INTERNATIONAL STANDARD

ISO 13658

First edition
2000-03-15

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

Reference number
ISO 13658:2000(E)

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Printed in Switzerland

Contents

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.

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

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General 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)

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

4.6 Hydrochloric acid (1+1)

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.

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.

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

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_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).

NOTE 2 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. 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:

$$fi_x = m_x/V_x \text{ for } x = 1 \text{ to } 3 \qquad (1a)$$

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:

$$f = (fi_1+fi_2+fi_3)/3 \qquad (1b)$$

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.

NOTE 1 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. 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.

NOTE 2 If the test sample contains cadmium, it will not be removed during the procedure given in 7.5. The cadmium 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_{Zn}) 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.

7.7 Determination of the cadmium content of the sample

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

8 Expression of results

8.1 Calculation of the zinc content of the test portions

$$\text{Zn\%} = \left[\frac{(V_t - V_b) \times f + m_{Zn}}{m} \times 100 \times \frac{100}{100 - H} \right] - 0{,}581 C_{Cd} \qquad (2)$$

where

V_t is the volume of EDTA used to titrate the sample aliquot, in millilitres;

V_b is the volume of EDTA used to titrate the reagent blank, in millilitres;

f is the zinc equivalent factor of the EDTA solution, in grams per millilitre;

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

m is the test portion mass, in grams;

H is the hygroscopic moisture of the test portion, expressed as a percentage by mass;

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.

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:

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 $E = |\mu_1 - \mu_2|$

where

μ_1 is the final result, in percent, reported by laboratory 1;

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

NOTE The critical difference is one of the factors used to derive the splitting limit.

If $E \leqslant R$, 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.

10.2 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:

$$\left|\mu_{\mathrm{c}} - A_{\mathrm{c}}\right| \leqslant C \tag{3}$$

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

$$\left|\mu_{\mathrm{c}} - A_{\mathrm{c}}\right| > C \tag{4}$$

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

Where

μ_{c} is the final result, in percent, of the certified reference material;

A_{c} is the certified value, in percent, of the certified reference material;

C is a quantity, in percent, depending on the type of certified reference material used as defined in 10.2.1.

Reference materials used for this purpose shall be prepared and certified in accordance with ISO Guide 35.

If the reference material has been certified/characterized by an inter-laboratory test programme,

$$C = 2\sqrt{\left[s_{\mathrm{R}}^2 - s_{\mathrm{r}}^{2*}\left(n - 1/n\right) + s^2\left\{A_{\mathrm{c}}\right\}\right]} \tag{5}$$

where

$s^2\{A_{\mathrm{c}}\}$ is the variance of the certified value;

n is the number of replicate determinations of the whole method.

If the reference material has been certified/characterized by only one laboratory,

$$C = 2\sqrt{\left[2s_{\mathrm{R}}^2 - s_{\mathrm{r}}^{2*}\left(n - 2/n\right)\right]} \tag{6}$$

where n is the number of replicate determinations of the whole method.

NOTE 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) identification of the sample;

b) reference to this International Standard, i.e., ISO 13658;

c) zinc content of the sample, expressed as a percentage by mass;

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)

An examination of potentially interfering elements

A.1 Scope

This annex describes the effect of potentially interfering elements and how the interference is minimized within the procedure.

A.2 Cadmium

Cadmium is not removed by precipitation. It is determined separately and the appropriate correction to the zinc concentration is made (see 7.7).

A.3 Lead

Lead is commonly present in large quantities in zinc concentrates. It is largely precipitated as lead sulfate in the dissolution stage (see 7.3). Small amounts of lead are completely eliminated in the filtration stage.

A.4 Iron and manganese

Iron and manganese are eliminated in the separation stage (see 7.4).

A.5 Copper

Copper is masked by the masking solution in the titration stage (see 7.5).

A.6 Nickel and cobalt

If the concentration of nickel and cobalt is less than 0,03 %, their influence is negligible. Levels above this value are not known to exist in internationally traded concentrates.

A.7 Calcium and aluminium

Calcium is partially precipitated as calcium sulfate in the dissolution stage (see 7.3) and aluminium is largely eliminated as a precipitate in the separation stage (see 7.4). Calcium and aluminium remaining in the filtrate are masked during the titration stage (see 7.5)

Annex B
(normative)

Procedure for the preparation and determination of the mass of a predried test portion

B.1 Scope

This annex sets out a method for the preparation and determination of the mass of a pre-dried test portion in the analysis of zinc sulfide concentrates. The method is applicable to zinc sulfide concentrates not susceptible to oxidation and having hygroscopic moisture contents ranging from 0,05 % (m/m) to 2 % (m/m).

