Water - Analysis, Treatment & Industrial Applications

Sources :—

Main source of water are :—

1) Surface water → It includes flowing water & still water
2) Underground water→ It includes water from wells & springs
3) Rain water

Impurities in water :—

a) Suspended impurities :— These impurities give turbidity, colour, & odour to water, it can be inorganic, organic in nature

b) Colloidal impurities :— Product from organic waste, finely divided silica & clay etc

c) Micro organisms :— It include bacteria, fungi & algae

d) Dissolved impurities :— It includes dissolved salts like carbonates, bicarbonates chlorides sulphates of calcium, magnesium, iron & sodium making water hard.

O_2 & CO_2 are also dissolved impurities

Classification of water :—

Ⓐ Hard water :— Water which does not produce lather with soap solution, but form a white curd is called hard water.
Hard water contain dissolved salts of calcium, magnesium etc.

Ⓑ Soft water :— Water which produce lather (foam) with soap solution is called soft water

Saft water do not contain dissolved calcium
and magnesium salt in it.

Hardness of water

" Hardness in water is that characteristic which prevent
the lathering of soap"

" Hardness is that property of water due to which it is
unable to give lather/foam with soap
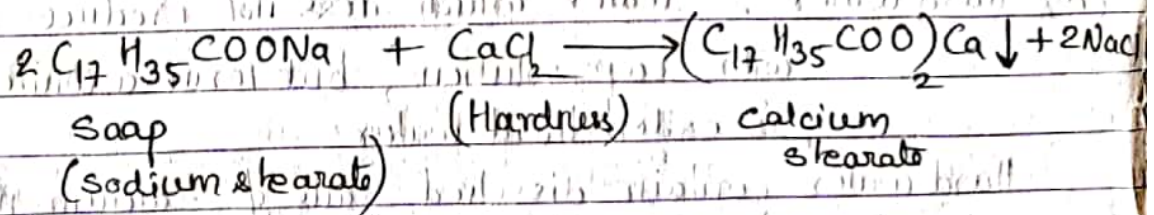
" Soap consuming capacity of water sample"

Reason of hardness in hard water :-

Hard water consumes lot of soap
Hard water do not give lather with soap due to the
presence of dissolved salts of Ca, Mg & other heavy metals
ions like Al^{3+}, Fe^{3+} & Mn^{2+}

Reaction of Hard water with Soap

Hard water do not produce lather/foam with soap.
but form insoluble white scum or precipitate
, it is due to formation of insoluble soaps of calcium &
magnesium.

$$2 C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2 Ca \downarrow + 2NaCl$$

Soap   (Hardness)   calcium
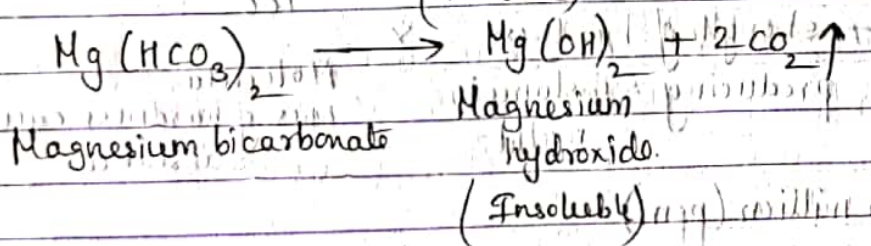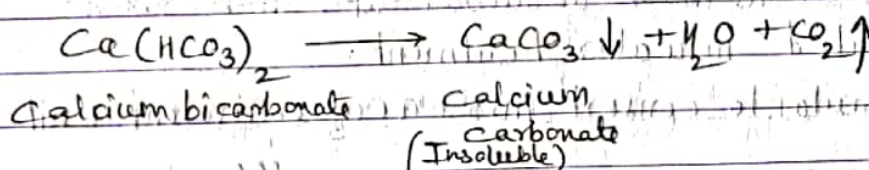(sodium stearate)   stearate

Types of Hardness :—

A) Temporary Hardness :—

i) It is caused by the presence of dissolved bicarbonates of calcium, magnesium & other heavy metals & the carbonate of Iron

$\{ Ca(HCO_3)_2 , Mg(HCO_3)_2 \} \longrightarrow$ Salts mainly responsible for temporary hardness.

ii) Temporary hardness is also called Carbonate hardness / alkaline hardness.

iii) Temporary hardness can be removed by boiling of water.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$
Calcium bicarbonate   Calcium Carbonate (Insoluble)

$$Mg(HCO_3)_2 \rightleftharpoons Mg(OH)_2 + 2CO_2 \uparrow$$
Magnesium bicarbonate   Magnesium hydroxide. (Insoluble)

Here bicarbonate decompose to insoluble carbonate or hydroxide, which get deposited as crust at bottom of vessel.

