EXPERIMENT – 1 | Estimation of Hardness of Water by EDTA Method

INTRODUCTION

Water hardness is the traditional measure of the capacity of water to precipitate soap. Hard water requiring a considerable amount of soap to produce leather. Scaling of hot water pipes, boilers and other house hold appliances is due to hard water. Hardness of water is no specific constituent but is a variable and complex mixture of cations and anions. It is caused by dissolved polyvalent metallic ions. In fresh water, the principle hardness causing ions are calcium and magnesium. The other ions like Strontium, Iron, Barium and Manganese also contribute. Hardness is commonly expressed as $CaCO_3$ in mg/L. The degree of hardness of drinking water has been classified in terms of the equivalent $CaCO_3$ concentration as follows:

Soft	0-60 mg/L;
Medium	60-120 mg/L;
Hard	120-180 mg/L;
Very hard	> 180 mg/L;

Although hardness is caused by cation, it may also be discussed in terms of carbonate (temporary) and non-carbonate (permanent) hardness. Carbonate hardness refers to the amount of carbonates and bicarbonates in solution that can be removed or precipitated by boiling. This type of hardness is responsible for the deposition of scale in hot water pipes and kettles. When total hardness is numerically greater than that of total alkalinity expressed as $CaCO_3$, the amount of hardness equivalent to total alkalinity is called 'carbonate hardness'. The amount of hardness in excess of total alkalinity expressed as $CaCO_3$ is non-carbonate hardness. Non carbonate hardness is caused by the association of the hardness of causing cation with sulphate, chloride or nitrate and is referred to as "permanent hardness" because it can not be removed by boiling.

AIM

To estimate the amount of total hardness (Ca & Mg) present (as $CaCO_3$) in the given water sample by EDTA method.

APPARATUS

1. Conical flasks (100 mL)   2. Burette   3. Pipette   4. Spatula

CHEMICALS

1. Buffer solution   2. Inhibitor   3. Eriochrome black T indicator
4. Muroxide Indicator   5. NaOH (2N)   6. Standard EDTA Solution 0.01M
7. Standard Calcium Solution

THEORY

When Eriochrome Black T dye is added to the hard water at pH around 10 it gives wine red coloured unstable complex with Ca^{+2} and Mg^{+2} ions of the sample water. Now when this wine red-coloured
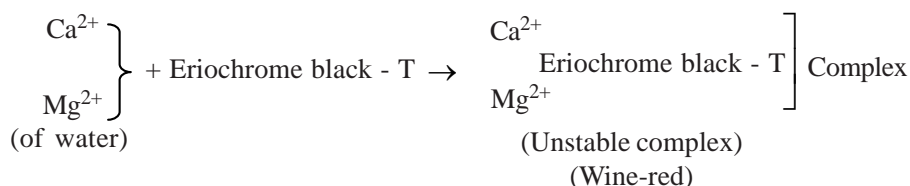
complex is titrated agianst EDTA solution (of known strength) the colour of the complex changes wine red to original blue colour showing the endpoint.

$$NaOOCH_2 \diagdown \atop HOOCCH_2 \diagup N - CH_2 - CH_2 - N \diagup CH_2COOH \atop \diagdown CH_2COONa$$
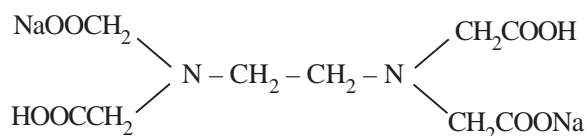
Disodium salt of ehtylenediamine tetraacetic acid: (Na_2H_2Y)

     where Y = deprotonated agent.

In aqueous solution EDTA ionises to give $2Na^+$ ions and act as a strong chelating agent.

$$\left. \begin{matrix} Ca^{2+} \\ \\ Mg^{2+} \end{matrix} \right\} + \text{Eriochrome black - T} \rightarrow \left. \begin{matrix} Ca^{2+} \\ \quad \text{Eriochrome black - T} \\ Mg^{2+} \end{matrix} \right] \text{Complex}$$

(of water)   (Unstable complex)

                                           (Wine-red)

$$\text{EDTA} \quad \left[\begin{matrix} Ca^{2+} \\ \quad \text{EDTA} \\ Mg^{2+} \end{matrix} \right] \text{Complex} + \text{Eriochrome black - T}$$

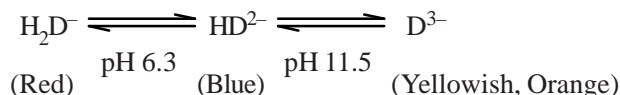   (blue)