B.2 Principle

Drying of the test portion to be used for analysis in air in an oven maintained at 105 °C ± 5 °C. Weighing of the dried test portion and using it for the analysis. No correction for moisture is required.

B.3 Reagents

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

WARNING — Care should be taken when disposing of exhausted magnesium perchlorate. It should be washed down the sink with a stream of running water.

B.4 Apparatus

B.4.1 Analytical balance, sensitive to 0,1 mg.

B.4.2 Weighing vessels, of glass or silica or corrosion-resistant metal having externally-fitting air-tight covers. For small test portions (less than 3 g), the mass of the vessel should be as small as possible, i.e., less than 20 g.

B.4.3 Laboratory oven, capable of maintaining a temperature of 105 °C ± 5 °C.

B.5 Procedure

B.5.1 Preparation of the weighing vessel

Dry the weighing vessel and vessel cover (B.4.2) by heating in a laboratory oven (B.4.3) at 105 °C ± 5 °C for 1 h. Transfer the vessel and vessel cover to a desiccator containing suitable fresh desiccant (B.3.1) and allow to cool to ambient temperature.

B.5.2 Test portion

Tare the dried weighing vessel and vessel cover (B.4.2). Immediately add a portion of the laboratory sample to provide a suitable predried test portion. An accurate total mass of the test portion and weighing vessel is not required at this point.

B.5.3 Determination of the test portion dry mass

Transfer the uncovered weighing vessel and test portion and vessel cover to the laboratory oven (B.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 and dry test portion and 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 to 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).

NOTE 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.

B.6 Calculation of the test portion dry mass

The dry mass of the test portion (m_3) is calculated from the equation:

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

where

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

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

m_3 is the mass, in grams, of the dry test portion.

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.

Annex C
(normative)

Determination of zinc content of acid-insoluble and hydroxide precipitation residues by atomic absorption spectroscopy

C.1 Scope

This annex sets out a method for the preparation and determination of the residual zinc content of the acid-insoluble and the hydroxide precipitate residues in the range 0,000 1 g to 0,000 5 g.

C.2 Principle

Dissolution of the hydroxide precipitate from the hydroxide separation in hydrochloric acid and combining the filter paper remaining with the filter paper containing the acid-insoluble residue. Ashing of both filter papers and fusion of the resultant residue with sodium peroxide. Leaching of this melt with hydrochloric acid and combination with the dissolved hydroxide precipitate. Determination of the zinc concentration of the combined solutions using atomic absorption spectroscopy or inductively-coupled plasma atomic emission spectroscopy.

C.3 Reagents

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

C.3.1 Hydrochloric acid (ρ_{20} 1,16 g/ml to 1,19 g/ml)

C.3.2 Hydrochloric acid (1+1)

Add 500 ml of hydrochloric acid (C.3.1) to 500 ml of water.

C.3.3 Nitric acid (ρ_{20} 1,42 g/ml)

C.3.4 Hydrofluoric acid (ρ_{20} 1,13 g/ml)

C.3.5 Sulfuric acid (ρ_{20} 1,84 g/ml)

C.3.6 Sulfuric acid (1+1)

Add carefully and slowly with stirring 500 ml of sulfuric acid (C.3.5) to 500 ml of water.

C.3.7 Iron solution

Dissolve 1 g of iron metal in 20 ml of hydrochloric acid (C.3.2). Add 5 ml of nitric acid (C.3.3) and transfer to a 100 ml volumetric flask. Dilute to volume with water and mix well.

C.3.8 Zinc stock standard (1 000 µg/ml)

Dissolve 1 g of high-purity zinc metal in 100 ml of hydrochloric acid (C.3.2). Cool and transfer into a 1 000 ml volumetric flask. Dilute to volume with water and mix well.

C.3.9 Zinc intermediate standard (100 µg/ml)

Transfer 25 ml of zinc stock standard (C.3.8) into a 250 ml volumetric flask. Dilute to volume with water and mix well.

