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DETERMINATION OF THALLIUM IN GEOLOGICAL SAMPLES BY ZEEMAN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Abstract

Thallium is a rare element, present in the earth crust below 1 ppm. During the weathering processes it is accumulated in sediments and soils where, furthermore, its content is increased as a result of human activity.

Besides the low abundance of thallium and its limited application, analysis of this element is important task due to the high toxicity of thallium compounds. On the territory of the Republic of Macedonia there are several thallium contamination sources: zinc and lead mines "Sasa” and "Toranica", zinc and lead metallurgical plant “Zletovo”, ferromanganese metallurgical plant “RZ Topilnica”, coal burning power plant “REK Bitola” and

cement factory “Usje”. A particularly geochemical, physical and analytical interest has a polymetallic sulfide deposit in region known as Allchar, on Mount Kozuf in R. Macedonia, rich with thallium minerals.

From these reasons, a method for thallium determination in geological and soil samples by electrothermal atomic absorption (ETAAS) was developed. Different procedures for sample decomposition have been examined for obtaining reliable results. Several ammonium salts as chemical modifiers have also been applied for stabilization of thallium species in graphite atomizer. The limit of thallium determination by this method was 0.1 μg/g Tl.

INTRODUCTION

Thallium is abundant in the Earth's crust at concentrations estimated to be about 0.1 ppm in ultrabasic rocks to 1.5 ppm in acid rock [1], and mainly occurs in association with potassium minerals in clays, soils and granites. Thallium minerals occur in nature as sulfide or selenide complexes with arsenic, antimony, copper, lead and zinc [2]. From the sulfide minerals thallium can be easily released during weathering, but its great ionic radius cause its fast fixation by hydroxides of Fe and Mn [3, 4], and by clay minerals [5].

In the Republic of Macedonia, in region known as Allchar mine on Mount Kozuf, uniquely polymetallic sulfide deposit of antimony, arsenic, thallium, gold and silver is situated. This region belongs to the large Vardar geotonic zone, and is mainly built up of triassic marbled limestones and other sedimentary rocks. The Kozuf metallogenic province contains copper-polymetallic mineralization in the central zone, lead-zinc and gold-silver in the middle and ore mineralization of antimony, arsenic and thallium (Allchar). Allchar polymetallic mineralization was formed as a result of low temperature hydrothermal deposit. Mainly antimony-realgar mineralization with marcasite and gold in sulfide parts lies in the southern part of deposit, while realgar-orpiment mineralization with large contents of thallium minerals prevail in the northern part [4, 6-8].

Thallium is an incredibly destructive poison, affecting many organs and the neural systems of body and is therefore of considerable analytical interest, particularly in the biological and environmental samples. Poisoning may occur due to the absorption of thallium after inhalation of dust or fume or as a result of skin contact and by consummation of contaminated food. The natural abundance of thallium in cultivated soils is below 1 μg/g [9], but thallium compounds can occurs in environmental as a result of atmospheric pollution. The main sources of contamination are ash from coal burning power plants, dust and gaseous from copper, lead and zinc metallurgical plants and cement industry.

From 1912 to 1930, thallium compounds were used extensively for medicinal purposes (e.g., in the treatment of dysentery and tuberculosis). The use of thallium salts as poison for rodents and later as insecticide led to increased use of thallium from 1925 to 1965. Significant quantities of the rodenticide were used in the period from 1959 to 1973. World production of thallium is only a few tons per year.

Thallium can be measured in geological samples at very low concentration by DC arc emission spectrometry [10], instrumental neutron activation analysis [11, 12], ICP-AES, ICP-MS [13], laser-excited atomic fluorescence spectrometry [14], differential pulse anodic stripping voltametry [15] and other methods.

