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CHEMISTRY

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In this class..

Estimation of total hardness, permanent and temporary hardness by EDTA method

Expt. No. : 2

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Experiment

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❏ **Aim :**

To estimate the amount of total hardness, permanent hardness and temporary hardness of a given sample of water by EDTA method using ammonia buffer (pH =10) and Eriochrome black-T indicator.

❏ **Materials required:**

Pipette, burette, conical flask, standard flask, funnel, beaker.

Chemicals required :

EDTA solution, standard hard water, sample water, Eriochrome black T indicator (EBT), NH_3-NH_4Cl buffer solution (pH 10).

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Hardness of water

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❏ Hard water is water that contains cations with a charge of +2, especially Ca^{2+} and Mg^{2+}

❏ At a **level over 100 mg/L** measured as calcium carbonate, a given water source is considered hard. (Not potable)

Hardness (mg/L)	Degree of hardness
0-75	Soft
75-100	Moderately hard
150-300	Hard
>300	Very hard

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Hardness of water, scale formation

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Types of hardness

❑ **Temporary hardness:**
  It is due to the presence of bicarbonates of calcium and magnesium and can be removed by boiling.

❑ **Permanent hardness:**
  It is due to the presence of sulphates, nitrates and chlorides of calcium and magnesium.

❑ Hardness is usually reported as **parts per million (ppm) of calcium carbonate (by weight)**.

❑ A water supply with a hardness of **100 ppm contains** the equivalent of **100 g of $CaCO_3$ in 1 million g of water or 0.1 g in 1 L of water**

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Hardness, representation

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Clark's degree (°Cl): The number of parts of calcium carbonate equivalent hardness present in **70,000 or (7×10⁴)** parts of water.

1° Clark = 1 part of $CaCO_3$ eq. hardness per 70,000 parts of water. (**14.254 ppm**)

Degree French (°Fr): The number of parts of calcium carbonate equivalent hardness presents in **10^5 parts of water**.

1° Fr = 1 part of $CaCO_3$ hardness eq per 10^5 parts of water. (**10 ppm**)

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Complexometric titration

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❑ A titration based on the formation of coordination complexes between a **metal ion and complexing agent** (or chelating agent) to form soluble complexes. **(Hardness in water)**

❑ Complex-forming reactions involving **many metal ions** can serve as a basis for accurate and convenient titrations for such metal ions. **High accuracies** and offer the possibility of determinations of metal ions at the **millimole levels**.

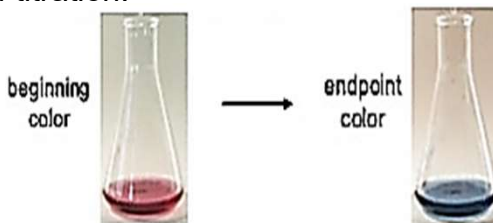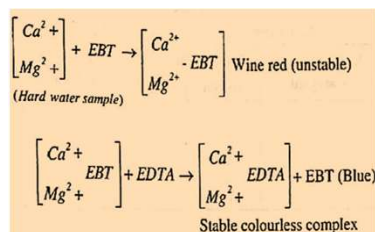Eriochrome Black-T + Ca^{2+}/Mg^{2+} ⟶ Eriochrome Black-T-Ca^{2+}/Mg^{2+}
(Wine red)

Eriochrome Black-T-Ca^{2+}/Mg^{2+} + EDTA ⟶ EDTA-Ca^{2+}/Mg^{2+} + Eriochrome Black-T
(Wine red) (Steel blue)
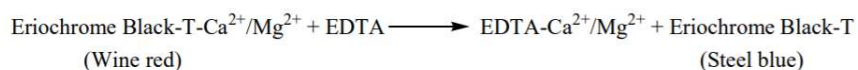
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Principle

❏ The hardness causing metal ions form a **wine–red coloured weak complex with Eriochrome black-T indicator** in the presence of buffer solution.

