B Tech Lab Experiments

9th December, 2022

Experiment 1

Aim of the experiment: To Determine the total hardness of pond water/ supplied water using Standard EDTA Solution

Apparatus used: burette, conical flask, dropper, measuring cylinder

Chemicals used: EDTA solution, ammonium buffer solution, eriochrome black T indicator

Theory: Hardness is a degree of ability of water to cause precipitation of insoluble calcium and magnesium salts of higher fatty acids from soap solutions. Hardness can be categorized into two types:

1. Temporary Hardness 2. Permanent Hardness

1. Temporary Hardness: Temporary Hardness mainly caused by the presence of dissolved bicarbonates of Calcium, Magnesium ($Ca(HCO_3)_2$, $Mg(HCO_3)_2$). Temporary Hardness can be largely removed by boiling of water.

2. Permanent Hardness: It is due to the presence of dissolved Chlorides, Nitrates and Sulphates of Calcium, Magnesium, Iron and other metals. Permanent hardness responsible salts are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$. Permanent Hardness cannot be removed by boiling but it can be removed by the use of chemical agents.

Hardness of water is significant in determining the suitability of water for domestic and industrial uses. The comparative amount of calcium and magnesium hardness, carbonate and non-carbonate hardness present in water is the aspects while determining the most economical type of softening process.

The determination of hardness is carried out by titrating water sample with Sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA) using Eriochrome Black-T (EBT) as an indicator and keeping the pH of the water at 9.0 - 10.0. The end point is the change in color from wine - red to blue, when the EDTA solution complexes the calcium and magnesium salt completely.

EBT is often used as indicator for the above titration. At pH 10, the calcium or magnesium ion first forms a complex with the EBT giving a wine red colored solution. After addition of EDTA, the stronger EDTA replaces the EBT ions to form a Ca – EDTA/ Mg-EDTA complex. This complex is more stable than the Ca – EBT/Mg-EBT complex. Now the EBT indicator is free and it gives a blue color.

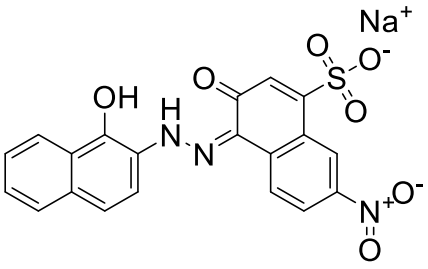


Fig: Eriochrome Black T

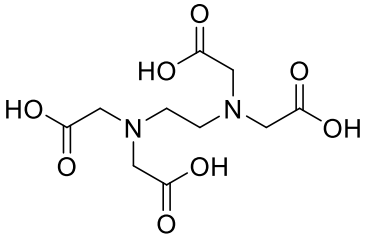


Fig: EDTA

Graphical Representation:

+ EBT

(Ca^{2+} or Mg^{2+}) Hardness-salts Colorless

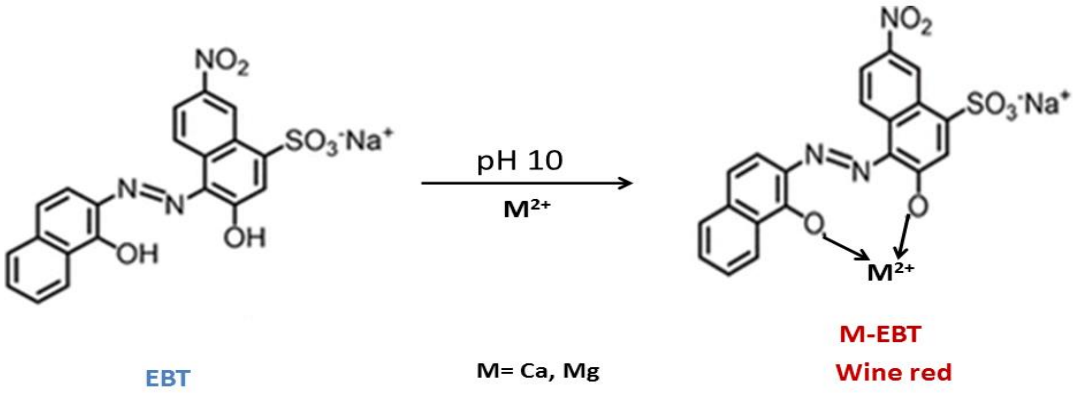
indicator

[Ca – EBT] (or) [Mg – EBT] unstable complex (wine red)

