

**DETERMINATION OF THALLIUM IN ORE SAMPLES FROM ALLCHAR
BY ATOMIC ABSORPTION SPECTROMETRY**

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The concentration of thallium was determined in samples from the Allchar deposit by flame and flameless atomic absorption spectrometry. Interferences of various elements were investigated. A concentration of 10–2000 ppm was found in samples from Allchar ore.

1. Introduction

The presence of thallium in ore from the Allchar deposit was observed at the end of the 19th century. Its minerals were of great interest then [1,2] and are of considerable interest now.

There are a number of investigations concerning the determination of thallium in geologic samples by atomic absorption spectrometry. In such cases, of particular interest is the influence of interfering elements. In samples with very low content of Tl, thallium was first extracted from the samples and then its determination by flame [3–7] or by furnace [8–11] atomic absorption spectrometry can be performed. Other authors have investigated the possibility of the determination of thallium directly from sample solutions in flame [12–16] or by direct determination of solid samples in a graphite furnace [17–19].

There are no reports on the determination of thallium in an arsenic–antimony ore, such as the Allchar ore. In this work, the influence of all elements present in the ore matrix, using flame and furnace atomic absorption, were investigated. During this work a new method for determination of thallium by flame and furnace atomic absorption spectrometry is suggested.

2. Experimental*2.1. Instrumentation*

A Perkin–Elmer atomic absorption spectrophotometer Model 703 equipped with a deuterium background

corrector, an HGA-400 graphite furnace and a M-56 recorder were used. A thallium hollow lamp was used as a source. Background correction was applied throughout the course of analyses. For flame analysis a C₂H₂–air flame was used.

Conditions of operation for thallium determination were established by extensive testing and are summarized in table 1.

2.2. Reagent and samples

All reagents and standards were of analytical grade. A stock solution of thallium was prepared by dissolving thallium (I) nitrate in redistilled water. The concentration of thallium was 4,893 mol dm⁻³ and from this solution other diluted solutions were prepared.

Table 1
Instrumental parameters

Model 703	
Wavelength	276.8 nm
Spectral slit width	0.7 nm
Calibration mode	Absorbance, peak height
Background correction	Deuterium arc lamp
HGA-400	
Dry	120 °C, 30 s, ramp 2 s
Char	400 °C, 30 s, ramp 2 s
Atomize	1800 °C, 5 s, maximum power and miniflow mode
Cleaning	2700 °C, 3 s

The investigated ore samples are from the arsenic-antimony mine "Allchar", near Kavadarci, SR Macedonia, Yugoslavia.

2.3. Sample preparation and procedure

For better homogeneity, ore samples were crushed in a jaw crusher to 10 mm and in a cone crusher to 2–5 mm. After that a 100 g sample was ground in a vibratory mill to 0.074 mm particle size.

Different methods of sample decomposition were applied depending on the way of determination of thallium, flame (procedure A) or furnace atomic absorption spectrometry (procedures B and C). For samples with low concentrations of thallium, furnace atomic absorption was used and two methods for decomposition were tested: decomposition by HF under pressure in an autoclave (procedure B) and by HF in platinum or teflon vessel (procedure C).

Procedure A: 5 g of finely powdered ore sample were put into a glass beaker and were heated for 2 h at 450 °C to eliminate sulfur [20]. After heating, the sample was dissolved according to the method proposed by Tindall [21,22]. In the beaker, 25 cm³ conc. HCl was added and the solution was heated on a plate for about 15 min. Then, 15 cm³ conc. HNO₃ was added and heated for about 20 min. After that, 25 cm³ conc. HCl and 25 cm³ redistilled water were added and heated to remove nitrogen oxide vapours. Redistilled water was added, filtered and the filtrate was collected in a 100 cm³ volumetric flask. This solution is then ready for introduction into the flame.

Procedure B: A 0.2 g sample was taken and was heated for 2 h at 450 °C in a furnace. Then this sample was transferred to a teflon vessel and 1 cm³ conc. HCl, 0.5 cm³ conc. HNO₃ and 5 cm³ conc. HF were added.

The autoclave was heated for 1 h at 130–140 °C. Then the solution was collected in a 100 cm³ volumetric flask and filled with H₂SO₄ (1 + 20).

Procedure C: A 0.2 g sample was heated for 2 h at 450 °C. This sample was then transferred to a teflon or platinum vessel and 0.5 cm³ conc. HNO₃, 0.5 cm³ conc. H₂SO₄ and 5 cm³ conc. HF were added. The mixture was heated to dryness. 5 cm³ HCl (1 + 1) were added and collected in a 100 cm³ volumetric flask and filled with H₂SO₄ (1 + 20).

