry, are givens.

The investigations showed that the presence of arsenic influence to the lead absorbance. Therefore, arsenic was separated in the process of mineral's dissolving.

Since the concentrations of lead in these minerals are very low, they had to be determined by electrothermal atomic absorption spectrometry.

INTRODUCTION

There are many data about the determination of lead by the methods of flame and flameless atomic absorption spectrometry in a variety of geological materials. The content of lead was determined in soils [1-5, 12], rocks [6-7, 12], ores [8-11, 12], and in other geological materials [12-13]. Also there are number of papers for lead determination in different types of sulfidic ores and minerals [14-16].

Until recently, there has been few data about the content of lead in the minerals from the Alshar mine near Kavadarci, Macedonia, Yugoslavia. There are

some data from Todt [17], who has determined the content of lead in lorandite, orpiment and realgar by mass spectrometry.

The determination of ^{205}Pb , which is produced in nuclear reaction between the solar neutrino and ^{205}Tl , and is accumulated in the thallium minerals [18], is of special interest. But, because of the possibility for finding ^{205}Pb which is obtained from the lead content in the other minerals and materials, it is necessary to determine the exact lead content in the other minerals, ores and rocks from Alshar. The most occurring arsenic minerals in Alshar, are realgar, orpiment and lorandite, so it is important to determine the lead content in these minerals.

In this paper a method for lead determination in orpiment (As_2S_3) and realgar (As_4S_4) from Alshar, by atomic absorption spectrometry is presented.

Since the previous investigations [19] showed that arsenic in mass ratio with lead up to 5000:1, influences the absorbance of lead, a method for dissolving the minerals, which makes possible complete removing of the arsenic was developed.

EXPERIMENTAL

INSTRUMENTATION

A Perkin-Elmer Model 703 atomic absorption spectrophotometer, equipped with a deuterium background corrector an HGA-400 graphite furnace, and a Model 056 stripchart recorder was used. A lead electrodeless discharge lamp was used as a source. Background corrector was applied throughout the analysis.

For lead determination by flame atomic absorption spectrometry, an air-acetylene flame was used.

Operating conditions for lead determination were established by extensive testing and are given in Table I.

REAGENTS AND SAMPLES

The mineral samples are from the Alshar arsenic-antimony mine. All reagents and standards were of analytical grade. Stock solution of lead was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ in aqueous media. The mass concentration of lead was 1000 mg/dm^3 and from this solution the other diluted solutions were prepared.

* location Crven Dol,

TABLE I
INSTRUMENTAL PARAMETERS FOR LEAD
DETERMINATION BY ETAAS

MODEL 703	
Wavelength	383.3 nm
Spectral slit	0.7 nm
Lamp power	10 W
Calibration mode	Absorbance, Peak height
Background corrector	Deuterium arc lamp
HGA - 400	
DRY	
Temperature	120 ⁰ C
Time	30 s
Time ramp	2 s
CHAR	
Temperature	550 ⁰ C
Time	20 s
Time ramp	1 s
ATOMIZE	
Temperature	2100 ⁰ C
Time	5 s
Time ramp	0
CLEANING	
Temperature	2700 ⁰ C
Time	3 s
GAS	Argon

SAMPLE PREPARATION AND PROCEDURE

Orpiment and realgar were dissolved by the following procedure:

About 1 g powdered mineral was transferred to a glass beaker and 20 cm³ 25% NH₄OH and 2 cm³ diluted solution of NH₄Cl were added. The mixture was gently heated and mixed, until it was dissolved. Then the reaction mixture was filtered through a filter paper. The arsenic was removed in filtrate in soluble form, and lead minerals and the other undissolved minerals remained as a residue. The residue was washed with 10% ammonia. Then, the filter paper was removed in a glass beaker and was dissolved with 20 cm³ HN0₃ (1:1). The solution was diluted, filtered off, and made to volume in the volumetric flask. From this solution, a volume of 20 mm³ was introduced in the graphite furnace with Eppendorf pipette, and lead was directly determined by electrothermal atomic absorption spectrometry (ETAAS).

To verify the procedure, series of samples with known concentration of lead were treated according to the previous procedure, and then lead was determined by flame atomic absorption spectrometry. Also, some mineral samples with standard addition of lead were made. The content of lead was checked in the reagent, too.

RESULTS AND DISCUSSION

Our previous investigations about the interference of some elements on lead determination by ETAAS [19], showed that the arsenic in mass ratio with lead up to 5000:1 interfered on the decreasing of the lead absorbance. This fact pointed out to the necessity of lead separation from arsenic when lead is determined in arsenic minerals by ETAAS. There are many different methods for lead separation from the matrix, before its determination by atomic absorption measurements. To this purpose, several methods are described, based on the extraction [4, 12, 20-29], ionic exchange [10-12, 30-33], or lead is occasionally separated from the matrix by precipitation methods [12, 34]. All these methods were developed to avoid interferences of matrix elements and to increase the sensitivity.

