

Water Quality Parameters

Examination of Water: Dissolved Oxygen (DO)

- What ?
- Why ?
- How ?



Dr Vinod Tare
Department of Civil Engineering
IIT Kanpur

Water Quality Parameters - Dissolved Oxygen and BOD

Dissolved Oxygen (DO)

- Why is oxygen present in water and How does Oxygen gets into water?
- Solubility of Oxygen in Water (Hennery's Law) and Presence of Oxygen in the Atmosphere ($\approx 20.9\%$; Dalton's Law of Partial Pressure; Partial Pressure of Oxygen in Atmosphere ≈ 0.209).
- Hennery's Constant, and hence solubility is a function of temperature and presence of certain substances in water such as Dissolved Solids.
- What is responsible for depletion of or demand of oxygen in water?
- Is Oxygen produced in water, and if yes, what is responsible for that?
- How does Oxygen enter or leave water & How does it move or get transported in water and air, move from water to air and vice-a-versa \rightarrow Diffusion of Oxygen.

Water Quality Parameters - Dissolved Oxygen and BOD

Saturation DO Concentrations in Water

Temperature, °C	Max. Concentration, mg/L
0	14.6
4	13.1
8	11.9
12	10.8
16	10.0
20	9.2
24	8.5
28	7.9
30	7.6

Water Quality Parameters - Dissolved Oxygen and BOD

Dissolved Oxygen (DO) in Water and Its Significance

- Dissolved Oxygen (DO) concentration in surface waters is of great importance.
- Reduction of DO values to less than 4 mg/L results in difficulties and even death for aquatic animals, i.e., fish.
- The normal DO level of a healthy surface water body ranges from 8-10 mg/L, while the value for groundwater may be as low as 1-2 mg/L.
- Low DO values may indicate organic pollution and/or presence of reduced species in the water bodies, resulting in DO depletion of the water.

Water Quality Parameters - Dissolved Oxygen and BOD

WINKLER

Dissolved Oxygen Determination

With the **Alsterberg Azide** Modification

AZIDE Destroys NITRITE

Water Quality Parameters - Dissolved Oxygen and BOD

DO Determination - Winkler Method

Iodometric Method



Free IODINE released in relation to DO in Sample

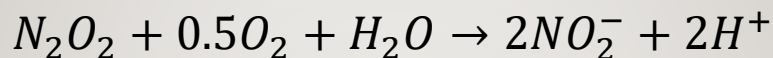
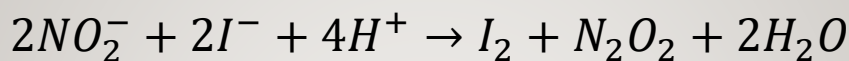
Water Quality Parameters - Dissolved Oxygen and BOD

The Azide Modification with the Winkler Method for DO Determination

- This modification is used to remove interference of nitrite ions.
- Nitrites occur in effluents from wastewater treatment plants employing biological processes, in river water and in incubated BOD samples.
- Nitrite does not oxidize Mn^{2+} but does oxidize I^- to I_2 under acidic conditions and gets reduced to N_2O_2 .
- When the reduced form of nitrite (N_2O_2) is oxidized by oxygen, it is converted to NO_2^- again, establishing the cycle again that can result in erroneous results, far in excess of amounts that would be expected.

Water Quality Parameters - Dissolved Oxygen and BOD

The Azide Modification

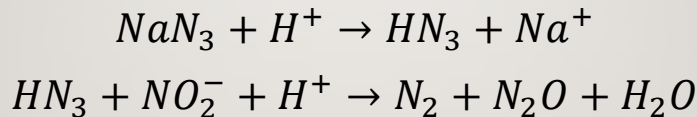


- When interference from nitrites is present, it is impossible to obtain a permanent end point.
- As soon as the blue color of the starch indicator has been discharged, the nitrites formed by the second reaction reacts with more iodide ions to produce I_2 and the blue color of the starch indicator will return.

Water Quality Parameters - Dissolved Oxygen and BOD

The Azide Modification

The nitrite interference is easily overcome with use of sodium azide (NaN_3), which is incorporated in the alkali-KI reagent. When sulfuric acid is added, following reactions happen:



