

# Unit - 1

water

## 1.1: Introduction

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Date: 23/08/25

### Water analysis-

1. Water is a clear, tasteless and odourless liquid that we find everywhere on earth.
2. It's made atwo molecules first is hydrogen atom and Second is a oxygen atom which chemist write  $H_2O$
3. The earth's 71% surface area is occupied by water and the remaining 29% by land.
4. This water is 97% are available on earth Surface.
5. This water is can not be used directly for drinking, agricultural and industrial purpose.
6. Hence, we are totally dependent on rain water and it necessary to store water available from rain.
7. In our daily life water is used for drinking, bathing, cooking and washing purpose.

1.2

Importance of water:-

- 1 Water is super important for plants, animals and even humans need it to survive we drink it to stay hydrated and it helps plants grow too.
- 2 Without food human being can survive for a number of days, but water is such an essential thing without which one cannot survive.

1.3

Properties of water

Water can exist as solid ice, liquid water or gas vapor depending on the temperature.

- (a) Liquid at Room Temperature — water is usually found as a liquid at room temperature, which means it flows easily and takes the shape of its container.
- (b) Transparent — water is clear and transparent, allowing us to see through it to the bottom of lakes, rivers and oceans.
- (c) Tasteless and Odorless — pure water does not have a taste or smell, making it pleasant to drink and use in cooking.

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USE OF WATER

- Drinking** — we drink water to satisfy our thirst and keep our body healthy.
- Cooking** — water is used for boiling, steaming and preparing food like rice, pasta and soups.
- Cleaning** — water is used for washing dishes, clothes and surfaces to keep them clean.
- Bathing** — we use water for showering and bathing to stay clean and fresh.
- Watering Plants** — water is used to give plants the moisture they need to grow.

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IMPURITIES IN WATER

## Impurities in water

Physical	Micro-Biological	Chemical
Suspended Impurities	Bacteria	Dissolved gases
Colloidal Colloidal Impurities	Fungi	Dissolved organic salts
	Algae	Dissolved Inorganic salts

1 Physical Impurities:— Physical Impurities in water refer to substances or particles that are physically present in the water but are not dissolved. These impurities can include:

- (a) Suspended Solids— Solid particle that float or sink in water but are not dissolved. These can include sediment, sand and other debris.
- (b) Floating Debris (colloidal impurities):— Larger objects like leaves, twigs, plastic or other debris that can be seen floating on the surface of water.

2 Chemical Impurities — Chemical impurities in water are things that mix into the water and change its properties. They can be minerals, like salt or iron or things from pollution like pesticides or oil. These impurities can make the water taste different or even unsafe to drink.

These impurities are three types, they are—

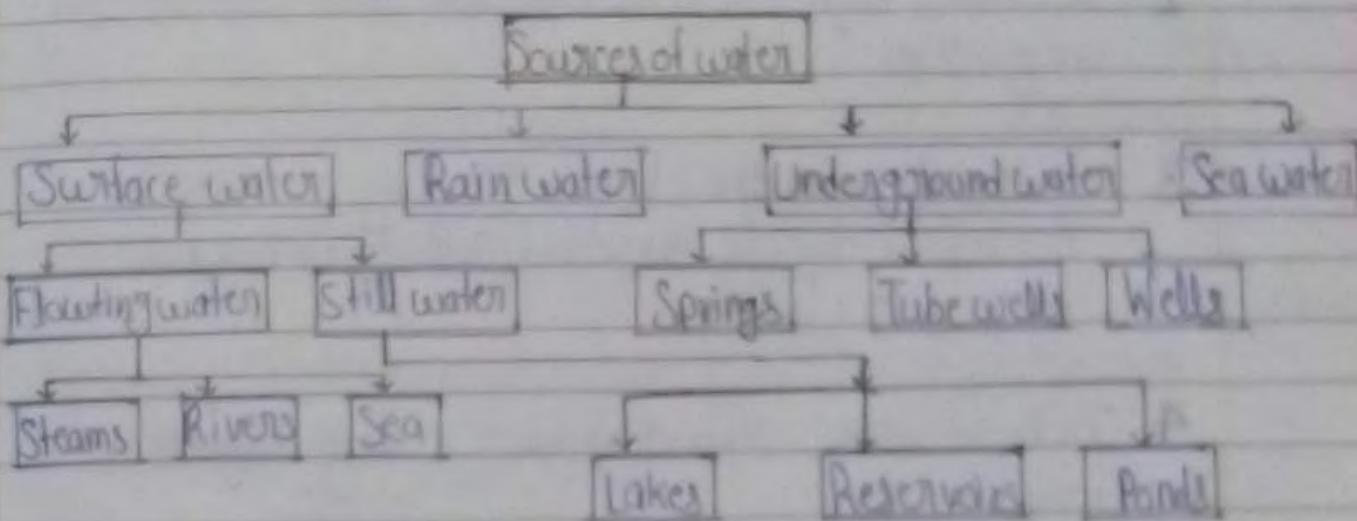
- (a) Inorganic impurities.
- (b) Organic impurities.
- (c) Dissolved gases.

3 Micro-Biological Impurities — Microbiological impurities in water are tiny living things like bacteria and viruses that can make water unsafe to drink. They can get into water from things like sewage, animal waste and dirty runoff from fields. It's important to clean water and treat water to remove these germs before drinking it to avoid getting sick.

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## Sources of water

Sources of water are places where we can find water. They include things like rivers, lakes, streams, ponds, wells and even rain. These sources provide us with the water we need for drinking, cooking, washing and many other daily activities.



- (a) Surface water**— This includes water found on the surface of Earth. Such as rivers, lakes, streams and ponds.
- (b) Rain water**— water that falls from the sky as precipitation including rain, snow, sleet and hail.
- (c) Underground water**— water that is stored beneath the Earth's surface in soil and rock formations, accessed through wells and aquifers.