In this work, the separation of lead from arsenic was done by lead precipitation and arsenic removing in the filtrate. Namely, the dissolving of the orpiment and realgar was done with ammonia. In this case the arsenic is in soluble form and lead minerals are undissolved. By filtration through filter paper, arsenic was removed in the filtrate, and lead remained as a residue.

To verify the method, some standard samples with known concentration of lead were prepared, and treated as it was described above. Also, some mineral samples, with addition of lead, were dissolved by this procedure and lead was determined by flame AAS. In some samples of orpiment an exact amount of standard solution of lead was added in the final solution and lead was determined by ETAAS

The results of lead determination by flame and flameless AAS, from the final solutions, of blank samples and samples with standard addition, are given in the Table II.

TABLE II
THE RESULTS OF LEAD DETERMINATION IN THE BLANK
SAMPLES AND IN THE SAMPLES WITH STANDARD ADDITION
OF LEAD, BY AAS

SAMPLE		Pb - added $\mu\text{g} \cdot \text{cm}^{-3}$	Pb found $\mu\text{g} \cdot \text{cm}^{-3}$
FLAME AAS			
1.	Standard solution of Pb	20	20
2.	Blank sample 1.	20	20
	Blank sample 2.	20	19.6
3.	Realgar with Pb-addition 1	20	19.2
	Realgar with Pb-addition 2.	20	20
4.	Orpiment with Pb-addition	20	19.2
ETAAS			
5.	Orpiment	0	5.55
6.	Orpiment with Pb-addition 1.	10	15.78
	Orpiment with Pb-addition 2.	25	30.29
	Orpiment with Pb-addition 3.	50	55.58

From these results, it can be seen that lead was not lost in the procedure of dissolving, but it remained as a residue (or was precipitated). Also, it can be seen that there is no interference arsenic, so it can be concluded that arsenic was removed in the process of dissolving. Therefore, according to the procedure above, greater number of samples of realgar and orpiment were dissolved, and lead was determined by ETAAS, according to the instrumental parameters given in Table I. ETAAS was applied because of the very low concentration of lead in these minerals. As it can be seen from Table I, very high atomization temperature (2100°C), and charge temperature (550°C) for lead determination is not necessary.

A calibration curve was constructed by introduction of suitable lead mass from the standard solutions prepared in the same way as the samples. With this method or a modification of the procedure (larger mass of samples and/or smaller volume of solution) it was possible to determine lead in these minerals down to $0.5 \mu\text{g}\cdot\text{g}^{-1}$. Relative standard deviation up to $2 \mu\text{g}\cdot\text{g}^{-1}$ are 5%, and from 2–10 $\mu\text{g}\cdot\text{g}^{-1}$ are < 9%.

The results of the determination of lead in mineral samples are given in Table III.

TABLE III

THE RESULTS FROM DETERMINATION IN
REALGAR AND ORPIMENT FROM ALSHAR

MINERAL	Pb ($\mu\text{g}\cdot\text{g}^{-1}$)
REALGAR	
Realgar 1.	4.8
Realgar 2.	1.1
Realgar 3.	2.2
Realgar 4.	6.2
ORPIMENT	
Orpiment 1.	8.0; 9.4; 8.4
Orpiment 2.	5.8; 5.3; 6,6

From the Table III, it can be considered that lead concentration in orpiment is from 5.3 to 9.4 $\mu\text{g}\cdot\text{g}^{-1}$ and in realgar from 1.1 to 6.2 $\mu\text{g}\cdot\text{g}^{-1}$. These results are in agreement with the results of lead determination by mass spectrometry in other samples of these minerals from Alshar, given by Todt [17] (11.60 for orpiment and 0,38 $\mu\text{g}\cdot\text{g}^{-1}$ for realgar)

