
**Copper sulfide concentrates —
Determination of copper —
Electrogravimetric method**

*Concentrés de sulfure de cuivre — Dosage du cuivre — Méthode
électrogravimétrique*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10469 was prepared by Technical Committee ISO/TC 183, *Copper, lead, zinc and nickel ores and concentrates*.

This second edition cancels and replaces the first edition (ISO 10469:1994), which has been technically revised.

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Introduction

ISO 10469:1994 underwent periodical review in 1999. Although the decision was made to confirm the International Standard at that time, significant comments were submitted by Japan. These comments were considered at a meeting of ISO/TC 183 in 2000, where it was agreed that Japan would re-draft ISO 10469 to indicate the proposed changes.

The most significant change was the elimination of the correction for impurities.

ISO/TC 183 agreed that the changes made do not warrant a new interlaboratory test programme. Details of the changes are as follows:

- a) Deletion of the determination of impurities in the deposited copper (7.9 in ISO 10469:1994).
- b) Adjustment of the expression of dissolution of the test portion according to ISO 10258:1994, *Copper sulfide concentrates — Determination of copper content — Titrimetric methods*.
- c) Adjustment of the expression of the sulfide separation method according to ISO 10258:1994.
- d) In the case of contained bismuth or tellurium, modification of the sulfide separation procedure. The method described in ISO 10469:1994 included a lot of copper in the iron hydroxide precipitation, which will lead to incorrect results. The method described in ISO 13658:2000, *Zinc sulfide concentrates — Determination of zinc content — Hydroxide precipitation and EDTA titrimetric method* has less copper in the iron hydroxide precipitation than the method described in ISO 10469:1994, so the method described in ISO 10469:1994 has now been modified with reference to ISO 13658.
- e) The procedure of treatment of the iron hydroxide precipitation (contained copper) is not given in ISO 10469:1994. The procedure of treatment has been added to the revised Standard.

Calibration solution A (4.34.1 in ISO 10469:1994) will be used in 7.7.1 (FAAS determination of copper in the filtrate of the sulfide precipitation). This filtrate contains iron ion, so calibration solution A should contain iron to achieve matrix matching. The preparation method of calibration solution A has been revised to include iron ion in the revised Standard.

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Copper sulfide concentrates — Determination of copper — Electrogravimetric method

WARNING — This International Standard may involve hazardous materials, operations and equipment. It is the responsibility of the user of this International Standard to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies an electrogravimetric method for the determination of the mass fraction of copper in copper sulfide concentrates in the range 15 % to 50 %.

2 Normative references

The following referenced documents are indispensable for the application of this document. 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 — One-mark pipettes*
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ISO 1042, *Laboratory glassware — One-mark volumetric flasks*
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ISO 4787, *Laboratory glassware — Volumetric glassware — Methods for use and testing of capacity*

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

3 Principle

The test portion is decomposed in nitric and sulfuric acids, and copper is separated from interfering elements:

- from silver by precipitation of silver chloride;
- from arsenic, antimony, selenium and tin by fuming with hydrobromic acid;
- from iron by precipitation of copper sulfide with sodium thiosulfate or by precipitation of iron(III) oxide hydrate (bismuth and tellurium are also separated in this way).

Electrogravimetric deposition of copper occurs in the presence of nitric acid, sulfuric acid and traces of chloride. Under these conditions, coprecipitation of molybdenum does not occur.

Traces of copper in the electrolyte, the filtrate of the copper sulfide precipitation, all precipitates and residues are determined by flame atomic absorption spectrometry (FAAS) or inductively coupled plasma atomic emission spectrometry.

The normal mass fraction of mercury in copper concentrates does not usually affect the copper result. At a level of 0,005 % or greater, the mass fraction of mercury in the copper deposit should be checked. This procedure is not described in this International Standard.

4 Reagents

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

4.1 Nitric acid, concentrated (ρ_{20} 1,42 g/ml).

4.2 Nitric acid, diluted 1 + 1.

Slowly add 500 ml of concentrated nitric acid (4.1) to 500 ml of water, while stirring.

