INTERNATIONAL STANDARD

ISO 10469

Second edition
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Copper sulfide concentrates — Determination of copper — Electrogravimetric method

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

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Foreword

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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.

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.

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*

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

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 % (*V*/*V*).

4.12 Methanol, minimum purity 95 % (*V*/*V*).

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 [$NH_4Fe(SO_4)_2 \cdot 12H_2O$] to 950 ml of water.

4.14 Iron(III) nitrate solution.

Add 30 g of iron(III) nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] 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.

Calibration solutions should be prepared freshly before use.

4.26.1 Calibration solutions A.

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 pargraph) 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) 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.

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

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.

WARNING — Extreme caution MUST be taken during this step.

NOTE This step may be omitted if the test sample contains less than 0,01 % (m/m) each of As, Sb, Sn and Se.

Add 100 ml of water and warm to dissolve soluble salts.

Precipitate silver completely as silver chloride by adding approximately 1 ml of sodium chloride solution (4.8).

NOTE This step may be omitted if the test sample contains less than 0,01 % (m/m) of Ag.

Heat until boiling, then allow to cool.

Filter through a dense filter paper (5.5), wash with cold water and collect the filtrate in a 400 ml or 500 ml conical or tall-form beaker, or a 500 ml Erlenmeyer flask (only for sulfide separation). Reserve the filter paper and residue for the determination of copper by FAAS (as described in 7.7.3), unless it has been proven by previous testing that the copper in the sample is completely soluble using the initial dissolution (7.3).

7.5 Copper separation

Separate copper from interfering ions in accordance with 7.5.1 or 7.5.2.

7.5.1 Sulfide separation

Dilute the filtrate to 200 ml with water and heat to 70 °C to 90 °C. Slowly add 50 ml of sodium thiosulfate solution (4.6) while stirring, to produce a yellow or yellowish-brown emulsion. Heat gradually and continue boiling gently until the precipitate coagulates.

Filter off the precipitate using a filter paper of medium porosity (5.5). Collect the filtrate in a 500 ml volumetric flask, and immediately wash the filter and precipitate with hot water. Reserve the filtrate for the determination of copper by FAAS (as described in 7.7.1).

Put the filter and copper sulfide precipitate back into the vessel used for precipitation, cover with a watch glass or drip catcher, add 30 ml of nitric acid (4.1) and 10 ml of sulfuric acid (4.3), heat to decompose the precipitate and filter paper, and continue heating until strong white fumes are evolved.

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

Should elemental sulfur be present, continue heating strongly to destroy any elemental sulfur. Add 10 ml of nitric acid (4.1) around the top of the beaker to rinse away the residual sulfur. Then add 2 ml of dilute sulfuric acid (4.5) and heat until strong white fumes are evolved. Allow to cool.

Dilute with water to approximately 100 ml, warm to dissolve the soluble salts, filter into a 400 ml tall-form beaker and wash the filter and vessel with water. Reserve the filter for the determination of copper by FAAS (as described in 7.7.3).

NOTE The following step may be omitted if the test sample contains less than 0,01 % (m/m) of Bi and/or Te.

Add 3 ml of iron(III) nitrate solution (4.14) and slowly add ammonia solution (4.15) while stirring, until the basic copper salt precipitated at first is dissolved again, then add a further 30 ml of ammonia solution (4.15) to make the solution alkaline. Heat until the onset of boiling, filter the precipitate using a filter paper of medium porosity (5.5) and wash with dilute ammonia solution (4.16). Collect the filtrate and washings in a 400 ml tall-form beaker.

Rinse the precipitate back into the original beaker with water and dissolve any precipitate adhering to the filter paper using 15 ml of warm dilute sulfuric acid (4.5) in small amounts. Wash the filter paper with warm water, collecting the washings in the original beaker. Dissolve the precipitate completely by adding 10 ml of dilute sulfuric acid (4.4), warm gently and dilute with water to obtain a volume of approximately 100 ml. Add ammonia solution (4.15) while stirring, until a slight precipitate of iron(III) hydroxide appears, then add a

further 30 ml of ammonia solution in excess. Heat until the onset of boiling, filter using the same filter paper again, wash with warm dilute ammonia solution (4.16) and collect the filtrate and washings in the 400 ml tall-form beaker already used.

