UNIT 3 WATER AND WASTE WATER ANALYSIS

Structure

3.1 INTRODUCTION

Water is one of the most essential substances needed by living organisms, i.e. human life, animals and plants. It is required for agricultural, industrial, domestic and recreation purposes. In our homes, we use water for drinking, cooking, bathing and cleaning. The need for pure and clean water is increasing very rapidly. Water is one of the most important engineering materials and is used for steam generation, as a coolant in power plants, for air-conditioning and fire fighting, and in buildings and other concrete constructions.

The physical and chemical requirements are different for different uses of water. Physical impurities impart odour, taste, colour and turbidity. The chemical impurities mostly comprise the following dissolved substances :

(a) Inorganic salts :

Cations : Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, Fe^{+2}, Al^{+3}, etc.

Anions : Cl^{-}, F^{-}, SO_4^{2-}, NO_3^{-}, HCO_3^{-}, CO_3^{2-} etc.

(b) Dissolved organic substances

(c) Dissolved gases : CO_2, O_2, N_2, H_2S, oxides of nitrogen.

Use of unsuitable water often leads to many problems like health complications for living organisms and decrease in the efficiency of industrial plants due to scale formation, priming and foaming, corrosion and caustic embrittlement etc. Thus, removal of all the undesirable substances from water used for drinking and industrial purposes is absolutely essential.

The treatment methods depend on the nature of impurities present, which can be determined by analysis. The extent of analysis is governed by the purpose for which water is to be used and the specifications laid down for the purpose.

There are different physical and chemical parameters like pH, conductivity, total hardness, temporary and permanent hardness, magnesium hardness, alkalinity, chloride content, dissolved oxygen, chemical oxygen demand (COD), biochemical oxygen demand (BOD), free chlorine in water, etc. which are essential to assess the quality of water. It may not be possible for you to evaluate all these parameters. In this unit, you would determine the following parameters in a water sample using chemical methods :

(a) Total hardness

(b) Temporary and permanent hardness

(c) Biochemical Oxygen Demand (BOD)

(d) Chloride content

Objectives

After performing water analysis experiments, you should be able to

- define total hardness, temporary hardness and permanent hardness,
- list the causes of hardness,
- discuss complex formation of metal ions,
- estimate total hardness, temporary hardness and permanent hardness in water by complexometric titration,
- explain the meaning of BOD and chloride content,
- estimate the BOD and chloride content in a water sample, and
- highlight the importance of BOD in water body.

3.2 EXPERIMENT NO. 5 : DETERMINATION OF TOTAL HARDNESS OF WATER BY COMPLEXOMETRY (USING EDTA)

Water containing salts of heavy metals, mainly calcium and magnesium, is called '**hard water**'. Hard water is not desirable for use at home or in industry. The knowledge of the magnitude and type of hardness is important in determining the suitability of water for domestic and industrial purposes. Hard water precipitates soap (soap forms scum), thus, reducing its cleaning action. Use of hard water for cleaning purposes is unsatisfactory as it increases the consumption of soap. The hardness can be classified into the following two types.

Temporary Hardness

This is due to bicarbonates of calcium and magnesium. The temporary hardness can be removed on boiling water. This involves the evolution of CO_2 and the simultaneous precipitation of the respective carbonates as shown below :

$$Ca(HCO_3)_2 \xrightarrow{\text{Boiling}} CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \xrightarrow{\text{Boiling}} Mg\,CO_3 + H_2O + CO_2 \quad (MgCO_3 \text{ is partially soluble})$$

Permanent Hardness

Permanent hardness of water is mainly attributed to the presence of sulphates, chlorides and nitrates of calcium and magnesium. It does not get removed on boiling and hence has to be removed by chemical methods.

Total hardness in water is the summation of both temporary hardness and permanent hardness.

Total Hardness = Temporary Hardness + Permanent Hardness

Hardness of water is expressed in terms of mg of $CaCO_3$ per dm^3 of water or as ppm.

Hardness of water sample can be determined by soap solution method or by compelxometric titration using EDTA (**ethylene diamine tetra acetic acid**) or by conductometric methods. In this unit, we will discuss the complexometric titration using EDTA.

3.2.1 Principle

Ethylene diamine tetra acetic acid (EDTA) is a powerful compexing agent because of its six donor atoms and is, therefore, also known as 'hexadentate' ligand (Figure 3.1). On chelation, it forms a strainless five membered ring. (**Chelation :** The attachment of a ligand to the central metal ion to form a ring like structure.)

