(1)

Hardness

It is characteristics which prevents the lathering of soap.

Soaps consuming capacity of water is called hardness of water.

Soaps are potassium & sodium salts of fatty acids.

oleic acid, Palmitic acid, stearic acid

$$C_{17}H_{35}COOH + NaOH \longrightarrow C_{17}H_{35}COONa + H_2O$$

$$C_{15}H_{31}COOH + KOH \longrightarrow C_{15}H_{31}COOK + H_2O$$

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

Type of Hardness

i) Temporary (Carbonate Hardness)
ii) Permanent (Non-Carbonate)

i) Temporary → Hardness due to Carbonates & bi-carbonates of Calcium (Ca^{2+}), Mg^{2+} & other metals.

ii) It is removed by Boiling of water

$CaCO_3$, $MgCO_3$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$

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

$$2C_{17}H_{35}COONa + MgCO_3 \rightarrow Mg(C_{17}H_{35})_2$$

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

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

→ Permanent Hardness

It is due to the presence of dissolved chlorids of Ca^{++}, Mg^{2+} and heavy metals.

$CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$

& $AlCl_3$, $FeCl_2$, $FeSO_4$

It cannot be removed by boiling. It can be removed by following methods (external)

i) Lime - Soda (L-S method)
ii) Zeolite or Permutit
iii) ~~Hight~~ exchange method.
Ion

40
71
111
2
5

100/2 50

40
2
24
96
162

64

48
12
60

40
32
64
136

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Measurement of Hardness

The intent of Hardness is measured in terms of concentration of ions contributing to hardness. It is usually expressed in terms of equivalent amount of $CaCO_3$. the reason for choosing $CaCO_3$ as the standard for expressing hardness of water. In the case of calculation as its molecular weight is exactly 100. it is the most insoluble compound that can be precipitated in water treatment

Equivalent of $CaCO_3$ = $\frac{\text{Equivalent wt } CaCO_3}{\text{Equivalent wt. of hardness producing substance}}$ x mass of hardness producing substance

= $\frac{100}{2 \times \text{Eq wt of hardness producing substance}}$ x mass of hardness producing substance

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23+27+3

$NaAlO_2$ Sodium Aluminate	82	82	100/64
$Al_2(SO_4)_3$	342	57	100/114
$FeSO_4 \cdot 7H_2O$	278	139	100/278
HCl	36.5	36.5	100/73
CO_2	44	22	100/44
HCO_3^-	61	61	100/122
CO_3^-	60	30	100/66
OH^-	17	17	100/34
H^+	1	1	100/2

A water sample

272 mg

27.2g per litres $CaSO_4$

40
32
64
136

Hardness in term of $CaCO_3$ equivalent

Eq. $\frac{100}{2 \times 136} \times 272$

= 200 mg / litre

32+64
96+56 152

How many $FeSO_4$ 210.5 ppm of Hardness

$\frac{2 \times 152 \times 210.5}{100}$ =

$1.52 \times 210.5 = 319.96$

210.5
1.52

Units of Hardness

1) ppm = part per million
parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.

2) Mg/L
No. of mg of $CaCO_3$ equivalent Hardness present per Litre of water.

1000
$\frac{1}{10^5 \times 10}$
1 ppm = 1 mg/L
1 mg

3) (°Cl) (degree Clark) = 1 part of $CaCO_3$ equivalent hardness per ~~Litre~~ 70,000 litres parts of water.

4) °Fr (degree French)
1 Part of $CaCO_3$ equivalent hardness per 10^5 parts of water.

