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IS 3025 (Part 32) (1988, Reaffirmed 2007): Method of Sampling and Test (Physical and Chemical) for Water and Wastewater, Part 32: Chloride (First Revision). ICS 13.060.50

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(Reaffirmed 2007)

Indian Standard

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

PART 32 CHLORIDE

(First Revision)

1. Scope — 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. Argentometric Method

2.1 *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.

2.2 *Interference* — Bromide, iodide and cyanide register 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 interfere. Iron in excess of 10 mg/l interferes by masking the end point.

2.3 *Apparatus*

2.3.1 *Erlenmeyer flask* — 250 ml.

2.3.2 *Burette* — 50 ml.

2.4 *Reagents*

2.4.1 *Potassium chromate indicator solution* — Dissolve 50 g of potassium chromate in a little distilled water. 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.

2.4.2 *Standard silver nitrate titrant* — 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 **2.5.1**. 1·00 ml = 500 µg of chloride. Store in a brown bottle.

2.4.3 *Standard sodium chloride solution* — 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.

2.4.4 *Special reagents for removal of interferences*

2.4.4.1 *Aluminium hydroxide suspension* — Dissolve 1·25 g of aluminium potassium sulphate or aluminium ammonium sulphate [$AlK(SO_4)_2.12H_2O$ or $Al\,NH_4(SO_4)_2.12H_2O$] in 1 litre of distilled water. Warm to 60°C and add 55 ml of concentrated ammonium hydroxide 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.

2.4.4.2 *Phenolphthalein indicator solution*

2.4.4.3 *Sodium hydroxide* — 1 N.

2.4.4.4 *Sulphuric acid* — 1 N.

2.4.4.5 *Hydrogen peroxide* — 30 percent.

Water Sectional Committee, CDC 26; Panel for Methods of Test for Water, Wastewater and Effluents, CDC 26 : P1 [Ref : Doc : CDC 26 (9300)]

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2.5 *Procedure*

2.5.1 Use 100 ml sample or a suitable portion diluted to 100 ml. If the sample is highly coloured, add 3 ml of aluminium hydroxide suspension, mix, let settle and filter. If sulphide, sulphite or thiosulphate is present, add 1 ml of hydrogen peroxide and stir for 1 minute. Directly titrate the samples in the *p*H range 7 to 10. Adjust sample *p*H to 7-10 with sulphuric acid or sodium hydroxide if it is not in the range. Add 1·0 ml of potassium chromate indicator solution. Titrate with standard silver nitrate solution to a pinkish yellow end point. Standardize silver nitrate solution and establish reagent blank value by titration method.

2.6 *Calculation*

$$\text{Chloride, mg/l} = \frac{(V_1 - V_2) \times N \times 35\,450}{V_3}$$

where

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

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

V_3 = volume in ml of sample taken for titration, and

N = normality of silver nitrate solution.

3. Mercuric Nitrate Method

3.1 *Principle* — Chloride can be titrated with mercuric nitrate because of the formation of soluble, slightly dissociated mercuric chloride. In the *p*H range 2·3 to 2·8, diphenyl carbazone indicates the end point by the formation of a purple complex with excess mercuric ions.

3.2 *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.

3.3 *Apparatus*

3.3.1 *Erlenmeyer flask* — 250 ml capacity.

3.3.2 *Microburette* — 5 ml with 0·01 ml graduation intervals.

3.4 *Reagents*

3.4.1 *Standard sodium chloride solution* — *See* **2.4.3**.

3.4.2 *Nitric acid* — 0·1 N.

3.4.3 *Sodium hydroxide* — 0·1 N.

3.4.4 *Reagents for chloride concentrations below 100 mg/l*

3.4.4.1 *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 (a) or (b) 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 *p*H in a 100 ml sample. Adjust amount of nitric acid to accommodate samples of alkalinity different from 150 mg/l.

a) 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.

b) Because *p*H control is critical, adjust *p*H 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 *p*H meter with a nonchloride type of reference electrode for *p*H adjustment. If only the usual chloride-type reference electrode is available for *p*H adjustment, determine amount of acid or alkali required to obtain a *p*H 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.

3.4.4.2 *Standard mercuric nitrate titrant* — 0·014 1 N. Dissolve 2·3 g mercuric nitrate [$Hg(NO_3)_2$ or 2·5 g $Hg(NO_3)_2 \cdot H_2O$] 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 **3.5.1**. 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 0·014 1 N and make a final standardization; 1·00 ml = 500 µg Cl^-. Store away from light in a dark bottle.

3.4.5 Reagent for chloride concentration greater than 100 mg/l.

3.4.5.1 *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.

3.4.5.2 *Strong standard mercuric nitrate titrant* — 0·141 N. Dissolve 25 g mercuric nitrate [$Hg(NO_3)_2 \cdot H_2O$] 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 **3.5.2**. 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 Cl.

3.5 *Procedure*

3.5.1 *Titration of chloride concentration less than 100 mg/l* — Use a 100 ml sample or small portions so that the chloride content is less than 10 mg. Add 1·0 ml indicator-acidifier reagent. For highly alkaline or acid waters, adjust *p*H to about 8 before adding indicator-acidifier reagent. Titrate with 0·014 1 N mercuric nitrate to a definite purple end point. The solution turns from green blue to blue a few drops before the end point. Determine the blank by titrating 100 ml distilled water containing 10 mg of sodium bicarbonate.

