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Module V

Water Technology and Sewage Water Treatment

About 75% earth's crust is water. Water is essential for living beings as well as for industries. It is used as an engineering material, as a coolant in power plants and also used for power generation purpose. But only 1% of earth's water resources are available for ready use. Hence it is urgently required to treat the water most carefully and economically. Such type of all treatments comes under the heading water technology.

Hardness of water

The property of water which prevents lather formation with soap solution is called hardness of water. It is due to the presence of dissolved salts of Ca, Mg and some other heavy metals. On the basis of hardness, water is of two types;

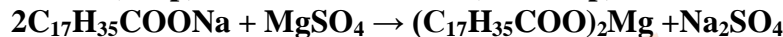
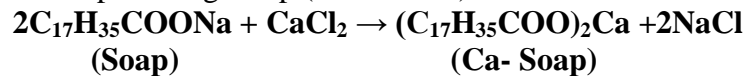
1. Soft water
2. Hard water

Soft water:

Water which can form ready and permanent lather with soap solution is called soft water.

Hard water:

Water which cannot form ready and permanent lather with soap solution is called hard water. Soap is sodium or potassium salts of higher fatty acid which when treated with hard water produces insoluble Ca-Soap and Mg-Soap (white scum).



Hardness is of two types.

1. Temporary (Carbonate) hardness
2. Permanent (Non-carbonate) hardness

Temporary (Carbonate) hardness:

Hardness which will remain for a shorter period and can be easily removed by boiling is called temporary (Carbonate) hardness. It is due to the presence of bicarbonates of Ca & Mg. On boiling, soluble bicarbonate changes to insoluble carbonates and hydroxides.



Removal of temporary hardness

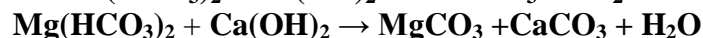
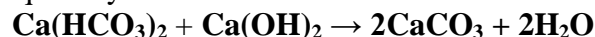
1. Boiling

On boiling, soluble bicarbonate changes to insoluble carbonates and hydroxides.



2. Clark's process

In this method, calculated quantity of lime is added to convert it as insoluble carbonate.



Permanent (Non-carbonate) hardness:

Hardness due to the presence of chlorides and sulphates of Ca, Mg, Al, Fe, etc. are called permanent hardness.

Removal of Permanent (Non-carbonate) hardness:

1. Lime soda process
2. Zeolite process
3. Ion exchange process

Degree of hardness

Hardness is expressed in terms of degree of hardness. Degree of hardness is expressed in terms of CaCO₃ equivalent hardness. The concentration of hardness producing ions and non-hardness producing ions are expressed in terms of equivalent amount of CaCO₃ and is called CaCO₃ equivalent hardness. The choice of CaCO₃ in particular due to,

1. Molecular weight is 100.
2. Equivalent weight is 50.
3. It is the most insoluble precipitate in most of the water treatment processes.

$$\text{CaCO}_3 \text{ equivalent hardness} = \frac{\text{Mass of HPS} \times \text{Equivalent weight of CaCO}_3}{\text{Equivalent weight of HPS}}$$

Where **HPS** is hardness producing substance.

The same formula can be modified by replacing the equivalent weight by molecular weight.

$$\text{CaCO}_3 \text{ equivalent hardness} = \frac{\text{Mass of HPS} \times \text{Molecular weight of CaCO}_3}{\text{Molecular weight of HPS}}$$

Let X be the mass of HPS, then **CaCO₃ equivalent hardness** = $\frac{X \times 100}{M \text{ HPS}}$

Units of hardness

The important units of hardness are

1. Ppm
2. Mg/L
3. Degree French (°F)
4. Degree Clark (°Cl)
5. Equivalents per million (epm)

Ppm:

It is the number of parts of CaCO₃ equivalent hardness present per million parts of water.

$$1 \text{ ppm} = \frac{1}{10^6}$$

$$10^6 \text{ ppm} = 1$$

Mg/L:

It is the number of milligrams of CaCO₃ equivalent hardness present per litre of water.

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

$$10^6 \text{ mg/L} = 1$$

Degree French:

It is the number of parts of CaCO₃ equivalent hardness present per 10⁵ parts of water.

$$1^\circ \text{F} = \frac{1}{10^5}$$

$$10^5^\circ \text{F} = 1$$

Degree Clark:

It is the number of parts of CaCO₃ equivalent hardness present per 70000 parts of water.

$$1^\circ \text{Cl} = \frac{1}{70000}$$

Equivalents per million:

It is the number of equivalents of CaCO₃ equivalent hardness present per million parts of water.

$$1 \text{ epm} = \frac{50}{10^6}$$

$$\frac{10^6}{50} \text{ epm} = 1$$

Inter conversion of various units of hardness

$$70000^\circ \text{Cl} = 1$$

$$10^6 \text{ Ppm} = 10^6 \text{ mg/L} = 10^5^\circ \text{F} = 70000^\circ \text{Cl} = \frac{10^6}{50} \text{ epm} = 1$$

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1^\circ \text{F} = 0.07^\circ \text{Cl} = 0.02 \text{ epm}$$

Disadvantages of hard water

- It doesn't form lather with soap solution. Instead it produces sticky precipitates of Ca-Soap and Mg-Soap. This will lead to the wastage of soap.
- Hard water used in boilers causes problems such as boiler corrosion, scales and sludges in boilers, priming and foaming, caustic embrittlement, etc.
- Water containing chlorides and sulphates if used for concrete mixing affects the hydration of cement and the final strength of hardened cement.
- The boiling point of hard water is high. So it leads to the wastage of fuel.
- Tea and coffee prepared in hard water have an unpleasant taste.
- Hard water cannot be used in dyeing industry. Since it cannot produce the exact shades of colours due to the adherence of Ca-Soap and Mg-Soap.
- It cannot be used in sugar industry. Since it causes difficulties in the crystallization of sugar and makes the sugar deliquescent.
- It cannot be used in paper industry, because it will affect the smoothness, glossiness, colour, etc. of the paper.

1. Calculate the hardness of water sample containing the following salts/litre. CaSO_4 – 16.2mg/L, $\text{Mg}(\text{HCO}_3)_2$ – 1.4mg/L, MgCl_2 – 9.5mg/L.

Constituents	Quantity	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
CaSO_4	16.2mg/L	136	$16.2 \times \frac{100}{136} = 11.9 \text{ ppm}$
$\text{Mg}(\text{HCO}_3)_2$	1.4mg/L	146	$1.42 \times \frac{100}{146} = 0.97 \text{ ppm}$
MgCl_2	9.5mg/L	95	$9.5 \times \frac{100}{95} = 10 \text{ ppm}$

$$\text{Total hardness} = 11.9 + 0.97 + 10 = 22.87 \text{ ppm}$$

$$\text{Temporary hardness} = 0.97 \text{ ppm}$$

$$\text{Permanent hardness} = \text{Total hardness} - \text{Temporary hardness} = 22.87 - 0.97 = 21.9 \text{ ppm}$$

2. A sample of water on analysis gives the following results: $\text{Ca}^{2+} = 30\text{mg/L}$, $\text{Mg}^{2+} = 18\text{mg/L}$, $\text{HCO}_3^- = 244\text{mg/L}$, $\text{Na}^+ = 11.5\text{mg/L}$. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
Ca^{2+}	30	40	$30 \times \frac{100}{40} = 75$
Mg^{2+}	18	24	$18 \times \frac{100}{24} = 75$
HCO_3^-	122	61	$122 \times \frac{100}{2 \times 61} = 100$
Na^+	11.5	-	-

$$\text{Total hardness} = 75 + 75 = 150 \text{ ppm}$$

$$\text{Temporary hardness} = 100 \text{ ppm}$$

$$\text{Permanent hardness} = \text{Total hardness} - \text{Temporary hardness} = 150 - 100 = 50 \text{ ppm}$$

3. A water sample is having 400 ppm permanent hardness and 100 ppm temporary hardness. If 42 mg/L NaHCO_3 is added to this water, calculate the new temporary and permanent hardness.

$$\text{Total hardness} = 400 + 100 = 500 \text{ mg/L}$$

Temporary hardness of water sample increases with the addition of 42 mg/L NaHCO_3 .

$$\text{Increase in temporary hardness} = \frac{42 \times 100}{2 \times 84} = 25 \text{ ppm}$$

$$\text{New temporary hardness} = 100 + 25 = 125 \text{ mg/L}$$

$$\text{New permanent hardness} = \text{Total hardness} - \text{New temporary hardness} = 500 - 125 = 375 \text{ mg/L}$$

4. A water sample contains $(\text{HCO}_3)_2$ – 36.5 ppm, $\text{Ca}(\text{HCO}_3)_2$ – 40.5 ppm, MgSO_4 – 30.0 ppm, CaSO_4 – 34.0 ppm, CaCl_2 – 27.75 ppm, NaCl – 10 ppm. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (ppm)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
$\text{Ca}(\text{HCO}_3)_2$	40.5	162	$40.5 \times \frac{100}{162} = 25 \text{ ppm}$
$\text{Mg}(\text{HCO}_3)_2$	36.5	146	$36.5 \times \frac{100}{146} = 25 \text{ ppm}$
MgSO_4	30.3	120	$30.0 \times \frac{100}{120} = 25 \text{ ppm}$
CaSO_4	34.0	136	$34.0 \times \frac{100}{136} = 25 \text{ ppm}$
CaCl_2	27.75	111	$27.75 \times \frac{100}{111} = 25 \text{ ppm}$
NaCl	10	-	-

Temporary hardness = Hardness due to $\text{Ca}(\text{HCO}_3)_2$ + Hardness due to $\text{Mg}(\text{HCO}_3)_2$
 $= 25 + 25 = 50 \text{ ppm}$

Permanent hardness = Hardness due to MgSO_4 + Hardness due to CaSO_4 + Hardness due to CaCl_2
 $= 25 + 25 + 25 = 75 \text{ ppm}$

