भारतीय मानक
Indian Standard

IS 3025 (Part 40) : 2024

जल एवं अपशिष्ट जल के नमूने लेने तथा परीक्षण (भौतिक एवं रसायन) की पद्धतियाँ

भाग 40 कैल्शियम

(दूसरा पुनरीक्षण)

Methods of Sampling and Test (Physical and Chemical) for Water and Wastewater

Part 40 Calcium

(Second Revision)

ICS 13.060.50

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भारतीय मानक ब्यूरो
BUREAU OF INDIAN STANDARDS
मानक भवन, 9 बहादुर शाह ज़फर मार्ग, नई दिल्ली - 110002
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110002
www.bis.gov.in www.standardsbis.in

July 2024 **Price Group 7**

Water Quality Sectional Committee, CHD 36

FOREWORD

This Indian Standard (Part 40) (Second Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Water Quality 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.

The Committee responsible for formulation of IS 3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry' and IS 2488 (Part V) : 1976 'Methods of sampling and test for industrial effluents, Part V' decided to revise the standard and publish it in separate parts. This standard was one of the different parts published under IS 3025 series of standards and superseded **33** of IS 3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry' and **5** of IS 2488 (Part V) : 1976 'Methods of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'. The first revision was published in 1988.

In this revision the following changes have been incorporated:

a) Amendment issued has been incorporated;

b) Inductively coupled plasma (ICP) spectroscopy methods have been incorporated;

c) References, ICS No. have been updated; and

d) Other editorial changes have been done to bring the standard in the latest style and format of Indian Standards.

In the preparation of this standard, considerable assistance has been derived from the method no. 3500-Ca A, B, and 3111 B, D, and E, and F of — Standard methods for the examination of water and wastewater, published by the American Public Health Association, Washington, USA, 23nd Edition, 2017.

The composition of the Committee responsible for the formulation of this standard is given in Annex B.

In reporting the results 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 : 2022 'Rules for rounding off numerical values (*second revision*)'.

Indian Standard

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

PART 40 CALCIUM

(Second Revision)

1 SCOPE

This standard (Part 40) prescribes following methods for determination of calcium in water and wastewater:

a) EDTA titrimetric method;

b) Atomic absorption spectrometric method;

c) Permanganate titration method; and

d) Inductively coupled plasma (ICP) spectroscopy methods.

2 REFERENCES

The standards listed in Annex A contain provisions which, through reference in this text, constitute provisions of this standard. At the time of publications, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent edition of these standards.

3 TERMINOLOGY

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

4 SAMPLING AND PRESERVATION

Sampling and sample preservation shall be done as prescribed in IS 17614 (Part 1) and IS 17614 (Part 3).

5 EDTA TITRIMETRIC METHOD

5.1 Principle

EDTA (ethylenediamine tetra-acetic acid or its salts), when added to water containing both calcium (Ca^{2+}) and magnesium (Mg^{2+}), EDTA first combines preferentially with calcium ions. At a high *p*H of around 12 to 13, the magnesium ions are largely precipitated as hydroxide, while the calcium ions remain in solution. This selective precipitation is done to separate the two ions. To determine the concentration of calcium, an indicator is used that forms a colored complex only with calcium ions and not with magnesium ions. This indicator undergoes a color change when all the calcium ions have been complexed by EDTA, indicating the endpoint of the titration at the *p*H of 12 to 13.

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, 5mg/l; lead, 5 mg/l; aluminium, 5 mg/l and tin, 5 mg/l. Orthophosphate may cause interference as it 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

Hot Plate — one 30 cm × 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) 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 is prepared by dissolving 150 mg of the dye in 100 mg 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 microns to 425 microns. Immediately, perform the titration after the addition of the indicator because it is unstable under alkaline conditions. To facilitate end-point recognition, a color comparison blank is prepared. This blank solution contains 2.0 ml of sodium solution, 0.21 g of solid indicator mixture (or 1 to 2 drops if a solution is used), and sufficient standard EDTA titrant (0.05 ml to 0.10 ml) to produce an unchanging colour.