$\frac{1}{0.07}$ $\frac{100}{14}$
1 ppm = 0.07° Cl = 0.1 Fr

1° Fr = 10 ppm = 10 mg/L = 0.7° Cl
1° Cl = 14.3 ppm = 14.3 ppm = 1.43° Fr

$\frac{1}{10^6}$ $\frac{1}{75*10^4}$ $\frac{95}{71}$ $\frac{71}{24}$

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$\frac{100}{146}$ $Mg(HCO_3)_2 = 73\ Mg/L$ (1+12+48)

$\frac{100}{162}$ $Ca(HCO_3)_2 = 162\ mg/L$

$\frac{100}{95}$ $95\ mg/L = MgCl_2$ $\frac{95}{2}$

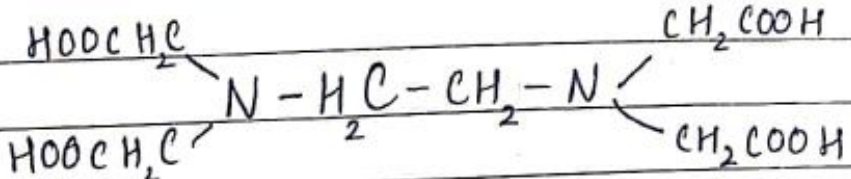
$\frac{100}{136}$ $CaSO_4 = 136\ Mg/L$

Dissolved Salt	mass	multiplication factor	equivalent to	
$Mg(HCO_3)_2$	73 Mg/L	$\frac{100}{146}$	50	T
$Ca(HCO_3)_2$	162 Mg/L	$\frac{100}{162}$	100	T
$MgCl_2$	95 Mg/l	$\frac{100}{95}$	100	P
$CaSO_4$	146 Mg/l	$\frac{100}{136}$	100	P

A water samples contain 410 mg $CaSO_4$ per litres Calculate the hardness in terms of equivalent of calcium carbonate

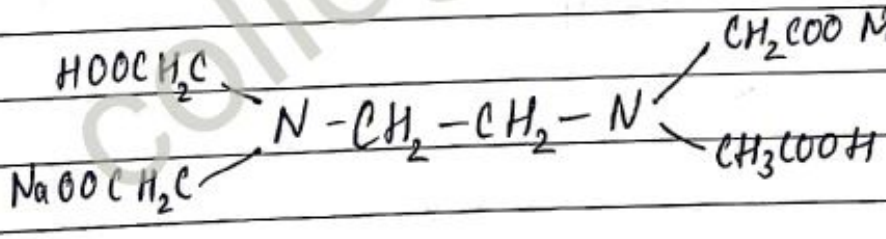
$$410 \times \frac{100}{136} = 301.47\ mg/L$$
$$= 301.47\ ppm$$

Determination of Hardness of Water by Complexo-metric Titration using EDTA solution.

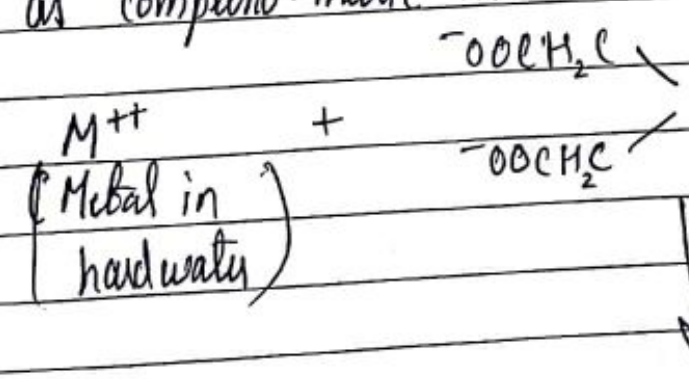


Water Hardness is generally caused by the presence of calcium (Ca^{++}) and Mg^{++} in water. The estimation of water is done by complexometric titration using standard EDTA as titrant and EBT as an indicator. EDTA (Ethylene Diamine Tetra Acetic Acid) is tetra propic acid.

The compound dissolves in water with great difficulty and very small quantity so for common experimental purpose its ~~Na~~ Di-Sodium salt derivative is used



EDTA is Hexa-dentate ligands it binds metal ions in water to give high stable chelate complex. Therefore this method is called as complexo-metric Titration



