Determination of temporary and permanent hardness of water sample by EDTA method

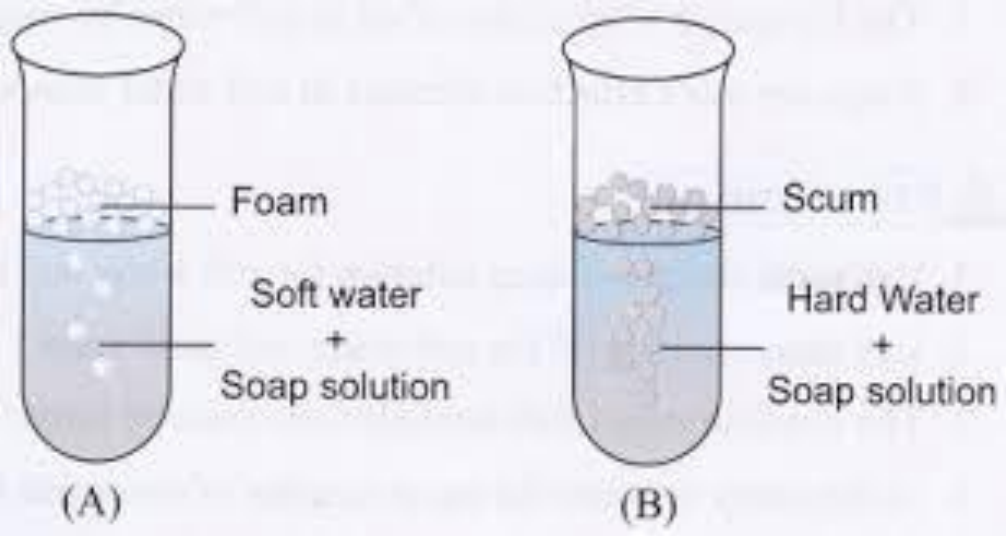
Hard Water :

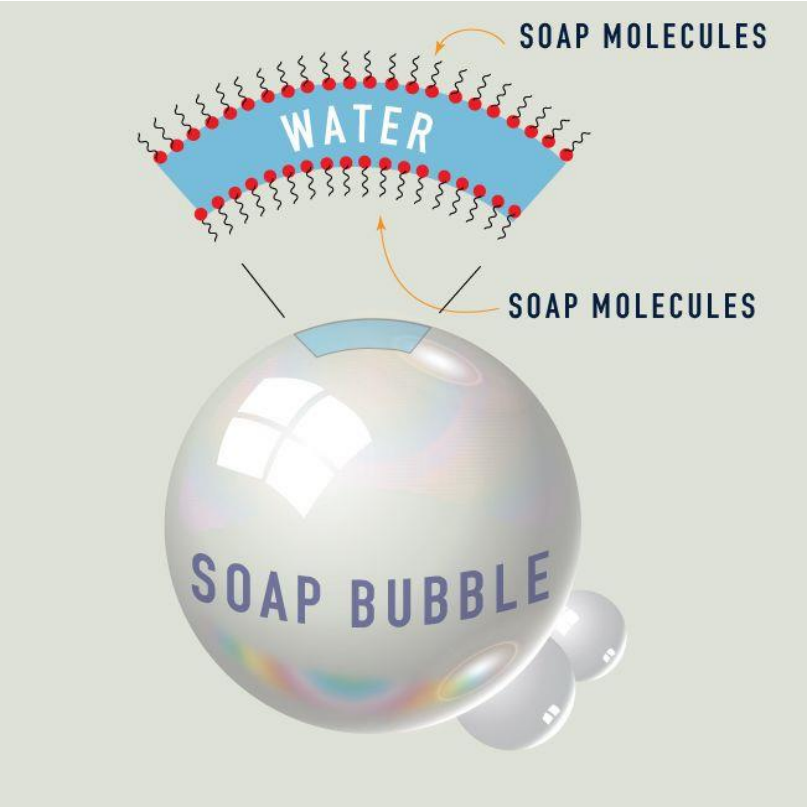
The water sample, which fails to produce foam/lather on addition of soap is called as **hard water**.