B) Permanent Hardness :—

i) It is caused by the presence of dissolved chlorides & sulphates of calcium, magnesium, iron & other heavy metals.

$CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , FeSO_4 , Al_2(SO_4)_3$
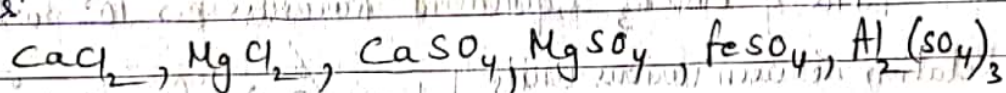
ii) Permanent hardness cannot be removed by boiling.

But it can be removed by following method
i) Lime Soda Method.
ii) Zeolite "
iii) Ion exchange"

iii) Permanent hardness, also called non carbonate/non alkaline hardness:

Units of Hardness :—

i) Hare $CaCO_3$ equivalent :— Hardness of water is conveniently expressed in terms of $CaCO_3$ equivalent, because calculation becomes easy as its molecular wt. is 100, and it is the most insoluble salt that can be precipitated in water treatment.

formula to convert into $CaCO_3$ equivalent unit

$$= \text{strength of hardness producing substance in mg/lit} \times \frac{100}{\text{Molecular mass of hardness causing substance.}}$$

ii) Parts per million (ppm)
"Number of parts by weight of calcium carbonate present per million (10^6) parts by weight of water

iii) Milligram per litre (mg/l)
"Number of milligrams of $CaCO_3$ present in one litre of water
$1mg/lit = 1 ppm$

iv) Degree clarke (°Cl)
"Parts of $CaCO_3$ equivalent hardness per 70,000 parts of water

v) Degree french (°fr)
"Parts of $CaCO_3$ equivalent hardness per 10^5 parts of water

Relation between various units $\boxed{1 ppm = 0.1°fr = 0.07°Cl = 1 mg/lit}$
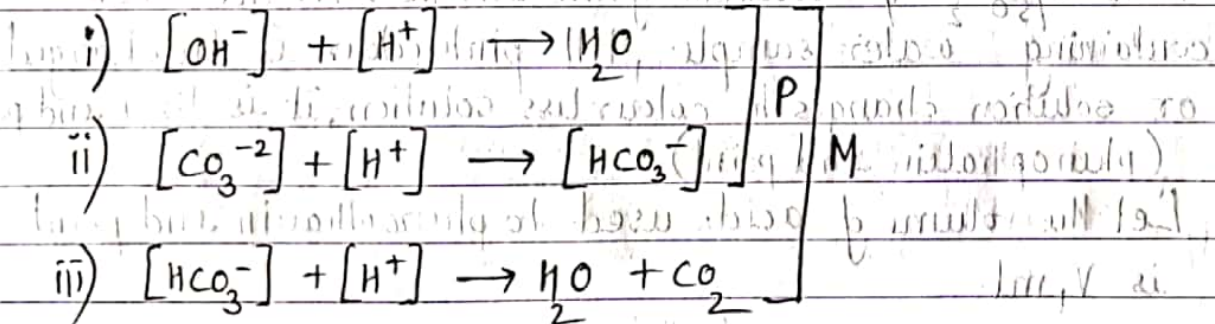
Alkalinity :—

Defination :— The total content of those substances in water which causes increased concentration of OH^- ion by dissociation or hydrolysis

Alkalinity of water is due to the presence of following

i) Caustic alkalinity (OH^- & CO_3^{--} ions)
ii) Temporary hardness (due to HCO_3^- ion)

