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Indian Standard

METHOD FOR DETERMINATION OF ZINC (VOLUMETRIC)

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INDIAN STANDARDS INSTITUTION
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

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Indian Standard

METHOD FOR DETERMINATION OF ZINC (VOLUMETRIC)

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Indian Standard

METHOD FOR DETERMINATION OF ZINC (VOLUMETRIC)

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 9 August 1979, after the draft finalized by the Chemical Standards Sectional Committee had been approved by the Chemical Division Council.

0.2 Zinc in small quantities is associated with a large variety of materials of industrial importance, such as basic chemicals, ores, clays, and non-ferrous alloys. The accuracy of the volumetric method compares favourably with that of the gravimetric method. The volumetric method is more rapid when many samples are to be analysed.

0.3 This standard is intended to achieve uniformity of the method of determination of zinc prescribed in various Indian Standards.

0.4 In the preparation of this standard assistance has been drawn from JIS M 8124-1965 'Methods for determination of zinc in ores', published by Japanese Standards Association.

0.5 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960*.

1. SCOPE

1.1 This standard prescribes the methods for the volumetric determination of zinc by using (a) potassium ferrocyanide, and (b) ethylenediamine tetraacetate (EDTA).

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*Rules for rounding off numerical values (*revised*).

2. QUALITY OF REAGENTS

2.1 Unless specified otherwise, pure chemicals and distilled water (*see* IS : 1070-1977*) shall be used in tests.

NOTE — 'Pure chemicals ' shall mean chemicals that do not contain impurities which affect the results of analysis.

3. POTASSIUM FERROCYANIDE METHOD

3.1 Outline of the Method — The sample is decomposed with hydrochloric acid and nitric acid and hydrogen sulphide gas is passed to precipitate cadmium and copper. Ammonium chloride, ammonium hydroxide and bromine water are added to the filtrate to remove iron and manganese. Hydrochloric acid is added to the solution which is titrated with potassium ferrocyanide standard solution using uranyl salt indicator.

3.2 Reagents

3.2.1 *Concentrated Hydrochloric Acid* — (*see* IS : 265 - 1976†).

3.2.2 *Hydrochloric Acid* — 1 : 1, 1 : 2, 1 : 5, and 1 : 50.

3.2.3 *Nitric Acid* — 1 : 1.

3.2.4 *Sulphuric Acid* — 1 : 2.

3.2.5 *Ammonium Hydroxide*

3.2.6 *Hydrogen Sulphide Gas*

3.2.7 *Bromine Water*

3.2.8 *Hydrogen Peroxide* — 1 : 10.

3.2.9 *Ammonium Chloride*

3.2.10 *Ammonium Persulphate*

3.2.11 *Ammonium Carbonate*

3.2.12 *Ammonium Chloride Wash Solution* — Dissolve 20 g of ammonium chloride in water, add 10 ml of ammonium hydroxide and dilute to 1 litre.

3.2.13 *Litmus Paper*

3.2.14 *Hydrogen Sulphide Water* — saturated.

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*Specification for water for general laboratory use (*second revision*).

†Specification for hydrochloric acid (*second revision*).

3.2.15 *Uranyl Salt Indicator* — Dissolve 10 g of uranyl acetate or uranyl nitrate in water and dilute to 100 ml.

3.2.16 *Potassium Ferrocyanide Standard Solution* — Dissolve 21·6 g of potassium ferrocyanide in water, and dilute with water to 1 litre. Standardize this solution as follows.

3.2.16.1 Weigh accurately 0·25 g of zinc into a 500-ml conical flask. Add 10 ml of hydrochloric acid to dissolve it completely. Then add 100 ml of water and 14 g of ammonium chloride and neutralize with ammonium hydroxide using litmus paper and add 5 ml of hydrochloric acid. Add 50 ml of hydrogen sulphide water (saturated) and dilute with water to about 250 ml. Titrate zinc in accordance with **3.3.5** and calculate the mass of zinc equivalent to 1 ml of potassium ferrocyanide solution as follows:

$$m = \frac{M}{V_1 - V_2}$$

where

m = mass in g of zinc equivalent to 1 ml of potassium ferrocyanide solution,

M = mass in g of zinc taken,

V_1 = volume in ml of potassium ferrocyanide solution consumed in titration, and

V_2 = volume in ml of potassium ferrocyanide solution consumed for the blank.

