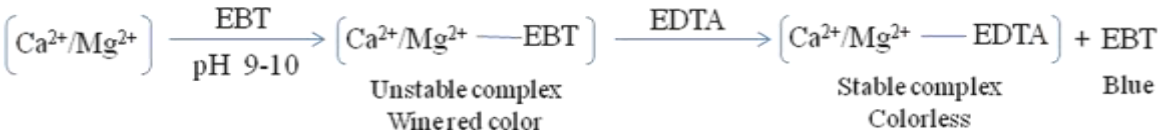
AIM: To determine the calcium and magnesium hardness in a given water sample

Theory: The property of water which restricts or checks the lather formation with soap is called hardness. In other words, the presence of multivalent cations, mostly calcium and magnesium ions, in water is referred to as hardness of water. Hardness is of two types: Temporary or carbonate hardness which can be removed by boiling and Permanent or Noncarbonate hardness which cannot be removed by boiling. The hardness is usually expressed in parts of $CaCO_3$ equivalent or calcium and magnesium salts per million parts of water i.e in ppm.

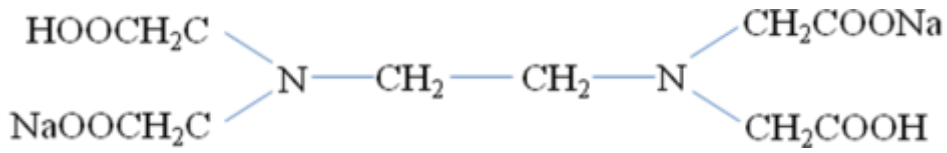
The hardness of water can be determined by complexometric titration using Ethylene diammine tetra acetic acid (EDTA). EDTA in the form of its di-sodium salt forms complex with Ca^{2+} and Mg^{2+} ions of water sample. When Eriochrome Black T (EBT) indicator is added to the hard water at pH around 9–10, it gives wine red colored unstable complex with Ca^{2+} and Mg^{2+} ions of water sample. When this wine red colored complex is titrated against EDTA solution of known strength the Ca^{2+} and Mg^{2+} ions forms stable metal complex with EDTA and color changes from wine red to blue (color of EBT indicator) at the end point.



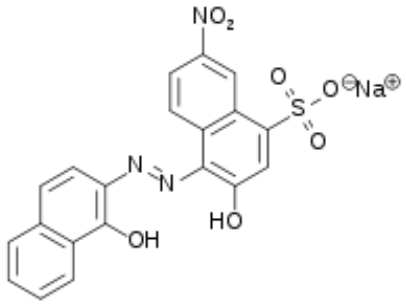
So titration at pH about 9–10 using EBT indicator gives the total amount of Ca^{2+} and Mg^{2+} ions in the water sample.

Titration against EDTA at pH around 12.5 gives the hardness due to Ca^{2+}only. A pH of about 12.5 required for this titration can be obtained by adding diethyl amine base with 3-4 drops of calcon indicator or NaOH base with murexide indicator. At this high pH, the Mg^{2+} ion is quantitatively precipitated as $Mg(OH)_2$ and Ca^{2+} ion alone can be estimated by complexometric method using EDTA. At the end point color changes from pink to pure blue.

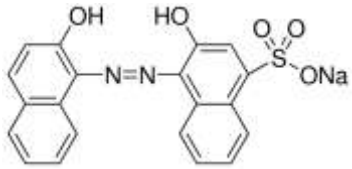
Structure of di-sodium salt of EDTA:



Structure of EBT Indicator:



Structure of Calcon Indicator:



Apparatus: Conical flask, burette, pipette, and measuring cylinder.

Chemicals: EDTA, $Zn(OAc)_2$, NH_4Cl, NH_4OH, Eriochrome Black T (EBT), Calcon, NaOH and ethyl alcohol.

Procedure:

1. Primary standard $Zn(OAc)_2$ solution was provided.
2. Secondary standard EDTA solution and NH_4Cl–NH_4OH buffer solution were provided.
3. **Standardization of EDTA solution:** Pipette out 10 mL of $Zn(OAc)_2$ solution in 100 mL conical flask, add 5 mL of NH_4OH solution (to neutralize the residual acid in the solution), 5 mL of buffer solution and 4–5 drops of EBT indicator. The solution becomes wine red color. Titrate with EDTA solution from the burette till the colour changes to clear blue. Repeat three times and find out the strength of EDTA from known strength of $Zn(OAc)_2$ solution.