5. A sample of water on analysis gives the following results: $\text{Ca}^{2+} = 400 \text{ mg/L}$, $\text{Mg}^{2+} = 240 \text{ mg/L}$, $\text{HCO}_3^- = 244 \text{ mg/L}$, $\text{Na}^+ = 92 \text{ mg/L}$. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (ppm)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
Ca^{2+}	400	40	$400 \times \frac{100}{40} = 1000$
Mg^{2+}	240	24	$240 \times \frac{100}{24} = 1000$
HCO_3^-	244	61	$244 \times \frac{100}{2 \times 61} = 200$
Na^+	92	-	-

Total hardness = 1000 + 1000 = 2000 ppm

Temporary hardness = 200 ppm

Permanent hardness = 2000 – 200 = 1800 ppm

6. A water sample contains $\text{Mg}(\text{HCO}_3)_2$ – 43.8 mg/L, $\text{Ca}(\text{HCO}_3)_2$ – 48.6 ppm, MgSO_4 – 24.0 ppm, CaSO_4 – 27.2 mg/L, NaHCO_3 – 16.8 mg/L. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
$\text{Ca}(\text{HCO}_3)_2$	48.6	162	$48.6 \times \frac{100}{162} = 30 \text{ ppm}$
$\text{Mg}(\text{HCO}_3)_2$	43.8	146	$43.8 \times \frac{100}{146} = 30 \text{ ppm}$
MgSO_4	24.0	120	$24.0 \times \frac{100}{120} = 20 \text{ ppm}$
CaSO_4	27.2	136	$27.2 \times \frac{100}{136} = 20 \text{ ppm}$
NaHCO_3	16.8	84	$16.8 \times \frac{100}{2 \times 84} = 10 \text{ ppm}$

Total hardness = 30+30+20+20 = 100 ppm

Temporary hardness = 30+30+10 = 70 ppm

Permanent hardness = 100 – 70 = 30 ppm

7. A sample of water on analysis gives the following results: $\text{Ca}^{2+} = 320\text{mg/L}$, $\text{Mg}^{2+} = 72\text{mg/L}$, $\text{HCO}_3^- = 610\text{mg/L}$, $\text{Na}^+ = 23\text{mg/L}$. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
Ca^{2+}	320	40	$320 \times \frac{100}{40} = 800$
Mg^{2+}	72	24	$72 \times \frac{100}{24} = 300$
HCO_3^-	610	61	$610 \times \frac{100}{2 \times 61} = 500$
Na^+	23	-	-

Total hardness = $800 + 300 = 1100$ ppm

Temporary hardness = 500 ppm

Permanent hardness = Total hardness - Temporary hardness = $1100 - 500 = 600$ ppm

8. Calculate the hardness of 0.1M CaCl_2 solution.

$$\begin{aligned}\text{Hardness} &= \text{Normality} \times \text{Eqnt Wt}_{\text{CaCO}_3} \times 1000 \\ &= 0.1 \times 2 \times 50 \times 1000 = 10000 \text{ ppm}\end{aligned}$$

9. Calculate the hardness of 0.4 N Ca^{2+} solution.

$$\begin{aligned}\text{Hardness} &= \text{Normality} \times \text{Eqnt Wt}_{\text{CaCO}_3} \times 1000 \\ &= 0.4 \times 50 \times 1000 = 20000 \text{ ppm}\end{aligned}$$

10. A sample of water is found to contain $\text{Mg}(\text{HCO}_3)_2 = 7.3\text{mg/L}$, $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/L}$, $\text{MgCl}_2 = 9.5 \text{ ppm}$ and $\text{CaSO}_4 = 13.6\text{mg/L}$. Calculate the temporary and permanent hardness of water sample. What happen to the temporary and permanent hardness of water sample if 10.6mg/L Na_2CO_3 is added?

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
$\text{Ca}(\text{HCO}_3)_2$	16.2	162	$16.2 \times \frac{100}{162} = 10 \text{ ppm}$
$\text{Mg}(\text{HCO}_3)_2$	7.3	146	$7.3 \times \frac{100}{146} = 5 \text{ ppm}$
MgCl_2	9.5	95	$9.5 \times \frac{100}{95} = 10 \text{ ppm}$
CaSO_4	13.6	136	$13.6 \times \frac{100}{136} = 10 \text{ ppm}$
Na_2CO_3	10.6	106	$10.6 \times \frac{100}{106} = 10 \text{ ppm}$

Total hardness = $10+5+10+10 = 35$ ppm

Temporary hardness = $10+5 = 15$ ppm

Permanent hardness = $35 - 15 = 20$ ppm

If 10.6mg/L Na_2CO_3 is added to water, it removes permanent Ca^{2+} as CaCO_3 and Mg^{2+} cannot be removed.

CaCO_3 equivalent hardness of $\text{Na}_2\text{CO}_3 = 10$ ppm. Thus 10 ppm permanent Ca is removed as CaCO_3 .

New total hardness = $35 - 10 = 25$ ppm

Temporary hardness = 15 ppm

New permanent hardness = $25 - 15 = 10$ ppm

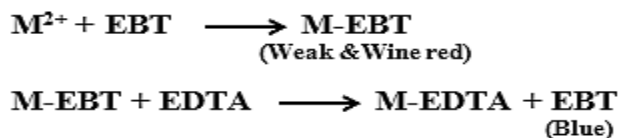
Estimation of hardness by EDTA process

It is a complexometric method used for the determination of hardness of water sample. In this method, EDTA is used as titrant and EBT (Erio-chrome Black-T) is the titrant. It is blue in

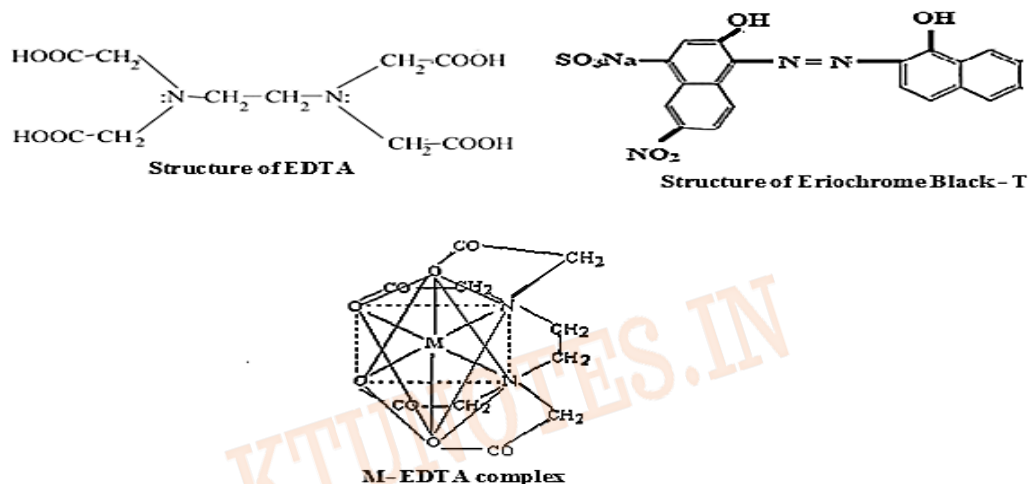
colour. It works effectively at the P^H of 10. So a buffer solution is required to maintain the P^H at 10. Usually used buffer is ammonium chloride- ammonium hydroxide buffer.

Principle and method of EDTA process:

At a P^H of 10, the Ca^{2+} & Mg^{2+} ions present in water forms a weak wine red coloured complex with EBT. When EDTA is added to this, weak EBT can be replaced by strong EDTA to form metal- EDTA complex. At the same time, wine red colour changes to blue due to the regeneration of EBT.



The PH is maintained around 10 using NH_4Cl and NH_4OH buffer, since indicator effective only at this PH. Initially M-EBT complex is formed, which is unstable. Then the addition of EDTA replaces EBT from the M-EBT complex produces M-EDTA complex and the colour changes from wine red to blue.



Procedure:

I. Preparation of solutions

a) Standard Hard Water (SHW)

Dissolve 1g pure dry $CaCO_3$ in minimum quantity dil.HCl and evaporate to dryness. The residue obtained is dissolved in distilled water and is made up to 1 litre. Each ml of this solution is equivalent to 1mg $CaCO_3$ equivalent hardness.

b) EDTA solution

Dissolve 4g EDTA crystals and 0.1g $MgCl_2$ in 1 litre distilled water.

c) EBT indicator

Dissolve 0.5g EBT powder in 100 ml alcohol.

d) Buffer solution

67.5g NH_4Cl is added to 570 ml of liquor NH_3 and is diluted to 1 litre using distilled water.

II. Standardisation of EDTA

50 ml SHW is mixed with 10 ml buffer solution and add 3-4 drops of EBT indicator. It is then titrated against EDTA till the wine red colour changes to blue.

Let the volume of EDTA consumed be V_1 ml & N_1 be its normality.

50 ml SHW = V_1 ml EDTA

(Each ml SHW contains 1mg $CaCO_3$ equivalent hardness.)

V_1 ml EDTA = 50mg $CaCO_3$ equivalent hardness

$$1 \text{ ml EDTA } (N_1) = \frac{50}{V_1} \text{ mg CaCO}_3 \text{ equivalent hardness}$$

III. Determination of Total hardness

50 ml Unknown Hard Water (UHW) is mixed with 10 ml buffer solution and add 3-4 drops of EBT indicator. It is then titrated against standardized EDTA till the wine red colour changes to blue.

Let the volume of EDTA consumed be V_2 ml.

