Methods of increasing selectivity of EDTA

- EDTA is very **unselective** because it can form stable complexes with **many** divalent, trivalent and tetravalent cations.
- Many methods can increase the selectivity of EDTA and so facilitate the titration of mixtures or the removal of interferences.
- Examples of these methods are illustrated in the following experiments:

Exp.(14): Complexometric determination of (Ca^{2+}/Mg^{2+}) mixture ($CaCl_2.6H_2O$ & $MgSO_4.7H_2O$)

Principle : *(direct titration)*

1) **First step: (Determination of Ca^{2+}only).**

By titrating 10 ml of the mixture ≠ standard EDTA using **8% NaOH** & **murexide** indicator.

$E.P_1 \equiv Ca^{2+}$ only.

2) **Second step: (Determination of total Ca^{2+} & Mg^{2+}).**

By titrating another 10 ml of the mixture ≠ standard EDTA using **amm. buffer** & **EBT** indicator.

$E.P_2 \equiv$ Total (Ca^{2+} & Mg^{2+}).

Notes:

1) **When we use 8% NaOH (pH=12) & murexide, we determine Ca^{2+} ONLY because:** Mg^{2+} does not form any complex with EDTA at pH=12 due to the precipitation of Mg^{2+} as $Mg(OH)_2\downarrow$ which is more stable than (Mg-EDTA) complex. IN OTHER WORDS, we can say that the selectivity of EDTA was increased to determine Ca^{2+} only without interference of Mg^{2+}.

2) **Ca^{2+} alone can not be directly determined ≠ EDTA using EBT ind. because:** EBT gives poor E.P. with Ca^{2+} (i.e. the color change at E.P. is not sharp) and that is because the binding between Ca^{2+} & EBT is very weak.

3) **Although EBT can not be used in direct complexometric determination of Ca^{2+} alone** *(as mentioned before)*, **BUT it can be used for determination of total Ca^{2+} & Mg^{2+}……HOW??!!**

That is because:

⇒*Before starting titration:* {*sample (Ca^{2+} & Mg^{2+})* + *amm. buffer* + *EBT*}

EBT will be complexed with Mg^{2+} only because **(Mg-EBT) complex is more stable than (Ca-EBT) complex** which is very weak *(as mentioned before)*.

i.e. We have { free Ca^{2+} + free Mg^{2+} + (Mg-EBT) } in the flask.

⇒*During titration, the following reactions occur:*

1) EDTA + free Ca^{2+} ↔ (Ca-EDTA) complex.

2) EDTA + free Mg^{2+} ↔ (Mg-EDTA) complex.

E.P. 3) EDTA + (Mg-EBT) ↔ (Mg-EDTA) + free EBT. *blue color*

i.e. EDTA reacts first with free Ca^{2+} then with free Mg^{2+} because **(Ca-EDTA) complex is more stable than (Mg-EDTA) complex** *(compare with EBT)*.

And finally EDTA reacts with (Mg-EBT) complex and so the color change at E.P. will be due to Mg-reaction and that gives sharp E.P. representing (or equivalent to) the total.

Procedure :

A Murexide reading ($E.P_1$) : (≡ Ca^{2+} only)

1) Transfer 10 ml of the mixture into a clean conical flask.

2) Add 2 ml of 8% NaOH.

3) Add few specks of murexide indicator.

4) Titrate ≠ 0.05 M EDTA.

{ **Color change at E.P.**: from **Rose Red (Pink)** to **Bluish Violet** }

Complexed murexide ind. *Free murexide ind.*

B EBT reading ($E.P_2$) : (≡ Ca^{2+} + Mg^{2+})

1) Transfer another 10 ml of the mixture into a clean conical flask.

2) Add 2 ml of Amm. buffer.

3) Add few specks of EBT indicator.

4) Titrate ≠ 0.05 M EDTA.

