

## Determination of Antimony and Bismuth in Technogenic Raw Materials

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**Abstract**—The paper describes determination of antimony and bismuth in the metal-containing technogenic raw materials by atomic absorption spectrometry with electrothermal atomization (AAS with ETA). To improve the metrological characteristics, we used modification of the graphite furnace by complex compounds of precious metals and in some cases separation and concentration of antimony and bismuth by N,S-containing heterochain polymeric sorbents.

**Keywords:** determination, antimony, bismuth, atomic absorption spectrometry with electrothermal atomization, technogenic raw materials, precious metals, sorption concentration, sorbents

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Determination of volatile toxic elements such as Sb and Bi in technogenic raw materials and objects in the environment is a problem of current interest. These elements are common and dangerous toxicants with a high degree of negative impact on people and the environment in which they fall from release of dust and gaseous waste of chemical and other industrial plants. Methodological support of control of antimony and bismuth emissions in the atmosphere requires use of highly sensitive methods of analysis. The problem of determining these and other toxic elements becomes even more important in connection with the publication of the Russian Federation Government Resolution no. 442 On the Transboundary Movement of Waste of July 17, 2003; no. 718 On Customs Tariff of the Russian Federation and the Commodity Nomenclature Applied in Implementation of Foreign-Economic Activity of November 27, 2006; and no. 78 On Amendments to Certain Acts of the Russian Government on the Implementation of Certain Powers of the Ministry of Natural Resources and Ecology of the Russian Federation and the Federal Service for Ecological, Technological, and Nuclear Supervision of February 15, 2011. Any movements of waste across the border should be controlled for the presence of these dangerous elements.

The study was carried out using samples of industrial raw materials containing antimony and bismuth selected on the territories of JSC "ELECTROZINC" and North Ossetia-Alania (Vladikavkaz). Samples were taken from the plant dumps containing products of processing of lead-zinc ores of the Sadonsk lead-zinc plant.

To determine the valuable and hazardous components of wastes (iron, manganese, copper, arsenic, lead, bismuth, silver, antimony, chromium, and zinc), several methods are used, the most popular of which is atomic absorption with electrothermal atomization (AAS-ETA) [1–4]. When determining antimony, bismuth and other volatile components by this method, chemical modification of graphite furnaces is needed in order to prevent loss of the analyte. There are various methods of applying a modifier to the cell surface [5].

The purpose of this study is to find approaches that allow one to minimize errors in the final stage of the analysis and obtain reliable results in determination of antimony and bismuth by atomic absorption spectrometry with electrothermal atomization in metal-containing technogenic raw materials.

Measurements were performed on an atomic absorption spectrometer (PerkinElmer, model Zeeman-3030) with an AS-60 automatic sample supply, graphite atomizer, and background correction based on the Zeeman effect. Graphite cells without pyrolytic coating and hollow cathode lamps were used. Argon was used as an inert gas.

Selection of analytical lines for atomic absorption determination of antimony and bismuth was performed. It was found that the lines at 231.1 nm for antimony and 223.1 nm for bismuth have the highest intensity and the best signal/noise ratio. The main problem in determination of Sb and Bi by the AAS-ETA method is high volatility of elements and their compounds, so thermal stabilization in the preliminary

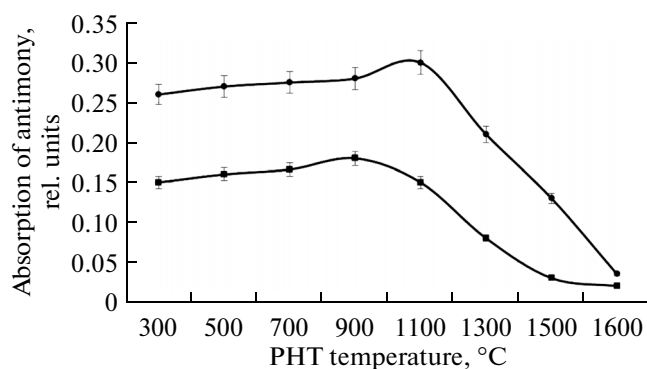


Fig. 1. Dependence of absorption of antimony on PHT temperature: (●) Rh modifier; (■) without modifier.