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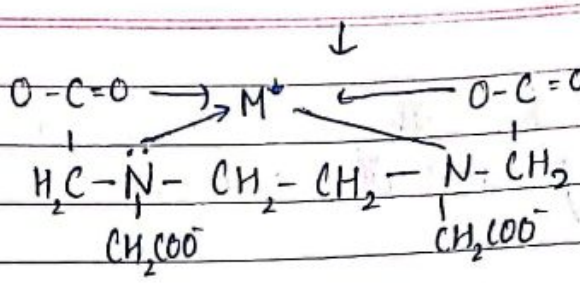
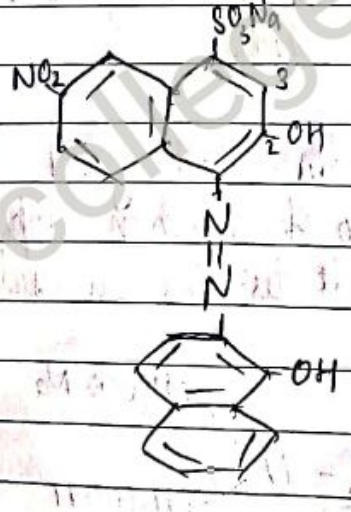


$[M^{++}\text{-EDTA}]$ complex

EBT

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



3/1/20

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Principle of EDTA method.

EDTA forms complexes ~~and~~ with (calcium & Mg) ions as well as with other mutal cations in aqueous solution. Thus in hard water sample the total hardness can be determined by titrating calcium and Magnesium ions present with

(Na - EDTA) solution using (NH_4OH - NH_4Cl) buffer solution of PH = 10 and EBT as an indicator

3→ at PH 10 EBT indicator form wine red complex (unstable) with (calcium & Mg) ion in hard water.

4) This complexes is broken by EDTA solution during titration giving stable complex with ions and reducing EBT indicator which is blue in colour so an end point the colour changes from wine red to blue.

$$Mg^{2+}/Ca^{2+} + EBT \xrightarrow[PH=10]{NH_4OH / NH_4Cl} \left[\begin{matrix} Mg^{2+} \\ Ca^{2+} \end{matrix} - EBT \right]$$

wine red

$$\left[\begin{matrix} Mg^{2+} \\ Ca^{2+} \end{matrix} - EDTA \right] + EBT$$

blue

Stable colourless complex

0.5

0.5g of $CaCO_3$ was dissolved in dilute HCl and diluted to 500 ml. 50ml of this solution required 48ml of EDTA solution for titration. 50 ml of given hard water required 15ml of EDTA solution for titration calculate Total Hardness in ppm or mg/L

40
+12
48
100

$$N_1 = \frac{0.5}{50/2} \times \frac{1}{500} \times 1000 \times 2$$

$$= \frac{N}{50} \times 1$$

SHW EDTA

$N_1V_1 = N_2V_2$

$$\frac{N}{50} \times 50ml = EDTA \; 48ml$$

$$\frac{N}{48} = EDTA$$

$$\frac{N}{48} \times \frac{15}{50} \times 1000 = N(HW)$$

$$\frac{N}{160} = N$$

$$\frac{1000}{160} \quad 6.25$$

$$\frac{250}{2} \quad 62.5$$

$$\frac{5 \times 1000}{16}$$

312.5 ppm

1.5g of $CaCO_3$ was dissolved in dilute HCl and solution was made to 1 litre by dilution. 100 ml of this solution required 44 ml of EDTA solution. While 50 ml of (sample Hard water) required 20 ml of EDTA solution

$$g = 1.5$$

$$N = \frac{1.5}{1050} = \frac{15}{500}$$

$$\frac{15}{500} \times \frac{100}{}$$

$$\frac{15}{500} = N_1 \quad V_1 = 100 \text{ ml}$$

$$\frac{3\,15}{500} \times \frac{100}{1000} \times = N_2 \times 44$$

$$\frac{3}{44} = N_2$$

$$N_2 V_2 = N_3 V_3$$

$$\frac{3}{2244} \times \frac{20}{50} = N_3$$

$$\frac{3}{110} \times \frac{50 \times 1000}{15000} = 136.36 \text{ Mg/L}$$

1g of $CaCO_3$ was dissolved in dilute HCl and diluted to 1000ml = 1l. 25ml of this solution required 25 ml of EDTA solution for titration 50ml of sample Hard water required 45 ml of EDTA solution. In another titration 50ml of same hard water on boiling, cooling & filtering required 20ml of EDTA solution using EBT. Temporary & Permanent