L2  
L3Hard Water and Soft WaterHARD WATERDefinition :-

1. Water which does not produce foam with soap is known as hard water.
2. Contains high levels of minerals like calcium and magnesium.
3. In hard water the cleaning property of soap is depressed due to dissolved salt. It is bad for washing & cleaning.
4. In hard water, skin and hair, causing dryness and irritation.

Soft WaterDefinition :-

1. Water which produces foam with soap is known as soft water.
2. Contains low level of minerals.
3. Soft water is used for daily routine like cooking, washing and cleaning.
4. In soft water, skin and hair feel smooth and moisturized.

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## Types of Hardness

### Types of Hardness

#### ① Temporary Hardness

by - carbonate Hardness

Alkaline Hardness

ex-  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  
 $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$

#### ② Permanent Hardness

carbonate Hardness

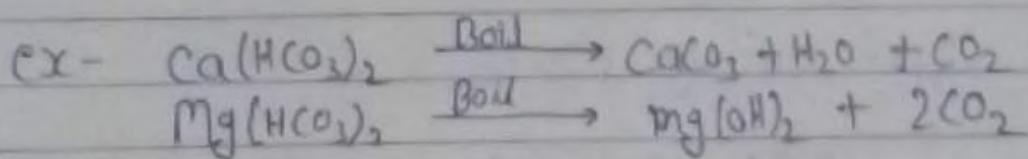
Non-Alkaline Hardness

ex-  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  
 $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$

### Temporary Hardness

1. It is due to the presence of dissolved carbonate and by-carbonate of calcium and magnesium known as temporary hardness.

2. The hardness of water which can easily removed by simple boiling of water is known as temporary hardness.



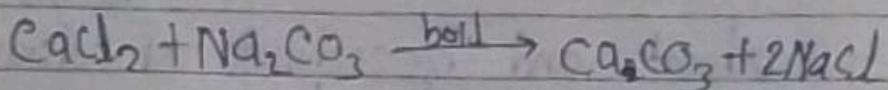
3. It is also known as carbonate hardness or Alkaline Hardness

(4) It is determined by titration with HCl using methic orange as indicator.

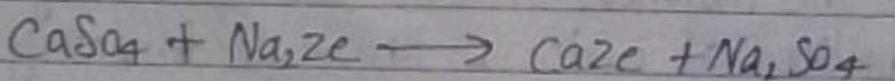
## Permanent Hardness :-

1. It is due to the permanent presence of dissolved chloride and sulphate of Ca, Mg and Al is known as permanent hardness.
2. The hardness of water which still remains after boiling of water is known as permanent hardness.
3. It cannot be destroyed by boiling. It can be removed by -

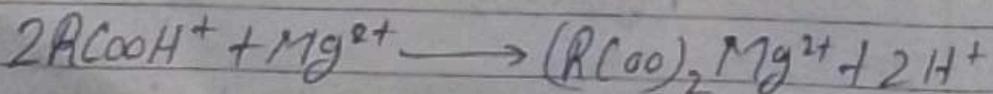
### (i) Lime Soda process



### (ii) Zeolite process :-



### (iii) Ayan exchange process



Total Hardness :- Total hardness is the measure of the concentration of calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) ions present in water.

$$\text{Total Hardness (mg/L as } \text{CaCO}_3) = \text{Calcium hardness} + \text{Magnesium hardness}$$

or

$$\text{Total Hardness} = \text{Temporary Hardness} + \text{Permanent Hardness}$$

## Table for multiplication factor of Salts/ions

Constituent Solution	molar mass	n-factor	Chemical equivalent = $\frac{\text{molar mass}}{\text{n-factor}}$	multiplication factor for converting into eq of $\text{CaCO}_3$
$\text{Ca}(\text{HCO}_3)_2$	162	2	$162/2 = 81$	$100/(2 \times 81) = 100/162$
$\text{Mg}(\text{HCO}_3)_2$	146	2	$146/2 = 73$	$100/(2 \times 73) = 100/146$
$\text{CaSO}_4$	136	2	$136/2 = 68$	$100/(2 \times 68) = 100/136$
$\text{MgSO}_4$	120	2	$120/2 = 60$	$100/(2 \times 60) = 100/120$
$\text{CaCl}_2$	111	2	$111/2 = 55.5$	$100/(2 \times 55.5) = 100/111$
$\text{MgCl}_2$	95	2	$95/2 = 47.5$	$100/(2 \times 47.5) = 100/95$
$\text{CaCO}_3$	100	2	$100/2 = 50$	$100/(2 \times 50) = 100/100$
$\text{MgCO}_3$	84	2	$84/2 = 42$	$100/(2 \times 42) = 100/84$
$\text{CO}_2$	44	2	$44/2 = 22$	$100/(2 \times 22) = 100/44$
$\text{Mg(NO}_3)_2$	148	2	$148/2 = 74$	$100/(2 \times 74) = 100/148$
$\text{HCO}_3^-$	61	1	$61/1 = 61$	$100/(2 \times 61) = 100/122$
$\text{OH}^-$	17	1	$17/1 = 17$	$100/(2 \times 17) = 100/34$
$\text{NaAlO}_2$	82	1	$82/1 = 82$	$100/(2 \times 82) = 100/164$
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	2	$278/2 = 139$	$100/(2 \times 139) = 100/278$
$\text{H}^+$	1	1	$1/1 = 1$	$100/(2 \times 1) = 100/2$
$\text{CO}_3^{2-}$	60	2	$60/2 = 30$	$100/(2 \times 30) = 100/60$
$\text{Al}_2(\text{SO}_4)_3$	392	6	$392/6 = 57$	$100/(2 \times 57) = 100/114$

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## Formula of Degree of Hardness:-

$\text{CaCO}_3 \text{ eq} = \frac{\text{mass of Hardness producing Substance}}{\times \text{multiplication factor}}$

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## Degree of Hardness:-

Degree of hardness define as the term of equivalent amount of  $\text{CaCO}_3$  because of taken of  $\text{CaCO}_3$  it is insoluble in water easily calculated, easily filtered its molecular weight is 100.

