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Therefore oxygen demanding wastes are termed as water pollutants because they deplete water from its dissolved oxygen. Thus sufficient oxygen may be present or supplied to maintain aerobic conditions and hence prevent bad odour, taste and colour.

### CHEMICAL OXYGEN DEMAND

Although BOD test is applicable to organic wastes, there are many drawbacks. Certain organic materials are not biodegradable and hence can give wrong conclusions that less organic matter is present because BOD of such water samples will be low. In this case COD, Chemical Oxygen Demand reveals the real organic content present. Here the oxidation of organic substances present in water is done chemically.

*COD, is the amount of oxygen required by organic matter in a sample of water, by its oxidation by a strong chemical oxidizing agent such as  $K_2Cr_2O_7$*

Since in COD determination, the organic matter, both biologically oxidizable (glucose) and biologically inert (cellulose) is completely oxidized to  $CO_2$  and  $H_2O$ , COD values are greater than BOD values.

### EXPERIMENT NO. 2.6



Determination of dissolved oxygen in the given sample of water.

**APPARATUS** Burette, pipette, conical flask, beakers etc.

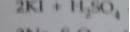
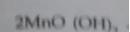
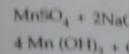
**CHEMICALS**  $Na_2S_2O_3$  (N/40),  $MnSO_4$  solution, KI, starch, conc.  $H_2SO_4$

**THEORY** Oxygen itself is not a pollutant in water but its deficiency is indicator of several types of pollution in water.

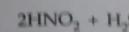
Dissolved oxygen (DO) is determined by Winkler's method or iodine titration.\* The dissolved oxygen in water oxidizes KI and an equivalent amount of iodine is liberated. This iodine is titrated against a standard hypo solution. However since dissolved oxygen in water is in molecular state and is incapable of reacting with KI, therefore an oxygen carrier such as manganese hydroxide is used.

\*Note: For details on iodometric titrations refer to chapter 1, page 64.

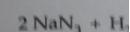
The method involves adding potassium iodide, aside reagent  $Mn(OH)_2$  which is formed, brown precipitate of basic MnO<sub>2</sub> is formed. This precipitate is dissolved in acidic medium and an equivalent amount of dissolved iodine is titrated against  $Na_2S_2O_3$  solution. The iodine ions involved are:



The nitrates present in water liberate  $I_2$  from KI



Thus to destroy nitrites



### PROCEDURE

1. A known amount of water is taken in a conical flask, stopper avoiding contact with the liquid.
2. Add 0.2 ml of  $MnSO_4$  solution well below the surface of the water and mix it.
3. Stopper the bottom of the flask with a cork containing a small quantity of  $MnO(OH)_2$  for about 10 minutes.
4. When some portion of the water is titrated with conc.  $H_2SO_4$  with  $Na_2S_2O_3$  solution, the iodine is completely dissolved.
5. Transfer 100 ml of the titrated water to a conical flask. Titrate the liberated iodine with  $Na_2S_2O_3$  solution until the sample becomes colourless.

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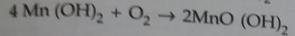
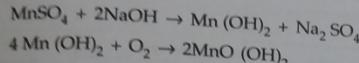
ren sample

c.  $\text{H}_2\text{SO}_4$

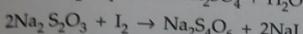
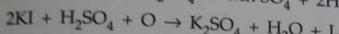
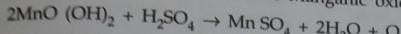
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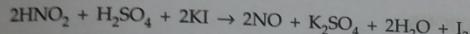
The method involves introducing a conc. solution of  $\text{Mn SO}_4$ ,  $\text{NaOH}$  and potassium iodide, azide reagent, into the water sample. The white precipitate of  $\text{Mn(OH)}_2$  which is formed, is oxidized by oxygen in water sample to give a brown precipitate of basic manganese oxide  $\text{MnO(OH)}_2$ . This  $\text{MnO(OH)}_2$ , in acidic medium dissolves and liberates free iodine from the added KI in an equivalent amount of dissolved oxygen in water sample. This liberated  $\text{I}_2$  is then titrated against  $\text{Na}_2\text{S}_2\text{O}_3$  solution using starch as indicator. The reactions involved are:



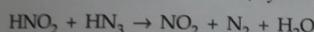
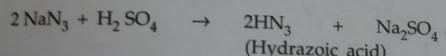
Basic Manganese oxide



The nitrites present in water, interfere with the titration as these can also liberate  $\text{I}_2$  from KI



Thus to destroy nitrite, sodium azide is used.



#### PROCEDURE

1. A known amount of sample water (say 250 ml) is taken in a stoppered bottle avoiding contact with air.
2. Add 0.2 ml of  $\text{MnSO}_4$  solution to it by means of a pipette, dipping the end well below the surface of water. Also add 2 ml of alkaline iodide-azide solution to it.
3. Stopper the bottle and shake thoroughly. Allow the brown precipitates of  $\text{MnO(OH)}_2$  formed, to settle down.
4. When some portion of the liquid below the stopper is clear, add 2 ml of conc.  $\text{H}_2\text{SO}_4$  with the help of pipette. Stopper and mix till the precipitate is completely dissolved. The characteristic brown colour of iodine is produced.
5. Transfer 100 ml of the above solution in a 250 ml flask with a pipette. Titrate the liberated  $\text{I}_2$  with standardized sodium thiosulphate solution until the sample solution becomes pale yellow.