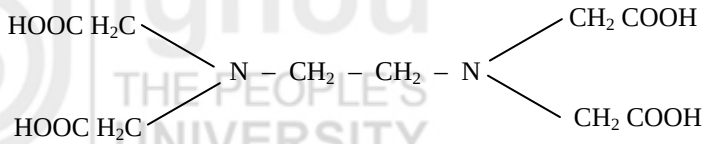

Figure 3.1 : Structure of EDTA

Thus, in a complexometric titration, EDTA forms soluble complexes with metal ions like Ca^{+2} and Mg^{+2} (Figure 3.2). Eriochrome black T is used as an indicator to detect the end point. As the stability of the complex and colour change of the indicator are sensitive to pH changes, the solution to be titrated must be well buffered by ammonium hydroxide-ammonium chloride buffer solution of pH 10.

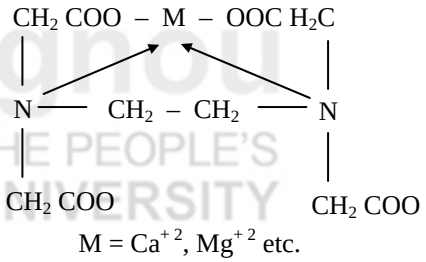

Figure 3.2 : EDTA Complex with a Divalent Metal Cation

EDTA is generally used in the form of disodium salt or tetrasodium salt on account of their greater solubility. Let EDTA be represented by the formula H_4Y; hence, the sodium salt will be $Na_2\,H_2Y$ which gives the complex forming ion H_2Y^{2-} in aqueous solution. The disodium salt reacts with metal ions in 1 : 1 ratio. The reaction with cations, e.g. divalent cation M^{+2}, may be written as follows :

$$M^{2+} + H_2Y^{-2} \rightarrow MY^{2-} + 2H^+ \qquad \ldots (3.1)$$

(M^{2+} may be taken as Ca^{+2}, Mg^{+2} etc.)

$$Ca^{+2} + H_2Y^{-2} \rightarrow CaY^{2-} + 2H^+ \quad \ldots (3.2)$$

$$Mg^{+2} + H_2Y^{-2} \rightarrow MgY^{2-} + 2H^+ \quad \ldots (3.3)$$

Similarly, for trivalent and other multivalent cations, the reactions may be represented as

$$M^{3+} + H_2Y^{-2} \rightarrow MY^- + 2H^+ \quad \ldots (3.4)$$

$$M^{4+} + H_2Y^{-2} \rightarrow MY + 2H^+ \quad \ldots (3.5)$$

$$M^{n+} + H_2Y^{-2} \rightarrow MY^{(n-4)+} + 2H^+ \quad \ldots (3.6)$$

From the above equation, it is evident that 1 mole of the complex forming H_2Y^{2-} reacts in all cases with one mole of the metal ion and two moles of hydrogen ions are liberated. Thus, the molarities are related as per the following equation.

$$\frac{M_1V_1}{M_2V_2} = \frac{1}{1} \quad \ldots (3.7)$$

$$M_1V_1 = M_2V_2 \quad \ldots (3.8)$$

where M_1 and M_2 are the molarities of EDTA salt and metal ion solutions, respectively.
V_1 and V_2 are the volumes of EDTA salt and metal ion solutions, respectively.

Thus, the equilibrium situation is determined by the strength of the bond between the metal ion and the ligand and the relative concentrations of metal ion versus hydrogen ion. It is clear that the stability of a metal-EDTA complex will be governed by the pH value of the solution (Table 3.1).

Table 3.1 : pH Value and the Corresponding Stability of some Metal-EDTA Complexes

Minimum pH at which Complex is Stable	Some Metal Ions
1 – 3	Zr^{+4}, Hf^{+4}, Th^{+4}, Bi^{+3}, Fe^{+3}
4 – 6	Pb^{+2}, Cu^{+2}, Zn^{+2}, Co^{2+}, Sb^{+2}, Mn^{+2} Ni^{+2}, Fe^{+2}, Cd^{+2}, Al^{+3}
8 – 10	Ca^{+2}, Mg^{+2}, Ba^{+2}, Sr^{+2}

From this table, it is found that EDTA complexes with alkaline earth metal ions are stable in alkaline solution, whilst complexes with tri- and tetravalent metal ions are more stable in more acidic solutions. Since the total hardness involves the metal ions like Ca^{+2} Mg^{+2} which are alkaline earth metals, then its determination is carried out at pH 10.

Metal Ion Indicators

Metal ion indicators are commonly used in EDTA titrations. At the end point, i.e. at the equilibrium position, the change occurs from the metal-indicator complex to the metal-EDTA complex.

$$M^{2+} + HIn^2 \rightarrow MIn^- + H^+ \quad \ldots (3.9)$$

This change should be very sharp and swift. To enhance the sharpness of the end point, a small amount of magnesium salt of EDTA is added to the buffer.