1 mole of  $\text{CaCO}_3$  = 100g of  $\text{CaCO}_3$

1 mole of  $\text{Mg}(\text{HCO}_3)_2$  = 186g of  $\text{Mg}(\text{HCO}_3)_2$

1 mole of  $\text{MgCl}_2$  = 95g of  $\text{MgCl}_2$

## 4 Types of Degree of Hardness:-

### ① PPM (Parts per million):-

- Part of  $\text{CaCO}_3$  in 1 million part of water.
- It's define as the number of parts of the  $\text{CaCO}_3$  equivalent.
- Present in  $10^6$  part of water

1 ppm = 1 part of  $\text{CaCO}_3$  in  $10^6$  parts of water

## (D) Calcium Hardness

- Number of milligram of calcium carbonate ( $\text{CaCO}_3$ ) present in 1 liter of water.

$1 \text{ mg/l} = 1 \text{ mg of parts of hardness in 1 liter of water}$

$$1 \text{ ppm} = 1 \text{ mg/l}$$

$$\text{M} = P \quad \Rightarrow \text{in case of water } P = 1$$

$$\text{M} = \text{N}$$

$$11 \times 1 \text{ mg} = 11 \text{ mg} = 1000 \times 1000 \text{ mg}$$

$$11 = 10^6 \text{ mg}$$

$$1 \text{ mg/l} = \frac{1 \text{ mg}}{10^6 \text{ mg}} = 10^{-6} = 1 \text{ ppm}$$

$$1 \text{ mg/l} = 1 \text{ ppm}$$

## (E) °CL (Degree Clarke) :-

- Number of parts of calcium carbonate ( $\text{CaCO}_3$ ) present in 70000 parts of water.

- It is define as the number of parts of  $\text{CaCO}_3$  if in 70000 parts of the water is known as clarke.

$$1^\circ \text{ CL} = 1 \text{ part of } \text{CaCO}_3 \text{ per 70000 part of water}$$

(ii)



### °Fr (Degree French) :-

- Number of parts of calcium carbonate ( $\text{CaCO}_3$ ) present in  $10^5$  part of water.
- It is defined as the number of parts of the  $\text{CaCO}_3$  eq. It is tendency power.  $10^5$  parts of the water is known as French.

$$1^{\circ}\text{Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ eq per } 10^5 \text{ part of water}$$

Note:-

### Relationship between various units of hardness:-

$$1 \text{ ppm} = 1 \text{ part per } 10^6 \text{ parts of water}$$

$$\text{and } 1^{\circ}\text{Fr} = 1 \text{ part per } 10^5 \text{ parts of water}$$

$$1^{\circ}\text{Cl} = 1 \text{ part per } 70,000 \text{ parts of water}$$

$$\therefore 10^6 \text{ ppm} = 10^5 {}^{\circ}\text{Fr} = 70,000 {}^{\circ}\text{Cl}$$

$$\text{Hence, } 1 \text{ ppm} = 0.1 {}^{\circ}\text{Fr} = \frac{70,000}{10^6} = 0.07 {}^{\circ}\text{Cl} = 1 \text{ mg/L}$$

	PPM	mg/L	°Fr	°Cl
PPM	1	1	0.1	0.07
mg/L	1	1	0.1	0.07
°Fr	10	10	1	0.7
°Cl	1/0.07	1/0.07	1/0.1	1

Classification of water hardness adapted from the WHO

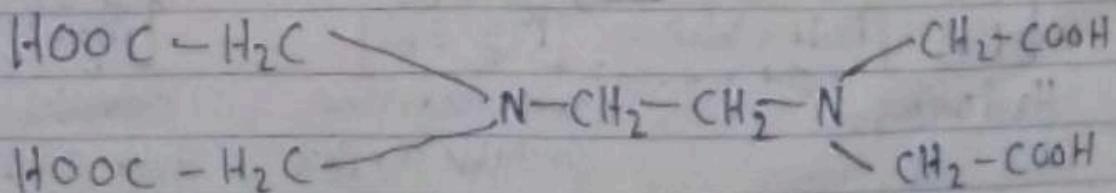
Classification	Soft	Slightly hard	Moderately hard	Hard	Very hard
Ppm or mg/L	0-17	17-60	60-120	120-180	180 and above

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## Determination of Hardness by Eddta EDTA method

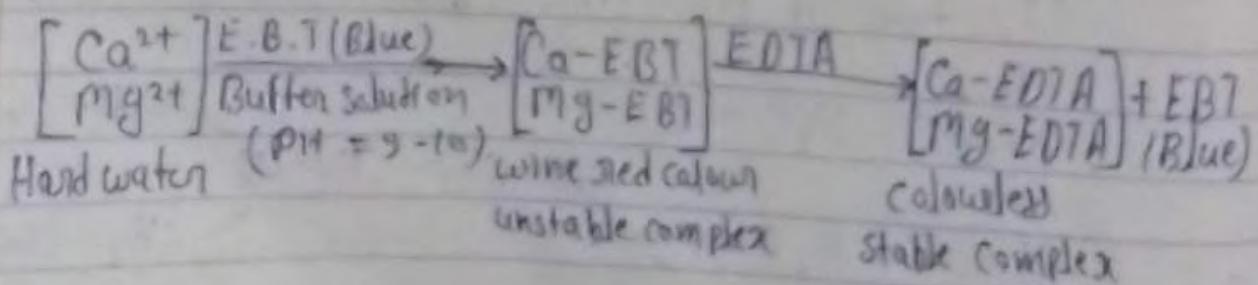
- EDTA is abbreviation of ethylene diamine tetra acetic acid.
  - EDTA ~~itself~~ dissolves in water with great difficulty and in a very very small quantity.
  - On the ~~contrary~~ contrary it's di-Sodium salt dissolves in water quickly and completely. Hence for common experimental purpose, in place of EDTA. It's di-Sodium derivative is used.
  - EDTA is a hexadentate ligand. It binds the metal ions in water i.e.  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  to give highly stable chelate complex (These metal ions are bonded via oxygen or nitrogen from EDTA molecule). Therefore this method is called as Complexometric Titration.