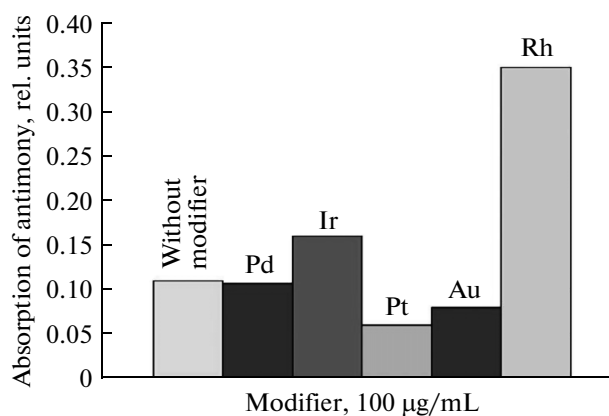


Fig. 2. Effect of different modifiers on absorption of antimony.

heat treatment by adjusting the temperature–time modes and use of modifiers is needed.

A properly selected temperature–time mode makes it possible to eliminate partially before the stage of atomization the matrix influence without loss of the analyte and to determine low contents of trace elements in matrices of complex composition.

The most important is the stage of preliminary heat treatment (PHT), the purpose of which is to remove most of the base with preservation of the assayed element within the atomizer in a stable form for atomization to proceed with minimal interference of the base.

The most suitable temperature of the PHT stage for antimony using a rhodium modifier is 1100°C (Fig. 1). Without the addition of the modifier, the PHT temperature is lower, namely, 900°C. The optimum temperature of PHT stage for bismuth is 600°C. Addition of a palladium-containing modifier allows one to increase this value to 800°C and increase the absorption signal.

The program chosen for atomic absorption determination of antimony and bismuth is shown in Table 1.

To achieve the maximum sensitivity of determination at the atomization stage, we reduced the flow of inert (shielding) gas from 300 to 30 mL/min for antimony and 100 mL/min for bismuth.

In order to select the most effective modifier, we studied the impact of salts of platinum metals on the absorption signal of Bi and Sb solution, such as Pd, Pt, Rh, Ir and Au, with a concentration of 100 µg/mL (mass of modifier was 2 µg). Rhodium has the biggest influence on the absorption of antimony, and palladium has the biggest influence on the absorption of bismuth (Figs. 2, 3).

To improve reproducibility, reduce the influence of the sample base, and shorten the analysis time, it is advisable to use a permanent modifier.

Using model solutions, we studied the effect of copper and other elements of the base (nickel, iron, cobalt, and lead) on the absorption signal of antimony and bismuth (Figs. 4, 5).

Absorption of Sb gradually decreases with increasing concentration of copper, nickel, iron, and cobalt, and lead, on the other hand, slightly increases the signal of antimony. The value of Bi absorbance gradually decreases with increasing concentration of copper, nickel, iron, and lead, while cobalt slightly increases the signal of bismuth. Therefore, in the analysis of real-world objects of technogenic raw materials with unknown content of interfering elements, separation

Table 1. Conditions of atomic absorption determination of antimony and bismuth

Stage	$T$ , °C		Heating time, s		Dwell time, s	Gas flow rate, mL/min	
	Sb	Bi	Sb	Bi		Sb	Bi
Drying	100	100	5	5	5	300	300
PHT*	1100	800	8	5	5	300	300
Atomization	2400	1800	1	1	4	30	100
Annealing	2600	2500	1	1	2	300	300
Returning to normal conditions	20	20	1	1	15	300	300

\* PHT temperature depends on the presence of modifier and the method of its introduction.

