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Copper, lead and zinc sulfide concentrates — Determination of cadmium —

Part 2:
Acid digestion and inductively coupled plasma atomic emission spectrometric method

Concentrés de sulfure de cuivre, de plomb et de zinc — Dosage du cadmium —

Partie 2: Méthode par digestion acide et spectroscopie d'émission atomique à plasma à couplage inductif

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Foreword

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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).

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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*.

A list of all parts in the ISO 19976 series can be found on the ISO website.

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, lead and zinc sulfide concentrates — Determination of cadmium —

Part 2:
Acid digestion and inductively coupled plasma atomic emission spectrometric method

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

1 Scope

This document specifies an acid digestion and inductively coupled plasma atomic emission spectrometric (ICP-AES) method for the determination of the mass fraction of cadmium in copper, lead and zinc sulfide concentrates as follows:

a) for copper sulfide concentrates, the method is applicable to the determination of mass fractions of cadmium from 0,01 % to 0,30 %;

b) for lead sulfide concentrates, the method is applicable to the determination of mass fractions of cadmium from 0,01 % to 0,30 %;

c) for zinc sulfide concentrates, the method is applicable to the determination of mass fractions of cadmium from 0,05 % to 1,00 %.

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 glassware — Volumetric instruments — Methods for testing of capacity and for use*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

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 — 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 sample is dissolved in hydrochloric acid, nitric acid and hydrofluoric acid with a final stage perchloric acid digestion. Yttrium is added as an internal standard to solutions of dissolved samples, reference materials and calibration solutions and cadmium determined by ICP-AES.

5 Reagents

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

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

5.2 Hydrochloric acid, dilute 1+1. Slowly add 500 ml of concentrated hydrochloric acid (5.1) to 500 ml of water while stirring.

5.3 Hydrochloric acid, dilute 1+9. Slowly add 50 ml of concentrated hydrochloric acid (5.1) to 450 ml of water while stirring.

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

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

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

5.7 Cadmium metal, minimum purity 99,99 %.

5.8 Cadmium, standard solution, 1 ml contains 1 mg of Cd.

Weigh, to the nearest 0,1 mg, 1,000 0 g of cadmium metal (5.7) into a 250 ml beaker. Add 10 ml of water and 5 ml of nitric acid (5.4). Cover and warm gently (if necessary) until the cadmium metal is dissolved. Heat to remove nitrogen oxides, then allow to cool, and add about 50 ml of water. Transfer the solution to a 1 000 ml one-mark volumetric flask, add 40 ml of hydrochloric 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.

5.9 Cadmium, standard solution, 1 ml contains 100 µg of Cd.

Pipette 10,00 ml of cadmium standard solution (5.8) into a 100 ml one-mark volumetric flask. Add 20 ml of hydrochloric 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 Cadmium, standard solution, 1 ml contains 10 µg of Cd.

Pipette 10,00 ml of cadmium standard solution (5.9) into a 100 ml one-mark volumetric flask. Add 18 ml of hydrochloric 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 Yttrium, standard solution, 1 ml contains 1 mg of Y.

Weigh, to the nearest 0,1 mg, 1,269 9 g of yttrium trioxide (≥99,99 %) and transfer to a 250 ml beaker. Add 100 ml of hydrochloric acid (5.3) and heat gently until the metal is dissolved, then cool to room temperature. Transfer to a 1 000 ml one-mark volumetric flask, fill up nearly to the mark with hydrochloric acid (5.3), mix and cool to room temperature, then fill up exactly to the mark with hydrochloric acid (5.3) and mix again.

5.12 Yttrium, standard solution, 1 ml contains 200 µg of Y.

Pipette 50,00 ml of yttrium standard solution (5.11) into a 250 ml one-mark volumetric flask. Add 40 ml of hydrochloric 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.

6 Apparatus

Ordinary laboratory equipment and the following.

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

It is permissible to use other measuring instruments, approved types, auxiliary devices and materials whose technical and metrological characteristics are not inferior to those mentioned above.

6.2 Polytetrafluoroethylene beaker, of capacity 200 ml, or glass-carbon beaker.

6.3 Analytical balance, sensitive to 0,1 mg.

6.4 ICP-AES. The emission wavelength should be set to 226,502 nm.

6.5 Insolubles filter paper, Whatman®[1] No. 40 or equivalent.

7 Sample

7.1 Laboratory sample

Laboratory samples 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 pre-dried test portions are to be used (see Annex A).