Biochemical Oxygen Demand Analyses

DO Procedure: Winkler Procedure

$$\text{mg/L DO} = \frac{\text{mL of Titrant} \times \text{Normality of Titrant} \times 8 \times 1000}{\text{mL of Sample}}$$

$$\frac{0.0125 \text{ N} \times 8 \times 1000}{100} = 1$$

1 mL of Titrant = 1 mg/L DO

$$\frac{0.025 \text{ N} \times 8 \times 1000}{200} = 1$$

1 mL of Titrant = 1 mg/L DO

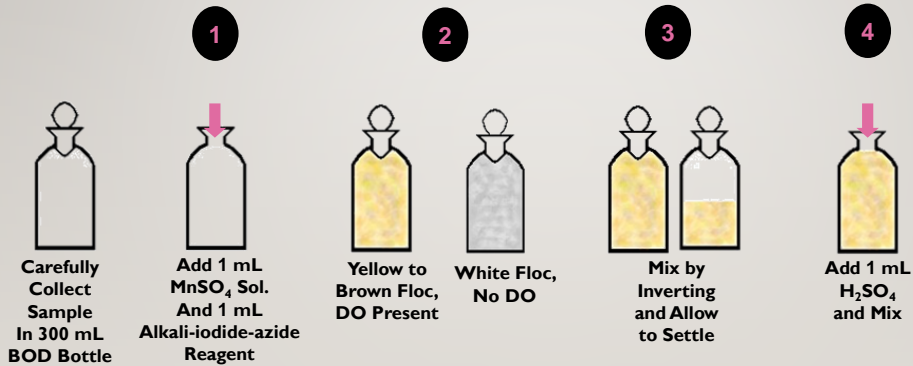
With Any of the Following Combinations of
Sample Volumes and Normalities

Sample Volume	Normality
100 mL	0.0125 N
200 mL	0.0250 N
300 mL	0.0375 N

Biochemical Oxygen Demand Analyses

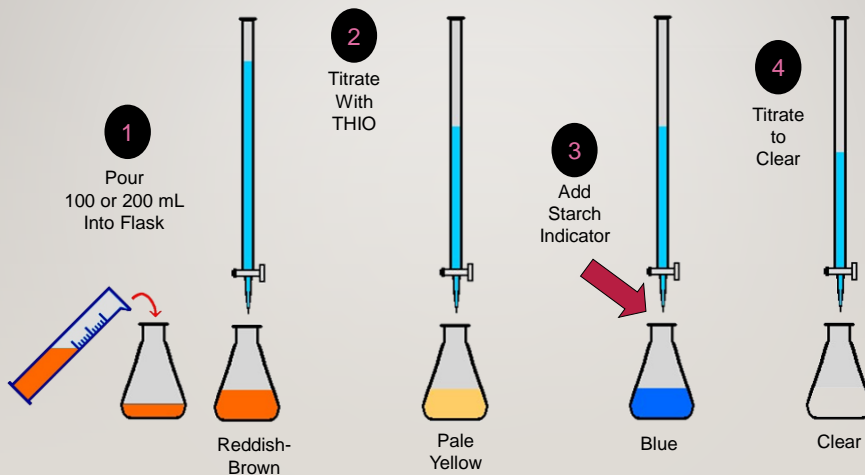
DO Procedure: Winkler Procedure

Outline Of Winkler Dissolved Oxygen Procedure



Biochemical Oxygen Demand Analyses

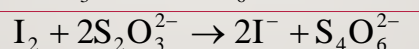
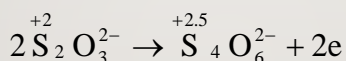
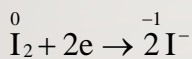
Titration of Iodine Solution



Water Quality Parameters - Dissolved Oxygen and BOD

I Titration of Iodine with $\text{Na}_2\text{S}_2\text{O}_3$

Iodine may be reduced to I^- when titrated with sodium thiosulfate. The relevant equations are as follows:



Starch is used as an indicator. Starch combines with iodine to give a dark blue colour. When thio-sulfate is added to this solution, it extracts iodine from the iodine-starch complex and reduces it to iodide. Once all iodine is thus extracted, the blue color of the solution is discharged, signifying the end-point of titration.

Water Quality Parameters - Dissolved Oxygen and BOD

Procedure:

- Prepare an iodine solution by adding 10 g of iodine to a 150 mL solution containing 10 g of potassium iodide. Let stand overnight. Decant 85 mL and dilute to 1000 mL. Label, "Standard Iodine Solution".
- To 25 g of soluble starch, add 500 mL of boiling distilled water. Stir and let settle overnight. Add 0.6 g of salicylic acid to the supernatant and store as, "Starch Indicator Solution".
- Prepare a 0.025 M $\text{Na}_2\text{S}_2\text{O}_3$ solution.
- Titrate 25 mL of the iodine solution with the thiosulfate solution until the yellow colour is almost discharged.
- Add 1 mL of starch indicator and titrate until the blue colour is discharged. Note the volume of titrant required.

Water Quality Parameters - Dissolved Oxygen and BOD

II Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ Solution

Potassium bi-iodate ($\text{KH}(\text{IO}_3)_2$) is first reduced to an equivalent amount of iodine by the addition of KI. This iodine is then quantified by titration with $\text{Na}_2\text{S}_2\text{O}_3$.