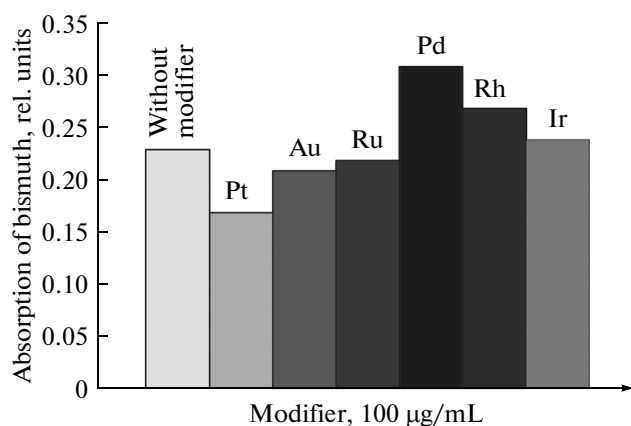


Fig. 3. Effect of different modifiers on absorption of bismuth.

and in some cases concentration of antimony and bismuth are necessary.

Preliminary sorption concentration is carried out if it is necessary to eliminate the effects of the sample base. In order to do so, 10 mL of sample solution is injected into a flask with a volume of 100–200 mL, the volume is adjusted to 0.1 M HCl, and 0.1–0.2 g of N,S-containing heterochain sorbent Diasorb is added. Sorption is carried for 45 minutes under heating to 80°C. The solution with sediment is cooled and the sediment (sorption concentrate) is separated by filtration through a White Ribbon ashless filter. The sediment is washed with hydrochloric acid (1 : 9) and water. The concentrate is then dissolved by heating in 5–10 mL of concentrated nitric acid, transferred into a flask with a volume of 100 mL, and adjusted to the mark by dilute nitric acid (1 : 12). Dilution of samples of technogenic raw materials, if necessary, is performed with hydrochloric acid solution (1 : 5).

A graphite cell without pyrolytic coating is used. The current of the hollow cathode lamp is set in the

Table 2. Validation of the developed methods using the “introduced–found” method

Sb		Bi	
introduced, µg	found, µg	introduced, µg	found, µg
5.00	4.97 ± 0.35	10.00	9.76 ± 0.47
10.00	9.95 ± 0.69	15.00	14.88 ± 0.65
12.50	12.48 ± 0.78	20.00	20.23 ± 0.76

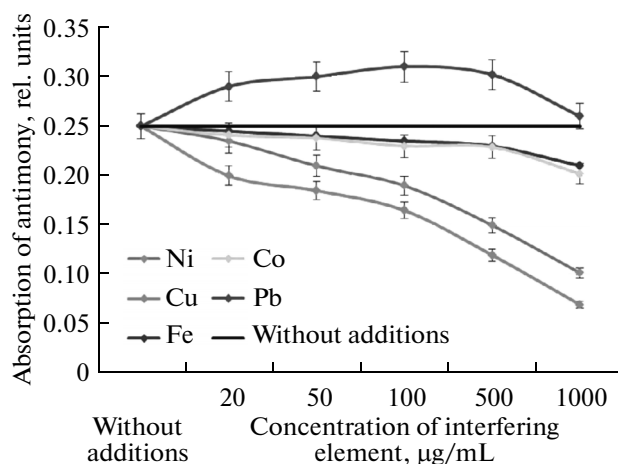


Fig. 4. Effect of Cu, Ni, Fe, Co, and Pb on analytical signal of antimony.