Add dilute sulfuric acid (4.4) to make the solution slightly acidic, then heat to evaporate the filtrate to a volume of approximately 250 ml. Reserve the beaker and precipitate for the determination of copper by FAAS (as described in 7.7.2).

Add 20 ml of dilute nitric acid (4.2) and 10 ml of sodium chloride solution (4.9), and dilute with water to approximately 300 ml. Use this solution for the electrolytic deposition of copper (as described in 7.6).

7.5.2 Hydroxide separation

Bring the filtrate retained in 7.4 to a volume of 150 ml, either by dilution with water or evaporation by heating.

Slowly add ammonia solution (4.15) while stirring, until the basic copper salt precipitated at first is dissolved again. Then add a further 30 ml of ammonia solution (4.15) in excess. Heat until the onset of boiling, filter using a filter paper of medium porosity (5.5), wash with warm diluted ammonia solution (4.16) and collect the filtrate and washing solutions in a 600 ml beaker.

If the test portion contains less than 50 mg of Fe [i.e. $< 2{,}5$ % (m/m) Fe]. add 10 ml of ammonium iron(III) sulfate solution (4.13) (equivalent to approximately 50 mg of iron) before the precipitation of iron(III) hydroxide.

Rinse the precipitate back into the original beaker with water and dissolve any precipitate adhering to the filter paper using 15 ml of warm dilute sulfuric acid (4.5) in small amounts. Wash the filter paper with warm water, collecting the washings in the original beaker. Dissolve the precipitate completely by adding 10 ml of dilute sulfuric acid (4.4), warm gently and dilute with water to obtain a volume of approximately 100 ml.

Add ammonia solution (4.15) while stirring, until a slight precipitate of iron(III) hydroxide appears, then add a further 30 ml of ammonia solution (4.15) in excess.

Heat until the onset of boiling, filter using the same filter paper again, wash with warm dilute ammonia solution (4.16) and collect the filtrate and washings in the 600 ml beaker already used. Reserve the precipitate and beaker for the determination of copper by FAAS (as described in 7.8).

Heat to evaporate the filtrate to a volume of approximately 250 ml.

NOTE The dark blue colour of the complex ion $[(Cu(NH_3)_4)]^{2+}$ should disappear.

Add 20 ml of dilute sulfuric acid (4.4), 20 ml of dilute nitric acid (4.2) and 10 ml of sodium chloride solution (4.9). Use this solution for the electrolytic deposition of copper (as described in 7.6).

7.6 Electrolytic deposition

Before starting, prepare the cathode in the same way as for finishing the copper deposition (see below). Weigh the cathode to the nearest 0,1 mg (m_1).

Carry out the electrolytic deposition of copper without stirring and without heating, preferably overnight, using platinum electrodes (5.7).

NOTE 1 A 'Winkler' net as the cathode and a spiral as the anode, touching the bottom of the electrolysis beaker, cover glasses (two halves of a watch glass), a current of approximately 0,3 A to 0,5 A (current density is approximately 5 mA/cm^2 to 10 mA/cm^2) and a voltage of between 2,5 V and 4 V are considered suitable.

NOTE 2 An addition of sulfamic acid (NH_2–SO_3H) is not necessary. The use of considerably higher currents, heating and stirring is not recommended.

When working during the day, continue with the electrolytic deposition until the electrolyte is colourless, then raise the current to approximately 1 A for at least one more hour.

After finishing the copper deposition (if working overnight, the next morning), wash the glass covers and wall of the beaker.

Remove the cathode, washing first with water, then with 2-propanol (4.10) or ethanol (4.11) or methanol (4.12), and dry in a drying oven at approximately 80 °C for 5 min to 10 min. Allow to cool in the desiccator (5.4) and weigh the cathode to the nearest 0,1 mg (m_2).

Reserve the electrolyte for the determination of copper by FAAS (as described in 7.7.2 or 7.8, as appropriate).

