(D) Determination of hardness of water by EDTA method

(i) Pipette out 50 mL of the given water sample into a 250 mL conical flask.

(ii) Add 3–5 mL of the (ammonia + ammonium chloride) buffer solution to elevate pH to approximately 10.0.

(iii) Add a tiny amount to dry eriochrome black (EBT) indicator. The solution turns wine red.

(iv) Titrate the sample of water *slowly* with 0.01 M EDTA until the last reddish tinge disappears from the solution.

(v) Add the last few drops at 3–5 second intervals to allow the end-point reaction to go to completion with the permanent blue colouration. Record the volume of EDTA used up at equivalence, V mL.

Example Calculate the hardness of the sample using: [Note: 1 L of water = 10^6 mg of water]

The total hardness of water = $\dfrac{V \times B \times 1000 \text{ mg}}{\text{volume of water taken}}$ $CaCO_3$/litre or ppm.

where: V is the mL of the EDTA used in the titration 'B' is the mg $CaCO_3$ equivalent to 1 mL of EDTA solution $B \equiv 1$ mL of 0.01 M EDTA solution $\equiv 1$ mg $CaCO_3$

The total hardness of water can also be reported in terms of parts per million (ppm).

Worked Examples

1. The following chemicals are dissolved in a litre of water. Calculate the hardness of this sample of water.
$CaSO_4$ = 20.0 mg; $Mg(HCO_3)_2$ = 14.6 mg; $MgCl_2$ = 12.5 mg.
Calculation of $CaCO_3$ equivalent in the water sample:
Conversion factor = Molecular weight $CaCO_3$/Mol weight of dissolved salt.

	Conversion factor	$CaCO_3$ equivalent
1. $CaSO_4$	100/136	$20.0 \times 100/136 = 14.70$ mg/L
2. $Mg(HCO_3)_2$	100/146	$14.6 \times 100/146 = 10.0$ mg/L
3. $MgCl_2$	100/95	$12.5 \times 100/95 = 13.6$ mg/L

Therefore, the total hardness due to dissolved salt = $[14.70 + 10.0 + 13.6] = 38.3$ mg/L
= 38.3 ppm

2. A water sample contains $Ca(HCO_3)_2$ = 22.4 mg/L; $Mg(HCO_3)_2$ = 19.2 mg/L; $CaSO_4$ = 23.5 mg/L.
Calculate the temporary and permanent hardness.
Conversion factor = Mol weight $CaCO_3$/Mol weight of dissolved salt.

	Conversion factor	$CaCO_3$ equivalent
1. $Ca(HCO_3)_2$	100/162	$22.4 \times 100/162 = 13.83$ mg/L
2. $Mg(HCO_3)_2$	100/142	$19.2 \times 100/142 = 13.5$ mg/L
3. $CaSO_4$	100/136	$23.5 \times 100/136 = 17.20$ mg/L

Therefore, (i) Temporary hardness due to [$Ca(HCO_3)_2$ + Mg $(HCO_3)_2$ = 27.33 mg/L
(ii) Permanent hardness due to $CaSO_4$ = 17.20 mg/L = 17.2 ppm.

3. A precipitate of 0.110 g of $CaC_2O_4.H_2O$ was obtained from 250 mL of water sample. Express the calcium content in the sample in ppm.
Gram molecular weight of $CaC_2O_4.H_2O$ is $[40 + 24 + 64 + 18] = 146$ g
If 146 g of $[CaC_2O_4.H_2O]$ is dissolved in water and then it contains 40 g of Ca in solution.
Weight of calcium oxalate in 250 mL of water = 0.110 g
Therefore, weight of calcium oxalate in litre (L) = $0.110 \times 4 = 0.440$ g.

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Now, 146 g of $CaC_2O_4.H_2O \equiv 40$ g of Ca

0.440 g contains $0.44 \times 40/146 = 0.1206$ g/L of Ca.