range of 8–10 µA. Either an aliquot of modifier of 20 µL is added simultaneously with the sample or modified cells are used. To apply a permanent modifier, the graphite cell without pyrolytic coating is treated with a mixture of nitric and hydrochloric acid (1 : 3), washed thoroughly with distilled water, and dried to remove moisture. The bottom of the cell is closed with a stopper, a Teflon bandage is put on the slot for injection of the sample, and then the cell is positioned into a holder. Then 2 mL of electrolyte is poured into the cell. A solution of standard sample of palladium or rhodium in sulfuric acid (1 : 5) may be used as electrolyte. Aluminum wire that is attached to the outer surface of the graphite cell is dipped into the solution of electrolyte. After completion of the reaction (electrolysis), the aluminum electrode is removed from the cell, washed with hydrochloric acid (1 : 5) and distilled water, and then dried. During electrolysis (10–15 min) on the inner surface of the cell, at least 60 µg of metal is precipitated out.

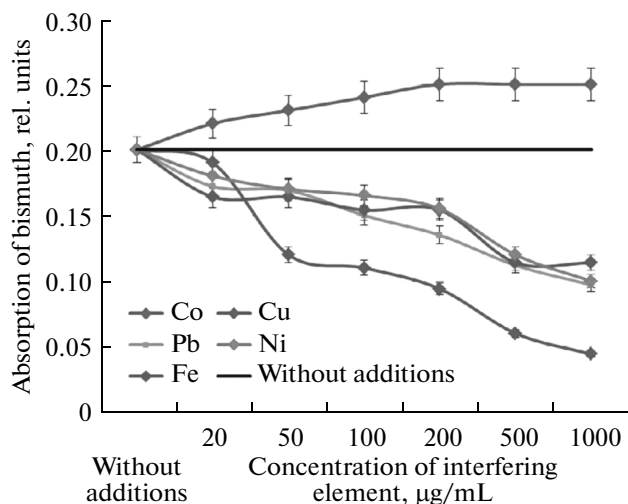
Further solutions of analyzed samples are successively introduced into a graphite cell (aliquot of 20 µL), each time heating the furnace according to a predetermined program and measuring the atomic absorption of the assayed element. For each of the solutions of the analyzed sample, at least two parallel measurements are carried out.

The correctness of the developed methods was assessed by the “introduced–found” method and by comparing the results with those obtained by atomic emission spectrometry with inductively coupled plasma (AES-ICP) (Tables 2, 3).

Thus, methods of atomic absorption determination of antimony and bismuth in samples of technogenic metal-containing raw materials using an electrothermal atomizer were developed. Instrumental methods of accounting for the background were studied (background correction on the basis of the Zeeman effect,

**Table 3.** Validation of the developed methods by comparison with results of AAS-ETA determination

Sample	Sb		Bi	
	AAS-ETA, $\mu\text{g/mL}$	AES-ICP, $\mu\text{g/mL}$	AAS-ETA, $\mu\text{g/mL}$	AES-ICP, $\mu\text{g/mL}$
1	$0.0100 \pm 0.0004$	$0.0090 \pm 0.0007$	$0.0120 \pm 0.0005$	$0.0110 \pm 0.0008$
2	$0.0150 \pm 0.0006$	$0.0160 \pm 0.0011$	$0.0650 \pm 0.0007$	$0.0640 \pm 0.0013$
3	$0.1330 \pm 0.0008$	$0.1320 \pm 0.0015$	$0.1160 \pm 0.0009$	$0.1170 \pm 0.0019$

**Fig. 5.** Effect of Cu, Ni, Fe, Co, and Pb on analytical signal of bismuth.

selection of temperature and time parameters of the graphite furnace heating, etc.), as well as the possibility of using different modifiers. The interval of assayed content of antimony and bismuth was from 0.05 to 0.5  $\mu\text{g/mL}$ . Validation of the procedures was performed by comparing the results with data obtained by atomic emission analysis with inductively coupled plasma and the “introduced–found” method. The developed atomic absorption techniques were introduced in analytical practice of the Laboratory for Separation and Concentration in Chemical Diagnosis of Functional Materials and Environmental Objects of the National University of Science and Technology (MISiS) and the Test Analytical and Certification Center of Giredmet.

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