❏ When EDTA is added, the **indicator is replaced by EDTA and a stable complex is formed**. Due to **liberation of Eriochrome black-T indicator**, wine *red colour changes to steel blue* which marks the end point of titration.


$$\begin{bmatrix} Ca^{2+} \\ Mg^{2+} \end{bmatrix} + EBT \rightarrow \begin{bmatrix} Ca^{2+} \\ Mg^{2+} \end{bmatrix} - EBT \text{ Wine red (unstable)}$$

(Hard water sample)

$$\begin{bmatrix} Ca^{2+} \\ Mg^{2+} \end{bmatrix} EBT + EDTA \rightarrow \begin{bmatrix} Ca^{2+} \\ Mg^{2+} \end{bmatrix} EDTA + EBT \text{ (Blue)}$$

Stable colourless complex

beginning color

endpoint color

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Role of Eriochrome black-T

❏ Eriochrome black T is an azo dye used as a complexometric indicator.
❏ In its **deprotonated form, Eriochrome black-T is blue**. It turns **red when it forms a complex** with calcium, magnesium, or other metal ions.

Eriochrome black -T
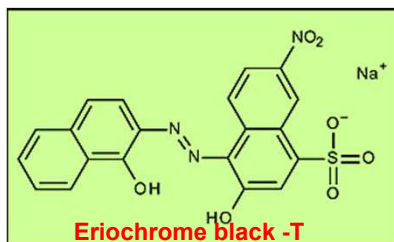
❏ The **characteristic blue end-point is reached** when sufficient EDTA is added and the metal ions bound to the indicator are chelated by EDTA, leaving the free indicator molecule.
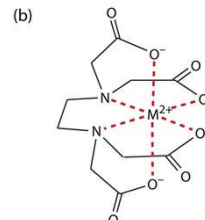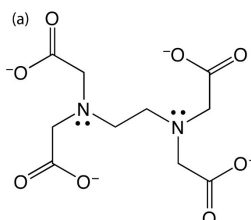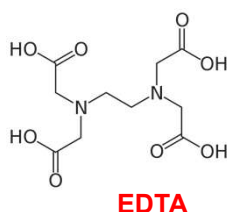
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Role of EDTA

❑ EDTA is a **hexadentate complexing or chelating agent** used to capture the metal ions.
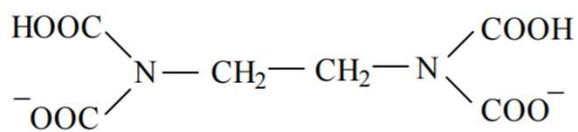

EDTA

❑ Capturing metal ions causes water to become softened, but metal ions are not completely removed from water.

❑ EDTA simply binds the metal ions to it very tightly thus forming a **strong and stable metal complex.**

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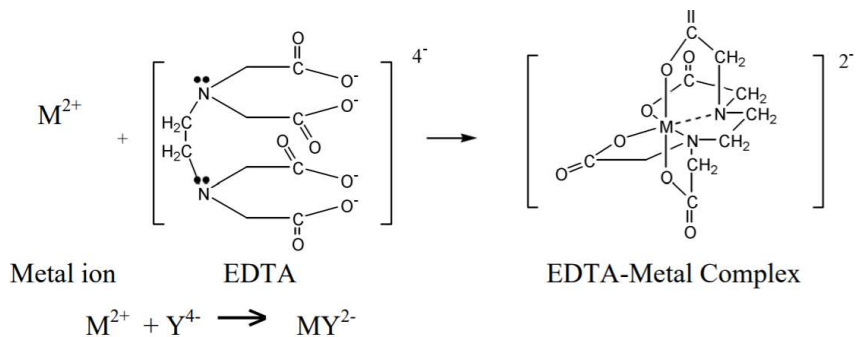

Role of EDTA

$$Ca^{2+}(aq) + H_2Y^{2-}(aq) \longrightarrow CaY^{2-}(aq) + 2H^+(aq)$$

EDTA (anionic form)

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Complexometric titration

Metal ion · · · · · EDTA · · · · · EDTA-Metal Complex

$$M^{2+} + Y^{4-} \longrightarrow MY^{2-}$$

❑ The **Y^{4-} ion that forms a 1:1 complex** with the metal ion is the completely deprotonated anion of ethylenediaminetetraacetic acid **("H_4Y").**

