********** 3^RD^ SECTION (PART II) **********

Examples of Complexometric titrations

Introduction :

General Principles for Complexometric Titrations:

- The complex is formed between **Metal & EDTA** or between **Metal & Indicator** {Not between EDTA & Indicator because both of them are electron- donors (ligands)}.
- **(Metal-EDTA)** complex must be **more stable** than **(Metal-Indicator)** complex.
- The **change in color** at the end point is due to change of:

  [complexed ind. *into* free ind.]……………………………………………in **direct** titration

  OR

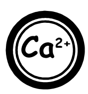
  [free ind. *into* complexed ind.]……………………………………………in **back** titration.

Sketch Diagrams for

Direct Complexometric Titrations ≠ EDTA

These symbols will be used in the following diagrams:

= Magnesium ion.



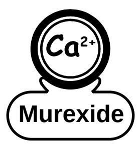
= Calcium ion.

= Disodium salt of ethylenediaminetetraacetic acid.

= Free EBT indicator.

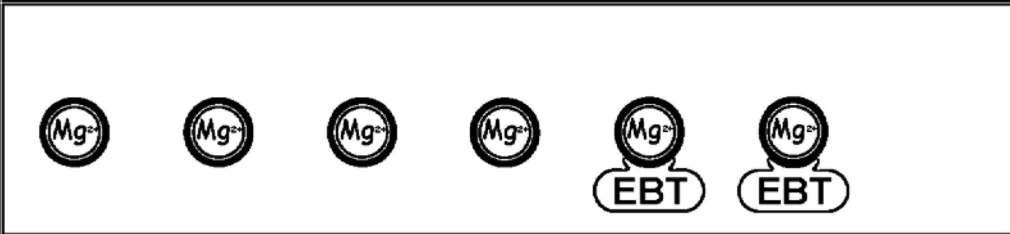
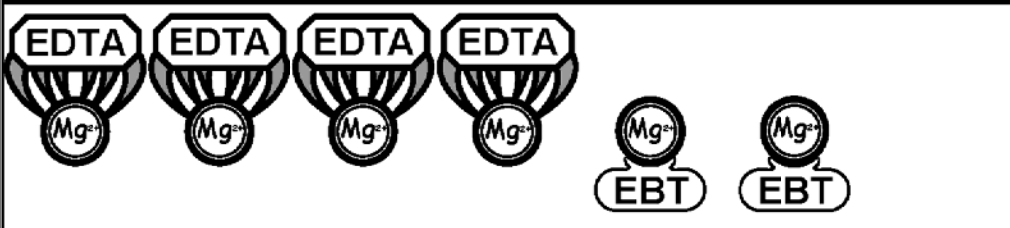
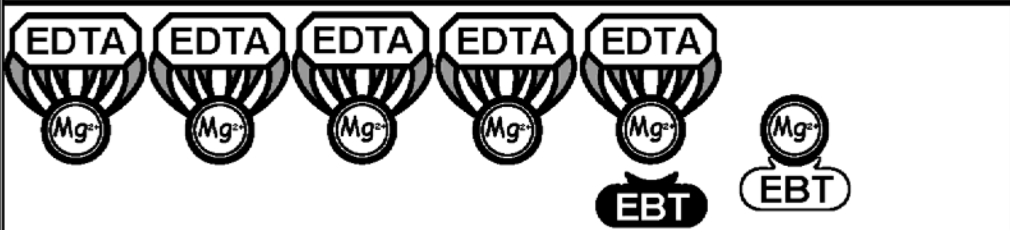
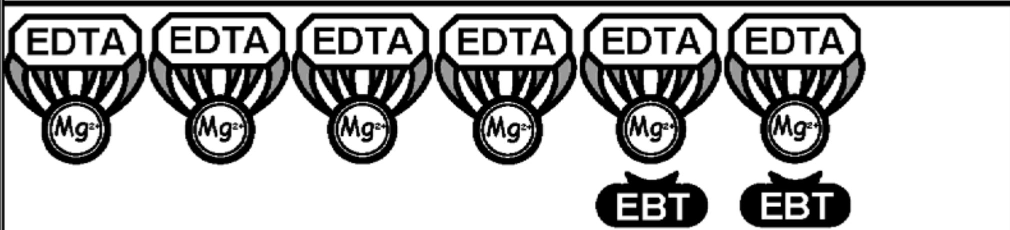
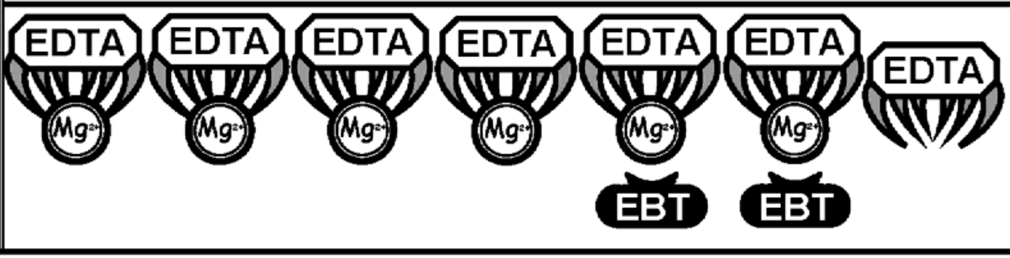
= Free Murexide indicator.

