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Expt: 1

DETERMINATION OF HARDNESS OF WATER

Aim: To determine the Total Hardness (CH+NCH) of water sample.

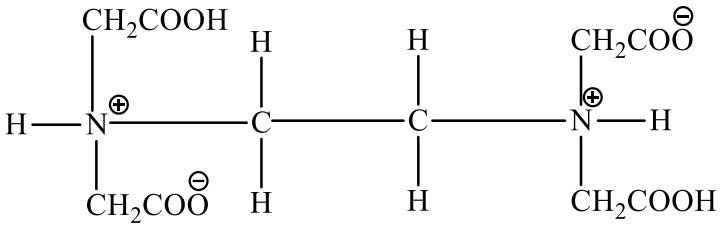
Principle:

The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of Ca and Mg. Temporary hardness or carbonate hardness (CH) is due presence of bicarbonates of Ca and Mg; which could be removed by boiling.

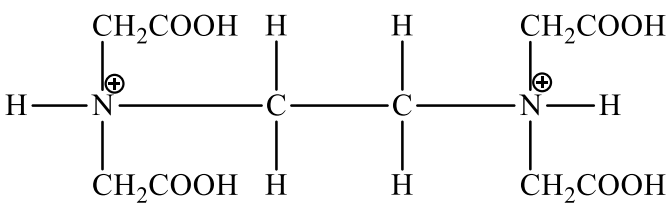
Permanent or non-carbonate hardness (NCH) is due to the presence of chlorides and sulphates of Ca and Mg. Hardness is usually expressed in terms of an equivalent amount of $CaCO_3$ (Eq. Wt. = 50; Mol.Wt. = 100). CH can be determined by titration against standardized HCl using methyl orange as an indicator. NCH can be determined by precipitation of Ca^{++} and Mg^{++} as $CaCO_3$ and $Mg(OH)_2$ respectively, by boiling with known excess of the soda reagent ($NaOH + Na_2CO_3$) filtering the precipitates and titrating the unused soda reagent against HCl as before. Soda reagent is not consumed by CH.

$$M(HCO_3)_2 + 2NaOH \rightarrow MCO_3(s) + Na_2CO_3 + 2H_2O$$

A more accurate method is based on the formation of 1:1 complexes with ethylene diamine tetraacetate ion (EDTA) by Ca^{++} and Mg^{++}
The formula of the ion of the disodium salt, Na_2H_2Y is represented as H_2Y^{2-} or as



Zwitter Ions(I)



Zwitter Ions(II)

The sodium salt ($Na_2C_{10}H_{14}O_8N_2.2H_2O$) has a Mol. Wt. of 372.2 and is normally used in 0.01M concentrations. H_2Y^{2-} forms single complex species with most metal ions except alkali metal ions and whatever be the charge on the metal ion, the complex has the formula MY.

$$M^{2+} + H_2Y^{2-} \longrightarrow MY^{2-} + 2H^+$$

$$M^{3+} + H_2Y^{2-} \longrightarrow MY^{-} + 2H^+$$

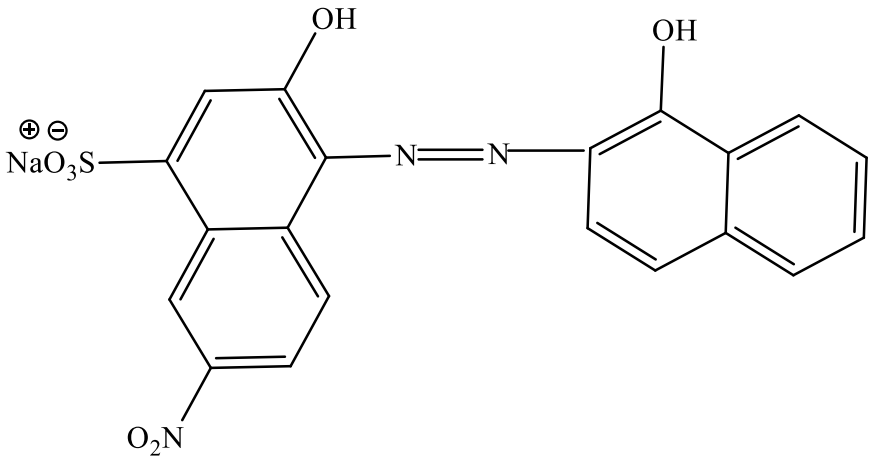
$$M^{4+} + H_2Y^{2-} \longrightarrow MY + 2H^+$$

$$M^{n+} + H_2Y^{2-} \longrightarrow MY^{(n-4)} + 2H^+$$

For such 1:1 complexes to be stable it is clear from the above equilibria that the medium should be alkaline. The pH is kept constant by using NH_3-NH_4Cl buffer mixture (pH-9-10) so that the stability of the complex is not affected by the H^+ ions produced.