❑ At **pH=10**, the EDTA is present in solution primarily as its monoprotonated form, **HY^{3-}**
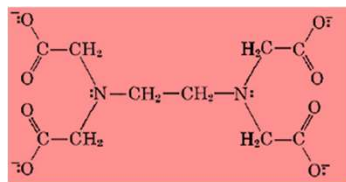
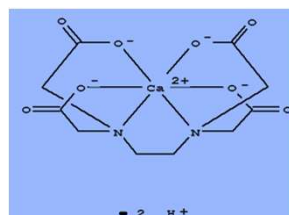5 October 2021 · · · · · Dr K Ananthanarayanan · · · · · 13

Role of ammonia buffer

❑ The buffer solution is used to resist the change in pH as all reactions between **metal ions and EDTA are pH dependent**.

❑ With increasing the pH, each hydrogen ion in the carboxyl groups of EDTA will start to dissociate. Above pH 10, $EDTA^{4-}$ is predominant. As we need $EDTA^{4-}$ to react with the metal ions present in the titration solution, we use **pH 10 buffer** such as ammonia/ammonium chloride.

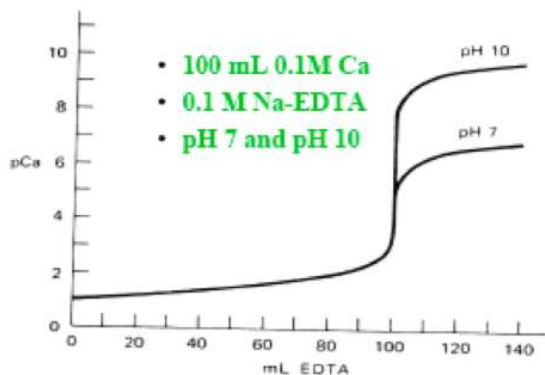**EDTA $^{4-}$** · · · · · **EDTA - metal complex**

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Role of pH
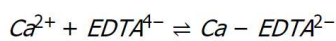

- 100 mL 0.1M Ca
- 0.1 M Na-EDTA
- pH 7 and pH 10

❑ EDTA versus metal ion titration, if pM (= -log[M^{n+}], where M^{n+} signifies the metal ion whose concentration is required) is plotted against the volume of EDTA solution added
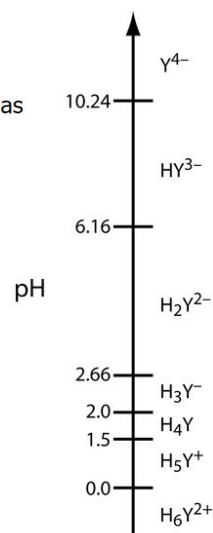
Formation constant and equilibrium

$$Ca^{2+} + EDTA^{4-} \rightleftharpoons Ca - EDTA^{2-}$$

with a corresponding equilibrium constant for ***formation*** expressed as

$$K_f \left(Ca - EDTA^{2-}\right) = \frac{[Ca-EDTA^{2-}]}{[Ca^+][EDTA^{4-}]}$$

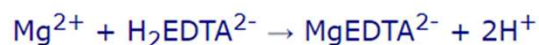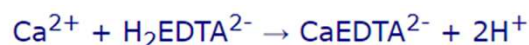**Formation constant is very large 2.9 x 10^{16}**, its equilibrium position lies far to the right.
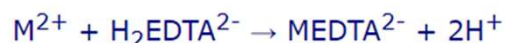

pH

10.24	Y^{4-}
6.16	HY^{3-}
2.66	H_2Y^{2-}
2.0	H_3Y^-
1.5	H_4Y
0.0	H_5Y^+
	H_6Y^{2+}

Equation, calculation

$$Ca^{2+} + H_2EDTA^{2-} \rightarrow CaEDTA^{2-} + 2H^+$$

$$Mg^{2+} + H_2EDTA^{2-} \rightarrow MgEDTA^{2-} + 2H^+$$

So if we let M^{2+} be the total of Ca^{2+} and Mg^{2+} ions in solution ther

$$M^{2+} + H_2EDTA^{2-} \rightarrow MEDTA^{2-} + 2H^+$$

Note that 1 mole of M^{2+} reacts with 1 mole of H_2EDTA^{2-}.
At the equivalence point of the titration:

$$moles\ M^{2+} = (moles\ Ca^{2+} + moles\ Mg^{2+})$$
$$= moles\ H_2EDTA^{2-}$$

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$CaCO_3$ as reference for hardness

