

INDIAN STANDARDS

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भारतीय मानक मसौदा

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

भाग 32 क्लोराइड

(दूसरा पुनरीक्षण)

Draft Indian Standard

**Methods of Sampling and Test (Physical and Chemical) For Water and Wastewater
Part 32 Chloride**

{*Second Revision of IS 3025 (Part 32)*}

ICS 13.060.50

Water Quality Sectional Committee, CHD 36

Last Date for Comments:

10.02.2025

FOREWORD

(Formal clause to be added later)

Chloride is one of the major inorganic anion in water and wastewater. In potable water, the salty taste produced by chloride concentrations is variable and dependent on the chemical composition. Chloride concentration is higher in wastewater than in raw water because sodium chloride (NaCl) is a common dietary component and passes unchanged through the digestive system.

The chloride alongside of sea coast, is found in high concentrations because of leakage of salt water into the sewerage system. And during industrial processes, high production of chloride A high chloride content may harm metallic pipes and structures as well as growing plants.

The Committee responsible for the formulation of IS 3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry' had decided to revise the standard and publish it as separate parts. This standard was one of the different parts published under IS 3025 series of standards and superseded **24** of IS 3025 : 1964 and **5** of IS 2488 (Part 3) : 1968 'Methods of sampling and test for industrial effluents'. The first revision of this standard was published in 1988.

In this second revision the following changes have been incorporated:

- The argentometric method, mercuric nitrate method, potentiometric method and automated ferricyanide method have been modified ;

- b) Dissolved anions by liquid chromatography of ions, liquid chromatographic separation using low-capacity anion exchanger, photometric detection have been added;
- 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 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*)'.

1 SCOPE

1.1 This standard (Part 32) prescribes the following methods for the determination of chloride in water and wastewater:

- a) Argentometric Method (applicable in the range of 0.15 mg to 10 mg of chloride);
- b) Mercuric nitrate method;
- c) Potentiometric method;
- d) Automated ferricyanide method; and
- e) Dissolved anions by liquid chromatography of ions (The lower limit of application is $\geq 0,1$ mg/l for chloride. The lower limit of application depends on the matrix and the interferences encountered.);
- f) Liquid chromatographic separation using low-capacity anion exchanger (working range 0.1 mg/l to 50 mg/l); and
- g) Photometric detection .

1.2 This standard prescribes four methods for the determination of chloride. The argentometric method is suitable for use in relatively clear waters when 0.15 to 10 mg of chloride is present in the portion titrated. The end point of mercuric nitrate method is easier to detect. Potentiometric method is suitable for coloured or turbid samples. The ferricyanide method is an automated technique. In case of any difference of opinion, the argentometric method shall be the referee method.

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 publication, 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 editions of the standards.

3 TERMINOLOGY

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

4 SAMPLING AND STORAGE

The sampling shall be done as prescribed in IS 17614 (Part 1) and IS 17614 (Part 3).

NOTE — The maximum required sample portion is 100 ml.

5 PURITY OF THE REAGENTS

5.1 Unless specified otherwise, only pure chemicals and iron free distilled water shall be used in tests.

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

6 ARGENTOMETRIC METHOD

6.1 Principle

In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated before red silver chromate is formed.



6.2 Interference

Bromide, iodide and cyanide register as equivalent chloride concentrations. Sulphite, thiosulphate and sulphide ions interfere but can be removed by treatment with hydrogen peroxide. Orthophosphates in excess of 25 mg/l interferes by precipitating as silver phosphate. Iron in excess of 10 mg/l interferes by masking the end point.

6.3 Apparatus

6.3.1 Erlenmeyer flask, 250 ml

6.3.2 Burette, 50 ml

6.3.3 Beaker, 500 ml

6.4 Reagents

6.4.1 Potassium Chromate Indicator Solution

Dissolve 50 g of potassium chromate in a little distilled water in 500 ml beaker. Add silver nitrate solution until a definite red precipitate is formed. Let it stand for 12 h, filter and dilute to 1 litre with distilled water.

6.4.2 Standard Silver Nitrate Titrant

Prepare a standard solution of silver nitrate of 0.014 1 N. Dissolve 2.395 g of silver nitrate in distilled water and dilute to 1 litre. Standardize against 0.014 1 N sodium chloride solution as prescribed in 6.5.3. Store in a brown bottle (1.00 ml = 500 µg of chloride).