These ions can be estimated seperately by titration against standard acid, using phenophthalein and methyl orange as indicator, the determination is based on the following reactions.
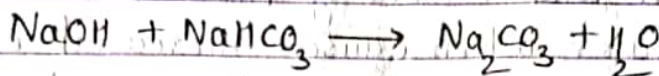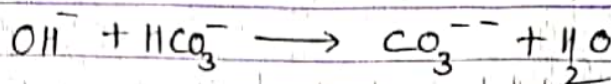
i) $[OH^-] + [H^+] \longrightarrow H_2O$

ii) $[CO_3^{-2}] + [H^+] \longrightarrow [HCO_3^-]$

iii) $[HCO_3^-] + [H^+] \longrightarrow H_2O + CO_2$

The possible combination of ions causing alkalinity in water are
i) OH^- only ii) CO_3^{--} only iii) HCO_3^- only iv) OH^- & CO_3^{--}
v) CO_3^{--} and HCO_3^-

Combination of ions not possible :—

a) Possibility of OH^- & HCO_3^- ion together is not possible because they combine to form CO_3^{--} ion.

$$OH^- + HCO_3^- \longrightarrow CO_3^{--} + H_2O$$

$$NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O$$

b) OH^-, CO_3^{--} & HCO_3^- also cannot exist together, due to same above reason.

Procedure :—

i) Pipette out 100 ml of water sample in a clean titration flask, then add 2-3 drops of phenopthalein indicator in above solution, pink coloured solution is obtained

ii) Run $N/50$ H_2SO_4 solution from burette into the flask containing water sample, till pink colour is discharged or solution changes to colourless solution, it is first end point (phenopthalein end point)

iii) Let the volume of acid used to phenophthalein end point is V_1 ml.

iv) In the same above solution add 2-3 drops of methyl orange and continue titration till the pink colour reappears, it is second end point (Methyl orange end point), let the volume of acid used to methyl orange end point is V_2 ml.
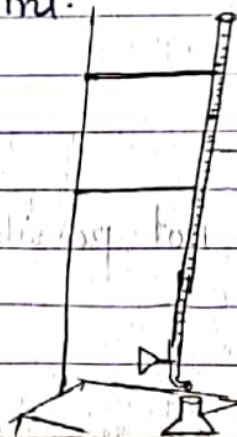
[The titration of water sample against standard acid upto phenopth alein end point marks the completiong. reaction (i) & (ii), & titration of water sample against standard acid to methyl orange end point marks completion of reaction (i)(ii) & (iii)]

Burette

conical flask

Calculation :—

100 ml of water upto phenopthalein end point = V_1 ml of $N/50$ H_2SO_4

$$100 \text{ ml} \times N_p = V_1 \text{ ml} \times (N/50)$$

$$(\text{normality}) \; N_p = \frac{V_1 \text{ ml}}{100 \text{ ml}} \times \frac{N}{50} = \frac{V_1}{5000} N$$

$$\boxed{\begin{aligned}
&\text{Normality} = \frac{gm \cdot \text{Equivalent}}{L} = \frac{x/Eq. wt.}{L} \quad x = wt. \text{ in gram} \\
&\text{Strength} \left(\frac{x}{L}\right) = N \times \text{Equivalent \& Eq. wt. of } CaCO_3, \; wt. = \frac{Mol. wt.}{2} = \frac{100}{2} = 50
\end{aligned}}$$

Strength of alkalinity upto phenopthalein end point in terms of $CaCO_3$ equivalent (P)

$$= \frac{V_1}{5000} \times (50g/L) \times 1000 \frac{mg}{g}$$

$$P = 10 \, V_1 \frac{mg}{L} = 10 \, V_1 \, PPM.$$

Now 100 ml of water upto methyl orange end point

$$= (V_1 + V_2) \text{ ml of } N/50 \, H_2SO_4$$

$$100 \text{ ml} \times N_M = (V_1 + V_2) \text{ ml} \times N/50$$

$$\text{normality, } N_M = \frac{(V_1+V_2) \text{ ml}}{100 \text{ ml}} \times N/50 = \frac{(V_1+V_2)}{5000} N$$

Strength of to alkalinity upto methyl orange end point in terms of $CaCO_3$ equivalent (M)