The surface of the copper deposit should appear bright. If there is a dark colour, the determination should be repeated, including the separation steps for the coprecipitated elements. Considerable amounts of selenium and tellurium can be detected as a dark layer between the copper and platinum surfaces, after dissolving the copper with **cold** dilute nitric acid (4.2).

7.7 FAAS determination of copper in the electrolyte, filter residues and sulfide precipitates

7.7.1 FAAS determination of copper in the filtrate of the sulfide precipitation

Dilute the filtrate (reserved in 7.5.1) in the 500 ml volumetric flask nearly to the mark with water, mix and equilibrate at room temperature; then fill up exactly to the mark and mix again.

Aspirate the test solution and the calibration solutions A (4.26.1) into the atomic absorption spectrometer (5.8) using an air/acetylene flame and a wavelength of 324,7 nm. Note the absorbances. For exact determination, use the test solution and the two nearest calibration solutions (one less concentrated than and the other more concentrated than the test solution). Repeat these measurements twice.

Calculate the mass of copper (m_3) in the test solution.

NOTE Alternatively, an ICP atomic emission spectrometer (5.9) can be used for the determination of copper at a wavelength of 324,7 mm.

During all FAAS or ICP-AES determinations, the test solutions and calibration solutions should have the same temperature, as well as the same acid(s) concentration.

7.7.2 Treatment of hydroxide precipitate in sulfide separation

Wash the precipitate from the filter paper containing the hydroxide precipitate from 7.5.1 into the original beaker with a minimum quantity of water. Rinse the filter paper alternately with warm hydrochloric acid and water. Collect the filter rinses in the same beaker as the original precipitate. Add 15 ml of hydrochloric acid (4.23) and boil to dissolve the hydroxide precipitate. Allow to cool and combine the solution with the electrolyte reserved in 7.6 in a 500 ml volumetric flask. Reserve the filter paper.

7.7.3 FAAS determination of copper in the electrolyte, filter residues and precipitates (sulfide separation method)

Transfer the filter papers reserved at 7.4, 7.5.1 and 7.7.2 to the original beaker (or Erlenmeyer flask) and dissolve the paper by heating with 30 ml of concentrated nitric acid (4.1) and 10 ml of concentrated sulfuric acid (4.3). Add 5 ml of perchloric acid (4.18) for the oxidation of sulfur and heat until strong white fumes of sulfuric acid are evolved.

If the residue appears dark (presence of carbon), slowly add a small amount of the nitration mixture (4.7) until the solution becomes colourless or bluish. Allow to cool.

Dilute with 20 ml of water, transfer the residue to a platinum dish (5.10) or a PTFE dish (5.11), add 20 ml of hydrofluoric acid (4.19) and heat again until fuming of sulfuric acid occurs.

If the use of perchloric acid is not possible, place the filter paper in a platinum cruicible and gently ash the paper in a muffle furnace at 800 °C. Allow to cool, then add 5 ml of concentrated sulfuric acid (4.3) and 10 ml of hydrofluoric acid (4.19) and heat again until fuming of sulfuric acid occurs.

Dissolve the residue with 20 ml of water and combine this solution with the electrolyte reserved in 7.6 in a 500 ml volumetric flask. Fill up with water nearly to the mark, mix and equilibrate at room temperature; then fill up exactly to the mark and mix again.

Aspirate the test solution and the calibration solutions B (4.26.2) into the atomic absorption spectrometer (5.8) using an air/acetylene flame and a wavelength of 324,7 nm. Note the absorbances. For exact determination, use the test solution and the two nearest calibration solutions (one less concentrated and the other more concentrated than the test solution). Repeat these measurements twice.

Calculate the mass of copper (m_4) in the test solution.

NOTE 1 Alternatively, an ICP atomic emission spectrometer (5.9) can be used for the determination of copper using a wavelength of 324,7 mm.

During all FAAS determinations, the test solutions and calibration solutions should have the same temperature, as well as the same acid(s) concentration.