Certain dyes, such as calmagite or erichrome-Black T used as colours indicators, also react with these metal ions, especially Ca^{+2} and Mg^{+2} forming coloured complexes.

$$MI_n^- + H_2Y^{2-} \rightarrow MY^{2-} + HIn^{2-} + H^+ \text{ (Q M = Ca, Mg)} \quad \ldots (3.10)$$

e.g. $Mg^{2+} + HIn^{2-} \rightarrow MgIn^{-} + H^{+}$ . . . (3.11)

$$\underset{\text{Wine Red}}{MgI_n^-} + \underset{\text{Colourless}}{H_2Y^{2-}} \rightarrow \underset{\text{Colourless}}{MgY^{2-}} + \underset{\substack{\text{Blue}\\ \text{(at the end point)}}}{HIn^{2-}} + H^+ \quad \ldots (3.12)$$

Eriochrome black T is sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4 -sulphonate (Figure 3.3).

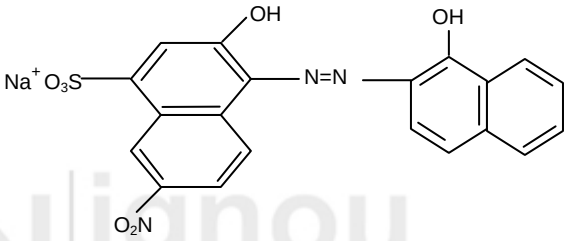

Figure 3.3 : Structure of Eriochrome Black T

SAQ 1

(a) Why is water sample buffered at pH 10 in the determination of hardness of water by complexometry using EDTA?

(b) Explain the changes in equilibrium point when water sample is titrated with EDTA using Eriochrome black T as indicator.

(c) Why is a small amount of magnesium salt of EDTA added to the buffer while titrating the water sample for hardness?

3.2.2 Requirements

You will need the following apparatus, chemicals and solutions for this experiment.

Apparatus	Quantity
Burette (50 cm^3)	1
Pipette (20 cm^3)	1
Conical flask (250 cm^3)	2
Volumetric flask (250 cm^3)	1
Weighing bottle	1
Funnel	1
Burette stand with clamp	1

Chemicals
Disodium salt of EDTA
Ammonium chloride
Ammonium hydroxide
Eriochrome black T
Ethanol
Magnesium chloride

Solutions Provided

(a) **Standard 0.01 M EDTA Solution**

Transfer 0.95 g of the disodium dihydrate EDTA ($Na_2H_2C_{10}H_{12}O_8N_2$. $2H_2O$) salt into a clean and dry 250 cm^3 volumetric flask through a glass funnel. Dissolve the salt in deionised or distilled water. Make up to the mark with distilled water and shake thoroughly to make a homogeneous solution.

(b) **Water Sample**

Take the water sample from the water tap of your laboratory.

(c) **NH_4OH – NH_4Cl Buffer Solution of pH 10**

Take 64 g of NH_4Cl in distilled water and add to it 570 cm^3 of ammonia solution (specific gravity 0.88 to 0.90). Stir and dilute the solution to 1 litre with distilled water.

(d) **Erichrome Black T Indicator (0.5% mass/volume)**

0.50 g indicator is weighed and dissolved in 100 cm^3 ethanol.

(e) **Mg – EDTA Complex (0.005 M) Solution**

It is the stoichiometric mixture of 0.01 M disodium salt of EDTA and 0.01 M $MgCl_2$. A portion of Mg – EDTA solution, when treated with a few drops of eriochrome black T at pH 10 should change to a wine red colour, which should change to pure blue on the addition of one drop of 0.01 M EDTA solution and wine red on addition of a single drop of 0.01 M $MgCl_2$ solution.

3.2.3 Procedure

The experimental procedure involves the following steps :

(a) Bring all the apparatus and prepared solutions to your working table. Then after rinsing the burette with EDTA salt solution, mount it on a stand. Now fill the burette with the EDTA salt solution (0.01 M EDTA) and note the reading in the burette. This reading should be recorded in the observation Table 3.2 under the 'initial reading' column.

(b) Pipette out 50 mL of the hard water sample into a 250 mL conical flask. To this, add 2 mL of the buffer solution, 0.5 mL of Mg – EDTA complex solution, and 3 to 4 drops of Erichrome black T indicator. Colour of the mixture at this stage must be wine red.

(c) Titrate with 0.01 M EDTA from the burette drop wise with constant swirling until the colour changes from wine red to clear blue. This is the end point. Note the reading in burette and record in the observation Table 3.2 under the 'final reading' column.

