

*Indian Standard***METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL)
FOR WATER AND WASTEWATER****PART 26 CHLORINE, RESIDUAL***(First Revision)*

1. Scope — Prescribes the iodometric or stabilized neutral ortho-toluidine method for determination of residual chlorine.

1.1 Iodometric method is more precise than colorimetric method where residual concentration exceeds 1 mg/l, but for lower concentration it is not so accurate.

1.2 Stabilized neutral ortho-toluidine is useful to determine free available chlorine and combined chlorine. This method is sensitive to low residual chlorine concentrations, in the range of 5 to 10 µg/l.

2. Sampling and Storage — Chlorine is not stable in aqueous solution. Exposure to sunlight or other light or agitation will accelerate the reduction of chlorine. Therefore, it is recommended that chlorine determinations be started immediately after sampling and exposure to light and agitation are to be avoided. The sample can not be stored. Sampling and storage shall be done as prescribed in IS : 3025 (Part 1)-1986 'Methods of sampling and test (physical and chemical) for water and wastewater : Part 1 Sampling (*first revision*)'.

3. Iodometric Method

3.1 Interferences — Oxidized forms of manganese and other oxidizing agents interfere. Reducing agents, such as organic sulphides also interfere. Although the neutral titration minimizes the interfering effect of ferric and nitric ions, the acid titration is preferred because some forms of combined chlorine do not react at pH 7. Use only acetic acid for titration; sulphuric acid will increase interferences ; never use hydrochloric acid.

3.2 Reagents

3.2.1 Unless otherwise stated, the reagents should be of analytical reagent grade.

3.2.2 Acetic acid, glacial — See IS : 695-1975 'Specification for acetic acid (*second revision*)'.

3.2.3 Potassium iodide — Crystals.

3.2.4 Standard sodium thiosulphate — 0.01 N.

3.2.5 Standard potassium dichromate — 0.1 N.

3.2.6 Starch indicator solution — See IS : 2263-1979 'Methods of preparation of indicator solutions for volumetric analysis (*first revision*)'.

3.3 Procedure

3.3.1 Select a sample volume which will require no more than 20 ml of 0.01 N sodium thiosulphate. Thus for residual chlorine concentration of 1 mg/l or less, take 1 000 ml of sample; for range of 1 to 10 mg/l, a 500 ml of sample and above 10 mg/l proportionately less sample.

3.3.2 Take appropriate volume of the sample as given in 3.3.1 and add acetic acid to bring down the pH to 3 to 4 in the flask. Add about 1.0 g of potassium iodide crystals and mix with a glass rod.

Add chlorine-free distilled water if larger volume is preferred for titration. Titrate with 0.01 N sodium thiosulphate until yellow colour of the liberated iodine is almost discharged. Add 1.0 ml of starch indicator and titrate until the blue colour is discharged. In many cases residual chlorine is very low and starch needs to be added before starting up the titration.

3.4 Calculation

$$3.4.1 \text{ Residual chlorine, mg/l} = \frac{V_1 \times N \times 35450}{V_2}$$

where

V_1 = volume of standard sodium thiosulphate used,

V_2 = volume of sample taken for test, and

N = normality of sodium thiosulphate used.

4. Stabilized Neutral Ortho-toluidine Method

4.1 Principle and Theory — The stability of oxidized ortho-toluidine decreases as pH increases. Anionic surface active reagents stabilize the colour development by free chlorine and ortho-toluidine at pH 7.0. Sodium di (2-ethyl-hexyl) sulphosuccinate, is the best stabilizing agent. The optimum concentration of stabilizer is 40 mg for each 100 ml of sample plus reagents. The final solution should have pH between 6.5 and 7.5.

4.2 Interferences — Strong oxidizing agents, such as bromine, chlorine dioxide, iodine, manganic compounds and ozone interfere. However, the reduced forms of these compounds do not interfere. Reducing agents like nitrites, ferrous compounds, hydrogen sulphide and oxidizable organic matter do not interfere, but may interfere by reducing the chlorine residual by reaction with chlorine to produce chlorine ion. Turbidity and colour also interfere unless the background turbidity or colour is compensated for using a blank.

4.3 Apparatus

4.3.1 Spectrophotometer — Suitable for use at 625 nm providing a light path of 1 cm or longer for ≤ 1 mg/l free residual chlorine, or a light path from 1 to 10 mm for free residual chlorine > 1.5 mg/l.

4.3.2 Magnetic stirrer assembly

4.4 Reagents

4.4.1 Distilled water — Chlorine demand free. Add sufficient chlorine to distilled water to destroy the ammonia and nitrate. The amount of chlorine required will be about 10 times the amount of ammoniacal nitrogen present; produce an initial residual of more than 1.0 mg/l free chlorine. Let the chlorinated distilled water stand overnight or longer; then expose to direct sunlight until all residual chlorine is discharged.

4.4.2 Neutral ortho-toluidine reagent — Add 5.0 ml of concentrated hydrochloric acid to 500 ml chlorine demand free distilled water. Add 10 ml of this acid solution, 20 mg mercuric chloride (Hg Cl_2), 30 mg of disodium salt of EDTA (dehydrated) and 1.5 g of ortho-toluidine dihydrochloride to chlorine demand free distilled water and dilute to 1 litre. Store in a brown bottle or in the dark at room temperature. Protect at all times from direct sunlight. Use for not more than 6 months and avoid contact with rubber. Do not let the temperature fall below 0°C because the resulting crystallization of ortho-toluidine can lead to deficient subsequent colour development.

