

Indian Standard

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

PART 38 DISSOLVED OXYGEN

(First Revision)

भारतीय मानक

**पानी और मल जल — नमूने लेने और परीक्षण (भौतिक तथा रासायनिक)
की पद्धतियां**

भाग 38 घुली आक्सीजन

(पहला पुनरीक्षण)

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Price Group 2

FOREWORD

This Indian Standard was adopted by the Bureau of Indian Standards on 30 November 1989, after the draft finalized by the Water Sectional Committee had been approved by the Chemical Division Council.

The dissolved oxygen level in natural and wastewater depends on the physical, chemical and biochemical activities in water. Analysis for dissolved oxygen is an important step in water pollution control and wastewater treatment process control.

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.

This standard supersedes clause 11 of IS 2488 (Part 1) : 1974 'Methods of sampling and test for industrial effluents, Part 1', and clause 50 of IS-3025 : 1964 'Methods of sampling and test (physical and chemical) for water used in industry'.

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 38 DISSOLVED OXYGEN

(First Revision)

1 SCOPE

1.1 This standard prescribes titrimetric and electrometric methods for determination of dissolved oxygen.

2 REFERENCES

2.1 The following Indian Standards are necessary adjuncts to this standard:

IS No.	Title
IS 3025 (Part 1) : 1986	Methods of sampling and test (physical and chemical) for water and wastewater: Part 1 Sampling (<i>first revision</i>)
IS 7022 (Part 1) : 1973	Glossary of terms relating to water, sewage and industrial effluents, Part 1
IS 7022 (Part 2) : 1979	Glossary of terms relating to water, sewage and industrial effluents, Part 2

3 TERMINOLOGY

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

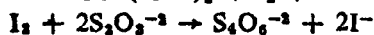
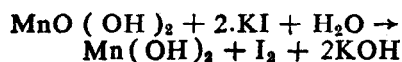
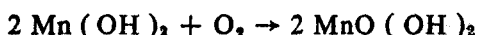
4 TITRIMETRIC METHOD

4.1 Winkler Method

4.1.1 Principle

Divalent manganese salt in solution is precipitated by strong alkali to divalent manganese hydroxide. It is rapidly oxidized by dissolved oxygen present in the sample to form trivalent or higher valency hydroxide. Iodide ions are added and acidified, which reduce tetravalent hydroxides back to their stable divalent state thereby liberating equivalent amount of iodine. This iodine is equivalent to dissolved oxygen present in the sample.

The sequence of reactions is as follows:



4.1.2 Interference

Oxidizing agents give positive interference and reducing agents give negative interference.

4.1.3 Sampling and Sample Preservation

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

NOTE — Analysis shall be carried out preferably at the time of collection. If immediate analysis is not possible dissolved oxygen shall be fixed.

4.1.4 Reagents

4.1.4.1 Manganous sulphate solution

Dissolve manganese sulphate (480 g of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ or 400 g of $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ or 364 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$) in freshly boiled and cooled water, filter and make up to 1 000 ml. The solution should not give blue colour by addition of acidified potassium iodide solution and starch.

4.1.4.2 Alkaline iodide solution

Dissolve 500 g of sodium hydroxide (or 700 g of potassium hydroxide) and 135 g of sodium iodide (or 150 g of potassium iodide) in freshly boiled and cooled water and dilute to 1 litre.

4.1.4.3 Sulphuric acid, concentrated.

4.1.4.4 Starch indicator

Dissolve 2 g of starch and 0.2 g of salicylic acid as preservative, in 100 ml of hot distilled water.

4.1.4.5 Sodium thiosulphate stock solution

Dissolve approximately 25 g of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in boiled distilled water and make up to 1 000 ml. Add 1 g of sodium hydroxide to preserve it.

4.1.4.6 Standard sodium thiosulphate solution

Dissolve 250 ml of stock solution (4.1.4.5) in boiled distilled water and make up to 1 litre and standardize sodium thiosulphate against known standard before use.