Therefore, the calcium content in the sample = 120.6 mg/L or 120.6 ppm

4. The standard hard water contains 15 g of $CaCO_3$ per litre. 20 mL of this required 25 mL of EDTA solution. (i) 100 mL of sample of water required 18 mL of EDTA solution (ii) The same sample after boiling required 12 mL of EDTA solution. Calculate the temporary hardness of the given sample of water, in terms of ppm.

A standard water contains 15 g of $CaCO_3$/L.

1000 mL of standard hard water (SHW), therefore, contain 15,000 mg of $CaCO_3$.

Therefore, 1 mL of standard water = $15,000/1000 = 15$ mg of $CaCO_3$ equivalent.

5 mL of EDTA solution = 20 mL of SHW contains $[20 \times 15] = 300$ mg of $CaCO_3$ equivalent.

Therefore, *1 mL of EDTA solution = 300/25 = 12 mg of $CaCO_3$ equivalent.*

(i) **Calculation of Hardness of water**

  100 mL of water $\equiv$ 18 mL of EDTA solution

      $\equiv [18 \times 12] = 216$ mg of $CaCO_3$ equivalent.

  Therefore, 1000 mL of water $\equiv$ 2160 mg of $CaCO_3$ equivalent.

  Hence, hardness of water = 2160 mg/L or ppm.

(ii) **Calculation of permanent hardness of water**

  100 mL of water (after boiling) = 12 mL of EDTA solution.

      $= [12 \times 12] = 144$ mg of $CaCO_3$ equivalent.

  Therefore, 1000 mL of water contains $144 \times 1000/100 = 1440$ mg of $CaCO_3$ equivalent.

  Hence, permanent hardness of water = 1440 ppm.

(iii) **Calculation of temporary hardness of water**

  Temporary hardness of water = [Total – Permanent] hardness

      $= [2160 – 1440] = 720$ ppm.

5. 50 mL of a standard hard water containing 1 mg of pure $CaCO_3$ per 1 mL, consumed 20 mL of EDTA. 50 mL of a water sample consumed 25 mL of EDTA solution using EBT indicator. Calculate the total hardness of water sample.

1 mL of SHW contains 1 mg of $CaCO_3$

50 mL of standard hard water (SHW) contains 50 mg of $CaCO_3$

20 mL of EDTA solution = 50 mL of SHW $\equiv$ 50 mg of $CaCO_3$ equivalent.

1 mL of EDTA solution $\equiv 50/20 = 2.25$ mg of $CaCO_3$ equivalent.

Therefore, 25 mL of EDTA solution $\equiv 2.25 \times 25 = 56.25$ mg of $CaCO_3$ equivalent.

Hence, 50 mL of water contains 56.25 mg of $CaCO_3$ equivalent.

Therefore, 1000 mL of water $\equiv 1000 \times 56.25/50 = 1,125$ mg/L

Hence, total hardness of water = 1125 ppm.

6. A water sample contains the following:

  $Mg(HCO_3)_2$: 95 mg/L

  $Ca(HCO_3)_2$: 203 mg/L

  $CaSO_4$: 136 mg/L

  $CaCl_2$: 111 mg/L

  $MgCl_2$: 95 mg/L

Calculate the temporary and permanent hardness of water.

Salt	mg/L	C. factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$	95	100/146	$95 \times 100/146 = 65.0$ mg/L
$Ca(HCO_3)_2$	203	100/162	$205 \times 100/162 = 125$ g/L
$CaSO_4$	136	100/136	$136 \times 100/136 = 100$ mg/L
$CaCl_2$	150	100/111	$150 \times 100/111 = 135$ mg/L
$MgCl_2$	95	100/95	$95 \times 100/95 = 100$ mg/L

$$CaCO_3 \text{ equivalent of salt} = \frac{\text{weight of salt (mg/L)} \times 100}{\text{Mol Weight of Salt}}$$

1. Temporary hardness of water $= [Mg(HCO_3)_2 + Ca(HCO_3)_2]$
   $= [65.0 + 125]$
   $= 190.00$ mg/L

2. Permanent hardness of water $= [CaSO_4 + CaCl_2 + MgCl_2]$
   $= [100 + 135 + 100]$
   $= 335.0$ mg/L (ppm)

7. An analysed sample of water containing only $Ca(HCO_3)_2$ is found to contain 150.00 mg/L of hardness. Calculate the amount of $Ca(HCO_3)_2$ dissolved in that water sample.