Store this standard solution in a brown bottle in a dark place and restandardize prior to use.

3.3 Procedure

3.3.1 Weigh accurately 0·3 to 1 g of the sample into a 300-ml beaker. Cover with a watch glass and moisten with small amount of water. Add 20 to 30 ml of hydrochloric acid and gently heat to volatilize sulphur contained in sulphide as hydrogen sulphide gas. Add 10 ml of nitric acid, continue the heating to decompose the sample completely and evaporate to nearly dryness. After cooling, add 10 ml of hydrochloric acid (1 : 1) to dissolve soluble salts and dilute with water to 3 percent by volume of hydrochloric acid solution.

3.3.2 Heat the solution to 80 to 90°C and immediately pass hydrogen sulphide gas for 20 to 30 minutes. After standing a while, filter, and wash the filter paper with hydrochloric acid (1 : 50) saturated with hydrogen sulphide gas. Collect the filtrate and washings in a 500-ml beaker and reserve as the main solution.

3.3.3 Place the original beaker under the funnel, add dropwise 9 ml of hydrochloric acid (1 : 2) into the filter paper to dissolve the precipitate and wash with about 100 ml of warm water.

3.3.4 Heat the solution and pass hydrogen sulphide gas to precipitate sulphides in the same way as prescribed in **3.3.2**. Filter, wash and combine the filtrate and washings with the main solution reserved in **3.3.2**.

3.3.5 Heat the solution to evaporate to about 50 ml and add a small amount of bromine water or hydrogen peroxide water. Heat the solution to oxidize iron, etc, and add 5 g of ammonium chloride. Add, under stirring, 15 ml of ammonium hydroxide to precipitate iron, etc, followed by 10 to 20 ml of bromine water or 0·5 g of ammonium persulphate, and boil the solution for a few minutes covered with a watch glass.

3.3.6 After standing a while, filter the solution into a 500-ml conical flask, and wash the filter paper several times with ammonium chloride wash solution. Reserve the filtrate and washings as the main solution. Wash the precipitate with water into the original beaker, add 10 ml of hydrochloric acid (1 : 1) and heat to dissolve the precipitate.

3.3.7 Add 3 g of ammonium chloride and repeat the procedure as in **3.3.5** with the addition to ammonium hydroxide and bromine water or ammonium persulphate to precipitate iron, etc. Filter the precipitate through the original filter paper, and wash with ammonium chloride wash solution. Combine the filtrate and washings with the main solution. Boil the solution for a few minutes to decompose the excess of bromine or ammonium persulphate present and adjust the volume of the solution to about 200 ml.

3.3.8 Add dropwise hydrochloric acid to neutralize the solution against litmus paper. Add additional 5 ml of the acid, followed by 50 ml of hydrogen sulphide water (saturated) and titrate the solution with potassium ferrocyanide solution using uranyl salt as the external indicator keeping the solution temperature at 75 to 80°C. In the titration, add potassium ferrocyanide solution in small increments at first and shake the flask every time. The precipitate produced will gradually become fine as the titration proceeds and becomes milky at the approach of the end point. Add 1 or 2 drops of the standard solution and shake the flask after each addition. Take one drop of the solution with a glass rod on a porcelain plate and mix with the external indicator placed on the plate. Continue the titration until the mixed solution changes colour from yellowish green to pale brown. Titrate three times to arrive at the exact volume of potassium ferrocyanide solution required. Run the blank for all reagents under the same condition and calculate the zinc content.

