

BUREAU OF INDIAN STANDARDS

DRAFT FOR COMMENTS ONLY

(Not to be reproduced without permission of BIS or used as an Indian Standard)

Draft Indian Standard

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

Part 38 Dissolved Oxygen

(Second Revision)

भारतीय मानक मसौदा

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

भाग 38 घुली ऑक्सीजन

(दूसरा पुनरीक्षण)

ICS 13.060.50

Water Quality Sectional Committee, CHD 36

Last date for Comments: 20.03.2025

FOREWORD

(Formal clause may be added later)

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.

The Technical 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 1): 1974 'Methods of sampling and test for industrial effluents, Part 1' decided to revise the standards and publish IS 3025 in separate parts. This method superseded clause **11** of IS 2488 (Part 1): 1974 'Methods of sampling and test for industrial effluents, and clause **50** of IS 3025: 1964 'Methods of sampling and test (physical and chemical) for water used in industry' and was one among the different parts published under IS 3025 series of standards. The first revision of this standard was published in 1989.

In this second revision the following modification have been made:

- a) The azide modification method has been updated; and
- b) References, and ICS No. have been updated; and
- c) 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 Standard Methods for the Examination of Water and Wastewater, published by the American Public Health Association, Washington, USA, 24th Edition, 2023.

In reporting the results of a test or analysis 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

This standard (Part 38) prescribes the following methods for determination of dissolved oxygen in water and wastewater:

- a) Titrimetric method; and
- b) Electrometric method.

2 REFERENCES

The standards listed below 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 indicated below:

<i>IS No.</i>	<i>Title</i>
---------------	--------------

IS 7022	Water Related-Glossary of Terms
(Part 1) : 2024	Part 1 Water, Sewage and Industrial Effluents (<i>first revision</i>)
(Part 2) : 2024	Part 2 Water Supply and Sewerage (<i>first revision</i>)
IS 17614	Water Quality Sampling
(Part 1) : 2021/ ISO 5667-1 : 2020	Part 1 Guidance on the design of sampling programmes and sampling techniques
(Part 3) : 2024/ 5667-3: 2024	Part 3 Preservation and Handling of Water Samples (<i>first revision</i>)

3 TERMINOLOGY

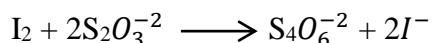
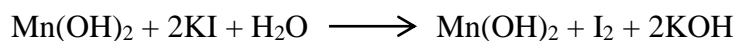
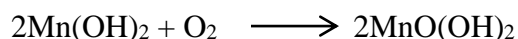
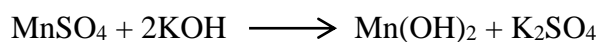
For the purpose of this standard, definitions given in IS 7022 (Part 1) and IS 7022 (Part 2) shall apply.

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 17614 (Part 1) and IS 17614 (Part 3).

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.

4.3.4.2 *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 min to 3 min 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 to 4 drops of starch indicator solution. The end point solution, adding 3-4 drops of starch indicator solution. The end point is pale blue to colorless.

4.1.6 *Calculation*

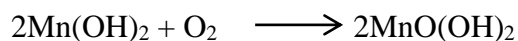
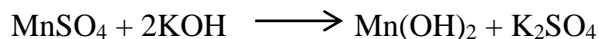
The dissolved oxygen mg/l is equal to the volume 1 ml of 0.025 N thiosulphate solution used for titration.

4.2 Azide Modification

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

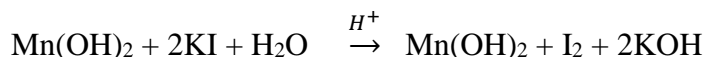
4.2.1 *Principle*

4.2.1.1 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:

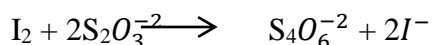


NOTE — Mn(OH)_2 floc acts as a ‘gathering agents’ for oxygen.

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



4.2.1.3 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 *Alkali—iodide-azide reagent:*

4.2.2.2.1 *For saturated and less than saturated sample*

In distilled water dissolve 500 mg of sodium hydroxide (or 700 mg of potassium hydroxide) and 135 g of sodium iodide (or 150 g of potassium iodide, KI) and make volume to 1 l. Dissolve 10 g of sodium azide (NaN_3) in 40 ml of distilled water and add this with constant stirring to the solution. The reagent should not give a color with starch when diluted and acidified.

