INTERNATIONAL STANDARD

ISO 10258

Second edition
2015-07-01

Copper sulfide concentrates — Determination of copper content — Titrimetric methods

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

Reference number
ISO 10258:2015(E)

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

Contents

Page

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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:

$$f_1 = \frac{m_1}{V_1} \tag{1}$$

$$f_2 = \frac{m_2}{V_2} \tag{2}$$

$$f_3 = \frac{m_3}{V_3} \tag{3}$$

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.

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

8 Expression of results

The copper content of the test portion w_{Cu}, expressed as a percentage by mass, is given by Formula (5):

$$w_{Cu} = \frac{(V \times f + m_4) \times 100}{m} \times \frac{100}{100 - H} \quad (5)$$

where

V is the volume, in millilitres, of sodium thiosulfate standard volumetric solution used;

f is the mean standardization factor, in grams of copper per millilitre, for the sodium thiosulfate standard volumetric solution, calculated in 4.20.1.2;

m_4 is the mass, in grams, of residual copper determined by FAAS, calculated in 7.3.5.3;

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

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

Calculate the copper content of 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 formulae:

a) Long iodide method

$$s_r = 0{,}000\,8\,\overline{X} + 0{,}048\,5 \quad (6)$$

$$s_L = 0{,}004\,2\,\overline{X} - 0{,}007\,7 \quad (7)$$

b) Short iodide method

$$s_r = 0{,}001\,4\,\overline{X} + 0{,}028\,2 \quad (8)$$

$$s_L = 0{,}000\,5\,\overline{X} + 0{,}081\,9 \quad (9)$$

where

$\overline{X}$ is the mean content of copper, expressed as a percentage by mass, 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:

a) Mean of duplicates

$$\bar{x} = \frac{x_1 + x_2}{2} \tag{10}$$

b) Within-laboratory standard deviation long iodide method

$$s_r = 0{,}000\,8\,\bar{X} + 0{,}048\,5 \tag{11}$$

c) Short iodide method

$$s_r = 0{,}001\,4\,\bar{X} + 0{,}028\,2 \tag{12}$$

d) Repeatability limit

$$r = 2{,}8\,s_r \tag{13}$$

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 the laboratories followed the same procedure.

Calculate the following quantities:

a) Mean of final results

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \tag{14}$$

b) Between-laboratories standard deviation

1) Long iodide method

$$s_L = 0{,}004\,2\,\mu_{1,2} - 0{,}007\,7 \tag{15}$$

2) Short iodide method

$$s_L = 0{,}000\,5\,\mu_{1,2} + 0{,}081\,9 \tag{16}$$

c) Within-laboratory standard deviation

1) Long iodide method

$$s_r = 0{,}000\,8\,\mu_{1,2} + 0{,}048\,5 \tag{17}$$

2) Short iodide method

$$s_r = 0{,}001\,4\,\mu_{1,2} + 0{,}028\,2 \tag{18}$$

d) Permissible difference

$$P = 2{,}8\sqrt{s_L^2 + \frac{s_r^2}{2}} \tag{19}$$

e) Range

$$E = |\mu_1 - \mu_2| \tag{20}$$

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 less than or equal to 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:

a) $|\mu_c - A_c| \leq C$ (21)

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

b) $|\mu_c - A_c| > C$ (22)

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

where

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 below.

The reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35.

Where the reference material is certified/characterized by an interlaboratory test programme, the quantity C (see 9.4), expressed by mass of copper, is given by the following formula:

$$C = 2\sqrt{s_L^2 + \frac{s_r^2}{n} + s^2\{A_c\}} \quad (23)$$

where

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

n is the number of replicate determinations.

Where the reference material is certified/characterized by one laboratory, the quantity C, expressed as a percentage by mass of copper, is given by the following formula:

$$C = 2\sqrt{2s_L^2 + \frac{s_r^2}{n}} \quad (24)$$

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

10 Test report

The test report shall contain the following information:

a) identification of the sample;

b) a reference to this International Standard, i.e. ISO 10258;

c) copper content of the sample, expressed as a percentage by mass;

d) date on which the test was carried out;

e) any occurrences noticed during the determination that could 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 General

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 having 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 moisture is required

A.3 Reagent

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

WARNING — Care needs to be taken whenever disposing of exhausted magnesium perchlorate and all other laboratory chemicals. Environmental regulations often apply. Users should seek specialist's advice to determine an appropriate, effective, health-conscious, safety-conscious, and environmentally sound means of disposal.

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 (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 vessel 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 test portion and 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 cooling to ambient temperature in the desiccator. When cool, remove the weighing vessel containing dry test portion and vessel cover from the desiccator and weigh to the nearest 0,1 mg (m_6) 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_7) 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 re-weigh the weighing vessel and test portion plus vessel cover to the nearest 0,1 mg (m'_6). The mass of the test portion can be considered to be constant if the difference ($m_6 - m'_6$) 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_8, in grams, is given by Formula (A.1):