5.4.4.2 *Eriochrome blue black R indicator solution*

Stable form of this indicator is prepared by grinding 200 mg powered dye and 100 g solid NaCl to 40 mesh to 50 mesh in a mortar. Store it in a tightly stoppered bottle. Use 0.2 g of ground mixture for titration in the same manner as murexide indicator. During the titration, colour changes from red through purple to bluish purple to a pure blue with no trace of reddish or purple tint. Use 8 N of NaOH to get a good colour changes, because the *p*H of some (not all) water raised to 14.

5.4.4.2 *Patton and reeder, 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

5.4.5.1 Dissolve 3.75 g of disodium ethylenediamine tetra-acetate dihydrate (EDTA) in water and make up to 1 000 ml in a volumetric flask. Standardize 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.

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

5.4.5.3 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 Ca/ml.

5.4.6 *Stock Calcium Solution*

Dry calcium carbonate ($CaCO_3$) at 180 °C for 1 h and allow it to cool in a desiccator. Suspend 2.50 g ± 0.01 g of the dried material in 1.0 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 (*see* **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 ml 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 ml 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 ml to 2 ml of concentrated nitric acid and warm slightly. And 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 mg 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 and add 0.1 g 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

$$\text{mg Ca/l} = \frac{A \times B \times 400.8}{V}$$

$$\text{Calcium hardness (as CaCO}_3\text{), mg/l} = \frac{A \times B \times 1\,000}{V}$$

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,.

6 ATOMIC ABSORPTION SPECTROMETRIC METHOD

6.1 Direct Air-Acetylene Flame Method

6.1.1 *Principle*

This method is applicable to the analysis of raw and drinking waters and can be used for waters having a calcium content from 0.2 mg/l to 20 mg/l. For samples containing higher concentration smaller volume of the sample must be taken for the analysis.

6.1.2 *Interferences*

Chemical interferences are common. These can be overcome by the addition of a releasing agent, that is, lanthanum chloride when air-acetylene (oxidizing) flame is used.

6.1.3 *Apparatus*

Atomic absorption spectrophotometer set up and equipped with an appropriate burner for air-acetylene flame and a hollow cathode lamp for calcium with wavelength of 422.7 nm.

6.1.4 *Reagents*

6.1.4.1 Unless otherwise specified, only AR grade chemicals should be used for all the tests.

6.1.4.2 *Air*, clean, dried and free from oil, water and other foreign substances. The source may be a compressor or commercially bottled gas.

6.1.4.3 *Acetylene* — standard commercial grade

CAUTION — Acetylene gas is an explosive threat in the laboratory. In plumbing and utilising this gas, follow the manufacturer's instructions. Allow no gas contact with copper, brass containing more than 65 percent copper, silver or liquid mercury. Use copper or brass tubing, regulators, and fittings that contain more than 65 percent copper.

6.1.4.4 *Calcium-free distilled water* should be used for preparing standards and reagent solution.

6.1.4.5 *Hydrochloric acid* (HCl), 1 percent, 10 percent, 20 percent (all v/v), 1 + 5, 1 + 1, and concentrated.

6.1.4.6 *Nitric acid* (HNO_3), 2 percent (all v/v), 1 + 5, 1 + 1, and concentrated.

6.1.4.7 *Lanthanum solution*

Dissolve 58.65 g lanthanum oxide (La_2O_3), in 250 ml concentrated hydrochloric acid. Add acid slowly until material is dissolved and dilute to 1 000 ml with water.

6.1.4.8 *Stock calcium solution*

Dissolve 0.249 7 g calcium carbonate, $CaCO_3$ (dried at 180 °C for 1 h before weighing) in water and dissolve cautiously with a minimum amount of 1 + 1 HNO_3. Add 10.0 ml conc. HNO_3 and dilute 1 000 ml with water (1.00 ml = 100 µg of Ca).

6.1.4.9 *Standard calcium solution*

Prepare a series of standard calcium solution by diluting stock calcium solution (**6.1.4.8**) with water containing 1.5 ml of concentrated HNO_3/l. Stock standard solution can be taken from a number of commercial supplier. Alternatively, it can be prepared as described in **6.1.4.8**.

