IS 3025 (Part 40) : 1991

(Reaffirmed 1998)

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भाग 40 कैलशियम

(पहला पुनरीक्षण)

Indian Standard

WATER AND WASTEWATER — METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL)

PART 40 CALCIUM

(First Revision)

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November 1991 **Price Group 2**

Environmental Protection Sectional Committee, CHD 12

FOREWORD

This Indian Standard (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Environmental Protection Sectional Committee had been approved by the Chemical Division Council.

Calcium is a major constituent of various types of rock. It is one the most common constituents present in natural waters ranging from zero to several hundred milligrams per litre depending on the source and treatment of the water. Calcium is a cause for hardness in water and incrustation in boilers.

This standard supersedes **33** of IS 3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry' and **5** of IS 2488 (Part V) : 1976 'Methods of sampling and test for industrial effluents, Part V'.

In the preparation of this standard, considerable assistance has been derived from Standard Methods for the Examination of Water and Wastewater; published by the American Public Health Association, Washington, USA, 16th edition, 1985.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*). The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

Indian Standard

WATER AND WASTEWATER — METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL)

PART 40 CALCIUM

(*First Revision*)

1 SCOPE

This standard prescribes following three methods for determination of calcium:

a) EDTA titrimetric method,

b) Atomic absorption spectrometric method, and

c) Permanganate titration method.

2 REFERENCES

The following Indian Standards are necessary adjuncts to this standard :

IS No.	*Title*
1070 : 1977	Water for general laboratory use (*second revision*)
3025 (Part 1) : 1986	Methods of sampling and test (physical and chemical) for water and wastewater : Part 1 Sampling (*first revision*)
7022 (Part 1) : 1973	Glossary of terms relating to water, sewage and industrial effluents, Part 1
7022 (Part 2) : 1979	Glossary of terms relating to water, sewage and industrial effluents, Part 2

3 TERMINOLOGY

For the purpose of this standard, definitions given in IS 7022 (Part 1) : 1973 and IS7022 (Part 2) : 1979 shall apply.

4 SAMPLING AND STORAGE

Sampling and storage shall be done as prescribed in IS 3025 (Part 1) : 1986.

5 EDTA TITRIMETRIC METHOD

5.1 Principle

In a solution containing both calcium and magnesium, calcium can be determined directly with EDTA (ethylenediamine tetra-acetic acid or its salts) when the *p*H is made sufficiently high (12 to 13) so that the magnesium is largely precipitated as the hydroxide and an indicator is used which combines, only with calcium.

5.2 Interference

Under conditions of this test, the following concentrations of ions cause no interference with the calcium determination : Copper, 2 mg/l; ferrous iron, 20 mg/l; ferric iron, 20 mg/l; manganese, 10 mg/l; zinc, 5 mg/l; lead, 5 mg/l; aluminium, 5 mg/l and tin 5 mg/l. Orthophosphate precipitates calcium at the *p*H of the test. Strontium and barium give a positive interference and alkalinity in excess of 300 mg/l may cause an indistinct end point in hard waters.

5.3 Apparatus

5.3.1 *Hot Plate* — One 30 × 50 cm heating surface is adequate.

5.4 Reagents

5.4.1 *Quality of Reagents*

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.

5.4.2 *Sodium Hydroxide Solution* — 1 N.

5.4.3 *Hydrochloric Acid* — 0·1 N.

5.4.4 *Indicator Solution*

Any of the following indicators shall be used.

5.4.4.1 *Murexide (ammonium purpurate) indicator solution*

This indicator changes from pink to purple at the end point. An indicator solution can be prepared by dissolving 150 mg of the dye in 100 g of absolute ethylene glycol. Water solutions of the dye are not stable for longer than a day. A ground mixture of the dye powder and sodium chloride provides a stable form of the indicator. It is prepared by mixing 200 mg of murexide with 100 g of solid sodium chloride and grinding the mixture to 300 to 425 microns. The titration should be performed immediately after the addition of the indicator because it is unstable under alkaline conditions. End point recognition is facilitated by the preparation of colour comparison blank containing 2·0 ml of sodium hydroxide solution, 0.2 g of solid indicator mixture (or 1 to 2 drops if a solution is used), and sufficient standard EDTA titrant (0·05 to 0·10 ml) to produce an unchanging colour.

5.4.4.2 *Patton and Reeder's indicator solution*

This indicator solution permits the direct titration of calcium in the presence of magnesium. It produces a sharp colour change from wine red to pure blue at the end point. It is prepared by mixing 1 g of Patton and Reeder's (Eriochrome Blue Black R) reagent with 100 g of sodium sulphate or potassium sulphate.

