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Copper sulfide concentrates — Determination of copper content — Titrimetric methods

Concentrés de sulfure de cuivre — Dosage du cuivre — Méthodes titrimétriques

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ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

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Foreword

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 183, *Copper, lead, zinc and nickel ores and concentrates*.

This second edition cancels and replaces the first edition (ISO 10258:1994), of which the warning in A.3.1 in Annex A has been revised.

Copper sulfide concentrates — Determination of copper content — Titrimetric methods

1 Scope

This International Standard specifies two titrimetric methods for the determination of the copper content of copper sulfide concentrates in the range 15 % (m/m) to 50 % (m/m), using sodium thiosulfate after separation (method 1) or without separation (method 2) of copper from interfering elements.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

ISO 9599, *Copper, lead, zinc and nickel sulfide concentrates — Determination of hygroscopic moisture content of the analysis sample — Gravimetric method*

3 Principle

3.1 Method 1 (Long iodide method)

A test portion is decomposed in nitric and sulfuric acids, and arsenic, antimony, and tin are removed by treatment with hydrobromic acid. Copper is separated from interfering elements by precipitation of copper sulfide with sodium thiosulfate. The precipitate is dissolved in nitric and sulfuric acids, ammonium hydrogen difluoride is added to eliminate interference of residual iron, and excess potassium iodide is also added. Free iodine isolated by reaction between iodide ions and copper(II) ions is titrated with sodium thiosulfate using soluble starch as the indicator.

3.2 Method 2 (Short iodide method)

A test portion is decomposed in nitric and sulfuric acids, and arsenic, antimony, and tin are removed by treatment with hydrobromic acid. Ammonium hydrogen difluoride is added to eliminate interference of iron, and excess potassium iodide is also added. Free iodine isolated by reaction between iodide ions and copper(II) ions is titrated with sodium thiosulfate using soluble starch as the indicator.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and distilled water or water of equivalent purity.

4.1 Copper metal, minimum purity 99,99 %.

4.2 Potassium iodide.

4.3 Ammonium hydrogen difluoride.

4.4 Sulfuric acid, diluted 1 + 1.

Slowly add 500 ml of concentrated sulfuric acid (ρ_{20} 1,84 g/ml) to 500 ml of water, while stirring and cooling.

4.5 Sulfuric acid, diluted 1 + 999.

Add 1 ml of dilute sulfuric acid (4.4) to 500 ml of water.

4.6 Nitrit acid, concentrated (ρ_{20} 1,42 g/ml).

4.7 Nitrit acid, diluted 1 + 1.

Slowly add 500 ml of concentrated nitric acid (4.6) to 500 ml of water.

4.8 Hydrofluoric acid (ρ_{20} 1,14 g/ml).

4.9 Bromine.

4.10 Bromine water, saturated.

4.11 Hydrobromic acid (ρ_{20} 1,50 g/ml).

4.12 Acetic acid, diluted 1 + 3.

Slowly add 25 ml of glacial acetic (ρ_{20} 1,05 g/ml) to 75 ml of water.

4.13 Nitration mixture.

Slowly add 250 ml of concentrated sulfuric acid (ρ_{20} 1,84 g/ml) to 250 ml of concentrated nitric acid (4.6).

4.14 Ammonium hydrogen difluoride, 250 g/l solution.

4.15 Sodium carbonate, 20 g/l solution.

4.16 Sodium thiosulfate pentahydrate, 200 g/l solution.

4.17 Potassium thiocyanate, 100 g/l solution.

4.18 Starch, 2 g/l solution.

Moisten 1 g of soluble starch with cold water, slowly pour into 500 ml of hot water while stirring, and boil for about 1 min.

4.19 Ethanol.

4.20 Standard solutions.

Standard solutions should be prepared at the same ambient temperature as that at which the determinations will be conducted.

4.20.1 Sodium thiosulfate, standard volumetric solution (20 g/l).

4.20.1.1 Preparation

Dissolve 20 g of sodium thiosulfate (pentahydrate) in 1 l of freshly boiled and cooled water. Add 0,2 g of sodium carbonate, stir to dissolve and allow to stand for at least one day. Standardize this solution as specified in 4.20.1.2.

4.20.1.2 Standardization

Clean a piece of copper metal (4.1) by immersing it in warm dilute acetic acid (4.12). Wash the copper thoroughly with water followed by ethanol (4.19) and allow to dry in air. Weigh into three separate 400 ml conical beakers to the nearest 0,1 mg, a mass of clean copper metal which approximates the copper content in the test portion. Record these masses as m_1, m_2, and m_3.

