INTERNATIONAL STANDARD

ISO 13546

First edition
2021-07

Copper concentrates — Determination of mercury content — Cold vapour atomic absorption spectrometric method

Concentrés de cuivre — Dosage du mercure — Méthode par spectrométrie d'absorption atomique de vapeur froide

Reference number
ISO 13546:2021(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

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 of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Copper concentrates — Determination of mercury content — Cold vapour atomic absorption spectrometric method

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

1 Scope

This document specifies an acid digestion and vapour generation atomic absorption spectrometric method for the determination of the mercury content in copper sulfide concentrates.

This document is applicable to mass fraction of mercury between 5 µg/g and 65 µg/g in copper sulfide concentrates.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 — Single-volume pipettes*

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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*

ISO 12743:2018, *Copper, lead, zinc and nickel concentrates — Sampling procedures for determination of metal and moisture content*

ISO Guide 35, *Reference materials — Guidance for characterization and assessment of homogeneity and stability*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

The test portion is decomposed by treatment with hydrochloric and nitric acid at a temperature between 60 °C and 80 °C followed by the addition of potassium permanganate as oxidizing agent. Subsequently, the potassium permanganate is reduced by hydroxylamine hydrochloride. The mercury

vapour is generated by vapour generation using tin (II) chloride as reduction agent. The equipment is set to measure the absorbance at 253,7 nm. The absorbances of the test and calibration solutions, including those of certified or other reference materials, are compared to determine the mercury content.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and grade 2 water in accordance with ISO 3696.

Reagents shall be selected or purified for the lowest possible blank value.

5.1 Tin (II) chloride dehydrate, ($SnCl_2.2H_2O$), containing < 5 mg/g mercury.

5.2 Potassium permanganate ($KMnO_4$).

5.3 Hydroxylamine hydrochloride ($HONH_2.HCl$).

5.4 Mercury (II) chloride ($HgCl_2$).

5.5 Nitric acid, ρ = 1,42 g/ml.

5.6 Hydrochloric acid, ρ = 1,16 g/ml to 1,19 g/ml.

5.7 Sulfuric acid, ρ = 1,84 g/ml.

5.8 Sulfuric acid solution, diluted 1 + 5.

5.9 Sulfuric acid solution, diluted 1 + 9.

5.10 Aqua regia. Mix 300 ml of hydrochloric acid (5.6) and 100 ml nitric acid (5.5). Prepare freshly for each batch of mercury determination.

5.11 Tin (II) chloride solution, 100 g/l. Add 10 g of tin (II) chloride (5.1) to 80 ml sulfuric acid solution (5.9). Heat and swirl to dissolve. Cool the solution and dilute with deionized water to 100 ml and mix thoroughly.

Continuously stir the solution with a magnetic stirrer for at least 2 h before use and maintain stirring during analysis. Prepare weekly.

Hydrochloric acid may be used instead of sulfuric acid.

Alternative procedure:

Tin (II) chloride solution, 100 g/l: add 10 g of tin (II) chloride (5.1) to 20 ml of deionized water. Add continuously 60 ml of sulfuric acid solution (5.8). Heat and swirl to dissolve. Cool, dilute to 100 ml with deionized water and mix thoroughly.

5.12 Potassium permanganate ($KMnO_4$) solution, 2 g/l. Add 0,2 g of potassium permanganate (5.2) to 100 ml of deionized water. Store in a glass bottle.

5.13 Hydroxylamine hydrochloride solution, 20 g/l. Add 2 g of hydroxylamine hydrochloride (5.3) to 100 ml of deionized water.

5.14 Mercury trapping solution. Add 10 g of potassium permanganate (5.2) to 100 ml of water and mix well. This reagent is used to oxidize mercury vapour to its Hg^{2+} state and trap it in solution.

5.15 Nitric acid solution, diluted (1+9).

5.16 Mercury standard solution A, 100 µg/ml. Weigh 0,1354 g of mercury (II) chloride (5.4) into a 250 ml beaker and dissolve in 100 ml of nitric acid (5.5). Quantitatively transfer to a 1-l volumetric flask with water. Mix and store in a labelled glass container.

Alternatively, use a suitable high-quality commercial standard solution.

5.17 Mercury standard solution B, 10 µg/ml. Pipette 10 ml of mercury standard solution A (5.16) into a 100-ml volumetric flask containing 10 ml nitric acid (5.5). Dilute to volume with water. Mix and store in a labelled volumetric flask.

Prepare the solution monthly.

5.18 Mercury standard solution C, 0,1 µg/ml. Pipette 10 ml of mercury standard solution B (5.17) into a 1-l volumetric flask containing 100 ml of nitric acid (5.5). Dilute to volume with water. Mix and store in a labelled volumetric flask.

The solution should be freshly prepared.

