DISSOLVED OXYGEN IN WATER (DO)

Since Oxygen is necessary for all living/non-living organisms, but dissolved oxygen in water is vital to fish and other aquatic life. Oxygen is transferred from atmosphere to surface water as well as produced by aquatic plants, algae and phytoplankton as a bye product of photosynthesis. After dissolving in water oxygen diffuses or distributed throughout the water body. Distribution depends on movement of water, currents and thermal upwelling. Oxygen in water measured as dissolved oxygen (DO). It is measured as parts per million (ppm), which is the number of oxygen (O_2) molecules per million total molecules in a sample.

It is also defined as the number of moles of molecular oxygen (O_2) dissolved in a litre of water at a temperature. It is expressed as mg O_2 / *l*. Dissolved oxygen can range from 0-18 mg O_2 / *l*. Most natural water systems require 5-6 mg O_2 / *l*. The oxygen is used by plants and animals for respiration and by the aerobic bacteria which consume oxygen during the process of decomposition. A high percentage of dissolved oxygen is conducive to aquatic flora & fauna. A low percentage indicates a negative impact on a body of water which results in a abundance of worms and fly larvae.

Factors Affecting Dissolved Oxygen

The following are the main factors which affects the dissolved oxygen (DO) in the water :

1. Water temperature.
2. Flow.
3. Aquatic plant population.
4. Atmospheric pressure.
5. Human Activities.
6. Water discharge.
7. Organic waste.
8. Runoff from streets.

Winkler's Method for DO Determination

The most precise and reliable titrimetric procedure for DO analysis is the Winkler's method (1888). It is the same as iodometric technique. It is based on the fact that dissolved oxygen oxidises Potassium Iodide (KI) to Iodine, which is titrated against standard sodium thiosulphate (Hypo) solution using starch as an Indicator. Since dissolved oxygen is in the molecular state, her.ce can not oxidise as such. For that Manganese hydroxide is used as an oxgen carrier to bring out the reaction. Manganese hydroxide is obtained by the action of KOH with Manganese sulphate.

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$$

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2$$

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

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

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

For oxidising and reducing agents present in water, two modification are given:

(i) Alsterberg's Modification : If oxidising agents like nitrate and ferric ions are present in water, they will oxiside I to I_2 and will give positive error. To over come with this problem sodium azide is used in alkaline solution to decompose them.

$$2NaN_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HN_3$$

$$HNO_3 + HN_3 \rightarrow N_2O + N_2 + H_2O$$

(ii) Rideat-Stewart Modification : If reducing agents like Fe^{+2}, SO_3^{-2}, S^{-2} etc. are present in sample. They will reduce I_2 to I^- and will produce negative error.

To overcome with this problem, $KMnO_4$ is used for pretreatment. Excess of $KMnO_4$ can be removed by reaction with Potassium oxalate.

CHEMICAL OXYGEN DEMAND (COD)

Chemical Oxygen Demand is a useful measure of water quality. It is defined as the amount of oxygen consumed under specified conditions in the oxidation of organic & oxidisable inorganic matter. COD expressed in milligrams per litre (*mg/l* or ppm).

COD of waste water is the number of *mg* of oxygen required to oxidise the impurities present in 1000 ml of waste water using strong oxidising agent like acidified $K_2Cr_2O_7$. COD represents the total amount of oxygen required to oxidise all oxidisable impurities in a given sample. Thus COD value for a sample is always higher than BOD value. Since time required for COD test is less, therefore it is always advantageous. In environmental chemistry COD test is indirect measure of organic compounds present in water.

Limitations of COD

COD test does not differentiate between bio-inert and biodegradable materials. It also not indicate the rate at which the biologically oxidisable material stabilize.

COD represents the total amount of oxygen required to oxidise all oxidisable impurities in a sample of sewage wastes COD is always greater than BOD since in COD measurement both biodegradable and non-biodegradable load are completely oxidised. The difference in COD and BOD is equivalent to the quantity of biologically resistant organic matter.

DETERMINATION OF COD

Principle

A known volume of the wastewater sample is refluxed with a known excess of $K_2Cr_2O_7$ solution in H_2SO_4 medium containing $HgSO_4$ (catalyst) and Ag_2SO_4 [which retains halides] for about $1\frac{1}{2}$ hr for the oxidation to be complete. A part of the $K_2Cr_2O_7$ is used up for the oxidation of impurities. The remaining $K_2Cr_2O_7$ is determined by titration with standard FAS (Ferrous Ammonium Sulphate) solution using ferroin as indicator. The endpoint is the change of colour from blue green to reddish brown.

A blanks is performed by titrating known volume of the acidified $K_2Cr_2O_7$ with the same FAS using the same indicator.

$$\text{COD of water sample} = \frac{(A - B) \times M\ 8000\ \text{ml}}{\text{Volume of sample}}\ \text{mg}/l$$

where A = Blank titre value of $K_2Cr_2O_7$ vs FAS and

B = Volume of FAS consumed for unreacted $K_2Cr_2O_7$ of the solution.

M = Molarity of FAS solution.

Procedure

25 ml of waste water is pipette out into a round bottomed flask. 10 ml of $K_2Cr_2O_7$ is pipette out into the same flask along with one test tube full of 1 : 1 H_2SO_4 containing $HgSO_4$ and Ag_2SO_4. The flask is filled with a reflux water condenser and the mixture is refluxed for 2 hours. The contents are cooled and transferred to a conical flask. 5 drops of ferroin indicator is added to it and titrated against FAS taken in the burette till the colour changes from blue green to red brown. Same volume of $K_2Cr_2O_7$ is pipette out, mixed with sulphuric acid and ferroin and titrated against same FAS to get blank titre value.

Calculation

$$\text{Chemical oxygen demand of water} = \frac{(A - B) \times M \times 8000}{V}$$

where A = FAS (ml) used for blank

B = FAS (ml) used for sample

M = Molarity of FAS

V = Volume of sample (ml)

BIOLOGICAL OXYGEN DEMAND (BOD)

Biological Oxygen Demand (BOD) is a measure of water quality. It is an important property. It is defined as a measure of oxygen needed (in mg/litre or ppm) by bacteria and other micro-organisms oxidise the organic matter present in water sample over a period. It may also be defined as the quantity of dissolved oxygen required by aerobic bacteria for the to oxidation of organic matter under aerobic conditions. The BOD of drinking water is less than one while sewages have more then several hundreds.

BOD is high, the dissolved oxygen becomes low. The greater the BOD, greater the pollution. Thus BOD is an indication of extent of pollution.

Micro-organisms such as bacteria and fungi are responsible for decomposing organic waste *i.e.*, dead plants, leaves, grass, manure, sewage or food waste. In this process much of the available dissolved oxygen is consumed by aerobic bacteria, robbing other aquatic organisms of the oxygen they need to live. The temperature of the water can also contribute to high BOD levels. Similarly Nitrates and Phosphates in a body of the water can contribute to high BOD levels.

Limitations of BOD

Effluents of industries like paper, pulp rayon & chemicals, have low value of BOD, although they contain enough organic matter. Thus BOD values should not be used as equivalent to organic load. In these cases COD reveals the real pollution potential.