Experiment No.: 2

Determination of the hardness of water sample by complexometric titration

Apparatus required :

(1) Pipette (2) Burette (3) Funnel (4) Conical flask (5) Beaker (5) Bunsen Burner (6) Stand (7) Wire gauge (8) Filter paper

Chemicals Required

(i) Ethylenediaminetetra acetic acid (EDTA)

(ii) Buffer solution

(iii) Eriochrome Black - T indicator

Theory:

The presence of salt of calcium or magnesium in water which forms a scum with soap and prevents the formation of a lather is known as hardness of water. Other soluble salts of metal like, aluminium, barium, strontium, iron and manganese can also form scum with soap and prevent the formation of lather, but these salts are present in natural water only in trace amount. Hence, the cause of hardness is due to soluble salt of calcium and magnesium only, specially due to presence of chlorides, sulphates and bicarbonates of calcium and magnesium.

Hardness of water is of two types:

1. Temporary hardness
2. Permanent hardness

Temporary hardness is caused due to the presence of bicarbonates (HCO_3^-) of calcium and magnesium. It can be easily removed by boiling.

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

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + CO_2 + H_2O$$

The temporary hardness is removed by adding lime (calcium hydroxide), which give a precipitates of calcium carbonate.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + H_2O$$

$$Mg(HCO_3)_2 + Mg(OH)_2 \longrightarrow 2MgCO_3 \downarrow + H_2O$$

Permanent hardness is caused due to the presence of sulphates and chlorides of calcium and magnesium. It can't be removed by boiling. But it can be removed by ion-exchange method using zeolites (e. g. permutit)*. or by treating with Na_2CO_3.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + NaCl$$

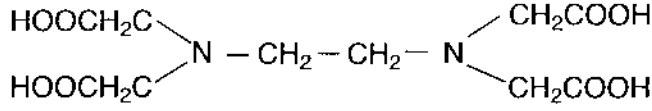
$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na2SO_4$$

$$CaCl_2 + Na_2Z \longrightarrow CaZ + 2NaCl$$

(Sodium Zeolite)

The hardness of water is not a pollution parameter but indicates water quality. Hard water poses considerable problem in washing, it reduces the efficiency of boiler, in certain industrial process.

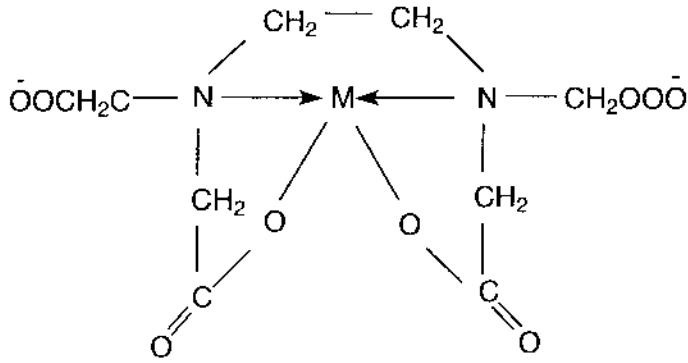
Ethylenediaminetetra acetic acid (EDTA) is a well known complexing agent which is widely used in analytical work on account of its powerful complexing action and commercial availability. This is also available under trade names as Versenecor Tritriplex-III. Its chemical formula can be represented as :



EDTA forms complexes with Ca^{2+} and Mg^{2+} ions as well as with many other metal cations in aqueous solution.

* hydrated sodium aluminium silicate (permutit) $Na_2Al_2Si_2O_8\ xH_2O$

These complexes have the general formula :



EDTA is generally used in the form of disodium salt or tetrasodium salt on account of their greater solubility.

During the titration with EDTA (H_2Y^{--}) when all Ca^{++} and Mg^{++} ions have reacted to form metal EDTA complex (MY^{--}) realizing free indicator (In) and the color changes from wine red to clear blue.

Ca^{++} + H_2Y ⟶ CaY

Mg^{++} + H_2Y ⟶ MgY

In-Mg + H_2Y › MgY + In

(wine red) (blue)

1 mole EDTA ≡ 1 mole of Ca^{2+} ≡ 1 mole of $CaCO_3$

Procedure :

Pipette out 50 ml of the water sample into a 250 ml conical falsk. Add 2 ml of the buffer solution and 3 drops of Eriochrome Black-T indicator. Titrate the solution with standard EDTA solution from the burette until the colour changes from violet to clear blue at the end-point. Note the titrate value which corresponds to total hardness.

Measure out 250 ml of the water sample in 500 ml breaker, boil gently for half-an-hour, filter the solution into a 250 ml measuring flask. Make the solution upto the mark with de-ionised water and

shake thoroughly. Pipette out 50 ml of this solution into a 250 ml conical flask, add 2 ml of the buffer solution and 3 drops of Eriochrome Black-T indictor. Titrate with EDTA solution until the voilet colour changes to clear blue at the end-point. This titre value corresponds to the permanent hardness.

Sample Observation:

S. No.	Volume of Water sample taken (ml)	Volume of 0.01 M EDTA solution run-down	
		Total hardness (ml)	Permanent harness (ml)
1.	50	14.1	5.0
2.	50	14.0	4.9
3.	50	14.0	4.9

Calculation:

1 mole EDTA $\equiv$ 1 mole of Ca^{2+} $\equiv$ 1 mole of $CaCO_3$

$\therefore$ 1 ml of 1 M EDTA $\equiv$ 100 mg of $CaCO_3$

1 ml of 0.01 M EDTA $\equiv$ 100 x 0.01 mg of $CaCO_3$

$= 1$ mg of $CaCO_3$

Total hardness:

14 ml of 0.01M EDTA $\equiv$

Hence, the hardness present in 50 ml of the water sample taken

$\equiv$ 14 mg of $CaCO_3$.

$\therefore$ The hardness present in 1000 ml of the water sample

$$\equiv 14 \times \frac{1000}{50} = 280\text{mg of } CaCO_3$$

$\therefore$ Total hardness = 280 mg/l = 280 ppm.

Permanent hardness:

4.9 ml of 0.01M EDTA $\equiv 100 \times 0.01 \times 4.9$ mg of $CaCO_3$

$= 4.9$ mg of $CaCO_3$

$\therefore$ The hardness present in 50 ml of the water sample taken

$\equiv 4.9$ mg of $CaCO_3$

$\therefore$ The hardness present in 1000 ml of the water sample

$$= 4.9 \times \frac{1000}{50} = 98 \text{ mg of } CaCO_3$$

$\therefore$ Permanent hardness $= 98$ mg/l $= 98$ ppm.

Temporary hardness:

Temporary hardness = Total hardness-permanent hardness

$= 280$ ppm $\quad 98$ ppm $= 182$ ppm

Results:

Hence, temporary hardness present in the water sample in terms of $CaCO_3$= 182ppm.,

Permanent hardness present in the water sample in terms of $CaCO_3$ = 98ppm.,

Total hardness present in the water sample in terms of $CaCO_3$ = 280ppm.

Precautions:

(1) No tinge of reddish hue should remain at the end-point, the solution should be clear blue.

(2) Titration should be performed slowly near the end-point.