6.4.3 Standard Sodium Chloride Solution

Prepare a standard solution of sodium chloride of 0.014 1 N. Dissolve 824.0 mg of sodium chloride (dried at 140 °C) in distilled water and dilute to 1 litre (1.00 ml = 500 µg of chloride).

6.4.4 Special Reagents for Removal of Interferences

6.4.4.1 Aluminium hydroxide suspension

Dissolve 1.25 g of aluminium potassium sulphate or aluminium ammonium sulphate [$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ or $\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] in 1 litre of distilled water. with stirring. Warm the solution upto 60 °C and add 55 ml of concentrated ammonium hydroxide (29 % of NH_4OH) slowly with stirring. Let it stand for 1 h, transfer to a large bottle and wash precipitate by successive additions, with thorough mixing and decanting with distilled water, until free from chloride. When freshly prepared, the suspension occupies a volume of about 1 litre.

6.4.4.2 Phenolphthalein indicator solution

6.4.4.3 Sodium hydroxide

Prepare a solution of sodium hydroxide of 1 N.

6.4.4.4 Sulphuric acid

Prepare a solution of sulphuric acid of 1 N.

6.4.4.5 Hydrogen peroxide, 30 %

6.5 Procedure

6.5.1 Wash the apparatus and prepare it for experiment. Pipette 100 ml of the sample or an appropriate portion diluted to 100 ml into a 250 ml Erlenmeyer flask. If the sample is highly coloured, add 3 ml of aluminium hydroxide suspension, stir, allow it to settle and filter the sample. Proceed to titration.

6.5.2 Alternatively, if sulphide, sulphite or thiosulphate is present in the sample. To remove the interference in the sample, boil the sample to a volume of approximately 70 ml and add 3 ml of hydrogen peroxide and stir for

1 min. Continue the boiling until the sample volume reduces to 50 ml, and cool the sample to room temperature. Proceed to titration.

6.5.3 Titration

Directly titrate the samples in the pH range 8 to 10. Adjust sample pH to 8 to 10 by adding sulphuric acid or sodium hydroxide if it is not in the range, using a pH electrode with a nonchloride-containing reference electrode. Add 1.0 ml of potassium chromate indicator solution. Titrate sample with standard silver nitrate solution to a clear pinkish yellow end point is observed. Standardize silver nitrate solution and establish reagent blank value by titration method.

6.6 Calculation

$$\text{Chloride (Cl}^{-}\text{), mg/l} = \frac{(V_1 - V_2) \times N \times 35.450}{V_3}$$

where,

V_1 = Volume of the silver nitrate used by the sample, in ml;

V_2 = Volume of the silver nitrate used in the blank titration, in ml;

V_3 = Volume of the sample taken for titration, in ml; and

N = Normality of the silver nitrate solution.

7 MERCURIC NITRATE METHOD

7.1 Principle

Chloride can be titrated with mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$) because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3 to 2.8, diphenyl carbazone indicates the end point by the formation of a purple complex with excess mercuric ions.

7.2 Interference

Bromide and iodide are titrated in the same manner as chloride. Chromate, ferric and sulphite ions interfere, when present in excess of 10 mg/l.

NOTE — Prepare a small portion sample of chloride (below 10 mg/l) to avoid the interference in the sample.

7.3 Apparatus

7.3.1 *Erlenmeyer Flask*, 250 ml capacity

7.3.2 *Microburette*, 5 ml with 0.01 ml graduation intervals

7.4 Reagents

7.4.1 *Standard Sodium Chloride Solution* — (see 6.4.3)

7.4.2 *Nitric Acid*

Prepare a solution of nitric acid of 0.1 N

7.4.3 *Sodium Hydroxide*

Prepare a solution of sodium hydroxide of 0.1 N

7.4.4 *Reagents for Chloride Concentrations below 100 mg/l*

7.4.4.1 *Indicator-acidifier reagent*

The nitric acid concentration of this reagent is an important factor in the success of the determination and can be varied as indicated in 7.4.4.1.1 or 7.4.4.1.2 to suit the alkalinity range of the sample. Reagent (a) contains sufficient nitric acid to neutralize a total alkalinity of 150 mg as CaCO_3/l to the proper pH in a 100 ml sample. Adjust amount of nitric acid to accommodate samples of alkalinity different from 150 mg/l.