Structure of EDTA(Ethylenediamine tetra acetic acid)



## Principle of EDTA method:-

- The di-Sodium salt of EDTA forms complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as well as with many other metal cations in aqueous solution.
- Thus the total hardness of a hardwater sample, can be determine by titrating  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  present in the sample with di-Sodium salt of EDTA ( $\text{Na}_2\text{EDTA}$ ) solution, using ammonical buffer solution containing  $\text{NH}_2\text{Cl}$ ,  $\text{NH}_4\text{OH}$  of  $\text{pH}$  10 using Eriochrome Black-T (EBT) as the metal indicator.
- At  $\text{pH}$  10, EBT indicator form wine red coloured unstable complex with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in hard water.
- This Complex is broken by EDTA solution during titration, giving stable complex with ions and releasing EBT indicator solution which is blue in color. Hence the colour changed is from wine red to blue (EBT's own colour).
- Thus noting the colour change, the point of equivalence can be trapped and hardness of water can be determined by this method.



## Advantages of EDTA method:-

- Greater accuracy
- Highly rapid
- Highly convenient

## Alkalinity and its determination:-

### Alkalinity:

- It can be defined as "the concentration of the salts present in water which increases the concentration of  $\text{OH}^-$  ions due to the hydrolysis thereby raising pH of water to alkaline range".
- Natural water when found alkaline, it is generally due to the presence of  $\text{HCO}_3^-$ ,  $\text{SiO}_3^{2-}$  and sometimes  $\text{CO}_3^{2-}$  ions. In addition to the above the alkalinity of boiler water is also due to the presence of  $\text{OH}^-$  &  $\text{PO}_4^{3-}$  ions.

The extent of alkalinity depends on the presence of ions which broadly can be categorized as presence of.

- (I)  $\text{OH}^-$  only (ii)  $\text{CO}_3^{2-}$  only (iii)  $\text{HCO}_3^-$  only (iv)  $\text{OH}^-$  &  $\text{CO}_3^{2-}$  together. (v)  $\text{HCO}_3^-$  &  $\text{CO}_3^{2-}$  together.

bicarbonates

hydroxyle

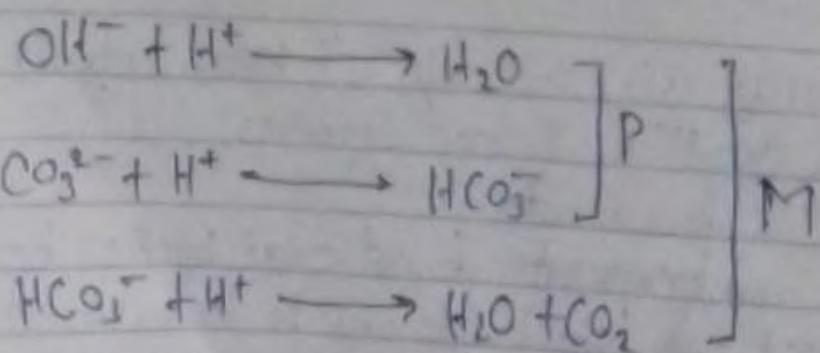
- Hydroxide and bicarbonates do not exist together because hydroxyle ions react with bicarbonate ions to form carbonate ions. Therefore existence of hydroxyle and bicarbonate ions together is ruled out.



The alkalinity of natural water is due to the presence of hydroxides, carbonates and bicarbonates of calcium and magnesium. Alkalinity is a measure of the ability of water to neutralize the acids. The constituents causing alkalinity in natural water are as follows:-

This is determined by titrating the sample with a standardised solution of a strong acid. When the pH of the sample is above 8.3, titration is first carried out using phenolphthalein indicator. At the end point when indicator changes from pink to colourless, the pH is lowered to about 4.5 due to addition of HCl. At this point complete neutralization of hydroxide and conversion of all the carbonate into bicarbonate occurs. The alkalinity measured upto this point is called phenolphthalein alkalinity - [P]. Titration is continued using methyl orange indicator. The color changes from yellow to red and shows complete neutralization of all the bicarbonate ions.

When standardised acid solution is added to alkaline water following reaction takes place



The total volume of acid used in both the stages corresponds to the neutralization of hydroxide, carbonate and bicarbonate and is thus a measure of total alkalinity. [M]

Calculation of Alkalinity of water by following table :-

Alkalinity	$\text{OH}^-$ (PPM)	$\text{CO}_3^{2-}$ (PPM)	$\text{HCO}_3^-$ (PPM)
$P=0$	0	0	M
$P = \frac{1}{2}M$	0	$2P$	0
$P < \frac{1}{2}M$	0	$2P$	$(M-2P)$
$P > \frac{1}{2}M$	$(2P-M)$	$2(M-P)$	0
$P=M$	$P=M$	0	0

Significance :-

- (1) For calculating the amount of lime and soda required for water softening.
- (2) In Conditioning boiler feed water highly alkaline water may cause caustic embrittlement and also may cause deposition of precipitates and sludge in boiler tubes and pipes.