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

Na-stereate (soap)

Ca-stereate (scum)





Hard water sample produces scum (curd like insoluble impurities) with addition of soap

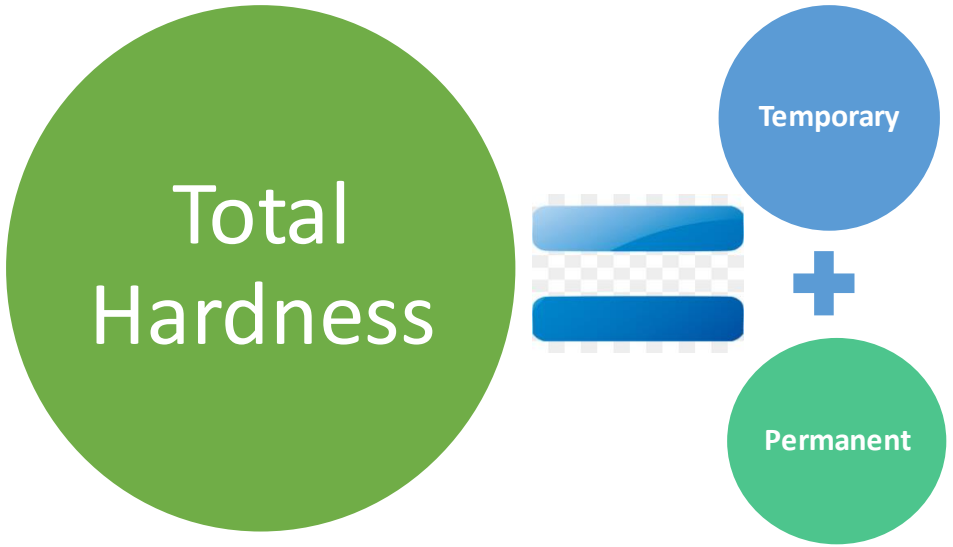
If chlorides, Sulphates, Nitrates, bicarbonates, carbonates of bivalent cations like Ca^{2+},Mg^{2+}, Fe^{2+}, Mn^{2+} are present in water, water becomes Hard.

Types of Hard Water:

Depending on the types of impurities present in water, it is mainly divided into following two types.

A) Temporary Hardness (or) Carbonate Hardness and

B) Permanent Hardness (or) Non-Carbonate Hardness.



Total Hardness = Temporary (Carbonate) Hardness + Permanent (Non- carbonate) Hardness

A) **Temporary Hardness (or) Carbonate Hardness:**

Hardness caused by Carbonates and/or bicarbonates of Ca^{2+} and Mg^{2+} is called Temporary or carbonate Hardness.

The salts responsible for causing Temporary or Carbonate Hardness are:

i. $Ca(HCO_3)_2$, ii. $Mg(HCO_3)_2$, iii. $CaCO_3$, iv. $MgCO_3$, etc.

Carbonate hardness is also called Temporary Hardness because, it can be removed by simple methods like

Boiling followed by Filtration.

B)Permanent Hardness (or) Non-carbonate Hardness:

Hardness caused by Chlorides, Sulphates, Nitrates of Ca2+ and Mg2+ is called Temporary or carbonate Hardness. The salts

responsible for causing Temporary or Carbonate Hardness are:

i. $CaCl_2$, ii. $MgCl_2$, iii. $CaSO_4$, iv. $MgSO_4$, v. $Ca(NO_3)_2$, vi. $Mg(NO_3)_2$, etc.

Non-Carbonate hardness is also called Permanent Hardness because it cannot be removed by simple methods. To remove Permanent Hardness some Chemical Treatment or other techniques are required.