   (Ca = 40, H = 1, C = 12 and O = 16)

   M.F of $Ca(HCO_3)_2 = 40 + (1 + 12 + 48)_2 = 162$

   Therefore, 100 mg/L of $CaCO_3$ equivalent = 162 mg/L of calcium bicarbonate

   $$150 \text{ mg/L of } CaCO_3 \text{ equivalent} = \frac{150 \times 162}{100}$$

   Therefore, amount of $Ca(HCO_3)_2 = 243.0$ mg/L (ppm)

8. A sample of hard water contains the following dissolved salts:

   $MgSO_4 = 10.0$ ppm
   $CaCl_2 = 85.0$ ppm
   $Ca(HCO_3)_2 = 162.0$ ppm
   $Mg(HCO_3)_2 = 73.0$ ppm
   $CaSO_4 = 68.0$ ppm.

   Find out the temporary and permanent hardness of water in ppm?

Salt	Quantity, ppm	C factor	$CaCO_3$ equivalent
$MgSO_4$	10.0	100/120	$10 \times 100/120 = 8.34$
$CaCl_2$	85.0	100/111	$85 \times 100/111 = 76.5$
$Ca(HCO_3)_2$	162.0	100/162	$162 \times 100/162 = 100$
$Mg(HCO_3)_2$	73.0	100/146	$73 \times 100/146 = 50$
$CaSO_4$	68.0	100/136	$68 \times 100/136 = 50$

Note: 1mg/L = 1 ppm.

Temporary hardness of water $= [Ca(HCO_3)_2 + Mg(HCO_3)_2]$
   $= \{100 + 50\} = 150$ ppm

Permanent hardness $= [MgSO_4 + CaCl_2 + CaSO_4]$
   $= \{8.34 + 76.5 + 50\} = 134.84$ ppm

Total hardness of water $= 150 + 134.84 = 284.84$ ppm

(E) Removal of temporary hardness on boiling hard water

Temporary hardness in water can be easily removed by boiling. On boiling, calcium/magnesium bicarbonate decomposes to give calcium/magnesium carbonate which is insoluble in water. Therefore, it precipitates out.

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2$$
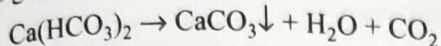
By the addition of slaked lime (Clark's process)

In Clark's process, slaked lime, $Ca(OH)_2$ is added to temporary hard water. Insoluble calcium carbonate precipitates out and no longer produce hardness.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2H_2O$$
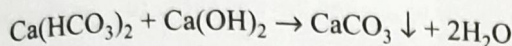
(Slaked lime)

The methods used to remove permanent hardness given in the next section can also be employed to remove the temporary hardness. However, the above methods cannot be used to remove the permanent hardness

8.3.2.2 Alkalinity

Alkalinity measures the acid-neutralizing capacity of a water sample. It is an aggregate property of the water sample and can be interpreted in terms of specific substances only when a complete chemical composition of the sample is also performed.

The alkalinity of surface water is primarily due to the carbonate, bicarbonate and hydroxide content and is often interpreted in terms of the concentrations of these constituents. Alkalinity may also include contributions from borates, phosphates, silicates or other bases if they are present.

Alkalinity is used to determine the suitability of water for irrigation, industrial use, raw water characterization and water and wastewater monitoring. Alkalinity is also important as an indicator of water body's ability to resist pH change with the addition of acid from an accidental spill or acid precipitation.