5.4.5 *Standard EDTA Solution* — 0·01 M.

Dissolve 3·75 g of disodium ethylenediamine tetra-acetate, dihydrate in water and make up to 1 000 ml in a volumetric flask. Standardise this with standard zinc solution. Pipette out 25 ml of standard zinc solution in a 250-ml conical flask. Adjust the *p*H to approximately 10 with buffer solution. Dilute to about 100 ml and add 3 to 4 drops of Eriochrome Black T indicator solution. This will give red colour. Titrate with 0·01 M EDTA solution to a clear blue end point free from violet tinge. This solution will be slightly stronger than 0·01 M, dilute the solution to exactly 0·01 M by adding calculated amount of water and recheck the strength by titrating 25 ml of standard zinc solution by exactly the same manner as mentioned above. This should consume exactly 25·0 ml of standard EDTA solution.

Alternatively, calcium solution may be used for standardization of EDTA subject to the availability of certified calcium carbonate according to the method given below:

Weigh 3·723 g of dry analytical reagent grade disodium ethylene diamine tetra acetate, dihydrate, dissolve in distilled water and dilute to 1 000 ml. Check the strength by standardizing against standard calcium solution as described in **5.5.3**. An exactly 0·01 M solution is equivalent to 0·400 8 mg of calcium per millilitre.

5.4.6 *Stock Calcium Solution*

Dry calcium carbonate (Ca Co_3) at 180°C for one hour and allow it to cool in a desiccator. Suspend 2·50 ± 0·01 g of the dried material in 100 ml of water. Add slowly the minimum amount of 0·1 N hydrochloric acid to dissolve the calcium carbonate (approximately 500 ml). Boil briefly to expel dissolved carbon dioxide, cool and transfer the solution quantitatively to a 1 000 ml volumetric flask and dilute to mark with 0·1 N hydrochloric acid.

5.4.7 *Standard Calcium Solution*

Dilute 100 ml of the stock solution (**5.4.6**) to 250 ml using 0·1 N hydrochloric acid. This solution is equivalent to 1·00 mg of calcium carbonate or 0·400 8 mg of calcium per millilitre. Store the solution in a polyethylene bottle.

5.5 Procedure

5.5.1 *Pretreatment*

Mix the sample and transfer a suitable volume (50 to 100 ml) to a beaker. Add 5 ml of concentrated nitric acid and evaporate on a hot plate at a slow boil to the lowest volume possible (about 15 to 20 ml) before precipitation or salting occurs. Add 5 ml of concentrated nitric acid, cover with a watch glass and heat to obtain a gentle refluxing action. Continue heating and adding concentrated nitric acid as necessary until digestion is complete as shown by a light-coloured clear solution. Do not let sample dry during digestion. Add 1 to 2 ml of concentrated nitric acid and warm slightly to dissolve any remaining residue. Wash down beaker walls and watch glass with water and then filter, if necessary. Transfer the filtrate to a 100-ml volumetric flask. Cool, dilute to mark and mix thoroughly. Take a portion of this solution for the determination of calcium.

5.5.2 *Sample Preparation*

Because of the high *p*H used in this procedure, the titration should be performed immediately after the addition of the alkali and indicator. Use 50 ml of sample or a smaller portion diluted to 50 ml so that the calcium content is about 5 to 10 mg. Analyse hard waters with alkalinity higher than 300 mg/l $CaCO_3$ by taking a smaller aliquot and diluting to 50 ml, or by neutralization of the alkalinity with acid, boiling for one minute and cooling before beginning the titration.

5.5.3 Add 2·0 ml of sodium hydroxide solution or a volume sufficient to produce a *p*H of 12 to 13. Stir. Add 0·1 to 0·2 g of the indicator murexide-sodium chloride mixture selected (or 1 to 2 drops if a solution is used). Alternatively, approximately 1 g of the mixture of Patton and Reeder's reagent and sodium sulphate or potassium sulphate may be used. Add EDTA titrant slowly with continuous stirring to the proper end point. Check the end point by adding 1 to 2 drops of titrant in excess to make certain that no further colour change occurs.

5.6 Calculation

$$\text{Calcium (Ca), mg/l} = \frac{A \times B}{V} \times 1\,000$$

where

A = volume in ml of EDTA solution used for titration,

B = mass in mg of calcium equivalent to 1 ml of EDTA solution, and

V = volume in ml of the sample taken for the test.

