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Zinc sulfide concentrates — Determination of zinc content — Hydroxide precipitation and EDTA titrimetric method

Concentrés sulfurés de zinc — Dosage du zinc — Méthode par précipitation d'hydroxydes et titrage à l'EDTA

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 13658 was prepared by Technical Committee ISO/TC 183, Copper, lead and zinc ores and concentrates.

Annexes B, C, D and E form a normative part of this International Standard. Annexes A and F are for information only. (standards.iteh.ai)

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Zinc sulfide concentrates — Determination of zinc content — Hydroxide precipitation 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 hydroxide precipitation and EDTA titrimetric method for the determination of the zinc content of zinc ores and concentrates containing 10 % (m/m) to 60 % (m/m) zinc.

2 Normative references

https://standards.iteh.ai/catalog/standards/sist/b07968fe-e424-47ea-bf14-ISO 385-1:1984, Laboratory glassware — Burettes and Part 1:6General requirements.

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

ISO 1042:1998, 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 5725-2:1994, Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.

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

ISO 12739:1997, Zinc sulfide concentrates — Determination of zinc content — Ion-exchange/EDTA titrimetric method.

ISO 13291:1997, Zinc sulfide concentrates — Determination of zinc content — Solvent extraction and EDTA titrimetric method.

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

3 Principle

Dissolution of a test portion of zinc concentrate in bromine and nitric acid. Dissolution of any remaining insoluble residue in hydrofluoric and sulfuric acids. Separation of aluminium, iron and manganese as hydroxides using precipitation with ammonia, ammonium chloride and ammonium persulfate. Separation of lead as sulfate. Copper is masked. Determination of zinc and cadmium together by complexometric titration (pH 5,5 to 5,7) in the presence of xylenol orange. Independent determination of cadmium and subtraction from the zinc value.

NOTE An examination of potential interfering elements is contained in annex A.

4 Reagents

During the analysis, use only reagents of recognized analytical reagent grade and water that complies with grade 2 of ISO 3696.

4.1 Zinc metal, minimum purity 99,99 %

The surface of the metal shall be free from oxide prior to use and may be cleaned by immersing the metal in hydrochloric acid (4.6) for 1 min, washing well with water followed by an acetone rinse and dried in an oven at 50 °C.

- 4.2 Ammonium chloride
- 4.3 Bromine
- **4.4** Nitric acid (*ρ*₂₀ 1,42 g/ml)
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- **4.5** Hydrochloric acid (ρ_{20} 1,16 g/ml to 1,19 g/m])_{SO 13658:2000}
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Add 500 ml of hydrochloric acid (4.5) to 500 ml of water.

- **4.7** Sulfuric acid (ρ_{20} 1,84 g/ml)
- 4.8 Dilute sulfuric acid (1+1)

Add carefully and slowly with stirring, 500 ml of sulfuric acid (4.7) to 500 ml of water.

4.9 Sulfuric acid (1 + 99)

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

- **4.10** Ammonia (*ρ*₂₀ 0,89 g/ml)
- 4.11 Ammonium persulfate

4.12 Ammonia washing solution

Dissolve 20 g of ammonium chloride in 1 000 ml of aqueous ammonia solution (1 + 100).

- 4.13 Ethanol, pure or denatured
- **4.14** Acetic acid (ρ_{20} 1,05 g/ml)

4.15 Bromothymol blue indicator solution (1 g/l)

Dissolve 0,1 g of bromothymol blue in ethanol (4.13) and dilute to 100 ml.

4.16 Hexamethylenetetramine buffer solution (250 g/l)

Dissolve 250 g of hexamethylenetetramine (hexamine) in water. Add 60 ml of acetic acid (4.14) and dilute to 1 l.

4.17 Masking solution

Dissolve 50 g of ammonium fluoride and 100 g of sodium thiosulfate pentahydrate in water and dilute to 1 l.

4.18 Xylenol orange indicator solution (1 g/l)

Dissolve 0,1 g of the sodium salt of xylenol orange in water and dilute to 100 ml.

4.19 Iron(III) solution (10 mg Fe/ml)

Dissolve 72,3 g of iron(III) nitrate nonahydrate in water and dilute to 1 l.

4.20 EDTA standard solution (0,1 mol/l)

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

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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 0.14mge84a94b/iso-13658-2000

5.3 Laboratory hotplate

5.4 pH meter

6 Sample

6.1 Test sample

Prepare an air-equilibrated test sample in accordance with ISO 9599.

