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 biodegredable 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 for 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

AIM **Determination of dissolved oxygen in the given sample of water.**

APPARATUS Burette, pipette, conical flask, beakers etc.

CHEMICALS $Na_2S_2O_3$ (N/40), Mn SO_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 iodometric 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 not capable of reacting with KI, therefore an oxygen carrier such as manganese hydroxide is used.

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

The method involves in
potassium iodide, azide reag
Mn $(OH)_2$ which is formed,
brown precipitate of basic
acidic medium dissolves and
lent amount of dissolved
titrated against $Na_2S_2O_3$ so
volved are:

$MnSO_4$ + 2NaO

4 Mn $(OH)_2$ +

2MnO $(OH)_2$

2KI + H_2SO_4

$2Na_2S_2O_3$ + I

The nitrites present i
liberate I_2 from KI

$2HNO_2$ + H_2

Thus to destroy nitri

2 NaN_3 + H_2

HNO_2 + HN

PROCEDURE

1. A known amount
   bottle avoiding co
2. Add 0.2 ml of Mn
   well below the su
   solution to it.
3. Stopper the bot
   of MnO $(OH)_2$ for
4. When some porti
   conc. H_2SO_4 with
   is completely diss
   duced.
5. Transfer 100 ml o
   Titrate the libera
   until the sample

The method involves introducing a conc. solution of $MnSO_4$, NaOH and potassium iodide, azide reagent, into the water sample. The white precipitate of $Mn(OH)_2$ which is formed, is oxidized by oxygen in water sample to give a brown precipitate of basic manganic oxide $MnO(OH)_2$. This $MnO(OH)_2$, in acidic medium dissolves and liberates free iodine from the added KI in a equivalent amount of dissolved oxygen in water sample. This liberated I_2 is then titrated against $Na_2S_2O_3$ solution using starch as indicator. The reactions involved are:

$$MnSO_4 + 2NaOH \rightarrow Mn(OH)_2 + Na_2SO_4$$

$$4\,Mn(OH)_2 + O_2 \rightarrow \underset{\text{Basic Manganic oxide}}{2MnO(OH)_2}$$

$$2MnO(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + O$$

$$2KI + H_2SO_4 + O \rightarrow K_2SO_4 + H_2O + I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

The nitrites present in water, interfere with the titration as these can also liberate I_2 from KI

$$2HNO_2 + H_2SO_4 + 2KI \rightarrow 2NO + K_2SO_4 + 2H_2O + I_2$$

Thus to destroy nitrite, sodium azide is used.

$$2\,NaN_3 + H_2SO_4 \rightarrow \underset{\text{(Hydrazoic acid)}}{2HN_3} + Na_2SO_4$$

$$HNO_2 + HN_3 \rightarrow NO_2 + N_2 + H_2O$$

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 $MnSO_4$ 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 $MnO(OH)_2$ formed, to settle down
4. When some portion of the liquid below the stopper is clear, add 2 ml of conc. H_2SO_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 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 $\quad O_2$ in water

$$N_1V_1 = N_2V_2$$

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

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

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

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

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

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

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

PRECAUTIONS

1. The water should be taken in the stoppered bottle very carefully w... trapping air bubbles which could raise oxygen level by aerating the...

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

2. $MnSO_4$ and alkaline ... just below the surfa...
3. Whole of the precip...

Instructions For the Lab A...

1. $MnSO_4$ sulphate: Di... volume to 1L.
2. Alkaline potassium ... distilled water, add ... and make up the v...
3. N/40 $Na_2S_2O_3$ solu... up this volume to ...
4. Starch solution.

1. Which method is ... and why?

Ans. *Winkler's method ... often less than 3 ... used to measure d... or the sample is hi... small differences i... versions, the Win...*

2. What is Dissolv...

Ans. *Oxygen gas that ... for rivers, stream... If there is an abs... ranges from very ... low, there is har...*

3. Where does dis...

Ans. *Most DO in w... tumbling water ... Photosynthesis is ... the afternoon bec... rapidly. Because ... nocturnal cycles...*

4. What are the ...

Ans. *Many factors c... one of the cause... warmer water. ... of the year, tim...*

2. $MnSO_4$ and alkaline iodine -azide solutions are added to the water sample just below the surface of water.
3. Whole of the precipitate of $MnO(OH)_2$ should be dissolved in H_2SO_4.

Instructions For the Lab Assistant:

1. $MnSO_4$ sulphate: Dissolve 50 g of $MnSO_4$ in distilled water and make up the volume to 1L.
2. Alkaline potassium iodide azide reagent: Dissolve 40 g of 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 $Na_2S_2O_3$ solution: Dissolve 6.20 g of $Na_2S_2O_3$ solution in water and make up this volume to 1L. Standardize with N/40 $K_2Cr_2O_7$ 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* 3×10^{-4} *M. In contrast, air is roughtly 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 cxygen 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 factrors 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 is 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*