5.7 Precision and Accuracy

A synthetic unknown sample containing 108 mg/l of calcium, 82 mg/l of magnesium, 3·1 mg/l of potassium, 19·9 mg/l of sodium, 241 mg/l of chloride, 1·1 mg/l of nitrate, 0·25 mg/l of nitrite, 259 mg/l of sulphate and 42·5 mg/l of total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 44 laboratories by the EDTA titrimetric method, with a relative standard deviation of 9·2 percent and a relative error of 1·9 percent.

6 ATOMIC ABSORPTION SPECTROMETRIC METHOD

6.1 This method is applicable to the analysis of dissolved calcium in raw and drinking water and can be used for water having a calcium content up to 50 mg/l. A smaller volume may be used for samples containing higher concentrations. In general nitrous oxide/acetylene flame should be used if the composition of the sample is complex or unknown especially for samples with a high content of dissolved matter, or which contain phosphate, sulphate, aluminium or silica.

6.2 Interference

Chemical interferences are common. These interferences can be overcome by the addition of a releasing agent, that is, lanthanum chloride (if air/acetylene flame is used) or cesium chloride (if nitrous oxide/acetylene flame is used).

NOTE — Silicon, aluminium phosphate and sulphate depress the sensitivity for calcium. Lanthanum or strontium at cencentration of 0·1 to 1·0 percent may be added to the samples and standards to control these interferences and simultaneously ionization interferences for calcium in air/acetylene flame. Acid concentration of the standards should be matched with that of the samples.

6.3 Apparatus

Atomic absorption spectrometer set up and equipped with an appropriate burner for air/acetylene flame or nitrous oxide/acetylene flame and a hollow cathode lamp for calcium with a wavelength of 422·7 nm.

6.4 Reagents

6.4.1 *Hydrochloric Acid* — 1 N.

6.4.2 *Hydrochloric Acid* — 0·1 N.

6.4.3 *Lanthanum Chloride (20 g/l of La)*

Take 24 g of lanthanum oxide (La_2O_3) into a 1-litre volumetric flask. Slowly and cautiously, add 50 ml of 1 N hydrochloric acid while stirring, to dissolve the lanthanum oxide. Make up to the mark with water.

6.4.4 *Cesium Chloride (20 g/l of Cs)*

Dissolve 25 g of cesium chloride in 1 litre of 0·1 N hydrochloric acid and make up to 1 000 ml.

6.4.5 *Standard Calcium Solution*

Take 5 ml of the stock calcium solution (**5.4.6**) and dilute with 0·1 N hydrochloric acid to 50 ml.

6.5 Procedure

6.5.1 *Preparation of Test Solution*

Samples containing particulate matter after acidification shall be filtered to prevent clogging of the nebulizer and burner systems. To a 100 ml volumetric flask, add 10 ml of the lanthanum chloride solution (**6.4.3**) (if air/acetylene flame is to be used), or 10 ml of cesium chloride solution (**6.4.4**) (if a nitrous oxide/acetyene flame is to be used). Add 10 ml of the sample and make up to the mark with 0·1 N hydrochloric acid.

NOTE — If the concentration of calcium in the sample is above 50 mg/l for air/acetylene flame or 20 mg/l for nitrous oxide/acetylene flame, then appropriately smaller volume of the sample shall be used.

6.5.2 *Blank Test*

Carry out a blank test simultaneously using the same reagents in the same quantities and following the same procedure, but replacing the volume of the test sample used in **6.5.1** by an equal volume of water.

6.5.3 *Preparation of the Set of Calibrations Solutions*

To a series of 100 ml volumetric flasks add 10 ml either of lanthanum chloride or cesium caloride as in **6.5.1**. With the aid of pipettes, add 0; 2·5; 5; 10; 15; 20 and 25 ml of the standard calcium solution. Make up to the mark with 0·1 N hydrochloric acid.

6.5.4 *Calibration and Determination*

Carry out the measurements at 422·7 nm. Aspirate the calibration and blank solutions in random order and aspirate 0·1 N hydrochloric acid in between. Prepare calibration graphs. Aspirate the test solutions, with an aspiration of 0·1 N hydrochloric acid in between and determine the absorbances.

6.6 Calculation

$$\text{Calcium (as Ca), mg/l} = C \times \frac{V_1}{V_0}$$

where

C = concentration, expressed in mg/l of calcium calculated from the calibration graph, having taken into account the blank value;

V_0 = volume in millilitres of the original sample taken for analysis; and

V_1 = volume in millilitres to which the sample has been diluted.