NOTE An air-equilibrated 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 from the test sample and weigh to the nearest 0,1 mg. At the same time as the test portions are taken for analysis, 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 Reagent blank

A reagent blank shall be determined. 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, with the exception that no laboratory sample test portion is required. The average volume of EDTA titrant used for the reagent blanks is $V_{\rm b}$.

7.3 Dissolution

Digest the sample as follows.

Transfer the test portion (6.2) to a 300 ml conical beaker. Moisten the material with about 5 ml of water and add 1 ml of bromine (4.3). Stand for 15 min, swirling the beaker and contents from time to time.

Cautiously add 15 ml of nitric acid (4.4). Place the beaker on a hotplate (5.3) and heat gradually until bromine and nitrogen oxides are expelled. Add 15 ml of sulfuric acid (4.8). Heat and evaporate the solution until the evolution of sulfuric acid fumes (approximately 5 ml).

NOTE Care needs to be taken to ensure no loss of material when fuming samples containing significant carbonaceous material, due to the sample climbing up the walls of the beaker.

Cool and cautiously add about 50 ml of water and heat the solution until boiling. Cool the solution to room temperature and filter it into a 500 ml conical beaker through a medium-speed cellulose filter paper. Wash the beaker and filter paper thoroughly with sulfuric acid (4.9). Collect the filtrate and washing solution in the same beaker.

Reserve the filter paper and acid-insoluble residue for determination of zinc by FAAS (as described in annex C) for the concentrate being analysed and the analyst performing the test, unless it has been statistically shown, by previous testing, that the zinc is completely soluble in the initial decomposition. If this step is not routinely performed, regular checks confirming the validity of its exclusion shall be carried out for each concentrate type by each analyst. Similarly, all documentation containing results where this step has been excluded shall contain a comment indicating this fact.

7.4 Separation of aluminium, iron and manganese as hydroxides

Add 15 g of ammonium chloride (4.2) to the solution and swirl gently to dissolve.

NOTE 1 If the iron content of the sample is only a few percent, then iron(III) solution (4.19) is added to the solution to increase the contained iron in solution to about 50 mg.

Heat to near boiling then add ammonia (4.10) to the solution until complete precipitation occurs and then 30 ml in excess. Add 1 g of ammonium persulfate (4.11) to the solution, heat until boiling and continue boiling for 1 min. Stand to allow the precipitate to settle out. Filter into another 500 ml beaker through a medium-speed cellulose filter paper and wash the precipitate several times with hot ammonia washing solution (4.12). Collect the filtrate and the washing solutions in the same beaker.

NOTE 2 Filtration will be slow for high lead content samples.

Wash the precipitate back into the original beaker without damaging the filter paper and dissolve it with 10 ml of hydrochloric acid (4.6). Add 5 g of ammonium chloride (4.2) to the solution. Repeat the precipitation by addition of ammonia (4.10) and ammonium persulfate (4.11). Boil, filter through the original filter paper and wash in the same manner as described above.

Collect the filtrate and washing solution in the same beaker used to collect the filtrate for the first separation and place the beaker on a hotplate (5.3). Heat gently and evaporate the solution to about 200 ml. Cool to room temperature.

Keep the hydroxide precipitate for later treatment.

7.5 Titration

7.5.1 Determination of the titration factor of the EDTA solution

NOTE 1 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.

The EDTA 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 0,1 mg, depending on the zinc content of the test sample. Record these masses as m_1 , m_2 and m_3 .

Add 10 ml of hydrochloric acid (4.6) and warm gently to aid the complete dissolution of the metal. Add 50 ml of water and 20 g of ammonium chloride (4.2), swirl gently to dissolve and dilute to about 200 ml with water.

Add 4 drops of bromothymol blue indicator solution (4.15) and neutralize by adding ammonia (4.10) dropwise until the yellow colour disappears. Add 7 drops of hydrochloric acid (4.5).

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NOTE 2 A pH meter (5.4) may be used to adjust the pH to a value of 05,6 instead of using the bromothymol blue indicator. Care should be taken to ensure that the electrodes are washed off with water before continuing the procedure.