7.8 FAAS determination of copper in the electrolyte, filter residues and precipitates (hydroxide separation method)

Take the precipitate containing the hydroxide precipitate from 7.5.2 and wash it into the original beaker with a minimum quantity of water. Rinse the filter paper alternately with warm hydrochloric acid (4.23) and water. Collect the filter rinses in the same beaker as the original precipitate. Add 15 ml of hydrochloric acid (4.23) and boil to dissolve the hydroxide precipitate. Allow to cool, combine the solution with the electrolyte reserved in 7.6 in a 500 ml volumetric flask. Reserve the filter paper and original beaker.

Transfer both filter papers (reserved in 7.4 and above) to the original beaker, and dissolve the paper by heating with 50 ml of concentrated nitric acid (4.1) and 10 ml of concentrated sulfuric acid (4.3). Add 5 ml of perchloric acid (4.18) for the oxidation of sulfur and heat until strong white fumes of sulfuric acid are evolved. If the residue appears dark (presence of carbon), slowly add a small amount of the nitration mixture (4.7) until the solution becomes colourless or bluish. Allow to cool.

Dilute with 20 ml of water, transfer the residue to a platinum dish (5.10) or PTFE dish (5.11), add 20 ml of hydrofluoric acid (4.19) and heat again until fuming of sulfuric acid occurs.

If the use of perchloric acid is not possible, place the filter paper in a platinum crucible and gently ash the paper in a muffle furnace at 800 °C. Allow to cool, then add 5 ml of concentrated sulfuric acid (4.3) and 10 ml of hydrofluoric acid (4.19) and heat again until fuming of sulfuric acid occurs.

Dissolve the residue with 5 ml of water and combine this solution with the electrolyte reserved above in a 500 ml volumetric flask. Fill up with water nearly to the mark, mix and equilibrate at room temperature, then fill up exactly to the mark and mix again.

Aspirate the test solution and the calibration solutions C (4.26.3) into the atomic absorption spectrometer (5.8) using an air/acetylene flame and a wavelength of 324,7 nm. Note the absorbances. For exact determinations, use the test solution and the two nearest calibration solutions (one less concentrated the other more concentrated than the test solution). Repeat these measurements twice.

Calculate the mass of copper (m_3) in the test solution.

NOTE Alternatively, an ICP atomic emission spectrometer (5.9) can be used for the determination of copper using a wavelength of 324,7 mm.

During all FAAS determinations, the test solutions and calibration solutions should have the same temperature, as well as the same acid(s) concentration.

8 Expression of results

The mass fraction of copper in the test portion, w_{Cu} expressed as a percentage, is calculated from the following equation:

$$w_{Cu} = \frac{m_2 - m_1 + m_3 + m_4 - m_5}{m} \times 100 \times \frac{100}{100 - H} \quad (1)$$

where

m_1 is the mass, in grams, of the electrode before copper deposition;

m_2 is the mass, in grams, of the electrode after copper deposition;

m_3 is the mass, in grams, of copper in the filtrate of the sulfide precipitation (in the case where hydroxide separation was used, m_3 = 0);

m_4 is the mass, in grams of copper in the electrolyte, hydroxide precipitation and residues;

m_5 is the blank value, in grams;

m is the mass, in grams, of the test portion;

H is the hygroscopic moisture content, in percent, of the test portion (in the case of a predried test portion being used, H = 0).

Calculate the mass fraction of copper in the test portion to the second decimal place.

9 Precision

9.1 Expression of precision

The precision of this analytical method is expressed by the following equations:

Sulfide separation method

s_r = 0,000 7 X + 0,037 0 (2)

s_L = 0,004 0 X – 0,010 5 (3)

Hydroxide separation method

s_r = 0,000 2 X + 0,043 9 (4)

s_L = 0,000 9 X + 0,051 4 (5)

where

X is the mean mass fraction of copper, expressed as a percentage, in the sample;

s_r is the within-laboratory standard deviation, expressed as a percentage by mass of copper;

s_L is the between-laboratories standard deviation, expressed as a percentage by mass of copper.

NOTE Additional information is given in Annex C.

