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Copper and zinc sulfide concentrates — Determination of thallium — Acid digestion and inductively coupled plasma-mass spectrometry

Concentrés sulfurés de cuivre et de zinc — Dosage du thallium — Digestion acide et plasma à couplage inductif-spectrométrie de masse

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Foreword

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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 and zinc sulfide concentrates — Determination of thallium — Acid digestion and inductively coupled plasma-mass spectrometry

WARNING — This Document may involve hazardous materials, operations and equipment. It is the responsibility of the user of this document to establish appropriate health and safety practices prior to use.

1 Scope

This Document specifies an acid digestion and inductively coupled plasma mass spectrometry (ICP-MS) procedure for determination of the mass fraction of thallium in copper and zinc sulfide concentrates as follows.

a) For copper sulfide concentrates, the method is applicable to the determination of mass fractions of thallium from 0,000 1 % to 0,002 5 %.

b) For zinc sulfide concentrates, the method is applicable to the determination of mass fractions of thallium from 0,000 1 % to 0,025 %.

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 4787, *Laboratory glass and plastic ware — 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, *Copper, lead, zinc and nickel concentrates — Sampling procedures for determination of metal and moisture content*

ISO/GUIDE 35, *Reference materials — General and statistical principles for certification*

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

4 Principle

The test portion is decomposed in hydrochloric, nitric, hydrofluoric and perchloric acids. The thallium concentration is determined by ICP-MS using a constant amount of iridium as the internal standard.

5 Reagents

During the analysis, use only reagents of recognized guaranteed reagent quality and distilled water or water of equivalent purity.

5.1 Hydrochloric acid, concentrated (ρ_{20} 1,19 g/ml).

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

5.3 Nitric acid, dilute 1 + 1.

5.4 Hydrofluoric acid, concentrated (ρ_{20} 1,15 g/ml).

5.5 Perchloric acid, concentrated (ρ_{20} 1,70 g/ml).

5.6 Hydrogen peroxide, concentrated (ρ_{20} 1,13 g/ml).

5.7 Thallium oxide (Tl_2O_3), minimum purity 99,99 %.

5.8 Thallium standard solution, 1 ml contains 100 μg of Tl.

Weigh, to the nearest 0,1 mg, 0,111 8 g of thallium oxide (5.7), transfer to a 250 ml beaker. Add 50 ml of nitric acid (5.3) and heat gently until the oxide is dissolved. Then cool to room temperature. Transfer to a 100 0 ml one-mark volumetric flask, dilute to the mark with water and mix thoroughly.

5.9 Thallium standard solution, 1 ml contains 10 μg of Tl.

Pipette 10,00 ml of thallium standard solution (5.8) into a 100 ml one-mark volumetric flask. Add 3 ml of nitric acid (5.2), fill up nearly to the mark with water, mix, and cool to room temperature, then fill up exactly to the mark with water and mix again.

5.10 Thallium standard solution, 1 ml contains 100 ng of Tl.

Pipette 2,00 ml of thallium standard solution (5.9) into a 200 ml one-mark volumetric flask. Add 6 ml of nitric acid (5.2), fill up nearly to the mark with water, mix, and cool to room temperature, then fill up exactly to the mark with water and mix again.

5.11 Iridium standard stock solution, 1 ml contains 1 mg of Ir.

Weigh, to the nearest 0,1 mg, 0,1 g of iridium powder ($w_{Ir} \geq 99,99$ %, transfer to a 50 ml glass tube. Add 8 ml of hydrochloric acid (5.1), 2 ml hydrogen peroxide (5.6), sealing pipe. Under the temperature of 150 °C to dissolve 48 h until the powder is dissolved, then cool to room temperature, open the tube. Transfer to a 100 ml one-mark volumetric flask, add 10 ml of hydrochloric acid (5.1), fill up nearly to the mark with water, mix, and cool to room temperature, then fill up exactly to the mark with water and mix again.

5.12 Iridium internal standard solution, 1 ml contains 1 μg of Ir.

Pipette 1,00 ml of iridium standard stock solution (5.11) into a 1 000 ml one-mark volumetric flask. Add 20 ml of hydrochloric acid (5.1), fill up nearly to the mark with water, mix, and cool to room temperature, then fill up exactly to the mark with water and mix again.

NOTE Commercial and certified standard solutions can also be used.

6 Apparatus

6.1 Usual laboratory equipment, including fume hoods, hotplates and a drying oven.

6.2 Ordinary laboratory glassware.

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

6.4 Polytetrafluoroethylene beaker, of capacity 200 ml.

6.5 Analytical balance, sensitive to 0,1 mg.

6.6 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The ICP-MS should be set up according to the manufacturer's guidelines. The mass number of thallium should be set to ^{205}Tl. The mass number of internal standard should be set to ^{193}Ir.