6 Apparatus

All laboratory glassware and equipment shall be free of mercury contamination. Use ordinary laboratory apparatus, including pipettes and volumetric flasks conforming with the specifications of ISO 648 and ISO 1042, respectively, and the following:

6.1 Analytical balance, sensitive to 0,1 mg.

6.2 Magnetic stirrers.

6.3 Laboratory glassware, of class A conforming with ISO 385, ISO 648, ISO 1042 and used in accordance with ISO 4787.

6.4 Atomic absorption spectrometer, equipped with a mercury hollow cathode lamp or electrodeless discharge lamp or a continuum radiation source.

WARNING — Follow the manufacturer's instructions to avoid possible explosion hazards when igniting and extinguishing the air-acetylene flame and possible burning from the hot electric furnace. Wear tinted safety glasses whenever the atomic absorption spectrometer is in operation. Good ventilation is necessary to prevent poisoning by mercury hydride.

The atomic absorption spectrometer used in this method shall meet the following criteria:

a) Minimum sensitivity: the absorbance of the highest concentration calibration solution (see 8.7) is at least 0,5 µg/ml.

b) Graph linearity: the slope of the calibration graph covering the top 20 % of the concentration range (expressed as a change in absorbance) is not less than 0,7 of the value of the slope for the bottom 20 % of the concentration range determined in the same way.

c) Minimum stability: the standard deviation of the absorbance of the most concentrated calibration solution and that of the zero-calibration solution, each being calculated from a sufficient number of repetitive measurements, are less than 1,5 % and 0,5 %, respectively, of the mean value of the absorbance of the most concentrated solution.

The use of a strip-chart recorder, digital readout device or both is recommended to evaluate criteria a), b) and c) and for all subsequent measurements.

Parameters will vary with each instrument.

6.5 Stopwatch.

6.6 Hotplate.

7 Sampling and sampling preparation

7.1 Test sample

Prepare an air-equilibrated test sample and a hygroscopic moisture test sample in accordance with ISO 9599.

Mercury can evaporate from samples at elevated temperatures, so a separate chemical analysis sample shall be prepared as described in ISO 12743:2021, 16.2.

7.2 Test portion

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

Table 1 — Recommended test portion masses

Mercury content of sample µg/g	Mass of test portion g
< 50	1,0000
50 to 65	0,5000

8 Procedure

8.1 Number of determinations

Carry out the determinations at least in duplicate in accordance with Annex A, independently, on each test sample.

NOTE The expression "independently" means that the second and any subsequent result is not affected by previous results. For this particular analytical method, this condition implies that the repetition of the procedure is carried out either by the same operator at a different time or by a different operator including, in either case, appropriate recalibration.

8.2 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 repeat the analysis.

8.3 Dissolution of the test portion

Transfer the test portion (7.2) to a conical beaker. Wash down the walls of the conical beaker with 5 ml of deionized water so that none of the sample remains on the walls. Carefully add 25 ml of aqua regia (5.10) while swirling the solution. Leave for 30 min at room temperature. Then, using a hotplate to maintain the temperature between 60 °C and 80 °C, digest the sample for 1 h.

If the mercury content of the test portion is to be determined within 6 h then proceed to 8.5. Otherwise, store the samples using the procedure described in 8.4.

8.4 Storage of digested solutions

Dilute the cooled solution from 8.3 to approximately 60 ml and add 10 ml of potassium permanganate solution (5.12), then cover the beaker with a watch glass or other suitable cover to minimize contamination of the sample.

When the mercury content of the sample is going to be determined, reduce the potassium permanganate by adding dropwise hydroxylamine hydrochloride solution (5.13) until the pink colour disappears, while swirling the conical beaker slowly to ensure adequate mixing.

8.5 Preparation of sample solutions

Dilute the sample solution from either 8.3 or 8.4 to approximately 80 ml with deionized water. If necessary, allow the solution to cool to room temperature and then dilute to 100 ml.

8.6 Preparation of test solutions

Prepare test solutions for each determination at least in duplicate.

Pipette 1 ml to 5 ml of the sample solution prepared in 8.5, containing between 0,1 µg and 0,5 µg of mercury, into the reaction vessel used for mercury determination. Dilute this solution to 100 ml with nitric acid solution (5.15).

8.7 Preparation of calibration solutions

Prepare all calibration solutions at least in duplicate.

With the mercury standard solution C 0,1 µg/ml Hg (5.18) and using Table 2 as a guide, prepare a series of calibration standards using pipettes to transfer the appropriate volumes into separate reaction vessels and dilute to 100 ml with nitric acid solution (5.15).

Table 2 — Calibrating solutions

Volume of mercury standard solution ml	Mercury content µg
1	0,1
2	0,2
3	0,3
4	0,4
5	0,5

8.8 Preparation of mercury calibration graph

Set up the atomic absorption spectrometer (6.4) according to the guidelines set out in 6.4. Adjust the instrument read-out scale to zero. Using vapour generation equipment, reduce the mercury in the first duplicate of the calibration solutions prepared in 8.7 with 5 ml of tin (II) chloride solution (5.11). Record the absorbance of the generated vapour with the atomic absorption spectrometer (6.4). If necessary, flush out any residual mercury vapour from the vapour generation apparatus and check for condensed water vapour on the absorption cell.