(d) The difference of the two readings gives the volume of EDTA salt solution consumed by Ca^{+2} and Mg^{+2} present in 50 mL of the hard water sample. Repeat the titration to get at least two concordant readings.

3.2.4 Observations

Approximate mass of the empty weighing bottle = m_1 = ... g

Mass of weighing bottle + estimated EDTA salt = m_2 = ... g

Mass of the weighing bottle (after transferring the EDTA salt) = m_3 = ... g

Actual amount of EDTA salt transferred = $m_2 - m_3 = m_4$ = ... g

Molar mass (M_m) of disodium salt of EDTA = 372.31 g mol^{-1}

Volume of EDTA salt solution prepared = 250 mL

Molarity of EDTA salt solution = $M_1 = \dfrac{m_4 \times 1000}{M_m \times 250}$ mol L^{-1}

$= \dfrac{m_4 \times 4}{372.31}$ mol L^{-1}

Table 3.2 : Observation Table

Sl. No.	Volume of Hard Water Sample (in mL)	Burette Reading (in mL)		Volume of 0.01 M EDTA Salt Solution in mL (Final – Initial)
		Initial	Final	
1	50			
2	50			
3	50			

3.2.5 Calculations

Estimation of Total Hardness of Water Sample

Molarity of EDTA salt solution = $M_1 = \dfrac{m_4 \times 4}{372.31} = \ldots\ldots \text{ mol L}^{-1}$

Volume of EDTA salt solution consumed = V_1 = mL (from Table 3.2)

Volume of water sample = V_2 = 50 mL

Molarity of Ca^{+2} / Mg^{+2} in the water sample = M_2 = ?

Using Eq. (3.8)

$$M_1 V_1 = M_2 V_2$$

Molarity of Ca^{+2} / Mg^{+2} in water sample,

$$M_2 = \frac{M_1 V_1}{V_2} \text{ mol L}^{-1} = \ldots\ldots \text{ mol L}^{-1}$$

Total hardness of water sample in mg of $CaCO_3$ in one litre (1 dm^3) of water

= M_2 × Molar mass of $CaCO_3$ × 1000

= M_2 × 100 × 1000 = . . . ppm of $CaCO_3$

(Q Molar mass of $CaCO_3$ = 100.0 g for all practical purposes. It is taken as 100 for the sake of convenience in calculations).

3.2.6 Result

Total hardness of the given water sample = . . . ppm of $CaCO_3$.

Permissible range of hardness of water is below 300 ppm.

3.3 EXPERIMENT NO. 6 : DETERMINATION OF PERMANENT AND TEMPORARY HARDNESS OF WATER

In this experiment, we have discussed that the total hardness of water is the summation of temporary and permanent hardness. Temporary hardness can be removed by simple boiling the water for sometime and the precipitate obtained can be filtered out. After removal of temporary hardness, the water sample contains permanent hardness only.

Total Hardness – Permanent Hardness = Temporary Hardness

The permanent hardness in the water sample is determined in the same way as we have done for the total hardness in Experiment 5.

Thus, in this experiment, you will first remove the temporary hardness by boiling and then titrate water sample for permanent hardness.

3.3.1 Principle

The principle is same as in Experiment 5 as you are going to use the same method.

SAQ 2

How can temporary hardness be removed from the water sample?

3.3.2 Requirements

You can use the same apparatus, chemicals and solutions which you have prepared for Experiment 5. Besides that you will need a 400 mL beaker, burner and filter paper.

3.3.3 Procedure

The following steps are to be followed :

(a) Determine the total hardness of water sample as given in Experiment 5. If you are using the same water sample, then there is no need to repeat this experiment.

(b) Take 250 mL of the water sample in a 400 mL beaker and boil it for 30 minutes. Cool the sample and filter it through Whatman No 1 filter paper into a 250 mL volumetric flask. Make up the filtered sample to the mark by adding distilled or deionised water. Thus, temporary hardness of water is removed and now you can titrate the filtered sample with 0.01 M EDTA salt solution for permanent hardness using the same steps, i.e. (b), (c) and (d) of Experiment 5.

