# Complex-formation titration

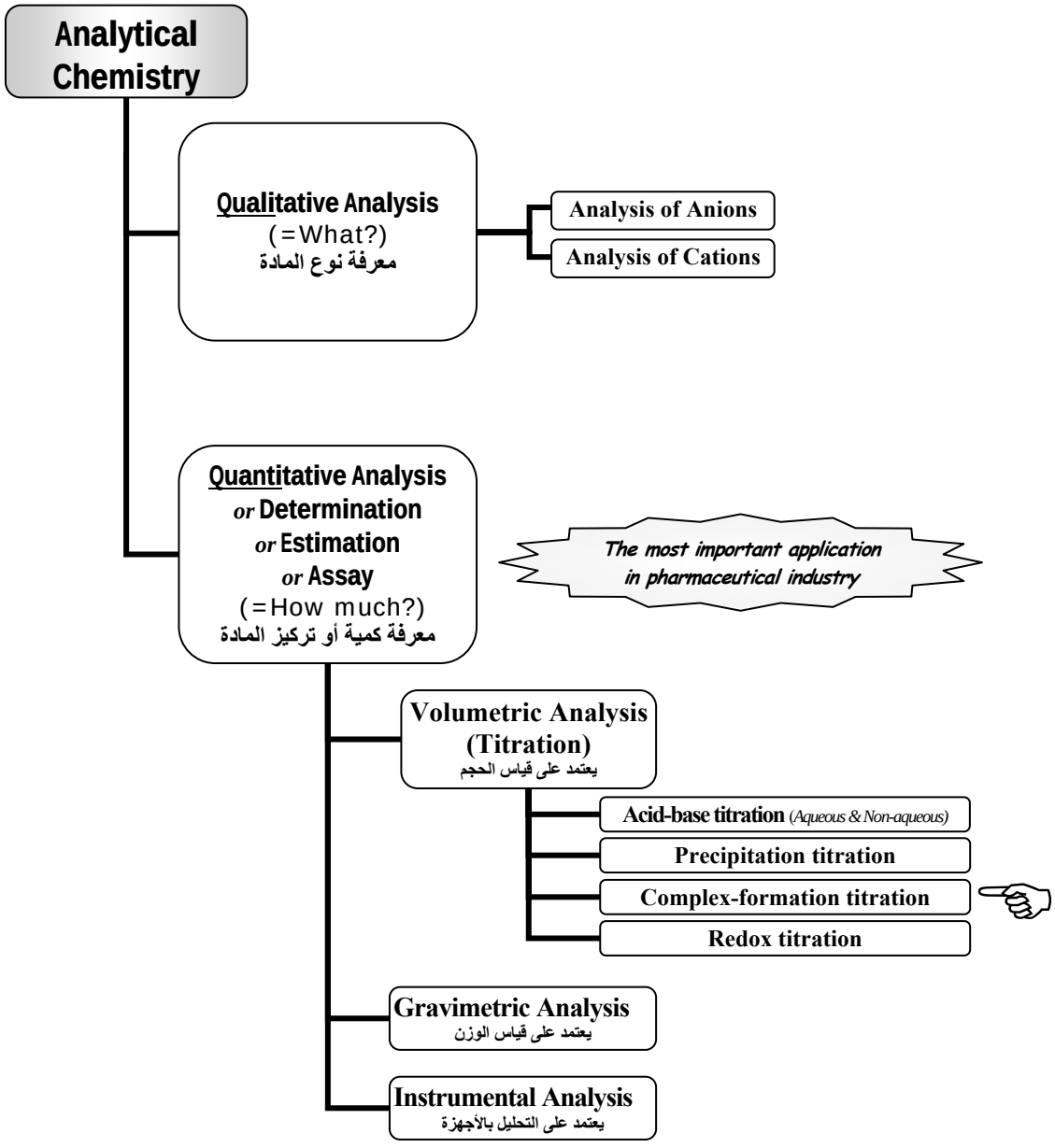
# (= Complexometric titration).

## Definition of Complex-formation titration :

It is a type of titrations that depends on the formation of soluble complexes.

⇒ ***Remember:***

## Classification of Analytical Chemistry



## Introduction :

- **Complex** = Coordination compound.
- **Complex** consists of an electron donor bonded to an electron acceptor by a coordination bond.

Donor —coordination bond→ Acceptor

(= Ligand)
(= Complexing agent)
⇓
can donate lone pair of electrons such as N̈, Ö & S̈.

(= Metal)
⇓
can accept lone pair of electrons in its vacant orbitals □ □ □.

- **Example of Complexes**:

Silver ammine complex " $[Ag(NH_3)_2]^+$ " where **$NH_3$** is the donor (ligand) while **$Ag^+$** is the acceptor (metal).

$$[H_3N: \rightarrow Ag^+ \leftarrow :NH_3]$$

# EDTA Titrations

- It is the most common type of complex-formation titrations.
- The main complexing agent (= ligand = donor) in these titrations is EDTA.
- **Basic components in any EDTA titration:**

  **1) Metal** (acceptor) ⇒ *sample* .

  **2) EDTA** (donor) ⇒ *the main complexing agent.*

  **3) Indicator** (donor).

  **4) Buffer** (to adjust pH of the medium).

## 1 Metal :

A very large number of metals can be determined complexometrically such as $Mg^{2+}$, $Ca^{2+}$, $Zn^{2+}$, $Al^{3+}$……etc.