❑ $CaCO_3$ is stable, non-hygroscopic and is obtained in pure form. Therefore a standard hard water solution can be prepared by dissolving accurately weighed $CaCO_3$ in HCl and can make up to a known volume.

❑ $CaCO_3$ is insoluble in water. Therefore it can be easily precipitated in water treatments.

❑ Molecular weight of $CaCO_3$ is 100, so mathematical calculations are easy.

1.0 gm of pure CaCO$_3$ dissolved in minimum quantity of conc. HCl and diluted to a one litre with distilled water.

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Procedure

Standardisation of EDTA

❏ Pipette out **20mL of standard hard water** into a clean conical flask.

❏ Add **5mL of the buffer solution and 3 or 4 drops** of eriochrome black-T indicator. The solution **turns wine red** in colour.

❏ Titrate the **wine red coloured solution against EDTA** taken in the burette.

❏ The change from **wine red to steel blue colour** is the end point. Repeat the titration for **concordant values**. Let the titer value be **V_1 mL**

Procedure

Determination of total hardness

❏ Pipette out **20mL of sample hard water** into a clean conical flask.

❏ Add 5mL of the buffer solution and 3 or 4 drops of eriochrome black-T indicator.The solution turns wine red in colour.

❏ Titrate the wine red coloured solution against EDTA taken in the burette.

❏ The change from wine red to steel blue colour is the end point.

❏ Repeat the titration for concordant values. Let **V_2 mL** be the volume of EDTA consumed.

Procedure

Determination of permanent hardness

❑ Take 100 mL of hard water sample in a 250 mL beaker and boil gently for about one hour. (***boiled water will be given)***

❑ Cool and filter into a 100mL standard flask and make the volume up to the mark. Take **20mL of this solution** and proceed the titration in the same way.

❑ The volume of EDTA consumed corresponds to the permanent hardness of the water sample. Let the titer value be **V_3 mL.**

❑ Temporary hardness is calculated by subtracting **permanent hardness from total hardness.**

Tabular column

Standardisation of EDTA

Table 1
Std Hard water Vs EDTA solution

S.No.	Vol. of Std. hard water ml	Burette Reading		Vol. of EDTA ml	Indicator
		Initial	Final		
					EBT

Calculation, standardisation

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1 ml of Standard hard water	=	1 mg of $CaCO_3$
Volume of standard hard water taken	=	20ml
20ml of Standard hard water	=	20mg of $CaCO_3$
Volume of EDTA consumed	=	V_1ml (from table-1)
V1ml EDTA solution	=	20mg $CaCO_3$
Therefore 1ml EDTA will be	=	$\dfrac{20}{V_1}$ mg of equivalent $CaCO_3$

A mg $CaCO_3$

Tabular column

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Determination of total hardness

Table 2
Sample Hard water Vs EDTA Solution

S.No.	Vol. of Sample hard water ml	Burette Reading		Vol. of EDTA ml	Indicator
		Initial	Final		
					EBT

Determination of Total hardness

Volume of EDTA consumed $\quad$ = **X mL (V_2 from Table-2)**
1 mL of EDTA $\quad$ = 20/**V1** [mg CaCO$_3$] $\quad$ = **A mg CaCO$_3$**
V_2 mL of EDTA $\quad$ = **A** × V_2 $\quad$ [mg CaCO$_3$] = **B mg of CaCO$_3$**

If 20 mL of sample hard water taken for titration = **B mg of CaCO$_3$**

Then, 1000 mL will contain = (**B** × 1000 mg CaCO$_3$) / 20

Total hardness = TH ppm

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Tabular column

Determination of permanent hardness

Table 3
Boiled sample hard water Vs EDTA solution

S.No.	Vol. of boiled water ml	Burette Reading		Vol. of EDTA ml	Indicator
		Initial	Final		
					EBT