Total Hardness = Temporary (Carbonate) Hardness + Permanent (Non-carbonate) Hardness

Expressing Hardness

- The concentrations of hardness as well as non-hardness constituting ions are usually expressed in terms of equivalent amount of $CaCO_3$

$$Equivalent\ amount\ of\ CaCO_3 = \frac{Mass\ of\ Solute \times Equivalent\ weight\ of\ CaCO_3}{Equivalent\ weight\ of\ Solute}$$

$$= \frac{m_{solute} \times EW_{CaCO3}}{EW_{solute}}$$

$$= \frac{m_{solute} \times 100/2}{MW_{solute}/n}$$

Example: $Ca(HCO_3)_2$

MW of $Ca(HCO_3)_2$ = 162 gm/mol

$$Multiplication\ factor = \frac{100/2}{162/2} = \frac{100}{162}$$

Example: $Al_2(SO_4)_3$

MW of $Al_2(SO_4)_3$ = 342 gm/mol

$$Multiplication\ factor = \frac{100/2}{342/6} = \frac{50}{57}$$

Expressing Hardness

- The concentrations of hardness as well as non-hardness constituting ions are usually expressed in terms of equivalent amount of $CaCO_3$

Salt	Molecular Weight	Equivalent Amount of $CaCO_3$
$Ca(HCO_3)_2$	162	100/162
$Mg(HCO_3)_2$	146	100/146
$CaSO_4$	136	100/136
$CaCl_2$	111	100/111
$MgSO_4$	120	100/120
$MgCl_2$	95	100/95
$CaCO_3$	100	100/100
$MgCO_3$	84	100/84
CO_2	44	100/44
$Ca(NO_3)_2$	164	100/164
$Mg(NO_3)_2$	148	100/148
HCO_3^-	61	100/122
OH^-	17	100/34
CO_3^{2-}	60	100/60
$NaAlO_2$	82	100/164
$Al_2(SO_4)_3$	342	100/114
$FeSO_4 \cdot 7H_2O$	278	100/278
H^+	1	100/2
HCl	36.5	100/73

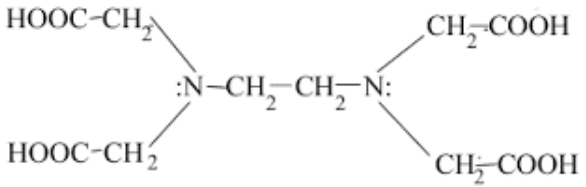
Units of Hardness

- Parts per million (ppm)
  1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.
- Milligrams per Litre (mg/L)
  1mg of $CaCO_3$ equivalent hardness of 1L of water.
  1 mg/L = 1 ppm
- Clarke's Degree (°Cl)
  one grain (64.8 mg) of CaCO3 per Imperial gallon (4.55 litres) of water equivalent to 14.254 ppm
- Degree French (°Fr)
  10 mg/L $CaCO_3$, equivalent to 10 ppm
- Milli-equivalents per Litre (meq/L)
  milli-equivalents of hardness present per liter

Water Hardness Scale		
Grains/Gallon	mg/L & ppm	Classification
Less than 1	Less than 17.1	Soft
1 to 3.5	17.1 to 60	Slightly hard
3.5 to 7.0	60 to 120	Moderately hard
7.0 to 10.5	120 to 180	Hard
10.5 and over	180 and over	Like a stone
Note - one grain per gallon = 17.1 parts per million (ppm)		

Procedure

Part A : Estimation of total hardness of given water sample



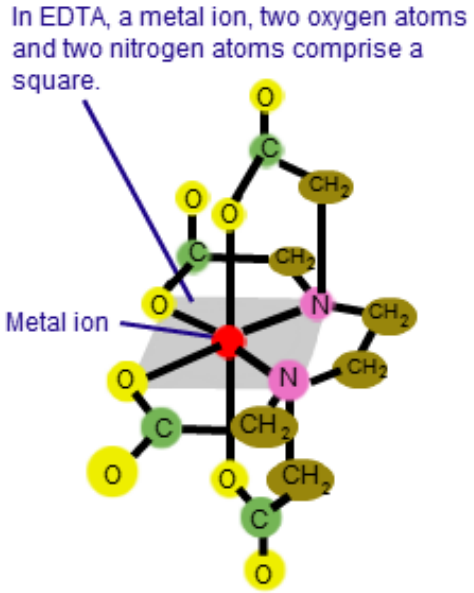
Structure of EDTA

In Burette : 0.01 M Ethylene Diamine Tetra Acetic Acid (EDTA)

In conical flask : 10ml water sample + 3ml buffer solution

Indicator : 1-2 drops of Erichrome black T (EBT)

