8. Environmental Chemistry

Syllabus: *Water: sources and ill effects of water pollutants – fluoride and nitrate; determination of total hardness of water by EDTA method -numerical problems. Sewage: determination of Biological Oxygen Demand by Winkler's method - numerical problems and determination of Chemical Oxygen Demand -numerical problems.*

WATER:

Water is abundant in nature and it covers 71% of the earth surface. Water is not only essential for existence of plant and animal life but also very much essential for the industrial development.

Sources of water: The sources of water classified as Surface water and Underground water

Surface water: Rain water, River water, Lake Water, Sea water

1) Rain water: Purest form of water contains many dissolved gases and suspended solid particles.
2) River water: Contains dissolved minerals of soil such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium, iron etc. It also contains the organic matter, small particles of soil and sand in suspension.
3) Lake water: It contains less dissolved minerals but high quantity of organic matters.
4) Sea water: It is the most impure form of natural water. It contains many dissolved salts such as NaCl, sulphates of Na and K, bicarbonates of Mg and Ca.

Underground water: Spring water and well water.

Impurities of Water: Water may be contaminated with various forms of impurities. The impurities present in water are classified into following types.

i) Dissolved Impurities: These are mostly inorganic ions and are completely soluble in water. Examples: Salts such as bicarbonates, chlorides, sulphates of calcium, magnesium, iron, sodium, potassium, and gases such as O_2, CO_2, N_2, H_2S, and NH3 etc.
ii) Suspended Impurities: This form of impurities is heavy and settles down to bottom. Examples: Inorganic compounds like sand, clay, rust powder etc, Organic compounds like vegetable and animal materials.
iii) Colloidal Impurities: These impurities are derived from suspended impurities. This type of impurity gives turbidity property to water sample. Examples: Finely divided matter of sand, clay, organic matter etc.
iv) Biological Impurities: This type of impurity is mainly due to micro-organisms like amoeba, bacteria, algae, and fungi etc which are found in surface water. These micro-organisms are produced due to discharge of organic matter in water.

Sources and ill effects of water pollutants

Fluoride

Most of the fluoride that people consume comes from fluoridated water, foods and beverages prepared with fluoridated water, and toothpaste and other dental products containing fluoride.

Sources

Fluoride is found naturally in soil, water, and foods. It is also produced synthetically for use in drinking water, toothpaste, mouthwashes and various chemical products.

ill effects of Fluoride

- Tooth Discoloration: Consumption of too much of fluoride leads to yellowed or browned teeth.
- Tooth Decay: High intake fluoridated water can lead to the weakening of enamel.
- Skeletal Weakness: Excess exposure to fluoride known as skeletal fluorosis.
- Neurological Problems
- High Blood Pressure
- Thyroid problems
- Acne and other skin problems
- Cardiovascular problems and heart failure
- Reproductive issues, such as lower fertility and early puberty in girls
- Affects the joints and bones, such as osteoarthritis and bone cancer.
- Fluoride poisoning: Acute, high-level exposure to fluoride can lead to abdominal pain, excessive saliva, nausea and vomiting

Nitrate

Sources

Nitrate can be found in some lakes, rivers, and groundwater. We cannot taste, smell, or see nitrate in water.

Nitrate can enter the water bodies from discharge of fertilizers, septic systems, animal feedlots, municipal and industrial waste, urban drainage, decaying plant debris and food processing waste.

ill effects of Nitrate

- Consuming too much nitrate can be harmful—especially for babies. Consuming too much nitrate can affect blood carries oxygen and can cause methemoglobinemia (also known as blue baby syndrome).
- Nitrate can turn hemoglobin (the protein in blood that carries oxygen) into methemoglobin. High levels can turn skin to a bluish or gray color and cause more serious health effects like weakness, excess heart rate, fatigue, and dizziness.
- Increased heart rate, nausea, headaches, and abdominal cramps.

- Headaches, dizziness, fainting, low blood pressure (hypotension) and irregular heart rhythms (arrhythmia).
- Damage blood vessels, making arteries more likely to harden and narrow, leading to heart disease.
- Nitrates may also affect the way our body uses sugar, making us more likely to develop diabetes.

Water Analysis by Na₂EDTA method

Aim: To estimate the Total Hardness present in the supplied sample of water by Na_2EDTA method.