N_2 be the normality of UHW.

$$50 \text{ ml UHW} = V_2 \text{ ml EDTA}$$

$$V_{\text{UHW}} \times N_{\text{UHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_2 = V_2 \times \frac{50}{V_1}$$

$$1 \text{ ml UHW } (N_2) = \frac{V_2}{V_1}$$

$$1 \text{ litre of UHW} = \frac{V_2}{V_1} \times 1000 \text{ mg CaCO}_3 \text{ equivalent hardness}$$

$$\text{Total hardness} = \frac{V_2}{V_1} \times 1000 \text{ mg/L or ppm}$$

IV. Determination of permanent hardness

250 ml UHW is boiled to 50 ml. During boiling, soluble bicarbonates changes to insoluble CaCO_3 & Mg(OH)_2 . These are precipitates are filtered off and the filtrate is collected and is made upto 250 ml. It contains only permanent hardness causing ingredients.

50 ml of this Boiled Hard Water (BHW) is mixed with 10 ml buffer solution and add 3-4 drops of EBT indicator. It is then titrated against standardized EDTA till the wine red colour changes to blue.

Let the volume of EDTA consumed be V_3 ml.

N_3 be the normality of BHW.

$$50 \text{ ml UHW} = V_2 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_3 = V_3 \times \frac{50}{V_1}$$

$$1 \text{ ml BHW } (N_3) = \frac{V_3}{V_1}$$

$$1 \text{ litre of BHW} = \frac{V_3}{V_1} \times 1000 \text{ mg CaCO}_3 \text{ equivalent hardness}$$

$$\text{Permanent hardness} = \frac{V_3}{V_1} \times 1000 \text{ mg/L or ppm}$$

V. Determination of temporary hardness

Temporary hardness = Total hardness – Permanent hardness

$$= \left\{ \frac{V_2}{V_1} \times 1000 - \frac{V_3}{V_1} \times 1000 \right\} \text{ mg/L or ppm}$$

$$= \frac{V_2 - V_3}{V_1} \times 1000 \text{ mg/L or ppm}$$

Advantages of EDTA process

- It is more accurate.
- It is more convenient.
- It is a rapid procedure.

1. Calculate the hardness of 0.1M CaCl_2 solution.

$$\begin{aligned} \text{Hardness} &= \text{Normality} \times \text{Eqnt. Wt. CaCO}_3 \times 1000 = \text{Molarity} \times 2 \times \text{Eqnt. Wt. CaCO}_3 \times 1000 \\ &= 0.1 \times 2 \times 50 \times 1000 = 10000 \text{ ppm} \end{aligned}$$

2. Calculate the hardness of 0.4 N Ca^{2+} solution.

$$\begin{aligned} \text{Hardness} &= \text{Normality} \times \text{Eqnt. Wt. CaCO}_3 \times 1000 \\ &= 0.4 \times 50 \times 1000 = 20000 \text{ ppm} \end{aligned}$$

3. A standard hard water containing 15g CaCO₃ per litre. 20ml of this required 25ml EDTA solution. 100ml of sample of water required 18ml EDTA solution. The same sample after boiling required 12ml EDTA solution. Calculate the temporary hardness.

Step I: Preparation of SHW

$$\begin{aligned} 1 \text{ litre SHW} &= 15\text{g CaCO}_3 \\ 1000 \text{ ml SHW} &= 15000\text{mg CaCO}_3 \\ 1 \text{ ml SHW} &= 15\text{mg CaCO}_3 \\ \text{Normality of SHW} &= 15\text{mg CaCO}_3 \end{aligned}$$

Step II: Standardisation of EDTA

$$\begin{aligned} 20 \text{ ml SHW} &= 25 \text{ ml EDTA} \\ V_{\text{SHW}} \times N_{\text{SHW}} &= V_{\text{EDTA}} \times N_{\text{EDTA}} \\ 20 \times 15 &= 25 \times N_{\text{EDTA}} \\ N_{\text{EDTA}} &= \frac{20 \times 15}{25} = 12\text{mg CaCO}_3 \end{aligned}$$

Step III: Estimation of total hardness

$$\begin{aligned} 100 \text{ ml UHW} &= 18 \text{ ml EDTA} \\ V_{\text{UHW}} \times N_{\text{UHW}} &= V_{\text{EDTA}} \times N_{\text{EDTA}} \\ 100 \times N_{\text{UHW}} &= 18 \times 12 \\ N_{\text{UHW}} &= \frac{18 \times 12}{100} = 2.16\text{mg} \end{aligned}$$

$$\text{Total Hardness} = 2.16 \times 1000 = 2160 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$\begin{aligned} 100 \text{ ml BHW} &= 12 \text{ ml EDTA} \\ V_{\text{BHW}} \times N_{\text{BHW}} &= V_{\text{EDTA}} \times N_{\text{EDTA}} \\ 100 \times N_{\text{BHW}} &= 12 \times 12 \\ N_{\text{BHW}} &= \frac{12 \times 12}{100} = 1.44\text{mg} \end{aligned}$$

$$\text{Permanent Hardness} = 1.44 \times 1000 = 1440 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 2160 - 1440 = 720 \text{ ppm}$$

4. A standard hard water was prepared by dissolving 1g CaCO₃ in dil. HCl. It is then evaporated and made upto 1 litre using distilled water. 50ml of this required 48ml EDTA solution. 50ml of test hard water required 15ml EDTA solution. 50 ml of the same test water sample after boiling and filtration required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$\begin{aligned} 1 \text{ litre SHW} &= 1\text{g CaCO}_3 \\ 1000 \text{ ml SHW} &= 1000\text{mg CaCO}_3 \\ 1 \text{ ml SHW} &= 1\text{mg CaCO}_3 \\ \text{Normality of SHW} &= 1\text{mg CaCO}_3 \end{aligned}$$

Step II: Standardisation of EDTA

$$\begin{aligned} 50 \text{ ml SHW} &= 48 \text{ ml EDTA} \\ V_{\text{SHW}} \times N_{\text{SHW}} &= V_{\text{EDTA}} \times N_{\text{EDTA}} \\ 50 \times 1 &= 48 \times N_{\text{EDTA}} \\ N_{\text{EDTA}} &= \frac{50 \times 1}{48} = 1.04\text{mg CaCO}_3 \end{aligned}$$

Step III: Estimation of total hardness

$$\begin{aligned} 50 \text{ ml UHW} &= 15 \text{ ml EDTA} \\ V_{\text{UHW}} \times N_{\text{UHW}} &= V_{\text{EDTA}} \times N_{\text{EDTA}} \\ 50 \times N_{\text{UHW}} &= 15 \times 1.04 \\ N_{\text{UHW}} &= \frac{15 \times 1.04}{50} = 0.312\text{mg} \end{aligned}$$

$$\text{Total Hardness} = 0.312 \times 1000 = 312 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$50 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_{\text{BHW}} = 10 \times 1.04$$

$$N_{\text{BHW}} = \frac{10 \times 1.04}{50} = 0.208 \text{ mg}$$

$$\text{Permanent Hardness} = 0.208 \times 1000 = 208 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 312 - 208 = 104 \text{ ppm}$$

5. 2.8g CaCO_3 was dissolved in dil. HCl and made upto 1 litre using distilled water. 100ml of this required 28ml EDTA solution. 100ml of test hard water required 35ml EDTA solution. 100 ml of the same test water sample after boiling and filtration when titrated against EDTA required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 2.8 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 2800 \text{ mg CaCO}_3$$

$$1 \text{ ml SHW} = 2.8 \text{ mg CaCO}_3$$

$$\text{Normality of SHW} = 2.8 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$100 \text{ ml SHW} = 28 \text{ ml EDTA}$$

$$V_{\text{SHW}} \times N_{\text{SHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times 2.8 = 28 \times N_{\text{EDTA}}$$

$$N_{\text{EDTA}} = \frac{100 \times 2.8}{28} = 10 \text{ mg CaCO}_3$$

Step III: Estimation of total hardness

$$100 \text{ ml UHW} = 35 \text{ ml EDTA}$$

$$V_{\text{UHW}} \times N_{\text{UHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times N_{\text{UHW}} = 35 \times 10$$

$$N_{\text{UHW}} = \frac{35 \times 10}{100} = 3.5 \text{ mg}$$

$$\text{Total Hardness} = 3.5 \times 1000 = 3500 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times N_{\text{BHW}} = 10 \times 10$$

$$N_{\text{BHW}} = \frac{10 \times 10}{100} = 1 \text{ mg}$$

$$\text{Permanent Hardness} = 1 \times 1000 = 1000 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 3500 - 1000 = 2500 \text{ ppm}$$

6. 0.30g CaCO_3 was dissolved in dil. HCl and made upto 1 litre using distilled water. 100ml of this required 30ml EDTA solution. 100ml of test hard water required 33ml EDTA solution. 100 ml of the same test water sample after boiling and filtration when titrated against EDTA required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 0.30 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 300 \text{ mg CaCO}_3$$

$$1 \text{ ml SHW} = 0.3 \text{ mg CaCO}_3$$

$$\text{Normality of SHW} = 0.3 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$100 \text{ ml SHW} = 30 \text{ ml EDTA}$$

$$V_{\text{SHW}} \times N_{\text{SHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times 0.3 = 30 \times N_{\text{EDTA}}$$

$$N_{\text{EDTA}} = \frac{100 \times 0.3}{30} = 1 \text{ mg CaCO}_3$$

Step III: Estimation of total hardness

$$100 \text{ ml UHW} = 33 \text{ ml EDTA}$$

$$V_{\text{UHW}} \times N_{\text{UHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times N_{\text{UHW}} = 33 \times 1$$

$$N_{\text{UHW}} = \frac{33 \times 1}{100} = 0.33 \text{ mg}$$

$$\text{Total Hardness} = 0.33 \times 1000 = 330 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times N_{\text{BHW}} = 10 \times 1$$

$$N_{\text{BHW}} = \frac{10 \times 1}{100} = 0.1 \text{ mg}$$

$$\text{Permanent Hardness} = 0.1 \times 1000 = 100 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 330 - 100 = 230 \text{ ppm}$$

