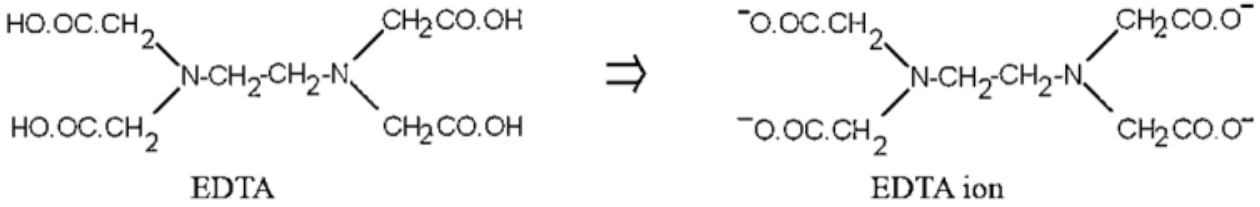
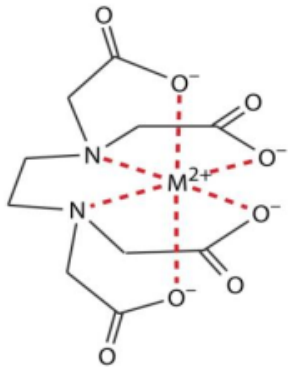
Complexometric Determination of Hardness of Water (EDTA Method)

Theory-EDTA Method

- Hardness of water determined by complexometric titration using standard ethlyene diamine tetraacetic acid (EDTA) and Eriochrome Black T (EBT) as an indicator
- EDTA is a weak acid - tetraprotic acid- lose four H on complete neutralization
- Because of limited solubility, EDTA used in the form of its disodium salt. The resultant anion will form stable complex with metal ion

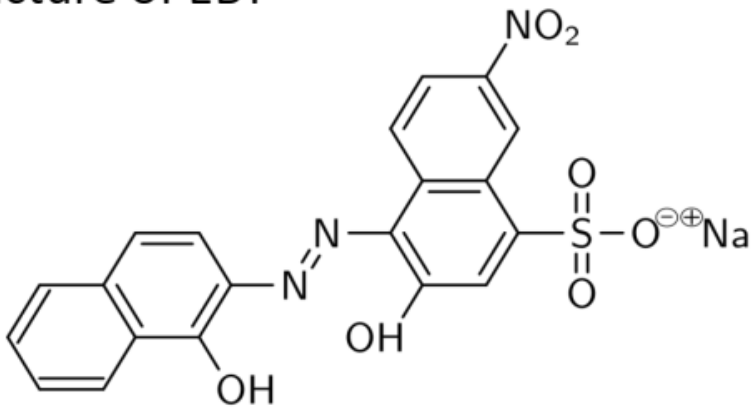


EDTA EDTA ion



- EDTA combines with metal ion in a 1:1 ratio, irrespective of the charge of the cation
- EDTA complex – stable – titration method
- Titration – determination of the equivalence point – completion of M-EDTA complex formation – M-EDTA complex not colored – requires indicator
- Eriochrome Black T (EBT) is used as indicator

- Structure of EBT



→ Weak acid

$$H_2O + H_2In^- \rightleftharpoons HIn^{2-} + H_3O^+$$
red blue

→ M-EBT complex - wine red, as in H_2In^-

- For metal ion detection – pH to be adjusted to basic side – blue form, i.e., HIn^{2-} predominates in the absence of metal ion
- Buffered at pH 10 using NH_4OH-NH_4Cl buffer

$$Ca^{2+} + \underset{\text{(Blue)}}{EBT} \xrightarrow{pH = 10} \underset{\text{Wine-red}}{[Ca\text{-}EBT]\ complex}$$

- During titration, EDTA combines with metal ions to form stable M-EDTA complex and releasing free EBT

$$\underset{\text{Wine-red}}{[Ca\text{-}EBT]\ complex} + EDTA \xrightarrow{\text{Titration}} \underset{\text{Colorless}}{[Ca\text{-}EDTA]\ complex} + \underset{\text{(Blue)}}{EBT}$$

- Until equivalence point – EBT complexes the excess metal ion, so wine red color retained – with first slight excess of EDTA, color changes to blue (end point)

Preparation of standard solutions/Reagents

- **Standard Hard Water (0.01M $CaCl_2$):** Weigh accurately 0.5 g of dried $CaCO_3$, transfer to 500 mL volumetric flask, add about 100 mL of water. Further add 1N HCl solution drop-wise till effervescence ceases and the solution become clear. Make up the solution to the mark with the distilled water and shake the flask well for uniform concentration.