The indicator used is a complex organic compound (sodium – 1 – (1-hydroxy 2-naphthylazo)-6-nitro-2-naphthol-4-sutphonate), commonly known as Eriochrome black T(EBT). It has two ionisable phenolic hydrogen atoms and for simplicity it is represented as $Na^+H_2In^-$:
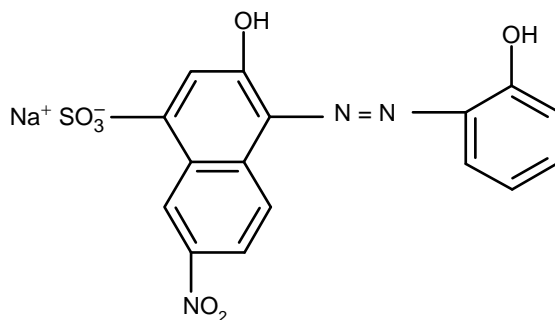

Eriochrome Black-T

Eriochrome Black-T(EBT) is the metal ion indicator used in the determination of hardness by complexometric titration with EDTA. This dye-stuff tends to polymerize in strongly acidic solutions to a red brown product, and hence the indicator is generally used in EDTA titration with solutions having pH greater than 6.5. The sulphuric acid gropus loses its proton much before the pH range of 7-12, which is of interest for metal ion indicator use. The dissociation of the two hydrogen atoms of the phenolic groups only should therefore be considered and hence the dye stuff may be represented by the formula
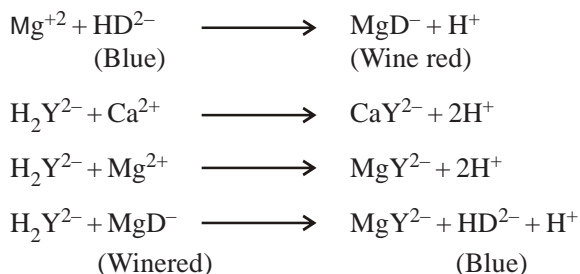
H_2D^-. This functions as acid-base indicator with two colour changes as follows:

$$H_2D^- \underset{\text{pH 6.3}}{\rightleftharpoons} HD^{2-} \underset{\text{pH 11.5}}{\rightleftharpoons} D^{3-}$$

(Red)   (Blue)   (Yellowish, Orange)

In the pH range 8-10, the blue form of the indicator HD^{2-} gives a wine red complex with Mg^{2+}:

$$Mg^{+2} + HD^{2-} \longrightarrow MgD^- + H^+$$

(Blue)   (Wine red)
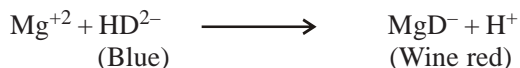
Now if EDTA (H_2Y^{2-}) is added to such a solution Mg^{2+} preferentially complexes with EDTA (since the metal EDTA complex is more stable than the metal-indicator complex) and liberates the free indicator HD^{2-} at the end point, thereby producing a sharp colour change from wine red to blue. These reactions during the EDTA titration may be summarized as follows

$$Mg^{+2} + HD^{2-} \longrightarrow MgD^- + H^+$$

(Blue)   (Wine red)

$$H_2Y^{2-} + Ca^{2+} \longrightarrow CaY^{2-} + 2H^+$$

$$H_2Y^{2-} + Mg^{2+} \longrightarrow MgY^{2-} + 2H^+$$

$$H_2Y^{2-} + MgD^- \longrightarrow MgY^{2-} + HD^{2-} + H^+$$

(Winered)   (Blue)

The metal ion-indicators of common use in EDTA titrations include:

Eriochrome Black-T (or Solochrome Black), Muroxide (ammonium salt of purpuric acid), Eriochrome Blue-Black B (or Solochrome Black-6B), Patton and Reeders indicator, Solochrome Dark Blue or Calcon, Zincon, Xylenon Orange .... etc.

The optimum pH for the determination of hardness of water is 10.0 + 0.1 and is adjusted by NH_4 OH – NH_4Cl buffer.

Advantages of EDTA method

This method is definitly preferable to the other methods, because of :

  (i)   Greater accuracy,

  (ii) convenience and

  (iii) more rapid procedure.

Units of Hardness

The followng units are used for expressing results.

1. *Parts per million (PPM) :* It is the number of parts of calcium carbonate equivalent hardness present in one million parts of water.
2. *Milligram per lite (mg/L):* It is the number of milligrams of Calcium carbonate equivalent hardness present in one litre of water.
3. *Degree Clarke (^{o}Cl):* It is the number of parts of $CaCO_3$ equivalent hardness present in 70,000 parts of water.
4. *Degree French (^{o}Fr):* It is the number of parts of $CaCO_3$ equivalent hardness present in 10^5 (1 Lac) parts of water.

