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DETERMINATION OF THALLIUM IN SOME SULFIDE MINERALS BY ZEEMAN  
ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

Trajče Stafilov and Anna Lazaru

Institute of Chemistry, Faculty of Science, University  
"St. Kiril and Metodij", POB 162, 91000 Skopje, Macedonia

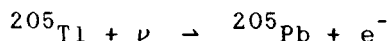
and Ernst Pernicka

Max-Planck Institut fur Kernphysik, P. fach 103980,  
6900 Heidelberg, Germany

Thallium was determined in arsenic (realgar and orpiment), antimony (stibnite) and iron (marcasite) sulfide minerals and dolomite by Zeeman electrothermal atomic absorption spectrometry. The extraction of thallium with isoamyl acetate in hydrochloric acid media was used. In the samples with higher iron concentration a correction for thallium was applied.

INTRODUCTION

The LOREX project is based on the idea that the mineral lorandite ( $TlAsS_2$ ) from Alshar deposit (Macedonia) could be used as a solar neutrino detector [1]. The aim of this project is to determine the content of  $^{205}Pb$  accumulated in the thallium minerals from Alshar, especially in lorandite, which is produced in the nuclear reaction between solar neutrinos and  $^{205}Tl$ :



Therefore, it is necessary to determine exactly the lead in thallium minerals [2,3], and also thallium content in non-thallium minerals present in Alshar deposit, such as: realgar ( $\text{As}_4\text{S}_4$ ), orpiment ( $\text{As}_2\text{S}_3$ ), stibnite ( $\text{Sb}_2\text{S}_3$ ), marcasite ( $\text{FeS}_2$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) etc.

There are a number of investigations concerning the determination of thallium in geological samples by electrothermal atomic absorption spectrometry (ETAAS). Some authors have investigated the determination of thallium directly from sample solutions [4-7]. In most cases the matrix interferences appeared. To overcome them the addition of different matrix modifiers such as ascorbic acid [8], EDTA [9], palladium and magnesium nitrate [10], or separation of thallium from the matrix were suggested. Separation methods used for thallium were adsorption of thallium complexes on activated carbon [11, 12] on polyurethane foam [13], on ion-exchanger [14], on cellulose [15], or extraction of thallium with different organic compounds, such as: iso-propyl ether [16], diethyldithiocarbamates in methylisobutyl ketone (MIBK) [17] or in toluene [18], brilliant green [19], MIBK [20,21], n-butyl acetate from HBr medium [22], trioctylmethyl ammonium ion [23,24] or trioctylphosphine oxide in MIBK [25].

There are no reports on the extraction of thallium from different minerals or geochemical samples with isoamyl acetate followed by the determination of thallium by ETAAS. In this work, a new procedure for determination of thallium by Zeeman ETAAS in different sulfide minerals (realgar, orpiment, stibnite, marcasite) and dolomite is suggested.

## EXPERIMENTAL

### Instrumentation

A Perkin-Elmer Zeeman 3030 atomic absorption spectrophotometer with HGA-600 and autosampler AS-60 was used. A thallium hollow cathode lamp was used. Pyrolytically coated graphite tubes with platform were used. Operation conditions

for thallium determination are given in Table I.

Table I

## Instrumental parameters

Wavelength	383.3 nm
Spectral band pass	0.7 nm
Lamp current	20 mA
Calibration mode	Absorbance, peak area
Background correction	Zeeman BG corrector
HGA-600	
DRY	
Temperature	120 °C
Time	30 s
Ramp time	1 s
CHAR	
I. Temperature	200 °C
Time	10 s
Ramp time	1 s
II. Temperature	350 °C
Time	30 s
Ramp time	1 s
ATOMIZE	
Temperature	2200 °C
Time	3 s
Ramp time	0 s
CLEAN	
Temperature	2650 °C
Time	3 s
Ramp time	1 s
GAS	Argon

## Procedures

### 1. Realgar and orpiment

0.1 to 0.2 g of powdered samples of realgar or orpiment were dissolved in 5 ml of concentrated  $\text{HNO}_3$ . The solution was evaporated to dryness. The residue was then dissolved in 10 ml of  $10 \text{ mol}\cdot\text{l}^{-1}$   $\text{HCl}$ . Few drops of  $\text{H}_2\text{O}_2$  were added and solution boiled for 5 minutes. Then, it was transferred to a separatory funnel. 10 ml of isoamyl acetate were added and the mixture was shaken for one minute. After the phases were separated the lower aqueous layer was transferred into a second separatory funnel and the extraction repeated with another 5 ml aliquot of isoamyl acetate. This operation was repeated once again. To the combined organic phase (20 ml) 0.5 ml of concentrated  $\text{H}_2\text{SO}_4$  was added. Thallium was determined in the organic phase by applying of 20  $\mu\text{l}$  of solution into a graphite furnace.