= Complexed EBT indicator.

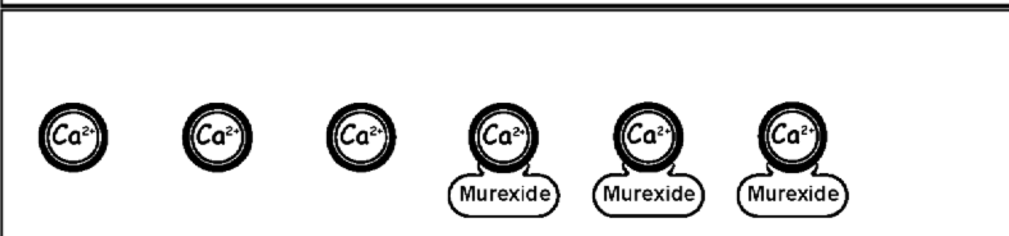
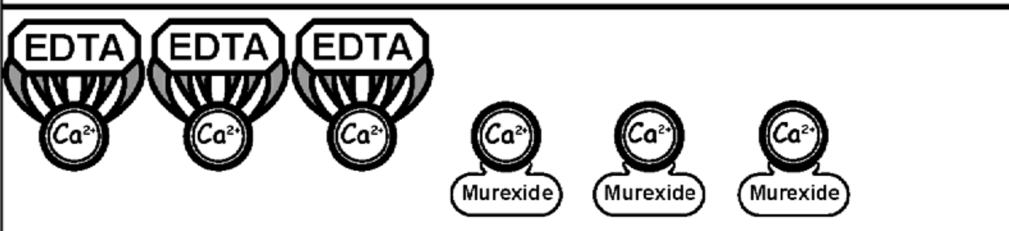
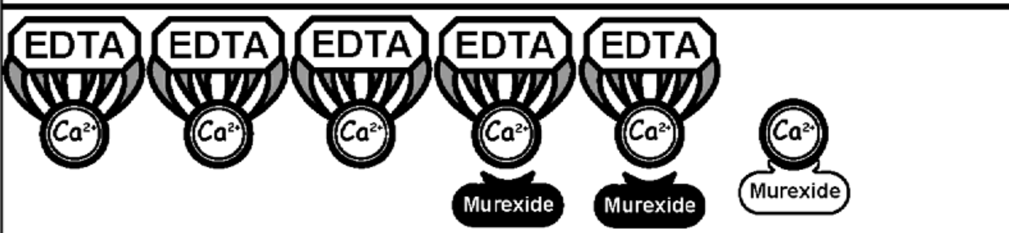
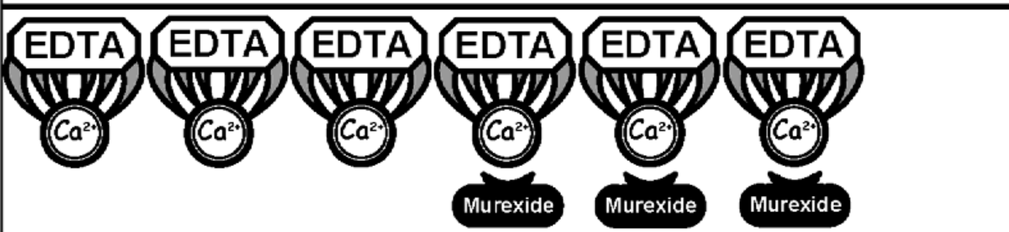
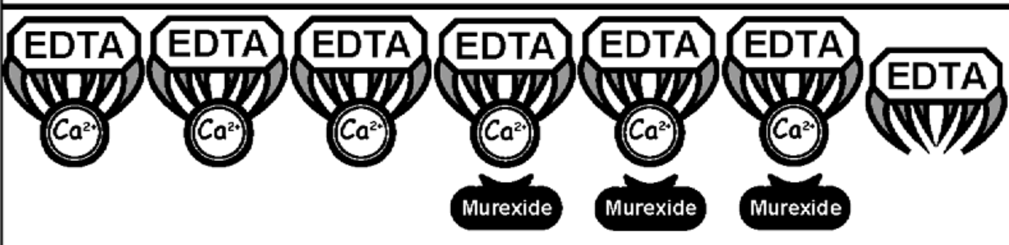