Apparatus: Burette, pipette, conical flask, volumetric flask, beakers, funnel and glass-rod.

Chemicals: Disodium salt of ethylene diamine tetra acetic acid crystals, Eriochrome Black-T indicator, Buffer solution (Mixture of NH_4OH and NH_4Cl).

Theory:

Hardness is that characteristic property of water, which prevents lather formation with soap solution. There are two types of hardness, viz., temporary and permanent hardness.

Temporary hardness of water is due to the presence of soluble salts of bicarbonates of calcium and magnesium in water that can be removed merely by boiling. Boiling of water converts the bicarbonates of soluble salts present in the water into insoluble carbonates and hydroxides of metal ions, which can be removed by filtration.

Permanent hardness of water is due to the presence of soluble salts of chlorides, sulphates and nitrates of Ca & Mg which cannot be removed by boiling the water. Hence permanent hardness is due to the presence of these salts.

Total hardness of water is the algebraic sum of temporary and permanent hardness and it is expressed in terms of $CaCO_3$ equivalent hardness in ppm. or mg./lit., because

1) The amount of Ca is maximum in the earth's crust compared to any other hardness producing substances.

2) Its molecular weight is 100, which makes mathematical calculations easier.

3) It is most insoluble salt, thus can be easily precipitated.

Total hardness of water permissible in potable water is 200 ppm. Water samples having Total hardness greater than 250 ppm causes scale deposits in plumbing, boilers and leads to corrosion.

The hardness of water is determined by using Std. disodium salt of EDTA solution and EBT indicator.

Procedure:

Preparation of Standard EDTA solution:

Dissolve the supplied disodium salt of EDTA ('W'g.) in a 250ml clean beaker by adding 4 test tubes of warm distilled water. Transfer this solution to 250ml volumetric flask. Wash the beaker 2-3 times with distilled water thoroughly and transfer the same to the volumetric flask. Dilute up to the mark of the volumetric flask using distilled water. Shake the flask well to make the solution homogeneous. Rinse and fill the burette with the prepared std. disodium salt of EDTA solution.

Weight of disodium salt of EDTA $\quad$ = 'W' g. Molecular weight of disodium salt of EDTA $\quad$ = 372.24

Molarity of disodium salt of EDTA $\quad = \dfrac{W \times 4}{372.24} = $ 'x' M.

Titration:

Pipette out **50 ml of the supplied hard water sample** into a clean conical flask. Add about **5ml of buffer solution, 2-3 drops of EBT indicator** and **titrate against std. disodium salt of EDTA solution** until a **sharp color changes from wine red to clear blue**. Note down the burette reading and perform another 2 sets of titrations for accuracy.

B.R. → B.L. ↓	I ml.	II ml.	III ml.	Mean BR
Final level				…' V ' ml
Initial level				
Difference				

Calculate the amount of total hardness present in the supplied sample of hard water in terms of calcium carbonate equivalent hardness, in ppm, using the standard conversion factor.

Calculation:

The given **Conversion Factor** is:

1000 ml of 1M Na_2EDTA solution $\equiv$ 100 g. of $CaCO_3$ equivalent hardness.

i.e. 1ml of 1M Na_2EDTA solution $\equiv$ 0.1 g. of $CaCO_3$ equivalent hardness.

Now, 'V' ml of 'x' M Na₂EDTA solution ≡ 0.1 x 'x' x 'V' = 'y' g. of CaCO₃.

i.e., **50 ml** of hard water sample contains = '**y**' g. of CaCO₃ equivalent hardness.

Therefore, **1000ml** of hard water sample ≡ '**y**' x 1000/50 = '**z**' g./lit. of CaCO₃

Hence, Total Hardness of water in terms of CaCO₃, in ppm. = '**z**' x 1000 mg/lit. = '**H**' ppm.

i.e., Total Hardness = 'H' ppm.

Result: Total Hardness of Water in terms of CaCO₃ equivalent hardness = '**H**' ppm.

Biological Oxygen Demand

BOD is defined as the number of milligrams of Dissolved Oxygen required for the oxidation of biologically oxidizable impurities present in 1000 ml of waste water under aerobic conditions at 20 ºC over a period of 5 days.

BOD Determination by Winkler's method

Aim: To estimate the amount of Biological Oxygen Demand present in the supplied sewage sample by Winkler's method.

