
**Zinc sulfide concentrates —
Determination of zinc — Solvent
extraction and EDTA titrimetric method**

*Concentrés sulfurés de zinc — Dosage du zinc — Méthode par
extraction à l'aide d'un solvant et titrage à l'EDTA*

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Contents

Page

Foreword.....	iv
1 Scope	1
2 Normative references	1
3 Principle	1
4 Reagents	2
5 Apparatus	3
6 Sample	3
6.1 Test sample	3
6.2 Test portion	3
7 Procedure	3
7.1 Number of determinations	3
7.2 Blank test	4
7.3 Dissolution of test portion	4
7.4 Extraction	4
7.5 Titration	4
7.6 Determination of the titration factor of the EDTA standard solution	5
8 Expression of results	5
9 Precision	6
9.1 Expression of precision	6
9.2 Procedure for obtaining the final result	6
9.3 Between-laboratories precision	6
9.4 Check of trueness	7
10 Test report	8
Annex A (normative) Procedure for the preparation and determination of the mass of a predried test portion	9
Annex B (normative) Flowchart of the procedure for the acceptance of analytical values for test samples	11
Annex C (normative) Elements that interfere with this method	12
Annex D (informative) Derivation of precision equations	13
Bibliography	18

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 13291 was prepared by Technical Committee ISO/TC 183, *Copper, lead, zinc and nickel ores and concentrates*.

This second edition cancels and replaces the first edition (ISO 13291:1997), which has been technically revised.

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Zinc sulfide concentrates — Determination of zinc — Solvent extraction and EDTA titrimetric method

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

1 Scope

This International Standard specifies a solvent extraction/titrimetric method for the determination of the mass fraction of zinc in zinc sulfide concentrates.

The method is applicable to zinc sulfide concentrates having a mass fraction of zinc in the range from 11 % to 62 %.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 385, *Laboratory glassware — Burettes*
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ISO 648, *Laboratory glassware — One-mark 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 glassware — Methods for use and testing of capacity*

ISO 9599, *Copper, lead and zinc sulfide concentrates — Determination of hygroscopic moisture in the analysis sample — Gravimetric method*

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

3 Principle

A test portion of zinc concentrate is dissolved in bromine and nitric acid. Any remaining insoluble residue is dissolved in sulfuric, nitric and hydrofluoric acids. A zinc thiocyanate complex is selectively extracted into methyl isobutyl ketone, after screening of some elements with thiourea and citrate ions. Partially extracted cadmium is screened with iodide ions before the final titration as explained in Annex C. Cobalt is extracted and determined separately, if present at concentration levels exceeding 0,05 %. Zinc is determined by titration with EDTA solution at pH 5,5.

4 Reagents

During the analysis, only reagents of recognized analytical grade and water that complies with grade 2 of ISO 3696 shall be used.

4.1 Zinc metal, minimum purity 99,99 %, free from oxide prior to use.

The surface of the metal may be cleaned by immersing the metal in hydrochloric acid (4.2), diluted 1 + 9 for 1 min, then washing well with water, followed by an acetone rinse and drying in an oven at 50 °C.

4.2 Hydrochloric acid, (ρ_{20} 1,16 g/ml to 1,19 g/ml).

4.3 Bromine.

4.4 Nitric acid, (ρ_{20} 1,42 g/ml).

4.5 Hydrofluoric acid, (ρ_{20} 1,13 g/ml to 1,15 g/ml).

4.6 Hydrochloric acid, (ρ_{20} 1,16 g/ml to 1,19 g/ml) diluted (1 + 4).

Add 200 ml of hydrochloric acid (4.2) to 800 ml of water.

4.7 Sulfuric acid, diluted (1 + 1).

Add carefully and slowly, with stirring, 500 ml of sulfuric acid (ρ_{20} 1,84 g/ml) to 500 ml of water.

4.8 Ammonia, (ρ_{20} 0,89 g/ml).

4.9 4-methyl-2-pentanone (methyl isobutyl ketone).

4.10 Ethanol, pure or denatured.

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4.11 Screening solution.

Dissolve 60 g of thiourea, 100 g of di-ammonium citrate and 200 g of ammonium thiocyanate in water and dilute to 1 l. Filter if necessary.

4.12 Sodium fluoride solution (20 g/l).

Dissolve 20 g of sodium fluoride in water. Dilute to 1 l.

4.13 Thiourea solution (100 g/l).

Dissolve 100 g of thiourea in water and dilute to 1 l.

4.14 Buffer solution.

Dissolve 250 g of hexamethylenetetramine in water. Add 60 ml of acetic acid (ρ_{20} 1,05 g/ml) and dilute to 1 l.

4.15 EDTA standard volumetric solution (0,05 mol/l).

Dissolve 18,6 g of the di-sodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA) in water. Dilute to 1 l.

4.16 Potassium iodide solution (1 000 g/l).

Dissolve 100 g of potassium iodide in water and dilute to 100 ml.