3.5.2 *Titration of chloride concentrations greater than 100 mg/l* — Use a sample portion requiring less than 5 ml titrant to reach the end point. Measure into a 150 ml beaker. Add approximately 0·5 ml mixed indicator reagent and mix well. The colour should be purple. Add 0·1 N nitric acid dropwise until the colour just turns yellow. Titrate with 0·141 N mercuric nitrate to first permanent dark purple. Titrate a distilled water blank using the same procedure.

3.6 *Calculation*

$$\text{Chloride (as Cl), mg/l} = \frac{(V_1 - V_2) \times N \times 35\,450}{V}$$

where

V_1 = volume in ml of titrant used for sample,
V_2 = volume in ml of titrant used for blank,
N = normality of mercuric nitrate solution, and
V = volume in ml of the sample taken for test.

4. Potentiometric Method

4.1 *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.

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

4.3 *Apparatus*

4.3.1 *Glass and silver-silver chloride electrodes*

4.3.2 *Electronic voltmeter*

4.3.3 *Mechanical stirrer*

4.4 *Reagents*

4.4.1 *Standard sodium chloride solution* — 0·014 1 N.

4.4.2 *Nitric acid* — concentrated.

4.4.3 *Standard silver nitrate titrant* — 0·014 1 N.

4.4.4 *Pretreatment reagents*

4.4.4.1 *Sulphuric acid* — 1:1.

4.4.4.2 *Hydrogen peroxide* — 30 percent.

4.4.4.3 *Sodium hydroxide* — 1 N.

4.5 *Procedure*

4.5.1 *Standardization* — Place 10·0 ml of standard sodium chloride solution in a 250 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 *p*H 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.

4.5.2 *Sample analysis* — 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 interferring substances, proceed as above.

In the presence of organic compounds, sulphite or other interferences, acidify sample with sulphuric acid using litmus paper. Boil for 5 minutes to remove volatile compounds. Add more sulphuric acid, if necessary, to keep solution acidic. Add 3 ml of hydrogen peroxide and boil for 15 minutes, 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 minutes, 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 4.5.1. 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.

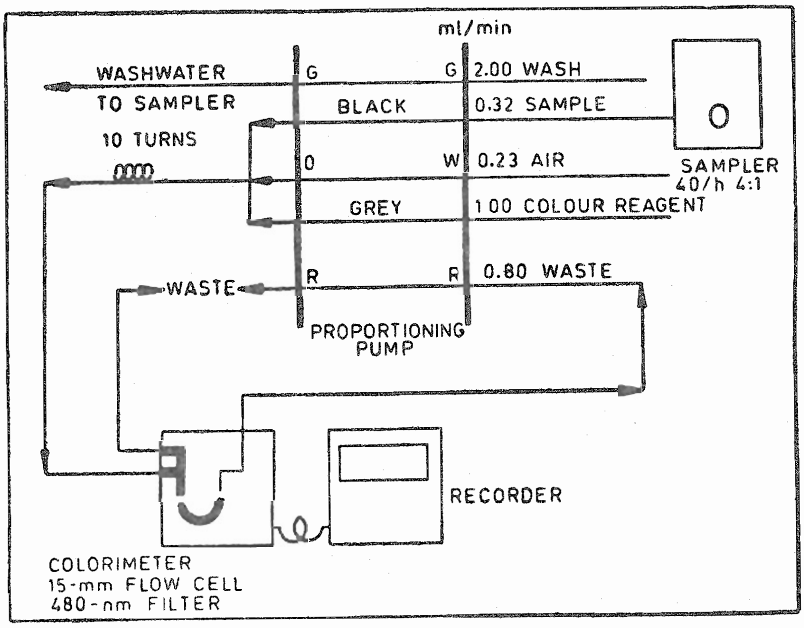

FIG. 1 FLOW SCHEME FOR AUTOMATED CHLORIDE ANALYSIS

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4.6 *Calculation*

$$\text{Chloride (as Cl), mg/l} = \frac{(V_1 - V_2) \times N \times 35\,450}{V}$$

where

V_1 = volume in ml of silver nitrate titrant used in sample;
V_2 = volume in ml of silver nitrate used in blank;
N = normality of titrant; and
V = volume in ml of the sample used in list.

5. Automated Ferricyanide Method

5.1 *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.

5.2 *Interference* — None of significance. Use a continuous filter on turbid sample.

5.3 *Apparatus*

5.3.1 *Automated analytical equipment* — The required continuous flow analytical instrument consists of the interchangeable components as shown in Fig. 1.

5.3.2 *Filters* — 480 nm.

5.4 *Reagents*

5.4.1 *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.

5.4.2 *Stock ferric nitrate solution* — Dissolve 202 g of ferric nitrate [$Fe(NO_3)_3, 9H_2O$] in about 500 ml of distilled water, then carefully add 21 ml of concentrated nitric acid. Dilute to 100 0 ml with distilled water and mix. Filter through paper and store in coloured bottle.

5.4.3 *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.

5.4.4 *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.

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

5.6 *Procedure* — Set up manifold as shown in Fig. 1 and follow general procedure prescribed by the manufacturer.

5.7 *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.

EXPLANATORY NOTE

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. A high chloride content may harm metallic pipes and structures as well as growing plants. This standard supersedes **24** of IS : 3025-1964 'Methods of sampling and test (physical and chemical) for water used in industry' and 5 of IS : 2488 (Part 3)-1968 'Methods of sampling and test for industrial effluents, Part 3'.