3.3.4 Observations

Sl. No.	Volume of Water Sample (after Boiling) (in mL)	Burette Reading in mL		Volume of 0.01 M EDTA Salt Solution (in mL) (Final – Initial)
		Initial	Final	
1				
2				
3				

3.3.5 Calculations

Permanent Hardness of Water Sample

The calculation for permanent hardness of water sample may be followed in the same way as in Experiment 5. Permanent hardness of water sample in mg of $CaCO_3$ in 1 litre of water

$$= M_2 \times 100 \times 1000 = \ldots \text{ ppm of } CaCO_3$$

Temporary Hardness of Water Sample

$$= \underset{\text{(From Experiment 5)}}{\text{Total Hardness}} - \underset{\text{(From Experiment 6)}}{\text{Permanent Hardness}} = \ldots \text{ ppm of } CaCO_3$$

3.3.6 Result

Permanent hardness of the given water sample = . . . ppm of $CaCO_3$

Temporary hardness of the given water sample = . . . ppm $CaCO_3$

3.4 EXPERIMENT NO. 7 : DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND (BOD) OF WATER

In the Experiments 5 and 6, you were introduced to the complexometric titration methods. Now, we are again going to discuss iodometric titration method indirectly to estimate the Biochemical Oxygen Demand (BOD) of water.

BOD is an empirical test that measures the amount of oxygen required for microbial oxidation of organic compounds in aqueous sample. BOD test is of great value in the analysis of sewage, highly polluted waters and industrial effluents.

3.4.1 Principle

The relation between BOD and DO (Dissolved Oxygen) is that when BOD is too high, the DO becomes too low to support the living organisms. BOD is commonly used to carry out the water quality measurement. When there is enough bacterial activity, there is depletion of oxygen in water down stream which is called the 'oxygen sag'.

In aerobic systems where oxygen is abundant, oxygen is the ultimate electron acceptor which is reduced while organic matter is being oxidised to CO_2 and H_2O.

$$CH_3COO^- + 2O_2 \xrightarrow{\text{bacteria}} CO_2 + HCO_3^- + H_2O$$

In-organic materials, S^{2-} and NH_3 are oxidised as follows :

$$S^{2-} + 2O_2 \xrightarrow{\text{bacteria}} SO_4^{2-}$$

$$NH_3 + 2O_2 \xrightarrow{\text{bacteria}} NO_3^- + H^+ + H_2O$$

Under an aerobic conditions (absence of oxygen), sulphate ions, phosphate ions, carbon dioxide etc. can act as electron acceptors and are reduced to hydrogen sulphide (H_2S), phosphine (PH_3), methane (CH_4), respectively.

$$2CH_3COO^- + 2SO_4^{2-} + 3H^+ \rightarrow 2CO_2 + 2HCO_3^- + H_2S + HS^- + 2H_2O$$

$$CH_3COO^- + PO_4^{3-} + 3H^+ \rightarrow CO_2 + HCO_3^- + PH_3 + H_2O$$

$$CH_3COO^- + CO_2 + 8H^+ \rightarrow 2CH_4 + HCO_3^- + H_2O$$

This test measures the amount of oxygen utilised during a specific incubation period (generally, 5 days) for biochemical oxidation of organic materials and oxidisable inorganic ions, such as Fe^{2+} and S^{2-}. The incubation is performed in the dark at 20 ± 1^oC.

BOD measures the amount of oxygen needed by the microbes to oxidize the organics in the wastewater. Therefore, oxygen must be supplied initially into the aqueous medium before incubation.

3.4.2 Requirements

You will need the following apparatus, chemicals and solutions for this experiment.

Apparatus	Quantity
Burette (50 mL)	1
Pipette (20 mL)	1
Conical flask (250 cm^3)	2
Volumetric flask (250 mL)	4
Volumetric flask (100 mL)	1
Weighing bottle	1
Funnel	1
Burette stand with clamp	1
BOD bottles (300 mL)	3
Thermostatically controlled air incubator or water bath	1
Beaker (250 mL)	1
Glass stopper bottle	1

Chemicals
Manganese sulphate ($MnSO_4$)
Potassium dichromate ($K_2Cr_2O_7$)
Sodium theosulphate ($Na_2S_2O_3 . 5H_2O$)
Potassium iodide (Kl)
Sodium azide (NaN_3)
Conc. HCl and Conc. H_2SO_4
Sodium bicarbonate ($NaHCO_3$)
Starch
Sodium hydroxide (NaOH)
Magnesium sulphate
Ferric chloride
Phosphate buffer (pH 7.2)

Solutions Prepared

(a) **Preparation of Standard $K_2Cr_2O_7$ Solution (N/20)**

Weight accurately 0.612 g $K_2Cr_2O_7$ in a weighing bottle. Transfer it to a clean 250 mL volumetric flask. Dissolve the salt with distilled water and make up the solution to the mark. Shake the solution till it is completely homogeneous.

(b) **Standard Sodium Thiosulphate Solution (N/20)**

Dissolve 3.102 g of sodium thiosulphate in 250 mL of distilled water.

(c) **Manganese Sulphate Solution**

Weigh accurately 100 g of $MnSO_4$ salt and transfer it to 250 mL volumetric flask. Dissolve it with distilled water and make it up to the mark.