7. In an EDTA experiment, the following values are obtained. Calculate the different types of hardness.

- i) 20ml standard hard water (10g CaCO₃ per litre) = 25ml EDTA solution
- ii) 50ml hard water sample = 25ml EDTA solution
- iii) 50ml boiled hard water sample = 14ml EDTA solution

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 10 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 10000 \text{ mg CaCO}_3$$

$$1 \text{ ml SHW} = 10 \text{ mg CaCO}_3$$

$$\text{Normality of SHW} = 10 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$20 \text{ ml SHW} = 25 \text{ ml EDTA}$$

$$V_{\text{SHW}} \times N_{\text{SHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$20 \times 10 = 25 \times N_{\text{EDTA}}$$

$$N_{\text{EDTA}} = \frac{20 \times 10}{25} = 8 \text{ mg CaCO}_3$$

Step III: Estimation of total hardness

$$50 \text{ ml UHW} = 25 \text{ ml EDTA}$$

$$V_{\text{UHW}} \times N_{\text{UHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_{\text{UHW}} = 25 \times 8$$

$$N_{\text{UHW}} = \frac{25 \times 8}{50} = 4 \text{ mg}$$

$$\text{Total Hardness} = 4 \times 1000 = 4000 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$50 \text{ ml BHW} = 14 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_{\text{BHW}} = 14 \times 8$$

$$N_{\text{BHW}} = \frac{14 \times 8}{50} = 2.24 \text{ mg}$$

$$\text{Permanent Hardness} = 2.24 \times 1000 = 2240 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 4000 - 2240 = 1760 \text{ ppm}$$

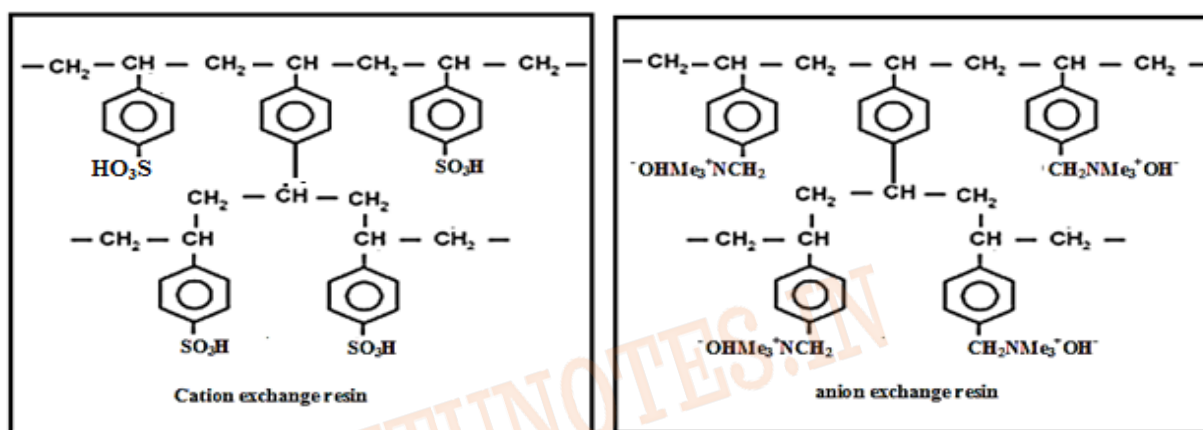
Water softening processes

The process by which hard water can be converted as soft water is called water softening process. One of the very important types of water softening process is called ion exchange process.

Ion exchange process : Ion exchange resins are insoluble cross linked long chain organic polymers having micro porous structure, where the functional group attached to the chain are responsible for their ion exchange capacity. Cation exchange resin (RH^+) contains acidic functional groups like $-\text{COOH}$, $-\text{SO}_3\text{H}$, etc. Anion exchange resin (ROH^-) contains basic functional groups like $-\text{OH}$, $-\text{NH}_2$, etc. Amberlite IR - 120, Dowex - 50 are commercially available cation exchange resins. Amberlite IR - 400, Dowex - 3 are commercially available anion exchange resins.

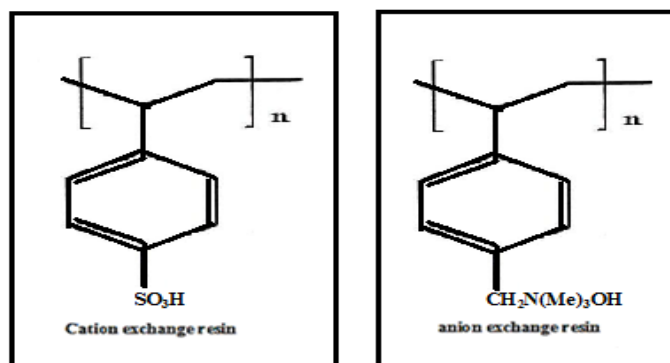
Cation exchange resins are basically styrene-divinyl benzene copolymers, which on sulphonation attain the capability to exchange its H^+ ions with cations of water.

Anion exchange resins are basically styrene-divinyl benzene or amine formaldehyde copolymers containing quaternary ammonium group, which on treatment with NaOH attain the capability to exchange its OH^- ions with cations of water.



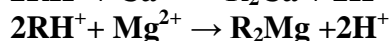
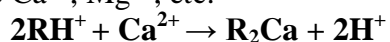
OR

Simply we can draw the structure of cation exchange resin and anion exchange resin in the following manner.

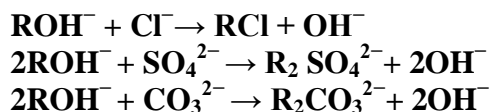


Procedure:

Initially hard water is allowed to pass through cation exchange resin column to remove all the cations like Ca^{2+} , Mg^{2+} , etc.



Then the hard water is allowed to pass through anion exchange resin column to remove all the anions like SO_4^{2-} , Cl^- , etc.

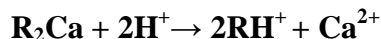


The H^+ ions and OH^- ions produced from cation and anion exchange resin column combine to form water.

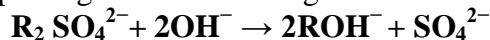


Water thus coming out of the exchanger will be free from both cations and anions. Hence it is called deionised water or demineralised water.

When the exchanger becomes exhausted, i.e. its capacity to exchange H^+ ions and OH^- ions is lost, it is regenerated. Cation exchangers are regenerated by passing dil.HCl or dil. H_2SO_4 through the column.



Anion exchangers are regenerated by passing dil.NaOH through the column.



In the deionization process, water is first passed through the cation exchanger and then through anion exchanger, Why?

When hard water is first passed through anion exchanger anions like Cl^- or SO_4^{2-} are replaced by OH^- of anion exchanger. Thus Ca^{2+} and Mg^{2+} ions of hard water produces $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ precipitates. These precipitates will lead to clogging. Thus in the deionization process, water is first passed through the cation exchanger and then through anion exchanger

Advantages:

1. Even highly acidic alkaline water can be softened by this method.
2. Gives water of very low hardness (2 ppm).
3. Water obtained by this method can be used even in high pressure boilers because of its low hardness.
4. No sludge is formed.

Disadvantages:

1. Equipment and chemicals used are costly.
2. Turbid water cannot be treated by this method.

Drinking water (Municipal water) (Potable water)

Water safe to drink is called drinking water (Municipal water) (Potable water).

Specifications of drinking water

- It must be very clear, odourless, and pleasant in taste.
- It must be soft, total hardness should not exceed 300 ppm and P^{H} should come within 6.5-8.5.
- It must be cool and free from dissolved toxic gases like H_2S .
- It should not contain harmful minerals like Pb, As, Cr, Mn, etc.
- TDS (Total Dissolved Solids) should not exceed 500 ppm.
- It should not contain any disease causing microorganisms.

Natural water from rivers, canals may not meet all the required specifications of drinking water. So it needs purification.

Methods are used for the purification of drinking water:

I. Removal of suspended impurities:

a) Screening:

In this method, water is passed through bar screens having large number of holes which removes floating matter.

b) Sedimentation:

In this method, water is taken big tanks (sedimentation tanks) for about 2-6 hours. At that time, suspended particles settle down by the force of gravity. The clear supernatant water can then be pumped out.

If the water to be purified contains fine clay particles and colloidal matter, then simple sedimentation fails. In that case, preferred method is **sedimentation with coagulation**. Usually used coagulants are alums ($K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$), $FeSO_4$, $NaAlO_2$, etc. These coagulants when added to water produce insoluble, gelatinous, flocculant precipitates, which descends through water entrap fine colloidal impurities in water forming bigger flocs that settle down easily.

c) Filtration:

In this method, water is passed through bed of fine sand and other proper sized granular materials to remove colloidal matter, bacteria, microorganisms, etc. Sand filter consists of a thick top layer of fine sand, a middle coarse particle layer and a bottom gravel layer. As water percolates through the sand filter, most of the impurities get retained in the pores of filter. So after a long time of filtration, due to clogging of filter bed with impurities, rate of filtration may become slow. In that situation, filtration is stopped and a 2-3cm portion of the top sand layer is scrapped off and is replaced with clean sand. Scrapped sand layer can be reused after washing with water and drying.

II. Removal of microorganisms (Disinfection methods)

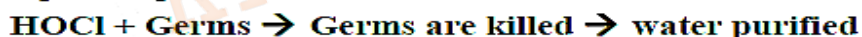
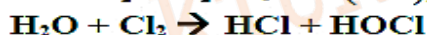
The process of removing bacteria and microorganisms from water are called disinfection. The chemicals used for this purpose is called disinfectants. Disinfection can be done by the following methods.

1. Boiling:

In this method water is boiled for a period of 10 minutes to remove the disease causing bacteria and microorganisms.

2. Addition of bleaching powder:

Bleaching powder is added at a rate of 1kg per 1000 kilo litres of water and allowed to stand undisturbed for several hours. Bleaching powder is calcium oxy chloride.



The hypochlorous acid produces is a powerful germicide. It reacts with enzymes in the cells of microorganisms, deactivating them and killing them.