- (3) Bicarbonates of calcium and magnesium induce temporary temporary hardness in water, which if untreated, cause scale formation in boilers.

Numerical based on Hardness & Strength :-

formula :-

Formula for Determination of Hardness :-

$$1) \text{ Hardness} = \frac{\text{Strength (in mg/l)} \times \text{chemical equivalent wt of } \text{CaCO}_3}{\text{chemical equivalent wt of hardness producing salt.}}$$

$$2) \text{ CaCO}_3 \text{ eq.} = \frac{\text{mass of hardness producing substance}}{\text{multiplication factor}}$$

- Q- A water sample contain 408 mg/L of calcium per liter calculate the hardness in term  $\text{CaCO}_3 \text{ eq}$

Solution Given that

water sample = 408 mg/L of  $\text{Ca}^{2+}$

and  $\text{CaCO}_3 \text{ eq} = ?$

$\text{CaCO}_3 \text{ eq} = \frac{\text{measured hardness}}{\text{Producing substance}} \times \text{multiplication factor of Producing substance}$

$$\text{CaCO}_3 \text{ eq} = \frac{408}{136} \times 100 \text{ mg/L}$$

$$\text{CaCO}_3 \text{ eq} = 300 \text{ mg/L}$$

- Q- Find the  $\text{CaCO}_3 \text{ eq}$ , Temporary Hardness, Permanent Hardness and Total Hardness of these salts and its value in mg/L °C and °F

Salts	Amount in mg/L
$\text{Ca}(\text{HCO}_3)_2$	5
$\text{Mg}(\text{HCO}_3)_2$	7
$\text{MgCO}_3$	4
$\text{MgCl}_2$	8
$\text{CaCl}_2$	3
$\text{CaSO}_4$	9

Solution

Salt	Amount (in mg/L)	multiplication factor	$\text{CaCO}_3 \text{ eq}$
$\text{Ca}(\text{HCO}_3)_2$	5	100/162	3.08 mg/L
$\text{Mg}(\text{HCO}_3)_2$	7	100/146	4.79 mg/L
$\text{MgCO}_3$	4	100/84	4.76 mg/L
$\text{MgCl}_2$	8	100/95	8.42 mg/L
$\text{CaCl}_2$	3	100/111	2.7 mg/L
$\text{CaSO}_4$	9	100/136	6.61 mg/L

$$\text{Temporary Hardness} = 7.88 \text{ mg/L}$$

$$\text{Permanent Hardness} = 22.5 \text{ mg/L}$$

$$\text{Total Hardness} = 30.38 \text{ mg/L}$$

Hardness	in mg/L	in °F	in °C
Temporary	7.88 mg/L	0.78	0.85
Permanent	22.5	2.24	1.37
Total	30.38	3.03	2.12

## Numerical Problems

QUESTION  
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(Q) - 60 ml of Standardized hardwater, calculate mg of pure  $\text{CaCO}_3$  per litre consumed 30 ml of TTD EDTA. 60 ml water sample consumed 35 ml of EDTA solution using the EBT as Indicator calculate the total hardness of water sample in ppm.

Solve:- Given that

$$\begin{aligned}\text{Standardized hardwater} &= 60 \text{ ml} \\ \text{EDTA} &= 30 \text{ ml} \\ \text{Water Sample} &= 60 \text{ ml} \\ \text{EDTA} &= 35 \text{ ml}\end{aligned}$$

$$\frac{30}{60} \text{ L.H.W} = 1 \text{ mg} = 1 \text{ ml}$$

(i) Standardization of EDTA solution -

1 ml of standard hardwater contains mg of  $\text{CaCO}_3$ ,

Now

$$30 \text{ ml of EDTA} = 60 \text{ ml of L.H.W}$$

$$30 \text{ ml of EDTA} = 60 \times 1 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA} = \frac{60}{30} \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA} = 2 \text{ mg of } \text{CaCO}_3$$

(ii) Determination of Permanent hardness -

(iii) Determination of total Hardness of water -

$$60 \text{ ml of water sample} = 35 \text{ ml of EDTA}$$

$$60 \text{ ml of water sample} = 35 \times 1 \text{ ml of EDTA}$$

$$60 \text{ ml of water sample} = 35 \times 2 \text{ mg of } \text{CaCO}_3$$

$$60 \text{ ml of water sample} = 70 \text{ mg of } \text{CaCO}_3$$

$$1\text{ ml of water sample} = \frac{70 \text{ mg of } \text{CaCO}_3}{60}$$

$$1\text{ L of water sample} = \frac{70 \times 1000 \text{ mg of } \text{CaCO}_3}{60}$$

$$1\text{ L of water sample} = 1166 \text{ mg of } \text{CaCO}_3$$

Hence, total hardness of water = 1166 mg = 1166 PPM

Q 100ml of standard hardwater calculate 1.5 mg of pure  $\text{CaCO}_3$  per litre consumed 44ml of EDTA 50 ml of water Sample Consumed 20ml of the same EDTA solution using the EBT indicator calculate the total hardness of water in ppm and °Cl unit.