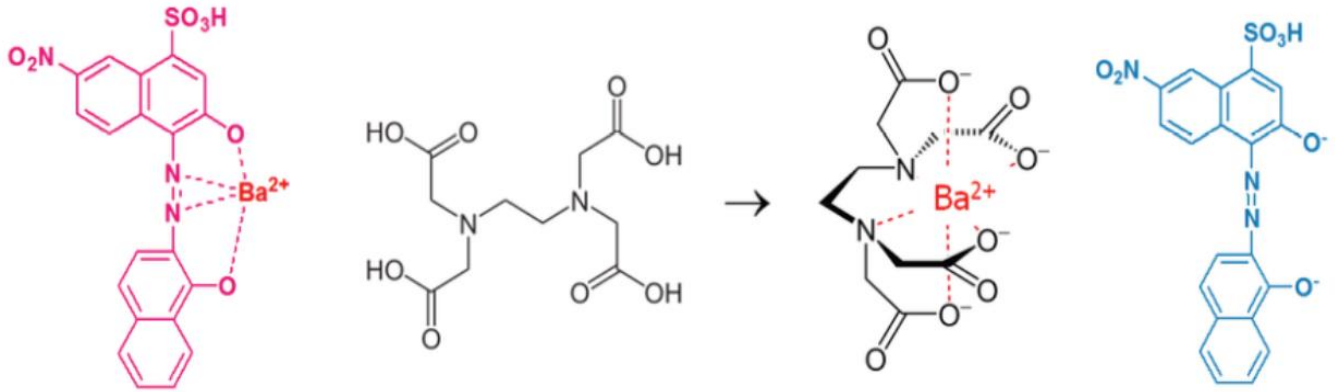
End –point : wine red to navy blue/peacock blue