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[1] This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

7.3 Test portion

Taking multiple increments, extract approximately 0,50 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 can be used to prepare pre-dried 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 reagents. 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 into a 200 ml polytetrafluoroethylene beaker (6.2) 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. Add 10 ml of nitric acid (5.4) and heat gently. Add 3 ml of hydrofluoric acid (5.5), then heat gradually until the solution is about 5 ml at 60 °C to 70 °C. Add 3 ml of perchloric acid (5.6), cover with a polytetrafluoroethylene lid, heat the solution until the strong white fumes evolve, then remove from the hotplate and cool. Wash the polytetrafluoroethylene lid and sides of the beaker with a minimum volume of water and add 2 ml of perchloric acid (5.6). Continue heating until the strong white fumes have evolved completely, then cool.

Add 40 ml of hydrochloric acid (5.2) [for lead concentrate samples, add 50 ml of hydrochloric acid (5.3)]. Wash down the cover and sides of the beaker, heat until the onset of boiling, then allow to cool.

8.4 Preparation of test solutions

Transfer the solution (8.3) and pipette 5,00 ml yttrium standard solution (5.12) to a 200 ml one-mark volumetric flask, dilute to the mark with water and mix thoroughly. For lead concentrate samples, filter the solution through an insoluble filter paper (6.5), then wash the precipitate with hydrochloric acid (5.3). Collect the filtrate in a 200 ml one-mark volumetric flask, and pipette 5,00 ml yttrium standard solution (5.12), dilute to the mark with hydrochloric acid (5.3) and mix thoroughly.

8.5 Preparation of calibration solutions

Using cadmium standard, prepare a series of calibration standards as per Table 1. Transfer 0,0 ml and 2,00 ml of cadmium standard (5.10) and 1,00 ml, 5,00 ml, 10,00 ml, 20,00 ml and 30,00 ml of cadmium standard (5.9), then transfer 2,50 ml yttrium standard solution (5.12) into 100 ml volumetric flasks, dilute to the mark with hydrochloric acid (5.3) and mix thoroughly.

Table 1 — Preparation of calibration solutions[a]

Concentration of cadmium standard µg/ml	Volume of cadmium standard ml	Concentration of cadmium µg/ml	Mass of cadmium contained µg
10	0,00	0,00	0
10	2,00	0,20	20
100	1,00	1,00	100
100	5,00	5,00	500
100	10,00	10,00	1 000
100	20,00	20,00	2 000
100	30,00	30,00	3 000

[a] Calibration solutions should be prepared at the same ambient temperature as that at which the determinations will be conducted.

8.6 Preparation of cadmium calibration curve

Set up the ICP-AES (6.4) according to the guidelines set out in 6.4. Adjust the instrument read-out scale to zero. Aspirate each calibration solution, as prepared in 8.5, through the ICP-AES and record the emission intensities. Manually or electronically plot a graph of the average emission intensities versus mass of cadmium (in µg) and repeat errant standards if necessary.

Use ISO 8466-2 as a guide to determine the acceptability of the calibration curve.

8.7 Determination of cadmium content in test solutions

Immediately after calibrating the ICP-AES (6.4), determine the cadmium content in the test solutions from 8.5. Adjust the instrument read-out scale to zero. Aspirate the first duplicate of each sample through the ICP-AES and record the emission intensities, checking the zero regularly.

Check the calibration of the instrument, then aspirate the second duplicate of each sample in the reverse order through the ICP-AES and record the emission intensities, checking the zero regularly.

Determine the mass of cadmium in each test sample (F_{Cd}, in µg) from the curve determined in 8.7.

9 Expression of results

The mass fraction of cadmium in the test portion, w_{Cd}, expressed as a percentage, is given in Formula (1):

$$w_{\mathrm{Cd}} = \frac{\left(F_{\mathrm{Cd}} - F_{\mathrm{Cdblank}}\right)}{m \times 10^6} \times \frac{100}{100 - H} \times 100 \qquad (1)$$

where

F_{Cd}	is the mass of cadmium found in the test sample aliquot, in µg;
F_{Cdblank}	is the mass of cadmium found in the blank test, in µg;
m	is the mass of the test portion, in g;
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, $H = 0$.