+ EDTA

[Ca – EBT] (or) [Mg – EBT] EDTA [Ca – EDTA] (or) [Mg – EDTA] + EBT

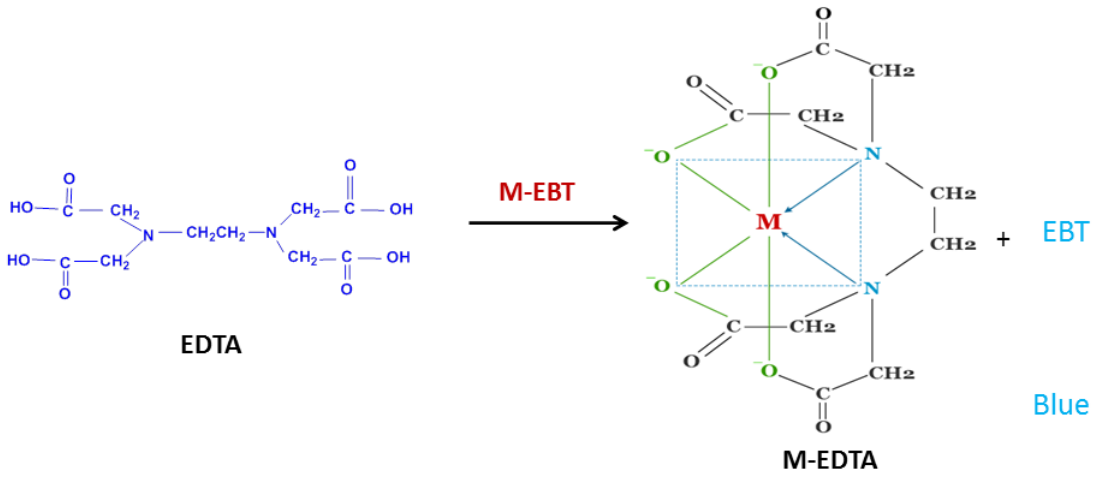
Unstable complex (wine red) stable complex (Colorless) blue



EBT

M= Ca, Mg

M-EBT
Wine red



EDTA

M-EDTA

Procedure:

1. The supplied EDTA solution (1M) is taken in the burette. The initial volume in the burette is noted.
2. 100 mL distilled water is taken in a conical flask. 2ml ammonia buffer is added to the conical flask followed by 2-3 drops of EBT indicator.
3. EDTA from the burette is added in the conical flask till the color of the solution changes from wine red to blue. The volume is noted.
4. The process is repeated for 2-3 times to get a concordant reading.

Observation:

Table: Titration of the water sample using EDTA

Sl No	Volume of sample taken (mL)	Burette reading (mL)		Volume of EDTA (mL)	Concordant reading (mL)
		Initial value	Final value		
1.	100	0	5.1	5.1	5.1
2.	100	5.1	10.3	5.2	
3.	100	10.3	15.4	5.1	
4.	100	15.4	20.7	5.3	

Calculation:

Formula weight of is $CaCO_3$ = 100 g/mol

Strength of the supplied EDTA solution= 1M

1000 mL of 1M EDTA is equivalent to 100 g of $CaCO_3$

5.1 mL of 1M EDTA is equivalent to $(100 * 5.1)/1000$ g of $CaCO_3$

$$= 0.51 \text{ g } CaCO_3$$

$$= 510 \text{ mg } CaCO_3$$

100 mL supplied sample contains 510mg of $CaCO_3$

1000 mL sample would contain $\frac{510*1000}{100}$ mg of $CaCO_3$

$$= 5100 \text{ mg of } CaCO_3$$

Result:

Hardness of the supplied sample is 5100 mg/L or 5100 ppm

Importance of buffer:

Experiment 2

Aim of the experiment: Estimation of magnesium from supplied solution using standard EDTA.

Theory:

Many metal ions react with electron pair donors to form coordination compounds or complex ions. The formation of a particular class of coordination compounds, called chelates, are especially well suited for quantitative methods. Complexometric titrations with EDTA have been reported for the analysis of nearly all metal ions. Because EDTA has four acidic protons, the formation of metal-ion/EDTA complexes is dependent upon the pH. For the titration of Mg^{2+}, pH of the solution should be maintained at 10 using a buffer so that complex formation will be quantitative. The endpoint of the titration is determined by the addition of Eriochrome Black T, which forms a wine red colored chelate with Mg^{2+} and undergoes a color change to blue when the Mg^{2+} is released to form a chelate with EDTA.