REFERENCES

- [1] H. L. Kahn, F. J. Fernanadez and S. Slavin, *At. Absort. Newsl.* **11**, 42 (1972).
- [2] J. L. Seeley, D. Dick, J. H. Arvik, R. L. Zimdahl and R. K. Skogerboe, *Appl. Spectrosc.*, **26**, 456 (1972).
- [3] W. Schmidt and F. Dietl, *Z. Anal. Chem.*, **291**, 213 (1978).
- [4] A. U. Azis Alrahman, U. A. Al-Hajja Al-Zamil, *Int. J. Environ. Anal. Chem.*, **15**, 9 (1982).
- [5] C. M. Jan, A. U. Ure, T.S. West, *Anal. Chim. Acta*, **146**, 171 (1983).
- [6] K. Govindaraju, G. Mevelle and C. Chanard, *Anal. Chem.*, **46**, 1672 (1974).
- [7] F. L. Langmyrh, J. R. Stuber, Y. Thomassen, J. E. Hanssen and J. Dolazel, *Anal. Chim. Acta*, **71**, 35 (1974).
- [8] A. G. Бажов. А. Б. Жербенко и П. А. Кока, *Ж. Анал. химии*, **26**, 1622 (1971).
- [9] B. G. Thomas, *At. Apsorpt. Newsl.*, **10**, 73 (1971).
- [10] T. W. Frendiger and C. T. Kenner, *Appl. Spectrosc.*, **26**, 302 (1972).
- [11] G. S. Negi, A. K. Das, *Indian J. Tehnol.*, **23**, 77 (1985).
- [12] J. Korkisch and H. Gross, *Talanta*, **21**, 1025 (1974).
- [13] R. F. Sanzolana and T. T. Chao, *Anal. Chim. Acta*, **86**, 163 (1976).
- [14] I. Rubeška. *Anal. Chim. Acta*, **40**, 187 (1968).
- [15] I Rubeška and M. Mikšovski, *Collect. Czech. Chem. Commun.*, **39**, 3485 (1974).
- [16] J. F. Alvin, F. R. Gardien, *Analyst*, **111**, 897 (1986).
- [17] W. Todt, *Nucl. Instr. Meth. Phys. Res.*, **A 271**, 251 (1988).
- [18] M. K. Pavićević, *Nucl. Instr. Meth. Phys. Res.*, **A 271**, 287 (1988).
- [19] T. Stafilov, V. Jordanovska and S. Aleksovska, *Glas hem. tehnol. Mcedonia*, **8**, 93 (1990).
- [20] E. Lakanen, *At. Absorpt. Newsl.*, **5**, 17 (1966)

- [21] D. Roosels and J. V. Vanderkeel, *At. Absorpt. Newsl.* **7**, 9 (1968).
 [22] M. E. Hofton and D. P. Hubbard, *Anal. Chim. Acta*, **52**, 425 (1970).
 [23] D. G. Mitchell, F. J. Ryan and K. M. Aldous, *At. Absorpt. Newsl.*, **11**, 6 (1972).
 [24] I. Tsukahara and T. Yamamoto, *Anal. Chim. Acta*, **61**, 33 (1972).
 [25] R. D. Olsen and M. R. Sommerfeld, *At. Absorpt. Newsl.*, **12**, 165 (1973).
 [26] B. M. Бырко, Л. Ф. Прищепов, И. А. Шихеева, *Завод. Лаб.*, **41**, 525 (1975).
 [27] S. Toda, K. Fuwa, P. Bodlaender and B. L. Valec, *Spectrosc. Lett.*, **9**, 225 (1976).
 [28] R. P. Mitcham, *Analyst*, **105**, 43 (1980).
 [29] J. Arnarez, F. Palacios and J. C. Vidal, *At. Absorpt. Newsl.*, **3**, 192 (1982).
 [30] D. G. Biechler, *Anal. Chem.*, **37**, 8 (1965).
 [31] N. G. Sellers, *Anal. Chem.*, **44**, 410 (1982).
 [32] J. Korkisch and A. Sorio, *Talanta*, **22**, 273 (1975).
 [33] A. H. Victor, F. W. E. Strelow, *Talanta*, **28**, 207 (1981).
 [34] V. Hudnik, S. Gomišček and B. Gorenc, *Anal. Chim. Acta*, **98**, 39 (1978).

ОПРЕДЕЛУВАЊЕ НА ОЛОВО ВО АРСЕНОВИ МИНЕРАЛИ ОД РУДНИКОТ "АЛШАР" СО АТОМСКА АПСОРПЦИОНА СПЕКТРОМЕТРИЈА

Т. Стафилов, В. Јордановска и С. Алексовска

Во овој труд се утврдени методи за растворање на некои арсен-сулфидни минерали, од рудникот "Алшар", како, на пример, реалгар и аурипигмент, а потоа е определувано оловото со методата на атомска апсорпциона спектрометрија.

Претходните испитувања покажаа дека присуството на арсен влијае на намалување на апсорбанцата на оловото, па затоа арсенот беше сепариран уште во текот на растворањето на минералите.

Поради ниските концентрации на оловото во овие минерали, неговото определување беше вршено со електротермичка атомска апсорпциона спектрометрија.

Институт за хемија. Природно-математички факултет,
 Универзитет "Кирил и Методиј", 91000 Скопје, П.фах 162