Dissolve the copper using 10 ml of dilute nitric acid (4.7) followed by 5 ml of dilute sulfuric acid (4.4). Heat to evaporate to dryness. Add 40 ml of water, heat to dissolve the soluble salts, and cool. Continue the standardization as specified in 7.3.4 for method 1 and in 7.4.2 for method 2. Record the volumes of sodium thiosulfate solution used in the titration as V_1, V_2, and V_3.

The standardization factor of the standard volumetric solution varies with the volume of sample solution, mass of potassium iodide, mass of copper, and temperature of solution. The same volume of solution and mass of potassium iodide as those used for the standardization should be used for the analysis of the test portion. The temperatures of standardization and determination should be essentially the same.

Calculate the standardization factors f_1, f_2, and f_3 using the following formulae:

$$f_1 = \frac{m_1}{V_1} \quad (1)$$

$$f_2 = \frac{m_2}{V_2} \quad (2)$$

$$f_3 = \frac{m_3}{V_3} \quad (3)$$

Calculate, to four significant figures, the mean standardization factor f for the sodium thiosulfate standard volumetric solution, provided that the range of the values of f_1, f_2, and f_3 does not exceed 10^{-5} g Cu/ml. If this range is exceeded, repeat the standardization.

4.20.2 Copper, standard solution (0,1 mg/ml).

Weigh, to the nearest 0,1 mg, 0,1 g of copper metal (4.1) into a 200 ml beaker, decompose with 10 ml of dilute nitric acid (4.7). Heat to remove nitrogen oxides, cool, and add about 50 ml of water. Transfer to a 1 000 ml volumetric flask, fill up nearly to the mark with water, mix and cool to room temperature; then fill up exactly to the mark and mix again.

5 Apparatus

Ordinary laboratory equipment and the following.

5.1 Volumetric glassware, of class A complying with ISO 385, ISO 648, and ISO 1042, and used in accordance with ISO 4787.

5.2 Analytical balance, sensitive to 0,1 mg.

5.3 Platinum crucibles.

5.4 Atomic absorption spectrometer (AAS), with a copper hollow cathode lamp.

Instrumental conditions:

— Flame: air/acetylene;

— Wavelength: 324,7 nm.

5.5 Inductively coupled plasma (ICP) atomic emission spectrometer (optional).

6 Sample

6.1 Test sample

Prepare an air-equilibrated test sample in accordance with ISO 9599.

NOTE A test sample is not required if predried test portions are to be used (see Annex A).

6.2 Test portion

Taking multiple increments, extract a test portion from the test sample as specified in Table 1 and weigh to the nearest 0,1 mg. At the same time as test portions are being weighed for analysis, weigh test portions for the determination of hygroscopic moisture in accordance with ISO 9599.

Alternatively, the method specified in Annex A can be used to prepare predried test portions directly from the laboratory sample.

Table 1 — Recommended test Portion masses

Copper content (presumed) % (m/m)		Mass of test portion
≥	<	g
15	25	0,8
25	50	0,4

7 Procedure

7.1 Number of determinations

Carry out the determinations at least in duplicate, as far as possible under repeatability conditions, on each test sample.

NOTE Repeatability conditions exist where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment, within short intervals of time.

7.2 Blank test

Carry out a blank test in parallel with the analysis using the same quantities of all reagents but omitting the test portion. The purpose of the blank test in this method is to check the quality of reagents. If a significant blank titration value is obtained as a result of the blank test, check all reagents and rectify the problem.

7.3 Determination — method 1: Long iodide method

7.3.1 Decomposition of test portion

Transfer the test portion to a 400 ml conical beaker and moisten with 10 ml of water. Add 20 ml of dilute nitric acid (4.7), cover with a watch glass and heat for about 10 min at 60 °C to 70 °C. Add 10 ml of dilute sulfuric acid (4.4) and heat gradually to decompose the test portion.

After the completion of the initial reaction, rinse the underside of the watch glass with a minimum volume of water, collecting the washings in the conical beaker. Continue heating until strong white fumes are evolved, then cool.

If the residue appears dark (presence of carbon), slowly add a small amount of the nitration mixture (4.13) to the hot solution until the solution becomes colourless or bluish and heat until strong white fumes are evolved.

If decomposition of the deposited sulfur is insufficient, add 5 ml of nitric acid (4.6) and 1 ml of bromine (4.9), and heat until strong white fumes are evolved.

Carefully add 5 ml of water and 10 ml of hydrobromic acid (4.11) and heat until strong white fumes are evolved. Remove from the source of heat and cool. After addition of 5 ml of dilute sulfuric acid (4.4) and 10 ml of hydrobromic acid (4.11), heat until strong white fumes are evolved. Remove from the source of heat and cool.

