EXP. No: 05	DETERMINATION OF HARDNESS OF WATER
DATE:	

Aim: To determine the total hardness of water by complexometric titration using EDTA solution.

Apparatus required: Burette, pipette, conical flask, volumetric flask, funnel, beaker, dropper etc.

Chemicals required: EDTA solution, standard $CaCl_2$ solution, given water sample,

buffer solution of pH = 10, Eriochrome black T Indicator etc.

Principle:

Total hardness of water is due to the presence of water-soluble bicarbonates, sulfates, chlorides, and nitrates of calcium and magnesium. Total hardness is the sum of temporary and permanent hardness. Temporary hardness is due to the presence of bicarbonates of calcium and magnesium which easily get decomposed when heated and form carbonates. Thus temporary hardness is also known as carbonate hardness.

Upon heating,

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2$$

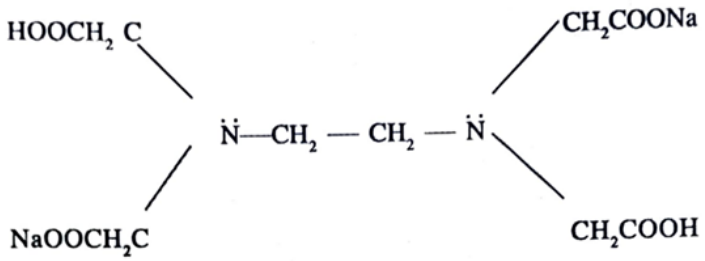
The hardness of water depends upon the concentration of $CaCO_3$.

Type of water sample	**Concentration of $CaCO_3$ (ppm)**
Soft	0 - 75 ppm
Moderately hard	75 - 150 ppm
Hard	150 - 300 ppm
Very hard	> 300 ppm

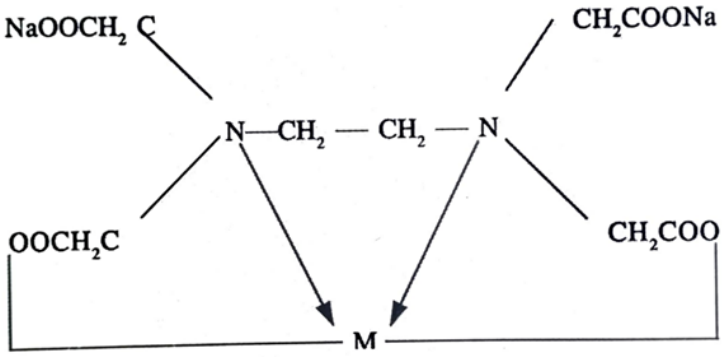
Permanent hardness arises from sulfates, chlorides, and nitrates of calcium and magnesium in water. To quantify the total hardness in a water sample, EDTA (ethylene diamine tetraacetic acid) is employed. The disodium salt of EDTA is chosen for water analysis because it effectively forms stable metal complexes with various metals, functioning as a superior chelating agent. The efficiency of EDTA complex formation is influenced by the pH of the solution and is most favorable under basic conditions. Therefore, an alkaline buffer of $NH_4OH + NH_4Cl$ is used to achieve optimal results.

This method is highly accurate due to the reaction of Eriochrome black-T (a blue dye) with hard water in an alkaline environment (around pH 10), which produces a wine-red unstable complex with Ca^{2+} and Mg^{2+} ions.

EDTA (ethylene diamine tetra acetic acid) takes Ca^{2+} and Mg^{2+} ions from the unstable Ca^{2+} chrome black - T and Mg^{2+} chrome black T complex and forms a colourless stable complex with the generation of blue coloured dye (Eriochrome black - T). Thus the colour of dye changes from wine red of its original blue colour at the endpoint.