$$N_M = \frac{(V_1+V_2)}{5000} \times 50 \, g/L \times 1000 \frac{mg}{g}$$

$$M = 10(V_1 + V_2) \frac{mg}{L} = 10(V_1 + V_2) ppm$$

Titration Curve

The titration Curve for neutralization of OH^- ions with H^+ ions is shown in fig. 1, Sudden change in pH near the equivalence point is characteristic of all analytically useful titrations. At the equivalence point the slope is greatest. The large change in pH at the equivalence point indicates that only a fraction of a drop of titrant causes a very large change in pH at this point in the titration.
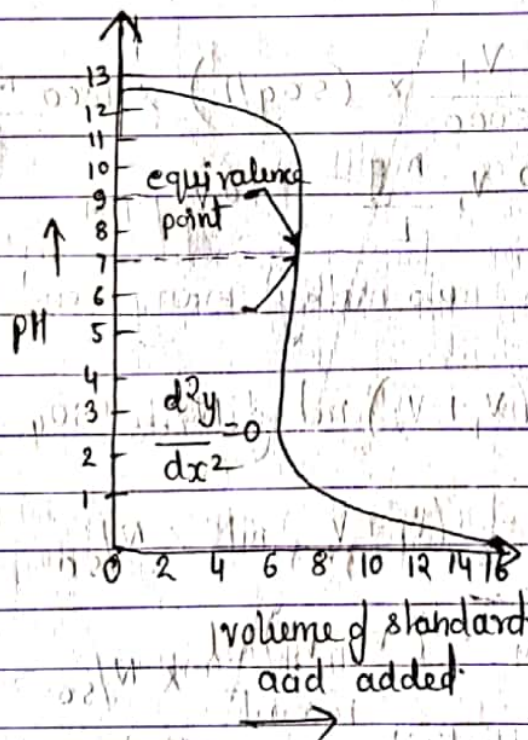
The titration curve for neutralization of OH^- ions with H^+ ions.

Acid base indicators are weak acids or weak bases. in which the acid form has a eto. colour characteristi- cally different from the colour of the basic form.

The colour change of indicator changes over a range of pH.

Different Cases :—

P = N then
① When given water sample is alkaline due to presence of OH⁻ ions only.

By phenopthalein as well as methyl orange. we can find out the end point, same amount of acid will be needed for neutralization of OH⁻ ions by any of the indicator (phenopthalein or methyl orange)

$$OH^- + H^+ \longrightarrow H_2O$$
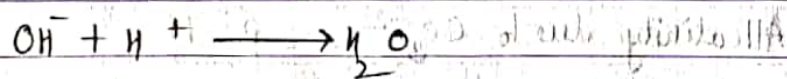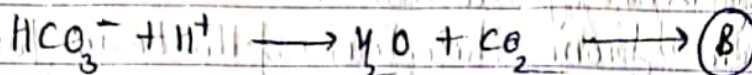
Thus when P = M then water sample is alkaline due to OH⁻ ion only.

alkaline
② When P = ½ M then given water sample is alkaline due to CO_3^{--} only

Titration of alkaline water sample against standard acid upto phenopthalein end point, indicates the completion of reaction Ⓐ

$$CO_3^{--} + H^+ \longrightarrow HCO_3^- \quad | \longrightarrow Ⓐ$$
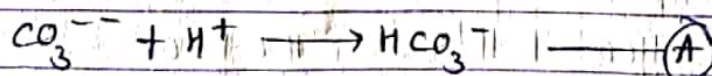
further when methyl orange indicator is added to same above solution then yellow solution is obtained. which turn pink at end point, the amount of acid.

used to methyl orange end point marks completion of reaction (B)

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2 \longrightarrow (B)$$

Both (A) & (B) reaction require same volume of acid.

$$V_1 = V_2$$

$$P = 10 V_1 \text{ ppm}$$
$$M = 10(V_1 + V_2) \text{ ppm}$$
$$= 10(2V_1) \text{ ppm}$$
$$= 20 V_1 \text{ ppm}$$

Thus when $p = \dfrac{1}{2} M$, CO_3^{-2} ion present in water sample.

Alkalinity due to $CO_3^{-2} = 2P$

③ When $P = 0$, then only HCO_3^- ion is present in alkaline water sample.

