# c. Biological Parameters

## i. Dissolved Oxygen

- Oxygen is very essential component for the existence of all forms of life. It is present in water in as dissolved oxygen.
- It enters water as dissolved oxygen by the process of diffusion from the surrounding air, or by aeration, and also as a byproduct of the process photosynthesis in plants.
- Dissolved oxygen is one of the best indicators of water quality and can be easily measured. The amount of oxygen dissolved in the water is called **dissolved oxygen or DO**.

- The most important oxidizing agent in natural waters is dissolved molecular oxygen ($O_2$). Each oxygen atom in $O_2$ is reduced from the zero oxidation state to the -2 state in $H_2O$ or $OH^-$.

In acidic solution, the redox half reaction is:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

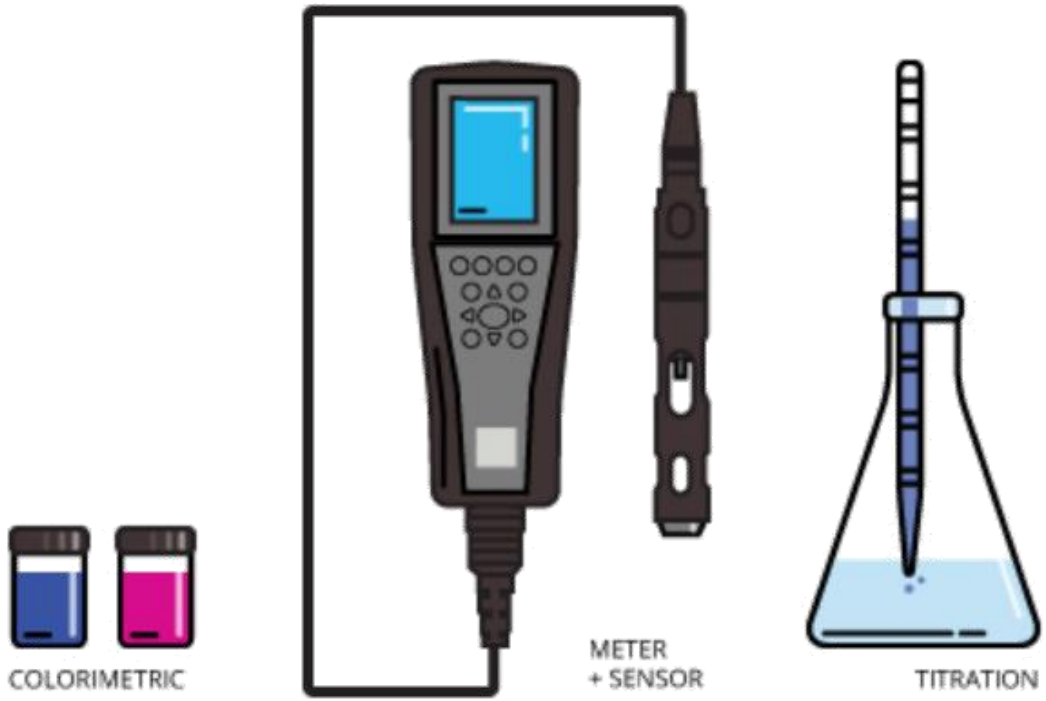
On the other hand in basic solutions is the redox half reaction is:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

The concentration of dissolved oxygen in water is small. The solubility is governed by Henry's law:

$$O_2\,(g) \Leftrightarrow O_2\,(aq.)$$

# *Dissolved Oxygen Measurement Methods*




Dissolved oxygen can be measured by colorimetry, a sensor and meter or by titration.

# Winkler Method

- Also known as the iodometric method, the Winkler method is a titrimetric procedure based on the oxidizing property of dissolved oxygen.
- Samples are collected, fixed and titrated, either in the field or in a lab.
- The sample should be fixed with the reagents as soon as possible to prevent oxygen levels from shifting due to agitation or atmospheric contact.

## Procedure*:

The sample in which DO is measured, a Mn(II) salt is added and the solution is made strongly alkaline. Mn(II) oxidized to $MnO_2$, which can be reacted with KI in acid medium liberates $I_2$ which is titrated with standard $Na_2S_2O_3$ solution using starch as an indicator.