Strength = 1g/L

$N = \frac{1}{50}$

$N_{EDTA} = \frac{1}{50}$

Total ~~Permanent~~ $= \frac{1}{50} \times \frac{45}{50} \times 50 \times \frac{20}{1000}$

$= 900\ mg/L = 900$ ppm =

Permanent $= \frac{1}{50} \times \frac{20}{50} \times 50 \times \frac{20}{1000}$

400×0.07

Permanent = 400 mg/L = 400ppm = $40^\circ fr$ = $28^\circ Cl$

Temporary = 500 mg/L = 500ppm = $50^\circ fr$ = $35^\circ Cl$

Unknown

Whose 20ml required 30ml EDTA.

10 ml of $CaCO_3$ whose strength 300 mg/200 ml

1500 mg/L

required 20ml of same EDTA.

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~~1500~~ ~~30 N~~ $\frac{1.5}{50} = \frac{15}{500}$ ~~3~~ ~~100~~

$\frac{1.5 \times 2}{T11} = \frac{3}{111}$

$\frac{3}{30} = N$ $\frac{1.5}{50}$

$\frac{3}{50} = N_{\text{unknown } CaCO_3}$ $\frac{1.5}{50}$

$\frac{3}{50} \times \frac{10}{20} = N_{EDTA}$ $\frac{1.5 \times 10}{50 \times 2}$

$\frac{3}{10} = N_{EDTA}$ $\frac{1.5}{100}$

$\frac{3}{10} \times \frac{30}{20} = N_{\text{unknown}}$ $\frac{1.5}{100} \times \frac{30}{20}$

$\frac{4.5}{10} = N_{\text{unknown}}$ $\frac{4.5}{200} \times 20 \times 1000$

450 mg/L

$\frac{450}{5000} = N_{\text{unknown}}$

$\frac{9}{5} \times 20 \times 1000$

$\frac{4.5}{100} \times \frac{30}{20} \times 50 \times 1000$

1125 ppm

0.28 g of $CaCO_3$ was dissolved in dilute HCl to 1L
100 ml of this solution 28 ml EDTA
while 100 ml of sample water required 33 ml
100 ml of boiled water sample 10 ml
0.28 g/L

$$S = \frac{0.28}{50} \times \frac{100}{28} = N_{EDTA}$$

$$\frac{1}{50} = N_{EDTA}$$

$$\frac{1}{50} \times \frac{33}{100} = N_{SW}$$

$$\frac{1}{50} \times \frac{33}{100} \times 50 \times 1000 = 330 \text{ ppm}$$

$$\frac{1}{50} \times \frac{10}{100} \times 50 \times 1000$$

100 ppm = permanent

Temporary 230 ppm.

Alkinity.

Alkinity of water means the total content of those substances which causes increased $OH^{\ominus}$ ion upon dissociation or due to hydrolysis.

Alkinitrity of water is due to the presence of

i) Caustic alkilinity due to $OH^{\ominus}$ ions
ii) Temp Carbonate alkanility due to (CO_3^{--} & HCO_3^-)

Alkinilinity is measure of ability of water to neutralize the acids. with respect to the constituents causing alkinilinity in water ~~in~~ following situation may arise.

i) $OH^{\ominus}$ only
ii) CO_3^{--} only
iii) HCO_3^- only
iv) HCO_3^- & CO_3^{--}
v) CO_3^- & $OH^{\ominus}$

Possibilities of $OH^{\ominus}$ & $HCO_3^{\ominus}$ existing togethes is ruled out because

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

On the basis of same reasoning all 3 ions cannot exists togethes the type and ~~exist~~ extent of alkilinity present in water sample can be determined by titrating the sample with standard acid using phenolphthelein & Methyl Orange indicates

$$OH^{\ominus} + H^{\oplus} \longrightarrow H_2O$$
$$CO_3^{\ominus\ominus} + H^+ \longrightarrow HCO_3^{\ominus} \quad \Big\} P \Big\} \text{M.O.}$$
$$HCO_3^{\ominus} + H^{\oplus} \longrightarrow H_2O + CO_2$$