- **EDTA solution (0.01M EDTA):** Dissolve 4 g of EDTA crystals along with 0.1 g $MgCl_2$ in little distilled water in 1L standard flask and make it upto the mark with distilled water. Shake the flask for uniform concentration. If the solution is turbid, add a few drops of 0.1N NaOH solution to the solution clear.

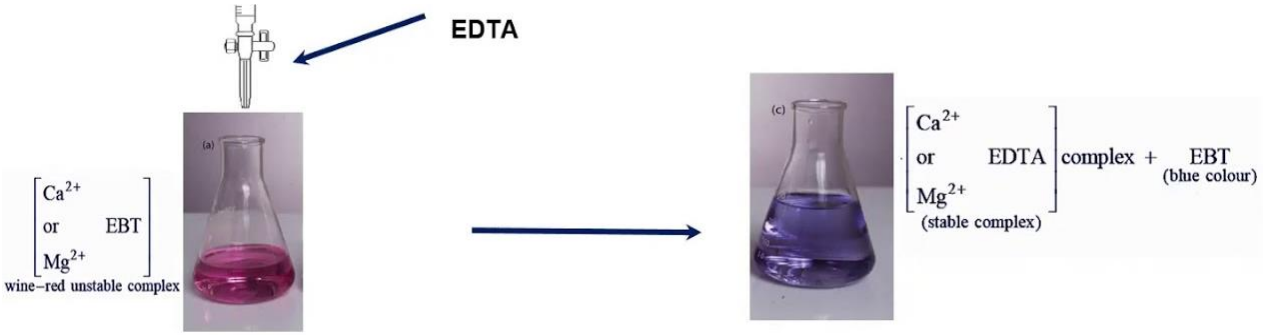
- **Indicator (EBT solution):** Dissolve 0.5 g of Erichrome Black-T in 100mL of ethanol/ methanol. Date the bottle. Solutions older than 6 weeks should not be used.

- **Buffer solution (pH 10):** Add 6.75 g of NH_4Cl to 57 mL of Conc. Ammonia solution and dilute with distilled water to one liter. pH will be slightly above 10.

Procedure:

PART- 1 : STANDARDISATION OF EDTA SOLUTION :

Take 10 mL of 0.1 M $CaCl_2$ solution in a conical flask & 1/2 test tube (T.T.) of buffer solution. Then add 2-3 drops of indicator solution. Titrate Carefully against EDTA solution to the end point where the color changes from wine-red to pure blue. The titration should be carried out slowly near the end point with constant stirring. No tinge of red color should remain in the solution. Repeat the titration with four other aliquots of the Ca^{++} solution. Calculate the molarity of the EDTA solution & the $CaCO_3$ equivalent of EDTA solution.

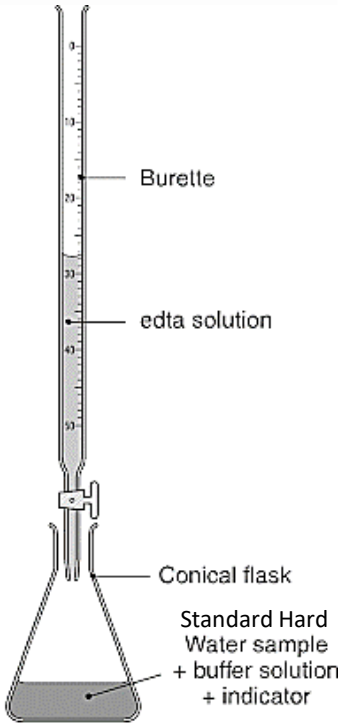


Hard Water + 8-10 ml buffer solution + 2-3 drops of EBT (Wine Red Colour)