6.1.5 *Procedure*

6.1.5.1 *Sample preparation*

Samples containing particulate matter after acidification shall be filtered to prevent clogging of the nebulizer and burner systems. Mix 10 ml of lanthanum solution (**6.1.4.7**) into 100 ml of sample solution before aspiration.

6.1.5.2 *Instrument operation*

6.1.5.2.1 It is difficult to formulate instructions as applicable to every instrument, because of differences between makes and models of atomic absorptions spectrometers. See manufacturer’s operating manual.

6.1.5.2.2 Install a hollow-cathode lamp for calcium in the instrument and set the wavelength at 422.7 nm. Set the slit width as suggested by manufacturer for calcium being measured. Turn on the instrument and apply current to hollow cathode lamp for 10 min to 20 min to stabilize the energy source. After adjusting the wavelength, install burner head. Turn on the air (**6.1.4.2**) and adjust the flow rate as suggested by the manufacturer to give maximum sensitivity for calcium being measured. Turn on acetylene (**6.1.4.3**) and adjust flow rate. Ignite the flame and let it stabilize for a few min.

6.1.5.2.3 Aspirate a blank consisting of distilled water (**6.1.4.4**) containing 1.5 ml of concentrated nitric acid and 10 ml lanthanum solution. Set zero the instrument. Aspirate the calcium standard solution. Check the aspiration rate of nebulizer and adjust it to obtain maximum sensitivity. Obtain maximum response by adjusting burner position vertically and horizontally. Aspirate the blank and re-zero the instrument. Aspirate standard calcium solution near middle of linear range. Prepare a fresh same standard and with a new hollow cathode lamp, record the absorbance of this standard. Check consistency of instrument setup and aging of hollow-cathode lamp and standard referring to these data on subsequent determinations of calcium.

6.1.5.2.4 The instrument is now ready to operate. At the end of analysis, first switch off acetylene than air.

6.1.5.3 *Standardization*

Prepare at least three standard calcium solutions containing lower concentration 0.1 mg/l calcium to bracket the expected metal concentration of a sample. Prepare a reagent blank of 100 ml volume with distilled water (**6.1.4.4**) containing 1.5 ml of concentrated nitric acid (**6.1.4.6**) and 10 ml lanthanum solution (**6.1.4.7**). Aspirate the reagent blank and carry out zero adjustment. Aspirate blank and zero the instrument. Mix 10 ml of lanthanum solution (**6.1.4.7**) into the standard solutions before aspiration. Aspirate each standard solution in turn into the flame and record the absorbance readings. Most modern instruments are equipped with micro-processors and digital read-out which permit calibration in direct concentration terms.

6.1.5.4 *Analysis of sample*

Rinse nebulizer by aspirating distilled water (**6.1.4.4**) containing 1.5 ml concentrated nitric acid/l and zero instrument. Aspirate a sample and determine its absorbance.

6.1.6 *Calculation*

Prepare a calibration curve on linear graph paper by plotting absorbance of the standard reading versus their original concentration of standards before dilution with lanthanum solution. Alternatively, read the concentration directly from the instrument read-out if the instrument is so equipped. If sample has been diluted, multiply by the appropriate dilution factor.

6.2 Direct Nitrous Oxide-Acetylene Flame Method

6.2.1 *Principle*

The calcium content of the sample is determined by atomic absorption spectrophotometry. For dissolved calcium, the filtered sample is directly aspirated to the atomizer. For total recoverable calcium, a pre-treatment with HCl is carried out prior to aspiration of the sample. This method is applicable in the range from 0.2 mg/l to 20 mg/l of calcium. However, the concentration range will vary with the sensitivity of the instrument used.

6.2.2 *Apparatus*

6.2.2.1 Atomic absorption spectrophotometer and associated equipment.

6.2.2.2 *Nitrous oxide burner head*

At roughly 20 min interval of operation, it may be necessary to dislodge the carbon crust that forms along the slit surface with a carbon rod or appropriate alternative.