The above four units are correlated as given below

$$1PPM = 1mg/L = 0.07^o \text{ Cl} = 0.1^oFr$$

Determination of Hardness

The following of any given water sample may be determined by the following methods.

  (i)   O.Hehner's method

 (ii)   Soap titration method

(iii)   EDTA method

EDTA Method

PREPARATION OF REAGENTS

1. *Buffer solution:* Dissolve 16.9 g NH_4Cl in 143 ml NH_4OH. Add 1.25 g magnesium salt of EDTA to obtain sharp change in colour of indicator and dilute to 250 ml. If magnesium salt of EDTA is not available, dissolve 1.179 g disodium salt of EDTA (AR grade) and 780 mg $MgSO_4.7H_2O$ or 644 mg $MgCl_2.6H_2O$ in 50 ml distilled water. Add this to above solution of NH_4Cl in NH_4OH and dilute to 250 ml.

2. *Inhibitor:* Dissolve 4.5 gm hydroxyl amine hydrochloride in 100 ml 95% ethyl alcohol or isopropyl alcohol.

3. *Eriochrome black T(EBT) indicator:* Mix 0.5 gm dye with 100 gm NaCl to prepare dry powder.

4. *Muroxide Indicator:* Prepare a ground mixture of 200 mg of murexide with 100 gm of solid NaCl.

5. *NaOH (2N):* Dissolve 80 gm NaOH and dilute to 1000 ml.

6. *Standard EDTA Solution 0.01M:* Dissolve 3.723 gm EDTA disodium salt and dilute to 1000 ml. Standardized against standard calcium solution, 1ml =1mg $CaCO_3$

7. *Standard Calcium Solution:* Weigh accurately 1gm $CaCO_3$ and transfer to 250 ml conical flask. Then add 1:1 HCl till $CaCO_3$ dissolve completely. Add 200 ml dist.water and boil for 20 to 30 min. then cool and add methyl red indicator. Add NH_4OH 3N drop wise till intermediate orange colour develops. Dilute to 1000 ml to obtain 1ml=1mg $CaCO_3$.

PROCEDURE

(a) Total hardness

   (i)   Take 25 or 50 ml or well mixed sample in a conical flask

  (ii)   Then add 1 to 2 ml buffer solution followed by 1 ml inhibitor

 (iii)   Add a pinch of Eriochrome black T and titrate with standard EDTA (0.01M) till **wine red** colour changes to **blue,** then note down the volume of EDTA required (**A**) .

 (iv)   Run a reagent blank. Note the volume of EDTA (**B**).

  (v)   Calculate volume of EDTA required by sample, **C = A – B** (from volume of EDTA required in steps (iii & iv).

(b) Calcium hardness

   (i)   Take 25 or 50 ml sample in a conical flask

  (ii)   Add 1 ml NaOH to raise pH to 12.0 and add a pinch of muroxide indicator.

(iii) Titrate immediately with EDTA till pink colour changes to **purple**. Note the volume of EDTA used (A_1).

(iv) Run a reagent blank. Note the ml of EDTA required (B_1) and keep it aside to compare end points of sample titrations.

(v) Calculate the volume of EDTA required by sample, $C_1 = A_1 - B_1$.

OBSERVATIONS AND CALCULATIONS

Water Sample Vs EDTA

S. No	Volume of water sample (ml)	Burette Reading		Volume of EDTA added (ml)
		Initial (ml)	Final (ml)	
1.				
2.				
3.				
4.				

(i) Total hardness as $CaCO_3$, mg /l $= \dfrac{C \times D \times 1000}{\text{Volume of sample in ml}}$

Where

C = Volume of EDTA required by sample (with EBT indicator)

D = mg $CaCO_3$ equivalent to 1 ml EDTA titrant (1 ml 0.01 MEDTA ≡ 1.000 mg $CaCO_3$)

$$\text{or } (D = 1 \times \frac{\text{Molarity of EDTA}}{0.01M})$$

(ii) Calcium hardness as $CaCO_3$, mg /l $= \dfrac{C_1 \times D \times 1000}{\text{Volume of sample in ml}}$

Where

C_1 = volume of EDTA used by sample (with murexide indicator)

D = mg $CaCO_3$ equivalent to 1 ml EDTA titrant

(iii) Magnesium hardness

Magnesium Hardness = Total hardness as $CaCO_3$, mg/l – Calcium hardness as $CaCO_3$, mg/l.

RESULT

Amount of total hardness present in the given water sample = ——— mg/l