Phenopthalein indicator is not suitable for estimation of HCO_3^-, it can be estimated by methyl orange indicator.
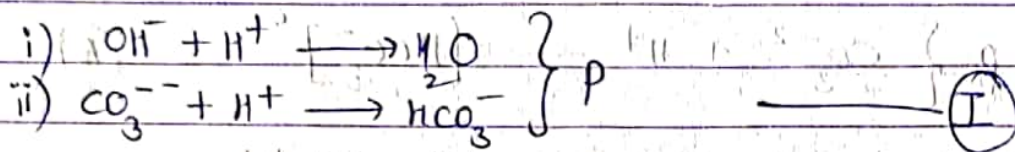
By titration of alkaline water sample against standard acid to methyl orange end point marks the completion of following reaction
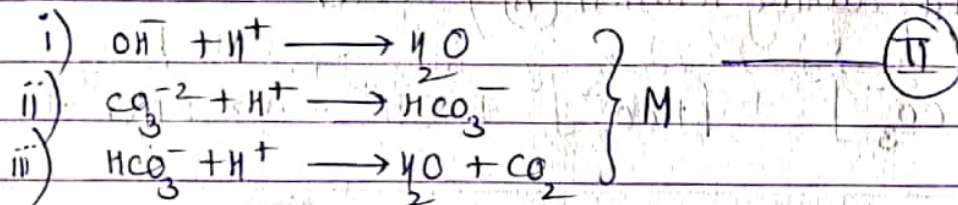
$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$$
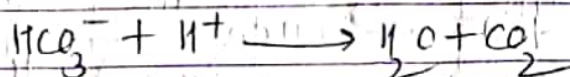
Thus when $P = 0$, alkalinity is due to HCO_3^- only.

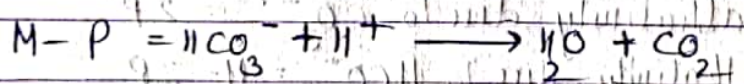(4) When $p > \frac{1}{2}M$, alkalinity of alkaline water sample. is due to CO_3^{-2} & OH^- ion.

Titration of alkaline water sample. against standard acid upto phenopthalein end point. marks the completion of neutralization of OH^- & CO_3^{--} (i & ii)

i) $OH^- + H^+ \longrightarrow H_2O$
ii) $CO_3^{--} + H^+ \longrightarrow HCO_3^-$ } P ———— (I)

further titration of same above water sample. with acid. upto methyl orange end point marks the complete neutraliz of OH^- & CO_3^{-2} ion (i, ii & iii)

i) $OH^- + H^+ \longrightarrow H_2O$
ii) $CO_3^{-2} + H^+ \longrightarrow HCO_3^-$ } M
iii) $HCO_3^- + H^+ \longrightarrow H_2O + CO_2$ ———— (II)

Subtract (I) from (II)

$M - P = HCO_3^- + H^+ \longrightarrow H_2O + CO_2$

HCO_3^- ion are neutralization product of CO_3^{-2} till half stage.

Half of CO_3^{-2} ion $= (M-P)$

alkalinity due to complete $CO_3^{-2} = 2(M-P)$
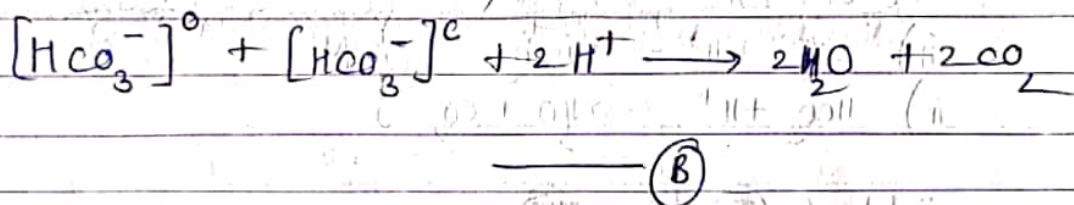
Alkalinity due to $OH^- = M - 2(M-P)$
$= 2P - M$

(5) When $P < \frac{1}{2}M$, given alkaline water sample is alkaline due to CO_3^{--} & HCO_3^- ions.

In titration of alkaline water sample against standard acid up to phenopthalein end-point marks neutralization of CO_3^{-2} ions till b. HCO_3^- stage only, thus following neutralization reaction completes

$$P \left\{ CO_3^{-2} + H^+ \longrightarrow [HCO_3^-]^c \xrightarrow{\quad\quad} (A) \right.$$

further when methyl orange is added to above solution the and then titration is done with acid to get pink end point then, neutralization of both HCO_3^- ions ($[HCO_3^-]^o$ originally present & $[HCO_3^-]^c$ formed during reaction (A)) occur.