(d) **Alkaline Iodide-azide Solution**

Dissolve 125 g of NaOH and 37.5 g of KI in distilled water in a 250 mL volumetric flask. Add 2.5 g of NaN_3 in 10 mL distilled water. Then make it up to the mark with distilled water.

(e) **Starch Solution**

Take 0.5 g of starch in a 250 mL beaker. To this add 100 mL of distilled water and boil it for a while with constant stirring.

(f) **Calcium Chloride Solution**

Dissolve 6.87 g of anhydrous $CaCl_2$ with distilled water in a 250 mL volumetric flask and make it up to the mark.

(g) **Magnesium Sulphate Solution**

Dissolve 6.87 g of MgSO4 . $7H_2O$ with distilled water in a 250 mL volumetric flask.

(h) **Ferric Chloride Solution**

Dissolve 0.06 g $FeCl_3$. $6H_2O$ in distilled water and dilute to 250 mL.

(i) **Phosphate Buffer Solution**

Dissolve 0.85 g of KH_2PO_4, 2.175 g of K_2HPO_4, 3.34 g of Na_2HPO_4 . $7H_2O$ and 0.17 g of NH_4Cl in 50 mL distilled water and make it up to 100 mL. The pH of this solution must be 7.2.

SAQ 3

Define BOD and give its significance.

3.4.3 Procedure

The experimental procedure involves the following steps.

(a) The concentration of DO before and after incubation is measured. DO in water may be determined by iodometric titration (in this experiment), i.e. Winkler method as follows in the subsequent steps. Divide the water sample into two parts : one part is put for incubation for 5 days at 20 ± 1^oC. The other part is used for DO test directly.

(b) A measured volume 300 mL of water sample is taken in a glass stoppered bottle. To this, add 2 mL of manganese solution ($MnSO_4$) followed by the addition of a strong base, i.e. 2 mL of alkaline iodide-azide solution. This will form precipitate.

(c) Stopper the bottle immediately and mix well by shaking the bottle. Then allow it to stand for 2 minutes.

(d) Add 1 mL of conc. H_2SO_4 and shake it to dissolve the precipitates (**Note :** If ferric ion is present, add phosphoric acid instead of H_2SO_4.)

(e) Then take 203 mL of the above clear solution (from (d)) into a 250 mL conical flask for titration (Table 3.3).

(f) Fill the burette with N/20 sodium thiosulphate solution.

(g) Pipette out 50 mL of sample in a conical flask (100 mL). To this, add 1 g of KI and 1 g of $NaHO_3$ and shake until the salts are dissolved.

(h) To this add 3 mL of conc. HCl slowly and then add 12 to 13 mL of N/20 $K_2Cr_2O_7$ solution and mix the solution well.

(i) Titrate with N/20 sodium thiosulphate solution from the burette with constant swirling. When the solution acquires a greenish-yellow colour, at this point, add 2 to 3 mL of starch indicator. The colour will change to black.

(j) Then continue the titration until the greenish-blue colour changes to light green by the addition of a single drop of sodium thiosulphate. This is the end point.

(k) Similar titration will be done for the 2nd part of the sample which was set for the incubation (Table 3.4).

Preparation or Dilution of 2nd Part of the Water Sample for Incubation

(a) Different volumes (50, 100, 150 and 200 mL) of water samples are placed in 300 mL incubation BOD bottles.

(b) These bottles are diluted with 'seeded' dilution water.

(c) The dilution of water (above b) is done by adding 1 to 2 mL of phosphate buffer solution to an equal volume of $MgSO_4 . 7H_2O$, $CaCl_2$, $FeCl_3 . 6H_2O$ solution and diluting into 1 litre by adding double distilled water.

(d) If the water sample is from sewage and sewage effluents, seeding is not necessary.

(e) If it is a fresh water sample, then 1 to 2 mL of water containing a good bacterial population is added to the dilution water which is known as seeding.

(f) Then the BOD bottles are filled to their full capacity with dilution water without leaving any headspace and tightly closed.

(g) The BOD bottles are then placed in a thermostatically controlled air incubator or a water bath at 20 ± 1^oC in the dark to prevent any photochemical reaction.