3.4 Calculation

$$\text{Zinc (as Zn), percent by mass} = \frac{m \times (V_1 - V_2)}{M} \times 100$$

where

m = equivalent in g of zinc to 1 ml of potassium ferrocyanide solution,

V_1 = volume in ml of potassium ferrocyanide solution consumed in titration,

V_2 = volume in ml of potassium ferrocyanide solution for the blank, and

M = mass in g of the sample taken in the test solution.

4. EDTA METHOD

4.1 Principle of the Method — The sample is decomposed with hydrochloric acid and nitric acid and zinc is retained on a strongly basic anion exchange resin. The resin column is washed with dilute hydrochloric acid and then zinc is eluted with dilute ammonium hydroxide containing ammonium chloride. The *p*H value of the eluate is adjusted to about 5·5 and titrated with EDTA standard solution using xylenol orange indicator.

4.2 Apparatus

4.2.1 *Ion-Exchange Resin Column* — Ion exchange resin column shall be as shown in Fig. 1. The resin, to be filled in the tube, shall be of strongly basic anion exchange resin of grain size 215 to 150 micron IS sieve (*see* IS : 460-1962*). Fill about 20 g of the resin with water into the tube and pour 100 ml of ammonium hydroxide (7 : 100) at a rate of 5 ml per minute, followed by about 50 ml of water at the same rate. Wash the column with 100 ml of hydrochloric acid (1 : 5) and finally with 50 ml of water. Repeat this procedure.

When the resin is used again, only one washing cycle is necessary.

4.3 Reagents

4.3.1 *Concentrated Hydrochloric Acid* — (*see* IS : 265 - 1976†).

4.3.2 *Hydrochloric Acid* — 1 : 5.

4.3.3 *Nitric Acid* — 1 : 1.

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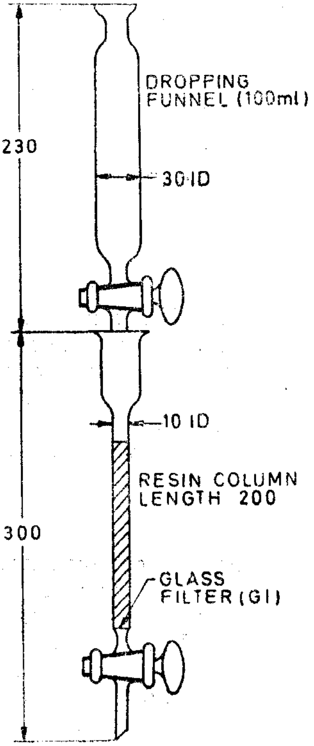
*Specification for test sieves (*revised*).

†Specification for hydrochloric acid (*second revision*).

4.3.4 *Sulphuric Acid* — 1 : 1 and 1 : 10.

4.3.5 *Acetic Acid* — 1 : 1.

4.3.6 *Ascorbic Acid - Hydrochloric Acid Solution* — Dissolve 0·25 g of ascorbic acid in hydrochloric acid (1 : 5) and dilute to 100 ml.



All dimensions in millimetres.

FIG. 1 ION EXCHANGE RESIN COLUMN

4.3.7 *Ammoniacal Eluent* — Dissolve 20 g of ammonium chloride in 1 litre of ammonium hydroxide (7 : 100).

4.3.8 *Buffer Solution* — Dissolve 250 g of ammonium acetate in water, add 25 ml of glacial acetic acid and dilute with water to 1 litre. Adjust the *p*H value to about 5·5 by means of a *p*H meter.

4.3.9 *Ammonium Fluoride Solution* — 5 percent (*m/v*).

4.3.10 *Sodium Thiosulphate Solution* — 10 percent (*m/v*).

4.3.11 *Xylenol Orange Indicator Solution* — Dissolve 9·1 g of xylenol orange in 100 ml of water or 100 ml of 50 percent ethyl alcohol (*v/v*).