Electrothermal atomic absorption spectrometry is a widely accepted method for the determination of trace thallium. Some authors have investigated the possibility of the determination of thallium directly from sample solutions [16-21] or by direct determination of solid samples in a graphite furnace [22-24]. In most cases the matrix interferences appeared. To overcome them the addition of different matrix modifiers such as ascorbic acid [25], EDTA [26], palladium and magnesium nitrate [27], or separation of thallium from the matrix were suggested. Separation methods used for thallium were adsorption of thallium complexes on activated carbon [28, 29], on ion-exchanger [30], on cellulose [31], or extraction of thallium with different organic compounds [32-45].

In this work, a method for thallium determination by ETAAS in geological samples using different matrix modifiers is presented.

EXPERIMENTAL

Instrumentation

The studies were carried out using a Varian SpectrAA 640Z atomic absorption spectrometer, equipped with a GTA-100 graphite tube atomizer, a transversally mounted Zeeman background corrector and a programmable sample dispenser PSD-100. Pyrolytically coated graphite tubes were used. The main instrumental parameters and the optimized heating program for graphite atomizer are given in Table 1.

Reagents and samples

All reagents were of analytical grade. Before use, reagents were check for thallium content by ETAAS. Stock solution of thallium was prepared by dilution of commercially standard solution of $TlNO_3$ (MERCK, Darmstadt) with distilled water.

Geological samples, samples of minerals and ores were taken from different regions of Republic of Macedonia. All samples, crushed previously to size ≤10 mm, were finally milled to a size ≤0.01 mm.

Table 1. Instrumental parameters for thallium determination by Varian 640 Z ETAAS

<table>
<tr><td colspan="4">Optical parameters</td></tr>
<tr><td colspan="2">Monochromator</td><td colspan="2">Czerny-Turner, 0.25 m</td></tr>
<tr><td colspan="2">Background corrector</td><td colspan="2">Transverse mounted Zeeman corrector</td></tr>
<tr><td colspan="2">Wavelength</td><td colspan="2">176.8 nm</td></tr>
<tr><td colspan="2">Lamp current</td><td colspan="2">4.5 mA</td></tr>
<tr><td colspan="2">Spectral width slit</td><td colspan="2">0.5</td></tr>
<tr><td colspan="2">Measurement mode</td><td colspan="2">Peak height</td></tr>
<tr><td colspan="4">Sample aliquots</td></tr>
<tr><td colspan="2">Sample solution volume</td><td colspan="2">15 µL</td></tr>
<tr><td colspan="2">Modifier solution volume</td><td colspan="2">5 µL</td></tr>
<tr><td colspan="2">Total injected volume</td><td colspan="2">25 µL</td></tr>
<tr><td colspan="4">Furnace parameters</td></tr>
<tr><td>Step</td><td>Temperature, °C</td><td>Time, s</td><td>Argon flow, L/min</td></tr>
<tr><td>0</td><td>50*</td><td>-</td><td>-</td></tr>
<tr><td>1</td><td>85</td><td>10</td><td>1</td></tr>
<tr><td>2</td><td>95</td><td>30</td><td>1</td></tr>
<tr><td>3</td><td>120</td><td>10</td><td>2</td></tr>
<tr><td>4</td><td>700</td><td>20</td><td>3</td></tr>
<tr><td>5</td><td>700</td><td>5</td><td>1</td></tr>
<tr><td>6</td><td>700</td><td>1</td><td>0</td></tr>
<tr><td>7</td><td>2200</td><td>1</td><td>0</td></tr>
<tr><td>8</td><td>2200</td><td>2</td><td>0</td></tr>
<tr><td>9</td><td>2400</td><td>2</td><td>3</td></tr>
</table>

* Temperature of graphite tube before the aliquot injection

Sample decomposition

The sample preparation step is frequently the major source of error in geochemical analysis of trace constituents [46]. In the last several years, the most widely used method for decomposition of geological and inorganic materials becomes digestion with strong acids (HCl, Aqua regia, HF) in PTFE bomb with conventional heating or in microwave oven. But, for many types of geochemical matrices, fusion with alkali flux (carbonates, borates) is necessary.

