
**Zinc sulfide concentrates — Determination
of zinc content — Ion-exchange/EDTA
titrimetric method**

*Concentrés sulfurés de zinc — Dosage du zinc — Méthode par échange
d'ions et titrage à l'EDTA*

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Contents

Page

| | | |
|----|-----------------------------|---|
| 1 | Scope | 1 |
| 2 | Normative references | 1 |
| 3 | Principle | 1 |
| 4 | Reagents | 2 |
| 5 | Apparatus | 3 |
| 6 | Sample | 3 |
| 7 | Procedure | 4 |
| 8 | Expression of results | 6 |
| 9 | Precision | 6 |
| 10 | Test report | 8 |

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Annexes

| | | |
|---|--|----|
| A | Ion exchange resins and columns | 9 |
| B | Procedure for the preparation and determination of the mass of a predried test portion | 11 |
| C | Determination of cadmium by atomic absorption spectrometry | 15 |
| | values for test samples | 15 |
| E | Effect of potentially interfering elements | 16 |
| F | Derivation of precision equations | 17 |
| G | Bibliography | 21 |

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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.

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.

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International Standard ISO 12739 was prepared by Technical Committee ISO/TC 183, *Copper lead and zinc ores and concentrates*.

Annexes A to D form an integral part of this International Standard.

Annexes E to G are for information only.
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Zinc sulfide concentrates — Determination of zinc content — Ion-exchange/EDTA titrimetric method

1 Scope

This International Standard specifies an ion-exchange titrimetric method for the determination of the zinc content of zinc concentrates. The method is applicable to zinc sulfide concentrates with zinc content in the range from 11 % (m/m) to 62 % (m/m).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements*.
<https://standards.iteh.ai/catalog/standards/iso/5840e6a-8d93-4631-8143-5513b1af6103/iso-12739-1997>

ISO 648:1977, *Laboratory glassware — One-mark pipettes*.

ISO 1042:—¹⁾, *Laboratory glassware — One-mark volumetric flasks*.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

ISO 4787:1984, *Laboratory glassware — Volumetric glassware — Methods for use and testing of capacity*.

ISO 9599:1991, *Copper, lead and zinc sulfide concentrates — Determination of hygroscopic moisture in the analysis sample — Gravimetric method*.

ISO Guide 35:1989, *Certification of reference materials — General and statistical principles*.

3 Principle

The test portion of zinc concentrate is dissolved in hydrochloric, nitric and sulfuric acids. The acidity is adjusted to about 2 mol/l with respect to hydrochloric acid. Zinc is adsorbed on a strongly basic anion exchange resin. Some interfering ions are removed by elution with 2 mol/l hydrochloric acid solution. Zinc is eluted with an ammonia-ammonium chloride solution. Zinc is determined in the eluate by titration with EDTA at a pH of approximately 5,6 using xylenol orange indicator.

¹⁾ To be published. (Revision of ISO 1042:1983)

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

The surface of the metal may be cleaned by immersing the metal in hydrochloric acid (4.3), diluted 1 + 9 for 1 min, washed well with water followed by an acetone rinse and dried in an oven at 50 °C.

4.2 Xylenol orange indicator (0,1 % *m/m*)

Mix 0,1 g of the sodium salt of xylenol orange with 100 g of potassium nitrate crystals by gently grinding in a ceramic mortar with a pestle. Mixing is considered complete when colour is uniform throughout.

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

4.4 Hydrochloric acid, diluted (1 + 1)

Add 500 ml of hydrochloric acid (4.3) to 500 ml of water.

4.5 Hydrochloric acid, diluted (1 + 5)

Add 100 ml of hydrochloric acid (4.3) to 500 ml of water.

4.6 Nitric acid (ρ_{20} 1,42 g/ml)

4.7 Nitric acid, diluted (1 + 1)

Add 500 ml of nitric acid (4.6) to 500 ml of water.

4.8 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.

4.9 Sulfuric acid, diluted (1 + 100)

Add 20 ml of dilute sulfuric acid (4.8) to 1 000 ml of water.

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

4.11 Ammonia solution, diluted (7 + 100)

Add 70 ml of aqueous ammonia solution (ρ_{20} 0,89 g/ml) to 1 000 ml of water.

4.12 Ammonia-ammonium chloride solution

Dissolve 20 g of ammonium chloride in 1 l of dilute ammonia solution (4.11).

4.13 Hydrochloric acid-ascorbic acid solution

Dissolve 0,25 g of ascorbic acid in 100 ml of dilute hydrochloric acid (4.5). Prepare fresh on day of use.

4.14 Ammonium fluoride solution (50 g/l)

Dissolve 50 g of ammonium fluoride in water and dilute to 1 l.