Titrations in which a metal ion is titrated against a complexion are called complexometric titrations. Since the concentration of the free metal ion changes as a result of complexation metal-ion-sensitive indicators such as Eriochrome Black – T (EBT) is widely used. This azo-dye forms wine-red coloured complexes with ions of Ca, Mg, Zn, Cd, Hg, Al, Fe(III), Ti(IV) etc.

Sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2napthol-4-sulphonate.



Erio – T (H_2I_n) or Solochrome Black T

Erio – T is an acid-base indicator, the colours at various pH ranges are shown below:

pH		***pH***	
5.3 to7.3	***blue***	***10.5 to 12.3***	***yellow - orange***

in the pH range 7 to 11 the indicator is pale blue, and the presence of Ca^{2+} and Mg^{2+} a pale red colour (wine red colour) develops.

$$Mg^{2+} + HIn^{2-} \longrightarrow MgIn^{-} + H^{+}$$
(wine red)

When a solution contains Ca^{2+} and Mg^{2+} (hard water) buffered to a pH of 9-10 and containing Erio – T indicator is titrated against H_2Y^{2-}, first of all the free Ca^{2+} and Mg^{2+} ions are complexed to give complexes of the type MY^{2-}. When all the free ions are complexed, the H_2Y^{2-} attacks the $MgIn^{-}$ and $CaIn^{-}$ complexes and converts these into the corresponding EDTA complexes, which are colourless.

$$\underset{\text{(wine red)}}{MgIn^{-}} + H_2Y^{2-} \longrightarrow \underset{\text{(blue)}}{MgY^{2-}} + HIn^{2-} + H^{+}$$

Since the indicator is set free in this reaction and at the pH 9-10, the solution assumes the blue colour of the indicator. Hence the end point is the sharp change of colour from wine red to pale blue.

The total hardness is first determined by titrating the sample of water against EDTA. An equal volume of the sample is boiled to decompose the bicarbonates of Ca and Mg and after filtering off the precipitate, the filtrate is titrated against EDTA. From this titre value, the NCH can be calculated.

Materials Required:

Chemicals:

1. 0.01M – EDTA (3.72 gm EDTA into 1 L dist. water)

2. Ammonical Buffer pH -10 (NH_4Cl-70 gm + NH_4OH{ammonia solution}-568 mL makeup in 1 L dist. water)

3. EBT Indicator (0.2 gm into 50 mL ethanol)

Glassware:

1. 250mL Conical Flask – 2No.

2. 50mL Burette – 1No.

3. 25mL Pipette – 1No.

4. Measuring Cylinder 25mL – 1No.

5. Measuring Cylinder 10mL – 1No.

6. Glass rod – 1No

7. Dropper – 1No

Procedure:

1. **Total Hardness (CH + NCH)**

Pipette out 25 ml of the sample of water into a clean conical flask, add 2 ml of the buffer solution (pH 9-10), 3-4 drops of EBT indicator. Titrate the wine-red solution against EDTA solution taken in a burette, till the contents of the conical flask assume a blue colour without any reddish tinge. Note down the volume of EDTA used. Repeat with another 25 ml of the sample to get concordant results. Let the volume of the EDTA used be V_1 ml.

Experimental Readings:

S. No.	Volume of Water sample (in ml) taken	Burette readings		*Volume of EDTA in ml (V1)*
		Initial	Final	
1.	**25**			
2.	**25**			

The total hardness in terms of an equivalent amount of $CaCO_3$ is calculated from the fact that.

1ml of 1M EDTA = 100 mg of $CaCO_3$

For x mL of M/100 EDTA,

x ml of 0.01M EDTA = $100 \times x \times \frac{1}{100}$ mg of $CaCO_3$

= y mg of $CaCO_3$

Total hardness of 25 ml of water sample = y mg of $CaCO_3$

So, Total hardness for 1 L of water sample = $y \times \frac{1000}{25}$ mg/L of $CaCO_3$

Total Hardness = ……mg/L or ppm