7 Sample

7.1 Laboratory sample

Laboratory sample shall be taken and prepared in accordance with the procedures described in ISO 12743.

7.2 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).

7.3 Test portion

Taking multiple increments, extract approximately 0,20 g from the test sample 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 may be used to prepare predried test portions directly from the laboratory sample.

8 Procedure

8.1 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.

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 the reagents, the environment of the laboratory room, the condition of the ICP-MS used, and the condition of the laboratory glass and plastic ware used. If a significant blank value is obtained as a result of the blank test, check all reagents and rectify the problem.

8.3 Dissolution of the test portion

Transfer the test portion (7.3) into a 200 ml polytetrafluoroethylene beaker (6.4) and moisten with 5 ml of water.

Add 10 ml of hydrochloric acid (5.1), and heat for 5 min at 60 °C to 70 °C and cool. Add 5 ml of nitric acid (5.2) and heat gently. Add 3 ml of hydrofluoric acid (5.4), then heat gradually until the solution is about 5 ml. Add 3 ml of perchloric acid (5.5), cover with a polytetrafluoroethylene lid, heat the solution at about 200 °C until the strong white fumes evolve completely, then remove the beaker from the hotplate and cool to room temperature.

Add 12 ml of nitric acid (5.3), rinse the sides of the beaker with a minimum volume of water and then heat until the onset of boiling, allow to cool.

8.4 Preparation of test solutions

Transfer the solution (8.3) and 2,00 ml iridium standard solution (5.12) into a 200 ml of one-mark volumetric flask, dilute to the mark with water and mix thoroughly. If a small amount of residue appears, dry filter.

8.5 Preparation of calibration solutions

Using thallium standard, prepare a series of calibration standards as Table 1. Transfer 0,00 ml, 0,50 ml, 1,00 ml, 10,00 ml volume of thallium standard (5.10) and 0,25 ml, 0,50 ml, 1,00 ml, 2,00 ml, 3,00 ml volume of thallium standard (5.9), then transfer 1,00 ml iridium standard solution (5.12) into a series of 100 ml volumetric flasks, add 6 ml nitric acid (5.3), fill up nearly to the mark with water, mix, and cool to room temperature, then fill up exactly to the mark with water and mix again.

Table 1 — Preparation of calibration solutions

Thallium standard solution	Volume of thallium standard, V1/ml	Volume of iridium standard (5.12), V2/ml	Volume after dilution, V/ml	Concentration of thallium, ng/ml
—	0,00	1,00	100	0,00
5.10	0,50	1,00	100	0,50
5.10	1,00	1,00	100	1,00
Calibration solutions should be prepared at the same ambient temperature as that at which the determinations will be conducted.				

Table 1 *(continued)*

Thallium standard solution	Volume of thallium standard, V1/ml	Volume of iridium standard (5.12), V2/ml	Volume after dilution, V/ml	Concentration of thallium, ng/ml
5.10	10,00	1,00	100	10,00
5.9	0,25	1,00	100	25,00
5.9	0,50	1,00	100	50,00
5.9	1,00	1,00	100	100,00
5.9	2,00	1,00	100	200,00
5.9	3,00	1,00	100	300,00
Calibration solutions should be prepared at the same ambient temperature as that at which the determinations will be conducted.				

NOTE Determination of thallium in copper sulfide concentrates, the concentration of calibration solutions to use are 0,00 ng/ml, 0,50 ng/ml, 1,00 ng/ml, 10,00 ng/ml, 25,00 ng/ml, 50,00 ng/ml.

8.6 Preparation of thallium calibration curve

Set up the ICP-MS according to the guidelines set out in 6.6. Aspirate each calibration solution, as prepared in step 8.5, through the ICP-MS and record the intensity ratio.

Manually or electronically plot a graph of the average intensity ratio versus concentration of thallium (in ng/ml) and repeat errant standards if necessary.

8.7 Determination of thallium content in test solutions

Immediately after calibrating the ICP-MS (8.6), determine the thallium content in the test solutions from step 8.4. Adjust the instrument read-out scale to zero. Aspirate the blank test solution (8.2) through the ICP-MS and record the concentration (ρ_0). Then aspirate the first duplicate of each sample through the ICP-MS and record the concentration (ρ).

Check the calibration of the instrument, then aspirate the second duplicate of each sample in the reverse order through the ICP-MS and record the concentration (ρ).

9 Expression of results

The mass fraction of thallium in the test portion, w_{Tl}, expressed as a percentage, is given in Formula (1).

$$w_{\mathrm{Tl}} = \frac{(\rho - \rho_0) \cdot V}{m \times 10^9} \times \frac{100}{100 - H} \times 100 \tag{1}$$

where

ρ is the concentration, in nanograms per millilitre, of thallium in the test solution obtained from the calibration curve;

ρ_0 is the concentration, in nanograms per millilitre, of thallium in the blank solution;

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

V is the total volume, in millilitre, of the test solution;

H is the hygroscopic moisture content of the sample, expressed as a percentage, determined using ISO 9599.