C.3.10 Sodium peroxide

C.3.11 Sodium chloride

C.4 Apparatus

C.4.1 Atomic absorption spectrometer or inductively-coupled plasma atomic emission spectrometer

C.4.2 Class A volumetric glassware, complying with ISO 385-1, ISO 648 and ISO 1042 and used in accordance with ISO 4787

C.4.3 Hotplate

C.4.4 Muffle furnace, capable of maintaining a temperature of 800 °C ± 10 °C

C.4.5 Zirconium crucible, 30 ml capacity

C.4.6 Platinum crucible, 50 ml capacity

C.5 Procedure

C.5.1 Treatment of hydroxide precipitate

Take the filter paper containing the hydroxide precipitate from step 7.4 and wash the precipitate into the original beaker with a minimum quantity of water. Rinse the filter paper with alternate warm hydrochloric acid (C.3.2) and water rinses. Collect the filter rinses in the same beaker as the original precipitate. Add 15 ml of hydrochloric acid (C.3.2) and boil to dissolve the hydroxide precipitate. Allow to cool.

Keep the filter paper for later treatment, unless it has been statistically shown, by previous testing, that no zinc remains on/in the filter paper after rinsing, for the concentrate being analysed and the analyst performing the test. If this step is not routinely carried out, regular checks confirming the validity of its exclusion shall be undertaken 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.

C.5.2 Treatment of acid-insoluble residue and hydroxide precipitate filter papers

Take the filter paper containing the acid-insoluble residue and the rinsed filter paper from the hydroxide precipitation and treat them using either of the following procedures:

a) Place both filter papers in a zirconium crucible (C.4.5). Gently ash the papers in a muffle furnace (C.4.4) at 800 °C. Allow the crucible and residue to cool. Add 2 g of sodium peroxide (C.3.10) and fuse over a gentle heat, gradually raising the heat of the melt to achieve complete fusion. When all the residue has fused, remove from heat and allow to cool. Transfer the crucible and melt to a 400 ml beaker containing 50 ml of warm water. Immerse the crucible to remove most of the melt and then add 25 ml of hydrochloric acid solution (C.3.2). Cover the beaker with a watch glass and heat gently to dissolve all the melt. Allow to cool, then remove the crucible and rinse the crucible well with water. Collect these rinsings in the same beaker as the dissolved melt.

b) Place both filter papers in a platinum crucible (C.4.6) and gently ash the paper in the muffle furnace (C.4.4) at 800 °C. Allow the crucible and residue to cool to ambient temperature. Add 2 ml of dilute sulfuric acid (C.3.6), 2 ml of nitric acid (C.3.3) and 2 ml of hydrofluoric acid (C.3.4) and evaporate the solution nearly to dryness. Cool and add water in small quantities to dissolve the soluble salts.

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

C.5.3 Determination of zinc content

Transfer the dissolved precipitate solution from C.5.1 and the dissolved acid-insoluble solution from C.5.2 to the same 250 ml volumetric flask. Dilute to volume with water and mix well

Prepare calibrating solutions by quantitatively transferring 0 ml, 0,5 ml, 2 ml and 5 ml of zinc intermediate standard (C.3.9) to separate 250 ml volumetric flasks. Add 40 ml of hydrochloric acid solution (C.3.2), 5 ml of iron solution (C.3.7) and if sodium peroxide was used add 3 g of sodium chloride (C.3.11). Dilute to volume with water and mix well.

The instrument shall be set up with appropriate background correction using a zinc hollow cathode lamp running at about 7 mA. The wavelength shall be set to 213,8 nm with a slit width of 0,5 nm. An oxidizing acetylene-air flame is used.

NOTE 1 The instrumental settings used for the determination of zinc should be in accordance with the manufacturer's recommendations. The above instructions are issued as guidelines only.

Aspirate the calibration solutions into the atomic absorption spectrometer and prepare a calibration graph of absorbance against zinc concentration in micrograms per gram. Ensure the calibration achieves better than 0,999 correlation and is suitably linear. Aspirate the test solutions and determine the zinc concentration of the test solutions from the calibration graph.

NOTE 2 An inductively-coupled plasma emission spectrometer can be used to determine the zinc concentration.

C.6 Expression of results

$$m_{\mathrm{Zn}} = c_{\mathrm{Zn}} \times \frac{250}{10^6} \tag{C.1}$$

where

m_{Zn} is the mass of zinc in the combined residues, expressed in grams;

c_{Zn} is the concentration of zinc in the test solution, expressed in micrograms per millilitre;

250 is the volume of the test portion solutions, expressed in millilitres;

10^6 is the conversion from micrograms to grams.

Annex D
(normative)

Determination of cadmium by atomic absorption spectrometry

D.1 Scope

This annex describes the procedure for the determination of cadmium in zinc sulfide concentrates containing cadmium in the range 0,05 % (*m*/*m*) to 0,2 % (*m*/*m*).