Calculate the average absorbance for each calibration solution. Plot a graph of the average absorbance versus micrograms of mercury and repeat any errant standards.

NOTE New instruments are usually equipped with software to calculate and draw the calibration curve.

8.9 Determination of mercury content in test solutions

Immediately after calibrating the atomic absorption spectrometer, determine the mercury content in the test solutions prepared in 8.6.

Adjust the instrument read-out scale to zero and using vapour generation equipment reduce the mercury in the first duplicate of the test solutions prepared in 8.6 with 5 ml of tin (II) chloride solution (5.11). Record the absorbance of the generated vapour with the atomic absorption spectrometer (6.4). If necessary, flush out any residual mercury vapour from the vapour generation apparatus and check for condensed water vapour on the absorption cell. Repeat this procedure for the second duplicate.

If the difference in absorbance between the two test solutions exceeds 5 % then re-prepare the test solution as per 8.6 and repeat the mercury determination.

9 Expression of results

From the graph determined in 8.8 establish the micrograms of mercury found (F_{Hg}) in the aliquot taken in 8.6 by calculating the mercury content of the sample according to Formula (1):

$$w_{Hg} = \left(\left(\left(F_{Hg} - B\right)*100\right)/\left(V_a * m\right)\right)*K \quad (1)$$

where

w_{Hg} is the mercury content of the sample, in µg/g;

F_{Hg} is the mass of mercury found in test sample aliquot, in µg;

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

V_a is the volume of the test sample aliquot, in ml;

B is the mass of mercury found in the blank test, in µg, corrected as follows: $\left(F_{Hg\,b} * V_a\right)/V_{a\,b}$;

$F_{Hg\,b}$ is the mass of mercury found in blank test, in µg;

$V_{a\,b}$ is the volume of blank test aliquot, in ml;

K is the hygroscopic moisture conversion factor determined as follows: $K = 100/(100 - H)$;

H is the hygroscopic moisture content of the sample determined by ISO 9599.

10 Procedure for obtaining the final result

Process the duplicate results for each test portion of the sample according to Figure A.1 and repeat the determination for a sample as necessary.

11 Precision

11.1 Expression of precision

The precision of this analytical method is expressed by Formulae (2) and (3):

$$S_r = 0{,}059\,4X + 0{,}074\,4 \quad (2)$$

$$S_L = 0{,}150\ 0X + 0{,}099\ 4 \quad (3)$$

where

X is the concentration of mercury in the sample, in µg/g;

S_r is the within-laboratory standard deviation;

S_L is the between-laboratory standard deviation.

11.2 Procedure for obtaining the final result

Calculate the quantities in Formulae (4) to (6) from the duplicate results X_1 and X_2 (%) and process according to Annex A.

Mean of duplicates:

$$X = (X_1 + X_2)/2 \quad (4)$$

Within-laboratory standard deviation (repeatability):

$$S_r = 0{,}059\ 4X + 0{,}074\ 4 \quad (5)$$

Repeatability limit:

$$r = 2{,}8S_r \quad (6)$$

11.3 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 quantities in Formulae (7) to (11).

Mean of final results:

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \quad (7)$$

where

μ_1 is the final result, in µg/g, reported by laboratory 1;

μ_2 is the final result, in µg/g, reported by laboratory 2.

Between-laboratory standard deviation:

$$S_L = 0{,}150\ 0X + 0{,}099\ 4 \quad (8)$$

Within-laboratory standard deviation:

$$S_r = 0{,}059\ 4X + 0{,}074\ 4 \quad (9)$$

Permissible tolerance:

$$P = 2{,}8\left[S_L^2 + \left(S_r^2/2\right)\right]^{1/2} \quad (10)$$

$$\text{Range } E = |\mu_1 - \mu_2| \tag{11}$$

where

μ_1 is the final result, in µg/g, reported by laboratory 1;

μ_2 is the final result, in µg/g, reported by laboratory 2.

If $E \leq P$, the final results are in agreement.

11.4 Check of trueness

11.4.1 General

The trueness of the analytical method can be checked by applying it to a certified reference material (CRM). When the precision has been confirmed, the final laboratory result can be compared with the certified value, A_c.

Two possibilities exist, as shown in Formula (12) and Formula (13):

$$|\mu_C - A_C| \leq C \tag{12}$$

where

μ_C is the final result, expressed as µg/g of mercury of the CRM;

A_C is the certified value, expressed as µg/g of mercury of the CRM;

C is a quantity, expressed as µg/g of mercury, depending on the type of CRM used, as defined in 11.4.2.

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

$$|\mu_C - A_C| > C \tag{13}$$

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

11.4.2 Type of certified reference material or reference material

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

11.4.3 Reference material certified or characterized by an interlaboratory test programme

The quantity C (see 11.4.1), in 5 µg/g, is given by Formula (14):

$$C = 2\sqrt{\left(S_L^2 + S_r^2 / n + S^2\{A_c\}\right)} \tag{14}$$

where

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

n is the number of replicate determinations.