{ **Color change at E.P.**: from **Wine Red** to **Pure Blue** }

Complexed EBT ind. *Free EBT ind.*

Calculations :

$$E.P_1 \{murexide\ reading\} \equiv Ca^{2+}$$

$$E.P_2 \{EBT\ reading\} \equiv Ca^{2+} + Mg^{2+}$$

$$\therefore (E.P_2 - E.P_1) \equiv Mg^{2+}$$

For Ca^{2+} :

$$Ca^{2+} + \underset{\substack{EDTA \\ (standard)}}{H_2Y^{2-}} \leftrightarrow CaY^{2-} + 2H^+$$

$$\therefore 1\ EDTA \equiv \underset{standard}{1}\ CaCl_2.6H_2O \quad \underset{sample}{}$$

Equivalence factor (F):

$$\text{each ml of 0.05 M EDTA} \equiv \frac{1 \times \text{M.W. of } CaCl_2.6H_2O \times 0.05}{1000} \equiv ..g\ CaCl_2.6H_2O$$

Concentration:

$$\text{Concn. of } CaCl_2.6H_2O = \frac{E.P_1 \times F \times 1000}{10} = \ldots\ldots\ g/L$$

For Mg^{2+} :

$$Mg^{2+} + \underset{\substack{EDTA \\ (standard)}}{H_2Y^{2-}} \leftrightarrow MgY^{2-} + 2H^+$$

$$\therefore 1\ EDTA \equiv \underset{standard}{1}\ MgSO_4.7H_2O \quad \underset{sample}{}$$

Equivalence factor (F):

$$\text{each ml of 0.05 M EDTA} \equiv \frac{1 \times \text{M.W. of } MgSO_4.7H_2O \times 0.05}{1000} \equiv ..g\ MgSO_4.7H_2O$$

Concentration:

$$\text{Concn. of } MgSO_4.7H_2O = \frac{(E.P_2 - E.P_1) \times F \times 1000}{10} = \ldots\ldots\ g/L$$

Use of masking and demasking agents to increase the selectivity of EDTA

Introduction :

- The selectivity of EDTA can be increased by the use of masking and demasking agents.
- **Definition of Masking:**

  It's the process in which a substance is transformed into a form that does not enter into the reaction without making physical separation of the substance or its reaction products.

Examples: **(CN^-)** ion is an effective masking agent that can form stable cyanide complex with some cations as **Cu^{2+}, Cd^{2+}, Hg^{2+} & Zn^{2+}** making them unable to react with EDTA or with indicators SO other cations as **Mg^{2+}, Mn^{2+} & Ca^{2+}** can be determined without interference of the above mentioned metals.

[Refer to the determination of (Cu^{2+}/Mg^{2+}) mix & (Hg^{2+}/Mg^{2+}) mix.].

- **Definition of demasking:**

  It's the process in which the masked substance regains its ability to enter into the reacton.

  Examples:

$$[Zn(CN)_4]^{2-} \xrightarrow{\text{demasking by (}\textit{formaldehyde / acetic acid}\text{)}} Zn^{2+}$$

- The use of masking agents can be illustrated in the following experiments.

Exp.(15): Complexometric determination of (Mg^{2+}/Cu^{2+}) mixture ($MgSO_4.7H_2O$ & $CuSO_4.5H_2O$)

Principle : *(direct titration)*

a) Determination of Mg^{2+} only (2 steps):

1st step: Masking of Cu^{2+} by KCN as follows:

- Cu^{2+} + 4 NH_3 ↔ $[Cu(NH_3)_4]^{2+}$
  amm. buffer — *Copper ammine complex (Blue color)*

- $[Cu(NH_3)_4]^{2+}$ + 4 CN^- ⟶ $[Cu(CN)_4]^{2-}$ + 4 NH_3
  masking agent — *very stable complex* ⇓ *Not react with EDTA*

2nd step: Titration of Mg^{2+} ≠ standard EDTA using EBT indicator without any interference of Cu^{2+}.

N.B. ***Role of Amm. buffer in this experiment:***

a) Consume the released protons from the reaction between metal and EDTA and so make the reaction go forward.