$$[HCO_3^-]^o + [HCO_3^-]^c + 2H^+ \longrightarrow 2H_2O + 2CO_2$$

$$\underline{\qquad\qquad (B) \qquad\qquad}$$

alkalinity due to $CO_3^{-2} = 2P$
alkalinity due to $HCO_3^- = M - 2P$

Alkalinity table :—

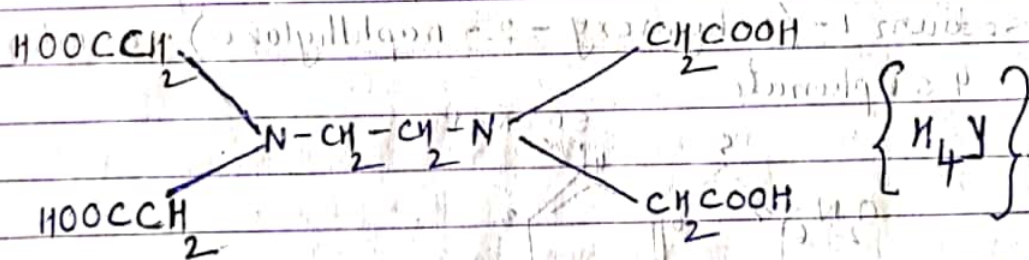| S.no	Result of Titration	Alkalinity due to		
		Hydroxide (OH^-)	Carbonate (CO_3^{2-})	Bicarbonate (HCO_3^-)
1.	$P = 0$	Nil	Nil	M
2.	$P = M$	P or M	Nil	Nil
3.	$P = \frac{1}{2}M$	Nil	2P	Nil
4.	$P > \frac{1}{2}M$	$(2P - M)$	$2(M - P)$	Nil
5.	$P < \frac{1}{2}M$	Nil	2P	M - 2P

EDTA Method

P Water hardness is generally caused by Ca^{++} & Mg^{++} ions, the estimation of water hardness is done by complexometric titration using standard EDTA as titrant & EBT as indicator.
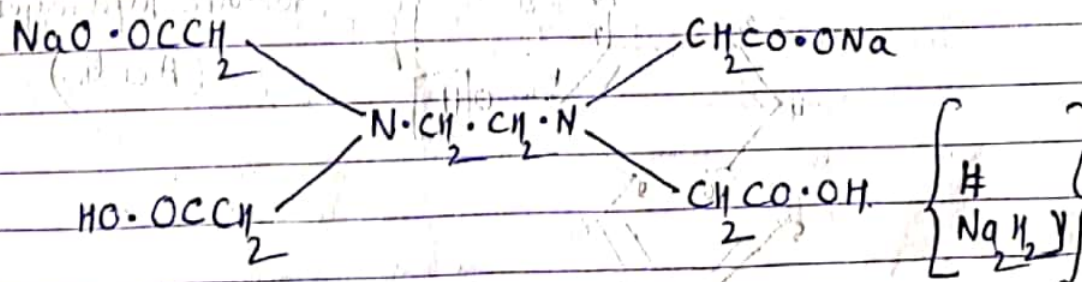
EDTA :— ethylene diammine tetra acetic Acid.

It is having less solubility so it is used in the form of soluble disodium salt dihydrate $(Na_2H_2Y \cdot 2H_2O)$ The EDTA solution combine with metal ion in 1:1 ratio.

EDTA is represented as H_4Y (Tetrabrotic acid) & its Disodium salt dihydrate is represented as $Na_2H_2Y \cdot 2H_2O$

Structure :—

HOOCCH₂ ... CH₂COOH
N–CH₂–CH₂–N
HOOCCH₂ ... CH₂COOH
$\{H_4Y\}$

EDTA structure :—

NaO·OCCH₂ ... CH₂CO·ONa
N·CH₂·CH₂·N
HO·OCCH₂ ... CH₂CO·OH
$\{Na_2H_2Y\}$
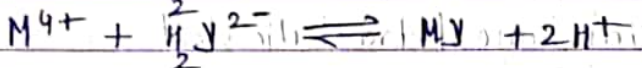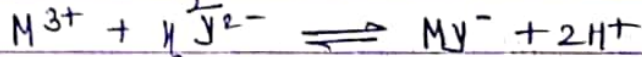
EDTA in disodium salt form

EDTA in the form of its disodium salt yields, anion in solution, this anion form complex with Ca^{++} & Mg^{++} ion   EDTA (H_2Y^{2-})

Reaction of cation with EDTA anion:

$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+$$
$$M^{3+} + H_2Y^{2-} \rightleftharpoons MY^- + 2H^+$$
$$M^{4+} + H_2Y^{2-} \rightleftharpoons MY + 2H^+$$

When EDTA anion (H_2Y^{2-}) react with metal ions, then it surrounds metal ion like large claw of a crab grasping its prey, it's called Such complex is called chelate

EBT → Eriochrome black T indicator.