6.2.2.3 *T-junction valve or other switching valve*

For rapidly changing from nitrous oxide to air, so that flame can be turned on or off with air as oxidant to prevent flashbacks.

6.2.2.4 *Standard volumetric glassware*

6.2.3 *Reagents*

6.2.3.1 Unless otherwise specified, only AR grade chemicals should be used for all the tests.

6.2.3.2 *Air* — clean, dried and free from oil, water and other foreign substances. The source may be a compressor or commercially bottled gas.

6.2.3.3 *Acetylene*, standard commercial grade

CAUTION — Acetylene gas represents an explosive hazard in laboratory. Follow instrument manufacturer’s directions in plumbing and using this gas. Do not allow gas contact with copper, brass with greater than 65 percent copper, silver and liquid mercury. Do not use copper or brass tubing, regulators and fittings with greater than 65 percent copper.

6.2.3.4 *Calcium-free distilled water* — should be used for preparing standards and reagent solution.

6.2.3.5 *Hydrochloric acid* (HCl) — 1 + 1, and concentrated.

6.2.3.6 *Nitric acid* (HNO_3) — concentrated

6.2.3.7 *Nitrous oxide*, standard commercial grade

CAUTION — Follow the manufacturer's instructions while using nitrous oxide. Improper sequencing of gas flows during instrument starting and shutdown might result in flashback explosions.

6.2.3.8 *Stock calcium solution*

Dissolve 0.249 7 g calcium carbonate, $CaCO_3$ (dried at 180 °C for 1 h before weighing) in water and dissolve cautiously with a minimum amount of 1 + 1 HNO_3. Add 10.0 ml conc. HNO_3 and dilute 1 000 ml with water (1.00 ml = 100 µg of Ca).

6.2.3.9 *Standard calcium solution*

Prepare a series of standard calcium solution by diluting stock calcium solution (**6.2.3.8**) with water containing 1.5 ml of concentrated HNO_3/l. Stock standard solution can be taken from a number of commercial supplier. Alternatively, it can be prepared as described in **6.2.3.8**.

6.2.4 *Procedure*

6.2.4.1 *Sample preparation*

Samples containing particulate matter after acidification shall be filtered to prevent clogging of the nebulizer and burner systems.

6.2.4.2 *Instrument operation*

6.2.4.2.1 It is difficult to formulate instructions as applicable to every instrument, because of differences between makes and models of atomic absorptions spectrometers. See manufacturer’s operating manual.

6.2.4.2.2 After adjusting wavelength, install a nitrous oxide burner head (**6.2.3.7**). Turn on acetylene (without igniting flame) and adjust flow rate to the value specified by manufacturer for a nitrous oxide-acetylene flame. Turn off acetylene. With both air and nitrous oxide supplies turned on, set T-junction valve to nitrous oxide and adjust flow rate according to manufacturer’s specifications. Turn switching valve to the air position and verify the flow rate in the same. Turn acetylene on and ignite to a bright yellow flame. With a rapid motion, turn switching valve to nitrous oxide. The flame should have a red cone above the burner. If it does not, adjust fuel flow to obtain the red cone. After nitrous oxide flame has been ignited, let burner come to thermal equilibrium before beginning analysis. Aspirate a blank consisting of distilled water containing 1.5 ml concentrated nitric acid. Check aspiration rate and adjust if necessary to a rate between 3 and 5 ml/min. Zero the instrument. Aspirate a calcium standard solution with a concentration near the mid-point of the optimum concentration range and adjust burner (both horizontally and vertically) in the light path to obtain maximum response. Aspirate blank again and re-zero the instrument. The instrument is ready to run standards and samples. To extinguish flame, turn switching valve from nitrous to air and turn off acetylene. This procedure eliminates the danger of flashback that may occur on direct ignition or shutdown of nitrous oxide and acetylene.