6. Add 2 ml of starch solution, the solution will turn blue.
7. Continue titration till the blue colour disappears.
8. Repeat to get another reading.

**OBSERVATIONS**

Volume of the water sample taken for titration = 100 ml

**Observation Table:**

S. No.	Volume of the solution taken in the titration flask (ml)	Burette Readings		Volume of the titrant used (Final-Initial reading) (ml)
		Initial Reading	Final Reading	
1.				
2.				
3.				

**CALCULATIONS**

Hypo O<sub>2</sub> in water

$$N_1 V_1 = N_2 V_2$$

$$\frac{1}{100} \times V_1 = N_2 \times 100$$

$$N_2 = \frac{V_1}{10000}$$

Strength of dissolved oxygen =  $N_2 \times$  Eq. wt

$$= \frac{V_1}{10000} \times 8 \text{ g/L}$$

$$= \frac{V_1}{10000} \times 8 \times 1000 \text{ mg/L}$$

$$= 0.8 V_1 \text{ ppm.}$$

**RESULT** The amount of dissolved oxygen in water = ... ppm.

**PRECAUTIONS**

1. The water should be taken in the stoppered bottle very carefully so as not to trap air bubbles which could raise oxygen level by aerating the water.

**Note.** Sodium azide is poisonous. It may also explode if exposed to heat.

**Water Analysis**

2. MnSO<sub>4</sub> and alkaline sulphite just below the surface.
3. Whole of the precipitate.

**Instructions For the Lab Assistant**

1. MnSO<sub>4</sub> sulphate: Dissolve 10 g in 1 L of distilled water.
2. Alkaline potassium iodide: Dissolve 10 g in 1 L of distilled water, add 10% NaOH and make up the volume to 1 L.
3. N/40 Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution: Dissolve 10 g in 1 L of distilled water and make up this volume to 1 L.
4. Starch solution.

1. Which method is better and why?

**Ans.** Winkler's method is often less than 3% error and is used to measure dissolved oxygen in water samples. It is more accurate than the D.O. method because small differences in results are easily detected.

2. What is Dissolved Oxygen?

**Ans.** Oxygen gas that is dissolved in water. It is present in rivers, streams, lakes, oceans etc. If there is an absence of oxygen in water, it ranges from very low to high. If oxygen is low, there is harm to aquatic life.

3. Where does dissolved oxygen come from?

**Ans.** Most DO in water comes from tumbling water. Photosynthesis is the main source of oxygen in the afternoon because plants grow rapidly. Because of the diurnal cycle, DO levels are higher at night and lower during the day.

4. What are the factors affecting DO levels?

**Ans.** Many factors can affect DO levels. One of the causes is temperature. Warmer water holds less oxygen than cold water. Another factor is time of the year, time of the day, and season.

2.  $\text{MnSO}_4$  and alkaline iodine -azide solutions are added to the water sample just below the surface of water.
3. Whole of the precipitate of  $\text{MnO(OH)}_2$  should be dissolved in  $\text{H}_2\text{O}_2$ .

**Instructions For the Lab Assistant:**

1.  $\text{MnSO}_4$  sulphate: Dissolve 50 g of  $\text{MnSO}_4$  in distilled water and make up the volume to 1L.
2. Alkaline potassium iodide azide reagent: Dissolve 40 g of  $\text{NaOH}$ , 20 g of KI in distilled water, add 0.5 g of reagent grade sodium azide to the cooled solution and make up the volume to 100 ml.
3. N/40  $\text{Na}_2\text{S}_2\text{O}_3$  solution: Dissolve 6.20 g of  $\text{Na}_2\text{S}_2\text{O}_3$  solution in water and make up this volume to 1L. Standardize with N/40  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.
4. Starch solution.

**EXERCISE**

1. Which method is used to determine the amount of dissolved oxygen in water and why?

**Ans.** *Winkler's method.* Oxygen is present in small amounts in water, at concentrations often less than  $3 \times 10^{-4} \text{ M}$ . In contrast, air is roughly 21% oxygen. Any technique used to measure dissolved oxygen must exclude atmospheric oxygen from the analysis or the sample is highly contaminated. Also, the technique must be highly precise, so that small differences in oxygen content of natural samples can be detected. In most of its versions, the Winkler method meets these two requirements.

2. What is Dissolved Oxygen?

**Ans.** Oxygen gas that is dissolved into water is dissolved oxygen, or DO. DO is essential for rivers, streams, lakes, and aquatic life. It is a positive sign to have DO in water. If there is an absence of oxygen in water, it can be a sign of severe pollution. Water ranges from very high levels of DO to very low levels of DO. Sometimes the DO is so low, there is hardly any aquatic life.

3. Where does dissolved oxygen come from?

**Ans.** Most DO in water comes from the atmosphere or plants. The oxygen comes from tumbling water on fast moving rivers that mix atmospheric oxygen with water. Photosynthesis is another way of oxygen entering water. DO levels are often highest in the afternoon because of high levels sunlight that cause plants and algae to photosynthesize rapidly. Because photosynthesis doesn't occur at night, DO levels exhibit diurnal and nocturnal cycles.

4. What are the factors which contribute to the DO?

**Ans.** Many factors contribute to how high or low a DO level may be. Water temperature is one of the causes. Oxygen and other gases dissolve more easily in cooler water than in warmer water. Certain factors affect the water temperature. These factors are seasons of the year, time of day, and water depth. DO is highest just before dark because the