4.3 Sulfuric acid, concentrated (ρ_{20} 1,84 g/ml).

4.4 Sulfuric acid, diluted 1 + 1.

Slowly add 500 ml of concentrated sulfuric acid (4.3) to 500 ml of water, while stirring. Cool the solution.

4.5 Sulfuric acid, diluted 1 + 4.

Slowly add 200 ml of concentrated sulfuric acid (4.3) to 800 ml of water, while stirring. Cool the solution.

4.6 Sodium thiosulfate pentahydrate, (450 g/l) solution.

4.7 Nitration mixture.

Slowly add 250 ml of concentrated sulfuric acid (4.3) to 250 ml of concentrated nitric acid (4.1).

4.8 Sodium chloride, 10 g/l solution.

4.9 Sodium chloride, 0,5 g/l solution.

4.10 2-propanol.

4.11 Ethanol, minimum purity 95 % (VII).

4.12 Methanol, minimum purity 95 % (VII).

4.13 Ammonium iron(III) sulfate solution.

Add 50 ml of dilute sulfuric acid (4.4) and 43 g of ammonium iron(III) sulfate dodecahydrate $[\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ to 950 ml of water.

4.14 Iron(III) nitrate solution.

Add 30 g of iron(III) nitrate nonahydrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ to 100 ml of water.

4.15 Ammonia solution (ρ_{20} 0,91 g/ml).

4.16 Ammonia solution, diluted 1 + 99.

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

4.18 Perchloric acid (ρ_{20} 1,53 g/ml).

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

4.20 Copper metal, minimum purity 99,999 %.

4.21 Sodium sulfate (Na_2SO_4), anhydrous.

4.22 Hydrochloric acid, concentrated (ρ_{20} 1,16 g/ml to 1,18 g/ml).

4.23 Hydrochloric acid, diluted 1 + 1.

Slowly add 500 ml of concentrated hydrochloric acid (4.22) to 500 ml of water, while stirring.

4.24 Bromine.

4.25 Copper standard solution, 1 ml contains 0,1 mg of Cu.

Dissolve 0,1 000 g of copper metal (4.20) in 10 ml of warm dilute nitric acid (4.2) and heat to evaporate to approximately 5 ml to remove nitrogen oxides. Transfer to a 1 000 ml volumetric flask, fill up nearly to the mark with water, mix and equilibrate at room temperature; then fill up exactly to the mark and mix again.

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

4.26 Calibration solutions.

Calibration solutions should be prepared at the same ambient temperature as that at which the determination will be conducted.

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Calibration solutions should be prepared freshly before use.

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4.26.1 Calibration solutions A.

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Pipette 0,0 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of copper standard solution (4.25) into a series of 500 ml one-mark volumetric flasks. Add 40 ml of dilute sulfuric acid (4.4), 13 g of sodium sulfate (4.21) and 50 ml (see third paragraph) of ammonium iron(III) sulfate (4.13) (corresponding to approximately 250 mg of iron) to each flask. Dilute with water, stir to dissolve the salts, fill up nearly to the mark, mix and equilibrate at room temperature, then fill up exactly to the mark and mix again.

These solutions contain 0 mg of Cu, 1 mg of Cu, 2 mg of Cu, 3 mg of Cu and 4 mg of Cu in a 500 ml volume.

If the test solution contains less than 50 mg of iron, only 10 ml of ammonium iron(III) sulfate (4.13) should be added to each flask.

In situations where the test solution contains more than 4 mg of Cu, dilute with the calibration solution containing 0,0 mg of Cu, until the copper concentration in the test solution is below 4 mg/500 ml.

4.26.2 Calibration solutions B.

Pipette 0,0 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of copper standard solution (4.25) into a series of 500 ml one-mark volumetric flasks. Add 30 ml of dilute sulfuric acid (4.4), 10 ml of dilute nitric acid (4.2), 15 ml of dilute hydrochloric acid (4.23) and 25 ml of ammonium iron(III) sulfate solution (4.13) to each flask. Fill up nearly to the mark with water, mix and equilibrate at room temperature; then fill up exactly to the mark and mix again.