Solve Given that

$$\text{Standard hardwater} = 100\text{ml}$$

$$\text{EDTA} = 44\text{ml}$$

$$\text{Water Sample} = 50\text{ml}$$

$$\text{EDTA} = 20\text{ml}$$

~~Find SHW~~

$$1\text{ ml SHW} = 1.5 \text{ mg } \text{CaCO}_3$$

Step-1 Standardization of EDTA Solution

1 ml of Standard hardwater contains 1.5 mg of  $\text{CaCO}_3$

Now

$$44 \text{ ml of EDTA} = 100 \text{ ml of SHW}$$

$$44 \text{ ml of EDTA} = 100 \times 1.5 \text{ mg of } \text{CaCO}_3$$

$$44 \text{ ml of EDTA} = 150 \text{ mg of } \text{CaCO}_3$$

1 ml of EDTA = 18% of mg of  $\text{CaCO}_3$

1 ml of EDTA = 3.40 mg of  $\text{CaCO}_3$

(ii) Determination of total hardness of water -

50 ml of water sample = 20 ml of EDTA

50 ml of water sample =  $20 \times 1 \text{ ml of EDTA}$

50 ml of water sample =  $20 \times 3.40 \text{ mg of } \text{CaCO}_3$

50 ml of water sample = 68 mg of  $\text{CaCO}_3$

1 ml of water sample =  $68/50 \text{ mg of } \text{CaCO}_3$

1 L of water sample =  $68/50 \times 1000 \text{ mg of } \text{CaCO}_3$

1 L of water sample = 1360 mg of  $\text{CaCO}_3$

Hence, Total hardness of water = 1360 mg = 1360 ppm

Total hardness =  $95.2^\circ\text{C}$

- Q. Calculate the hardness of a water sample, where 20 ml required 3 ml EDTA. 10 ml of standard calcium chloride solution, whose strength is equivalent to 300 mg of  $\text{CaCO}_3$  per 20 ml, required 20 ml of the same EDTA solution.

Ans

$$\begin{aligned} 20 \text{ ml of EDTA} &= 200 \text{ ml of hardwater} \\ &= 200 \times 300 \text{ mg of } \text{CaCO}_3 \text{ eq hardness} \\ &= 6 \times 10^4 \text{ mg of } \text{CaCO}_3 \text{ eq hardness} \end{aligned}$$

Thus, 1 ml of EDTA =  $\frac{6 \times 10^4}{20} = 3000 \text{ mg of } \text{CaCO}_3 \text{ eq}$

Determination of hardness of water sample

$$20 \text{ ml of Sample water} = 30 \text{ ml of EDTA} = 30 \times 3000$$

$$\begin{aligned} \text{Thus, 1L of Sample water} &= \frac{30 \times 3000}{20} \\ &= 4500 \text{ mg of } \text{CaCO}_3 \text{ eq hardness} \end{aligned}$$

(Q) One gm of  $\text{CaCO}_3$  was dissolved in dilute HCl and the solution was made to one litre by dilution. 50 ml of this solution required 40 ml of EDTA solution, while 50 ml of the sample water required 20 ml of EDTA solution. Calculate total hardness of water sample.

Solve - We calculate the total hardness in two steps -

(i) Standardization of EDTA solution

1000 ml of standard water = 1g of  $\text{CaCO}_3$   
or 1ml of standard water = 1mg of  $\text{CaCO}_3$

Now, 40 ml of EDTA solution = 50 ml of standard water

40 ml of EDTA solution =  $50 \times 1 \text{ mg of } \text{CaCO}_3 \uparrow$

$\therefore 1 \text{ ml of EDTA solution} = \frac{50}{40} \text{ mg of } \text{CaCO}_3$

(ii) Determination of total hardness of water sample

Further, 50 ml of sample water = 20 ml of EDTA solution  
 $= \frac{20 \times 50}{40} \text{ mg of } \text{CaCO}_3 \uparrow$

1000 ml of sample water =  $\frac{20 \times 50 \times 1000}{40 \times 50} \text{ mg of } \text{CaCO}_3 \uparrow$   
 $= 500 \text{ mg/l } \text{CaCO}_3$

Total hardness = 500 mg/l or 500 ppm

Q - 10 ml  $\text{CaCO}_3$  of strength 1 gm/litre required 8 ml EDTA on titration. 10 ml of a water sample required 6 ml of the same EDTA solution on titration. Calculate the total hardness of water sample.

Soln (i) Standardization of EDTA Solution

$$1\text{L of Standard water} = 1\text{g of } \text{CaCO}_3$$

$$\therefore 1\text{ml of Standard water} = 1\text{mg of } \text{CaCO}_3$$

$$\text{Now, } 3\text{ml of EDTA} = 10\text{ ml of Standard water}$$

$$\therefore 8\text{ml of EDTA sol.} = 10 \times 1\text{mg of } \text{CaCO}_3$$

$$\therefore 1\text{ml of EDTA sol.} = \frac{10}{8} \text{ mg of } \text{CaCO}_3$$

(ii) Determination of total hardness of water sample

$$\text{Further, } 10\text{ ml of sample water} = 6\text{ ml of EDTA solution}$$

$$= \frac{6 \times 10}{8} \text{ mg of } \text{CaCO}_3$$

$$10\text{ ml of sample water} = 6 \times \frac{10}{8} \text{ mg of } \text{CaCO}_3$$

$$= 75 \text{ mg of } \text{CaCO}_3$$

$$\text{Total hardness} = 75 \text{ mg/L or } 75 \text{ ppm}$$

(c) 50 ml of standard hard water containing 1000 mg of pure  $\text{CaCO}_3$  per litre, consumed 20 ml of EDTA solution. Using ethylene chrome black-T as indicator, calculate the total hardness of water sample in ppm.

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(i) Standardization of EDTA solution

$$50 \text{ ml of standard water} = 1000 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of standard water} = 20 \text{ mg of } \text{CaCO}_3$$

$$\text{Now, } 20 \text{ ml of EDTA} = 50 \text{ ml of standard hard water} \\ = 50 \times 20 \text{ mg of } \text{CaCO}_3 \text{ e.g. hardness}$$

$$\text{Hence } 1 \text{ ml of EDTA} = \frac{50 \times 20}{20} = 50 \text{ mg of } \text{CaCO}_3 \text{ e.g. hardness}$$

(ii) Determination of total hardness of water sample

$$50 \text{ ml of Sample water} = 25 \text{ ml of EDTA}$$

$$= 25 \times 50 \text{ mg of } \text{CaCO}_3 \text{ e.g. hardness}$$

$$\text{Hence, } 1000 \text{ ml of Sample water} = \frac{25 \times 50 \times 1000}{50}$$

$$= 25000 \text{ mg of } \text{CaCO}_3 \text{ e.g. hardness}$$

Thus, total hardness of water = 25000 ppm

(c) 100 ml of standard hard water containing 1.5 mg of pure  $\text{CaCO}_3$ . Per ml contained 44 ml of EDTA. 50 ml of a water sample consumed 20 ml of the same EDTA solution, using Calichrome black-T as indicator, calculate the total hardness of water sample in ppm and °C<sub>L</sub> units.

