

## Experiment - 2

**Aim-** Determination of hardness in the given water sample.

**Objective-** To determine the temporary and permanent hardness of a given water sample by titrating it against a standard (M/100) solution of disodium salt of Ethylenediaminetetraacetic acid (EDTA) using Eriochrome Black (T) (EBT) as an internal metallochromic indicator via complexometric titration.

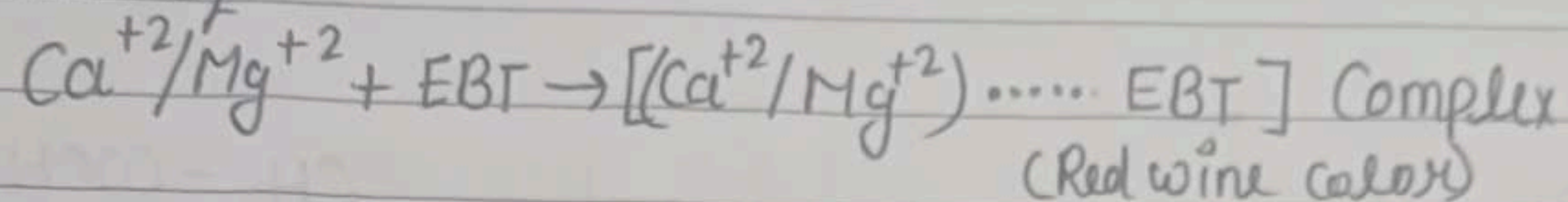
### Theory:-

- The Total amount of soluble salts of calcium and magnesium present in water is known as hardness, and water containing these salts is called hard water.
- It is due to the presence of bicarbonates, sulfates and chlorides of calcium and magnesium salts.
- It is determined by complexometric titration.
- EDTA is used as a complexing reagent.
- The calcium and magnesium ions present in water are complexometrically titrated with EDTA using EBT as an internal indicator.
- The indicator Eriochrome Black T (EBT), which is a blue-colored organic dye, forms an unstable complex with calcium and magnesium ions in hard water at  $\text{pH} = 10$ .

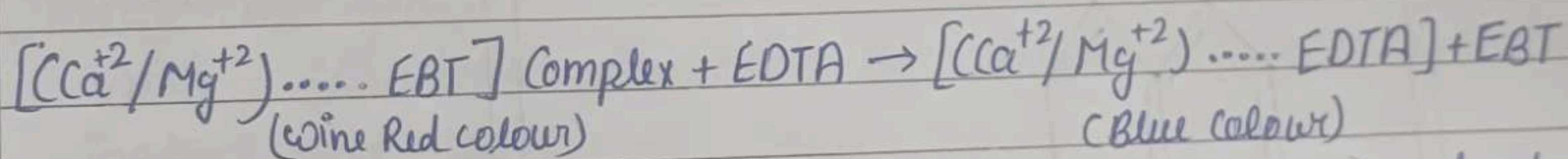
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The Complex formed is wine-red in color.