3. Results and discussion

3.1. Flame atomic absorption spectrometry

Tindall's method for decomposition of sulphide ore samples and determination of gold and silver by atomic absorption allow a great amount of sample and great concentration of these elements in solution. On the

Table 2
Average concentrations of thallium in some Allchar ore samples

Sample no	Tl [$\mu\text{g g}^{-1}$]
2	880 \pm 9 ^{a)} ; 872 \pm 6 ^{c)}
6	1970 \pm 15 ^{a)} ; 1850 \pm 20 ^{b)} ; 1890 \pm 9 ^{c)}
11	1150 \pm 10 ^{a)} ; 1300 \pm 20 ^{b)} ; 1170 \pm 17 ^{c)}
12	122 \pm 3 ^{a)} ; 125 \pm 4 ^{c)}
114	328 \pm 8 ^{a)} ; 316 \pm 5 ^{c)}
124	54 \pm 2 ^{a)} ; 55 \pm 1 ^{c)}
150	890 \pm 11 ^{a)} ; 965 \pm 6 ^{c)}
161	1070 \pm 13 ^{a)} ; 1120 \pm 22 ^{b)} ; 1050 \pm 10 ^{c)}

^{a)} Procedure A, flame AA

^{b)} Procedures B and C, flame AA.

^{c)} Procedures B and C, furnace AA.

other hand, some ore samples from Allchar have a relatively high concentration of thallium (table 2). In these cases the direct determination of thallium by flame atomic absorption from solution, without any preconcentration, is possible.

The background absorption and interferences of the present matrix could be a serious problem [13] especially in cases of samples with a great concentration of the matrix. Therefore, the interferences of elements which may influence the analysis of thallium have been investigated. For this investigation a series of solutions with the same concentration of thallium and a different concentration of the elements which are commonly present in Allchar ore samples (Sb, As, Ca, Mg, Al, Fe, Cu, Zn and Pb) were prepared. The solutions contained either a single element or a mixture of several interfering elements. Concentrations of these elements in the prepared solutions were similar to their concentration in ore samples. Interferences of present elements were determined by measuring the absorbance of thallium in a sample without any additions.

All measurements were performed with and without background correction. In case where the concentration of interfering elements was higher the background absorption was more evident so that it was necessary to use a background corrector.

The present matrix did not significantly influence the absorbance of thallium when the concentration of interfering elements in the matrix was up to 10 g dm⁻³ (procedure A). For thallium concentrations higher than 0.1% analytical procedures by atomic absorption according to procedures B and C were chosen. There are no interferences from the matrix on thallium absorbance. The lower limit of detection of thallium by procedure A is 10 $\mu\text{g g}^{-1}$.

The procedure for flame determination of thallium was checked by the method of additions. An exact amount of standard sample of thallium was added to the samples of ore prepared by procedure A and mea-

Table 3
Calculated and found concentrations of Tl ($\mu\text{g cm}^{-3}$) in sample solutions after adding a certain amount of standard solution of thallium

Sample no.	Concentration of Tl [$\mu\text{g cm}^{-3}$]	Added mass of Tl [μg]	New concentration of Tl	
			Calculated	Found
2	88.00	200	88.94	88.20
114	32.80	200	44.00	43.60
124	5.38	200	21.15	20.38
150	89.05	200	90.87	91.36

surement of absorbance of thallium was performed. Results are shown in table 3.

3.2. Furnace atomic absorption spectrometry

For the determination of low contents of thallium by furnace atomic absorption spectrometry, extraction of thallium is usually used (isopropil ether [8], brilliant green [9] or iso-BuCOMe [11]).

However, since the concentration of thallium in ore samples from Allchar is above $1 \mu\text{g g}^{-1}$ (table 2) there is the possibility of direct determination from the solution by graphite furnace. Decomposition of samples is possible by one of the methods B or C. In both cases the presence of matrix elements which could interfere with thallium absorption is very small. The influence of the matrix was investigated by a determination of the absorbance of thallium in a series of solutions where the concentration of thallium was the same and the concentration of the interfering elements was changed. Concentrations of these elements were limited by their presence in the ore. It was established that, even when the concentration of elements present is too high (up to 30% in the ore samples), there was no interference. Background absorption was present and it is necessary to apply background corrections. This method was also checked by the method of additions.

We confirmed Fuller's results [16] that the highest absorbance of thallium by furnace atomic absorption is obtained in the presence of sulfuric acid and therefore

all samples and standard solutions were complemented with sulfuric acid (1 + 20).

The lower limit for the thallium determination by these procedures and furnace atomic absorption is $1 \mu\text{g g}^{-1}$. Operation conditions for the determination of thallium were found by extensive testing and measuring of the absorbance of thallium in the samples with the same mass of thallium and by changing the temperature and the time. These values are given in table 1.

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