Calculate the mass fraction of cadmium in the test portion to the second decimal place and to the third decimal place if the mass fraction of cadmium is less than 0,1 %.

10 Precision

10.1 Expression of precision

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

a) For copper concentrates

$$s_r = 0{,}012\,3\bar{X} \tag{2}$$

$$s_L = 0{,}032\,9\bar{X} + 0{,}000\,5 \tag{3}$$

b) For lead concentrates

$$s_r = 0{,}026\,2\bar{X} \tag{4}$$

$$s_L = 0{,}037\,1\bar{X} + 0{,}001\,1 \tag{5}$$

c) For zinc concentrates

$$s_r = 0{,}009\,2\bar{X} + 0{,}000\,7 \tag{6}$$

$$s_L = 0{,}027\,0\bar{X} \tag{7}$$

where

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

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

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

10.2 Method for obtaining the final result

Calculate the quantities in Formulae (8) and (9) from the duplicate results x_1 and x_2 (%) and process according to the flowchart in Annex B.

a) Mean of duplicate results:

$$\bar{x} = \frac{x_1 + x_2}{2} \tag{8}$$

Within-laboratory standard deviation (s_r), using Formula (2) for copper sulfide concentrates, Formula (4) for lead sulfide concentrates and Formula (6) for zinc sulfide concentrates.

b) Repeatability limit:

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

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 quantities in Formulae (10) to (12).

a) Mean of final results:

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

Between-laboratories standard deviation (s_L) substitutes μ_{12} for $\overline{X}$ when using Formula (3) for copper sulfide concentrates, Formula (5) for lead sulfide concentrates and Formula (7) for zinc sulfide concentrates.

Within-laboratory standard deviation (s_r) substitutes μ_{12} for $\overline{X}$ when using Formula (2) for copper sulfide concentrates, Formula (4) for lead sulfide concentrates and Formula (6) for zinc sulfide concentrates.

b) Permissible tolerance:

$$P = 2{,}8 \times \sqrt{s_\mathrm{L}^2 + \frac{s_\mathrm{r}^2}{2}} \tag{11}$$

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 cadmium;

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

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. There are two possibilities: Formula (13) and Formula (14).

$$\left| \mu_\mathrm{c} - A_\mathrm{c} \right| \le C \tag{13}$$

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

$$\left| \mu_\mathrm{c} - A_\mathrm{c} \right| > C \tag{14}$$

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 cadmium of the CRM;

A_c is the certified value, expressed as a percentage by mass of cadmium of the CRM;

C is a quantity, expressed as a percentage by mass of cadmium depending on the type of CRM used as defined in 10.4.2.

10.4.2 Type of CRM or reference material

10.4.2.1 General

The reference materials used for this purpose shall 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 cadmium is given by Formula (15).

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

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 cadmium is given by Formula (16).

$$C = \sqrt{2s_L^2 + \frac{s_r^2}{n}} \tag{16}$$

It is recommended that this type of certified reference material 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) a reference to this document;

b) identification of the sample;

c) mass fraction of cadmium 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
(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, lead, zinc and nickel sulfide concentrates. The method is applicable to 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 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. 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 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 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.

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 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 desiccator. When cool, remove the weighing vessel containing the dry test portion and the vessel cover from the desiccator and weigh to the nearest 0,1 mg (m_{1a}) after slightly lifting the cover and quickly replacing it.

Transfer the test portion into the appropriate analytical apparatus and immediately re-weigh the empty weighing vessel and vessel cover. Record the mass to the nearest 0,1 mg (m_2).

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_{1b}). The test portion can be considered stable if the difference between m_{1a} and m_{1b} is within ± 0,5 mg. If this condition is not achieved, the drying and weighing steps should be repeated.

A.6 Calculation of the test portion dry mass

The dry mass of the test portion (m_3) is calculated from Formula (A.1).

$$m_3 = m_{1a} - m_2 \tag{A.1}$$

where

m_{1a} is the mass of the dried test portion plus weighing vessel and its vessel cover, in grams;

m_2 is the mass of the empty weighing vessel plus its cover, in grams.

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