4.3.12 *Sodium Diethyl Dithiocarbamate*

4.3.13 *Eriochrome Black T Indicator Solution* — Dissolve 0·5 g of eriochrome black T in 100 ml of ethyl alcohol and add 4 g of hydroxylamine hydrochloride.

4.3.14 *Zinc Standard Solution* — 0·05 M. Weigh accurately 3·269 g of zinc into a 500-ml conical flask and add 20 ml of hydrochloric acid to dissolve it. Heat the solution and dilute with water to exactly 1 litre. Standardize this solution with EDTA standard solution (0·05 M) as follows.

4.3.14.1 To 10 ml of EDTA standard solution add 180 ml of ammoniacal eluent and a few drops of Eriochrome black T indicator solution and titrate with the zinc solution until the colour changes from blue to violet.

4.3.15 *EDTA Standard Solution* — 0·5 M. Dissolve 18·610 g of disodium ethylenediamine tetraacetate dihydrate in water and dilute to 1 litre. One millilitre of this solution is equivalent to about 3·269 mg of zinc. Standardize this solution as follows.

4.3.15.1 Weigh accurately 0·15 g of zinc into a 500-ml conical flask and add 10 ml of hydrochloric acid to dissolve it. Add 180 ml of ammoniacal eluent, neutralize with acetic acid (1 : 1) and proceed as prescribed in **4.4.3**. Calculate the mass of zinc equivalent to 1 ml of EDTA solution as follows:

$$m = \frac{M}{V_1 - V_2}$$

where

m = mass of zinc equivalent to 1 ml of EDTA solution,

M = mass in g of zinc taken,

V_1 = volume in ml of EDTA solution consumed in titration for sample, and

V_2 = volume in ml of EDTA solution consumed in titration for the blank.

4.3.15.2 For the sample containing small amount of zinc, EDTA solution (0·01 M) shall be prepared.

4.4 Procedure

4.4.1 Weigh accurately 0·3 to 1 g of the sample into a 250-ml beaker. Cover with a watch glass and moisten with a small amount of water.

Add 20 to 30 ml of hydrochloric acid and gently heat to volatilize sulphur contained in sulphide as hydrogen sulphide gas. Then add 10 ml of nitric acid, continue heating to decompose the sample completely. Add 10 ml of sulphuric acid (1 : 1) and heat to evolve white fumes. After cooling add 50 ml of water, heat to dissolve soluble salts and allow to cool to room temperature. Filter the precipitate and wash several times with cold sulphuric acid (1 : 10). Collect the filtrate and washings in a 250-ml beaker and pour into the dropping funnel of the apparatus. Add 16 ml of hydrochloric acid and water to make to 100 ml and mix well.

4.4.2 Pour the solution on to the column at a rate of about 6 ml per minute and allow the zinc to be adsorbed in the column. After completion of the pouring, add 100 ml of hydrochloric acid followed by 100 ml of ascorbic acid-hydrochloric acid solution and finally 100 ml of hydrochloric acid to wash the column, adding about 7 ml of each solution per minute.

4.4.3 Add 180 ml of the ammoniacal eluent at a rate of about 6 ml per minute to elute the zinc from the column and collect the effluent in a 500-ml beaker. Neutralize the solution with acetic acid and add 20 ml of buffer solution to adjust the *p*H value to 5·0 to 5·5. Then add 2·5 ml of ammonium fluoride solution 5 percent (*m*/*v*), 5 ml of sodium thiosulphate solution [10 percent (*m*/*v*)] and a few drops of xylenol orange indicator solution and titrate with EDTA solution until the solution changes colour from pink to yellow.

4.5 Calculation

4.5.1 Calculate the zinc content as follows:

$$\text{Zinc (as Zn), percent by mass} = \frac{m \times (V_1 - V_2)}{M} \times 100$$

where

m = mass in g of zinc equivalent to 1 ml of EDTA solution,

V_1 = volume in ml of EDTA solution consumed in titration for sample,

V_2 = volume in ml of EDTA solution consumed for the blank, and

M = mass in g of the sample taken.