4.1.5 Procedure

To the sample collected in 300 ml bottle, add 2 ml of manganese sulphate solution followed by 2 ml of alkaline iodide solution. Use separate pipettes of 2 ml capacity for each reagent and take care that tip of the pipette in each case is

dipped well below the liquid surfaces carefully. Replace the stopper without the inclusion of any air bubble and thoroughly mix the content by shaking the bottle several times; allow the precipitate formed to settle. After 2-3 minutes of settling, carefully remove the stopper and immediately add 2 ml of concentrated sulphuric acid by running the acid down the neck of the bottle and mix thoroughly to dissolve the liberated iodine. Take 200 ml of the solution and titrate immediately against standard sodium thiosulphate solution, adding 3-4 drops of starch indicator solution. The end point is pale blue to colourless.

4.1.6 Calculation

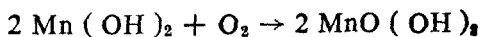
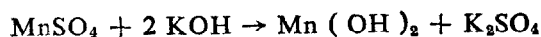
The dissolved oxygen in mg per litre is equal to the volume in ml of 0.025 N thiosulphate solution used for titration.

4.2 Azide Modification

Azide modification effectively removes interference caused by nitrate which is the most common interference in biologically treated effluents and incubated BOD samples.

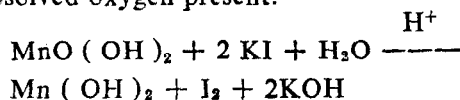
4.2.1 Principle

This method is a modification of the Winkler method for the determination of dissolved oxygen, and the principle is the same. The method depends on the formation of a precipitate of manganous hydroxide. The oxygen dissolved in the water is rapidly absorbed by manganous hydroxide, forming a higher oxide, which may be in the following form:



$\text{Mn}(\text{OH})_2$ flocc acts as a 'gathering' agent for oxygen.

Upon acidification in the presence of iodide, iodine is released in a quantity equivalent to the dissolved oxygen present.



The liberated iodine is then titrated with standard sodium thiosulphate solution using starch indicator



4.2.2 Reagents

4.2.2.1 Manganous sulphate solution

(see 4.1.4.1).

4.2.2.2 Alkaline iodide sodium azide solution

Dissolve 10 g of sodium azide (NaN_3) in 40 ml of distilled water and add this with constant stirring to the cool alkaline iodide solution prepared as in 4.1.4.2.

4.2.2.3 Potassium fluoride solution

Dissolve 40 g of potassium fluoride ($\text{KF} \cdot 2\text{H}_2\text{O}$) in 100 ml of distilled water.

4.2.2.4 Sulphuric acid, concentrated.

4.2.3 Procedure

To the sample collected in 300 ml bottle, add 2 ml of manganous sulphate solution followed by 2 ml of alkaline iodide sodium azide solution. Replace the stopper without inclusion of any air bubble and mix the contents thoroughly by shaking the bottle several times; allow the precipitate formed to settle. After 2-3 minutes of settling, carefully remove the stopper and immediately add 2 ml of concentrated sulphuric acid by running the acid down the neck of the bottle; restopper and mix thoroughly to dissolve the liberated iodine. Take 200 ml of the solution and titrate immediately against standard sodium thiosulphate solution adding 3-4 drops of starch indicator solution. The end point is the pale blue to colourless.

4.2.4 Calculation

The dissolved oxygen in mg/litre is equal to the volume in ml of the standard thiosulphate solution used for titration.

4.3 Alum Flocculation Modification

This method is suitable for effluent samples containing suspended solids.

4.3.1 Reagents

All reagents listed under 4.2.2 are required besides the following:

a) *Ammonium hydroxide* — Concentrated, and

b) *Alum solution* — Dissolve 10 g of aluminium potassium sulphate [$\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$] in distilled water and dilute to 100 ml.