### 2. Stibnite and dolomite

0.1 to 0.2 g of powdered mineral samples were dissolved in 5 ml concentrated  $\text{HCl}$ , 1 ml of concentrated  $\text{HNO}_3$  and a few drops of  $\text{H}_2\text{O}_2$ . The solution was evaporated to dryness and the residue dissolved in 10 ml of  $10 \text{ mol}\cdot\text{l}^{-1}$   $\text{HCl}$ . Then the same procedure followed as in the case of realgar and orpiment.

### 3. Marcasite

The same procedure for the extraction of thallium from marcasite was applied as in the case of stibnite. The only difference was in the dissolving procedure, where 5 ml of concentrated  $\text{HCl}$  and 5 ml of concentrated  $\text{HNO}_3$  were added.

## RESULTS AND DISCUSSION

In most papers on the determination of thallium by ETAAS in different geological samples acid digestion is suggested for sample dissolution. However, these solutions contain different ions which may interfere in the determination of

thallium. Therefore, it is necessary to separate thallium from the matrix.

The interferences of matrix elements of the minerals studied (As, Sb, Fe, Ca and Mg) on the thallium determination were investigated. Series of solutions with the same concentration of thallium and different concentrations of interfering elements were prepared so that the concentrations of these elements were similar to the concentrations in the sample solutions. The results of these investigations are presented in Table II.

Table II  
Influence of As, Sb, Fe, Ca and Mg on thallium determination by ETAAS

Mass ratio $m_{Tl}:m_M$	Tl absorbance			
	M=As	M=Sb	M=Ca, Mg	M=Fe
1:0	0.0706	0.0706	0.0706	0.0706
1:10	0.0711	0.0703	0.0706	0.0711
1:50	0.0706	0.0703	0.0709	0.0709
1:100	0.0712	0.0703	0.0711	0.0709
1:500	0.0708	0.0701	0.0711	0.0711
1:1000	0.0703	0.0701	0.0713	0.0701
1:5000	0.0686	0.0670	0.0690	0.0930
1:10000	0.0660	0.0650	0.0687	0.1062

It is evident from Table II, that the interference effect of As, Sb, Ca and Mg on thallium determination are practically negligible while the influence of Fe is not, at lower Tl/Fe ratios. Expected mass ratios were in the order of 1:10000 or even less, so it was necessary to separate thallium from the other interferent elements.

In the case of solutions where As(V), Sb(V), Ca and Mg are present in higher concentrations, we attempted, to use

isoamyl acetate for thallium extraction from hydrochloric acid solution [26]. For this purpose, the first task was to determine the optimal concentration of HCl for this extraction. Solutions were prepared with different concentration of HCl and it was found that the highest efficiency of extraction (89%) was achieved at the concentration of  $10 \text{ mol}\cdot\text{l}^{-1}$  of HCl. To obtain 100% extraction of thallium it is necessary to repeat the procedure for 3 times.

We also found, that it is necessary to use matrix modifier [27] ( $\text{H}_2\text{SO}_4$  about  $0.5 \text{ mol}\cdot\text{l}^{-1}$  in the organic phase) in the determination of thallium by ETAAS.

To check whether As, Sb, and Ca coextract with Tl in isoamyl acetate, the analysis of As and Sb in organic phase, after the extraction of sample solution of realgar and stibnite, were made by neutron activation analysis. It was found that only 5-6% of all arsenic coextract in isoamyl acetate but 35-38% of the antimony. So arsenic interferences were expected to be negligible and interferences of antimony very small. Ca was determined by flame AAS after the evaporation and dissolution of residue. Only about 20% of Ca coextract in isoamyl acetate so its interference effects are not expected.

Iron is completely extracted together with thallium and the influence of Fe on Tl absorbance cannot be avoided by the procedure. To determine the influence of iron on the Tl absorbance a series of samples with different mass ratios of Tl and Fe were extracted and Tl was analyzed. It is evident from Fig. 1 that Tl absorbance is in linear relationship to the iron content in the sample:

$$m_{\text{Tl}}(\text{correct})/m_{\text{Tl}}(\text{found}) = -0.00001964 m_{\text{Fe}}/m_{\text{Tl}}(\text{found}) + 0.8064$$

where  $m$  is the mass (in  $\mu\text{g}$ ) of the particular element in the sample.