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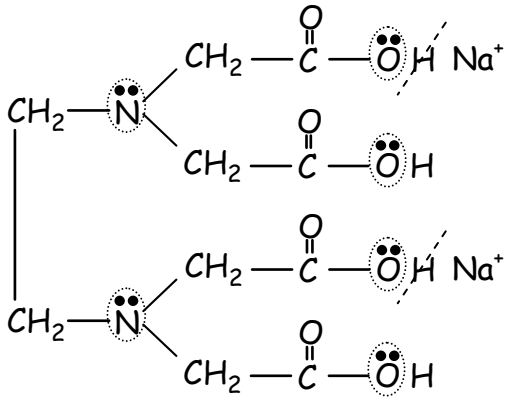
## 2 EDTA :

**{ EDTA** = Ethylenediaminetetraacetic acid **}**

It is used as **disodium salt**
because the parent acid is insoluble in water while the disodium salt is soluble.



- **EDTA** is a **hexadentate** ligand [ i.e. it can bind to metal ion with 6 coordination bonds because it contains 6 ligand (donor) atoms as shown in the structure].

  N.B. Generally, multidentate ligands (i.e. bi-, tri-, hexa- …… etc) are called "**Chelating agents**".

- **EDTA** can form stable **1:1** complex with many divalent (ثنائي التكافؤ), trivalent and tetravalent metal ions (i.e. 1 mole of EDTA ≡ 1 mole of metal ion) so EDTA is always prepared as **Molar** solutions.

- The parent acid of **EDTA** is represented as $H_4Y$ while its disodium salt is represented as $H_2Y^{2-}$.

## 3 Indicator :

- The indicators used in complexometric titrations are **metal-sensitive** indicators so these indicators are called "**Metal indicators**".
- The color of the free indicator must differs from the color of the [metal-indicator] complex.

. . . . . .

- Also, these indicators are **pH-sensitive** indicators BUT during titration, we adjust pH by using a suitable buffer and so the indicators will be affected by the metal only.
- **Examples of metal indicators:**

| **1 EBT indicator (Eriochrome Black T)** | **2 Murexide indicator** |
|---|---|
| • It is a salt of an acid.<br>• Its parent acid is represented as ($H_3In$)<br>• EBT ind. is represented as follows:<br>$H_2In^-$ ⇌ **$HIn^{2-}$** ⇌ $In^{3-}$<br>(pH < 7) **(pH 7-11)** (pH > 11)<br>Red **Blue** orange | • It is a salt of an acid.<br>• Its parent acid is represented as ($H_5In$)<br>• Murexide is represented as follows:<br>$H_4In^-$ ⇌ $H_3In^{2-}$ ⇌ **$H_2In^{3-}$**<br>(pH < 9) (pH 9-11) **(pH>11)**<br>Reddish Violet Violet **Bluish Violet** |
| • EBT is used at pH 10 (adjusted by Ammonia Buffer) so the color of the free EBT will be Blue. | • Murexide is most commonly used at pH 12 (adjusted by 8% NaOH) so the color of free murexide will be Bluish Violet.<br>Also, murexide is sometimes used at pH 10 (amm. buffer) where the color of free murexide is Violet. |
| • The color of [metal-EBT] complex is usually Wine-red color. | • The color of [metal-murexide] complex differs according to the metal & pH. |
| • Ex. of metals determined using EBT:<br>$Mg^{2+}$, $Zn^{2+}$, $Hg^{2+}$ | • Ex. of metals determined using murexide:<br>$Ca^{2+}$ *(at pH 12)* & $Ni^{2+}$ *(at pH 10)*. |

***Question: (Choose the correct answer)***

*EBT and murexide are (metal sensitive - pH sensitive - both)*

## 4 Buffer:

- **Role of buffer in complexometric titrations:**

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

$$\text{Metal} + \text{EDTA} \rightleftharpoons \text{(metal-EDTA) complex} + 2H^+$$

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

- **Examples of buffers used:**

1) Ammonia buffer (pH = 10).

2) 8% NaOH (pH = 12).

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# Methods of EDTA titrations

**1. Direct titrations:**

Direct titration of **metal sample** ≠ standard EDTA.

**2. Back (Residual) titrations:**

**Metal sample** + known excess of standard EDTA

↓

Back titration of the remaining unreacted EDTA ≠ standard metal soln.

**3. Replacement (Substitution) titrations:**

**Metal sample** + (Mg-EDTA) soln. → (metal-EDTA) + equivalent amount of $Mg^{2+}$

↓

Titr. ≠ standard EDTA.

**4. Alkalimetric titrations:**

**Metal sample** + EDTA soln. ⇌ (metal-EDTA) complex + $2H^{\pm}$

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Titr. ≠ standard NaOH

**5. Miscellaneous methods:** طرق متنوعة

Ex.: Determination of $Ag^+$ sample.

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*****>> *Best wishes* >>*****