However, a different procedure is used if calcium is present with magnesium. Mg (II) can be directly determined at pH 10 using EBT indicator when present alone in a solution. But the ion cannot be determined directly if present in a mixture with Ca (II). Ca (II) and Mg (II) form wine red coloured complexes with EBT. EDTA decomposes both the metal-indicator complexes at pH=10. Hence Mg can't be determined in presence of Ca. In fact the total amount of Ca (II) and Mg (II) in a mixture is determined using EBT indicator. KOH is added to the solution of Ca (II)-Mg (II), which precipitates the Magnesium ion as $Mg(OH)_2$. Then the remaining calcium ion can be determined using PR indicator. Amount of Mg (II) is then calculated by subtracting the amount of Ca (II) from the total amount.

Apparatus used: burette, conical flask, dropper, measuring cylinder

Chemicals used: Mg solution, EDTA solution, ammonium buffer solution, eriochrome black T indicator.

Graphical Representation:

+ EBT

(Mg^{2+}) indicator [Mg – EBT]

Colorless unstable complex (wine red)

+ EDTA

[Mg – EBT] EDTA [Mg – EDTA] + EBT

Unstable complex (wine red) stable complex (Colorless) blue

Procedure:

1. The supplied EDTA solution (1M) is taken in the burette. The initial volume in the burette is noted.
2. 25 ml of Mg solution is taken out using a pipette in a conical flask. 50 mL distilled water, 2ml ammonia buffer and 2-3 drops of EBT indicator is added.
3. EDTA from the burette is added in the conical flask till the color of the solution changes from wine red to blue. The volume is noted.
4. The process is repeated for 2-3 times to get a concordant reading.

Observation:

Table: Titration of the water sample using EDTA

Sl No	Volume of sample taken (mL)	Burette reading (mL)		Volume of EDTA (mL)	Concordant reading (mL)
		Initial value	Final value		
1.	25	0	9	9	9
2.	25	0	9.2	9.2	
3.	25	0	9	9	
4.	25	0	9.1	9.1	

Calculation:

Strength of the supplied EDTA solution= 1M

1000 mL of 1M EDTA is equivalent to 24.32 g of Mg

9 mL of 1M EDTA is equivalent to $(24.32 * 9)/1000$ g of Mg

$$= 0.218 \text{ g of Mg}$$

$$= 218 \text{ mg of Mg}$$

25 mL supplied sample contains 218 mg of Mg

1000 mL sample would contain $\frac{218*1000}{25}$ mg of Mg

$$= 8700 \text{ mg of Mg}$$

Result:

Amount of Mg in the supplied sample is 8700 mg/L or 8700 ppm

Experiment 3

Aim of the experiment: Estimation of calcium from supplied solution using standard EDTA

Theory:

Calcium (II) can be directly determined with EDTA using Patton and Reeder's indicator (PR) when present alone or in a mixture. This blue dye forms a complex with the calcium ions changing colour from blue to pink/red in the process, but the dye–metal ion complex is less stable than the EDTA–metal ion complex. As a result, when the calcium ion–PR complex is titrated with EDTA the Ca (II) ions react to form a stronger complex with the EDTA.

For the titration, the indicator is added to the sample solution containing the calcium ions and forms the pink/red calcium ion-indicator complex (Ca-PR). This solution is then titrated with EDTA. The endpoint occurs when the solution turns blue; indicating that the Ca-PR complex has been completely replaced by the calcium ion-EDTA complex and the PR indicator reverts to its blue colour. The reaction is:

$Ca\text{-}PR + EDTA^{4-} \rightarrow PR + [Ca\text{-}EDTA]^{2-}$

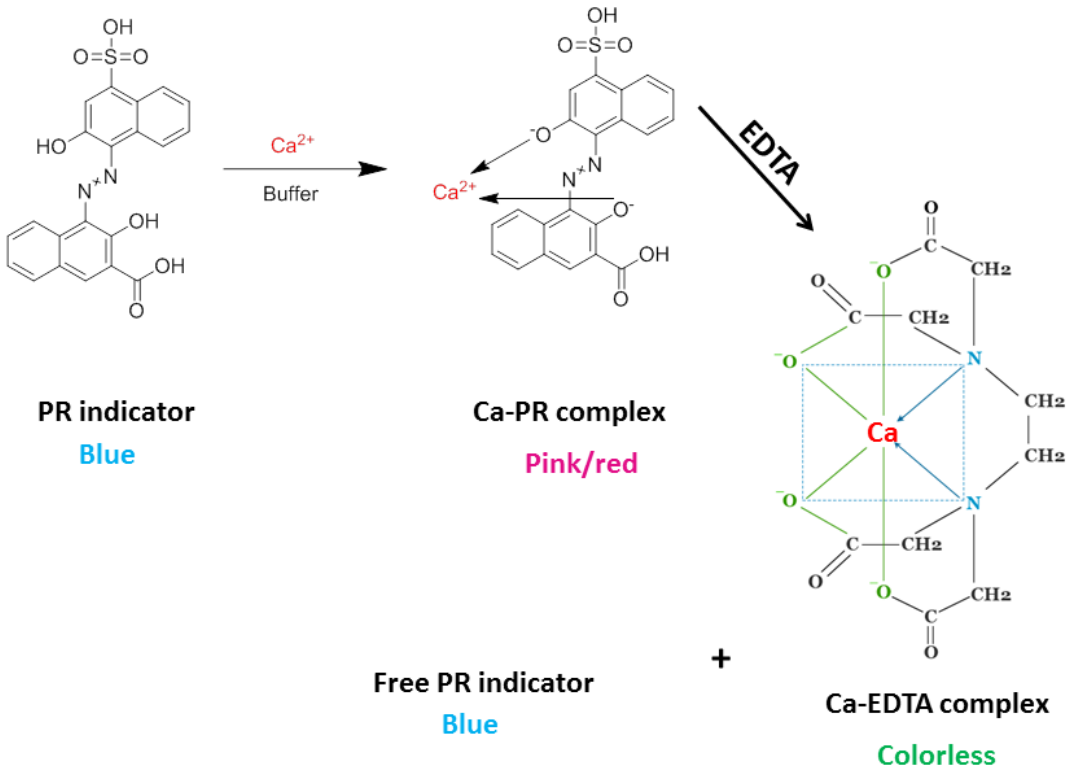


Fig: Schematic representation

Procedure:

5. The supplied EDTA solution (1M) is taken in the burette. The initial volume in the burette is noted.
6. 25 ml of Ca solution is taken out using a pipette in a conical flask. 25 mL distilled water, 2ml ammonia buffer and 2-3 drops of PR indicator is added.
7. EDTA from the burette is added in the conical flask till the color of the solution changes from wine red to blue. The volume is noted.
8. The process is repeated for 2-3 times to get a concordant reading.

Observation:

Table: Titration of the water sample using EDTA

Sl No	Volume of sample taken (mL)	Burette reading (mL)		Volume of EDTA (mL)	Concordant reading (mL)
		Initial value	Final value		
5.	25	0	5	5	5
6.	25	0	5.2	5.2	
7.	25	0	5	5	
8.	25	0	5.1	5.1	

Calculation:

Strength of the supplied EDTA solution= 1M

1000 mL of 1M EDTA is equivalent to 40.08 g of Ca

5 mL of 1M EDTA is equivalent to $(40.08 * 5)/1000$ g of Ca

= 0.200 g of Ca

= 200 mg of Ca

25 mL supplied sample contains 200 mg of Mg

1000 mL sample would contain $\frac{200*1000}{25}$ mg of Mg

= 8000 mg of Mg

Result:

Amount of Ca in the supplied sample is 8000 mg/L or 8000 ppm

Experiment 4

Aim of the experiment: Determination of Dissolved oxygen (D.O) of lake water

Introduction:

The major inputs of Dissolved Oxygen (DO) to natural water are from the atmosphere and photosynthetic reactions. Where the algae and phytoplankton production is high, the saturation of oxygen can occur during the daytime. The solubility of oxygen in water depends on temperature and other factors. The presence of oxygen is essential for the survival of aquatic life in water. A rapid fall of DO in river water is one of the first indications of pollution.

Dissolved oxygen (DO) levels in environmental water depend on the physiochemical and biochemical activities in the water body and it is important and useful in pollution and waste treatment process control. Oxygen reacts with Mangnous hydroxide to form higher hydroxides, which, when acidified, liberate iodine equivalent to the amount of oxygen fixed. This iodine is titrated with a standardized Sodium thiosulfate solution using starch as an indicator.

Two methods are commonly used to determine to DO concentration: (1) The iodometric method which is a titration-based method and depends on the oxidizing property of DO and (2) The membrane electrode procedure, which works based on the rate of diffusion of molecular oxygen across a membrane.