4.4.3 Buffer stabilizer reagent — Dissolve 34.4 g dipotassium hydrogen phosphate (K_2HPO_4), 12.6 g potassium dihydrogen phosphate (KH_2PO_4) and 8.0 g 100 percent solid di (2-ethyl hexyl) sulphosuccinate in a solution of 500 ml chlorine demand free water and 200 ml diethylene glycol monobutyl ether. Dilute to 1 litre with chlorine demand free water.

4.4.4 Potassium iodide solution — Dissolve 0.4 g potassium iodide in chlorine demand free distilled water and dilute to 100 ml, store in a brown glass stoppered bottle, preferably in a refrigerator. Discard when yellow colour is developed.

4.4.5 Sulphuric acid solution — Add cautiously 4.00 ml of concentrated sulphuric acid to chlorine demand free water and dilute to 100 ml.

4.4.6 Sodium carbonate solution — Dissolve 5.0 g of sodium carbonate in chlorine demand free distilled water and dilute to 100 ml.

4.4.7 Sodium arsenite solution — Dissolve 5.0 g of sodium arsenite in distilled water and dilute to 1 litre.

4.4.8 Standard chlorine solution — Obtain suitable solution from the chlorinator gas solution hose or by bubbling chlorine gas through distilled water. Improve the solution stability by storing in the dark or brown, glass-stoppered bottle. Standardize it each day of use. Alternatively, dilute household hypochlorite solution, which contains about 30 000 to 50 000 mg/l chlorine equivalent. This is more stable than chlorine solution, but do not use for more than 1 week without restandardization. Use the same chlorine concentration actually applied in plant treatment to determine chlorine demand. Depending on intended use, a suitable strength of chlorine solution usually will be between 100 and 1 000 mg/l. Use a solution of sufficient concentration so that adding the chlorine solution will not increase the volume of treated portion by more than 5 percent. Standardize the solution using 0.025 N thiosulphate solution. 1 ml of 0.025 N thiosulphate titrant is equivalent to 0.9 mg chlorine.

4.5 Procedure

4.5.1 Construct a calibration curve by making dilutions of standardized hypochlorite solution. Take care when diluting to low concentrations because of possible consumption of small amounts of chlorine by trace impurities. Use chlorine demand free distilled water for dilution.

4.5.1.1 Use 5.0 ml neutral ortho-toluidine and 5.0 ml buffer stabilizer reagent with 100 ml sample. Place the neutral ortho-toluidine and buffer stabilizer mixture in a beaker on a magnetic stirrer. Mix and add sample to the reagents with gentle stirring. Measure the absorbance at 625 nm. The value obtained (*A*) from the calibration curve represents the free chlorine residual.

4.5.1.2 Monochloramine — Return any position used for measuring free chlorine in 4.5.1.1 to the sample. Add with stirring 0.5 ml potassium iodide solution to each 100 ml sample or similar ratio for other sample volumes. Again measure the absorbance and obtain value (*B*) from calibration curve. This will give free residual chlorine plus monochloramine.

4.5.1.3 Dichloramine — Return any portion used for measuring the monochloramine in 4.5.1.2 to the sample. Add with stirring, 1 ml of sulphuric acid to each 100 ml of sample, or a similar ratio for other sample volumes. After 30 seconds for colour development add 1 ml of sodium carbonate solution, slowly with stirring or until a pure blue solution returns. Measure the absorbance of total residual chlorine, free chlorine, monochloramine and dichloramine and obtain the value (*C*) from the calibration curve.

4.5.2 Compensation for interferences — Compensate for the presence of natural colour or turbidity as well as manganic compounds by adding 5.0 ml arsenite solution to 100 ml of sample. Add this blank sample to the reagents as above. Use the colour of the blank to set zero absorbance on the spectrophotometer. Measure all samples in relation to this blank. Read from the calibration curve the concentrations of chlorine present in the sample.

4.6 Calculation

Free residual chlorine, mg/l = *A*, including $\frac{1}{2}$ trichloramine, if present (see 4.5.1.1).

Monochloramine, mg/l = (*B* - *A*) as mg/l of chlorine (see 4.5.1.2).

Dichloramine, mg/l = 1.03 *C* - *B* as mg/l of chlorine (see 4.5.1.2 and 4.5.1.3).

Total chlorine, mg/l = 1.03 *C* as mg/l chlorine (see 4.5.1.3).

EXPLANATORY NOTE

Chlorination of water and wastewater serves primarily to destroy or deactivate disease-producing micro-organisms. The other benefit is the overall improvement in water quality. Chlorination may produce adverse effects. Taste and odour characteristics of phenols and other organic compounds present in water may be intensified. Potentially carcinogenic chloro-organic compounds, such as chloroform may be formed. Combined chlorine formed on chlorination of ammonia or amine bearing waters adversely affects some aquatic life. To fulfil the primary purpose of chlorination and to minimize any adverse effects, it is essential that proper test methods be used with a fore knowledge of limitations of analytical determination. This method supersedes 45 of IS : 3025-1934 'Methods of sampling and test (physical and chemical) for water used in industry'.