7.4.4.1.1 Dissolve, in the order named, 250 mg s-diphenylcarbazone, 4.0 ml. concentration nitric acid and 30 mg xylene cyanol FF in 100 ml 95 percent ethyl alcohol or isopropyl alcohol. Store in a dark bottle in a refrigerator. This reagent is not stable indefinitely. Deterioration causes a slow end point and high results.

7.4.4.1.2 Because pH control is critical, adjust pH of highly alkaline or acid samples to 2.5 ± 0.1 with 0.1 N nitric acid or sodium hydroxide not with sodium carbonate (Na_2CO_3). Use a pH meter with a non-chloride type of reference electrode for pH adjustment. If only the usual chloride-type reference electrode is available for pH adjustment, determine amount of acid or alkali required to obtain a pH of 2.5 ± 0.1 and discard this sample portion. Treat a separate sample portion with the determined amount of acid or alkali and continue analysis. Under these circumstances, omit nitric acid, from indicator reagent.

7.4.4.2 *Standard mercuric nitrate titrant*

0.0141 N. Dissolve 2.3 g mercuric nitrate [$\text{Hg}(\text{NO}_3)_2$ or 2.5 g $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$] in 100 ml distilled water containing 0.25 ml concentrated nitric acid. Dilute to just under 1 litre. Make a preliminary standardization by following the procedure described in 7.5.1. Use replicates containing 5.00 ml standard sodium chloride solution and 10 mg sodium bicarbonate (NaHCO_3) diluted to 100 ml with distilled water. Adjust titrant to 0.0141 N and make a final standardization. Store away from light in a dark bottle (1.00 ml = 500 µg of Chloride).

7.4.5 *Reagent for Chloride Concentration greater than 100 mg/l*

7.4.5.1 *Mixed indicator reagent*

Dissolve 0.50 g diphenylcarbazone powder and 0.05 g bromophenol blue powder in 75 ml 95 percent ethyl or isopropyl alcohol and dilute to 100 ml with the same alcohol.

7.4.5.2 *Strong standard mercuric nitrate titrant*

0.141 N. Dissolve 25 g mercuric nitrate [$\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$] in 900 ml distilled water containing 5.0 ml concentrated nitric acid. Dilute to just under 1 litre and standardize by following the procedure described in 7.5.2. Use replicates containing 25.00. ml standard sodium chloride solution and 25 ml distilled water. Adjust titrant to 0.141 N and make a final standardization (1.00 ml = 5.00 mg of Chloride).

7.5 Procedure

7.5.1 *Titration of Chloride Concentration less than 100 mg/l*

Prepare a sample of 100 ml or less than. Add 1.0 ml of the indicator-acidifier reagent to the sample. At this point, a green-blue colour has been observed. For highly alkaline or acidic waters, adjust the pH to 8.0 before adding the indicator-acidifier reagent. Titrate the sample with 0.0141 N mercuric nitrate solution until the endpoint is reached, indicated by a colour change from green-blue to purple. The solution should transition from green-blue to blue before adding a few drops of the endpoint indicator, at which point the endpoint should be recorded. For the blank, prepare a 100 ml sample of distilled water and titrate it with 10 mg of sodium bicarbonate to determine the blank value.

7.5.2 *Titration of Chloride Concentrations greater than 100 mg/l*

Take a sample portion that requires less than 5 ml of titrant to reach the endpoint. Transfer the sample into a 150 ml beaker. Add approximately 0.5 ml of the mixed indicator reagent and stir the mixture thoroughly. The colour should be purple. Then, add 0.1 N nitric acid dropwise until the colour just changes to yellow. Next, titrate the sample with 0.141 N mercuric nitrate solution until the first permanent dark purple colour appears. For the blank, titrate a distilled water sample using the same procedure.

7.6 Calculation

$$\text{Chloride (as } \text{Cl}^- \text{), mg/l} = \frac{(V_1 - V_2 \times N \times 35.450)}{V}$$

where,

V_1 = Volume of titrant used for sample, in ml;

V_2 = Volume of titrant used for blank, in ml;

N = Normality of mercuric nitrate solution, in ml; and

V = Volume of the sample taken for test, in ml.

8 POTENTIOMETRIC METHOD

8.1 Principle

Chloride is determined by potentiometric titration with silver nitrate solution with a glass and silver-silver chloride electrode system. The end point of the titration is that instrument reading at which the greatest change in voltage has occurred for a small and constant increment of silver nitrate.