D.2 Principle

Dissolution of the sample in hydrochloric, nitric and sulfuric acids. Evaporation of the mixture to dryness and dissolution of the soluble salts with dilute hydrochloric acid. Determination of cadmium concentration using atomic absorption spectroscopy or inductively-coupled plasma atomic emission spectrometry.

D.3 Reagents

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

D.3.1 Hydrochloric acid (ρ_{20} 1,16 g/ml to 1,19 g/ml)

D.3.2 Hydrochloric acid (1 + 1)

Add 500 ml of hydrochloric acid (D.3.1) to 500 ml of water.

D.3.3 Nitric acid (ρ_{20} 1,42 g/ml)

D.3.4 Nitric acid (1 + 1)

Add 500 ml of nitric acid (D.3.3) to 500 ml of water.

D.3.5 Sulfuric acid (ρ_{20} 1,84 g/ml)

D.3.6 Sulfuric acid (1 + 1)

Add carefully and slowly, with stirring, 100 ml of sulfuric acid (D.3.5) to 100 ml of water.

D.3.7 Cadmium stock standard (500 µg/ml)

Dissolve 0,5 g of high-purity cadmium metal in 20 ml of nitric acid (D.3.4) by heating gently. Cool and transfer to a 1 000 ml volumetric flask. Make up to volume with water.

D.3.8 Cadmium intermediate standard (20 µg/ml)

Quantitatively transfer, by pipette, 10 ml of cadmium stock solution (D.3.7) into a 250 ml volumetric flask. Make up to volume with water. Prepare on the day of use.

D.4 Apparatus

D.4.1 Class A volumetric glassware, complying with ISO 385-1, ISO 648 and ISO 1042 and used in accordance with ISO 4787

D.4.2 Balance, capable of being read to 0,1 mg

D.4.3 Hotplate

D.4.4 Atomic absorption spectrometer or inductively-coupled plasma atomic emission spectrometer

D.5 Procedure

Taking multiple increments, extract a test portion of 0,5 g (m_{Cd}) weighed to the nearest 0,1 mg from a predried test sample (see annex B) and place in a 200 ml beaker.

NOTE If a predried test sample is not used, appropriate correction of the cadmium content will be required.

Add 10 ml of hydrochloric acid (D.3.1) and 5 ml of nitric acid (D.3.3). Cover the beaker with a watch glass and boil gently. Cool and add 5 ml of sulfuric acid (D.3.6). Remove the watch glass and evaporate the solution to dryness.

Cool and add 10 ml of hydrochloric acid (D.3.2) and 30 ml of water. Dissolve the soluble salts by heating gently. Allow to cool to ambient temperature and transfer to a 100 ml volumetric flask, make up to volume with water and mix well.

D.6 Determination of cadmium by atomic absorption spectrometry

Prepare calibrating solutions by quantitatively transferring 0 ml, 10 ml, 20 ml and 50 ml of cadmium intermediate standard (D.3.8) to separate 100 ml volumetric flasks. Add 10 ml of hydrochloric acid solution (D.3.2). Dilute to volume with water and mix well.

The instrument shall be set up with a cadmium hollow cathode lamp running at about 4 mA. The wavelength shall be set to 228,8 nm with a slit width of 0,5 nm. An oxidizing acetylene-air flame is used.

NOTE 1 The instrumental settings used for the determination of cadmium should be in accordance with the manufacturer's recommendations. The above instructions are issued as guidelines only.

Rotate the burner slightly until a calibration solution containing 10 µg/ml of cadmium gives an absorbance reading of 0,4 absorbance units.

Aspirate the calibration solutions into the atomic absorption spectrometer and prepare a calibration graph of absorbance against cadmium concentration in micrograms per gram. Ensure the calibration achieves better than 0,999 correlation and is suitably linear. Aspirate the test solutions and determine the cadmium concentration C_{Cd} of the test solutions from the calibration graph.

NOTE 2 An inductively-coupled plasma emission spectrometer can be used to determine the zinc concentration.

D.7 Expression of results

$$C_{\mathrm{Cd}} = \frac{c_{\mathrm{Cd}}}{m_{\mathrm{Cd}}} \times \frac{100}{10^4} \qquad \text{(D.1)}$$

where

C_{Cd} is the cadmium content of the sample, expressed as a percentage by mass;

c_{Cd} is the concentration of cadmium in the test solution, expressed in micrograms per millilitre;

m_{Cd} is the test portion mass, expressed in grams;

100 is the volume of the test portion solution, expressed in millilitres;

10^4 is the conversion from micrograms to percentage by mass.

Annex E
(normative)

Flowsheet of the procedure for the acceptance of analytical values for test samples