Add 80 ml of water, warm to dissolve soluble salts, and heat until boiling. Filter through a medium porosity filter paper, wash well with hot water, and collect the filtrate in a 400 ml conical beaker. Reserve the filter paper and residue for the determination of copper by flame atomic absorption spectrometry (FAAS) (as described in 7.3.5) unless it has been proven, through previous testing, that the copper in the sample is completely soluble using the initial dissolution.

7.3.2 Separation of copper

Dilute the filtrate to 200 ml and heat to 70 °C to 90 °C, slowly add 40 ml of sodium thiosulfate solution (4.16) while stirring, to produce a yellow or yellowish brown emulsion. Heat gradually and continue boiling gently until the precipitate coagulates. Filter the solution through a medium porosity filter paper and wash the filter paper and precipitate with hot water. Retain the filtrate for FAAS measurements of copper (as described in 7.3.5).

Using water, rinse away the copper sulfide precipitate into the original conical beaker and decompose the remaining precipitate on the filter paper using drop by drop addition of bromine water (4.10) followed by nitric acid (4.6). Repeat this treatment as required, then wash well with hot water, collecting this solution in the beaker containing the main precipitate. Retain the filter paper for FAAS measurements of copper (as described in 7.3.5).

NOTE Instead of using the above step, the following method can be used: Transfer the precipitate and filter paper into the original beaker, cover with a watch glass, and add 30 ml of nitration mixture (4.13). Heat slowly to decompose the precipitate and the filter paper, and evaporate to dryness. Use more nitration mixture if the residue appears dark. Continue heating strongly to destroy any elemental sulfur. After adding 10 ml of nitric acid (4.6) around the top of the beaker to rinse away the residual sulfur, add 2 ml of dilute sulfuric acid (4.4) and heat until strong white fumes are evolved. Remove from the heat source and cool. Add 40 ml of water, warm to dissolve the soluble salts, and cool. Proceed to 7.3.4.

7.3.3 Dissolution of copper precipitate

Add 2 ml of dilute sulfuric acid (4.4) and 10 ml of nitric acid (4.6), heat slowly to decompose the precipitate, and then evaporate to dryness. Continue heating strongly to destroy any elemental sulfur. After adding 10 ml of nitric acid (4.6) around the top of the beaker to rinse away the residual sulfur, add 2 ml of dilute sulfuric acid (4.4), and heat until strong white fumes are evolved. Remove from the source of heat and cool.

7.3.4 Titration

Add 40 ml of water, warm to dissolve the soluble salts, and cool the solution. Add sodium carbonate solution (4.15) until the copper precipitate appears, then add dilute acetic acid (4.12) until the copper precipitate disappears and an excess of 3 ml to 5 ml. Add 1 ml of ammonium hydrogen difluoride solution (4.14) and swirl. Add 15 g of potassium iodide (4.2), swirl to dissolve, and immediately titrate with sodium thiosulfate standard volumetric solution (4.20.1). When the yellow brown iodine colour fades to a pale yellow, add 5 ml of starch solution (4.18) as the indicator.

NOTE 1 Instead of using the above step, the following method can be used. Add 3 g of potassium iodide (4.2), swirl to dissolve, and immediately titrate with sodium thiosulfate standard volumetric solution (4.20.1). When the yellow brown iodine colour fades to a pale yellow, add 5 ml of starch solution (4.18) as the indicator, and continue the titration until the colour of the solution becomes light blue. Then add 5 ml of potassium thiocyanate solution (4.17).

NOTE 2 The presence of Ag, Bi, Hg, and Pb can obscure the colour change. In this case, add the starch solution (4.18) earlier in the titration, when the solution is a light brown colour.

Continue the titration until the blue indicator colour just disappears. Record the volume, *V*, of sodium thiosulfate standard volumetric solution used in the titration.

7.3.5 FAAS determination of copper in the insoluble residue, filtrate, and filter paper

7.3.5.1 Decomposition of the insoluble residue

Place the retained residue and the filter paper in a platinum crucible (5.3), dry, and ignite at 750 °C to 800 °C. Allow the crucible to cool, add 5 ml of dilute sulfuric acid (4.4) and 5 ml to 10 ml of hydrofluoric acid (4.8), heat to evaporate almost to dryness, and volatilize the silicon as silicon tetrafluoride. Dissolve with a small quantity of water and 1 ml of dilute sulfuric acid (4.4) by heating. Proceed to 7.3.5.3.