= Complexed Murexide ind.

Sketch diagram for direct titration of $Mg^{2+} \neq$ EDTA using EBT indicator

Stage of Titration	Representative Diagram	Indicator State	Color	Equation
1 Before starting the titration		Complexed	Wine Red	$Mg^{2+} + \underset{(EBT)}{HIn^{2-}} \leftrightarrow MgIn^{-} + H^{+}$
2 During the titration		Complexed	Still Wine Red	$Mg^{2+} + \underset{(EDTA)}{H_2Y^{2-}} \leftrightarrow MgY^{2-} + 2H^{+}$
3 Just before the end point		Complexed + Free	Wine Red + Blue	$MgIn^{-} + H_2Y^{2-} \leftrightarrow MgY^{2-} + H^{+} + HIn^{2-}$
4 At the end point		Free	Blue	*Mg-EDTA complex is more stable than Mg-EBT complex*
5 After the end point		Free	Still Blue	No more reactions after the end point

Sketch diagram for direct titration of $Ca^{2+} \neq$ EDTA using Murexide indicator

Stage of Titration	Representative Diagram	Indicator State	Color	Equation
1 Before starting the titration		Complexed	**Rose Red**	$Ca^{2+} + \underset{\text{(Murexide)}}{H_2In^{3-}} \leftrightarrow CaH_2In^{-}$
2 During the titration		Complexed	**Still Rose Red**	$Ca^{2+} + \underset{\text{(EDTA)}}{H_2Y^{2-}} \leftrightarrow CaY^{2-} + 2H^{+}$
3 Just before the end point		Complexed + Free	**Rose Red + Bluish Violet**	$CaH_2In^{-} + H_2Y^{2-} \leftrightarrow CaY^{2-} + 2H^{+} + H_2In^{3-}$
4 At the end point		Free	**Bluish Violet**	*Ca-EDTA complex is more stable than Ca-murexide complex*
5 After the end point		Free	**Still Bluish Violet**	No more reactions after the end point

Exp.(9): Complexometric Determination of $MgSO_4.7H_2O$

Principle :

Direct titration of Mg^{2+} with standard EDTA at pH = 10 (amm. buffer) using EBT indicator.