chemical eq<sup>n</sup> -



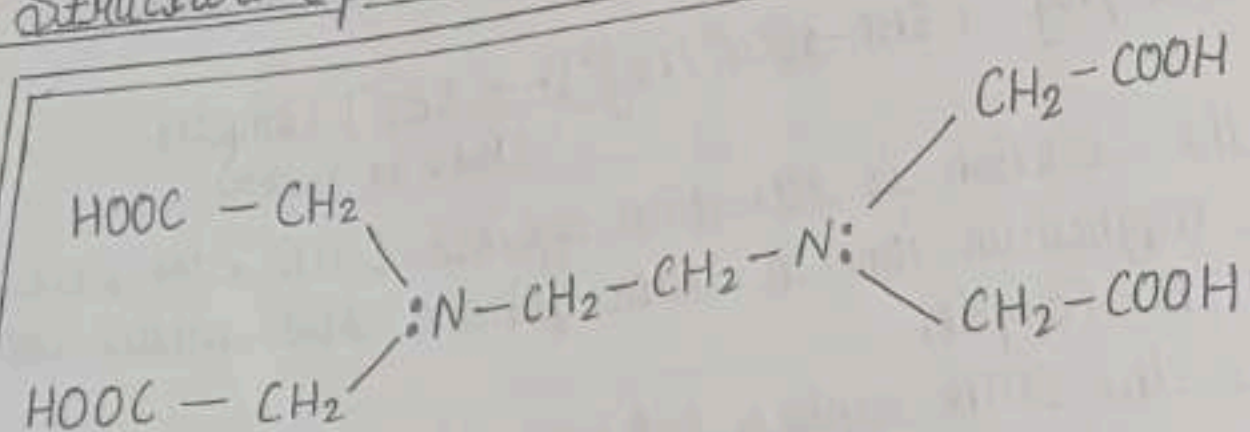
- As the solution is titrated against EDTA, the free Calcium and magnesium ions in water form a stable metal ion-EDTA complex.
- Once the EDTA replaces calcium and magnesium ions from the unstable indicator complex to form a stable complex, the indicator is set free. Since the indicator (EBT) is blue color at pH=10, the end point is marked by the appearance of a blue color.



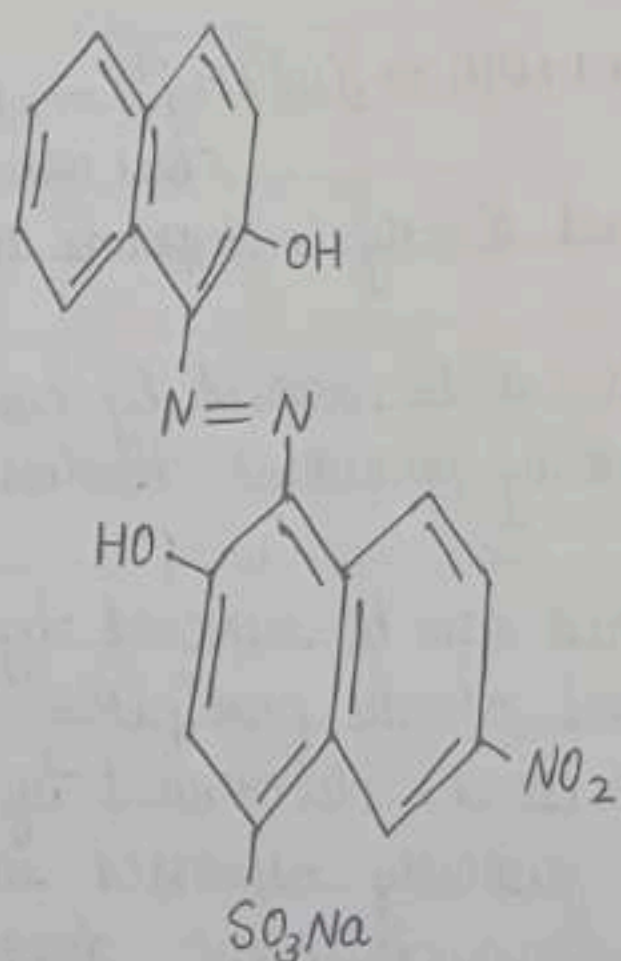
- The amount of EDTA used directly corresponds to the hardness of water.
- the temporary hardness can be removed by boiling. It is calculated by subtracting permanent hardness from the total hardness.
- the temporary hardness can be removed by boiling, and after the removal of the precipitate, the permanent hardness in the filtrate is determined by titrating with EDTA.
- Hardness in water is generally expressed in terms of calcium carbonate ( $\text{CaCO}_3$ ) equivalent because it is the most insoluble salt and its molecular weight is 100, which makes the calculation easy.

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### Structure of EDTA



### Structure of EBT



Sodium-[1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-Sulfonate]

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Apparatus - Burette, pipette, conical flask, beaker, dropper and funnel.