Disadvantages:

- It increases the Ca content in the water and makes the water harder.
- Excess of bleaching powder produces an unpleasant taste to water.

3. Chlorination:

Chlorine is added to water either in the gaseous form or concentrated solution form produces HOCl. Chlorinator is the apparatus used for chlorination, which uses liquid chlorine.



Advantages:

- It is very effective and economical.
- Storage is easy.
- It can be used at low and high temperatures.
- No salt impurities in the treated water.

Disadvantages:

- Excess of chlorine, produces an unpleasant taste and odour to water.
- It causes irritation to mucous membrane.
- It is not an effective disinfectant above 6.5 P^H.

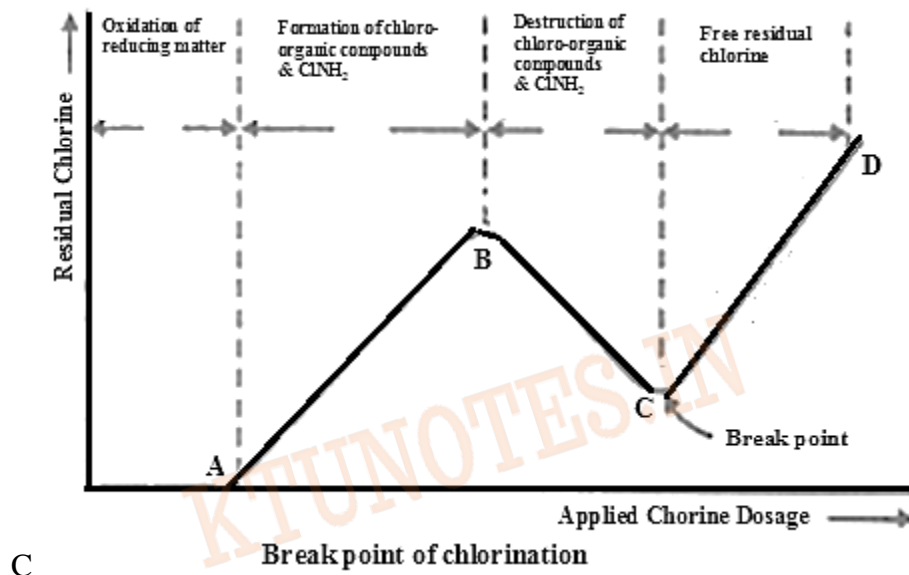
Break point of chlorination:

Break point of chlorination is defined as the addition of sufficient amount of chlorine to kill the microorganisms and to destroy them completely by the oxidation of reducing matter, organic matter, and free ammonia and leave behind free residual chlorine to continue the further disinfection.

If we plot, residual chlorine against applied chlorine, we get a curve. The dip in the curve 'C' shows the break point.

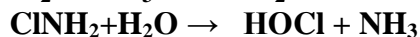
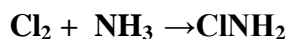
At the break point all the colour, odour, taste disappears and all the disease causing microorganisms get killed. It completely oxidises the organic compounds, ammonia and reducing compounds. After the break point, any further addition of chlorine appears to be present as free residual chlorine which will continue the further disinfection.

The amount of free chlorine required for continuing further disinfection is 0.1-0.2 ppm. If over chlorination occurs, excess chlorine can be removed by passing the water through molecular sieve or by stirring it with activated carbon followed by filtration. Excess chlorine can be removed by adding dechlorinating agents like SO_2 , Na_2SO_3 , sodium thiosulphate, etc.



4. Addition of ClNH_2

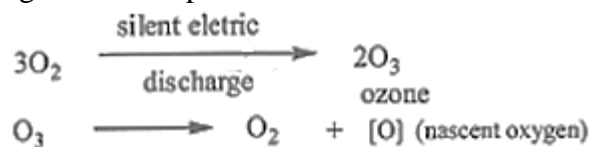
Chlorine on reaction with ammonia produces ClNH_2 .



ClNH_2 is a better disinfectant than chlorine, since its residuals remain in water for a longer period and will continue the disinfection. Its excess does not produce any irritating odour. Its presence imparts good taste to water.

5. Using ozone

Ozone is an excellent disinfectant and it is used in the gaseous form. Ozone is produced by passing silent electric discharge through cold and dry oxygen. Ozone thus produced is unstable and breaks down liberating nascent oxygen, which is a powerful oxidizing agent. It destroys all the bacteria and oxidises organic matter present in water.



Advantages

- Simultaneous removal of colour, odour, taste without leaving any residual in water.

- Its excess does not cause any harm to water as nascent oxygen is unstable and can be easily converted as molecular oxygen.

Disadvantages

- This method is costly.
- Microbial growth may again start in the treated water as it contains no residuals. In order to prevent this; add a small amount of Cl_2 after ozonation.

Small scale disinfection

1. Disinfection by UV light

Disinfection can be brought about by exposing water to UV light. A quartz tube containing Hg-lamp is used as a source of UV light.

Advantages

- No chemicals are used in this treatment.
- No taste or odour is imparted to water.
- It is mainly employed in swimming pools as disinfection using chemicals may cause harmful effects to the skin of the people swimming.

Disadvantages

- It requires costly equipment.
- Technical skill is required for this method.

2. Disinfection by sunlight

Sunlight can destroy microorganisms without imparting any colour, odour, and taste to water. But it has the disadvantage that it cannot penetrate into the depth of the water.

3. Disinfection by KMnO_4

KMnO_4 is a powerful oxidizing agent. It provides nascent oxygen, which will oxidise organic matter in the water.

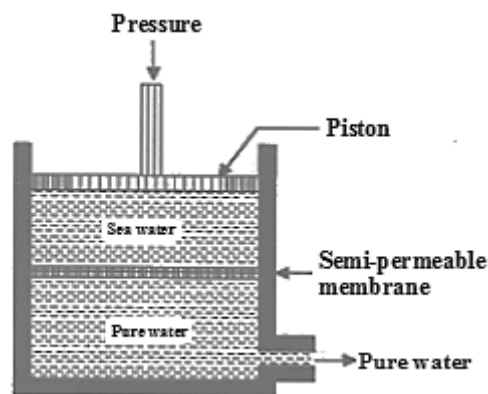
Brackish water treatment

Water containing high concentration of dissolved salt with a brackish taste is called brackish water. Eg: Brine

Brackish water is unfit for drinking. Hence it needs desalination. Reverse osmosis is the best method used for the desalination of brackish water.

Reverse osmosis

When two solutions of unequal concentrations are separated by a semipermeable membrane, then the solvent flows from dilute to the concentrated solution due to osmosis. But if the hydrostatic pressure is greater than the osmotic pressure, then the solvent flows through the semipermeable membrane in a direction opposite to that of natural osmosis i.e. from concentrated to the dilute solution. This is called reverse osmosis. Usually a pressure of $15\text{--}40\text{kgm}^{-2}$ is required. Membranes made up of cellulose acetate or polymethacrylate can be used as the semipermeable membrane.



Sea water can be purified by this method. The apparatus used for this process contains two chambers separated by semipermeable membrane. Sea water to be purified is taken in one of the chambers. If a pressure of $15\text{-}40\text{kgm}^{-2}$ is applied on the sea water side to force the pure water alone present in it through the semipermeable membrane to leave behind the dissolved solids. Hence we get the pure water from the other chamber.

Advantages

- It is simple, low cost and is the best method to convert sea water to fresh water.
- It helps for the removal of ionic matter, non-ionic matter, colloidal matter and high molecular weight organic matter.
- Colloidal silica which cannot be removed by demineralization can be removed effectively by this method.
- Life time of semipermeable membrane is quite high and is about 2 years.
- Semipermeable membrane can be replaced within a few minutes. Thus providing nearly uninterrupted water supply.

Disadvantage

- High pressure has to be maintained throughout the process which is very difficult.

Sewage (Waste water)

Sewage is the liquid waste which includes human waste, house hold waste, industrial waste, etc. It contains 99.99% of water and 0.01% of organic matter, inorganic matter, suspended impurity, colloidal impurity, etc. Sewage contains both aerobic and anaerobic bacteria that bring out the oxidation of organic compounds in it. Aerobic oxidation is the oxidation of organic matter in the sewage by aerobic bacteria in the presence of excess oxygen. Anaerobic oxidation is the oxidation of organic matter in the sewage by anaerobic bacteria in the presence of limited quantity oxygen.

Distinguish between aerobic and anaerobic oxidation

Aerobic oxidation	Anaerobic oxidation
<ul style="list-style-type: none"> • It occurs in presence of excess oxygen. • Oxidation by aerobic bacteria. • The products of oxidation are CO_2, nitrates, phosphates, sulphates. • The products are non-offensive smelling. • During decomposition, carbohydrates are converted as CO_2 and water. • Energy released is more and rate of decomposition is slow. • No bio-gas fuel is produced. 	<ul style="list-style-type: none"> • It occurs in presence of limited quantity oxygen. • Oxidation by anaerobic bacteria. • The products of oxidation are acetic acid, methane, H_2S, NH_3, phosphine. • The products are offensive smelling. • During decomposition, carbohydrates are converted as CO_2 and methane. • Energy released is less and rate of decomposition is fast. • Bio-gas fuel like methane is produced.

Dissolved oxygen (DO)

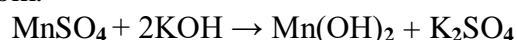
Dissolved oxygen is defined as the free oxygen present in water or any other liquid. It is the parameter used to assess water quality. Low dissolved oxygen content can cause harm to aquatic life and it also affect the water quality.