Apparatus: 300 ml BOD bottle, Burette, 10 ml pipettes, 100 ml measuring cylinder, 250 ml volumetric flask, beakers, conical flasks and funnel.

Chemicals: Manganese sulphate, alkaline potassium iodide, sodium thiosulphate, sulphuric acid and starch indicator.

Theory:

Dissolved oxygen is used as an indicator for the health of a water body. Aquatic animals need dissolved oxygen (DO) to live.

Winkler's Method is a technique used to measure **D**issolved **O**xygen (DO) in freshwater systems. The amount of dissolved oxygen available in waste water is determined before and after 5 days of incubation by Iodometric titration.

$$\text{Biodegradable load (CHONS)} + O_2 \longrightarrow CO_2 + H_2O + NO_3^- + SO_4^{2-}$$
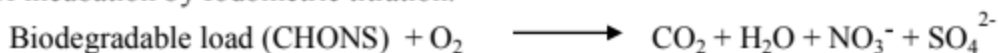
The **principle** involved in this method is the **DO in water oxidizes KI solution to liberate equivalent quantity of iodine**, which is then **titrated against std. Na2S2O3** solution using **starch as an indicator**.

Procedure:

A definite known volume ('**A**' ml) of sewage sample is diluted to a known volume ('**B**' ml) with fresh water. Equal quantities of diluted sewage samples are taken in two BOD Bottles.

Blank Titration:

Dissolved Oxygen (D1) in BOD **Bottle-1** is determined immediately as given below. To the Bottle-1 sample, add with the help of pipette 5ml of MnSO₄ and 5ml of alkaline KI reagents. Stopper the bottle immediately and shake well by inverting the bottle 3 to 4 times and allow it stand for 5 minutes. The brown precipitate of basic manganic oxide, MnO(OH)₂ gets settles down. Now, add one test tube of dil. H₂SO₄, insert the stopper and shake well till the precipitate is completely dissolved. The reaction mixture acquires brownish yellow colour due to the liberation of iodine.

Take **100 ml of the above reaction mixture into** a conical flask and titrate **against Na₂S₂O₃** solution until the reaction mixture becomes **pale yellow color**, then add 1ml of freshly prepared **starch solution**. The reaction mixture turns into deep **blue color due** to the formation of less stable starch-**iodide complex**. Continue the titration till the blue **colour disappears**. Note down the burette reading and perform another 2 sets of titrations for accuracy.

B.R. ⟶ B.L. ↓	I ml.	II ml.	III ml.	Mean BR
Final level				
Initial level				…' V_1 ' ml
Difference				

Sample Titration:

The BOD **Bottle-2** is incubated for 5 days under aerobic conditions at 20 ℃. After 5 days of incubation, the unconsumed **Dissolved Oxygen (D2)** in BOD **Bottle-2** is determined as described above in blank titration.

B.R. ⟶ B.L. ↓	I ml.	II ml.	III ml.	Mean BR
Final level				
Initial level				…' V_2 ' ml
Difference				

Calculation:
Volume of sewage sample before dilution = **A**
Volume of sewage sample after dilution = **B** ml.
Volume of reaction mixture (sewage sample) used for both blank and sample titration = '**Vs**'
Normality of reaction mixture (sewage sample) in **Bottle-1** = N_{DO1}
Normality of reaction mixture (sewage sample) in **Bottle-2** = N_{DO2}
Volume of Na₂S₂O₃ consumed for blank titration in **Bottle-1** = V_1 ml
Volume of Na₂S₂O₃ consumed for sample titration in **Bottle-2** = V_2 ml
Normality of Na₂S₂O₃ solution = N1

Dissolved Oxygen – D1 in Bottle-1:

$$V_{sewage} \, N_{DO1} = V_1 \, N_1$$
$$N_{DO1} = V_1 \, N_1 \, / \, V_{sewage}$$

Dissolved Oxygen in Bottle-1 = D_1 = Normality of reaction mixture (sewage sample) in Bottle-1 x Equivalent weight of Oxygen x 1000 ppm

$D1 = N_{DO1}$ x 8 x 1000 ppm.