Step 1 $2Mn^{2+}_{(aq)} + 4OH^-_{(aq)} + O_{2(aq)} \rightarrow 2MnO_{2(s)} + 2H_2O_{(l)}$

Step 2 $MnO_{2(s)} + 2I^-_{(aq)} + 4H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + I_{2(aq)} + 2H_2O_{(l)}$

Step 3 $2S_2O_3{}^{2-}_{(aq)} + I_{2(aq)} \rightarrow S_4O_6{}^{2-}_{(aq)} + 2I^-_{(aq)}$

# Oxygen Demand

- The amount of oxygen required by the pollutants for their oxidation is measured in terms of oxygen demand, which is done in two ways:

I. Biochemical Oxygen Demand (BOD)

II. Chemical Oxygen Demand (COD)

# ii. Biochemical Oxygen Demand (BOD)

- It is the standard measure of concentration of the oxygen required by the microorganisms to cause bio degradation of a part of the *organic and inorganic pollution* load.

- Microorganisms consume the organic matter like starch and sugars as food.

- The inorganic constituents like sulfides, sulfites and ferrous ions are attacked by oxygen in presence of enzymes released by microorganisms.

# Determination of BOD

- It depends upon the value of dissolved oxygen (DO) over a specified period of time. For convenience, the BOD test is made over a five day period, also called as a "Five Day BOD", or a $BOD_5$.

- A $BOD_5$ test quantitatively measures the amount (or concentration) of DO in the sample at the beginning of the study and again 5 days later. The difference of DO value initially and after 5 days, is the $BOD_5$.

- This is achieved by putting a sample of waste into a stoppered bottle for 5 days and measuring the amount of DO initially and after 5 days.

To determine the value of the BOD in mg/L, use the following formula:

$$BOD_5 = \frac{DO_i - DO_f}{\frac{\text{Volume of waste water}}{\text{Diluted volume}}}$$

$DO_i$: Initial DO of the diluted waste water, immediately after preparation.

$DO_f$: Final DO of thr diluted waste water, at the end of 5 days incubation.

P: The dilution factor

- The environmental impacts of BOD are:

1. It can quantitatively estimate the strength of domestic wastes and industrial wastewaters.
2. Sewage having high value of BOD creates environmental and health problems.
3. High value of BOD interferes with the aquatic life.

| Water Quality | BOD Level mg/L |
| --- | --- |
| Very good | 1-2 |
| Fair | 3-5 |
| Poor | 6-9 |
| Very poor | 100 or more |

# iii. Chemical Oxygen Demand (COD)

- BOD does not give accurate results of pollution load because non-biodegradable wastes like pesticides and detergents are resistant to microbial degradation and hence do not affect BOD.
- Thus, during the five days period required for elucidation of BOD, these may be only partially oxidized.
- Chemical oxygen demand (COD) is an indirect measurement of the amount of organic matter in a sample. With this test, you can measure virtually all organic compounds that can be digested by a digestion reagent.
- COD is also used to measure to BOD (Biochemical Oxygen Demand) because both are strongly correlated, however COD is a much faster, more accurate test.

- The process involves a two-hour digestion under acidic conditions and high temperature. Potassium dichromate is used as an oxidant in this process.
- The reduction process of $Cr^{6+}$ to $Cr^{3+}$ indirectly measures the oxygen demand. This can be done by titration or spectrophotometry.

$$3\{CH_2O\} + 16H^+ + 2Cr_2O_7^{-2} \longrightarrow 4Cr^{+3} + 3CO_2 + 11H_2O$$

- **Procedure:**

In determination of COD, a strong oxidant like acidify $K_2Cr_2O_7$ is used. All organic compounds and several inorganic chemicals are simultaneously oxidized. This test is faster than the BOD test. The sample is refluxed with $K_2Cr_2O_7$ and $H_2SO_4$. The excess of potassium dichromate is titrated against ferrous ammonium sulfate using ferroin as an indicator. The amount of $K_2Cr_2O_7$ used is proportional to the oxidizable matter present in the sample.

# iv. Total Organic Carbon (TOC)

- Total organic carbon is a measure of total concentration of all organic carbon atoms covalently bonded in the organic molecules of a given sample of water.
- The measurement of total organic carbon is the best method of evaluating the organic content of a water sample.
- The TOC is independent of the oxidation state of the carbon in an organic compound.

# TOC Detection Methods

- Several methods exist for measuring TOC, however each method has two common objectives:
  1. Oxidize organic carbon to carbon dioxide.
  2. Measure the carbon dioxide generated.

- Common oxidation methods include;
  - chemical agents (such as persulfate)
  - combustion (usually aided by a catalyst)
  - exposure to ionizing radiation (such as ultra violet light)
  - exposure to heat
  - some combination of these methods