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Determination of lead in lorandite and marcasite by electrothermal atomic absorption spectrometry

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With 4 tables in the text

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Abstract: In this paper, the methods and the results of lead determination in lorandite and marcasite from the Allchar deposit, by electrothermal atomic absorption spectrometry, are presented. Since the investigations of the matrix interferences showed that matrix elements, both in lorandite and marcasite, decrease the lead absorbance, it was necessary to separate the lead from the matrix. For this purpose, after the decomposition of the lorandite sample, thallium was extracted by isoamyl acetate, first, and then lead was extracted by sodium diethyldithiocarbamate in carbon tetrachloride. By adjusting the pH in the range from 10.5 to 12.5, arsenic was not coextracted with the lead. In the case of marcasite, iron was extracted by isoamyl acetate, and then lead was determined directly from the aqueous phase. Using these methods several samples of lorandite and marcasite from the Allchar deposit were analyzed, and it was found that the lead concentration in lorandite varies from 1 to 2.3 $\mu g \cdot g^{-1}$ and from 0.7 to 2 $\mu g \cdot g^{-1}$ in marcasite.

Key words: Lead determination, lorandite, marcasite, electrothermal atomic absorption spectrometry.

Introduction

The purpose of the LOREX project is to use mineral lorandite ($TlAsS_2$) from Allchar (FYR Macedonia) as a solar neutrino detector (Freedman et al. 1976). The amount of ^{205}Pb ($t_{1/2} = 1.5 \cdot 10^7$ y) accumulated in lorandite (Pavićević 1988) by the nuclear reaction between the solar neutrino and ^{205}Tl:

$$^{205}Tl + \nu\ ^{205}Pb + e^-$$

The ^{205}Pb content in lorandite has to be determined, and can give information on the solar neutrino flux over the last million years. Apart from its production by solar neutrinos, ^{205}Pb is also produced by cosmic radiation, such as, for example, by the (n, 2n) reaction on ^{206}Pb. Therefore, it is necessary to determine the lead content in lorandite, but because lorandite is closely associated with other sulfide minerals such as: orpiment (As_2S_3), realgar (AsS),

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antimonite (Sb_2S_3), marcasite (FeS_2) etc., it is necessary to determine the lead content in these minerals.

Until recently, there are few data on the content of lead in lorandite and the other sulfide minerals from Allchar. TODT (1988), has determined the content of lead in two samples of lorandite, using mass spectrometry. Also, in the same work, there are some data about the lead concentration in realgar and orpiment. Recently, we reported about the determination of lead in realgar, orpiment (STAFILOV et al. 1990 a) and in antimonite (STAFILOV et al. 1990 b) by electrothermal atomic absorption spectrometry (ETAAS).

Continuing the investigations on the lead concentration in minerals and ores from Allchar, in this paper we present the analytical procedures for lead determination in lorandite and marcasite by ETAAS.

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 chart recorder was used. A lead hollow cathode lamp was used as source. Background corrector was applied through the course of analysis. Operation conditions for lead determination are given in Table 1.

Table 1. Instrumental parameters for lead determination by ETAAS.

Atomic absorption spectrophotometer	
Wavelength	383.3 nm
Spectral slit	0.7 nm
Lamp current	10 mA
Calibration mode	Absorbance, peak height
Background corrector	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	3 s
Gas	Argon

Reagents and samples

Samples were collected in the Allchar mine, near Kavadarci, FYR Macedonia (the lorandite samples were from the locality Crven Dol). 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 diluted solutions were prepared.

Procedure

1. Determination of lead in lorandite

Powdered lorandite (0.2 to 0.5 g) were dissolved in $15\,cm^3$ concentrated HCl and $3\,cm^3$ concentrated HNO_3. The solution was evaporated to dryness, cooled and then the residue was dissolved in $15\,cm^3$ concentrated HCl and a few drops of H_2O_2 with a minimum of boiling. Then, it was transferred to a separating funnel, $25\,cm^3$ of isoamyl acetate were added and the mixture was shaken for a minute. The phases were allowed to separate, the lower aqueous layer was run into a second separate funnel and the extraction was repeated with further $25\,cm^3$ of isoamyl acetate. The aqueous phase was run back into a beaker and evaporated to near dryness. After cooling, $5\,cm^3$ 50 % ammonium citrate were added and 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. Then $5\,cm^3$ 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 again 1 – 2 min, and after 10 min the organic layer was transferred to an erlenmayer flask and evaporated to dryness. Then, the residue was dissolved with $5\,cm^3$ 10 % HCl. From this solution a volume of $20\,mm^3$ was introduced to a graphite furnace with Eppendorff pipette and lead was determined by ETAAS.