Prepare fresh on the day of use.

4.17 Xylenol orange indicator (1 % *m/m*).

Mix 1 g of the sodium salt of xylenol orange with 99 g of potassium nitrate crystals, by gently grinding in a ceramic mortar with a pestle. Mixing is considered complete when the colour is uniform throughout.

4.18 Iron stock solution.

Dissolve 45 g of iron(III) nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] in water and dilute to 1 l.

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 Platinum crucibles, of 25 ml capacity.

5.3 Balance, capable of being read to 0,1 mg.

5.4 Oven, with its temperature controlled at $105\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$.

5.5 Muffle furnace, having a maximum required operating temperature higher than $800\text{ }^\circ\text{C}$.

5.6 Laboratory hotplate.

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6 Sample

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6.1 Test sample

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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 in such a manner that it is representative of the dish or tray. Weigh, to the nearest 0,1 mg, 2,5 g of test sample. At the same time as the test portion is weighed, weigh test portions for the determination of hygroscopic moisture in accordance with ISO 9599.

Alternatively, the method specified in Annex A may be used to prepare predried test portions directly from the laboratory sample.

7 Procedure**7.1 Number of determinations**

Carry out the determinations at least in duplicate, as far as possible under repeatability conditions, on each test sample.

NOTE Repeatability conditions exist where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator, using the same equipment within short intervals of time.

7.2 Blank test

Determine a reagent blank. It is advisable to perform duplicate blank determinations every time an analysis is carried out on a laboratory sample. The blank samples are carried through the whole procedure, apart from where no laboratory-sample test portion is required. However, 5 ml of iron stock solution (4.18) should be added to assist in the determination of turbidity. The volume of EDTA titrant used is V_b .

7.3 Dissolution of test portion

Place the test portion in a 300 ml narrow-necked conical flask. Moisten the material with about 20 ml of water and add 2 ml to 3 ml of bromine (4.3). Allow to react at ambient temperature for 15 min, swirling the flask and contents from time to time. Add 15 ml of nitric acid (4.4) and leave for a further 15 min. Place the flask on a hotplate (5.6) and bring gently to the boil, to expel all bromine vapours. Cool, add 100 ml of water, heat to boiling and cool.

If no insoluble material is present, transfer the liquid to a 500 ml one-mark volumetric flask, rinsing the conical flask thoroughly. Make up to the mark with water.

If insoluble residue is present, filter through a medium-speed cellulose filter paper into a 500 ml one-mark volumetric flask. Rinse the filter thoroughly with water. Place the filter and insoluble residue in a platinum crucible (5.2) and gently ash in the muffle furnace (5.5) set at 800 °C. Add 2 ml of dilute sulfuric acid (4.7), 2 ml of nitric acid (4.4) and 2 ml of hydrofluoric acid (4.5) and evaporate the solution nearly to dryness. Cool and add water in small quantities, to dissolve the soluble salts. Filter through a medium-speed cellulose filter paper and add the filtrate and washing solution to the 500 ml one-mark volumetric flask used above. Make up to the mark with water.

If the sample contains lead, damage to the platinum crucible may occur. In this case, insoluble material should be treated as follows.

Rinse the insoluble residue into a polytetrafluoroethylene beaker with a fine jet of water. Place the filter in a porcelain crucible and gently ash the paper in the muffle furnace (5.5) at 600 °C to 700 °C. Allow the crucible to cool to ambient temperature.

Rinse the material in the crucible by washing with a small quantity of water into the polytetrafluoroethylene beaker used above. Add 2 ml of dilute sulfuric acid (4.7), 2 ml of nitric acid (4.4) and 2 ml of hydrofluoric acid (4.5) and evaporate the solution nearly to dryness. Cool and add water in small quantities, to dissolve the soluble salts. Filter through a medium-speed cellulose filter paper and add the filtrate and washing solution to the 500 ml one-mark volumetric flask used above. Make up to the mark with water.

Should it be confirmed that the filter paper contains no zinc, the procedure of ashing the filter may be omitted.

7.4 Extraction

Pipette 50,00 ml of the solution obtained in 7.3 into a 250 ml separating funnel. Add ammonia (4.8) dropwise until a slight turbidity develops. Add 5 ml of dilute hydrochloric acid (4.6) and 50 ml of screening solution (4.11). Mix well. Add 80 ml of 4-methyl-2-pentanone (4.9) and shake for 1 min. Allow the phases to separate and slowly transfer the lower aqueous phase to another separating funnel. Perform a second extraction with 20 ml of 4-methyl-2-pentanone (4.9). Separate the phases and discard the aqueous phase. Combine the two separate organic phases in a 400 ml low-form beaker.

Place 1 ml of dilute hydrochloric acid (4.6) and 70 ml of ethanol (4.10) in each of the two separating funnels. Shake well and discharge the contents from both funnels into the 400 ml low-form beaker.