Add 20 ml of hexamethylenetetramine buffer solution (4.16) and 20 ml of masking solution (4.17). Add 10 drops of xylenol orange indicator (4.18) to the solution. Swirl to dissolve and titrate with EDTA standard solution (4.20) until a colour change to yellow occurs. Record the volumes as V_1 , V_2 and V_3 .

Calculate the intermediate factors, fi_x , for each beaker using the following equation:

$$fi_x = m_x/V_x$$
 for $x = 1$ to 3

where

- fi_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 solution, in millilitres.

If the range of values for fi_1 , fi_2 and fi_3 exceeds 0,000 01 g/ml, then repeat the standardization.

Otherwise calculate the mean factor as follows:

$$f = (fi_1 + fi_2 + fi_3)/3$$

(1b)

(1a)

7.5.2 Titration of samples

To the sample prepared in 7.4, add 4 drops of bromothymol blue indicator solution (4.15) and neutralize by adding hydrochloric acid (4.5) dropwise until the blue colour disappears. Add 7 drops in excess.

A pH meter (5.4) may be used to adjust the pH to a value of 5,6 instead of using the bromothymol blue indicator. NOTE 1 Care should be taken to ensure that the electrodes are washed off with water before continuing the procedure.

Add 20 ml of hexamethylenetetramine buffer solution (4.16) and 20 ml of masking solution (4.17). Add 10 drops of xylenol orange indicator (4.18) to the solution. Swirl to dissolve and titrate with EDTA standard solution (4.20) until a colour change to yellow occurs. Record the volume of titrant used as V_{t} .

If the test sample contains cadmium, it will not be removed during the procedure given in 7.5. The cadmium NOTE 2 concentration is determined separately and a correction made for its presence. The method for the determination of cadmium is given in annex D.

7.6 Determination of mass of zinc in the acid-insoluble residue and hydroxide precipitate

Determine the mass of zinc (m_{7n}) contained in both the acid-insoluble residue from the dissolution step (7.3) and the hydroxide precipitate from the separation step (7.4) as described in annex C.

Determination of the cadmium content of the sample 7.7

Determine the cadmium content C_{Cd} of the sample as described in annex D.

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Expression of results 8

Calculation of the zinc content of the test portions 8.1

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$$Zn\% = \left[\frac{(V_{t} - V_{b}) \times f + m_{Zn}}{m} \times 100 \times \frac{100^{c4ab} 8e84a94b/iso-13658-2000}{100 - H} - 0,581C_{Cd}\right]$$

where

- is the volume of EDTA used to titrate the sample aliquot, in millilitres; V_{t}
- $V_{\rm h}$ is the volume of EDTA used to titrate the reagent blank, in millilitres;
- is the zinc equivalent factor of the EDTA solution, in grams per millilitre; f

 m_{Zn} is the mass of zinc in the residues as determined in annex C, in grams;

- is the test portion mass, in grams; т
- is the hygroscopic moisture of the test portion, expressed as a percentage by mass; Η

 C_{Cd} is the cadmium concentration as determined in annex D, expressed as a percentage by mass.

NOTE In the case of a predried test portion, H is equal to zero. (2)

8.2 Calculation of the zinc content of the test sample

Process the duplicate test portion results for the test sample as per the chart in annex E. If necessary, analyse extra test portions as required by annex E.

NOTE The replicate limit is calculated as follows:

 $E = |\mu_1 - \mu_2|$

Replicate limit = $2,8\sqrt{2s_r^2} = 0,16$

where s_r is the repeatability standard deviation, in percent (see 10.1)

9 Application to the trading of zinc concentrates

Between-laboratory precision is used to determine the agreement between the results reported by two laboratories. The assumption is that both laboratories followed the same procedure.

Calculate the following quantities:

Critical difference R = 0.34

Range

where

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 μ_1 is the final result, in percent, reported by laboratory 1: (standards.iteh.ai)

 μ_2 is the final result, in percent, reported by laboratory 2. ISO 136582000

NOTE The critical difference is one of the factors used to derive the splitting limit.^{47ea-bf14-}

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If $E \leq R$, the results are in agreement and the average of the two results can be used for commercial purposes.

10 Accuracy

10.1 Expression of precision

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

NOTE Additional information is given in annex F.

 $s_r = 0,041$

 $s_{R} = 0,12$

where

*s*_r is the repeatability standard deviation, in percent;

*s*_R is the reproducibility standard deviation, in percent.