Factors that governs the amount of dissolved oxygen in water

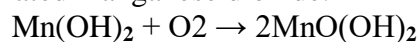
- Dissolved oxygen varies with water temperature. Pure water at 30°C contains 7.8 ppm dissolved oxygen, whereas that at 20°C contains 9.2 ppm dissolved oxygen. That means cold water is having greater dissolved oxygen than hot water.
- Dissolved oxygen in water gets affected by the presence of oxidisable impurities or pollutants like starch, cellulose, etc.
- Dissolved oxygen also varies with altitude. At higher altitudes, lesser the atmospheric pressure and hence lesser will be the DO.

Experimental determination of DO by Winkler's titration method

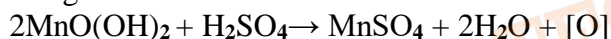
Take a 125 mL glass bottle having air tight stopper. Fill the bottle completely with water without bubbling. 1 mL MnSO_4 solution and 1 mL alkaline KI solution are introduced into the solution using a graduated pipette. Close the lid of the bottle without leaving any air bubble and shaken vigorously and allowed to stand for about 15 minutes. The precipitate formed gets settled at the bottom.



The DO present in the sample oxidizes some of the Mn^{2+} to Mn^{4+} , which is precipitated as brown hydrated manganese dioxide.



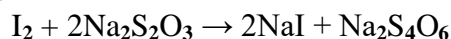
Add 2 mL 1:1 H_2SO_4 from the top using graduated pipette. Close the lid and shaken well till all the precipitate get dissolved.



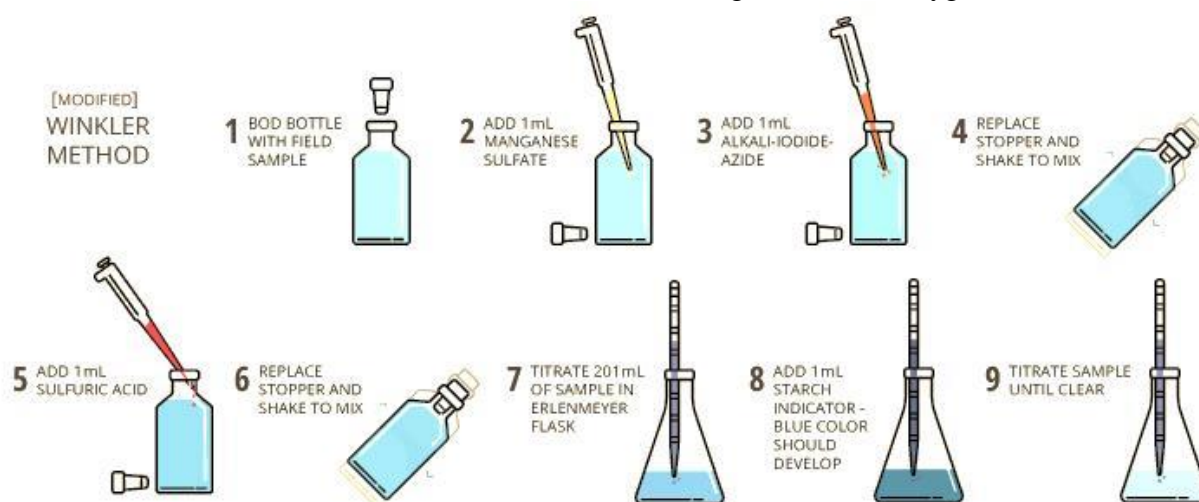
The nascent oxygen reacts with KI in the solution in presence of H_2SO_4 to liberate iodine.



The solution is then transferred to a 250 mL conical flask and titrated against standard thiosulphate solution taken in the burette using starch as indicator. Thus the liberated iodine is estimated.



1ml of 0.01N $\text{Na}_2\text{S}_2\text{O}_3$ solution = 0.1mg Dissolved Oxygen



BOD & COD

The extent of water pollution is assessed in terms of BOD & COD. It indicates the extent of treatment required for sewage water to make it safe for discharge into rivers.

Biological Dissolved Oxygen (BOD)

It is defined as the total amount of oxygen required for the complete oxidation of biologically active organic matter under aerobic conditions by bacteria and microorganisms at 20°C for a period of 5 days or 27°C for a period of 3 days.

Significance of BOD

- Larger the concentration of organic matter, greater will be the BOD.
- Larger the BOD, greater will be the pollution.
- BOD helps for finding the degree of pollution. It also helps for pollution study.

Disadvantage

- The results are obtained only after 5 days.

Experimental determination of BOD of water sample

A known volume of sewage is diluted with fresh water whose DO content is predetermined. Then it is kept in a closed vessel at 20°C for a period of 5 days or 27°C for a period of 3 days in an incubator. After this time period, the dissolved oxygen content in the water sample is measured. From the difference in the dissolved oxygen content, it is possible to calculate the BOD of the sample.

$$\text{BOD} = \frac{(D_1 - D_2) \text{ Volume of the sample after dilution}}{\text{Volume of the sample before dilution}}$$

Where D_1 is the DO of the sample in mg/l at the beginning of the experiment & D_2 is the DO of the sample in mg/l after 5 days

Chemical Oxygen Amount (COD)

It is the amount of oxygen required for the complete oxidation of biologically active and biologically inert materials present in sewage water using strong oxidizing agent like acidified $\text{K}_2\text{Cr}_2\text{O}_7$ for a period of 3 hours. Only less time is required for the determination of COD. COD is always greater than BOD, since it causes the oxidation of both biologically active and biologically inert material.

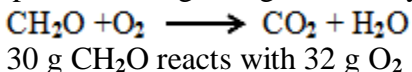
Experimental determination of COD of water sample

A known volume of sewage is mixed with a fixed volume of $\text{K}_2\text{Cr}_2\text{O}_7$ solution and dil. sulphuric acid and is refluxed for about 2-3 hours in presence of small amount of Ag_2SO_4 catalyst. The solution is then cooled and titrated with standard ferrous ammonium sulphates solution. Thus the unreacted $\text{K}_2\text{Cr}_2\text{O}_7$ in the solution can be determined. A blank experiment is conducted with pure water. From the difference between the titre values of the blank and the test solution, COD can be calculated.

$$\text{COD} = \frac{(V_1 - V_2) \times N \times 8}{V_e} \times 1000$$

Where V_1 & V_2 are the volumes of Mohr salt used by the blank and test samples respectively. V_e is the volume of effluent sample taken for test and N is the normality of Mohr's salt solution.

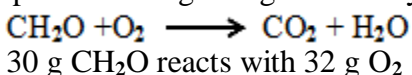
1. Find the BOD of the water sample containing 60mg of carbohydrate (CH_2O) per litre.



Therefore, 60 mg carbohydrate requires $60 \times \frac{32}{30} = 64$ mg oxygen

Thus the BOD of the water sample = 64mg/L = 64 ppm

2. Find the BOD of the water sample containing 75mg of carbohydrate (CH_2O) per litre.



Therefore, 75 mg carbohydrate requires $75 \times \frac{32}{30} = 80$ mg oxygen

Thus the BOD of the water sample = 64mg/L = 80 ppm

3. 100ml of water sample after reaction with fixed amount of acidified $K_2Cr_2O_7$ consumes 15ml, 0.1N Ferrous solution. For blank titration the ferrous solution consumed is 25ml. Find the COD of water sample.

$$COD = \frac{(V_1 - V_2) \times N \times 8}{V_e} \times 1000$$

$$COD = \frac{(25 - 15) \times 0.1 \times 8}{100} \times 1000 = 80 \text{ ppm}$$

4. 100 mL sewage water is diluted to 500 mL with dilution water; the initial dissolved oxygen was 7.5 ppm. The dissolved oxygen level after 5 days of incubation was 3.5 ppm. Find the BOD of the sewage.

$$BOD = \frac{(D_1 - D_2) \text{ Volume of the sample after dilution}}{\text{Volume of the sample before dilution}}$$

$$BOD = \frac{(7.5 - 3.5) 500}{100} = 20 \text{ ppm}$$

Sewage treatment

Sewage treatment is carried out using an artificial process called sewerage. It occurs via different steps. They are

1. Primary treatment
2. Secondary treatment
3. Tertiary treatment

1. Primary treatment

In this process, large solids and inorganic matter, which are suspended in the sewage, are removed. This can be done by

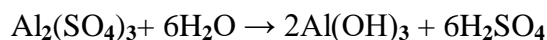
- a) Screening
- b) Sedimentation

Screening

In this process, sewage is passed through bar screen or mesh screen which removes the suspended impurities.

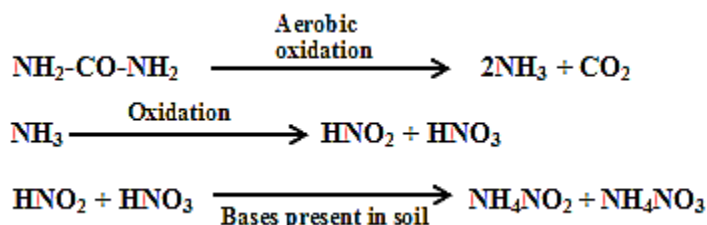
Sedimentation

Majority of suspended impurities present in the sewage can be removed by this process. In this process, sewage is taken in sedimentation tank. Along with sewage, some coagulants like alums, $Al_2(SO_4)_3$, $NaAlO_2$, etc. are added before sedimentation. Coagulants form gelatinous precipitate, which can entrap small sized organic matter to form bigger precipitate. Then settling occurs rapidly.