2. Determination of lead in marcasite

About 1 g of powdered mineral marcasite (FeS_2) was transferred to a glass beaker and $10\,cm^3$ conc. HCl and $10\,cm^3$ conc. HNO_3 were added. The mixture was heated and mixed until it was totally dissolved. The solution was evaporated to dryness and after cooling the residue was dissolved in $15\,cm^3$ conc. HCl. Then, it was transferred to a separating funnel, $25\,cm^3$ of isoamyl acetate, for iron extraction, were added and the mixture was shaken for a minute. The phases were allowed to separate, the lower aqueous layer was put into a second separating funnel and the extraction was repeated with further $25\,cm^3$ of isoamyl acetate. The aqueous phase was run back into a beaker and evaporated almost to dryness. Complete dryness should be avoided as it will cause uncompletely dissolving of the residue. The purpose of this evaporation is to remove the excess acid. The residue was redissolve with $10\,cm^3$ 10 % (w/w) HCl. From this solution a volume of $20\,mm^3$ was introduced to a graphite furnace with Eppendorf pipette and lead was determined by ETAAS.

Results and discussion

Because it is sensitive and specific, atomic absorption spectrometry (AAS) is widely used in geochemical analysis. Korkish & Gross (1974) and Sanzolone & Chao (1976) have reviewed the application of AAS for lead determination in geological materials. Lead determination in various types of sulfide minerals and ores, has investigated Rubeška (1968, 1974). In all these papers, for sample dissolution, usually, an acid digestion is used. However, acid digestion, produces solutions that contain different ions of elements dissolved from the sample matrix, which may interfere with the determination of lead by ETAAS.

There are no data on interferences of arsenic and thallium with lead determination by ETAAS. Sedikh et al. (1980) studied the interferences of K, Ca, Mg, Al, Co, Ni, Fe, and Cu on the lead absorbance. But their investigations do not include all elements which are present in our samples (for example Tl and As), and also in this paper iron interferences with the lead absorbance were investigated to 1 : 20,000 ($m_{Pb}:m_{Fe}$), which is not in the same concentration range as in marcasite samples. Therefore, the first step in this work, was to investigate the matrix interferences on lead determination by ETAAS (iron interferences for marcasite samples, on one hand, and thallium and arsenic interferences, on the other). For this purpose, series of solutions with constant mass of lead and varying masses of thallium and arsenic were prepared, as well as, with iron, for lead determination in marcasite, and lead was determined by ETAAS. The mass ratios for Pb and Tl varied from 1 : 0 to 1 : 500,000, for Pb and As from 1 : 50,000, and for Pb and Fe from 1 : 0 to 1 : 100,000. The measurements were performed in 2 mol · dm^{-3} HCl solutions. The results of lead determination by ETAAS in these samples are given in Table 2.

As it can be seen from the Table 2, thallium, arsenic and iron interfere on the determination of lead by decreasing the Pb absorbance, when the mass ratios for Pb and Tl is up to 1 : 50,000, for Pb and As, up to 1 : 5000, and for Pb and Fe up to 1 : 1000. Therefore, it was necessary to separate the lead from the matrix, before its determination by ETAAS. Also, the separation and concentration of lead is necessary, because of the very low concentrations of lead in lorandite and marcasite. For this purpose, a method of solvent extraction was chosen.

As mentioned in the experimental part, lorandite was dissolved with HCl and HNO$_3$, so thallium and arsenic are present as Tl(III) and As(V). There are no literature data about the lead extraction when Tl(III) and As(V) are both present, because, usually the lead extraction from Tl(III) takes place in acid

Table 2. Influence of thallium, arsenic and iron on lead determination by ETAAS.

Sample No.	Mass ratios $m_{\mathrm{Pb}}:m_{\mathrm{M}}$	Lead absorbance M = Tl	M = As	M = Fe
1.	1 : 0	0.180	0.180	0.180
2.	1 : 500	0.180	0.180	0.180
3.	1 : 1000	0.180	0.180	0.180
4.	1 : 5000	0.180	0.150	0.180
5.	1 : 10,000	0.180	0.130	0.050
6.	1 : 50,000	0.175	0.080	0.050
7.	1 : 100,000	0.170	–	0.030
8.	1 : 200,000	0.160	–	0.020
9.	1 : 500,000	0.150	–	0.020

medium (Kish et al. 1984, Bagreev & Zolotov 1963) an from As(V) in alkaline medium (Bode 1954). On the other hand, there are some data about the lead extraction from As(V) in acid medium but this method can not be applied in the case of lorandite, because thallium will be coextracted (Ikramuddin 1983). Therefore, two methods of extraction were used. Because of the fact that during the extraction of Pb from Tl(III) in acid medium, arsenic was coextracted, it was necessary to use the extraction of thallium from the matrix, first.