4.3.2 Procedure

Collect the sample in a glass stoppered bottle of 500 ml capacity. Add 10 ml of alum solution followed by 2 ml of ammonium hydroxide, mix the contents gently by inverting the bottle and allowing to settle for 15 minutes. Collect the supernatant liquid into 300 ml dissolved oxygen bottle. Avoid aeration and keep the siphon sufficiently submerged during transfer. Follow the remaining steps as given in 4.2.3.

4.3.3 Calculation

The dissolved oxygen in mg/litre is equal to the volume in ml of the standard thiosulphate solution used for titration.

4.4 Permanganate Modification

This method is useful for samples containing iron (Fe^{2+}) ions. Interference due to Fe^{3+} ions

can be suppressed by addition of 1 ml of potassium fluoride and azide solution and the titration is done immediately after acidification. This method is not useful when sulphites, thiosulphates and high BOD in wastewater are present.

4.4.1 Reagents

All the reagents listed under 4.2.2 are required besides the following:

- a) *Potassium permanganate solution* — Dissolve 6.3 g of potassium permanganate in distilled water and dilute to 1 litre; and
- b) *Potassium oxalate solution* — Dissolve 2 g of potassium oxalate ($K_2C_2O_4 \cdot H_2O$) in 100 ml distilled water, 1 ml will be equivalent to 1.1 ml of permanganate solution.

4.4.2 Procedure

Collect the sample in 300 ml bottle, add 0.7 ml of concentrated sulphuric acid, 1 ml of potassium permanganate solution and 1 ml of potassium fluoride solution. Stopper the bottle and mix by inverting. The sulphuric acid addition should not be in excess. Add sufficient quantity of potassium permanganate solution to get a violet tinge that persists for 5 minutes. If the violet tinge disappears before 5 minutes, add more permanganate solution but avoid large excess. Remove the permanganate colour completely by adding 0.5 to 1.0 ml of potassium oxalate solution. Avoid excess amount of potassium oxalate so that it does not interfere in the results. Follow the procedure for azide modification method (4.2.2) using 3 ml of alkaline iodide solution instead of 2 ml.

4.4.3 Calculation

The dissolved oxygen in mg/litre is equal to the volume in ml of the standard thiosulphate solution used for titration.

5 MEMBRANE ELECTRODE METHOD

5.1 Principle

This method is based on the principle that a diffusion current is established when a solid electrode system, sensitive to oxygen concentration

is immersed in water sample. The current is linearly proportional to the concentration of molecular oxygen in the test sample. The system is composed of solid metal electrodes electrically connected by a suitable electrolyte and separated from the water sample by the membrane which is permeable to molecular oxygen but impermeable to impurities. The diffusion current is amplified and converted into a suitable concentration scale. The scale is calibrated at a given temperature using saturated solution of oxygen in water. The method is well established with accuracy of ± 0.05 mg/l and the range of 0.15 mg/l. The method has the disadvantages like temperature dependency, effect of salt concentration in the sample and changes in electrode sensitivity due to corrosion, fouling of membrane or changes in the thickness of membrane. The plastic films used with membrane electrode systems are permeable to certain gases like hydrogen sulphide, chlorine, etc. Prolonged use of membrane electrodes in water containing such gases tends to lower the cell sensitivity.

5.2 Apparatus

Dissolved oxygen sensitive membrane electrode with appropriate amplifier meter.

5.3 Procedure

5.3.1 Calibration

Follow the manufacturer's instructions exactly to get specified accuracy and precision. Generally, calibrate membrane electrodes by reading against distilled water sample of known dissolved oxygen concentration as well as with a sample with zero dissolved oxygen (add excess of sodium sulphite and a trace of cobalt chloride to a sample of distilled water to bring dissolved oxygen to zero concentration).

5.3.2 Sample Measurement

Follow the manufacturer's instructions to get good results. While changing membrane, take care to avoid any contamination of electrodes and trapping of minute air bubbles under the membrane. Provide sufficient stirring of sample or flow of sample across the membrane, till constant reading is obtained.

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