Dissolved Oxygen – D2 in Bottle-2:

$$Vs \, N_{DO2} = V_2 \, N_1$$
$$N_{DO2} = V_2 \, N_1 \, / \, Vs$$

Dissolved Oxygen in Bottle-2 = D_2 = Normality of reaction mixture (sewage sample) in Bottle-2 x Equivalent weight of Oxygen x 1000 ppm

$D2 = N_{DO2}$ x 8 x 1000 ppm.

Biological Oxygen Demand (BOD):

$$\textbf{BOD} = \frac{(D1 - D2) \times B}{A} \textbf{ ppm.}$$

Chemical Oxygen Demand

COD is defined as the number of milligrams of Oxygen required for the oxidation of both biologically and chemically oxidizable impurities present in 1000 ml of waste water using strong oxidizing agent like $K_2Cr_2O_7$.

Determination of COD

Aim: To estimate the amount of **Chemical Oxygen Demand** present in the supplied sewage sample by redox reaction.

Apparatus: Round bottom flask, water condenser, Burette, pipette, conical flasks and funnel.

Chemicals: Potassium dichromate, 1:1 sulphuric acid, mercuric sulphate, silver sulphate and ferrous ammonium sulphate (FAS) and ferroin indicator.

Theory:

Chemical Oxygen Demand represents the total amount of oxygen required to oxidize all oxidizable impurities present in a sample of sewage wastes. COD is always greater than BOD since in COD measurement, both biodegradable and non-biodegradable load are completely oxidized. The difference in COD and BOD is equivalent to the quantity of biologically resistant organic matter.

COD is a satisfactory quantitative method for measuring total organic load. It is preferable to BOD as the results are reliable. COD is a rapidly measurable parameter and needs 2 hours for completion.

Procedure:

1. Sample Titration:

A definite known volume ('V_s' ml) of **sewage sample** was pipetted out into a round bottom flask. A **definite known excess of $K_2Cr_2O_7$** was pipetted out into the same round bottom flask. To the reaction mixture, one test tube of **1:1 H_2SO_4** containing **$HgSO_4$** and **Ag_2SO_4** was added ($HgSO_4$ prevents Cl^- ion interference and Ag_2SO_4 catalyzes the oxidation of organic compounds). The round bottom flask was fitted with a **water condenser** and the reaction mixture was **refluxed for 2 hours**.

The above reaction mixture was cooled and transferred into a conical flask. Now, **4-5 drops** of **ferroin indicator** was added and the **reaction mixture** turns into **blue-green colour**. The **reaction mixture** was **titrated** against **ferrous ammonium sulphate** taken in the burette until a **sharp colour changes from blue-green to red-brown.** Note down the burette reading ('**A**' ml).

Burette Level	Burette Reading
Final level	
Initial level	
Difference	…'A' ml

2. Blank Titration:

Same volume of **$K_2Cr_2O_7$** was pipetted out into a conical flask. To this, one test tube of **1:1 H_2SO_4** containing $HgSO_4$ and Ag_2SO_4 and **4-5 drops of** ferroin **indicator were** added and the **reaction mixture** turns into **blue-green colour**. This **reaction mixture** was **titrated** against **ferrous ammonium sulphate** taken in the burette until a **sharp colour changes from blue-green to red-brown.** Note down the burette reading ('**B**' ml).

Burette Level	Burette Reading
Final level	
Initial level	
Difference	…'B' ml

Calculation:

Volume of sewage sample taken = 'V_{sewage}' ml
Normality of reaction mixture (sewage sample) in terms of COD = N_{sewage}
Volume of FAS consumed in sample titration = **A** ml.
Volume of FAS consumed in blank titration = **B** ml.
Volume of $K_2Cr_2O_7$ consumed in satisfying COD in terms of FAS solution = V_{FAS} = (**B-A**) ml
Normality of FAS solution = N_{FAS}

Chemical Oxygen Demand (COD):

V_{FAS} = (**B-A**) ml

$V_{Sewage} \, N_{Sewage} = V_{FAS} \, N_{FAS}$

$N_{sewage} = V_{FAS} \, N_{FAS} \, / \, V_{sewage}$

Chemical Oxygen Demand of sewage sample = **COD** = Normality of reaction mixture (sewage sample) in terms of COD x Equivalent weight of Oxygen x 1000 ppm

$COD = N_{Sewage}$ x 8 x 1000 ppm.