4.15 Sodium thiosulfate solution (100 g/l)

Dissolve 100 g of sodium thiosulfate pentahydrate in water and dilute to 1 l.

4.16 Buffer solution (pH = 5,5)

Dissolve 250 g of ammonium acetate and 25 ml of concentrated acetic acid (ρ_{20} 1,05 g/ml) in water and dilute to 1 l.

4.17 Para-nitrophenol indicator solution (2 g/l)

Dissolve 0,2 g of para-nitrophenol in water and dilute to 100 ml.

4.18 EDTA standard volumetric solution (0,1 mol/l)

Dissolve 37,2 g of the di-sodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA) in water and dilute to 1 l.

5 Apparatus

5.1 Class A volumetric glassware complying with ISO 385-1, ISO 648 and ISO 1042 and used in accordance with ISO 4787.

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

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5.3 Laboratory hotplate <https://standards.iteh.ai/catalog/standards/sist/bf840e6a-8d93-4631-8143-5513b1af6103/iso-12739-1997>

5.4 Muffle furnace, capable of operating at 800 °C.

5.5 Platinum crucibles, of 25 ml capacity.

5.6 Ion exchange columns, with general dimensions shown in annex A.

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 B).

6.2 Test portion

Taking multiple increments, extract a test portion of 0,5 g, weighed to the nearest 0,1 mg, from the test sample in such a manner that it is representative of the contents of the dish or tray. 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 B 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. The volume of EDTA titrant used is V_b .

7.3 Dissolution of test portion

Place the test portion in a 300 ml conical beaker. Add 25 ml of hydrochloric acid (4.3). Cover with a watch glass and heat beaker and contents gently for 5 min.

Add 20 ml of dilute nitric acid (4.7) and 15 ml of dilute sulfuric acid (4.8). Heat and evaporate the solution to about 5 ml. Cool and add with caution about 50 ml of water and boil the solution.

Cool the solution to room temperature and filter it into a 300 ml beaker through a medium-speed cellulose filter paper. Wash the beaker and filter paper thoroughly with dilute sulfuric acid (4.9), collecting the washings in the same beaker.

If an acid-insoluble material is present, place the filter and insoluble residue in a platinum crucible (5.5) (see note below) and gently reduce the paper to ashes in the muffle furnace (5.4) at 800 °C. Allow the crucible and residue to cool to ambient temperature. Add 2 ml of dilute sulfuric acid (4.8), 2 ml of nitric acid (4.6) and 2 ml of hydrofluoric acid (4.10) 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 initial solution obtained above as described in paragraphs 1 to 3.

Heat to evaporate the combined filtrates to a volume of 60 ml to 80 ml. Cool and add 16 ml of hydrochloric acid (4.3). Dilute to 100 ml with water.

NOTE — If the sample contains lead, damage to the platinum crucible may occur. An alternative fusion with a zirconium crucible and sodium peroxide may be preferable.

7.4 Preparation of the ion-exchange column

Examples of ion-exchange columns which are suitable for use are shown in annex A. Pack water-soaked cotton or glass wool pads into the bottom of the column to a thickness of about 5 mm. This will retain resin in the column during use.

Soak the resin overnight in distilled water to make a slurry. With the stopcock open carefully transfer the slurry into the column to form a settled bed. This resin bed is formed by about 16 ml of the swollen resin. Close the stopcock and put about a 5 mm thickness of water-soaked glass wool or cotton wool on top of the resin.

NOTE — It is essential to ensure that the resin is covered by liquid at all times because air trapped in a resin causes "channelling", i.e. uneven flow rate and poor efficiency in the ion exchanger. If air enters the resin bed, it is recommended that the column be emptied and then repacked.

Pass about 100 ml of hydrochloric acid (4.5) through the column ensuring that the resin is covered at all times. Adjust the flow rate to about 5 ml/min using the stopcock control. The resin can be rapidly regenerated at any time by passing 100 ml of water and then 100 ml of dilute hydrochloric acid (4.5) through the column ensuring that the resin is always covered with liquid.

7.5 Adsorption of zinc on ion-exchange column

Quantitatively transfer the test solution obtained in 7.3 to the ion-exchange column at a flow rate of about 5 ml/min.

Rinse the beaker with small increments of dilute hydrochloric acid (4.5) and transfer the washings to the column. A total washing volume of 100 ml should be sufficient. Continue to drain the column until the liquid is 5 mm above the top wool plug.

Pass 100 ml of hydrochloric-ascorbic acid solution (4.13) through the column in small quantities. Then pass 100 ml of dilute hydrochloric acid (4.5) through the column. Collect the eluate in a 500 ml beaker and discard.