Metal + EDTA ⇌ (metal-EDTA) complex + $2H^+$

b) Keep pH constant and so keep the correct color of the indicator.

NEW c) Give blue color with Cu^{2+} and so complete masking of Cu^{2+} will be indicated by the disappearance of this blue color. *{that is the cause of adding amm. buffer **before** KCN}.*

b) Determination of Cu^{2+} only:

by titrating another 10 ml of the mixture ≠ standard EDTA using **PAN indicator & Acetate buffer** without interference of Mg^{2+}.

{PAN = **P**yridyl**a**zo**n**aphthol}

Color change: from **Pink** (complexed PAN) to **Yellowish Green** (free PAN).

N.B. PAN indicator allows selective titration of **Cu^{2+}** in presence of Ba^{2+}, Ca^{2+}, Mg^{2+} & Mn^{2+}.

Procedure :

A For Mg^{2+} only ($E.P_1$) :

1) Transfer 10 ml of the mixture into a clean conical flask.

2) Add 2 ml of amm. buffer. → *gives blue color.*

3) Add few drops of 10% KCN by a dropper till the blue color disappears. → *that means complete masking of Cu^{2+}.*

Warning: KCN is Very Very Toxic

4) Add few specks of EBT indicator.

5) Titrate ≠ 0.05 M EDTA.

{ Color change at E.P.: from **Wine Red** to **Pure Blue }**

Complexed EBT ind. *Free EBT ind.*

B For Cu^{2+} only ($E.P_2$) :

1) Transfer another 10 ml of the mixture into a clean conical flask.

2) Add 2 ml of acetate buffer.

3) Add 5 drops of PAN indicator.

4) Titrate ≠ 0.05 M EDTA.

{ Color change at E.P.: from **Pink** to **Yellowish Green }**

Complexed PAN ind. *Free PAN ind.*

Calculations :

$$E.P_1 \equiv Mg^{2+}$$

$$E.P_2 \equiv Cu^{2+}$$

For Mg^{2+}: $Mg^{2+} + \underset{EDTA}{H_2Y^{2-}} \leftrightarrow MgY^{2-} + 2H^+$

$\therefore$ 1 EDTA $\equiv$ $\underset{standard}{\underline{1}}$ $\underset{sample}{MgSO_4.7H_2O}$

Equivalence factor (F):

each ml of 0.05 M EDTA $\equiv \frac{\underline{1} \times \text{M.W. of } MgSO_4.7H_2O \times 0.05}{1000} \equiv ..g\ MgSO_4.7H_2O$

Concentration:

$$\text{Concn. of } MgSO_4.7H_2O = \frac{E.P_1 \times F \times 1000}{10} = \ldots\ldots\ g/L$$

For Cu^{2+}: $Cu^{2+} + \underset{EDTA}{H_2Y^{2-}} \leftrightarrow CuY^{2-} + 2H^+$

$\therefore$ 1 EDTA $\equiv$ $\underset{standard}{\underline{1}}$ $\underset{sample}{CuSO_4.5H_2O}$

Equivalence factor (F):

each ml of 0.05 M EDTA $\equiv \frac{\underline{1} \times \text{M.W. of } CuSO_4.5H_2O \times 0.05}{1000} \equiv ..g\ CuSO_4.5H_2O$

Concentration:

$$\text{Concn. of } CuSO_4.5H_2O = \frac{E.P_2 \times F \times 1000}{10} = \ldots\ldots\ g/L$$

Exp.(16): Complexometric determination of (Mg^{2+}/Hg^{2+}) mixture ($MgSO_4.7H_2O$ & $HgCl_2$)

Principle: *(direct titration)*

a) Determination of Mg^{2+} only (2 steps):

1st step: Masking of Hg^{2+} by KCN:

$Hg^{2+} + \underset{masking\ agent}{4\ CN^-} \longrightarrow \underset{very\ stable\ complex}{[Hg(CN)_4]^{2-}}$

$\Downarrow$

Not react with EDTA

2nd step: Titration of Mg^{2+} ≠ standard EDTA using EBT indicator & amm. buffer without any interference of Hg^{2+}.

b) Determination of Total (Mg^{2+} & Hg^{2+}):

by titrating another 10 ml of the mixture ≠ standard EDTA using EBT indicator & amm. buffer.