In our examination, both the acid dissolution and the fusion with carbonate or borate flux were employed. The main problem in the course of the sample preparation for determination of thallium is volatility of its compounds (which appears if the fusion methods are applied), and interference of some anions (phosphate, sulfate or chloride) in the atomization stage (if corresponding acid were used for dissolution). Volatility of thallium was suppressed by using a flux with a strong oxidizing agent (V_2O_5, KNO_3, MnO_2 etc.) [47].

Silicate samples and soils. Due to the strong influence of the chloride ions on the behavior of thallium in graphite atomizer, HCl was excluded from the acid mixture for dissolution. Dissolution was performed by nitric acid. Sodium fluoride or hydrofluoric acid can be added in the course of dissolution because fluorides, for distinction of chlorides, don’t give molecular absorption bands [48]. From the other side, nitric acid has a relatively low efficiency in the decomposition of a silicate matrix, so that a relative large insoluble residue is remained after the acid dissolution. Due to this reason, insoluble residue was fused with sodium carbonate and potassium nitrate (in ratio 10:1). For prevention of the loss of thallium during the ashing of the filter paper, it was decomposed at low temperature by heating with concentrated nitric acid into the platinum crucible. Excess of the acid was expelled and residue was fused with the mentioned flux. Flux with a mass of 2 g was enough for decomposition of residues, remained after the acid dissolution of 1 g sample.

If the relative large insoluble residue remained after the acid decomposition, sample was fused directly, without acid attack.

Iron and manganese ores. Some types of iron and manganese ores (siderite, limonite, rodohrosite), with a low content of silica (below 5 %) were decomposed only by the dissolution in concentrated nitric acid. Samples of the other types of Fe and Mn ores, due to the difficult decomposition by HNO_3, were fused by sodium carbonate and potassium nitrate (mass ratio 10:1) (Fe ores) or lithium tetraborate and V_2O_5 (mass ratio 10:1) (Mn ores).

Zinc, lead and copper minerals and ores. Zinc, lead and copper ores were treated previously by dilute nitric acid (1:1). Insoluble residue was decomposed by fusion with mixture of lithium tetraborate and V_2O_5 (mass ratio 10:1) [49]. After the fusion at 1000 °C, the molten mass was dissolved in diluted nitric acid (1:1), and the solutions were collected into 200 mL volumetric flask (2.000 g sample weight). In the case of sample weight of 2.000 g and 5 g of flux were used, amounts of salts, injected into graphite atomizer, don't exceed 500 μg (aliquot of 0.15 μL).

Arsenic and antimony minerals. Geological samples, taken from the mentioned Allchar deposit, were decomposed by dissolution in nitric acid (1:2). Usually, only an elementary sulfur was remained after the acid attack of arsenic and antimony sulfide minerals.

Procedures

Procedure A (acid dissolution): Heat the sample (mass of 2.5000 g) with HNO_3 (volume of 50 mL, c = 14 mol/dm^3) in a glass beaker. Periodically, add nitric acid to keep the solution volume in the glass near to the start volume. After 2-3 hours, evaporate solution to the dryness and keep the beaker at 120-140 ^{o}C for one hour. Add 15 mL diluted HNO_3 (1:3), heat and filter through filter paper (“white band”). Wash the silica with diluted nitric acid (2 %) and collect the solutions into a 250 mL volumetric flask. Diluted to the mark with distilled water.

Procedure B (combination of acid dissolution and fusion): If the precipitate, obtained after acid dissolution, is dark or gray, transfer the filter into a platinum crucible, dry at 120 ^{o}C, and decompose by heating with concentrated nitric acid. After a drying, add 1-2 g mixture of sodium carbonate and potassium nitrate (10:1) into a crucible. Fuse the mass at a temperature of 950-1000 ^{o}C for a short time (7-8 minutes). After a cooling, dissolve the molten mass in diluted nitric acid (1:2). Collect the solutions into a volumetric flask of 200 or 250 mL.