Significance:

- It is necessary to know the DO level to assess quality of raw water and to keep a check on stream pollution.
- A minimum DO of 4 to 5 mg/l is desirable for the survival of aquatic life.
- Higher values of DO may cause corrosion of Iron and steel.
- DO test is used to evaluate the pollution strength of domestic and industrial wastes.

Winkler's Modified Method:

The Winkler's Method is the technique used to measure DO in freshwater structures. It is used as an indicator of the health of a water body, where higher DO concentrations are associated with high production and little contamination. This test is performed on-site, as delays between sample collections and testing may result in a variation in oxygen content.

In this method of analysis the oxygen present in the water sample oxidizes the divalent manganous ion to its higher valency, which precipitates as a brown hydrated oxide after addition of sodium hydroxide (NaOH) and potassium iodide (KI). Upon acidification, manganese reverts to divalent state and liberates iodine from KI equivalent to DO content in the sample. The liberated iodine is titrated against sodium thiosulphate (0.01N), using freshly prepared 1% starch solution as indicator. If the oxygen is absent in the sample, the $MnSO_4$ react with the alkali to form white precipitate $Mn(OH)_2$.

When $MnSO_4$ and alkali-iodide reagent (NaOH + KI) are added to a sample in the absence of oxygen, a pure white precipitate is formed.

$$Mn^{2+} + 2OH^- \rightarrow Mn\ (OH)_2 \text{ (white precipitate)}$$

Mn^{2+} is oxidized to Mn^{4+} and precipitates brown hydrated oxide in the presence of oxygen.

$$Mn^{2+} + 2OH^- + 0.5O_2 \rightarrow MnO_2 \text{ (brown hydrated precipitate)} + H_2O$$

The oxidation of Mn^{2+} to MnO_2 is called fixation of the oxygen, and occurs slowly at low temperature.

$$Mn(OH)_2 + 0.5O_2 \rightarrow MnO_2 + H_2O$$

After the floc has settled, sulfuric acid is added. MnO_2 is oxidized to produce I_2 under low pH conditions. I_2 is insoluble in water and forms complexes when there is an excess of iodide ions in solution, preventing iodine ions from escaping.

$$MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O$$

$$I_2 + I^- \leftrightarrow I_3$$

The sample is now ready to be titrated with thiosulfate solution. The reaction between thiosulphate and iodine can be represented as below

$6\ Na_2S_2O_3 + 3I_2 \rightarrow \quad 3\ Na_2S_4O_6 + 6NaI$

Procedure:

Take 100 mL water sample in a conical flask. Add 1 ml $MnSO_4$ solution and 1 mL alkaline KI solution to it. Shake the flask and cover the mouth of the flask with a paper. Keep the flask for 5 mins for settling the brown precipitate. Add 1-2 mL conc. H_2SO_4 and shake well to dissolve the precipitate. The solution becomes brown. Titrate this solution with the standard hypo ($Na_2S_2O_3$) solution. When the brown color changes to pale yellow, add 1-2 mL starch (1%) solution to it. Continue the titration till the dark brown/ violet color changes to colorless which is the endpoint of the titration. Repeat the titration to get concordant volume. Calculate the amount of dissolved oxygen in ppm.

Table:

Sl no	Volume of supplied solution (mL)	Burette reading (mL)		Vol. of hypo consumed (ml)	Concordant volume of hypo (ml)
		Initial	Final		
1.	100				Z
2.	100				
3.	100				

Calculation:

Given, the strength of hypo solution= 0.01N

1000ml 1N hypo ($Na_2S_2O_3$) solution= 8 gm of oxygen

1ml 1N hypo ($Na_2S_2O_3$) solution= 0.008 gm of oxygen

1ml 1N hypo ($Na_2S_2O_3$) solution= 8 mg of oxygen

Z ml 0.01N hypo ($Na_2S_2O_3$) solution= 8 x 0.01 x Z mg oxygen

Dissolved oxygen/L $= \frac{8\ x\ 0.01\ x\ Z\ x\ 1000}{100} ppm$

Conclusion:

Amount of dissolved oxygen= _____ mg/L (ppm)

Experiment 5

Aim of the experiment: Determination of total alkalinity of supplied aqueous solution

Introduction:

Alkalinity is the presence of sufficient alkaline ions in water. The absence of alkalinity makes the water acidic. Water is said to be alkaline when pH of water is above 7.00. The determination of alkalinity is very useful in water and waste water because it provides buffering to resist changes in pH value. The alkalinity and acidity in water usually changes in natural waters with large algal growth. The alkalinity of natural waters is primarily due to the salts of week acids and bicarbonates represent the major form of alkalinity. Alkalinity can be expressed as follows:

$$\text{Alkalinity (mol/l)} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

The presence of alkalinity in surface waters primarily indicates the concentration of carbonate, bicarbonate and hydroxide contents. Alkalinity in excess of Alkaline earth metal concentrations is significant in determining the suitability of water for irrigation. Alkalinity measurements are used in the interpretation and control of water and waste water treatment processes. Raw domestic waste water has an alkalinity less than or only slightly greater than that of the water supply.

Alkalinity of water is the capacity of water to neutralize acid. It is usually expressed as Total Alkalinity or Caustic Alkalinity in water. It is significant in many uses and treatments of natural waters and wastewaters. Alkalinity is measured titrimetrically by titrating against dilute Sulphuric Acid. Phenolphthalein and Methyl Orange are used as indicator to indicate pH 8.3 and pH 4.3. Phenolphthalein process a pink color when pH is above 8.3 and colorless when pH is below 8.3.

Natural water alkalinity is caused primarily by the presence of weak acid salts, though strong bases (i.e. OH^-) may also contribute in extreme environments. Bicarbonates are the most

common type of alkalinity found in natural waters, and they are formed by the partitioning of CO_2 from the atmosphere and the weathering of carbonate minerals in rocks and soil. Other salts of weak acids, such as borate, silicates, ammonia, phosphates, and organic bases from natural organic matter, may be present in small amounts. Alkalinity is frequently identified as mg/L $CaCO_3$ because the majority of alkalinity is derived from the weathering of carbonate minerals.

Titration with standardized acid determines the total amount of hydroxyl ions in a solution. This is a well-known water-analysis procedure for estimating the concentrations of hydroxyl, carbonate ion, and bicarbonate ions. This titration has two pH endpoints, P and M, which correspond to the phenolphthalein and methyl orange indicators.

As previously stated, alkalinity in natural waters is primarily caused by carbonate species, and the following chemical equilibriua are established in waters.

$$CO_2 + H_2O <=> H_2CO_3^*$$

$$H_2CO_3 <=> HCO_3^- + H^+$$

$$HCO_3^- <=> CO_3^{2-} + H^+$$

where $H_2CO_3^*$ represents the total concentration of dissolved CO_2 and H_2CO_3. The first chemical equation represents the equilibrium of CO_2 in the atmosphere with dissolved CO_2 in the water. The equilibrium constant, Henry's Law, for this reaction is

$$K_{CO_2} = \frac{[H_2CO_3]}{P_{CO_2}} = 10^{-1.47}$$

The equilibrium relationships for the last two reactions may be expressed as

$$K_1 = \frac{[H^+][HCO_3^-]}{H_2CO_3} = 10^{-6.35}$$

Procedure:

Take 100 ml of water sample in a conical flask and add 2-3 drops of phenolphthalein indicator. If the color changes to pink, then titrate the solution with standard sulphuric acid solution. (Note: If there is no color change with the addition of phenolphthalein indicator, then titration is not necessary). Then add 2-3 drops of methyl orange indicator to the same solution when the color changes to yellow. Now titrate the solution again with the same sulphuric acid solution until the color of the solution changes to reddish/orange color which is the end point of the titration. Repeat the titration until concordant volume is obtained.

Table1:

Sl no	Volume of sample taken (mL)	Burette reading (ml)		Vol. of acid used (ml) with phenolphthalein indicator	Concordant volume (ml)
		Initial	Final		
4.	100				A
5.	100				
6.	100				

Table2:

Sl no	Volume of sample taken (mL)	Burette reading (ml)		Vol. of acid used (ml) with methyl orange indicator	Concordant volume (ml)
		Initial	Final		
7.	100				B
8.	100				
9.	100				

Calculation:

Strength of sulphuric acid= 0.01 N

Total alkalinity as CaCO3= $\frac{\{(A+B)\ x\ normality\ of\ \mathrm{H2SO4}\ x\ 50\ x\ 1000\}}{vol\ of\ sample}$ ppm

Where A= ml of H_2SO_4 acid with phenolphthalein indicator

B= ml of H_2SO_4 acid with methyl orange indicator

Conclusion:

Total alkalinity of water as $CaCO_3$ = _____ ppm