4.2.2.2.2 *For supersaturated samples*

In distilled water dissolve 480 mg of sodium hydroxide and 750 g of sodium iodide and make volume to 1 l. Dissolve 10 g of sodium azide (NaN_3) in 40 ml of distilled water and add this with constant stirring to the solution.

CAUTION — Don’t acidify this solution because toxic hydrazoic acid fumes may be produced.

4.2.2.3 *Standard sodium thiosulphate titrant*

Dissolve 6.205g sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in distilled water. To this add 0.4 g of solid sodium hydroxide or 6M NaOH and make volume up to 1000 ml. Standardize with potassium bi-iodate [$\text{KH(IO}_3)_2$] solution.

4.2.2.4 *Sulphuric acid, concentrated.*

4.2.2.5 *Standard potassium bi-iodate solution (0.0021 M)*

Dissolve 812.4 mg of $\text{KH(IO}_3)_2$ is dissolved in distilled water and volume made up to 1 l with distilled water.

STANDARDIZATION — Dissolve approximately 2 g of KI, free from iodate, in an Erlenmeyer flask with 100 to 150 ml of distilled water. Add a few drops of concentrated sulfuric acid and 20 ml of sodium bi-iodate solution. Dilute the mixture to 200 ml, then titrate the liberated iodine with thiosulfate titrant. Add starch toward the end of the titration when a pale straw color is reached. Ensure that when solutions are of equal strength, 20.00 ml of 0.025 M $\text{Na}_2\text{S}_2\text{O}_3$ is required.

4.2.3 *Procedure*

Collect sample in 300 ml bottle, add 1 ml of manganous sulphate solution followed by 1 ml of alkaline iodide – sodium azide solution. Rinse the pipets dipped into sample bottles, before returning them to reagent bottles. Otherwise, hold pipet tips just above liquid surface when adding reagents. Replace the stopper of the BOD bottle carefully to exclude any air bubbles. Mix the bottle contents by inverting a few times. Allow precipitate to settle for 2 min to 3 min (to approximately half the bottle volume). When precipitate has settled enough, immediately add 1 ml of concentrated sulphuric acid by running the acid down the neck of the bottle. Re-stopper and mix by inverting the BOD bottle several times until the precipitate is completely dissolved. Titrate a volume corresponding to 200 ml original sample after correction for sample loss by displacement with reagents. Thus, for a total of 2 ml (1 ml each) of MnSO_4 and alkaline iodide – sodium azide reagents in a 300 ml bottle, titrate $200 \times 300 / (300 - 2) = 201$ ml. Titrate immediately with standard sodium thio-sulphate solution (~0.025 M) solution to a pale straw colour. Add a few drops of starch solution and continue titration to the first disappearance of blue colour. Note the titre value. If endpoint has overrun, back titrate with 0.002 M bi-iodate solution by adding it drop by drop.

4.2.4 Calculation

The dissolved oxygen 1 mg/l is equal to the volume 1 ml of 0.025 N thiosulphate solution used for titration.

4.3 Alum Flocculation Modification

This method is suitable for effluent samples containing suspended solids. Interferences caused may be removed by alum flocculation.

4.3.1 Reagents

All reagents as specified in 4.2.2 as well as following are required:

4.3.1.1 Ammonium hydroxide, Concentrated.

4.3.1.2 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, stopper and mix the contents gently by inverting the bottle and allowing to settle for 15 min. 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/l 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 as specified in 4.2.2 as well as the following:

4.4.1.1 Potassium permanganate solution

Dissolve 6.3 g of potassium permanganate in distilled water and dilute to 1 litre; and

4.4.1.2 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.

4.4.1.3 Potassium fluoride (KF) solution

Dissolve 40 g $KF \cdot 2H_2O$ in distilled water and dilute to 100 ml.

4.4.2 Procedure

Collect the sample in 300 ml bottle, add 0.7 ml of concentrated sulphuric acid (4.2.2.4) by placing the glass bottle below the surface. After collecting sample add 1 ml of potassium permanganate solution (4.4.1.1) and 1 ml of potassium fluoride solution (4.4.1.3). Stopper the bottle and allow mixing by inverting it. 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 min. If the violet tinge disappears before 5 min, add more permanganate solution but avoid large excess. Remove the permanganate colour completely by adding 0.5 ml 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

Oxygen-sensitive membrane electrode with appropriate amplifier meters.

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.