Procedure C (direct fusion): If the sample is difficulty soluble in acid or acid mixture (*Procedure 1*), fusion with suitable flux is used. Mixture of sodium carbonate or lithium tetraborate with a strong oxidizing agent (KNO_3 or V_2O_5) (mass ratio 10:1) is enough efficient for decomposition of most of geological samples.

Place a part of the flux into a platinum crucible, add a mixture of sample and oxidizing agent and cover by the rest of the flux. After the fusion, dissolve the fused mass in diluted nitric acid (1:2) and transfer into a volumetric flask.

Procedure D (dissolution in HCl or acid mixture containing HCl): If the sample contain a large amount of thallium (>1µg/g), hydrochloric acid can be used for dissolution alone or in mixture with nitric acid (aqua regia). After the complete decomposition of the sample, expel an excess of acid(s), add a 20 mL of HNO_3 (14 mol/dm^3) and evaporated again. Dissolve a residue in diluted nitric acid, transfer into a volumetric flask and fill to the mark by distilled water.

It this method of dissolving is used, a solution of chemical modifier (1 g ammonium sulfate and 1 mL H_2SO_4 in 100 mL distilled water) must be added for suppression of the interference of non removed chloride anions. This method of dissolution can’t be used if the thallium content is below 10 μg/g.

RESULTS AND DISCUSSION

The behavior of thallium species in the both thermal stages, pyrolyse and atomization, depends on the several factors: types of the thallium species obtained on the furnace wall after the drying stage and in the pyrolysis stage; type of the matrix constituents; the temperature gradient in the pyrolysis and in the atomization stage; presence of modifier(s); condition of the graphite tube wall.

Drying step

Many analysts don’t dedicate enough attention to the first temperature step - drying of the injected solution. Correctly chosen temperature gradient in this step significantly influence on the reproducibility of analytical results. For the reduction of penetration of solution into a graphite tube wall, pre-heating of tube is necessary. Our examination was shown that an injection into a tube, preheated at 50 °C, gives satisfactory reproducible results. Slow evaporation of injected solution lead to smaller salt crystals and uniform behavior in pyrolysis step. A temperature program in drying step was selected for injected volume of 25 μL (Table 1). For smaller volumes (15 -20 μL), the time of heating may to be shorter. The final temperature and the temperature gradient in this stage depend, also, from the acid(s) present in the injected solution. If sulfuric acid is used in dissolution process or added as a modifier, appropriate temperature step (120 - 350 °C) must be inserted for expelling the acid fumes.

Pyrolysis step

Because only an inorganic matrix is present in the atomizer on the occasion of analysis of geological samples (excluding a small quantity of organic materials present in the soil samples), pyrolysis step must ensures only decomposition of the present salts: nitrates, or nitrates and borates in case of fusion was used. Nitrates of the usually matrices decomposed between 100 °C ($Fe(NO_3)_3$, $Mn(NO_3)_2$) and 600 °C ($Sr(NO_3)_2$, $LiNO_3$). Temperature higher then 550 °C must be applied for decomposition of nitrates of Ca, Sr, Pb (analysis of carbonate samples, galena etc.). It must keep accounts that thallium nitrate decomposed above 430 °C. Prolonged heating at 700 °C or higher temperature must be used for completely decomposition of nitrates. In any case, appropriate modifier must be added for prevention of loss of thallium species.

Borate matrix has a high melting point (>700 °C), and in this case the pyrolysis step must be finished at higher temperature, 900 or 1000 °C, for decomposition of different forms of borate compounds to B_2O_3.

Atomization step

Choice of an appropriate atomization temperature is not so critical as a choice of the previously temperature step. Thallium can be efficiency atomized at a temperature above 1800 °C. Our investigation was shown that, in the case of a type of graphite atomizer which is used in Varian's atomic absorption spectrometers, temperature gradient in the atomization step of 1000 °C/s is enough for obtaining a regular and sharp thallium absorption signals.