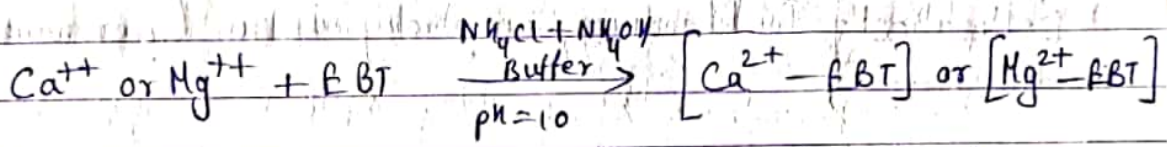It is a metal ion indicator, chemically it is sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-napthol-4 sulphonate

$SO_3^- Na^+$

Phenolic hydrogen (Acidic)
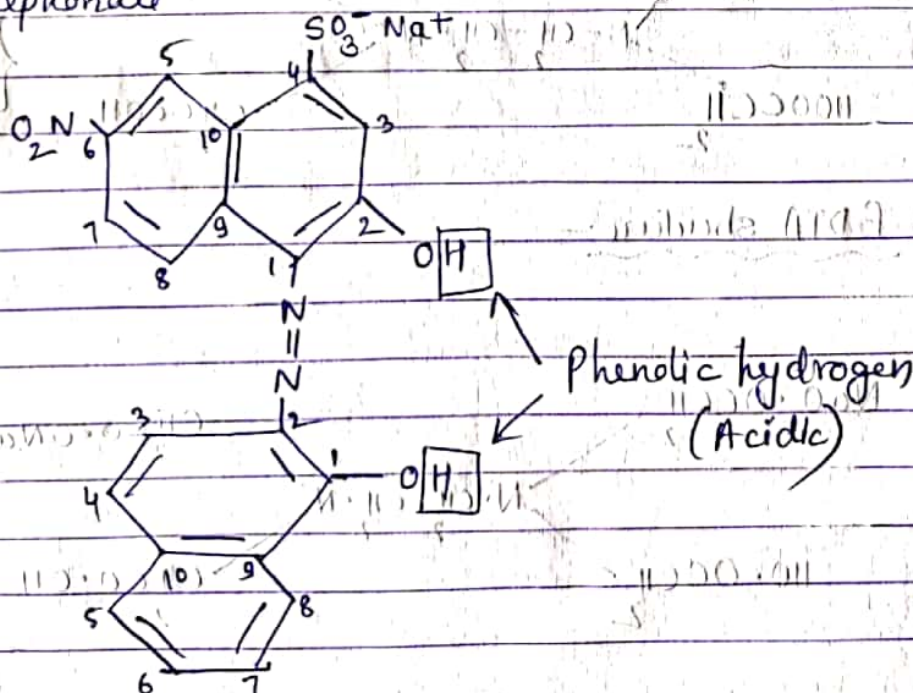
EBT (H_2In^-)

Principle of EDTA Titration :—

The hardness of water is determined by titration with a standard solution of EDTA which is a complexing agent , since EDTA is insoluble in water the disodium salt of EDTA is used $\left(Na_2Y^{2-}\right)$

Theory

1) In this method buffer solution is used to attain the maintain the pH value of ~10 in hard water by using $NH_4OH - NH_4Cl$ solution, then further EBT indicator is added (few drop). in above solution, EBT form weak complex with metal ions. which has wine red colour.
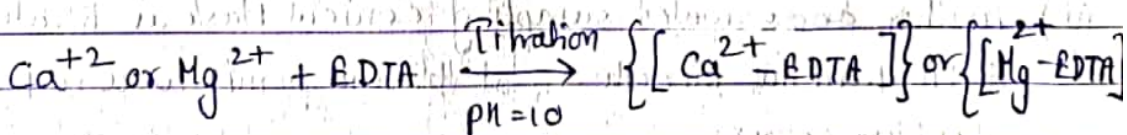
$$Ca^{++} \text{ or } Mg^{++} + EBT \xrightarrow[pH=10]{\underset{Buffer}{NH_4Cl + NH_4OH}} \left[Ca^{2+} - EBT\right] \text{ or } \left[Mg^{2+} - EBT\right]$$

from hard water   Indicator   Metal – indicator unstable complex (wine red)