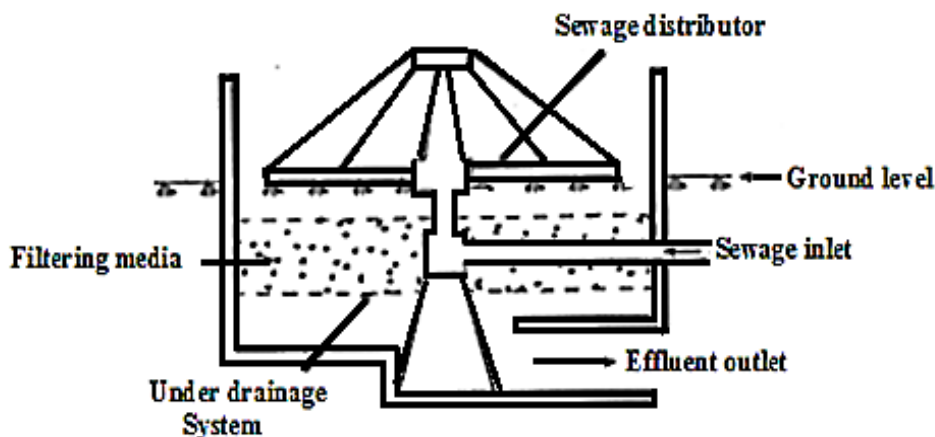
2. Secondary treatment or biological treatment

Secondary treatment is the biological treatment. In this process, aerobic oxidation of sewage occurs. During this process, carbon and nitrogen in the sewage get oxidised to CO_2 and NH_3 . Ammonia on further oxidation produces nitrites and nitrates.



a. Trickling filter process

It is a type of biological treatment carried out using a special type of filter called trickling filter.



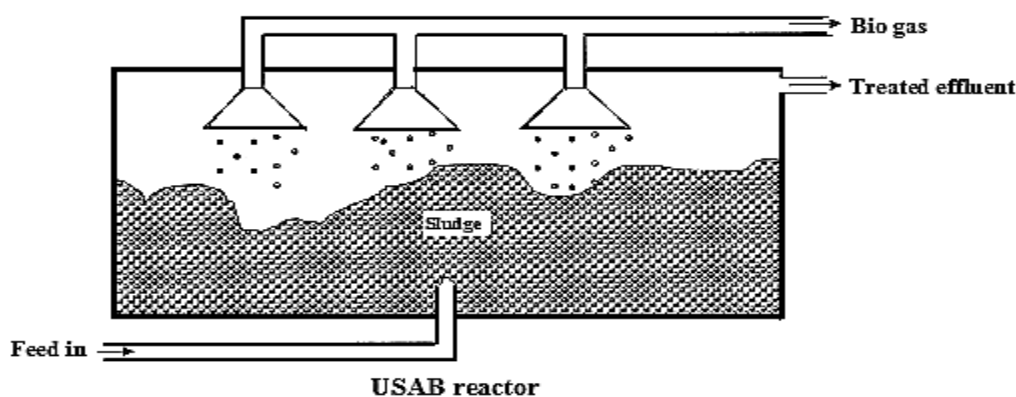
Trickling Filter

It is rectangular in shape with 2m depth. It is filled with crushed rocks, broken bricks, etc. on that microbial growth occurs and fitted with rotating distributor. Sewage trickles through the filter with the help of rotating distributor. Then it moves down through the filtering medium. During this movement, microorganisms start consuming organic matter in the sewage. A more or less clear effluent is collected through the under drainage system.

b. Activated sludge process

It is also a biological treatment. In this process, aerobic oxidation of sewage is carried out in the presence of activated sludge. Activated sludge is the sludge taken from previous oxidation process.

c. Upflow Anaerobic Sludge Blanket (UASB) (USAB) process



It is an anaerobic treatment. In this process, effluent is fed from the bottom of the reactor and it moves upwards through the sludge blanket. Sludge blanket is composed of biological granules containing large number of bacteria. As the waste comes in contact biological granules, anaerobic oxidation takes place producing gases like methane.

The gases with biological granules move towards the upper region of the reactor, where the gases only set free and the granules come back to the sludge blanket. Gases are collected at the gas collector dome at the top of the reactor. The Upflow velocities are 0.6-0.9m/hour.

3. Tertiary treatment

This is the advanced phase of sewage treatment. By this process, nitrogen and phosphorous content in the effluent get reduced. Three important processes employed for this purpose are

a) Precipitation

In this process, effluent obtained after the secondary treatment is treated with CaO, so that phosphorous get precipitated as $\text{Ca}_3(\text{PO}_4)_2$.

b) Nitrogen stripping

By this process, ammonia gas can be removed by passing the effluent through a series of baffle plates. Since ammonia is having lower density than air.

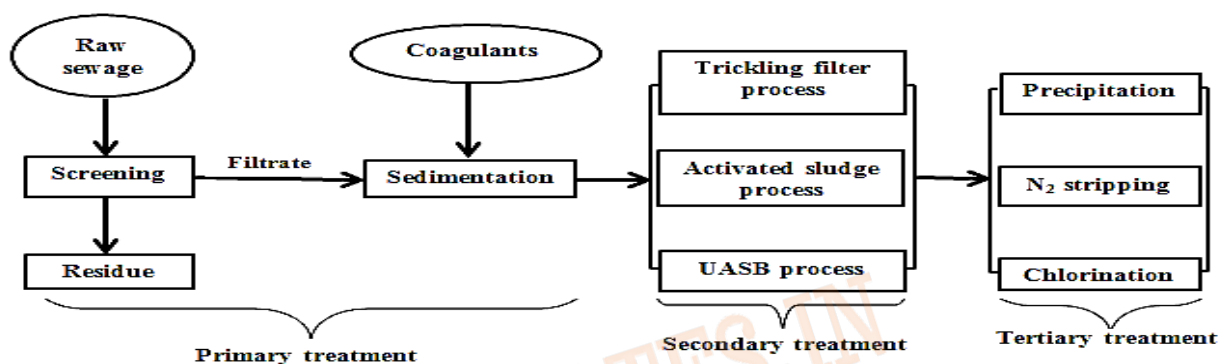
c) Chlorination

Disinfection of effluent is done by treating it with chlorine.



The hypochlorous acid produces is a powerful germicide. It reacts with enzymes in the cells of microorganisms, deactivating them and killing them.

Flow diagram of sewage(Wastewater) treatment



Problems

1. Calculate the hardness of water sample containing the following salts/litre. CaSO_4 – 16.2mg/L, $\text{Mg}(\text{HCO}_3)_2$ – 1.4mg/L, MgCl_2 – 9.5mg/L.

Constituents	Quantity	M _{HP}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{\text{MHPS}}$
CaSO_4	16.2mg/L	136	$16.2 \times \frac{100}{136} = 11.9 \text{ ppm}$
$\text{Mg}(\text{HCO}_3)_2$	1.4mg/L	146	$1.42 \times \frac{100}{146} = 0.97 \text{ ppm}$
MgCl_2	9.5mg/L	95	$9.5 \times \frac{100}{95} = 10 \text{ ppm}$

$$\text{Total hardness} = 11.9 + 0.97 + 10 = 22.87 \text{ ppm}$$

$$\text{Temporary hardness} = 0.97 \text{ ppm}$$

$$\text{Permanent hardness} = \text{Total hardness} - \text{Temporary hardness} = 22.87 - 0.97 = 21.9 \text{ ppm}$$

2. A sample of water on analysis gives the following results: $\text{Ca}^{2+} = 30\text{mg/L}$, $\text{Mg}^{2+} = 18\text{mg/L}$, $\text{HCO}_3^- = 244\text{mg/L}$, $\text{Na}^+ = 11.5\text{mg/L}$. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M _{HP}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{\text{MHPS}}$
Ca^{2+}	30	40	$30 \times \frac{100}{40} = 75$
Mg^{2+}	18	24	$18 \times \frac{100}{24} = 75$

HCO_3^-	122	61	$122 \times \frac{100}{2 \times 61} = 100$
Na^+	11.5	-	-

Total hardness = $75 + 75 = 150$ ppm

Temporary hardness = 100 ppm

Permanent hardness = Total hardness - Temporary hardness = $150 - 100 = 50$ ppm

3. A water sample is having 400 ppm permanent hardness and 100 ppm temporary hardness. If 42 mg/L NaHCO_3 is added to this water, calculate the new temporary and permanent hardness.

Total hardness = $400 + 100 = 500$ mg/L

Temporary hardness of water sample increases with the addition of 42 mg/L NaHCO_3 .

Increase in temporary hardness = $\frac{42 \times 100}{2 \times 84} = 25$ ppm

New temporary hardness = $100 + 25 = 125$ mg/L

New permanent hardness = Total hardness - New temporary hardness = $500 - 125 = 375$ mg/L

4. A water sample contains $\text{Mg}(\text{HCO}_3)_2$ – 36.5 ppm, $\text{Ca}(\text{HCO}_3)_2$ – 40.5 ppm, MgSO_4 – 30.0 ppm, CaSO_4 – 34.0 ppm, CaCl_2 – 27.75 ppm, NaCl – 10 ppm. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (ppm)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
$\text{Ca}(\text{HCO}_3)_2$	40.5	162	$40.5 \times \frac{100}{162} = 25$ ppm
$\text{Mg}(\text{HCO}_3)_2$	36.5	146	$36.5 \times \frac{100}{146} = 25$ ppm
MgSO_4	30.3	120	$30.0 \times \frac{100}{120} = 25$ ppm
CaSO_4	34.0	136	$34.0 \times \frac{100}{136} = 25$ ppm
CaCl_2	27.75	111	$27.75 \times \frac{100}{111} = 25$ ppm
NaCl	10	-	-

Temporary hardness = Hardness due to $\text{Ca}(\text{HCO}_3)_2$ + Hardness due to $\text{Mg}(\text{HCO}_3)_2$
 $= 25 + 25 = 50$ ppm

Permanent hardness = Hardness due to MgSO_4 + Hardness due to CaSO_4 + Hardness due to CaCl_2 = $25 + 25 + 25 = 75$ ppm

5. A sample of water on analysis gives the following results: $\text{Ca}^{2+} = 400$ mg/L, $\text{Mg}^{2+} = 240$ mg/L, $\text{HCO}_3^- = 244$ mg/L, $\text{Na}^+ = 92$ mg/L. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (ppm)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
Ca^{2+}	400	40	$400 \times \frac{100}{40} = 1000$
Mg^{2+}	240	24	$240 \times \frac{100}{24} = 1000$
HCO_3^-	244	61	$244 \times \frac{100}{2 \times 61} = 200$
Na^+	92	-	-