Procedure:

- Accurately prepare a 0.0021 M $\text{KH}(\text{IO}_3)_2$ solution. Label, “**Standard KH (IO_3)₂ Solution**”.
- To 80 mL of distilled water add 1 mL of concentrated H_2SO_4 , 10 mL of $\text{KH}(\text{IO}_3)_2$ and approximately 1 g of KI.

Water Quality Parameters - Dissolved Oxygen and BOD

- Titrate with 0.025 M $\text{Na}_2\text{S}_2\text{O}_3$ until the colour is almost discharged.
- Add 1 mL of starch indicator and titrate until the blue colour is discharged. Note the volume of titrant required.
- Based on the volume of titrant required, calculate the actual strength of the $\text{Na}_2\text{S}_2\text{O}_3$ solution.
- Using the above strength of the $\text{Na}_2\text{S}_2\text{O}_3$ solution, calculate the strength of the iodine solution.

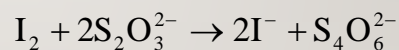
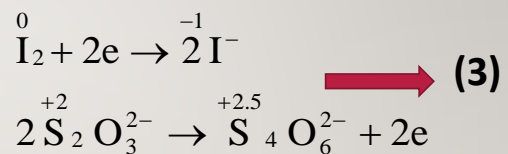
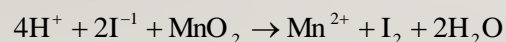
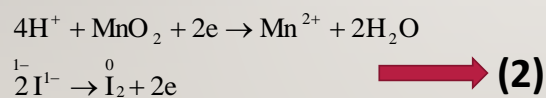
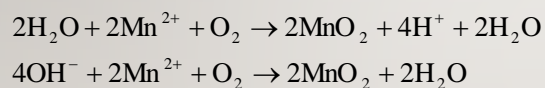
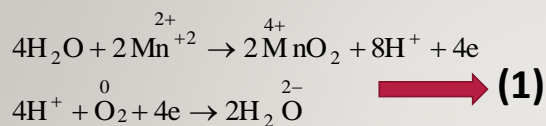
Water Quality Parameters - Dissolved Oxygen and BOD

Theory:

- Dissolved oxygen in the sample is converted to an equivalent amount of manganese dioxide (MnO_2) precipitate by addition of manganous sulphate.
- Precipitated manganese dioxide (MnO_2) is converted to an equivalent amount of iodine by addition of excess potassium iodide in acidic media.
- Iodine is quantified by titration with sodium thiosulfate in the presence of starch indicator.
- Based on iodine quantification, the dissolved oxygen concentration in the original sample may be calculated.

Water Quality Parameters - Dissolved Oxygen and BOD

Relevant Equations:



Water Quality Parameters - Dissolved Oxygen and BOD

Procedure for Dissolved Oxygen Determination

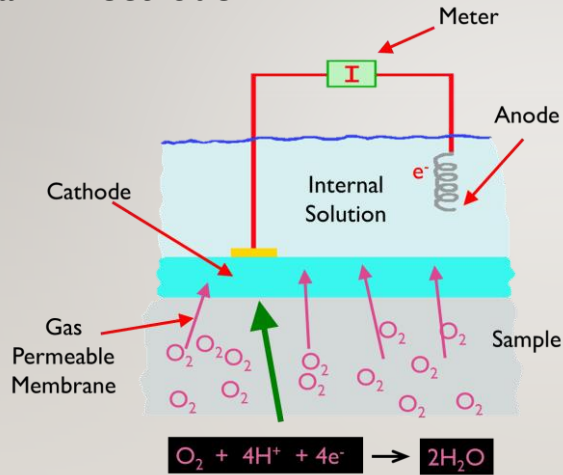
- Dissolve 48 g $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ or 40 g of $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ or 36.4 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in distilled water, filter and dilute to 100 mL. Label the bottle, "Manganous Sulfate Solution for DO Determination".
- Dissolve 50 g of NaOH and 15 g KI in distilled water, and dilute to 100 mL. Add 1 g of NaN_3 in 4 mL of distilled water. Mix together. Label the bottle, "Alkali-Azide-Iodide Reagent for DO Determination of Saturated or Less than Saturated Samples."

DO Meter



Dissolved Oxygen Probe: Membrane Electrode Method

Clark Electrode



The membrane electrode is composed of two solid metal electrodes in contact with supporting electrolyte separated from the test solution by a gas permeable membrane. Oxygen dissolved in the sample diffuses through the membrane on the DO probe and is chemically reduced (accepts electrons), producing an electrical current between the anode and cathode in the probe. The amount of current is proportional to the concentration of DO. Following proper calibration, the meter relates this current to the concentration of DO.