467.5 mg/L

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Neutalization titration

Result of Titration	$OH^{\ominus}$	$CO_3^{\ominus\ominus}$	$HCO_3^{\ominus}$
P=0	NIL	NIL	M
P= M	P or M	NIL	NIL
P=1/2M	NIL	2P	NIL
$P > \frac{1}{2}M$	2P-M	2(M-P)	NIL
$P < \frac{1}{2}M$	NIL	2P	M-2P

$N_{SHW} = \frac{0.768}{50}$

$\frac{0.768}{50} \times \frac{20}{12.9} = N_{EDTA_1} = 0.0243$

$\frac{0.768}{50} \times \frac{20}{12.7} = N_{EDTA_2} = 0.0241$

$N_{EDTA} = 0.023$

$\frac{0.023 \times 8.3}{20} = N_{HW} = 0.0092$

$0.023 \times \frac{8.3}{20} = N_{HW} = 0.0095$

$N_{HW} = 0.018$

$= 0.0093$

$0.0093 \times 50 \times 1000$

A sample of water was alkaline to both Phenolphthalin & M.O 100 ml of this water sample required 12.4 ml H_2SO_4 (N/50) 15.2 ml of the acid to M.O. end point. determine the type & extent of alkanility present.

$$\frac{1}{50} \times \frac{12.4}{100} = N$$

$$\text{Strength } [P] = \frac{1}{50} \times \frac{12.4}{100} \times 50 \times 1000$$

$$= 124 \text{ ppm}$$

$$\text{Strength } [M] = \frac{1}{50} \times \frac{15.2}{100} \times 50 \times 1000 = 152 \text{ ppm}$$

$P = 124$ ppm

$M = 152$ ppm

$P > \frac{1}{2} M$

$OH^{\ominus} \Rightarrow 2P - M = 2 \times (124) - 152 = 96$ ppm

$CO_3^{\ominus\ominus} \Rightarrow 2(M-P) = 2 \times (152-124) = 56$ ppm

Total = 152 ppm

[Check $\Rightarrow$ Total = M]

A water is alkaline to both Phenolphthalein & Methyl Orange 200ml of water sample on titration with N/50 HCl required 9.4 ml acid to phenolphthalein end point When few drops of Methy orange are added to the solution & titration further continued yellow colours of the solution just turned to pink after addition of another 21ml. of acid solution Determine the type & intent of alkanilinity present in water.

$N_2 = \frac{1}{50} \times \frac{9.4}{200}$

Strength [P] $= \frac{1}{50} \times \frac{9.4}{200} \times 1000 \times 50$

$= 47$ ppm

$N_3 = \frac{1}{50} \times \frac{30.4}{200}$

Strength [M] $= \frac{1}{50} \times \frac{30.4}{200} \times 50 \times 1000$

$= 152$

$\frac{1}{2}M = 76$

$\frac{1}{2}M = 76$ ppm

$P = 47$ ppm

$P < \frac{1}{2}M$

$CO_3^{\ominus\ominus} \Rightarrow 94$ ppm

$HCO_3^{\ominus\ominus} \Rightarrow 152 - 2 \times 47$

$\Rightarrow 58$ ppm

Total $= 152$ ppm $= M$

A water sample is alkaline to both Phenolphthalein and Methyl Orange. 500ml of water sample on titration with N/50 H_2SO_4 gave the value of 29 ml to Phenolphthalein end point. and another 500 ml water on titration with same acid gave value of 58 ml to M.O. end point. Calculate Alkalinity of water sample in term of $CaCO_3$.

$$N_P = \frac{1}{50} \times \frac{29}{500}$$

$$\text{Strength } [P] = \frac{1}{50} \times \frac{29}{500} \times 50 \times 1000 = 58 \text{ ppm}$$

$$N_{MO} = \frac{1}{50} \times \frac{58}{500}$$

$$\text{Strength } [M] = \frac{1}{50} \times \frac{58}{500} \times 1000 \times 50$$

$$= 116 \text{ ppm}$$

$P = 1/2M$

$CO_3^{--} = 116$