Determination

1. Accurately measure 100 mL of your sample into a 250 mL conical flask. Insert a bar magnet and place sample on magnetic stir plate.
2. Record initial pH of the sample. If the pH is above 8.3, add several drops of phenolphthalein indicator.
3. Titrate the sample with 0.02 N H_2SO_4 or HCl until the pH end-point (colourless) is reached. Note the total volume (V_1 mL) of acid needed to reach the end-point. This is the *phenolphthalein alkalinity, P.*

1000 mL of 1 N $CaCO_3$ $\equiv$ 50 g = 50,000 mg of $CaCO_3$/L

1 mL of 1 N $CaCO_3$ = 50000/1000 = 50 mg of $CaCO_3$

100 mL of water (V) $\equiv$ V_1 mL of N/50 H_2SO_4

Amount of $CaCO_3$ equivalent in V_1 mL N/50 H_2SO_4

$V_1 \times N/50$ $H_2SO_4 \times 50$ mg $CaCO_3$

100 mL of water (V) = $V_1 \times N/50$ $H_2SO_4 \times 50$ mg $CaCO_3$ equivalent.

Therefore, 1000 mL (L) of water = $\dfrac{V_1 \times N/50\ H_2SO_4 \times 50 \times 1000\ mg}{\text{Volume of water } (V)}$ $CaCO_3$ equivalent.

In general,

$$P = \frac{V_1 \times N \times 50,000\ mg}{\text{volume of water } (V)} CaCO_3/L$$

where V_1 is the volume in mL of the standard acid used N is the normality of the standard acid used $[50 \times 1000] = 50,000$ is a conversion factor to change the normality into units of mg $CaCO_3$/L.

4. If pH is below 8.3, add several drops of bromocresol green indicator. Titrate the water sample with 0.02 N H_2SO_4 or HCl until the pH 4.5 end-point (colour changes from blue to yellow) is reached. Note the volume (V_2) of acid needed to reach the endpoint. This gives the total alkalinity, T, of the sample.

5. The total alkalinity of the sample can be calculated using:

$$\text{Total alkalinity, } T = \frac{V \times N \times 50{,}000 \text{ mg}}{\text{volume of water } (V)} \text{ mg CaCO}_3/\text{L}$$

where $V = (V_1 + V_2)$, is the total volume in mL of the standard acid used. N is the normality of the standard acid used. 50,000 is a conversion factor to change the normality into units of mg $CaCO_3/L$. Calculation of alkalinity of water: (Table 8.1).

(Assuming all of the alkalinity is due to carbonate, bicarbonate or hydroxide)

Result of titration	OH⁻ alkalinity as $CaCO_3$	CO_3^- alkalinity as $CaCO_3$	HCO_3^- alkalinity as $CaCO_3$
$P = 0$	0	0	T
$P = \frac{1}{2}T$	0	2P	0
$P > \frac{1}{2}T$	2P–T	2 (T – P)	0
$P < \frac{1}{2}T$	2T	0	(T – 2P)
$P = T$	T	0	0

Table 8.1

Types of alkalinity in water

where P = phenolphthalein alkalinity T = total alkalinity

9. 100 mL of a water sample required 20 mL of N/50 H_2SO_4 for neutralization to phenolphthalein end-point. After this, methyl orange indicator was added to this and further acid required was again 20 mL. Calculate the alkalinity of water as $CaCO_3$ in ppm.

Volume of N/50 H_2SO_4 required to neutralize 100 mL water to phenolphthalein end-point V_a = 20 mL.

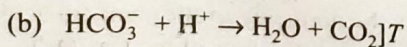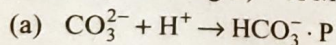$$P = \frac{V_1 \times N \times 50{,}000 \text{ mg}}{\text{volume of water } (V)} \text{ mg CaCO}_3/\text{L}$$

where V_1 is the volume in mL of the standard acid used N is the normality of the standard acid used $[50 \times 1000] = 50{,}000$ is a conversion factor to change the normality into units of mg $CaCO_3/L$.

$$\textit{Phenolphthalein Alkalinity, } P = \frac{20 \times 0.02 \times 50{,}000}{100} \text{ mg CaCO}_3/\text{L}$$

$$= 200 \text{ mg/L.}$$

Now 100 mL of water up to methyl orange end-point $= 20 + 20 = 40$ mL N/50 H_2SO_4

$$\textit{Total alkalinity, } T = \frac{[20 + 20] \times 0.02 \times 50{,}000}{100} \text{ mg CaCO}_3/\text{L}$$

$$= 400 \text{ mg/L.}$$

Now, P (= 200 mg/L) = $\frac{1}{2}$ M [$\frac{1}{2} \times 400$], so the alkalinity is only due to CO_3^{2-}.