7.3.5.2 Decomposition of the precipitate remaining on the filter paper

Transfer the retained filter paper into a beaker and add 30 ml of nitration mixture (4.13). Heat to evaporate to dryness. If the residue appears dark (presence of carbon), repeat this step. Dissolve with a small quantity of water and 1 ml of dilute sulfuric acid (4.4) by heating. Proceed to 7.3.5.3.

7.3.5.3 Spectrometric measurement

Transfer the solutions prepared in 7.3.5.1, 7.3.5.2, and the retained filtrate from 7.3.2 into a 500 ml volumetric flask and make up to the mark with water.

Prepare calibration solutions by adding, from a pipette or a micro-burette, 0,0 ml, 0,50 ml, 1,00 ml, 1,50 ml, 2,00 ml, and 3,00 ml of copper standard solution (4.20.2) into a series of 200 ml one-mark volumetric flasks, add 1 ml of dilute sulfuric acid (4.4) to each one, and make up to the marks with water.

Aspirate the test solution and the calibration solutions into the atomic absorption spectrometer (5.4) using an air/acetylene flame and a wavelength of 324,7 nm with background correction.

Prepare a calibration graph of masses of copper in the calibration solutions versus absorbances and read the mass, in micrograms, of copper in the test solution from the calibration graph.

NOTE Alternatively, the ICP atomic emission spectrometer (5.5) can be used for the determination of copper at a wavelength of 324,7 mm.

Calculate the mass of copper in the residue and filtrate using Formula (4):

$$m_4 = m_5 \times 10^{-6} \quad (4)$$

where

m_4 is the mass, in grams, of copper in the insoluble residue, the precipitate remaining on the filter paper, and the filtrate;

m_5 is the mass, in micrograms, of copper in the test solution.

7.4 Determination — method 2: Short iodide method

7.4.1 Decomposition of the test portion

Transfer the test portion to a 400 ml conical beaker and moisten with 10 ml of water. Add 20 ml of dilute nitric acid (4.7), cover with a watch glass, and heat for about 10 min at 60 °C to 70 °C. Add 10 ml of dilute sulfuric acid (4.4) and heat gradually to decompose the test portion.

After completion of the initial reaction, rinse the underside of the watch glass with a minimum volume of water, collecting the washings in the conical beaker. Continue heating until strong white fumes are evolved, then cool.

If the residue appears dark (presence of carbon), slowly add a small amount of the nitration mixture (4.13) to the hot solution until the solution becomes colourless or bluish and heat until strong white fumes are evolved.

If decomposition of the deposited sulfur is insufficient, add 5 ml of nitric acid (4.6), 1 ml of bromine (4.9), and 2 ml of dilute sulfuric acid (4.5), and heat until strong white fumes are evolved.

Carefully add 5 ml of water, 10 ml of hydrobromic acid (4.11), and 5 ml of dilute sulfuric acid (4.4), and heat until strong white fumes are evolved. Remove from the source of heat and cool. Add 5 ml of dilute sulfuric acid (4.4) and 10 ml of hydrobromic acid (4.11), and heat until strong white fumes are evolved. Continue heating to evaporate to complete dryness and then cool.

If it has not been proven, through previous testing, that the copper in the sample is completely soluble using the initial dissolution described above, the following procedure should be carried out. Add 20 ml of water, warm to dissolve soluble salts, then heat until boiling. Filter through a medium-porosity filter paper, wash well with hot water collecting the filtrate and washings in a 400 ml conical beaker, and then heat to evaporate to dryness. Determine the copper content of the insoluble residue in accordance with 7.3.5.

7.4.2 Titration

Add 40 ml of dilute sulfuric acid (4.5), warm to dissolve the soluble salts, and cool the solution. Add 3 g of ammonium hydrogen difluoride (4.3) to the test solution and swirl to dissolve.

Add 15 g of potassium iodide (4.2), swirl to dissolve, and immediately titrate with sodium thiosulfate standard volumetric solution (4.20.1). When the yellow brown iodine colour fades to a pale yellow, add 5 ml of starch solution (4.18) as the indicator.

NOTE 1 Instead of using the above step, the following method can be used: Add 3 g of potassium iodide (4.2), swirl to dissolve, and immediately titrate with sodium thiosulfate standard volumetric solution (4.20.1). When the yellow brown iodine colour fades to a pale yellow, add 5 ml of starch solution (4.18) as the indicator and continue the titration until the colour of the solution becomes light blue. Then add 5 ml of potassium thiocyanate solution (4.17).

NOTE 2 The presence of Ag, Bi, Hg, and Pb can obscure the colour change. In this case, add the starch solution (4.18) earlier in the titration, when the solution is a light brown colour.