Solve (i) Standardization of EDTA Solution

$$100 \text{ ml of standard water} = 1.5 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of standard water} = 0.015 \text{ mg of } \text{CaCO}_3$$

$$\text{Now } 44 \text{ ml of EDTA} = 100 \text{ ml of standard hard water}$$

$$= 100 \times 0.015 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA} = \frac{100 \times 0.015}{44} = \frac{15}{44} = 0.034 \text{ mg of } \text{CaCO}_3$$

(ii) Determination of total hardness of water sample

$$50 \text{ ml of Sample water} = 20 \text{ ml of EDTA}$$

$$= 20 \times 0.034 \text{ mg of } \text{CaCO}_3$$

$$\text{Hence, 100 ml of Sample water} = \frac{20 \times 0.034}{50} \times 100$$

$$= 13.6 \text{ mg of } \text{CaCO}_3 \text{ or hardness}$$

$$1 \text{ PP} = 1 \text{ mg/L}$$

$$\text{So, } = 13.6 \text{ PPM}$$

$$1 \text{ PPM} = 0.07 \text{ °C}_L$$

$$\text{So, } 13.6 \text{ PPM} = 13.6 \times 0.07 \text{ °C}_L$$

$$= 0.952 \text{ °C}_L$$

Q. One gram of  $\text{CaCO}_3$  was dissolved in dil. HCl and the solution diluted to one litre. 100 ml of this solution required 90 ml of EDTA solution, while 100 ml of the sample water required 40 ml of EDTA. On the other hand, 100 ml of boiled water sample when titrated against EDTA consumed 20 ml of it. Calculate total, permanent and temporary hardness of water sample in ppm.

### Solve (i) Standardization of EDTA solution

$$100 \text{ ml of Standard water} = 1 \text{ g of } \text{CaCO}_3$$

$$1 \text{ ml of standard water} = 1 \text{ mg of } \text{CaCO}_3$$

$$\text{Now } 90 \text{ ml of EDTA} = 100 \text{ ml of Standard water}$$

$$90 \text{ ml of EDTA} = 100 \times 1 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA} = \frac{100}{90} \text{ mg of } \text{CaCO}_3$$

### (ii) Determination of hardness

$$\text{Further, } 100 \text{ ml of Sample water} = 40 \text{ ml of EDTA solution}$$

$$= 40 \times \frac{100}{90} \text{ mg of } \text{CaCO}_3$$

$$1000 \text{ ml of Sample water} = \frac{40 \times 100}{90} \times \frac{1000}{100} \text{ mg of } \text{CaCO}_3$$

$$\text{Total hardness} = \frac{4000}{9} = 444.44 \text{ mg/L} = 444.44 \text{ ppm}$$

$$\text{Also, } 100 \text{ ml of boiled Sample water} = 20 \text{ ml of EDTA solution}$$

$$= 20 \times \frac{100}{90} \text{ mg of } \text{CaCO}_3$$

$$1000 \text{ ml of boiled Sample water} = \frac{20 \times 100}{90} \times \frac{1000}{100} \text{ mg of } \text{CaCO}_3$$

$$\text{Permanent hardness} = \frac{2000}{50} = 222.22 \text{ ppm}$$

Hence,

$$\text{Temporary hardness} = 444.44 - 222.22 = 222.22 \text{ ppm}$$

- (c) 0.5g of  $\text{CaCO}_3$  was dissolved in HCl and the solution was made to 500 ml with distilled water. 50 ml of this solution required 25 ml of EDTA solution for titration. 50 ml of hard water sample required 20 ml of EDTA. After boiling 50 ml of boiled water sample required 15 ml of the same EDTA. Calculate each type of hardness in mg/l.

### Solution

#### (i) Standardization of EDTA Solution

$$500 \text{ ml of Standard water} = 0.5 \text{ g of } \text{CaCO}_3 \\ \text{or} \quad 1 \text{ ml of Standard water} = 1 \text{ mg of } \text{CaCO}_3$$

$$\text{Now, } 25 \text{ ml of EDTA Solution} = 50 \text{ ml of Standard water}$$

$$\text{Also, } 25 \text{ ml of EDTA Solution} = 50 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml of EDTA Solution} = \frac{50}{25} \text{ mg of } \text{CaCO}_3$$

#### (ii) Determination of total hardness of water sample

$$\text{Further, } 50 \text{ ml of Sample water} = 20 \text{ ml of EDTA solution} \\ = \frac{20 \times 50}{25} \text{ mg of } \text{CaCO}_3$$

$$500 \text{ ml of Sample water} = \frac{20 \times 50 \times 50}{25 \times 10} = 400 \text{ mg/l of } \text{CaCO}_3$$

$$\text{Total hardness} = 400 \text{ mg/l}$$

50 ml of boiled water sample = 15 ml of EDTA solution  
 $= \frac{15}{50} \text{ mg of } \text{CaCO}_3$

Thus 1L of water sample =  $\frac{15}{50} \times 1000 = 300 \text{ mg of } \text{CaCO}_3$

Potassium Hardness = 300 mg/l

Temporary hardness = Total hardness - Potassium hardness  
 $= 900 - 300$   
 $= 600 \text{ mg/l}$

(Q) - 0.28 g of  $\text{CaCO}_3$  was dissolved in 1 litre of water 100 ml of this water on titration required 28 ml of EDTA 100 ml of unknown hard water sample required 33 ml of EDTA after boiling and cooling 100 ml of this sample required 10 ml of EDTA. Calculate the temporary hardness of water.