7.6 Elution of zinc from ion-exchange column

Elute the adsorbed zinc from the column by passing 180 ml of ammonia-ammonium chloride solution (4.12) through the resin at a flow rate of less than 5 ml/min. Collect the eluate in a 500 ml beaker.

NOTE — The column should now be regenerated in preparation for the next test solution using the procedure described in 7.4.

7.7 Titration

Add 2 to 3 drops of para-nitrophenol indicator solution (4.17) to the column eluate obtained in 7.6. Add dilute hydrochloric acid (4.4) until the colour of the solution changes from yellow to colourless.

NOTE 1 A pH meter may be used to adjust the pH to a value 5,5 to 5,7 instead of using the para-nitrophenol indicator. Care should be taken to ensure that the electrodes are washed off with water before continuing the procedure.

Add successively to the solution, 20 ml of buffer solution (4.16), 3 ml of ammonium fluoride solution (4.14) and 5 ml of sodium thiosulfate solution (4.15). Add 0,5 g of xylene orange indicator (4.2) and swirl to dissolve. Titrate with EDTA standard solution (4.18) until the colour changes from red to yellow. Record the volume, V_t , of EDTA standard solution required.

NOTE 2 If the test sample contains cadmium it will be eluted with the zinc and will be titrated during the procedure in 7.7. The cadmium concentration must be determined separately and a correction made for its presence. The method for the determination of cadmium is given in annex C. The effect of other elements commonly found in zinc concentrates is discussed in annex E.

7.8 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 standard 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.

The EDTA standard solution should be standardized as follows:

- Weigh into three separate 500 ml beakers between 0,055 g and 0,31 g of high purity zinc metal (4.1), to the nearest 0,000 1 g, depending on the zinc content of the test sample. Record these masses as m_1 , m_2 and m_3 .
- To each beaker add 15 ml of dilute hydrochloric acid (4.4). Heat gently to dissolve the metal, cool and add 150 ml of ammonia-ammonium chloride solution (4.12).
- Add 2 to 3 drops of para-nitrophenol indicator solution (4.17). Add dilute hydrochloric acid (4.4) until the colour changes from yellow to colourless. Alternatively a pH meter may be used as indicated in note 1 in 7.7
- Add successively 20 ml of buffer solution (4.16), 3 ml of ammonium fluoride solution (4.14) and 5 ml of sodium thiosulfate solution (4.15). Add 0,5 g of xylene orange indicator (4.2) and swirl to dissolve. Titrate each beaker with EDTA standard solution (4.18) until the colour changes from red to yellow and record the volume as V_1 , V_2 and V_3 .

— Calculate the intermediate factor, f_{i_x} , for each beaker using the following formula:

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

where

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

m_x is the mass of zinc weighed, in grams;

V_x is the volume of EDTA standard solution, in millilitres.

If the range of values for f_{i_1} , f_{i_2} and f_{i_3} exceeds 0,000 01 g/ml then repeat the standardization.

Otherwise calculate the mean factor as follows:

$$f = \frac{f_{i_1} + f_{i_2} + f_{i_3}}{3} \quad \dots (1b)$$

8 Expression of results

The zinc content of the test portion, W_{zn} , expressed as a percentage by mass, is given by the following equation:

$$W_{zn} = \left[\frac{(V_t - V_b) \times f \times 100}{m} - 0,581c \right] \times \frac{100}{100 - H} \quad \dots (2)$$

where

V_t is the volume of EDTA standard solution (4.18), in millilitres, used to titrate the test solution;

V_b is the volume of EDTA standard solution (4.18), in millilitres, used to titrate the blank solution;

f is the zinc equivalence factor, in grams per millilitre, determined in 7.7;

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

c is the cadmium concentration, expressed as a percentage by mass;

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

Calculate the zinc 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 equations:

$$s_r = 0,000 2\bar{X} + 0,054 3 \quad \dots (3)$$

$$s_L = 0,002 0\bar{X} + 0,052 4 \quad \dots (4)$$

where

\bar{X} is the mean content of zinc, expressed as a percentage by mass, 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.

See annex F.

9.2 Procedure for obtaining the final result

See annex D.

Calculate the following quantities from the duplicate results X_1 and X_2 (%) and process according to the flowchart in annex F:

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

Within-laboratory standard deviation (repeatability)
$$s_r = 0,000 2\bar{X} + 0,054 3 \quad \dots (3)$$

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

9.3 Between-laboratories precision

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

Calculate the following quantities:

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

Between-laboratories standard deviation
$$s_L = 0,002 0\mu_{12} + 0,052 4 \quad \dots (8)$$

Within-laboratory standard deviation
$$s_r = 0,002 0\mu_{12} + 0,054 3 \quad \dots (9)$$

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

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

where

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

μ_2 is the final result 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 a 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 . There are two possibilities as follows:

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