Equations: *(Please, Refer to previous sketch diagrams)*

Before starting titration:

$$\underset{\text{sample}}{Mg^{2+}} + \underset{\text{EBT ind.}}{HIn^{2-}} \leftrightarrow \underset{\substack{\text{complexed EBT}\\\text{(wine red)}}}{MgIn^{-}} + H^{+}$$

During titration ≠ EDTA:

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

Just before & at the E.P.:

$$MgIn^{-} + H_2Y^{2-} \leftrightarrow MgY^{2-} + H^{+} + \underset{\substack{\text{Free EBT}\\\text{(blue)}}}{HIn^{2-}}$$

(This reaction occurs because Mg-EDTA complex is more stable than Mg-EBT complex)

Procedure :

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

2) Add 2 ml of Amm. buffer.

3) Add few specks (مقدار ضئيل) of EBT indicator.

4) Titrate ≠ 0.01 M EDTA.

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

Wine Red → Complexed EBT ind.

Pure Blue → Free EBT ind.

Calculations :

(Refer to Calculations for Titrations in the 1^{st} term course, p. 1-10)

Calculations in complexometric titrations differ from that in other types of titration in the calculation of equivalence factor where (**b**) in complexometric titrations is **Absent** because we always use **Molar** concentrations in complexometric titrations.

Equivalence factor (F):

$$\underset{sample}{Mg^{2+}} + \underset{standard}{H_2Y^{2-}} \leftrightarrow MgY^{2-} + 2H^+$$

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

$$\text{each ml of 0.01 M EDTA} \equiv \frac{\underline{1} \times M.W.\ of\ MgSO_4.7H_2O \times 0.01}{1000} \equiv ..g\ MgSO_4.7H_2O$$

. . . .

Concentration:

$$Concn. = \frac{E.P. \times F \times 1000}{10} = ...\ g/L$$

Exp.(10): Complexometric Determination of $ZnSO_4.7H_2O$

The same Principle, Procedure and Calculations as $MgSO_4.7H_2O$ but

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

Exp.(11): Complexometric Determination of $CaCl_2.6H_2O$

Principle :

Direct titration of Ca^{2+} with standard EDTA at pH = 12 (8% NaOH) using murexide indicator.

Equations: *(Please, Refer to previous sketch diagrams)*

Before starting titration:

$$\underset{sample}{Ca^{2+}} + \underset{\text{murexide ind.}}{H_2In^{3-}} \leftrightarrow \underset{\text{complexed murexide (rose red)}}{CaH_2In^-}$$

During titration ≠ EDTA:

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

Just before & at the E.P.:

$$CaH_2In^- + H_2Y^{2-} \leftrightarrow CaY^{2-} + 2H^+ + \underset{\text{Free murexide (bluish violet)}}{H_2In^{3-}}$$

(This reaction occurs because Ca-EDTA complex is more stable than Ca-murexide complex)

Procedure :

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

2) Add 2 ml of 8% NaOH.

. . . . ✍

. . . .

3) Add few specks of murexide indicator.

4) Titrate ≠ 0.01 M EDTA.

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

Complexed murexide ind. — *Free murexide ind.*

Calculations :

<u>Equivalence factor (F)</u>:

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

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

$$\text{each ml of 0.01 M EDTA} \equiv \frac{\underline{1} \times \text{M.W. of } CaCl_2.6H_2O \times 0.01}{1000} \equiv ..g\ CaCl_2.6H_2O$$

. . . . ✍

<u>Concentration:</u>

$$\text{Concn.} = \frac{\text{E.P.} \times F \times 1000}{10} = \text{.........}\ \ g/L$$

Exp.(12): Complexometric Determination of $AgNO_3$

Principle : *(classified under miscellaneous methods)*

- Ag^+ ion can not be directly titrated against EDTA because Ag^+ can not form stable complex with EDTA *(because Ag^+ is a univalent metal).*
- The determination depends on an Exchange Reaction between:

  Tetracyanonickelate (II) ion $[Ni(CN)_4]^{2-}$ **&** Ag^+

  where Ni^{2+} is liberated & then titrated against EDTA using murexide indicator and amm. buffer (pH = 10). **{حالة خاصة}**

Equations:

$$\underset{\textbf{sample}}{2\,Ag^{2+}} + [Ni(CN)_4]^{2-} \leftrightarrow 2\,[Ag(CN)_2]^{-} + Ni^{2+}$$

then the liberated Ni^{2+} is titrated $\neq$ standard EDTA where:

$$1\,Ni^{2+} \equiv 1\,EDTA$$

- *The color change at E.P. from* ***Yellow*** *to* ***Violet***.

Color of (Ni-murexide) complex at pH = 10.	Color of free murexide at pH = 10 (H_3In^{2-}).

- This method is classified under (miscellaneous methods).
- **N.B.**

  8% NaOH (pH = 12) can not be used in this method due to the precipitation of $Ni(OH)_2\downarrow$ at this pH.

Procedure :

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

2) Add 10 ml of $[Ni(CN)_4]^{2-}$ by a **Burette**.

Warning: $[Ni(CN)_4]^{2-}$ is Very Toxic

3) Add 2 ml of amm. buffer.

4) Add few specks of murexide indicator.

5) Titrate ≠ 0.01 M EDTA.

{ **Color change at E.P.**: from **Yellow** to **Violet** }

Yellow: Complexed murexide ind.
Violet: Free murexide ind.

Calculations:

Equivalence factor (F):

From the above equations:

$$\therefore \underset{\textit{standard}}{1\ EDTA} \equiv 1\ Ni^{2+} \equiv \underset{\textit{sample}}{\underline{\underline{2}}\ AgNO_3}$$

$$\text{each ml of 0.01 M EDTA} \equiv \frac{\underline{\underline{2}} \times \text{M.W. of } AgNO_3 \times 0.01}{1000} \equiv \text{..........g } AgNO_3$$

. . . .

Concentration:

$$\text{Concn.} = \frac{\text{E.P.} \times F \times 1000}{10} = \text{.........} \ g/L$$

Exp.(13): Complexometric Determination of Potash alum $\{KAl(SO_4).12H_2O\}$

Principle: *(back titration)*

Al^{3+} salts can not be directly titrated ≠ EDTA because (Al-EDTA) complex is formed **slowly** so Al^{3+} salts are best determined by **back** titration.

Equation:

$$\underset{\text{sample}}{Al^{3+}} + \underset{\text{known excess of st. EDTA}}{H_2Y^{2-}} \leftrightarrow \underset{\text{(Al-EDTA) complex}}{AlY^{-}} + 2H^{+}$$

*then the remaining unreacted EDTA is back titrated ≠ standard **$MgSO_4$** using EBT indicator & amm. buffer.*

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

Blue: *Free EBT ind.* ; Wine Red: *Complexed EBT ind.*

Procedure:

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

2) Add 25 ml of 0.05 M EDTA.

3) Add 2 ml of amm. buffer.

4) Add few specks of EBT indicator.

5) Titrate ≠ 0.05 M $MgSO_4$.

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

Blue: *Free EBT ind.* ; Wine Red: *Complexed EBT ind.*

Calculations:

Equivalence factor (F):

$$\therefore \underset{\text{standard}}{1\ EDTA} \equiv \underset{\text{sample}}{1\ Al^{3+}}$$

$$\text{each ml of 0.05 M EDTA} \equiv \frac{1 \times M.W. \text{ of } KAl(SO_4).12H_2O \times 0.05}{1000} \equiv \ldots\ldots\ldots\text{g } KAl(SO_4).12H_2O$$

Concentration:

$$\text{Concn.} = \frac{(25 - E.P.) \times F \times 1000}{10} = \ldots\ldots\ldots \text{ g/L}$$

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