4. **Estimation of Ca^{2+} and Mg^{2+} in water:** Pipette out 20 mL of hard water sample in a 100 mL conical flask, add 5 mL of NH_4OH solution (to neutralize the residual acid in the solution), 5 mL of buffer solution and 4–5 drops of EBT indicator. Titrate with standard EDTA solution till wine red color changes to clear blue. Repeat three times.
5. **Estimation of Ca^{2+} in presence of Mg^{2+} in water:** Pipette out 20 mL of water sample in a 100 mL conical flask, add 3 mL of diethyl amine/NaOH solution. Shake the solution thoroughly to precipitate all Mg^{+2} ions as $Mg(OH)_2$. Add 4-5drops of calcon indicator and titrate with standard EDTA solution till the pink colour of the solution changes to clear blue. Repeat three times.

Observations and Calculations:

Table1:- Standardization of EDTA solution

Strength of $Zn(OAc)_2$ solution (S_1) = 0.1(M)

Entry	Volume of $Zn(OAc)_2$ solution mL (V_1)	Burette Reading (mL)		Volume of EDTA required (mL)	Mean volume of EDTA required (V_2) (mL)
		Initial	Final		
1	10				
2	10				
3	10				

$$V_1S_1 = V_2S_2$$

$\therefore$ Strength of EDTA solution (S_2) = (V_1S_1/ V_2) (M) = p(M)

Table 2:- Estimation of Ca^{2+} and Mg^{2+} in given water sample

Entry	Volume of water sample taken (mL)	Burette Reading (mL)		Volume of EDTA required (mL)	Mean volume of EDTA required (V_m) (mL)
		Initial	Final		
1	20				
2	20				
3	20				

EDTA forms 1:1 complex with Ca^{2+} and Mg^{2+}

1000 mL of 1(M) EDTA solution = 1 mole of $CaCO_3$ = 100 g of $CaCO_3$

1 mL of 1(M) EDTA solution = [100 x (1/1000)] g of $CaCO_3$

V_m mL of p(M) EDTA solution = [100 x (1/1000) x p x V_m] g of $CaCO_3$

= A g (say)

20 mL of water sample contain A g of $CaCO_3$

1000 mL of water sample contain [(A/20) x 1000] g of $CaCO_3$

Table 3:- Estimation of Ca^{2+} in given water sample

Entry	Volume of water sample taken (mL)	Burette Reading (mL)		Volume of EDTA required (mL)	Mean volume of EDTA required (V_n) (mL)
		Initial	Final		
1	20				
2	20				
3	20				

1000 mL of 1(M) EDTA solution = 1 mole of $CaCO_3$ = 100 g of $CaCO_3$

1 mL of 1(M) EDTA solution = [100 x (1/1000)] g of $CaCO_3$

(V_m–V_n) mL of p(M) EDTA solution = [100 x (1/1000) x p x (V_m–V_n)] g of $CaCO_3$

= B g (say)

20 mL of water sample contain B g of $CaCO_3$

1000 mL of water sample contain [(B/20) x 1000] g of $CaCO_3$

Conclusion: Total hardness of water sample w.r.t $CaCO_3$ = [(A/20) x 1000] g/L

Magnesium hardness of water w.r.t $CaCO_3$ = [(B/20) x 1000] g/L

Calcium hardness of water w.r.t $CaCO_3$ = [(A/20) x 1000]–[(B/20) x 1000] g/L

Discussion:

To determine the temporary and permanent hardness separately in the water sample, same EDTA method can be used first to determine the total hardness (H_1). Then boil the sample water gently for about one hour, cool it and filter it. Take this sample of water and estimate the permanent hardness (H_2) by the same EDTA method. As it is known that, temporary hardness can be removed just by boiling. The difference (H_1−H_2) is the temporary hardness in the given water sample.

Precautions:

i) All the glass apparatus should be washed thoroughly with distilled water before use.

ii) The burette and pipette should be rinsed with solution to be taken in it.

iii) There should not be any leakage in the burette.

iv) All the solution should be freshly prepared.

v) Same amount of indicator should be added each time.

vi) pH of the solution should be maintained during titration.

vii) Shaking should be proper during titration.

viii) The titration flask should be placed on white paper or board to identify properly the colour change at the end point.