Chemicals - Standard solution of m/100 EDTA, hard water sample, boiled water sample, buffer solution ( $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ )

Indication - Eriochrome black-T (EBT)

### Experimental Procedure:-

Rinse the glassware with distilled water, fill the burette with standard solution of m/100 EDTA solution. Pipette out 10 ml of hard water sample in a conical flask and 2 ml of buffer solution ( $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ ) then add two drops of EBT indicator to it. The solution turns into wine red colour. Titrate this wine red colour solution with m/100 EDTA till the solution becomes blue in colour. This is the end point of titration. Repeat the process till two concordant readings are obtained. Repeat the above process with boiled water.

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Crystal field effects and nature of ligands  
 order which is called natural order, is sometimes also called the spectrochemical series.  
 William Order of Stability: This series is consistent with the order of increasing ionic potential (charge/radius) of the metal ions.  
 $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$   
 are primarily octahedral complexes. Transition elements are

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Observations:-

for hard water Sample [Total hardness]

| S.No. | Volume of hard water taken in flask | Burette reading (ml) |         |            | Volume of m/100 EDTA Sol <sup>n</sup> |
|-------|-------------------------------------|----------------------|---------|------------|---------------------------------------|
|       |                                     | Initial              | Final   | Difference |                                       |
| 1.    | 10 ml                               | 0 ml                 | 18.0 ml | 18.0 ml    | 18 ml.                                |
| 2.    | 10 ml                               | 0 ml                 | 18.5 ml | 18.5 ml    |                                       |
| 3.    | 10 ml                               | 0 ml                 | 18.0 ml | 18.0 ml    |                                       |

- Calculation:-
- 10 ml of hard water = 18 ml of EDTA
- 1000 ml of hard water =  $18/10 \times 1000 = 1800$  ppm (or mg/L as  $CaCO_3$ )
- Total hardness = 1800 ppm.

for Boiled Distilled water Sample [permanent Hardness]

| S.No. | Volume of Boiled water in flask | Burette readings ml |        |            | Volume of m/150 EDTA Sol <sup>n</sup> ml |
|-------|---------------------------------|---------------------|--------|------------|------------------------------------------|
|       |                                 | Initial             | Final  | Difference |                                          |
| 1.    | 10 ml                           | 0                   | 5.0 ml | 5.0 ml     | 5 ml                                     |
| 2.    | 10 ml                           | 0                   | 4.7 ml | 4.7 ml     |                                          |
| 3.    | 10 ml                           | 0                   | 5.0 ml | 5.0 ml     |                                          |

- Calculation:-
- 10 ml of boiled water = 5 ml of EDTA
- 1000 ml of boiled water =  $5/10 \times 1000 = 500$  ppm (or mg/L as  $CaCO_3$ )
- permanent hardness = 500 ppm.

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Order of Stability: This series is consistent in the order:  
 $\text{Fe}^{2+} (= 0.83) > \text{Co}^{2+} (= 0.82) > \text{Ni}^{2+} (= 0.79)$   
These ions are primarily octahedral complexes. The transition elements as

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$$\begin{aligned} \text{for Temporary Hardness} &= \text{Total Hardness} - \text{Permanent hardness} \\ &= 1800 \text{ ppm} - 500 \text{ ppm} = 1300 \text{ ppm} \end{aligned}$$

Result :- The given water sample contains following types of hardness

- Total hardness : 1800 ppm
- Permanent hardness : 500 ppm
- Temporary hardness : 1300 ppm

Result analysis and discussion: It is important to determine the hardness of water because hard water causes excessive consumption of soap used for cleaning purposes. In industries using high-temperature boilers, calcium and magnesium carbonate precipitate. This forms scales in boilers, water pipes, and vessels which reduces the efficiency of the boiler.

The results obtained from the above experiment show that both water samples have different hardness values. The value of hardness for the first sample is \_\_\_\_\_ ppm and for the second sample is \_\_\_\_\_ ppm.

The difference in hardness values arises due to the fact that the first sample, which shows higher values of hardness (ppm), contains both types of hardness.

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