8.2 Interference

Iodide and bromide also are titrated as chloride. Ferricyanide causes high results and should be removed. Chromate and dichromate interfere.

8.3 Apparatus

8.3.1 Glass and Silver-Silver Chloride Electrodes

8.3.2 Electronic Voltmeter

8.3.3 Mechanical Stirrer

8.4 Reagents

8.4.1 Standard Sodium Chloride Solution, 0.014 1 N

8.4.2 Nitric Acid, concentrated

8.4.3 Standard Silver Nitrate Titrant, 0.014 1 N.

8.4.4 Pre-Treatment Reagents

8.4.4.1 Sulphuric acid, 1 : 1.

8.4.4.2 Hydrogen peroxide, 30 percent.

8.4.4.3 Sodium hydroxide, 1 N.

8.5 Procedure

8.5.1 Standardization

Place 10.0 ml of standard sodium chloride solution in a 260 ml beaker; dilute to about 100 ml and add 2.0 ml concentrated nitric acid. Immerse stirrer and electrodes. Set instrument to desired range of millivolts or pH units. Start stirrer. Add standard silver nitrate titrant, recording scale reading after each addition. At the start large increments of silver nitrate may be added, then as the end point is approached, add small and equal increments at longer intervals so that the exact end point can be determined. Determine the volume of silver nitrate used at the point at which there is the greatest change in instrument reading per unit addition of silver nitrate. Plot a differential titration curve if the exact end point cannot be determined by inspecting the data. Plot change in instrument reading for equal increments of silver nitrate against volume of silver nitrate added, using average of burette readings before and after each addition.

8.5.2 Sample Analysis

8.5.2.1 Pipette 100 ml of sample or a portion containing not more than 10 mg of chloride, into a 250 ml beaker. In the absence of interfering substances, proceed as above.

8.5.2.2 In the presence of organic compounds, sulphite or other interferences, acidify sample with sulphuric acid using litmus paper. Boil for 5 min to remove volatile compounds. Add more sulphuric acid, if necessary, to keep solution acidic. Add 3 ml of hydrogen peroxide and boil for 15 min, adding chloride free distilled water to keep the volume above 50 ml. Dilute to 100 ml, add sodium hydroxide solution dropwise until alkaline to litmus, then 10 drops in excess. Boil for 5 min, filter into a 250 ml beaker, and wash precipitate and paper several times with hot water. Add concentrated nitric acid dropwise until acidic to litmus paper, then 2.0 ml in excess. Cool and dilute to 100 ml, if necessary. Immerse stirrer and electrodes and start stirrer. Make necessary adjustments according to manufacturer's instructions and set selection switch to appropriate setting for measuring the difference of potential between electrodes. Complete determination as detailed in **8.5.1**. If an end point reading

has been established from previous determinations for similar samples and conditions, use this predetermined end point. For the most accurate work, make a blank titration by carrying chloride free distilled water through the procedure.

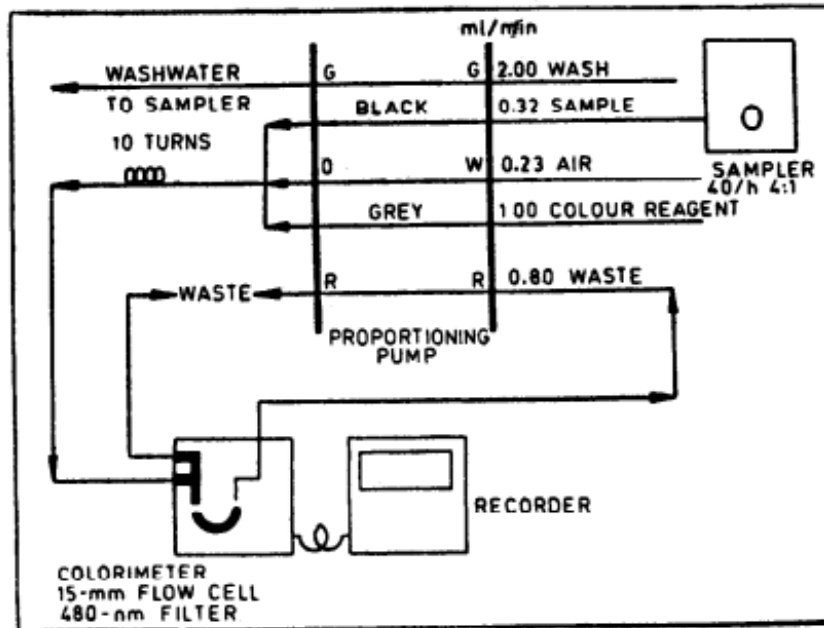


FIG. 1 FLOW SCHEME FOR AUTOMATED CHLORIDE ANALYSIS

8.6 Calculation

$$\text{Chloride (as } Cl^-), \text{ mg/l} = \frac{(V_1 - V_2 \times N \times 35.450)}{V}$$