It follows that the exact value of Tl concentration can be calculated using:

$$m_{\text{Tl}}(\text{correct}) = -1.964 \cdot 10^{-5} \cdot m_{\text{Fe}} + 0.8064 \cdot m_{\text{Tl}}(\text{found})$$

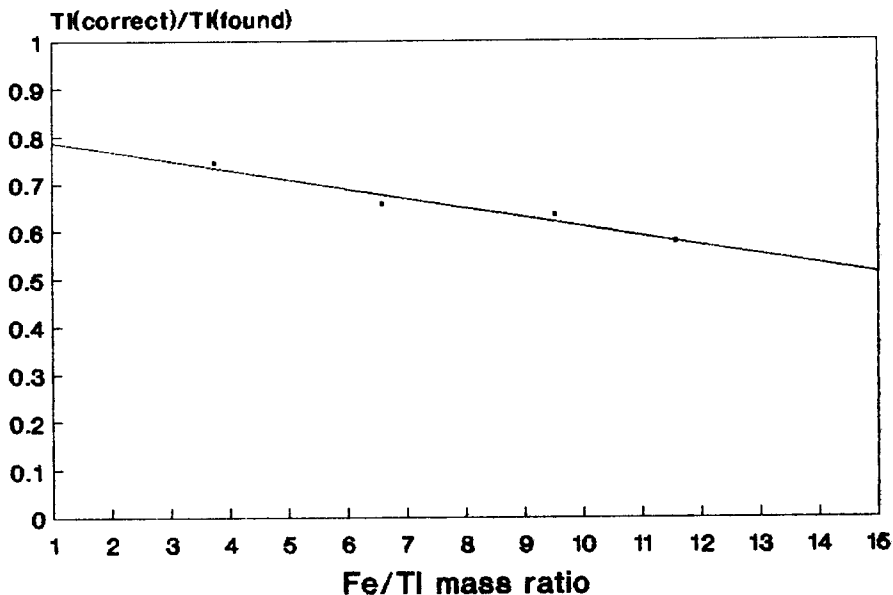


Fig. 1. The ratio of corrected and found content of thallium in dependence of iron/thallium mass ratio.

Using these procedures, some samples of realgar, orpiment, stibnite and dolomite (without and with standard additions) were dissolved, extracted and Tl was determined. The results are given in Table III. In the cases where single samples measured, the results are the mean values of three determinations. The results for dolomite in Table III are for two various samples.

One sample of marcasite was also analyzed and a reference standard sample (G-2) [28] with  $1.02 \pm 0.08 \mu\text{g g}^{-1}$  Tl and 1.87% of Fe. The measured values for Tl (three parallel determinations) were corrected for Fe content by the proposed equation. The results are presented in Table IV. It can be seen that Tl value, very similar to the recommended value for reference standard sample of G-2, is obtained.

Table III

The concentration of Tl in realgar, orpiment, stibnite and dolomite (in  $\mu\text{g g}^{-1}$ ), determined by ETAAS

Sample	Tl added	Tl calc.	Tl found	Recovery (%)
REALGAR				
	-	-	55.32	-
	8	63.32	62.29	98.29
	20	75.32	71.88	95.43
	40	95.32	89.40	93.79
ORPIMENT				
	-	-	92.85	-
	10	102.85	101.35	98.54
	25	117.85	119.00	100.97
	50	142.85	145.90	102.13
STIBNITE				
	-	-	27.90	-
	20	47.90	44.90	93.74
	50	77.90	74.80	96.02
DOLOMITE				
	-	-	27.80	-
			33.80	

Table IV

The concentration of Tl in marcasite and in reference standard sample G-2, determined by ETAAS

Sample mass (mg)	$m_{\text{Fe}}$ (mg)	Tl(measured) ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Tl(calculated) ( $\mu\text{g} \cdot \text{g}^{-1}$ )	Recommended value ( $\mu\text{g} \cdot \text{g}^{-1}$ )
MARCASITE				
93	44.2	58.9	46.6	-
G-2				
1000	18.7	1.68	0.988	1.02

A calibration curve (for organic solutions containing up to 20 ng Tl) was made using the proposed extraction procedure for standard solutions of thallium. The standard deviation (SD) for 1 ng Tl is 0.03. A relative standard deviation for this method is from 3 to 5,5%. The detection limit of the method, calculated as 3 SD of the blank, was found to be  $0.1 \mu\text{g} \cdot \text{g}^{-1}$ .

#### CONCLUSION

It was shown that isoamyl acetate can be successfully applied for thallium extraction from arsenic (realgar and orpiment), antimony (stibnite) and iron (marcasite) sulfide minerals as well as from dolomite. The method of Zeeman electrothermal atomic absorption spectrometry was used for determination of thallium. The extraction was performed in hydrochloric acid media ( $10 \text{ mol} \cdot \text{l}^{-1}$ ). When iron is present in high concentration (mass ratio of Tl/Fe higher than 1:5000), it was found that thallium absorbance is a linear function of the iron content. From the established relationship, the exact thallium concentration was calculated.

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