(a) $CO_3^{2-} + H^+ \rightarrow HCO_3^- \cdot P$

(b) $HCO_3^- + H^+ \rightarrow H_2O + CO_2]T$

Hence, total alkalinity (due to CO_3^{2-} only), T, is 400 mg/L

10. 100 mL of water sample required 20 mL of N/50 H_2SO_4 for neutralization to phenolphthalein end-point. After methyl orange addition to this, further acid required was 2.5 mL. Calculate the alkalinity of water in terms of $CaCO_3$ equivalent.

$$P = \frac{V_1 \times N \times 50,000}{\text{volume of water } (V)} \text{ mg } CaCO_3/L$$

where V_1, is the volume in mL of the standard acid used N is the normality of the standard acid used $[50 \times 1000] = 50,000$ is a conversion factor to change the normality into units of mg $CaCO_3/L$.

Phenolphthalein alkalinity, $P = \dfrac{20 \times 0.02 \times 50,000}{100}$ mg $CaCO_3/L$

$$= 200 \text{ mg/L.}$$

Now 100 mL of water up to methyl orange end-point in terms end methyl orange point.

$$= 20 \text{ mL} + 2.5 \text{ mL} = 22.5 \text{ mL of } N/50 \text{ } H_2SO_4$$

Total alkalinity of the sample can be calculated using:

Total alkalinity, $T = \dfrac{V \times N \times 50,000 \text{ mg}}{\text{volume of water } (V)}$ mg $CaCO_3/L$
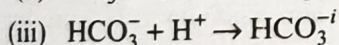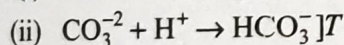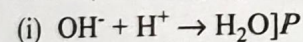
where $V = (V_1 + V_2)$, is the total volume in mL of the standard acid used

N is the normality of the standard acid used

50,000 is a conversion factor to change the normality into units of mg $CaCO_3$

Total alkalinity, $T = \dfrac{[20 + 2.5] \times N \times 50,000}{\text{volume of water } (V)}$ mg $CaCO_3/L$

$$= \dfrac{22.5 \times 0.02 \times 50000}{100} = 225 \text{ mg/L.}$$

Now $P(= 200 \text{ mg/L}) > \frac{1}{2}T [\frac{1}{2} \times 225]$, so alkalinity is due to OH^- and CO_3^{-2}

(i) $OH^- + H^+ \rightarrow H_2O]P$

(ii) $CO_3^{-2} + H^+ \rightarrow HCO_3^-]T$

(iii) $HCO_3^- + H^+ \rightarrow HCO_3^{-i}$

Therefore, Alkalinity due to CO_3^{-2} ions $= 2[T - P] = 2[225 - 200] = 2 \times 25 = 50$ ppm.

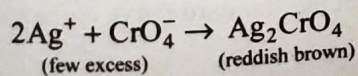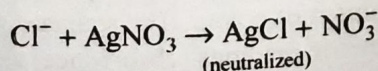And alkalinity due to OH^- ions $= [2P - T] = [2 \times 200 - 225] = 175$ ppm.

Therefore, Total alkalinity $= (50 + 175) = 225$ ppm.

8.3.2.3 Chloride

Argentometric method

Take 100 cc of water in a conical flask and then it is neutralized with N/50 H_2SO_4 using methyl orange as indicator. 2–3 drops of K_2CrO_4 indicator is added. The sample is titrated against N/50 silver nitrate solution till the colour changes from yellow to reddish brown.