Effect of chemical modifiers on the thallium absorption signal

Many modifiers were examined in ETAAS determination of thallium [50]. Our attention was focused on different ammonium salts with oxidizing characteristic. Efficiency of examined modifiers is presented in Table 2. All used modifiers don't change the analytical signal of thallium, and don't increase background signal.

Table 2. Maximum pyrolysis temperature, achieved in presence of different ammonium salts

Modifier	Maximum pyrolysis temperature (°C)
Ammonium nitrate	1000
Ammonium molybdate	700
Ammonium vanadate	1000
Ammonium dichromate	1200
Ammonium cerium sulfate	700
Sulfuric acid	650
Ammonium molybdate + sulfuric acid	900

Ammonium molybdate as a chemical modifier. In the pyrolysis stage, ammonium molybdate decomposes to different molybdenum oxides. Thallium species are incorporated into this molten product of decomposition and rest in the graphite tube up to 700 ^{o}C. Ammonium molybdate is a very efficient for many matrixes (for example, phosphate, halogenide etc.). Absorption signal of thallium is sharp and regular. In presence of large amount of chlorides (≥1 % NaCl, LiCl), H_2SO_4 must be added to prevent a loss of thallium prior the decomposition of ammonium molybdate (Fig. 1).

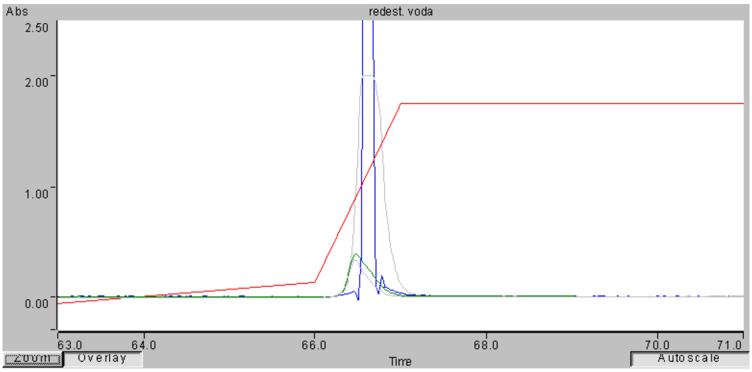

Fig. 1. Tl absorption signals, obtained from chloride solution (1 % NaCl) in absence (1) (nonregular signal) and in presence (2) of ammonium molybdate as a modifier

Ammonium nitrate and ammonium sulfate as modifiers. Ammonium nitrate and ammonium sulfate are good modifiers for inorganic matrix, except in presence of high concentration of alkaline halogenides (e.g., above 5 g/L sodium chloride, these modifiers are not enough efficient). If the temperature gradient in ashing stage is enough small (below 20 ^{o}C/min), ammonium sulfate may expel a large part of chloride matrix. These modifiers aren’t efficient in presence of phosphate or perchlorate matrix. Maximum ashing temperature in presence of ammonium nitrate is 1000 ^{o}C. Absorbance signal of thallium is the same as a signal of thallium from a pure solution of thallium nitrate, while the background signal is low.

Ammonium dichromate as a modifier. Ammonium dichromate can't prevent a loss of thallium in presence of halogenides (especially alkaline halogenides). But, in other matrix, this modifier is very efficient. Pyrolysis temperature can be increased up to 1200 ^{o}C, while the intensity of analytical signal is constant in atomization stage up to 2700 ^{o}C. Absorbance signal is a more extended in comparison with absorption signals in presence of other modifiers, Fig. 2. A negative aspect of usage of ammonium dichromate is contamination of graphite parts of atomizer, which influence on the reproducibility and the detection limit of chromium analyze by the same instrument.