Total hardness = $1000 + 1000 = 2000$ ppm

Temporary hardness = 200 ppm

Permanent hardness = $2000 - 200 = 1800$ ppm

6. A water sample contains $\text{Mg}(\text{HCO}_3)_2$ – 43.8 mg/L, $\text{Ca}(\text{HCO}_3)_2$ – 48.6 ppm, MgSO_4 – 24.0 ppm, CaSO_4 – 27.2 mg/L, NaHCO_3 – 16.8 mg/L. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
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Ca(HCO ₃) ₂	48.6	162	$48.6 \times \frac{100}{162} = 30 \text{ ppm}$
Mg(HCO ₃) ₂	43.8	146	$43.8 \times \frac{100}{146} = 30 \text{ ppm}$
MgSO ₄	24.0	120	$24.0 \times \frac{100}{120} = 20 \text{ ppm}$
CaSO ₄	27.2	136	$27.2 \times \frac{100}{136} = 20 \text{ ppm}$
NaHCO ₃	16.8	84	$16.8 \times \frac{100}{84} = 20 \text{ ppm}$

Total hardness = 30+30+20+20 = 100 ppm

Temporary hardness = 30+30+10 = 70 ppm

Permanent hardness = 100 – 70 = 30ppm

7. A sample of water on analysis gives the following results: Ca²⁺ = 320mg/L, Mg²⁺ = 72mg/L, HCO₃⁻=610mg/L, Na⁺ =23mg/L. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M _{HPS}	CaCO ₃ equivalent hardness = Quantity X $\frac{100}{M_{HPS}}$
Ca ²⁺	320	40	$320 \times \frac{100}{40} = 800$
Mg ²⁺	72	24	$72 \times \frac{100}{24} = 300$
HCO ₃ ⁻	610	61	$610 \times \frac{100}{61} = 1000$
Na ⁺	23	-	-

Total hardness = 800 + 300 = 1100 ppm

Temporary hardness = 500 ppm

Permanent hardness = Total hardness - Temporary hardness = 1100 – 500 = 600 ppm

8. Calculate the hardness of 0.1M CaCl₂ solution.

Hardness = Molarity X M_{CaCO₃} X 1000

= 0.1 X 100 X 1000 =10000 ppm

9. Calculate the hardness of 0.4 N Ca²⁺ solution.

Hardness = Normality X Eqnt. Wt. CaCO₃ X 1000

= 0.4 X 50 X 1000 =20000 ppm

10. A standard hard water containing 15g CaCO₃ per litre. 20ml of this required 25ml EDTA solution. 100ml of sample of water required 18ml EDTA solution. The same sample of water, after boiling required 12ml EDTA solution. Calculate the temporary hardness.

Step I: Preparation of SHW

1 litre SHW = 15g CaCO₃

1000 ml SHW = 15000mg CaCO₃

1 ml SHW = 15mg CaCO₃

Normality of SHW = 15mg CaCO₃

Step II: Standardisation of EDTA

20 ml SHW = 25 ml EDTA

V_{SHW} X N_{SHW} = V_{EDTA} X N_{EDTA}

20 X 15 = 25 x N_{EDTA}

N_{EDTA} = $\frac{20 \times 15}{25} = 12 \text{mg CaCO}_3$

Step III: Estimation of total hardness

100 ml UHW = 18 ml EDTA

V_{UHW} X N_{UHW} = V_{EDTA} X N_{EDTA}

100 X N_{UHW} = 18 X 12

N_{UHW} = $\frac{18 \times 12}{100} = 2.16 \text{mg}$

Total Hardness = 2.16 X 1000 = 2160 ppm

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 12 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times N_{\text{BHW}} = 12 \times 12$$

$$N_{\text{BHW}} = \frac{12 \times 12}{100} = 1.44 \text{ mg}$$

$$\text{Permanent Hardness} = 1.44 \times 1000 = 1440 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 2160 - 1440 = 720 \text{ ppm}$$

11. A standard hard water was prepared by dissolving 1g CaCO_3 in dil. HCl. It is then evaporated and made up to 1 litre using distilled water. 50ml of this required 48ml EDTA solution. 50ml of test hard water required 15ml EDTA solution. 50 ml of the same test water sample after boiling and filtration required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 1 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 1000 \text{ mg CaCO}_3$$

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

$$\text{Normality of SHW} = 1 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$50 \text{ ml SHW} = 48 \text{ ml EDTA}$$

$$V_{\text{SHW}} \times N_{\text{SHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times 1 = 48 \times N_{\text{EDTA}}$$

$$N_{\text{EDTA}} = \frac{50 \times 1}{48} = 1.04 \text{ mg CaCO}_3$$

Step III: Estimation of total hardness

$$50 \text{ ml UHW} = 15 \text{ ml EDTA}$$

$$V_{\text{UHW}} \times N_{\text{UHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_{\text{UHW}} = 15 \times 1.04$$

$$N_{\text{UHW}} = \frac{15 \times 1.04}{50} = 0.312 \text{ mg}$$

$$\text{Total Hardness} = 0.312 \times 1000 = 312 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$50 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_{\text{BHW}} = 10 \times 1.04$$

$$N_{\text{BHW}} = \frac{10 \times 1.04}{50} = 0.208 \text{ mg}$$

$$\text{Permanent Hardness} = 0.208 \times 1000 = 208 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 312 - 208 = 104 \text{ ppm}$$

12. 2.8g CaCO_3 was dissolved in dil. HCl and made up to 1 litre using distilled water. 100ml of this required 28ml EDTA solution. 100ml of test hard water required 35ml EDTA solution. 100 ml of the same test water sample after boiling and filtration when titrated against EDTA required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 2.8 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 2800 \text{ mg CaCO}_3$$

$$1 \text{ ml SHW} = 2.8 \text{ mg CaCO}_3$$

$$\text{Normality of SHW} = 2.8 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$100 \text{ ml SHW} = 28 \text{ ml EDTA}$$

$$V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times 2.8 = 28 \times N_{EDTA}$$

$$N_{EDTA} = \frac{100 \times 2.8}{28} = 10 \text{mg CaCO}_3$$

Step III: Estimation of total hardness

$$100 \text{ ml UHW} = 35 \text{ ml EDTA}$$

$$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{UHW} = 35 \times 10$$

$$N_{UHW} = \frac{35 \times 10}{100} = 3.5 \text{mg}$$

$$\text{Total Hardness} = 3.5 \times 1000 = 3500 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{BHW} = 10 \times 10$$

$$N_{BHW} = \frac{10 \times 10}{100} = 1 \text{mg}$$

$$\text{Permanent Hardness} = 1 \times 1000 = 1000 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 3500 - 1000 = 2500 \text{ ppm}$$

13. 0.30g CaCO₃ was dissolved in dil. HCl and made upto 1 litre using distilled water. 100ml of this required 30ml EDTA solution. 100ml of test hard water required 33ml EDTA solution. 100 ml of the same test water sample after boiling and filtration when titrated against EDTA required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 0.30 \text{g CaCO}_3$$

$$1000 \text{ ml SHW} = 300 \text{mg CaCO}_3$$

$$1 \text{ ml SHW} = 0.3 \text{mg CaCO}_3$$

$$\text{Normality of SHW} = 0.3 \text{mg CaCO}_3$$

Step II: Standardisation of EDTA

$$100 \text{ ml SHW} = 30 \text{ ml EDTA}$$

$$V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times 0.3 = 30 \times N_{EDTA}$$

$$N_{EDTA} = \frac{100 \times 0.3}{30} = 1 \text{mg CaCO}_3$$

Step III: Estimation of total hardness

$$100 \text{ ml UHW} = 33 \text{ ml EDTA}$$

$$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{UHW} = 33 \times 1$$

$$N_{UHW} = \frac{33 \times 1}{100} = 0.33 \text{mg}$$

$$\text{Total Hardness} = 0.33 \times 1000 = 330 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{BHW} = 10 \times 1$$

$$N_{BHW} = \frac{10 \times 1}{100} = 0.1 \text{mg}$$

$$\text{Permanent Hardness} = 0.1 \times 1000 = 100 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 330 - 100 = 230 \text{ ppm}$$

14. A sample of water is found to contain Mg(HCO₃)₂ – 7.3mg/L, Ca(HCO₃)₂ – 16.2 mg/L, MgCl₂ – 9.5 ppm and CaSO₄ – 13.6mg/L. Calculate the temporary and permanent hardness of

water sample. What happen to the temperory and permanent hardness of water sample if 10.6mg/L Na_2CO_3 is added?

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{HPS}}$
$\text{Ca}(\text{HCO}_3)_2$	16.2	162	$16.2 \times \frac{100}{162} = 10 \text{ ppm}$
$\text{Mg}(\text{HCO}_3)_2$	7.3	146	$7.3 \times \frac{100}{146} = 5 \text{ ppm}$
MgCl_2	9.5	95	$9.5 \times \frac{100}{95} = 10 \text{ ppm}$
CaSO_4	13.6	136	$13.6 \times \frac{100}{136} = 10 \text{ ppm}$
Na_2CO_3	10.6	106	$10.6 \times \frac{100}{106} = 10 \text{ ppm}$

Total hardness = 10+5+10+10 = 35 ppm

Temporary hardness = 10+5 = 15 ppm

Permanent hardness = 35 – 15 = 20 ppm

If 10.6mg/L Na_2CO_3 is added to water, it removes permanent Ca^{2+} as CaCO_3 and Mg^{2+} cannot be removed.

CaCO_3 equivalent hardness of Na_2CO_3 = 10 ppm

Thus 10 ppm permanent Ca is removed as CaCO_3 .

New total hardness = 35 – 10 = 25 ppm

Temporary hardness = 15 ppm

New permanent hardness = 25 – 15 = 10 ppm

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