The volume of $AgNO_3$ solution added is calculated as ppm of sodium chloride as $CaCO_3$ in the following manner:

$$Cl^- + AgNO_3 \rightarrow AgCl + NO_3^-$$
$$\text{(neutralized)}$$

$$2Ag^+ + CrO_4^- \rightarrow Ag_2CrO_4$$
$$\text{(few excess)} \quad \text{(reddish brown)}$$

59. (a) What is hardness of water? Give causes for hardness.

(b) Calculate the amount of temporary and permanent hardness of water sample that contains the following impurities. $Ca(HCO_3)_2$ = 12.5 ppm, $Mg(HCO_3)_2$ = 1168 ppm, $MgCl_2$ =79.8 ppm, $CaSO_4$ = 102 ppm. [JNTU June, 2014]

60. A water sample is nonalkaline to phenolphthale in indicator. 100 mL of the same sample on titration with 0.02 N H_2SO_4 requires 14.5 mL of acid to obtain the end-point using methyl orange indicator. Identify the type of alkalinity and determine its content.

[Pune University, Dec, 2014]

61. (a) Describe ion exchange method for softening water.

(b) Define caustic embrittlement. Give causes and prevention of caustic embrittlement in boiler.

(c) A water sample is not alkaline to phenolphthalein. However, 100 mL of water sample on titration with N/50 HCL required 16.9 mL of acid to get methyl orange end-point. Identify the type and determine the extent of alkalinity.

[Pune University, May, 2014]

62. (a) Explain caustic corrosion and caustic embrittlement as ill effects of water in boilers. State their causes and its preventive measures.

(b) A 50 mL of hard water containing 1.2g of $CaCO_3$ per L required 15 mL of EDTA solution for the end-point. Whereas 50 mL of water sample required 19 mL of EDTA solution and 50 mL of boiled sample of water required 11 mL of EDTA solution for the end-point. Calculate, temporary and permanent hardness of sample water in ppm. [Pune University, April, 2013]

63. (a) Explain the formation in boilers, give their disadvantages and methods of removal.

(b) A zeolite softener gets exhausted on softening 4000 L of hard water. Calculate the hardness of water, if the exhausted zeolite

requires 10 L of 10 percent NaCl for regeneration. [Pune University, Dec, 2013]

64. 50 mL of water required 12.1 mL of N/50 HCL to reach phenolphthalein end-point and 18.5 mL of the same acid for the methyl orange end-point. Calculate types and amount of alkalinities present.

[Pune University, Dec, 2015]

65. (a) What are zeolites? Explain zeolite process of softening of water. Give regeneration reactions, advantages and disadvantages of the process.

(b) 50 mL of water requires 18 mL of 0.05 M EDTA during titration. Whereas 50 mL of boiled water requires 12.5 mL of same EDTA in the titration. Calculate total, temporary and permanent hardness of water sample. [Pune University, June, 2015]

66. (a) Explain the methods for internal treatment of Boiler feed water.

[Pune University, Oct, 2012]

67. State Zeolite process for the removal of hardness of water. Discuss its merit over soda lime.

[UPTU, 2012]

68. (a) What are ion exchange resins? How will you purify water using the resins?

(b) Calculate the lime and soda needed for softening 50,000 L of water containing the following:

$CaSO_4$ = 13.6mg/L, $MgCl_2$ = 9.5 mg/L, $Mg(HCO_3)_2$ = 7.3 mg/L, $Ca(HCO_3)_2$ = 16.2 mg/L.

Given the molar mass of $Ca(HCO_3)_2$ is 162 and that of $MgCl_2$ is 95.

(c) Discuss the different methods of internal treatment of boiler feed water.

[UPTU, 2012]

69. (a) What is boiler feed water? Explain the priming and foaming in boilers.

(b) Define COD? Discuss the experimental determination of waste water.

(c) Explain the activated sludge treatment of sewage water.

(d) Discuss the desalination of seawater by reverse osmosis. [VTU, June/July, 2015]