NOTE If pre-dried test samples are used, H = 0.

10 Precision

10.1 Expression of precision

The precision of this analytical method is expressed by Formulae (2) to (7).

a) For copper sulfide concentrates:

$$s_r = 0{,}036\ \overline{X} + 0{,}000\ 003 \tag{2}$$

$$s_L = 0{,}000\ 03\ln(\overline{X}) + 0{,}000\ 3 \tag{3}$$

$$s_R = 0{,}07\ \overline{X} + 0{,}000\ 02 \tag{4}$$

b) For zinc sulfide concentrates:

$$s_r = 0{,}018\ 8\ \overline{X} + 0{,}000\ 03 \tag{5}$$

$$s_L = 0{,}031\ \overline{X} + 0{,}000\ 07 \tag{6}$$

$$s_R = 0{,}034\ 91\ \overline{X} + 0{,}000\ 09 \tag{7}$$

where

$\overline{X}$ is the mean mass fraction of thallium in the sample, expressed as a percentage;

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

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

s_R is the reproducibility standard deviation, expressed as a percentage by mass of thallium.

10.2 Method for obtaining the final result

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 duplicate results:

$$\overline{X} = \frac{X_1 + X_2}{2} \tag{8}$$

Within laboratory standard deviation (s_r), using Formula (2) for copper sulfide concentrates, Formula (5) for zinc sulfide concentrates.

b) Repeatability limit, *r*

$$r = 2{,}8s_r \tag{9}$$

10.3 Between-laboratories precision

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

Calculate the following quantities in Formula (10) to Formula (12):

a) Mean of final results:

$$\mu_{12} = \frac{\mu_1 + \mu_2}{2} \tag{10}$$

Between-laboratories standard deviation (s_L) by substituting μ_{12} for $\overline{X}$ in Formula (3) for copper sulfide concentrates and Formula (6) for zinc sulfide concentrates.

Within-laboratory standard deviation (s_r) by substituting μ_{12} for $\overline{X}$ in Formula (2) for copper sulfide concentrates and Formula (5) for zinc sulfide concentrates.

b) Permissible tolerance:

$$P = 2{,}8 \times \sqrt{s_L^2 + \frac{s_r^2}{2}} \tag{11}$$

c) Range

$$E = \left|\mu_1 - \mu_2\right| \tag{12}$$

where

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

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

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

10.4 Check of trueness

10.4.1 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.

The two possibilities shown in: Formula (13) and Formula (14) exist:

a) $$\left|\mu_c - A_c\right| \le C \tag{13}$$

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

b) $$\left|\mu_c - A_c\right| > C \tag{14}$$

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 thallium of the certified reference material;

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

C is a quantity, expressed as a percentage by mass of thallium depending on the type of certified reference material used as defined in Clause 10.4.2.

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

10.4.2.1 General

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

10.4.2.2 Reference material certified/characterized by inter-laboratory test programme

The quantity C (see 10.4.1) expressed as a percentage by mass of thallium, is given by Formula (15):

$$C = 2 \times \sqrt{s_L^2 + \frac{s_r^2}{n} + s^2(A_c)} \quad (15)$$

where

$s^2(A_c)$ is the variance of the certified value;

n is the number of replicate determinations.

10.4.2.3 Reference material certified/characterized by one laboratory

The quantity C (see 10.4.1) expressed as a percentage by mass of thallium, is given by Formula (16):

$$C = \sqrt{2s_L^2 + \frac{s_r^2}{n}} \quad (16)$$

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.

11 Test report

The test report shall contain the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) reference to this document;

d) details necessary for the identification of the sample;

e) result of the analysis;

f) reference number of the result;

g) any characteristics noticed during the determination and any operations not specified in this document which may have had an influence on the results, either for the test sample or the CRM(s);

h) the date of the test.

Annex A
(informative)

Procedure for the preparation and determination of the mass of a pre-dried test portion

A.1 General

This annex specifies a method for the preparation and determination of the mass of a pre-dried test portion in the analysis of copper and zinc sulfide concentrates. The method is applicable to sulfide concentrates not susceptible to oxidation and with hygroscopic moisture mass fractions of contents ranging from 0,05 % to 2 %.

A.2 Subclause autonumber

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 Reagents

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

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

A.4 Apparatus

Ordinary laboratory equipment is to be used in addition to 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 air-tight covers. For small test portions (of mass less than 3 g) the mass of the vessel should 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 a laboratory oven (A.4.3) at 105 °C ± 5 °C for 1 h. Transfer the vessel and its cover to a desiccator containing suitable fresh desiccant (A.3.1) and allow to cool to ambient temperature.