These solutions contain 0 mg of Cu, 1 mg of Cu, 2 mg of Cu, 3 mg of Cu and 4 mg of Cu in a 500 ml volume.

In situations where the test solution contains more than 4 mg of Cu, dilute with the calibration solution containing 0,0 mg of Cu, until the copper concentration in the test solution is below 4 mg/500 ml.

4.26.3 Calibration solutions C.

Pipette 0,0 ml, 10,00 ml, 20,00 ml, 30,00 ml and 40,00 ml of copper standard solution (4.25) into a series of 500 ml one-mark volumetric flasks. Add 20 ml of dilute sulfuric acid (4.4), 10 ml of dilute nitric acid (4.2) and 50 ml (see third paragraph) of ammonium iron(III) sulfate solution (4.13) (corresponding to approximately 250 mg of Fe) to each flask. Fill up nearly to the mark with water, mix and equilibrate at room temperature; then fill up exactly to the mark and mix again.

These solutions contain 0 mg of Cu, 1 mg of Cu, 2 mg of Cu, 3 mg of Cu and 4 mg of Cu in a 500 ml volume.

If the test portion contains less than 50 mg of Fe [$< 2,5 \% (m/m) \text{ Fe}$], only 10 ml of ammonium iron(III) sulfate solution (4.13) should be added each time.

In situations where the test solution contains more than 4 mg of Cu, dilute with the calibration solution containing 0,0 mg of Cu, until the copper concentration in the test solution is below 4 mg/500 ml.

5 Apparatus

5.1 Usual laboratory equipment, including fume hoods, hotplates, a drying oven, an analytical balance and a water bath with a thermostat for the temperature control of solutions.

5.2 Ordinary laboratory glassware.

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

5.4 Desiccator.

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5.5 Filter papers, of different porosity (dense and medium).

5.6 Equipment for static electrolysis.

5.7 Platinum electrodes, net electrodes as cathodes; spiral electrodes as anodes.

NOTE Winkler electrodes have been found suitable.

5.8 Atomic absorption spectrometer (AAS).

Instrument conditions:

Flame: air/acetylene

Wavelength 324,7 nm

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

5.10 Platinum dish.

5.11 Polytetrafluoroethylene (PTFE) dish.

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 approximately 2 g from the test sample and weigh to the nearest 0,1 mg (*m*). 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 may be used to prepare predried test portions directly from the laboratory sample.

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

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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 value is obtained as a result of the blank test, check all reagents and rectify the problem.

7.3 Dissolution of test portion

Transfer the test portion into a 400 ml or 500 ml conical or tall-form beaker, or a 500 ml Erlenmeyer flask. Moisten with 10 ml of water. Add 20 ml of dilute nitric acid (4.2), cover the beaker with a watch glass or, if using an Erlenmeyer flask, with a drip catcher and heat for about 10 min at 60 °C to 70 °C. Add 40 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 or drip catcher with a minimum volume of water, collecting the washings in the conical beaker or Erlenmeyer flask. Continue heating until strong white fumes are evolved, then cool.

If the residue appears dark (presence of carbon), slowly add a small amount of nitration mixture (4.7) to the hot solution until the solution becomes colourless or bluish, then heat until strong white fumes are evolved.

If decomposition of the deposited sulfur is insufficient, add 5 ml of nitric acid (4.1) and 1 ml of bromine (4.24) and heat until strong white fumes are evolved.

7.4 Separation of arsenic, antimony, tin, selenium and silver

Carefully add 5 ml of water and 10 ml of hydrobromic acid (4.17), heat until strong white fumes are evolved, then cool. Add 5 ml of dilute sulfuric acid (4.4) and 10 ml of hydrobromic acid (4.17) and heat until strong white fumes are evolved, then cool.