3.4.4 Observations

Approximate mass of the weighing bottle = m_1 = ... g

Mass of the weighing bottle + sodium thiosulphate salt = m_2 = ... g

Mass of the weighing bottle (after transferring the salt) = m_3 = ... g

Actual amount of sodium thiosulphate salt transferred = $m_2 - m_3 = m_4$ = ... g

Molar mass of sodium thiosulphate (M_m) = 248.17 g mol^{-1}

Volume of sodium thiosulphate solution prepared = 250 mL

Molarity of sodium thiosulphate salt solution $= M_1 = \frac{m_4 \times 1000}{M_m \times 250}\ \text{mol L}^{-1}$

$$= \frac{m_4 \times 4}{248.17}\ \text{mol L}^{-1}$$

Table 3.3 : Water Sample before Incubation vs Sodium Theosulpate Salt Solution

Sl. No.	Volume of Water Sample (in mL)	Burette Reading (in mL)		Volume of $Na_2S_2O_3$ Salt (in mL) (Final – Initial)
		Initial	Final	
	50			
	50			
	50			

Table 3.4 : Water Sample after Incubation vs $Na_2S_2O_3$ Solution

Sl. No.	Volume of Water Sample (in mL)	Burette Reading (in mL)		Volume of $Na_2S_2O_3$ Salt (in mL) (Final – Initial)
		Initial	Final	
	50			
	50			
	50			

3.4.5 Calculations

Estimation of DO in Water Sample

Molarity of sodium theosulphate salt solution $= M_1 = \frac{m_4 \times 4}{248.17} = \ldots \text{mol L}^{-1}$

Volume of $Na_2S_2O_3$ salt solution used (from Table 3.3) = V_1 = . . . mL

Molarity of the water sample with respect to DO = M_2 = ?

$$M_1 V_1 = M_2 V_2$$

$$M_2 = \frac{M_1 V_1}{V_2} \text{ mol L}^{-1} = \ldots \text{mol L}^{-1}$$

Strength of DO in the given water sample will be $= \frac{M_1 V_1}{V_2} \times 8000 = \text{mg DO L}^{-1}$.

(Q The milli equivalent weight for oxygen is 8000.)

Calculation for BOD

$$\text{BOD, mg L}^{-1} = \frac{(P_1 - P_2)\, V_2}{V_1}$$

where P_1 = Initial conc. DO mg L^{-1} before incubation of water sample,

P_2 = Conc. DO mg L^{-1} after incubation of water sample,

V_1 = mL sample diluted, and

V_2 = Volume of the BOD bottle (300 mL).

When seeded dilution water is used, the BOD is calculated as follows :

$$\text{BOD mg L}^{-1} = \frac{[(P_1 - P_2) - (q_1 - q_2)\ f\,]\, V_2}{V_1}$$

where, q_1 = DO of seed control before incubation, mg L^{-1}, and

q_2 = DO of seed control after incubation, mg L^{-1}.

$$f = \frac{\text{\% seed in diluted sample}}{\text{\% seed in seed control}}$$

3.4.6 Result

The BOD of the given water sample = . . . ppm or (mg L^{-1}).

SAQ 4

(a) What is the relationship between BOD and DO?

(b) In which type of water seed control is necessary and why?

3.5 EXPERIMENT NO. 8 : ESTIMATION OF CHLORIDE CONTENT IN A WATER SAMPLE

Chlorides (Cl^-) are one of the most commonly occurring anions in the environment and are present in water usually as NaCl, $MgCl_2$ and $CaCl_2$. Chloride ion is the most mobile ion in the water body. It may react with many metals and non-metal to form complex compounds which are very harmful to aquatic biota. The chloride ion concentration in the water body should be within the permissible range (< 250 ppm). It can be analysed using several different methods, but here we will use Argentometric tritrimetry or Mohr's method.

3.5.1 Principle

Chloride ions can be determined by titration with standard silver nitrate solution, using potassium chromate as indicator. As the titration proceeds, the silver nitrate reacts with chloride ions in neutral or slightly alkaline solution (pH 7 to 8) quantitatively precipitating silver chloride, as shown below :

$$AgNO_3 + NaCl \rightarrow \underset{\text{white ppt.}}{AgCl\downarrow} + NaNO_3 \qquad \ldots (A)$$

Potassium chromate also reacts with $AgNO_3$ to form real silver chromate

$$K_2CrO_4 + 2\,AgNO_3 \rightarrow AgCr\,O_4 + 2\,KNO_3 \qquad \ldots (B)$$

The reaction B is less favourable than A. Therefore, K_2CrO_4 can be used as an indicator.

3.5.2 Requirements

Apparatus	Quantity
Burette (50 mL)	1
Pipette (20 mL)	1
Conical flask (100 mL)	1
Beaker (100 mL)	2
Volumetric flask (100 mL)	1
Weighing bottle	1
Funnel	1
Volumetric flask (1 litre)	2
Burette stand	1

Chemicals
Sodium Chloride
Silver Nitrate
Potassium Chromate
Hydrogen Peroxide (30%)

Solutions Provided

(a) **Standard N/20 NaCl Solution**

Weight 2.922 g of pure and dry NaCl in a weighing bottle and transfer it into a 1 litre volumetric flask. Dissolve it with 1 litre distilled water.