Disodium salt of EDTA



Metal- Ca^{2+}, Mg^{2+}

Chemical Reaction:

1) **Ca^{2+} + Eriochrome black -T** (blue dye) → **Ca-EBT** (wine red complex)

   i.e. Metal + Indicator → Metal indicator complex

2) **Ca-EBT + EDTA → Ca-EDTA** (colorless complex) + **Eriochrome black -T** (blue dye)

   (Metal Indicator) + EDTA Metal →Metal EDTA (colourless complex) + **Indicator** (blue dye)

Procedure:

Part I - Standardization of EDTA Solution:

1. Rinse the burette with a little quantity of EDTA solution and fill it up to the mark.

2. Pipette out 10 ml of standard $CaCl_2$ solution in a conical flask.

3. Add half of the test tube of the buffer solution to it.

4. Then add a pinch of Eriochrome black T indicator.

5. Titrate the solution with EDTA solution till the wine red color changes to sky blue.

6. Repeat the procedure 3 to 4 times till you get a constant titration reading. Let the volume used be X ml.

Part II - Estimation of Total Hardness:

1. Pipette out 10 mL of the water sample in a conical flask.

2. Add half the test tube of buffer solution to it.

3. Then add a pinch of Eriochrome black T indicator.

4. Titrate the solution with EDTA solution till the wine red color changes to sky blue.

5. Repeat the procedure 3 to 4 times till you get a constant titration reading. Let the volume used be Y ml.

Observations:

Part I - Standardization of EDTA Solution:

In Burette - EDTA solution

In conical flask - 10 mL standard solution of $CaCl_2$ or hard water

Indicator- EBT

Endpoint - Wine red to sky blue

Observation Table (Part 1)

Sr. No.	Pilot Reading (ml)	Burette Reading (ml) accurate			M.B.R. (mL)
		I	II	III	
1	Final				X mL
2	Initial				
3	Difference				

Volume of EDTA used = …….. mL (x)

Part II - Estimation of Total Hardness:

In Burette - EDTA solution

In conical flask - 10 mL of given water sample

Indicator- EBT

Endpoint - Wine red to sky blue

Observation Table (Part 2)

Sr. No.	Pilot Reading (ml)	Burette Reading (ml) accurate			M.B.R. (mL)
		I	II	III	
1	Final				Y mL
2	Initial				
3	Difference				

Volume of EDTA used = …. mL (Y)

Calculations:

Standardization of EDTA:

As,

1 ml of standard hard water = 1 mg of $CaCO_3$ equivalent hardness

10 ml of standard hard water = 10 mg of $CaCO_3$ equivalent hardness

10 ml of standard hard water = X mL of EDTA

10 mg of $CaCO_3$ equivalent hardness = X mL of EDTA

So, 1 mL of EDTA = 10/ X mg of $CaCO_3$ equivalent hardness.

Now,

10 mL of given water sample = Y mL of EDTA

= Y × 1 mL of EDTA

= Y ×10 / X mg of $CaCO_3$ equivalent hardness

1000 mL of given water = (Y × 10×1000) / (10× X) mg/litre or ppm

Total hardness of given water sample = (Y × 1000) / X ppm

= ……..mg/litre or ppm

Result:

Total hardness of the given sample of water is

1: In mg/litre …….

2: In ppm …..

3:In ^{o}Cl……

4: In ^{o}Fr…..

1 ppm = 1 mg/lit = 0.07 ^{o}Cl = 0.1 ^{o}Fr

Exercise:

1. What is Complexometric titration?

2. Why is the hardness of water necessary to determine?

3. Why is hard water unfit for drinking?

4. 1.0 gm of $CaCO_3$ was dissolved in HCl and the solution was made up to 1000 ml with distilled water. 50 ml of the solution required 45 ml of EDTA solution for titration. 50 ml of hard water sample required 28 ml of EDTA and after boiling and filtering required 15 ml of EDTA solution. Calculate the hardness of water.

Components	**Max Marks**	**Marks Awarded**
Write Up	**2**	
Understanding	**3**	
Performance	**3**	
Timely Submission	**2**	
Total Marks	**10**	