ICS 77.120.30
CCS H 13

NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 3884.9-2025

Replacing GB/T 3884.9-2012

Methods for chemical analysis of copper concentrates - Part 9: Determination of arsenic, antimony and bismuth contents

铜精矿化学分析方法 第9部分：砷、锑和铋含量的测定

Issued on: August 29, 2025 **Implemented on: March 1, 2026**

Issued by: State Administration for Market Regulation;
Standardization Administration of the PRC

Table of Contents

1 Scope

This document describes methods for the determination of arsenic, antimony, and bismuth contents in copper concentrates and copper slag concentrates using hydride generation - atomic fluorescence spectrometry (Method 1), potassium bromate titration (Method 2), and silver diethyldithiocarbamate spectrophotometry (Method 3).

This document is applicable to the determination of arsenic, antimony, and bismuth contents in copper concentrates and copper slag concentrates. The determination ranges are. in Method 1, 0.010%~1.00% for arsenic, 0.010%~1.00% (mass fraction) for antimony, and 0.010%~1.00% for bismuth; in Method 2, 0.10%~4.50% (mass fraction) for arsenic; and in Method 3, 0.010%~0.40% (mass fraction) for arsenic.

2 Normative references

GB/T 6682

3 Terms and definitions

There are no terms and definitions requiring definition in this document.

4 Method 1 -- Hydride generation - atomic fluorescence

spectrometry

4.1 Principle

The test material is decomposed using a mixture of potassium chlorate-nitric acid solution,

ammonium hydrogen fluoride, and sulfuric acid. Arsenic, antimony, and bismuth are precipitated from the solution in an ammoniacal medium - utilizing the iron present in the test material and a specific amount of added lanthanum - thereby separating them from copper. The precipitate is dissolved in hot hydrochloric acid. An aliquot of the solution is taken, pre-reduced with ascorbic acid, and residual copper is masked with thiourea. In a hydride generator, arsenic, antimony, and bismuth are reduced to their respective hydrides by potassium borohydride. These hydrides are swept by argon gas into a quartz furnace atomizer, and their fluorescence intensity is measured using an atomic fluorescence spectrometer with a hollow cathode lamp as the light source.

4.2 Reagents

Unless otherwise specified, only confirmed analytically pure reagents are used in the analysis.

4.2.1 Water. complying with GB/T 6682, of Grade II purity or higher.

4.2.2 Hydrochloric acid (rho = 1.19 g/mL). guaranteed reagent.

4.2.3 Aqueous ammonia (rho = 0.90 g/mL). guaranteed reagent grade.

4.2.4 Potassium chlorate-nitric acid solution (80 g/L). weigh 40 g of potassium chlorate

and dissolve it in nitric acid (rho = 1.42 g/mL, guaranteed reagent). Dilute to 500 mL with nitric acid (rho = 1.42 g/mL, guaranteed reagent). Mix well.

4.2.5 Ammonium hydrogen fluoride solution (300 g/L).

4.2.6 Hydrochloric acid (1+24). 4.2.7 Sulfuric acid (1+1).

4.2.8 Ammonia washing solution (5+95).

4.2.9 Thiourea-ascorbic acid mixed solution. weigh 10 g of thiourea and 5 g of ascorbic acid separately, dissolve them in water, dilute to 100 mL, and mix well.

4.2.10 Lanthanum nitrate solution (50 g/L). weigh 5 g of lanthanum nitrate, dissolve in water, dilute to 100 mL, and mix well.

4.2.11 Ferric nitrate solution. weigh 73.40 g of ferric nitrate [Fe(NO3)3-9H2O] into a

250 mL beaker. Add 10 mL of nitric acid (rho = 1.42 g/mL, guaranteed reagent). Add an appropriate amount of water to dissolve the salt. Transfer the solution to a 1000 mL volumetric flask, dilute to the mark with water, and mix well. This solution contains 10 mg of iron per 1 mL.

4.2.12 Potassium borohydride solution (15 g/L). weigh 15 g of potassium borohydride

and dissolve it in 1000 mL of sodium hydroxide solution (2 g/L). Prepare when needed.