Solve (i) Standardization of EDTA Solution  
 Given, 1L of standard hardwater containing 0.28 gm  $\text{CaCO}_3$ . Hence, each ml of standard hardwater contains 0.28 mg  $\text{CaCO}_3$ .

As,

$$28 \text{ ml of EDTA} = 100 \text{ ml of standard hardwater}$$
 $= 100 \times 0.28$ 
 $= 28 \text{ mg of } \text{CaCO}_3$

$$1 \text{ ml of EDTA} = \frac{28}{100} = 1 \text{ mg of } \text{CaCO}_3$$

(ii) Determination of hardness of water.

$$\text{Given, 100 ml of unknown hardwater sample} = 33 \text{ ml of EDTA}$$
 $= \frac{33}{100} \times 1$ 
 $= 3.3 \text{ mg of } \text{CaCO}_3$

$$100 \text{ mg (or l) of unknown hard water sample} = \frac{330}{100} \times 1000$$

= 330 mg CaCO<sub>3</sub>, eq. hardness

$$\text{Total hardness} = 330 \text{ ppm}$$

$$100 \text{ ml of boiled water} = 10 \text{ ml of EDTA}$$

$$= 10 \text{ ml}$$

= 10 mg of CaCO<sub>3</sub>, eq. hardness

$$1000 \text{ ml (or l) of boiled water} = \frac{10}{100} \times 1000 = 100 \text{ mg of CaCO}_3, \text{eq. hardness}$$

Permanent hardness of water = 100 ppm

$$\text{Hence, temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

$$= 330 - 100 = 230 \text{ ppm}$$

- (Q.) 100 ml of a water sample on titration with N/50 H<sub>2</sub>SO<sub>4</sub> gave a titre value of 8.5 ml to phenolphthalein end point and 17.0 ml to methyl orange end point. Calculate alkalinity of water sample.

Solve

100 ml water sample on titration with  $\frac{N}{50}$  H<sub>2</sub>SO<sub>4</sub> required

$$= 8.5 \text{ ml } \frac{N}{50} \text{ H}_2\text{SO}_4$$

$$\therefore 100 \text{ ml} \times N_F = 8.5 \text{ ml} \times \frac{N}{50}$$

$$\text{Normality, } N_F = \frac{8.5}{100} \times \frac{1}{50} N$$

Now, Strength of alkalinity of upto phenolphthalein end point  
in terms of  $\text{CaCO}_3$  eq.

$$P = N_p \times 50 \times 1000 \text{ ppm}$$

$$P = \frac{8.5}{100} \times \frac{1}{50} \times 1000 = 17 \text{ ppm}$$

As, 100 ml of water sample upto methyl orange end point  
consumed

$$= 8.5 + 17 \text{ ml of } \text{N } 1/2 \text{ NaOH}$$

$$100 \times N_m = \frac{25.5}{50} \text{ N}$$

$$N_m = \frac{25.5}{100} \times \frac{1}{50} \text{ N}$$

Strength upto methyl orange end point in terms of  $\text{CaCO}_3$  equivalent,

$$M = N_m \times 50 \times 1000 \text{ ppm}$$

$$= \frac{25.5}{100} \times \frac{1}{50} \times 1000 \text{ ppm} = 51 \text{ ppm}$$

Since,  $P > \frac{1}{2} M$  Hence,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions present,

and alkalinity due to  $\text{CO}_3^{2-} = 2P = 2 \times 17 = 34 \text{ ppm}$

and alkalinity due to  $\text{HCO}_3^- = M - 2P = 51 - 34 = 17 \text{ ppm}$

Hence, the given water sample containing  $\text{CO}_3^{2-}$  alkalinity = 34 ppm  
and  $\text{HCO}_3^-$  alkalinity = 17 ppm

Q 100 ml of a water sample required 20 ml of N  $\text{H}_2\text{SO}_4$  for neutralization to phenolphthalein end point.  
 After this methyl orange indicator was added to this and further acid required was 15 ml. calculate the type and extent of alkalinity.

Soln 100 ml of water sample on titration with  $\text{N } \frac{\text{H}_2\text{SO}_4}{50}$  required

$$= 20 \text{ ml of } \text{N } \frac{\text{H}_2\text{SO}_4}{50}$$

$$100 \text{ ml} \times N_p = 20 \times \text{N } \frac{\text{H}_2\text{SO}_4}{50}$$

$$100 \text{ ml} \times N_p = 20 \times \text{N } \frac{50}{50}$$

$$N_p = \frac{20}{100} \times \frac{1}{50} \text{ N}$$

Now, Strength of alkalinity upto phenolphthalein end point in terms of  $\text{CaCO}_3$  eq

$$P = N_p \times S \times 1000 \text{ ppm}$$

$$P = \frac{20}{100} \times \frac{1}{50} \times 50 \times 1000 \text{ ppm}$$

$$P = 200 \text{ ppm}$$

As, 100 ml of water sample upto methylorange end point consumed

$$= 20 + 15 = 35 \times \text{N } \frac{\text{H}_2\text{SO}_4}{50}$$

$$100 \times N_m = \frac{35 \times N}{50}$$

$$N_m = \frac{35 \times N}{100 \times 50}$$

Strength upto methyl orange endpoint informed at 50% eq

$$M = N_m \times 50 \times 1000 \text{ ppm}$$

$$M = \frac{35}{100} \times \frac{1}{50} \times 50 \times 1000 \text{ ppm} = 350 \text{ ppm}$$