Blue Colour at End Point

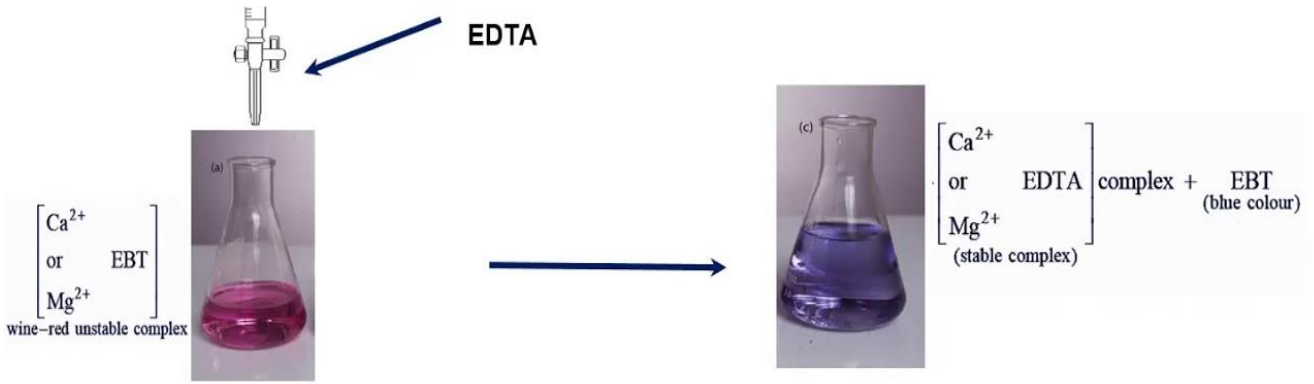
Reaction: Ca^{+2} + EBT = Ca-EBT Complex
Blue Wine Red

Ca-EBT + EDTA = Ca-EDTA Complex + EBT
Colorless Blue in color



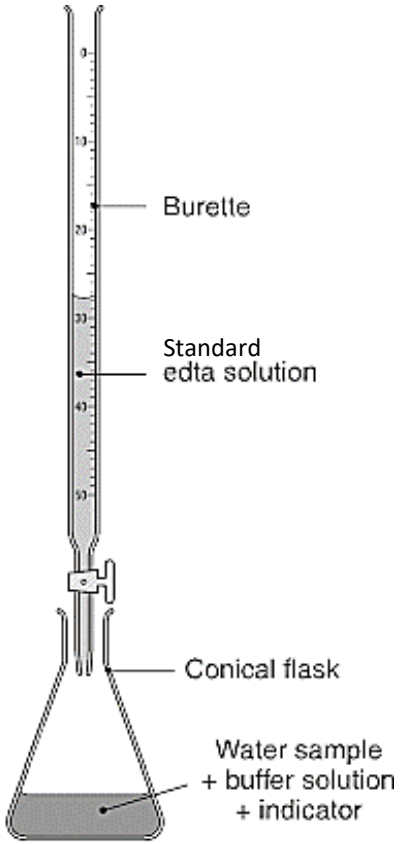
PART- 2 : ESTIMATION OF HARDNESS OF WATER :

Take 50 mL of given water sample in a conical flask. To this sample add ¼ T.T. of buffer solution & 2-3 drops of indicator solution. Titrate with EDTA solution from burette. End point a marked by a color change from wine red to pure blue. Repeat the titration with 4 other aliquots. Calculate the total hardness of the water as ppm (Parts per million) of $CaCO_3$



Hard Water + 8-10 ml buffer solution + 2-3 drops of EBT (Wine Red Colour)

Blue Colour at End Point



OBSERVATION :

PART-I : STANDARDIZATION OF EDTA SOLUTION :

Burette : 0.01 M EDTA solution

Flask : 10 ml 0.01 M $CaCl_2$ solution + 1/2 T.T. of buffer solution

Indicator : Eriochrome Black-T (EBT) solution (2-3drops)

End Point : Wine red to blue

OBSERVATION TABLE :

Sr. No.	Initial Burette Reading (ml)	Final Burette Reading (ml)	Differences (ml)	Concurrent Reading (ml)
1				
2				
3				
4				

Calcuiation :

Part-I :

1 mole of Ca^{+2} = 1 mole of sodium EDTA

Hence,

Molarity of EDTA solution x volume of EDTA solution

= Molarity of Ca^{+2} solution x volume of ca^{+2} solution

$M_2 \times BR = 0.01 \times 10$ (BR = Burette Reading)