$$m_8 = m_6 - m_7 \tag{A.1}$$

where

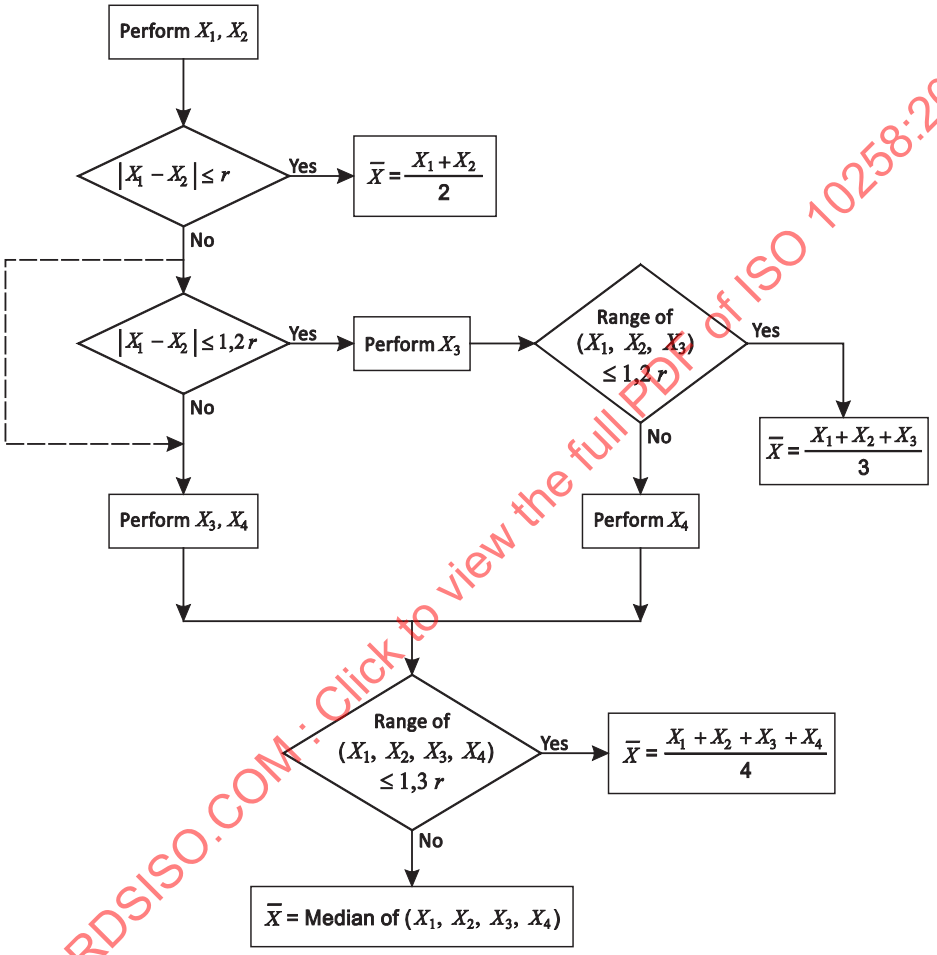
m_6 is the mass, in grams, of the dried test portion plus the weighing vessel and its cover;

m_7 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
(informative)

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



NOTE r is defined in 9.2.

Figure B.1 — Flowsheet of the procedure for the acceptance of analytical values for test samples

Annex C
(informative)

Derivation of precision formulae

C.1 General

This International Standard was tested in an interlaboratory test programme involving 8 countries and 18 laboratories. Five samples of copper concentrate covering the range 20 % (m/m) to 60 % (m/m) were analysed to determine the copper content. 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.

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.

Table C.1 — Composition of copper concentrated samples

Element	Unit	Sample numbers				
		85–6[a]	85–7[b]	85–8[c]	87–12[d]	87–18[e]
Cu	% (m/m)	≈ 20	≈ 25	≈ 35	≈ 50	≈ 30
Ag	g/t	1 250	35	170	100	≈ 70
Au	g/t	1	1	1	1	≈ 25
Zn	% (m/m)	13	< 1	1	0,1	< 1
MgO	% (m/m)	≈ 0,1	≈ 5	0,1	< 1	≈ 0,5
Bi	% (m/m)	≈ 0,01	< 0,01	≈ 0,005	< 0,001	≈ 0,005
Se	g/t	≈ 50	≈ 50	≈ 50	≈ 10	≈ 150
Te	g/t	≈ 10	< 5	< 5	≈ 5	≈ 5
SiO_2	% (m/m)	< 1	17	6	15	≈ 6
Fe	% (m/m)	23	2	22	1	≈ 25
S	% (m/m)	33	9	34	15	≈ 30
As	% (m/m)	0,1	0,1	0,2	0,1	≈ 0,02
Sb	% (m/m)	1,1	0,01	0,1	< 0,1	≈ 0,03
Sn	% (m/m)	≈ 0,05	≈ 0,05	< 0,01	< 0,1	≈ 0,01
Cd	% (m/m)	≈ 0,002	≈ 0,002	≈ 0,002	< 0,01	≈ 0,001
Ni	% (m/m)	≈ 0,02	≈ 0,02	< 0,01	< 0,01	< 0,01
CaO	% (m/m)	< 1	≈ 12	≈ 0,1	1	≈ 0,5
Al_2O_3	% (m/m)	< 1	≈ 6	≈ 2	1	≈ 2
Pb	% (m/m)	6	1	0,03	≈ 5	≈ 0,02
K_2O	% (m/m)	n.d.	0,2	≈ 1	< 0,01	≈ 0,2

[a] Rammelsberg concentrate (Germany).

[b] Polish concentrate (Poland).

[c] Caridad concentrate (Mexico).

[d] Coro-Coro concentrate (Bolivia).

[e] Bougainville concentrate (Papua New Guinea).

n.d. = not determined

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.