Procedure :

A For Mg^{2+} only ($E.P_1$) :

1) Transfer 10 ml of the mixture into a clean conical flask.

2) Add 10 drops of 10% KCN by a dropper.

Warning: KCN is Very Very Toxic

3) Add 2 ml of amm. buffer.

4) Add few specks of EBT indicator.

5) Titrate ≠ 0.05 M EDTA.

{ Color change at E.P.: from **Wine Red** to **Pure Blue** }

Complexed EBT ind. *Free EBT ind.*

B For Total (Mg^{2+} & Hg^{2+}) ($E.P_2$) :

1) Transfer another 10 ml of the mixture into a clean conical flask.

2) Add 2 ml of amm. buffer.

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3) Add few specks of EBT indicator.

4) Titrate ≠ 0.05 M EDTA.

{ Color change at E.P.: from **Wine Red** to **Pure Blue** }

Complexed EBT ind. *Free EBT ind.*

Calculations :

$$E.P_1 \equiv Mg^{2+}$$

$$E.P_2 \equiv Mg^{2+} + Hg^{2+}$$

$$\therefore (E.P_2 - E.P_1) \equiv Hg^{2+}$$

For Mg^{2+} :

$$Mg^{2+} + \underset{\substack{EDTA \\ (standard)}}{H_2Y^{2-}} \leftrightarrow MgY^{2-} + 2H^+$$

$$\therefore 1\ EDTA \equiv \underset{standard}{1}\ \underset{sample}{MgSO_4.7H_2O}$$

Equivalence factor (F):

$$\text{each ml of 0.05 M EDTA} \equiv \frac{1 \times \text{M.W. of } MgSO_4.7H_2O \times 0.05}{1000} \equiv ..g\ MgSO_4.7H_2O$$

Concentration:

$$\text{Concn. of } MgSO_4.7H_2O = \frac{E.P_1 \times F \times 1000}{10} = \ldots\ldots\ g/L$$

For Hg^{2+} :

$$Hg^{2+} + \underset{\substack{EDTA \\ (standard)}}{H_2Y^{2-}} \leftrightarrow HgY^{2-} + 2H^+$$

$$\therefore 1\ EDTA \equiv \underset{standard}{1}\ \underset{sample}{HgCl_2}$$

Equivalence factor (F):

$$\text{each ml of 0.05 M EDTA} \equiv \frac{1 \times \text{M.W. of } HgCl_2 \times 0.05}{1000} \equiv ..g\ HgCl_2$$

Concentration:

$$\text{Concn. of } HgCl_2 = \frac{(E.P_2 - E.P_1) \times F \times 1000}{10} = \ldots\ldots\ g/L$$

Summary

(The use of masking and demasking in the determination of mixtures)

How to use masking in the determination of a mixture of X & Y?

⇓

1 **1st**: 10 ml sample → masking of X → and then detn. of Y …… *($E.P_y$).*

2nd: another 10 ml sample → detn. of total X & Y …… *($E.P_{total}$).*

$\therefore E.P_x = E.P_{total} - E.P_y$

{ ex: Hg^{2+}/Mg^{2+} mixture}
X Y

OR

2 **1st**: 10 ml sample → masking of X → and then detn. of Y …… *($E.P_y$).*

2nd: another 10 ml sample → detn. of X only by using a selective indicator for X in presence of Y …… *($E.P_x$).*

{ ex: Cu^{2+}/Mg^{2+} mixture}
X Y

OR

3 10 ml sample → masking of X → and then detn. of Y …… *($E.P_y$)*

And then on the same solution, make demasking of X and titrate it on the same solution …… *($E.P_X$).*

{ ex: Refer to determination of (Mg^{2+}, Zn^{2+} & Cu^{2+}) mixture منهج النظري }

THE END

***** *Best wishes* *****