# Hardness of water

**Hardness is the property or characteristics of water which does not produce lather with soap.**

**How to detect hardness ?**

**Hardness of water can be detected into two ways**

**1. When water is treated with soap solution, if it prevents lathering and forms white scum, the water contain hardness.**

$$2\,C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca + 2Nacl$$

Soap — hardness — hard soap

Producing salt

**Water containing hardness give wine - red colour with Erichrome black - T ( EBT ) indicator.**

Types of hardness :

1. Temporary hardness
2. Permanent hardness

Temporary hardness (or) Carbonate hardness (or) Alkaline hardness

This is due to the presence of bicarbonate of calcium and magnesium.

It can be removed by

1. Boiling the water

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$$

2. Adding lime to the water

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$$

## Permanent hardness (or) Non - Carbonate hardness ( or ) Non - Alkaline hardness:

This is due to the presence of chlorides and sulphates of calcium and magnesium.

It cannot be removed by boiling the water.

It can be removed by

1. Lime - Soda process ($Na_2CO_3$)

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

Soda

2. Zeolite process ( $Na_2Ze$ )

$$CaSO_4 + Na_2Ze \longrightarrow CaZe + Na_2SO_4$$

zeolite

Total  hardness :

The sum of temporary hardness and permanent hardness.

Hardness = Temporary hardness + permanent hardness

Exprssion of hardness in term of equivalents of $CaCO_3$

The Concentration of hardness producing salt is usually expressed in terms of an equivalent amount of $CaCO_3$

$CaCO_3$ is chosen as a standard because, its molecular weight (100 ) and equivalent weight ( 50 ) is a whole number, so the calculation in water analysis can be simplified.

It is most insoluble salt that can be precipitate in water treatment

$$\text{Amount of equivalent to } CaCO_3 = \frac{X \times 100}{\text{Molecular weight of hardness Producing salt}}$$

Where

X = Amount of hardness producing salt

100 = molecular weight of $CaCO_3$

## Example :

If the concentration or weight of $CaSO_4$ is 43 mg/lit then weight equivalent to $CaCO_3$ = $\frac{43 \times 100}{136}$ mgs / lit = 31.61 mgs/lit

## Units of hardness :

1. Parts per million (ppm)
2. Milligrams per liter (mg/lit )
3. Clarke's degree (°Cl )
4. French degree (°Fr )

## Parts per million (ppm)

It is defined as the number of parts of the $CaCO_3$ equivalent hardness per 10 6. Parts of water.

1 ppm = 1 part of $CaCO_3$ equivalent hardness per 10*6 parts of water.

## Milligrams per liter ( mg /lit )

It is defined as number milligram of $CaCO_3$ equivalent hardness per 1 liter of water.

1 mg/lit = 1 mg of $CaCO_3$ equivalent hardness per liter of water.

## Clarke's degree ( °Cl )

It is defined as the number of parts $CaCO_3$ equivalent hardness per 70,000 parts of water.

1° Cl = 1 part of $CaCO_3$ equivalent hardness per

70,000 parts of water.

French degree (° Fr )

It is define as the number of parts of the CaC03 equivalent hardness per $10^5$ parts of water.

Relation between units :

1 ppm = 1 mg/lit= 0.1 °Fr = 0.07 ° Cl

1 mg/lit = 1 ppm = 0.1 ° Fr = 0.007 °Cl

Mill equivalent per litre ( meq/L )

The number of milli equivalents of hardness present per litre

Thus, 1 meq/L = meq of CaCO3 per L of water.

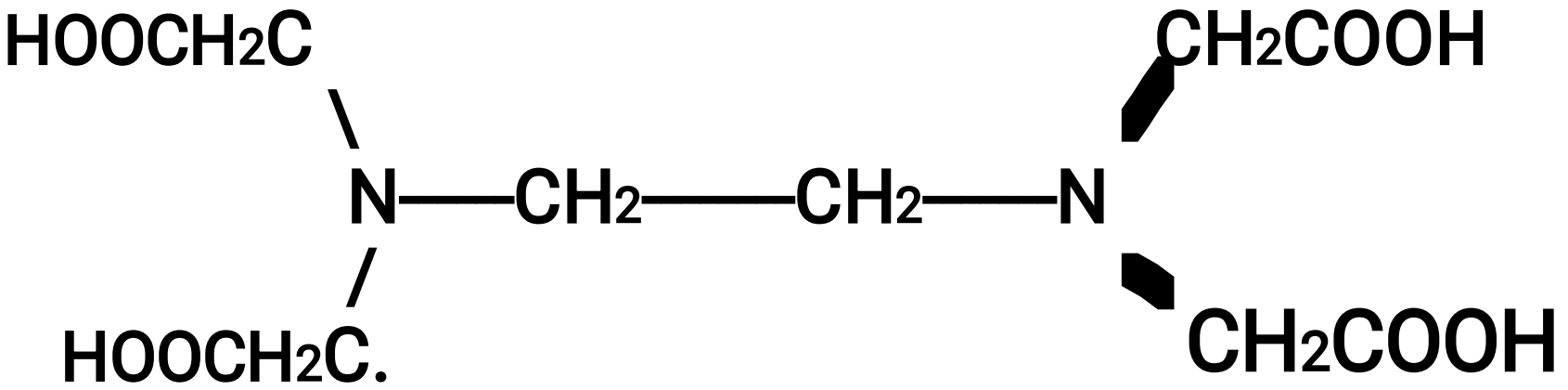
= 10-3 x 50 g of $CaCO_3$ equivalent per L

= 50 mg of CaCO3 equivalent per L

## Estimation of hardness by EDTA method :

EDTA is Ethylene Diamine Tetra Acetic acid

The structure of EDTA is



EDTA is insoluble in water.