(b) **Silver Nitrate Solution (N/20)**

8.494 g of pure solid silver nitrate is taken in a 1 litre volumetric flask. Dissolve it with distilled water and make it up to the mark.

(c) **Potassium Chromate Indicator (K_2CrO_4)**

Dissolve 5 g of potassium chromate in 100 mL distilled water in a 100 mL volumetric flask.

3.5.3 Procedure

The experimental procedure involves the following steps :

Standardisation of $AgNO_3$ Solution

(a) Fill the burette with the $AgNO_3$ solution after rinsing it with this solution and note the reading in the burette and record it in the observation Table 3.5 under the initial reading column.

(b) Pipette out 25 mL of the NaCl (N/20) solution into a 250 mL conical flask, add 1 mL of 30% H_2O_2 and 1 mL of K_2CrO_4 indicator into it.

(c) Titrate it with $AgNO_3$ (N/20) solution with constant swirling. End point is detected by the change of colour to pink. Note the burette reading and record in the observation Table 3.5 under the final reading column. Repeat the titration to get at least two concordant readings.

Titration with the Test Sample

The steps mentioned above from (a) to (c) will be followed in the same way and note down the observations in Table 3.6. Similarly, one blank titration will be carried out with distilled water.

Note

(a) 30% H_2O_2 is added into the test solution to remove the interfering agents like bromide, iodide, cyanide, sulphide, sulphate and thiosulphate.

(b) The pH of the water sample should be adjusted between 7 to 8, i.e. neutral or slightly alkaline.

3.5.4 Observations

Approximate mass of the weighing bottle = m_1 = ... g

Mass of the weighing bottle + Ag NO_3 salt (before transferring) = m_2 = ... g

Mass of the weighing bottle (after transferring) = m_3 = ... g

Actual amount transferred = $m_2 - m_3 = m_4$ = ... g

Molar mass (M_m) of solid silver nitrate salt = 169.87 g mol^{-1}

Equivalent mass (M_N) of solid silver nitrate salt = 169.87 g mol^{-1}

Volume of Ag NO_3 solution prepared = 1000 mL

Normality of Ag NO_3 solution $= N = \dfrac{m_4 \times 1000}{M_N \times 1000}$ mol L^{-1}

$$= \frac{m_4}{M_N} \text{ mol L}^{-1}$$

Table 3.5 : Sodium Chloride vs Silver Nitrate Solution

Sl. No.	Volume of NaCl (in mL)	Burette Reading (in mL)		Volume of $AgNO_3$ Salt (in mL) (Final – Initial)
		Initial	Final	
1	25			
2	25			
3	25			

Table 3.6 : Water Test Sample vs Silver Nitrate Solution

Sl. No.	Volume of Water Test Sample (in mL)	Burette Reading (in mL)		Volume of $AgNO_3$ Salt (in mL) (Final – Initial)
		Initial	Final	
1	25			
2	25			
3	25			

Table 3.7 : Distilled Water vs Silver Nitrate Solution

Sl. No.	Volume of Distilled Water (in mL)	Burette Reading (in mL)		Volume of $AgNO_3$ Salt (in mL) (Final – Initial)
		Initial	Final	
1	25			
2	25			
3	25			

3.5.5 Calculations

Estimation of chloride in water sample is done as follows :

Standardisation of $AgNO_3$ from Table 3.5

$$N_1 V_1 = N_2 V_2$$

where, N_1 = N/20 of NaCl,

V_1 = 25 mL of NaCl,

N_2 = ? normality of Ag NO_3, and

V_2 = . . . mL of $AgNO_3$ (burette reading)

$$N_1 V_1 = N_2 V_2$$

$$= \frac{N}{20} \times 25 = N_2 \times V_2 \quad \text{or} \quad N_2 = \frac{N \times 25}{V_2 \times 20}$$

$$\text{Cl}^- \text{ in g L}^{-1} = \frac{(X - Y)\, N_2 \times 35.45}{\text{Volume of water test sample (25 mL)}} \text{ g L}^{-1}$$

where, X = Volume of $AgNO_3$ titrant (mL) required for water test sample,

Y = Volume of $AgNO_3$ titrant (mL) required for blank titration, and

N_2 = Normality of titrant, $AgNO_3$.

3.5.6 Result

Chloride present in the water sample = . . . g L^{-1}.

SAQ 5

(a) Why is K_2CrO_4 used as an indicator, in the Mohr's method for estimation of chloride in water?

(b) Why is H_2O_2 (30%) added to the water sample while estimating chloride in water sample?