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Determination of Permanent hardness:

Volume of EDTA consumed = **X mL (V$_3$ from Table-3)**
1 mL of EDTA = 20/V$_1$ [mg CaCO$_3$] = A mg CaCO$_3$
V$_3$ mL of EDTA = **A** × V$_3$ [mg CaCO$_3$] = **C mg of CaCO$_3$**

If 20 mL of sample hard water taken for titration = **C** mg of CaCO$_3$

Then, 1000 mL will contain = (**C** × 1000 mg CaCO$_3$) / 20

= PH ppm

Permanent hardness = ppm

Estimation of Temporary hardness

Temporary Hardness = Total hardness – Permanent hardness

RESULT:

❑ The total hardness of sample hard water is   =

❑ The permanent hardness of sample hard water is =

❑ The temporary hardness of sample hard water is   =

Limitations of EDTA titration

1. Many EDTA titrations are carried out under alkaline pH which may lead to **formation of insoluble hydroxides** or basic salts that may compete with the complexation process.

2. Since EDTA forms stable complexes with most of the metal ions, **it lacks selectivity** if it is used to estimate a single metal cations from a solution of mixture of metal ions.

3. The change in equilibrium from metal-indicator complex to the metal-EDTA complex should be **sharp and rapid**.

4. Conditional formation constant of the metal-EDTA complex K' MY to K'In should **be of the order 10^4** to provide a good end point

Table-1 Standard Hard water vs EDTA Solution

Sl.No.	Volume of Sample Hard water (mL)	Burette Reading (mL)		Volume of EDTA solution (mL)	Indicator
		Initial	Final		
1	20	0	22.9	**22.9**	Eriochrome Black-T
2	20	0	22.9		

Table-2 Sample Hard water vs EDTA Solution SRM

Sl. No.	Volume of Sample Hard water (mL)	Burette Reading (mL)		Volume of EDTA solution (mL)	Indicator
		Initial	Final		
1	20	0	10.8	**10.8**	Eriochrome Black-T
2	20	0	10.8		

Table-3 Boiled sample water vs EDTA Solution SRM

Sl.No.	Volume of Sample Hard water (mL)	Burette Reading (mL)		Volume of EDTA solution (mL)	Indicator
		Initial	Final		
1	20	0	7.1	**7.1**	Eriochrome Black-T
2	20	0	7.1		

Determination of Total hardness:

Volume of EDTA consumed   = **10.8 mL (V_2 from Table-2)**
1 mL of EDTA   = 20/V1 mg $CaCO_3$ = **0.873 mg $CaCO_3$**
V_2 mL of EDTA   = **20/V_1 × V_2** mg $CaCO_3$
$\qquad\qquad\qquad\qquad$ = **9.432 mg of $CaCO_3$**

If 20 mL of sample hard water taken for titration =
20/V_1 × V_2 mg $CaCO_3$
Then, 1000 mL will contain
= (20/V_1 × V_2 × 1000) / 20
= **0.471.6 ×1000**

Total hardness = 471.61 ppm

Determination of Permanent hardness:

Volume of EDTA consumed = **7.1 mL (V_3 from Table-3)**
1 mL of EDTA   = 20/V_1 mg CaCO3   = 0.873 mg $CaCO_3$
V_3 mL of EDTA   = 20/V_1 × V_3 mg $CaCO_3$ = **6.198 mg of $CaCO_3$**

If 20 mL of sample hard water taken for titration
= 20/V_1 × V_3 mg $CaCO_3$

Then, 1000 mL will contain = (20/V_1 × V_3 × 1000) / 20

= 309.91 ppm

Permanent hardness = 309.91 ppm

Estimation of Temporary hardness

Temporary Hardness = Total hardness – Permanent hardness
= 471.60 ppm – 309.91 ppm
= 161.69 ppm

Result:

Total Hardness = **471.61 ppm**
Permanent Hardness = 309.91 ppm
Temporary Hardness = 161.70 ppm

Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.