It disodium salt is used as a complexion agent.

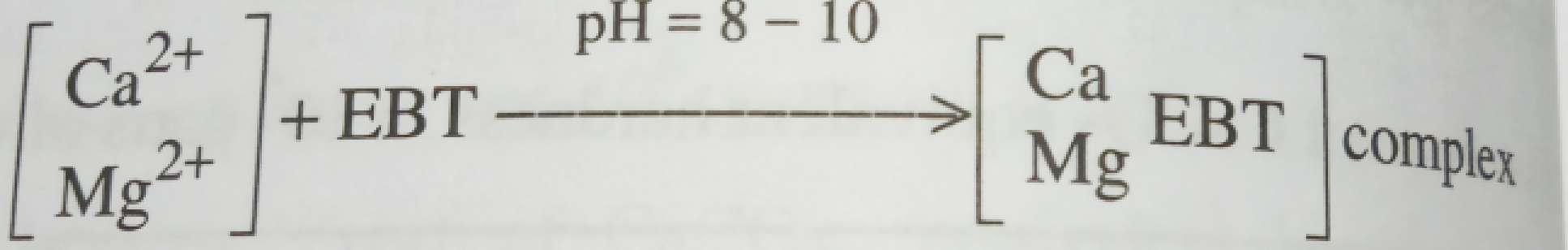
It is more accurate and fast.

Principle :

The amount of hardness causing ion (Ca+ and Mg +) can be estimated by titrating the Water sample against EDTA using Erichrome black T indicator ( EBT) at a PH of 8-10 in order to maintain the pH buffer solution.

Buffer solution = $NH_4Cl$ + $NH_4OH$ mixture

When the EBT indicator is added to the water sample if forms wine red colour weak complex with Ca2+ and Mg2+ ion.


[ Ca2+ Mg2+ ] + EBT
pH = 8 – 10
[ Ca Mg EBT ] complex
Wine red coloured weak complex

When this solution is titrated against EDTA it replaces.

The indicator  from the weak  complex from stable EDTA complex

When all the hardness causing ion are  complexes by EDTA the indicator is set free.

The colour of the free indicator is steel blue.

Thus the end point is the change of colour from wine red to steel blue.

$$\left[\begin{matrix}\text{Ca}\\\text{Mg}\end{matrix}\ \text{EBT}\right]\ \text{complex} + \text{EDTA} \xrightarrow{\text{pH} = 8 - 10}$$

Wine red coloured weak complex

$$\left[\begin{matrix}\text{Ca}\\\text{Mg}\end{matrix}\ \text{EDTA}\right]\ \text{complex} + \text{EBT}$$

Steel Blue

Stable complex

colourless

## Preparation of solution :

### EDTA solution :

It is prepared by dissolving 4 gms of EDTA in 1000 ml of distilled water.

### Standard hard water :

1 gms of pure $CaCO_3$ is dissolved in minimum quantity of HCl and then made up to 1000 ml using distilled water.

### EBT indicator

0.5 gms of EBT is dissolved in 100 ml of alcohol.

### Buffer solution :

67.5 gms of $NH_4Cl$ and 570 ml $NH_4OH$ are dissolved the solution is made up to 1000 ml using distilled water.

## Experimental procedure :

### ( I) Standardization of EDTA

1. Pipette out 50 ml of standard hard water into ba clean conical flask.

2. Added in 10 ml of buffer solution.

3. 4 - 5 drops EBT indicator ( Erichrome black T )

4. Titrate against EDTA ( Buffer ) solution.

5. The end point is the change of colour from wine red to steel blue.

6. Let the volume of EDTA consumed V1 ml.

## ( II ). Estimation of total hardness of water sample :

1. Pipette out 20 ml of given hard water sample II in clean conical flask.

2. Titrating against EDTA as before let the volume of EDTA consumed V2 ml.

## (III) Estimation of permanent hardness of water sample :

1. Take 100 ml the hard water sample in 250 ml beaker.

2. Boil it for 15 minutes
3. During boiling temporary hardness gets removed cool and filter the solution and the make up to 100 ml in a standard flask . By adding distilled water.

4. Pipette out 20 ml of the made up solution into a clean conical flask and titrate it against EDTA as before , let the volume of EDTA consumed V3 ml

# Titration - 1

## Standardisation of EDTA
## std Hard water Vs EDTA

Volume of std.Hard water V1 = 20ml

Normality of Std. Hard water N1= 0.01N

Volume of EDTA. V2= ----- ml(Burette reading)

$$\text{Normality of EDTA } N2 = \frac{V1 \times N1}{V2}$$

Titration - II

Estimation of total hardness:-

Volume of std. EDTA. V1 = ------ ml ( Burette reading )

Normality of EDTA. N1 = ------ N

Volume of water sample (II) V2 = ------ml

$$\text{Normality of water sample (II )} N2 = \frac{V1 \times N1}{V2}$$

Amount of total hardness in given solution
= Eq. Weight of ca x Normality of sample water (II) x 1000

= 50 x ------x 1000

= 50x 0.0065x 1000

= 325 ppm

**Titration : III**

**Volume of std EDTA v1= ------ ml (Burette reading)**

**Normality of EDTA N1 = -------N**

**Volume of water sample (III) V2= -------ml**

$$\text{Normality of water sample (III) } N2 = \frac{V1 \times N1}{N2}$$

$$= \text{--------N}$$

Amount of permanent hardness = Normality X Eq. Weight of Ca x 1000

= N x 50 x 1000
= 0.00225 x 50 x 1000

permanent hardness = 112.5 ppm

Total hardness = Permanent hardness + Temporary hardness

=Permanent hardness - Total hardness
= 325 –-112.5
= 212 ppm