

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 ($\text{Ca}^{2+}/\text{Mg}^{2+}$) mixture ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ & $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)

Principle : (*direct titration*)

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

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

$$\text{E.P}_1 \equiv \text{Ca}^{2+} \text{ only.}$$

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

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

$$\text{E.P}_2 \equiv \text{Total } (\text{Ca}^{2+} \text{ \& } \text{Mg}^{2+}).$$

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 $\text{Mg}(\text{OH})_2 \downarrow$ 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 \neq 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:

\Rightarrow 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.

\Rightarrow During titration, the following reactions occur:

1) $\text{EDTA} + \text{free } \text{Ca}^{2+} \leftrightarrow (\text{Ca-EDTA}) \text{ complex.}$

2) $\text{EDTA} + \text{free } \text{Mg}^{2+} \leftrightarrow (\text{Mg-EDTA}) \text{ complex.}$

 3) $\text{EDTA} + (\text{Mg-EBT}) \leftrightarrow (\text{Mg-EDTA}) + \text{free EBT.}$
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.P₁) : ($\equiv \text{Ca}^{2+}$ 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 \neq 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.P₂) : ($\equiv \text{Ca}^{2+} + \text{Mg}^{2+}$)

- 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 \neq 0.05 M EDTA.

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

Complexed
EBT ind.

Free
EBT ind.

Calculations :

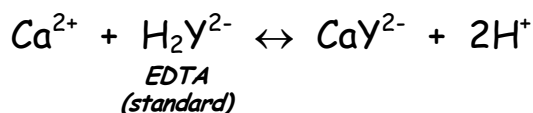


$$E.P_1 \{murexide \text{ reading}\} \equiv Ca^{2+}$$

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

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

For Ca^{2+} :



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

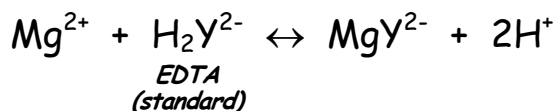
Equivalence factor (F):

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

Concentration:

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

For Mg^{2+} :



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

Equivalence factor (F):

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

Concentration:

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

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.



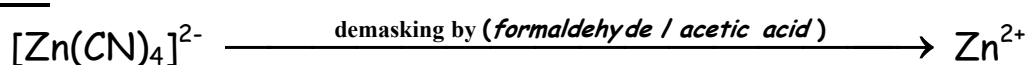
Examples: (CN^-) ion is an effective masking agent that can form stable cyanide complex with some cations as Cu^{2+} , Cd^{2+} , Hg^{2+} & Zn^{2+} making them unable to react with EDTA or with indicators SO other cations as Mg^{2+} , Mn^{2+} & Ca^{2+} can be determined without interference of the above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

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

- **Definition of demasking:**

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

Examples:



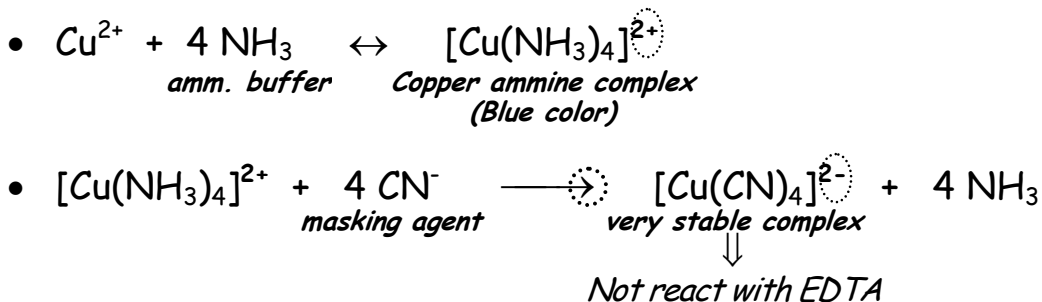
- The use of masking agents can be illustrated in the following experiments.

Exp.(15): Complexometric determination of ($\text{Mg}^{2+}/\text{Cu}^{2+}$) mixture ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ & $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

Principle : (direct titration)

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

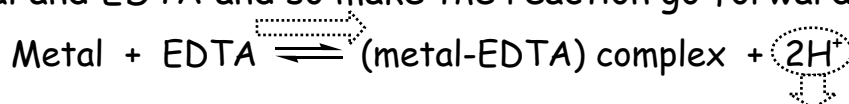
1st step: Masking of Cu^{2+} by KCN as follows:



2nd step: Titration of Mg^{2+} \neq 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.



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 \neq standard EDTA using **PAN indicator & Acetate buffer** without interference of Mg^{2+} .

{PAN = Pyriddylazonaphthol}

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.P₁) :

- 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 \approx 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.P₂) :

- 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 \approx 0.05 M EDTA.

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

Complexed
PAN ind.

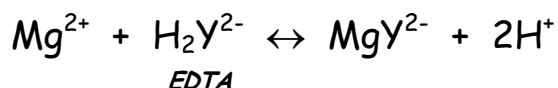
Free
PAN ind.

Calculations :

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

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

For Mg^{2+} :



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

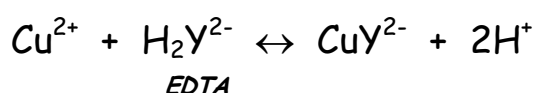
Equivalence factor (F):

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

Concentration:

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

For Cu^{2+} :



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

Equivalence factor (F):

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

Concentration:

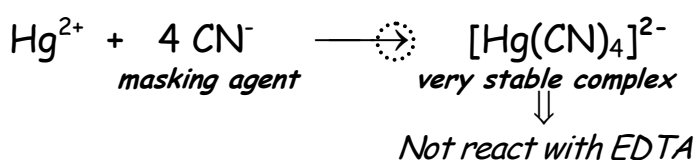
$$\text{Concn. of } CuSO_4 \cdot 5H_2O = \frac{E.P_2 \times F \times 1000}{10} = \dots\dots\dots g/L$$

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

Principle : (direct titration)

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

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



2nd step: Titration of Mg^{2+} \neq 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 \neq standard EDTA using EBT indicator & amm. buffer.

Procedure :

A For Mg^{2+} only (E.P₁) :

- 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 \approx 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.P₂) :

- 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 \approx 0.05 M EDTA.

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

Complexed
EBT ind.

Free
EBT ind.

Calculations :

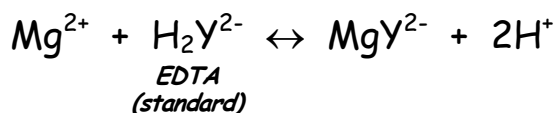


$$E.P_1 \equiv Mg^{2+}$$

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

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

For Mg^{2+} :



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

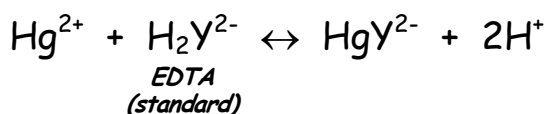
Equivalence factor (F):

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

Concentration:

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

For Hg^{2+} :



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

Equivalence factor (F):

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

Concentration:

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

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 *****