9.2 Method for obtaining the final result (see Annex B)

Calculate the following quantities from the duplicate results X_1 and X_2 and process according to the flowchart in Annex B:

Mean of duplicates: $X = (X_1 + X_2)/2$ (6)

Within-laboratory standard deviation: Sulfide separation method $s_r = 0{,}000\ 7\ X + 0{,}037\ 0$ (7)

Hydroxide separation method $s_r = 0{,}000\ 2\ X + 0{,}043\ 9$ (8)

Repeatability limit: $r = 2{,}8\ s_r$ (9)

9.3 Precision between laboratories

The precision between laboratories is used to determine the agreement between the results reported by two (or more) laboratories. It is assumed that all laboratories followed the same procedure.

Calculate the following quantities:

Mean of final results: $\mu_{1,2} = (\mu_1 + \mu_2)/2$ (10)

Between-laboratories standard deviation : Sulfide separation method $s_L = 0{,}004\ 0\ \mu_{1,2} - 0{,}010\ 5$ (11)

Hydroxide separation method $s_L = 0{,}000\ 9\ \mu_{1,2} + 0{,}051\ 4$ (12)

Within-laboratory standard deviation : Sulfide separation method $s_r = 0{,}000\ 7\ \mu_{1,2} + 0{,}037\ 0$ (13)

Hydroxide separation method $s_r = 0{,}000\ 2\ \mu_{1,2} + 0{,}043\ 9$ (14)

Permissible difference $P = 2{,}8\sqrt{s_L^2 + s_r^2/2}$ (15)

Range: $E = |\mu_1 - \mu_2|$ (16)

where

μ_1 is the final result, expressed as a percentage by mass of copper, reported by laboratory 1.

μ_2 is the final result, expressed as a percentage by mass of copper, reported by laboratory 2.

If E is equal to or less than P, the final results are in agreement.

9.4 Check of trueness

The trueness of the analytical method can be checked by applying it to a certified reference material (CRM). The procedure is the same as that described in Clause 7. When the precision has been confirmed, the final laboratory result can be compared with the certified value, A_c.

The following two possibilities exist:

$$|\mu_c - A_c| \leq C \quad (17)$$

If this condition exists, the difference between the reported result and the certified value is statistically insignificant.

$$|\mu_c - A_c| > C \quad (18)$$

If this condition exists, the difference between the reported result and the certified value is statistically significant.

In Equations (17) and (18), the symbols have the following meanings:

μ_c is the final result, expressed as a percentage by mass of copper, of the certified reference material;

A_c is the certified value, expressed as a percentage by mass of copper, of the certified reference material;

C is a quantity, expressed as a percentage by mass of copper, depending on the type of the certified reference material used, as defined in 9.4.1.

9.4.1 Type of certified reference material (CRM) or reference material (RM)

The reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35:2006, *Reference materials — General and statistical principles for certification*.

9.4.1.1 Reference material certified/characterized by an interlaboratory test programme

The quantity C (see 9.4), expressed as a percentage by mass of copper, is given by the following equation:

$$C = 2\sqrt{s_L^2 + s_r^2 / n + S^2\{A_c\}} \qquad (19)$$

where

$S^2\{A_c\}$ is the variance of the certified value;

n is the number of replicate determinations.

9.4.1.2 Reference material certified/characterized by one laboratory

The quantity C (see 9.4), expressed as a percentage by mass of copper, is given by the following equation:

$$C = 2\sqrt{2s_L^2 + s_r^2 / n} \qquad (20)$$

It is recommended that this type of certified reference material should be avoided, unless the particular CRM is known to have an unbiased certified value.

10 Test report

The test report shall include the following information.

a) identification of the sample;

b) a reference to this International Standard, i.e. ISO 10469;

c) mass fraction of copper in the sample, expressed as a percentage;

d) date on which the test was carried out;

e) any occurrences noticed during the determination which may have had an influence on the results.

Annex A
(normative)

Procedure for the preparation and determination of the mass of a predried test portion

A.1 Scope

This annex specifies a method for the preparation and determination of the mass of a predried test portion in the analysis of copper sulfide concentrates.

The method is applicable to copper sulfide concentrates not susceptible to oxidation, and with hygroscopic moisture contents ranging from 0,05 % to 2 %.