7 PERMANGANATE TITRATION METHOD

7.1 Principle

The calcium present in the solution is precipitated as oxalate filtered off and washed. The washed precipitate is dissolved in dilute sulphuric acid, and the oxalic acid liberated is titrated against standard potassium permanganate solution. The homogeneous precipitation approach using the urea hydrolysis method is best suited for the precipitation of calcium oxalate. Initially the *p*H of the solution is adjusted to approximately

1·0 by adding sufficient amount of acid. This is followed by ammonium oxalate and urea. Upon boiling the solution, the urea gradually undergoes hydrolysis and the *p*H rises to the point of calcium oxalate precipitation. The precipitate is filtered off immediately after formation. This eliminates the digestion period which is otherwise required. The solution must remain clear until boiling is commenced to hydrolyse the urea.

7.2 Interference

The sample should be free of interfering elements of strontium, silica, aluminium, iron, manganese, phosphate and suspended matter. Strontium may precipitate as oxalate and cause high results. In such cases, determine strontium by flame photometry. Interference of silica may be eliminated by classical dehydration procedure. Precipitate aluminium, iron, and manganese by ammonium hydroxide after treatment with persulphate. Precipitate phosphate as the ferric salt. Remove suspended matter by centrifuging or by filtration through sintered glass crucible or a cellulose acetate membrane.

7.3 Apparatus

7.3.1 *Beakers with Glass Rod* — 400 ml capacity and cover glass.

7.3.2 *Filtration Set Up*

A coarse filter paper or a small filter paper supported in a Gooch crucible with suction.

7.4 Reagents

7.4.1 *Quality of Reagents*

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

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

7.4.2 *Hydrochloric Acid* — 1 N.

7.4.3 *Methyl Red Indicator Solution*

Dissolve 100 mg of methyl red sodium salt in 100 ml of hot water or dissolve in 60 ml of ethanol dilute with 40 ml of water.

7.4.4 *Ammonium Oxalate Solution* — Saturated solution in water.

7.4.5 *Urea*

7.4.6 *Dilute Sulphuric Acid* — 1 N.

7.4.7 *Sodium Oxalate*

7.4.8 *Standardization of Potassium Permanganate Solution*

Weigh about 1·6 g of AR grade potassium permanganate on a watch glass, transfer it to a 1 500-ml beaker, add 1 litre of water, cover the beaker with a watch glass, heat the solution to boiling; boil gently for 15-30 minutes and allow the solution to cool to the laboratory temperature. Filter the solution through a funnel, containing a plug of purified glass wool, or through a Gooch crucible provided with a pad of purified asbestos, or most simply, through a sintered glass or porcelain filtering crucible. Collect the filtrate in a vessel which has previously been cleaned with chromic acid mixture and then thoroughly washed with distilled water. Store the filtered solution in a clean, glass stoppered bottle. Keep it in the dark or in an amber coloured bottle or in diffused light except while in use.

Weigh out accurately about 1·7 g of dry sodium oxalate into a 250-ml volumetric flask, dissolve it in water and make up to the mark. Pipette out 25 ml of this solution into a 400-ml beaker and add 150 ml of 1 N sulphuric acid. Titrate this solution rapidly at room temperature with potassium permanganate solution to be standardized while stirring, to a slight pink end point that persists for at least 1 minute. Do not let the temperature fall below 85°C. If necessary, warm beaker contents during titration. Repeat the titration with two more aliquots of the oxalate solution.

Calculate the normality of the permanganate solution using the following relationship:

$$\text{Normality of potassium permanganate solution} = \frac{100 \times m_1}{67 \times V_1}$$

where

m_1 = mass in g of sodium oxalate taken, and

V_1 = volume in ml of the potassium permanganate solution consumed by 25 ml of the oxalate solution.

7.5 Procedure

Pipette out 50 ml of the sample (containing about 10 mg of calcium) into a 250-ml beaker. Add dilute hydrochloric acid drop by drop to a *p*H of approximately 1·0. Add a few drops of methyl red indicator solution (sufficient acid must be present in the solution to prevent the precipitation of calcium oxalate when ammonium oxalate solution is added). Add about 10 ml of saturated ammonium oxalate solution gently until the methyl red changes colour to yellow (*p*H 5). Filter through a coarse filter paper or with suction on a small filter paper supported in a Gooch crucible. Wash the precipitate with cold water till the filtrate is free from chloride. Transfer the filter paper and the precipitate (or the Gooch crucible and precipitate) to the original beaker, dissolve the precipitate in hot dilute sulphuric acid and titrate immediately with standard 0·05 N potassium permanganate solution as described in **7.4.8.1**.

7.6 Calculation

$$\text{Calcium (as Ca) mg/l} = \frac{A \times B \times 100}{V}$$

where

A = volume in ml of permanganate solution used for the titration,

B = mass in mg of calcium equivalent to 1 ml of potassium permanganate solution, and

V = volume of the sample taken for the test.

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Review of Indian Standards

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