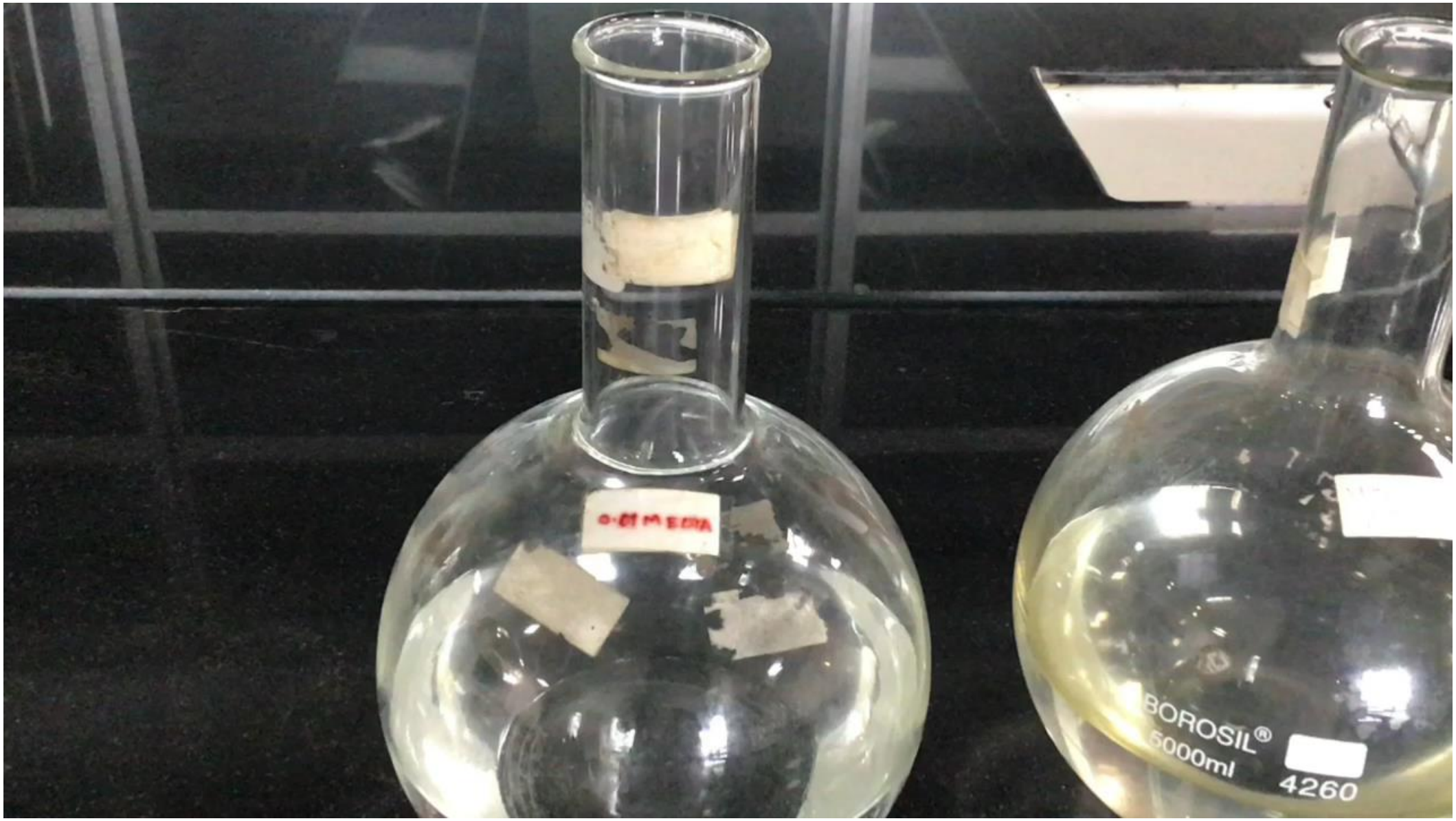


Reaction : M^{2+} + EBT → [M- EBT] $\xrightarrow{\text{EDTA}}$ [M-EDTA] + [M-EBT] $\xrightarrow{\text{EDTA}}$ [M-EDTA] [EBT]

dye — **Wine red** — Metal –Ligand complex — Colorless complex — **navy blue**

$$M^{2+} + EBT \longrightarrow [M - EBT] \xrightarrow{EDTA} [M - EDTA] + [M - EBT] \xrightarrow{EDTA} [M - EDTA] + EBT$$




BOROSIL®
5000ml
4260

Observation Table

Reading	1 (ml)	2 (ml)	3 (ml)	Constant Burette Reading (CBR)
Final	X1	X2	X3	X ml
Initial	0	0	0	
Difference				

$$\mathbf{1000\ mL\ of\ 1M\ EDTA \equiv 100\ gm\ of\ CaCO_3}$$

$$1000\ mL\ of\ 0.01M\ EDTA \equiv 100 \times 0.01\ gm\ of\ CaCO_3$$

$$X\ mL\ of\ 0.01M\ EDTA \equiv 100 \times 0.01 \times \frac{X}{1000}\ gm\ of\ CaCO_3$$

For 10 mL of water sample

$$\therefore Concentration\ (Eqv.CaCO_3) = 100 \times 0.01 \times \frac{X}{1000} \times \frac{gm}{10\ mL} = 100 \times 0.01 \times \frac{X}{1000} \times \frac{10^3 mg}{10 \times 10^{-3} L}$$

$$= X \times 10^2 \frac{mg}{L} = X \times 10^2\ ppm$$ ← Total Hardness

Part B : Estimation of Permanent hardness of given water sample

In Burette : 0.01 M EDTA

In conical flask : 10ml boiled water sample + 3ml buffer soln

Indicator : 1-2 drops of Erichrome black T (EBT)

End –point : wine red to navy blue

Reaction : $M^{2+} + EBT \rightarrow [M\text{- }EBT] \xrightarrow{EDTA} [M\text{-}EDTA] + [M\text{-}EBT] \xrightarrow{EDTA} [M\text{-}EDTA]\,[EBT]$

Observation Table

Reading	1 (ml)	2 (ml)	3 (ml)	Constant Burette Reading (CBR)
Final	Y1	Y2	Y3	Y ml
Initial	0	0	0	
Difference				

$$\mathbf{1000\ mL\ of\ 1M\ EDTA \equiv 100\ gm\ of\ CaCO_3}$$

$$1000\ mL\ of\ 0.01M\ EDTA \equiv 100 \times 0.01\ gm\ of\ CaCO_3$$

$$Y\ mL\ of\ 0.01M\ EDTA \equiv 100 \times 0.01 \times \frac{Y}{1000}\ gm\ of\ CaCO_3$$