2) Further the wine red coloered solution is titrated against EDTA, EDTA combines with free Ca^{++} or Mg^{++} ions. to give very stable , colourless and water soluble metal – EDTA complex

$$Ca^{+2} \text{ or } Mg^{2+} + EDTA \xrightarrow[pH=10]{Titration} \left\{\left[Ca^{2+} - EDTA\right]\right\} \text{ or } \left\{\left[Mg^{2+} - EDTA\right]\right\}$$

free hardness   Metal- EDTA stable
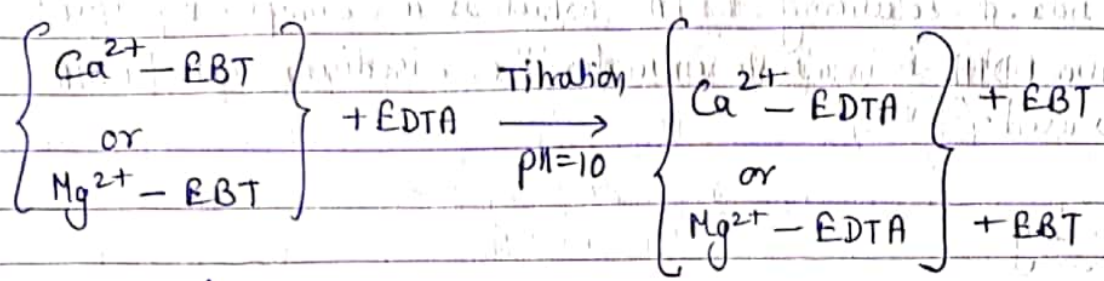causing ion   Complex
                                    (colourless/water
                                     soluble)

When all the free metal ions (Ca^{+2}, Mg^{2+}) are consumed , then next drop of added EDTA solution. displace the indicator

EBT, from Metal-EBT complex ; the free indicator gives blue colour.

$$\left.\begin{array}{c} Ca^{2+}-EBT \\ or \\ Mg^{2+}-EBT \end{array}\right\} \xrightarrow[pH=10]{Titration \; + EDTA} \left.\begin{array}{c} Ca^{2+}-EDTA \\ or \\ Mg^{2+}-EDTA \end{array}\right\} \begin{array}{c} + EBT \\ \\ + EBT \end{array}$$

Wine red.   Colourless   free indicator
complex   (Blue)
                                           colour

Thus at equivalent point / end point there is change from wine red to blue colour.

Estimation of Total hardness, temporary hardness & permanent hardness :—

Total hardness :— It is due to presence of bicarbonates, chlorides & sulphates of calcium & magnesium ions.

Estimation

i) 20 ml of given water sample is pipetted out into a clean conical flask

ii) 5 ml ammonia buffer & 2 drops of EBT indicator is added into conical flask, wine red coloured solution is formed.

iii) further above water sample of conical flask is titrated against EDTA from the burette., at the end point wine red change to blue colour.

iv) The titration is repeated to get concordant titre value.

Permanent hardness :— It is due to presence of chlorides & sulphates of calcium & magnesium ions. Permanent hardness cannot be removed by boiling. The filtrate obtained after boiling water contain permanent hardness producing substance.

Estimation

i) 100 ml of given sample of water is pipetted out into a clean beaker and boiled for 20 minutes.

ii) The above solution is then filtered to remove the precipitate formed due to decomposition of temporary hardness producing salts.

iii) The filtrate is made up to 100 ml in standard measuring flask using distilled water.

iv) 20 ml of a the above made up solution (iii) is pipetted into a conical flask, then 5ml ammonia buffer is added & 2 drops of EBT is added into the conical flask solution. & then, wine red solution is formed.

v) The above wine red coloured solution is titrated against the EDTA, at end point wine red colour changes to blue

• The titration is repeated to get concordant titre value.

Temporary hardness :— It is due to presence of bicarbonates of calcium & magnesium ions, it can be removed by boiling. When water is boiled temporary hardness producing substances are precipitated as insoluble carbonates or hydroxides. This precipitate can be removed by filtration. (The filtrate is used for determining permanent hardness)

Estimation

Temporary hardness is calculated from total & permanent hardness.

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

Role of Buffer Solution. ($NH_4OH - NH_4Cl$)

following important reaction require basic medium ($pH = 10$), which is maintained by addition of Buffer solution

a) Wine red coloured metal – eriochrome balack-T complex formation

b) Colourless metal- EDTA stable complex formation

c) Displacement of blue coloured free eriochrome black T indicator.