6.2.4.3 *Standardization*

Prepare at least three standard calcium solutions containing lower concentration 0.1 mg/l calcium to bracket the expected metal concentration of a sample. Prepare a reagent blank of 100 ml volume with distilled water (**6.2.3.4**) containing 1.5 ml of concentrated nitric acid (**6.2.3.6**). Aspirate the reagent blank and carry out zero adjustment. Aspirate blank and zero the instrument. Aspirate each standard solution in turn into the flame and record the absorbance readings. Most modern instruments are equipped with micro-processors and digital read-out which permit calibration in direct concentration terms.

6.2.4.4 *Sample analysis*

Rinse atomizer by aspirating distilled water (**6.2.3.4**) containing 1.5 ml conc. nitric acid/l and zero instrument. Aspirate a sample and determine its absorbance.

6.2.4.5 *Calculation*

Calculate the concentration of calcium in microgram per litre by referring to the calibration curve prepared. Alternatively, read the concentration directly from the instrument read-out if the instrument is so equipped. If sample has been diluted, multiply by the appropriate dilution factor.

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 of immediately after formation. This eliminates the digestion period which is otherwise required. The solution must remain clear until boiling is commenced to hydrolyze 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) 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*

7.4.8.1 Weigh about 1.6 g of analytical reagent (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 min to 30 min 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.

7.4.8.2 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 min. Do not let the temperature fall below 85 ºC. If necessary, warm beaker contents during titration. Repeat the titration with two more aliquots of the oxalate solution.

7.4.8.3 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

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

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, in ml, of the sample taken for the test.

8 INDUCTIVELY COUPLED PLASMA SPECTROSCOPY

Calcium can also be determined by inductively coupled plasma optical emission spectroscopy with reference to procedure given in IS 3025 (Part 2). Likewise, inductively coupled plasma mass spectroscopy with reference to procedure given in IS 3025 (Part 65) can also be used for the determination of calcium in water and wastewater.

ANNEX A

(*Clause 2*)

LIST OF REFERRED STANDARDS

IS No.	*Title*
IS 1070 : 2023	Reagent grade water — Specification (*fourth revision*)
IS 3025	Methods of sampling and test (physical and chemical) for water and wastewater:
(Part 2) : 2019/ ISO 11885 : 2007	Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)
(Part 65) : 2022/ ISO 17294 (Part 2) : 2016	Application of inductively coupled plasma mass spectrometry (ICP-MS) — Determination of selected elements including uranium isotopes (*first revision*)
IS 7022 (Part 1) : 1973	Glossary of term relating to water, sewage and industrial effluents: Part 1
IS 7022 (Part 2) : 1979	Glossary of term relating to water, sewage and industrial effluents: Part 2
IS 17614	Water quality — Sampling
(Part 1) : 2021/ ISO 5667 (Part 1) : 2020	Guidance on the design of sampling programmes and sampling techniques
(Part 3) : 2021/ ISO 5667 (Part 3) : 2018	Preservation and handling of water samples

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ANNEX B

(*Foreword*)

COMMITTEE COMPOSITION

Water Quality Sectional Committee, CHD 36

Organization	*Representative(s)*
Chief Scientist, Environment Protection Training and Research Institute, Hyderabad	Dr N. Raveendhar (***Chairperson***)
Andhra Pradesh Pollution Control Board, Vijayawada	Shrimati M. Sreeranjan Shrimati A. Sri Samyuktha (*Alternate*)
Bhabha Atomic Research Centre, Mumbai	Shri S. Jayakumar Shri Manoj Mohapatra (*Alternate*)
Bharat Heavy Electricals Limited, Haridwar	Shri Shailendra Kumar Shri Sudhir Bhartiya (*Alternate* I) Shri Avinash Kumar (*Alternate* II)
Central Pollution Control Board, New Delhi	Shri P. K. Mishra Shri Vishal Gandhi (*Alternate*)
CII Triveni Water Institute, New Delhi	Shri Kapil K. Narula Dr Sipika Chauhan (*Alternate*)
CSIR - Central Institute for Mining and Fuel Research, Dhanbad	Dr Abhay Kumar Singh
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CSIR - Indian Institute of Toxicology Research, Lucknow	Dr Satyakam Patnaik
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