There are many methods for thallium extraction in acid medium using: isopropyl ether (Sighinolfi 1973); methylisobutyl ketone (Bode 1954, Elson & Albuquarque 1982); 8-hydroxyquinoline (Almarin & Zolotov 1962, Schweitzer & Norton 1964) etc. The literature data show that when thallium was extracted by methyl-isobutyl ketone (Mulford 1966), or by 8-hydroxyquinoline in acid medium (Stary 1963), lead was coextracted too, so we selected isopropyl ether. Isopropyl ether was, also, very successfully used for iron extraction when lead was determined in high-alloy steels by AAS (Hofton & Hubbard 1970). Dagnal et al. (1966) have determined trace amounts of lead in steels, brass and bronze alloys by AAS after extraction of tetraiodoplumbate into methylisobutyl ketone. In the case of steel samples, they found it was necessary to remove the iron by extraction with isoamyl acetate. By analogy to iron extraction with isoamyl acetate in strong acid medium (Dangall et al. 1966), it was attempted to use this method for thallium extraction too. For this purpose, some solutions with known concentrations of Tl, Pb and As (the same as in lorandite), and other solution with known concentration of Pb and Fe (the same as in marcasite) were prepared and thallium and iron were extracted by isoamyl acetate, as well as, by isopropyl ether. After the extraction, thallium and iron was determined in the aqueous layer on one hand (Stafilov et al. 1988), and lead in the organic layer, on the other, by atomic absorption spectrometry. It was concluded that lead was not present in the organic layer, in both cases, which means that it was not coextracted neither with the thallium, neither with iron. The results of thallium and iron determination showed that they were extracted very successfully in both cases, but the results are somewhat better when isoamyl acetate was used, about 99.95 % Tl and 99.99 % Fe in comparison with 99.5 % Tl and Fe for isopropyl ether. Therefore, in this work, the method using isoamyl acetate for iron, as well as for thallium extraction, was chosen. Since the marcasite samples were pure and only the iron interferences were possible, further extraction of the lead was not necessary. But in the case of lorandite it was necessary to separate the lead from the arsenic.

Keil (1967) showed that lead was successfully extracted by sodium diethyldithiocarbamate in CCl_4 in alkaline medium, in presence of arsenic. Bode (1954) 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 solutions with known concentration of arsenic (the same as in lorandite), and varying concentrations of lead were prepared, lead was extracted by this procedure and than it was determined by ETAAS. The obtained results were in agreement with the results of standard solutions of lead, so it can be concluded that lead was successfully extracted. Therefore, for lead separation from arsenic, this method was chosen.

Using these two methods, several series of solutions with known concentrations of lead with thallium and arsenic were prepared and treated as it was given in the procedure. The mass concentrations of thallium and arsenic were the same as in the 0.5 g lorandite. The results of lead determination by ETAAS in these samples, are in agreement with the results of the samples with same concentration of lead, but without thallium and arsenic, so it can be concluded that lead was quantitatively separated from the matrix.

Using the complete procedure, some samples of lorandite from Allchar (about 0.5 g) were dissolved, treated as it was described above, and lead was determined by ETAAS. Also, some samples of lorandite 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 3. From these results, it can be seen that lead concentration in these samples of lorandite from Allchar is from 1 to 2.3 $\mu g \cdot g^{-1}$. These results are in agreement with the TODT's data (1988) (0.79 and 2.02 $\mu g \cdot g^{-1}$).

Also, some marcasite samples from Allchar (about 1 g) were dissolved, treated as it was described in the experimental part, and lead was determined by ETAAS. Some samples of marcasite with standard addition of lead were prepared and treated in the same manner, as well. The results of lead determination by ETAAS in these samples are given in Table 4. It can be seen from

Table 3. The results of lead determination in lorandite from Allchar.

Sample No.	Pb added $\mu g \cdot g^{-1}$	Pb calc. $\mu g \cdot g^{-1}$	Pb found $\mu g \cdot g^{-1}$
1	–	–	1.02
1′	2	3.02	2.82
2	–	–	2.21
2′	4	6.21	6.52
3	–	–	1.07

Table 4. The results of lead determination in marcasite from Allchar.

Sample No.	Pb added $\mu g \cdot g^{-1}$	Pb calc. $\mu g \cdot g^{-1}$	Pb found $\mu g \cdot g^{-1}$
1.	–	–	0.77
2.	1.0	1.77	1.71
3.	2.0	2.77	2.73
4.	3.0	3.77	3.90
5.	–	–	1.48
6.	–	–	1.89

this Table that the lead concentration in these samples varies from 0.7 to 2 $\mu g \cdot g^{-1}$.

The calibration curves were constructed by a similar treatment of samples containing from 0 to 12 ng lead. The relative standard deviation for 1 $\mu g \cdot g^{-1}$ is 4.8 %, for the lorandite samples, and 5.7 % for the marcasite samples. Applying the 2σ detection limit rule, a detection limit of 0.1 $\mu g \cdot g^{-1}$ is obtained.

Conclusion

Lead in lorandite and marcasite can be determined by electrothermal atomic absorption spectrometry. After the decomposition of the lorandite, thallium is extracted by isoamyl acetate, and then lead is extracted by sodium diethyldithiocarbamate in carbon tetrachloride. In the case of marcasite, iron is extracted by isoamyl acetate, and then lead is determined directly from the aqueous phase.

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