Calibration: Comparison with Winkler Method

Membrane Electrode Method

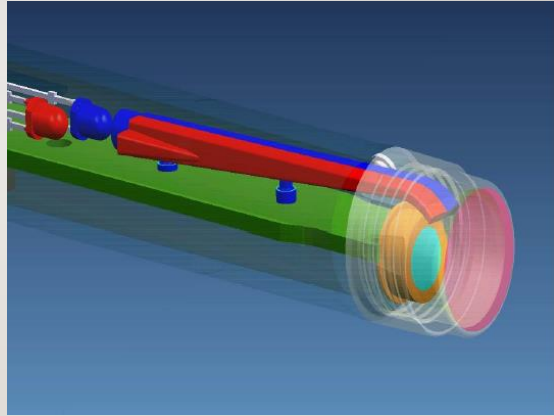
Calibration

Comparison with Winkler Titration

1. Fill two BOD bottles completely full of BOD dilution water, being very careful not to introduce air into either bottle.
2. Analyze one bottle for DO using the Winkler titration.
3. Insert the electrode into the second bottle, turn on the stirring mechanism, and wait for the reading to stabilize.
4. Calibrate the meter to the DO value obtained in the titration.
5. The meter is now ready for sample analysis

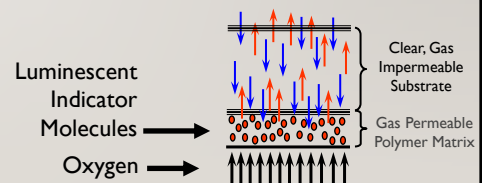
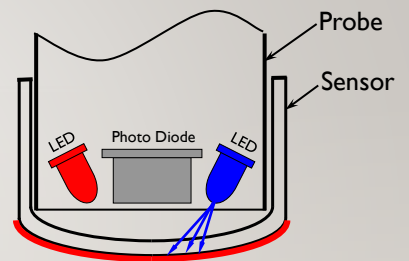


Luminescence DO Probe



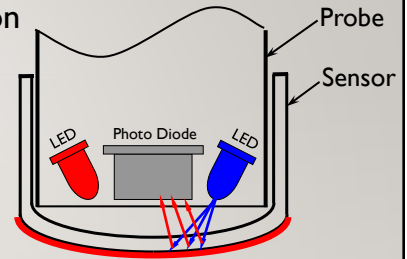
How Does LDO Work?

- A sensor is coated with a luminescent material.
- Blue light from an LED strikes the luminescent chemical on the sensor.
- The luminescent chemical instantly becomes excited.
- As the excited chemical relaxes, it releases red light.
- The red light is detected by a photo diode.
- The time it takes for the chemical to return to a relaxed state is measured
- When oxygen contacts the luminescent chemical, the intensity of the red light decreases
- The amount of time it takes for the material to relax is reduced



How Does LDO Work?

- The intensity of the red light is not what's being measured.
- What's being measured is the time it takes after excitation for red light to be given off.
- Lifetime of luminescence
- A red LED is also present in the probe.
- Between flashes of the blue LED, a red LED of known intensity, is flashed on the sensor.
- The red LED acts as an **internal standard** (or reference) for a comparison to the red light given off by the luminescent chemical



Advantages of Luminescence DO Probe

Reduced Maintenance

- **No membrane to replace**
 - No more stretching of Teflon and worrying about air bubbles
 - No more punctured membranes
- **No electrolyte to foul or poison**
 - No H₂S poisoning of the electrolyte
- **No anode or cathode**
 - No cleaning of anodes
 - No more coating of electrodes
- **Frequent Calibration Not Required**
 - No anode to consume and no electrolyte to deplete means extremely stable measurements
 - Internal standard with Red LED
 - No interference from pH swings, wastewater chemicals, H₂S, or heavy metals

- **Accurate and Stable Readings**
 - With nothing to interfere with the readings, LDO produces more stable measurements for a longer time
- **Speed!**
 - Turn it on and it's running!
 - Response time of less than 30 seconds to 90%
- **Simple Operation and Maintenance**
 - Only one replacement part
 - Inexpensive sensor cap is simple to replace quickly

Listed as ASTM Method D888-09 (C)
Footnote 63 – Hach Method 10360
(BOD and cBOD)
Footnote 64 In-Situ Method 1002-8-2009
(Dissolved Oxygen Measurement by Optical Probe)
Listed In Federal Register Vol. 77, No. 97
Friday, May 18, 2012

DO Meter

Advantages

Saves Time
Continuous Monitoring
Less Chemical Interference
Portable

Limitations

(Membrane Electrode)
Daily Calibration
Flow Past Membrane
Membrane May Foul
Requires Training