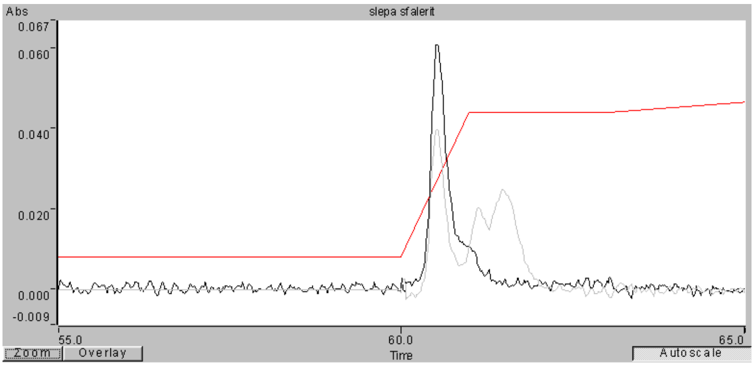

Fig. 2. Thallium absorption signal, obtained in the course of analysis of contaminated soil (Veles region) in presence of ammonium dichromate as a modifier

Ammonium vanadate as a modifier. Ammonium vanadate is a good modifier for different matrix (phosphate, perchlorate etc.), but not for the chloride matrix. In presence of ammonium vanadate, pyrolysis temperature can be extended up to 1000 °C. Absorbance of thallium is constant within the temperature interval of atomization from 1800 to 2700 °C. This modifier is suitable for determination of trace thallium (Fig. 3).

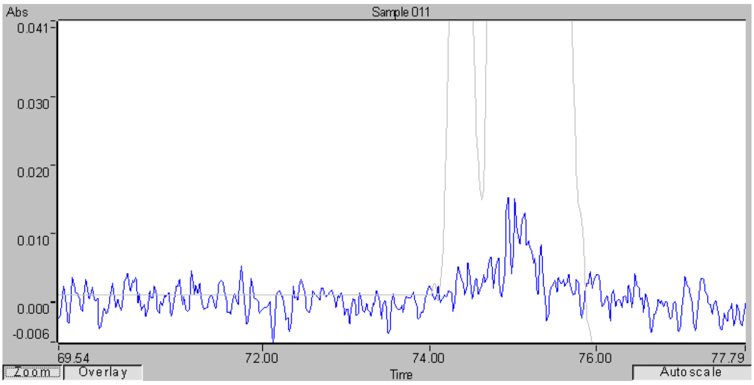

Fig. 3. Thallium absorption signal obtained in the course of analysis of limonite iron ore, in a presence of ammonium vanadate as a modifier

In the presence of alkaline chlorides, ammonium vanadate isn't enough efficient. For other matrix, analytical signal of thallium in presence of vanadate is regular, while the background signal, produced by the modifier, is low.

Results for thallium content, obtained for some geological samples, are presented in Table 3. As it can be seen, very high content of thallium is present in minerals from thallium minerals rich Allchar mine and from soil samples taken near lead and zinc smelting plant near Veles City.

Table 3. Content of thallium in some type of geological samples, taken from the territory of Republic of Macedonia (LOD = 0.1 μg/g).

Sample	Tl content, μg/g
Manganese ore (Mountain Stogovo)	0.4-0.6
Copper ore (chalkopyrite, Bucim)	1.0
Iron ore (hematite, Damjan)	<LOD
Iron ore (limonite, Pehcevo)	0.2
Lead ore (galena, Sasa)	1.4
Lead&zinc ore (Toranica)	2.6
Realgar (Allchar mine)	55.3
Orpiment (Allchar mine)	92.8
Stibnite (Allchar mine)	27.9
Dolomite (Allchar mine)	27.8
Marcasite (Allchar mine)	46.6
Marble (Prilep)	<LOD
Lime (Ograzden)	<LOD
Soil (Skopje region)	0.25
Soil (Bitola region)	0.2
Soil (Ohrid region)	<LOD
Soil (Veles region, near zinc&lead smelter)	20-50

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