A.2 Principle

The test portion to be used for analysis is dried in air in an oven maintained at 105 °C ± 5 °C. The dried test portion is then weighed and used for the analysis. No correction for hygroscopic moisture is required.

A.3 Chemicals

A.3.1 Dessiccant, such as self-indicating silica gel or anhydrous magnesium perchlorate.

WARNING — Care must be taken when disposing of exhausted magnesium perchlorate. It must be washed down the sink with a stream of running water.

A.4 Apparatus

Ordinary laboratory equipment and the following.

A.4.1 Analytical balance, sensitive to 0,1 mg.

A.4.2 Weighing vessels, of glass or silica or corrosion-resistant metal, with externally fitting airtight covers. For small test portions (of mass less than 3 g), the mass of the vessel shall be as small as possible, i.e. less than 20 g.

A.4.3 Laboratory oven, capable of maintaining a temperature of 105 °C ± 5 °C.

A.5 Procedure

A.5.1 Preparation of the weighing vessel

Dry the weighing vessel and its cover (A.4.2) by heating in the laboratory oven (A.4.3) at 105 °C ± 5 °C for 1 h. Transfer the vessel and its cover to a desiccator containing a suitable fresh desiccant (A.3.1) and allow to cool to ambient temperature.

A.5.2 Test portion

Tare the dried weighing vessel and its cover (A.5.1). Immediately add the mass of laboratory sample specified for analysis. An accurate total mass of the test portion and weighing vessel is not required at this point.

A.5.3 Determination of the test-portion dry mass

Transfer the uncovered weighing vessel and the test portion and the vessel cover to the laboratory oven (A.4.3) and dry at 105 °C ± 5 °C for 2 h. After the 2 h period, remove the weighing vessel and dry test portion from the oven, replace the vessel cover and allow to cool to ambient temperature in the dessicator. When cool, remove the weighing vessel containing the dry test portion and the vessel cover from the dessicator, and weigh to the nearest 0,1 mg (m_8) after slightly lifting the cover and quickly replacing it.

Transfer the test portion into the appropriate analytical apparatus and immediately reweigh the empty weighing vessel and its cover. Record the mass (m_9) to the nearest 0,1 mg.

For new concentrates of unknown characteristics, it is advisable to repeat the drying for another 2 h at 105 °C ± 5 °C, and to reweigh the weighing vessel containing the test portion and the vessel cover to the nearest 0,1 mg (m'_8). The mass of the test portion can be considered to be constant if the difference ($m_8 - m'_8$) is less than or equal to 0,5 mg. If this condition is not achieved, the drying and weighing steps should be repeated.

A.6 Calculation of the dry mass of the test portion

The dry mass of the test portion (m_{10}, in grams) is given by the following equation:

$$m_{10} = m_8 - m_9 \qquad \text{(A.1)}$$

where

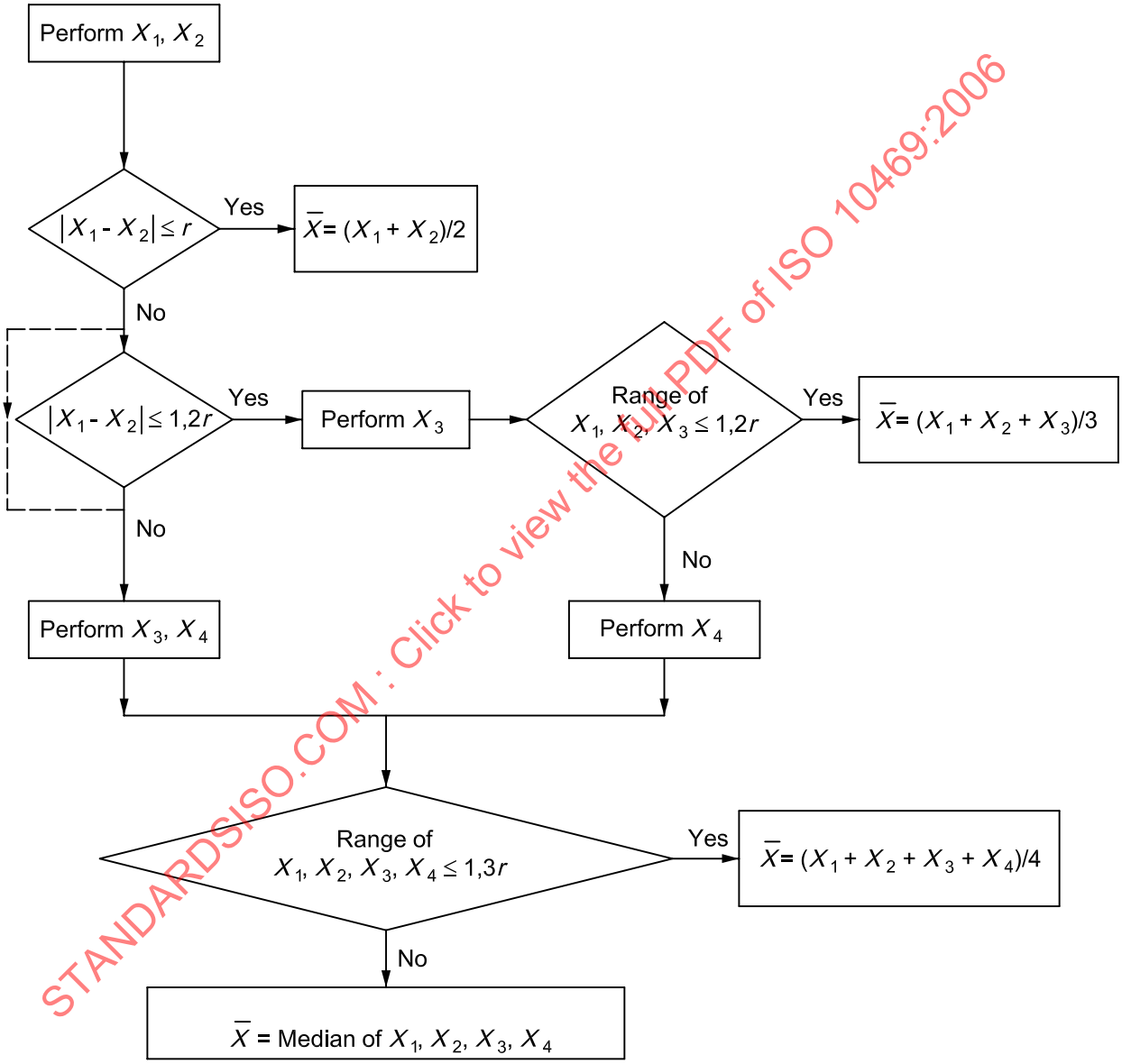
m_8 is the mass, in grams, of the dried test portion plus the weighing vessel and its cover;

m_9 is the mass, in grams, of the empty weighing vessel plus its cover.

The mass of the dry test portion is the mass to be used to calculate the element content in the laboratory sample on a dry basis. No correction for hygroscopic moisture is required.

Annex B
(normative)

Flowsheet of the procedure for the acceptance of analytical values for test samples



Annex C
(informative)

Derivation of precision equations

C.1 Introduction

This International Standard was tested in an interlaboratory test programme involving seven countries and 20 laboratories. Five samples of copper concentrate covering the range 20 % (m/m) to 54 % (m/m) were analysed to determine their mass fraction of copper. The test programme was designed to determine the repeatability and within-laboratory and between-laboratories reproducibilities in general, using the principles of ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

C.2 Design of the test programme

The analytical test programme was designed with the aim of providing maximum information. Each laboratory used two samples (two bags) of each concentrate, and each sample was analysed twice independently.

C.3 Test samples

This test programme used five samples of copper concentrate. The composition of these samples is shown in Table C.1.

C.4 Statistical evaluation

The procedure for statistical evaluation is illustrated schematically in Figure C.1. The results of the statistical evaluation are summarized in Table C.2.

The estimated precisions (s_r, s_L, r and P) are plotted against their corresponding sample means on a graph as shown in Figure C.2 (sulfide separation method) and Figure C.3 (hydroxide separation method), and the regression equations of these precisions against sample means were computed and are presented in Table C.2.