4.2.13 Arsenic standard stock solution. weigh 0 1320 g of primary standard arsenic

trioxide (previously dried at 100°C~105°C for 1 h and cooled to room temperature in a desiccator) into a 100 mL PTFE beaker. Add 5 mL of sodium hydroxide solution (200 g/L). Heat gently to dissolve, then allow to cool. Add 50 mL of water and 2 drops of phenolphthalein-ethanol solution (1 g/L). Neutralize with sulfuric acid (4.2.7) until the red color just disappears, then add an excess of 2 mL. Transfer the solution to a 1000 mL volumetric flask, dilute to the mark with water, and mix well. This solution contains 100 µg of arsenic per 1 mL.

4.2.14 Antimony standard stock solution. weigh 0 1000 g of metallic antimony (wSb >=

99.99%) into a 200 mL beaker. Add 50 mL of nitric acid (1+1) and 3 g of tartaric acid.

Heat gently to dissolve. Allow to cool. Transfer to a 1000 mL volumetric flask, dilute to the mark with water, and mix well. This solution contains 100 µg of antimony per 1 mL.

4.2.15 Bismuth standard stock solution. weigh 0 1000 g of bismuth metal (wBi >= 99.99%) into a 250 mL beaker. Add 50 mL of nitric acid (1+1). Cover with a watch glass. Heat gently to dissolve. Boil to expel nitrogen oxides. Allow to cool. Transfer the solution to a 1000 mL volumetric flask using nitric acid (1+24), dilute to the mark with water, and mix well. This solution contains 100 µg of bismuth per 1 mL.

4.2.16 Mixed standard solution. pipette 5.00 mL of arsenic standard stock solution

(4.2.13), 5.00 mL of antimony standard stock solution (4.2.14), and 5.00 mL of bismuth standard stock solution (4.2.15) into a 500 mL volumetric flask. Add 50 mL of hydrochloric acid (4.2.2). Dilute to the mark with water and mix well. 1 mL of this solution contains 1 µg each of arsenic, antimony, and bismuth.

4.2.17 Argon gas (purity >=99.99%).

4.3 Instruments

Atomic fluorescence spectrometer. equipped with a shielded quartz furnace atomizer and specialized hollow cathode lamps (or high-intensity hollow cathode lamps) for arsenic, antimony, and bismuth.

Provided the instrument is operating under optimal conditions, any setup capable of meeting the following specifications may be used.

- Limit of detection. no greater than 9 x 10-10 g/mL;

- Precision. measure the fluorescence intensity 10 times using a 0.1 μg/mL standard solution of arsenic, antimony, or bismuth. The standard deviation shall not exceed 5.0% of the mean fluorescence intensity.

4.4 Sample

4.4.1 The particle size of the sample shall be no greater than 100 μm.

4.4.2 The sample shall be dried at 100°C~105°C for 1 h and then cooled to room temperature in a desiccator.

4.5.1 Test material

Weigh 0.2 g of the sample (4.4), accurate to 0 0001 g.

4.5.2 Parallel test

Perform the test in duplicate and take the average value.

4.5.3 Blank test

Conduct a blank test alongside the test material.

4.5.4 Determination

4.5.4.1 Place the test material (4.5.1) into a 300 mL PTFE beaker. Moisten with a small amount of water. Add approximately 2 mL of ammonium hydrogen fluoride solution (4.2.5). Add 10 mL of potassium chlorate-nitric acid solution (4.2.4). Cover with a watch glass. Once the vigorous reaction has ceased, place on a hot plate and heat to dissolve the sample, reducing the volume to 3 mL~5 mL. Remove from the heat and allow to cool slightly. Add 5 mL of sulfuric acid (4.2.7) and mix well. Heat until dense white fumes appear. Remove from the heat and allow to cool. Rinse the watch glass and the inner walls of the beaker with water, bringing the total volume to approximately 50 mL. Heat to boiling, then remove from the heat and allow to cool slightly.

4.5.4.2 Add 5 mL of lanthanum nitrate solution (4.2.10). Dilute with water to

approximately 150 mL. Place on a hot plate and heat until near boiling. Remove from the heat. While stirring, add ammonia solution (4.2.3) until the resulting copper hydroxide precipitate completely dissolves. Add an additional 20 mL of ammonia solution (4.2.3). Slowly heat to boiling. Move to a lower-temperature area (approximately 60°C) and