For 10 mL of water sample

$$\therefore Concentration\ (Eqv.CaCO_3) = 100 \times 0.01 \times \frac{Y}{1000} \times \frac{gm}{10\ mL} = 100 \times 0.01 \times \frac{Y}{1000} \times \frac{10^3 mg}{10 \times 10^{-3} L}$$

$$= Y \times 10^2 \frac{mg}{L} = Y \times 10^2\ ppm$$ ←Temporary Hardness

$$Total\ Hardness = Temporary\ Hardness + Permanent\ Hardness$$

$$Temporary\ Hardness = Total\ Hardness\ (From\ part\ A) - Permanent\ Hardness\ (From\ part\ B) = \_\_\_\_\_\ ppm$$

Part C : Estimation of total hardness of given Tap water

In Burette : 0.01 M EDTA

In conical flask : 50ml Tap water + 3ml buffer soln

Indicator : 1-2 drops of Erichrome black T (EBT)

End –point : wine red to navy blue

Reaction : $M^{2+} + EBT \rightarrow [M\text{- }EBT] \xrightarrow{EDTA} [M\text{-}EDTA] + [M\text{-}EBT] \xrightarrow{EDTA} [M\text{-}EDTA]\,[EBT]$

Wine red

navy blue

Observation Table

Reading	1 (ml)	2 (ml)	3 (ml)	Constant Burette Reading (CBR)
Final	Z1	Z2	Z3	Z ml
Initial	0	0	0	
Difference				

$$\mathbf{1000\ mL\ of\ 1M\ EDTA \equiv 100\ gm\ of\ CaCO_3}$$

$$1000\ mL\ of\ 0.01M\ EDTA \equiv 100 \times 0.01\ gm\ of\ CaCO_3$$

$$Z\ mL\ of\ 0.01M\ EDTA \equiv 100 \times 0.01 \times \frac{Z}{1000}\ gm\ of\ CaCO_3$$

For 50 mL of water sample

$$\therefore Concentration\ (Eqv.CaCO_3) = 100 \times 0.01 \times \frac{Z}{1000} \times \frac{gm}{50\ mL} = 100 \times 0.01 \times \frac{Z}{1000} \times \frac{10^3 mg}{50 \times 10^{-3} L}$$

$$= Z \times 20\ \frac{mg}{L} = Z \times 20\ ppm$$

←Total Hardness

$$Total\ Hardness = Temporary\ Hardness + Permanent\ Hardness$$

$$Temporary\ Hardness = Total\ Hardness\ (From\ part\ A) - Permanent\ Hardness\ (From\ part\ B) = \_\_\_\_\_\ ppm$$

Expected Result :

1) **Total Hardness of given water sample = 400-600 ppm**
2) **Permanent hardness of water sample = 200-300 ppm**
3) **Temporary hardness of water sample = 200-300 ppm**
4) **Total Hardness of tap water = 20-50 ppm**

Note : Numbers vary person to person and with experimental conditions

- Calculate the temporary and permanent hardness of water sample containing $Mg(HCO_3)_2$= 7.3mg/L, $Ca(HCO_3)_2$= 16.2mg/L, $MgCl_2$= 9.5mg/L, $CaSO_4$=13.6mg/L)

- Calculate the temporary and total hardness of a water sample containing $Mg(HCO_3)_2$= 73mg/L, $Ca(HCO_3)_2$= 162mg/L, $MgCl_2$= 95mg/L, $CaSO_4$=136mg/L

- 50ml of a sample water consumed 15ml of 0.01 EDTA before boiling and 5ml of the same EDTA after boiling. Calculate the degree of hardness, permanent hardness and temporary hardness.

- 0.5g of $CaCO_3$ was dissolved in HCl and the solution made up to 500ml with distilled water. 50ml of the solution required 48ml of EDTA solution for titration. 50ml of hard water sample required 15ml of EDTA and after boiling and filtering required 10ml of EDTA solution. Calculate the hardness.