$M_2 = \frac{0.01 \times 10}{BR}$ = ... M

Molarity of EDTA solution = ... M

1.0 ml of EDTA solution = Molarity of EDTA x 100(Mole. Wt of $CaCO_3$)

Equivalent to $CaCO_3$ = ... mg. Of $CaCO_3$ (A)

(Use in calculation of Part-II)

For example:

OBSERVATION :

PART-I : STANDARDIZATION OF EDTA SOLUTION :

Burette : 0.01 M EDTA solution

Flask : 10 ml 0.01 M $CaCl_2$ solution + 1/2 T.T. of buffer solution

Indicator : Eriochrome Black-T (EBT) solution (2-3drops)

End Point : Wine red to blue

OBSERVATION TABLE :

Sr. No.	Initial Burette Reading (ml)	Final Burette Reading (ml)	Differences (ml)	Concurrent Reading (ml)
1	0.0	9.0	9.0	8.7
2	0.0	8.7	8.7	
3	0.0	8.7	8.7	
4				

Calculation :

Part-I :

1 mole of Ca^{+2} = 1 mole of sodium EDTA

Hence,

Molarity of EDTA solution x volume of EDTA solution

= Molarity of Ca^{+2} solution x volume of ca^{+2} solution

$M_2 \times BR = 0.01 \times 10$ (BR = Burette Reading)

$M_2 = \frac{0.01 \times 10}{BR}$ = $\frac{0.01 \times 10}{8.7} = 0.014$ ..... M

Molarity of EDTA solution = 0.014 ..... M

1.0 ml of EDTA solution = Molarity of EDTA x 100(Mole. Wt of $CaCO_3$)

Equivalent to $CaCO_3$ = 1.14 ..... mg. Of $CaCO_3$ (A)

(Use in calculation of Part-II)

PART-II:

Burette : _____ M EDTA solution (From Part-I calculation)

Flask : 50 ml water sample + ¼ T.T. Buffer solution

Indicator : Erichrome Black-T solution (2-3 drops)

End Point : Wine red to Pure Blue

OBSERVATION TABLE :

Sr. No.	Initial Burette Reading (ml)	Final Burette Reading (ml)	Differences (ml)	Concurrent Reading (ml)
1				
2				
3				
4				

CALCULATIONS Part-II :

(1) Amount of $CaCO_3$ present in 50.0 ml waer sample

= _____ (BR) x A (from Part-I)

= _____ mg(B)

(2) Total hardness of given water sample as ppm of $CaCO_3$

$= \frac{B \times 1000}{50.0}$

= _____ ppm=Mg/Litre

RESULTS:

The given sample of water has total hardness of _____ ppm of $CaCO_3$

For example:

PART-II:

Burette : 0.011 M EDTA solution (From Part-I calculation)

Flask : 50 ml water sample + ¼ T.T. Buffer solution

Indicator : Erichrome Black-T solution (2-3 drops)

End Point : Wine red to Pure Blue

OBSERVATION TABLE :

Sr. No.	Initial Burette Reading (ml)	Final Burette Reading (ml)	Differences (ml)	Concurrent Reading (ml)
1	0.0	12.4	12.4	12.4
2	0.0	12.3	12.3	
3	0.0	12.4	12.4	
4				

Reaction : Ca^{+2} + EBT = Ca-EBT Complex

Blue Wine Red

Ca-EBT + EDTA = Ca-EDTA Complex + EBT (Blue in colour)

Colorless (EBT=Eriochrome Black-T)

CALCULATIONS Part-II :

(1) Amount of $CaCO_3$ present in 50.0 ml waer sample

= 12.4 (BR) x A (from Part-I)

= 9.57 mg(B)

(2) Total hardness of given water sample as ppm of $CaCO_3$

$= \frac{B \times 1000}{50.0} = \frac{9.57 \times 1000}{50}$

= 282.72 ppm=Mg/Litre

RESULTS :

The given water sample has total hardness of 282.72. ppm of $CaCO_3$.

- **Advantages of EDTA method:** greater accuracy, convenience & rapid procedure

- **Significance of hardness determination:** useful analytical test - provides a measure of quality of water- particularly important to industry - hard water while heating precipitates $CaCO_3$ which clogs boilers & pipes