where,

V_1 = Volume of silver nitrate titrant used in sample, in ml;

V_2 = Volume of silver nitrate used in blank, in ml;

N = Normality of titrant; and

V = Volume of the sample used in limit, in ml.

9 AUTOMATED FERRICYANIDE METHOD

9.1 Principle

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms a highly coloured ferric thiocyanate, of which the intensity is proportional to the chloride concentration.

9.2 Interference

None of significance. Use a continuous filter on turbid sample.

9.3 Apparatus

9.3.1 Automated Analytical Equipment

The required continuous flow analytical instrument consists of the interchangeable components as shown in Fig. 1

9.3.2 Filters, 480 nm.

9.4 Reagents

9.4.1 Stock Mercuric Thiocyanate Solution

Dissolve 4.17 g of mercuric thiocyanate in about 500 ml of methanol, dilute to 1 000 ml with methanol, mix and filter through filter paper.

9.4.2 Stock Ferric Nitrate Solution

Dissolve 202 g of ferric nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ in about 500 ml of distilled water, then carefully add 21 ml of concentrated nitric acid. Dilute to 1 000 ml with distilled water and mix. Filter through paper and store in coloured bottle.

9.4.3 Colour Reagent

Add 150 ml stock mercuric thiocyanate solution to 150 ml of stock ferric nitrate solution. Mix and dilute to 1 000 ml with distilled water. Add 0.5 ml of polyoxyethylene 23 lauryl ether.

9.4.4 Stock Chloride Solution

Dissolve 1.648 2 g sodium chloride, dried at 140 °C in distilled water and dilute to 1 000 ml (1.00 ml = 1.00 mg of chloride).

9.4.5 Standard Chloride Solutions

Prepare chloride standards in the desired concentration range, such as 1 mg/l to 200 mg/l, using stock chloride solution.

9.6 Procedure

Set up manifold as shown in Fig. 1 and follow general procedure prescribed by the manufacture.

9.7 Calculation

Prepare standard curves by plotting peak heights of standards processed through the manifold against chloride concentrations in standards. Compute sample chloride concentration by comparing sample peak height with standard curve.

10 OTHERS METHODS FOR DETERMINATION OF CHLORIDE

Chloride can also be determined by photometric detection with reference to procedure as given in IS 3025 (Part 75). Likewise, determination of chloride in water with low contamination with reference to procedure given in IS 3025 (Part 81) and determination of dissolved anions by liquid chromatography of ions with reference to procedure given in IS 3025 (Part 82) can also be used for the determination chloride in water and wastewater.

(Clause 2)

LISTS OF REFERRED STANDARDS

<i>IS No.</i>	<i>Title</i>
IS 3025	Methods of sampling and test physical and chemical for water and wastewater
(Part 75) : 2022/ISO 10304-1 : 2007	Determination of dissolved anions by liquid chromatography of ions — Determination of bromide, chloride, fluoride, nitrate, nitrite phosphate and sulfate
(Part 81) : 2024/ISO 10304-4 : 2002	Determination of chlorate chloride and chlorite in water with low contamination
(Part 82) : 2024/ISO 15923-1 : 2013	Ammonium nitrate nitrite chloride orthophosphate sulfate and silicate with photometric detection
IS 7022	Water related — Glossary of terms
(Part 1) : 2024	Water, sewage and industrial effluents (<i>first revision</i>)
(Part 2) : 2024	Water supply and sewerage (<i>first revision</i>)
IS 17614	Water quality — Sampling:
(Part 1) : 2025/ISO 5667-1 : 2023	Guidance on the design of sampling programmes and sampling techniques (<i>first revision</i>)
(Part 3) : 2021/ISO 5667-3 : 2024	Preservation and handling of water samples (<i>first revision</i>)