7.5 Titration

Add, successively, 10 ml of sodium fluoride solution (4.12), 10 ml of thiourea solution (4.13), 20 ml of buffer solution (4.14), 5 ml of potassium iodide solution (4.16) and 0,1 g of xylenol orange indicator (4.17).

Titrate with EDTA solution (4.15) until the colour changes from red to yellow. Titrate very slowly when approaching the equivalence point. Note the volume, V_t , of titrant used.

7.6 Determination of the titration factor of the EDTA standard solution

NOTE In order to obtain a relative accuracy of between 0,1 % and 0,2 %, it is necessary to standardize the EDTA solution with zinc at the same time and under the same conditions as the analysis. It is thus advisable for the calibration to follow the complete set of operating conditions set down for the analysis. Likewise, to improve the repeatability of the calibration, it is useful to prepare several zinc reference solutions. Iron is added to the standard solution to assist in the determination of turbidity in 7.4.

The EDTA standard solution should be standardized as follows:

- Weigh into three separate 300 ml conical flasks, between 0,25 g and 1,625 g of zinc (4.1), to the nearest 0,000 1 g, depending on the mass fraction of zinc in the test sample. Record these masses as m_1 , m_2 and m_3 .
- Add 15 ml of water, 15 ml of nitric acid (4.4) and 5 ml of iron stock solution (4.18). After dissolution of the zinc, boil gently to expel nitrogen oxide gases.
- Cool and transfer to a 500 ml one-mark volumetric flask. Rinse the initial flask thoroughly and add the washings to the volumetric flask. Make up to the mark. Continue the procedure as described in 7.4 and 7.5. Record the volumes of EDTA standard solution used in the titrations as V_1 , V_2 and V_3 .

Calculate the intermediate factor, f_{ix} , for each beaker using the following equation:

$$f_{ix} = m_x / V_x \quad \text{for } x = 1 \text{ to } 3 \quad (1a)$$

where

f_{ix} is the factor obtained from the titration;

m_x is the mass of zinc weighed, in grams;

V_x is the volume of EDTA solution, in millilitres.

If the range of values for f_{i1} , f_{i2} , f_{i3} exceeds 0,000 01 g/ml then repeat the standardization. Otherwise, calculate the mean factor as follows:

$$f = \frac{f_{i1} + f_{i2} + f_{i3}}{3} \quad (1b)$$

8 Expression of results

The mass fraction of zinc in the test portion, w_{Zn} , expressed as a percentage, is given by the following equation:

$$w_{Zn} = \frac{(V_t - V_b) \times f \times 100}{m} \times \frac{100}{100 - H} \quad (2)$$

where

f is the zinc equivalence factor, in grams per millilitre, determined in 7.6;

H is the hygroscopic moisture content, as a percentage of the test portion (in the case of a predried test portion being used, $H = 0$);

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

V_b is the volume of EDTA solution (4.15), in millilitres, used to titrate the blank solution;

V_t is the volume of EDTA solution (4.15), in millilitres, used to titrate the sample solution.

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

9 Precision

9.1 Expression of precision

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

$$s_r = 0,000\ 8\bar{X} + 0,038\ 2 \quad (3)$$

$$s_L = 0,001\ 6\bar{X} + 0,053\ 9 \quad (4)$$

where

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

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

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

NOTE Additional information is given in Annex D.

9.2 Procedure for obtaining the final result

See Annex B.

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

Mean of duplicates $\bar{X} = \frac{(X_1 + X_2)}{2}$ (5)

Within-laboratory standard deviation (repeatability) $s_r = 0,000\ 8\bar{X} + 0,038\ 2$ (3)

Repeatability limit $r = 2,8s_r$ (6)

9.3 Between-laboratories precision

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

Calculate the following quantities:

Mean of final results $\mu_{12} = \frac{\mu_1 + \mu_2}{2}$ (7)

Between-laboratories standard deviation $s_L = 0,001\ 6\mu_{12} + 0,053\ 9$ (8)

Within-laboratory standard deviation $s_r = 0,000\ 8\mu_{12} + 0,038\ 2$ (9)

Permissible difference $P = 2,8\sqrt{s_L^2 + \frac{s_r^2}{2}}$ (10)

Range $E = |\mu_1 - \mu_2|$ (11)

where

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

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

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

9.4 Check of trueness

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

$$|\mu_c - A_c| \leq C \quad (12)$$

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

$$|\mu_c - A_c| > C \quad (13)$$

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

In Equations (12) and (13), the symbols are defined as follows:

μ_c is the final result, as a percentage of zinc mass of the certified reference material;

A_c is the certified value, as a percentage of zinc mass of the certified reference material;

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

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

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

9.4.1.1 Reference material certified/characterized by an interlaboratory test programme

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

$$C = 2\sqrt{s_L^2 + \frac{s_r^2}{n} + s^2\{A_c\}} \quad (14)$$

where

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

n is the number of replicate determinations.