



Complexometric Titration II

Lecture four 2024-2025

Indicators

- **Indicator** is a dye which is capable of acting as a chelating agent to give a dye-metal complex.
- The latter is different in colour from the dye itself and also **has a low stability constant than the chelate-metal complex**.
- The colour of the solution, therefore, remains that of the dye complex until the end point, when an equivalent amount of sodium EDTA has been added.
- As soon as there is the slightest excess of EDTA, the **metal-dye** complex decomposes to produce free dye; this is accomplished by a change in colour.

❖ Metal indicators must comply with the following requirements:

- Metal-indicator complex **must be less stable than the metal-EDTA complex**, ie. the metal-indicator complex **should be 10 to 100 times less stable** than the metal-titrant complex.
- Binding between metal and indicator **must not be too weak**. It has to avoid EDTA replacing at the beginning of the titration.
- Colour of the indicator and the metal complexed indicator **must be sufficiently different**.

$\text{Zn-Ind.}^- + \text{H}_2\text{Y}^{2-} \longrightarrow \text{ZnY}^{2-} + \text{H Ind.}^{2-} + \text{H}^+$ (during titration)
wine red Blue

EDTA Titration Techniques

Back Titration (indirect)

- It can be performed for the determination of several metal ions which can not be titrated directly but form stable EDTA complexes.

The procedure, a known amount of EDTA is added to the analyte sample solution and the excess is back titrated with a standard solution of "weak" metal ion, Mg^{2+} .

The weak metal ion will not displace the analyte from its EDTA complex.

It is used in the following cases: (when can be used?)

- Insoluble substances e.g. $BaSO_4$, CaC_2O_4 , $PbSO_4$, $Mg_3(PO_4)_2$... etc. Usually soluble in hot EDTA.
- The reaction between M^{n+} & EDTA is slow (incomplete) e.g. Fe^{3+} , Al^{3+} , Cr^{3+} , Th^{4+} , ... etc.
- The M^{n+} is pptd. at the pH suitable for titration e.g. $Al(OH)_3$.

EDTA Titration Techniques

Displacement Titration (what is the conditions??)

- A. The technique **only works** when the unknown metal has tighter binding to EDTA than the Zn^{2+} or Mg^{2+} .
 - B. Metal ions with no satisfactory indicator.
- MgY^{2-} or ZnY^{2-} complex is added to the solution of unknown metal ion composition.
 - The unknown metal displaces the Mg^{2+} or Zn^{2+} , which is then back titrated.



$$K_f' \text{ for } MY^{n-2} > K_f' \text{ for } MgY^{n-2}$$

K_f' is constant of complex formation

Titration of Mixtures

- EDTA is not a selective reagent (it chelates with most metal ions)
- Selectivity of *EDTA* can be increased by one of the following procedures:
 - a) Control of pH of the medium
 - b) Adjustment of oxidation number of metal ion
 - c) Masking and demasking agent

a) Control of pH of the medium

- **First group:** Trivalent & tetravalent cations e.g. (Bi^{3+} , Fe^{3+} , Th^{4+}) and Hg^{2+} titrated (form stable complex) at pH 1-3 using conc. HNO_3 .
- **Second group:** Divalent metals e.g. (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , pb^{2+} and Cd^{2+}) titrated (form stable complex) at pH 4-6 using acetate buffer.
- **Third group:** Alkaline earth metal e.g. (Ba^{2+} , Sr^{2+} , Ca^{2+}) and Mg^{2+} titrated (form stable complex) at pH=10 using ammonia buffer or 8% NaOH .
- From the mentioned above, we can titrate M^{n+} of the first group at pH 1-3 without interference of the second and third groups or at pH 4-6 we can titrate M^{n+} of the second group without interference of the third group.
- e.g. Mixture of Bi^{3+} & pb^{2+} : First titrating Bi^{3+} at pH = 2 using xylenol orange as ind., then increased pH to 5 by adding hexamine and titrating pb^{2+} .

b) Adjustment of oxidation number of metal ion

➤ This solves the interference between M^{n+} of the same group of pH.

➤ Examples:

❖ Ascorbic acid (vit. C) is reducing agent used in:

- Removal of interference of Fe^{3+} in first group (pH 1-3) → reduced to Fe^{2+}
- Removal of interference of Hg^{2+} in first group (pH 1-3) → reduced to Hg^0 (pptd.).
- Removal of interference of Cu^{2+} in second group (pH 4-6) → reduced to cuprous Cu^{1+} .

❖ Oxidation of Cr^{3+} $\xrightarrow[H_2O_2]{\text{alkaline}}$ to CrO_4^{2-}

➤ Fe^{2+} , Hg^0 , Cu^{1+} , CrO_4^{2-} do not react with EDTA

c) Masking and demasking agent

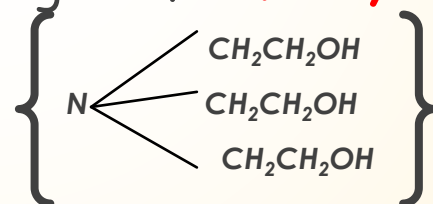
- **Masking agents:** Protect some component of analyte from reacting with EDTA. These reagents form complexes with interfering ions which are more stable than complexes formed with ind. & EDTA.

- Examples of masking agent: (give examples of masking agent)

KCN: It is used as masking agent for Ag^+ , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , ... etc.



Triethanolamine: It is used as masking agent for Fe^{3+} , Al^{3+} and Sn^{2+}

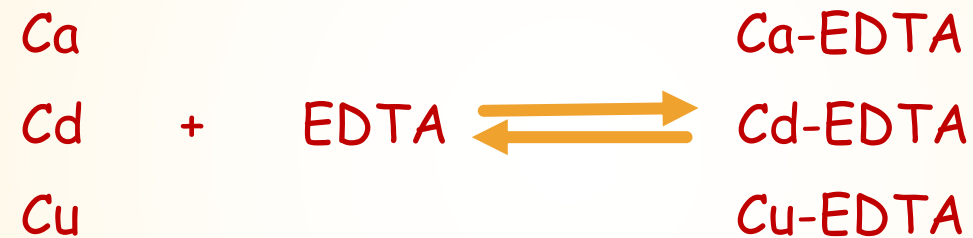


Fluoride (e.g. NH_4F): It is used as masking agent for Fe^{3+} and Al^{3+} to give $[\text{FeF}_6]^{3-}$ and $[\text{AlF}_6]^{3-}$

Iodide (KI): It is used as masking agent for Hg^{2+} to give tetraiodo complex (HgI_4)

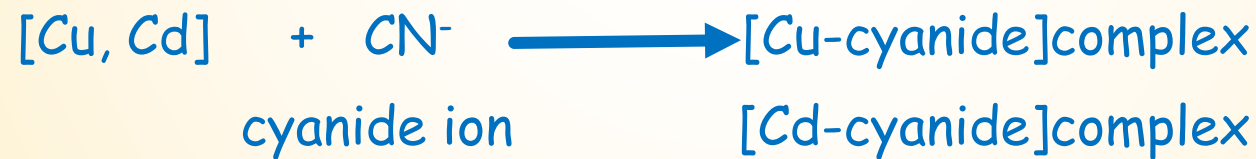
- **Demasking agent** : Releasing masking agent from analyte.
- Example of using masking and demasking agents in complexometry is the analysis of 3 metals, Cu, Cd and Ca. the following method of analysis is followed

Step 1: All metals are titrated



How can we determine a mixture of metals using complexometric titration?

Step 2: Only Ca titrated



➤ Step 3: Cd and Cu are titrated

➤ $[\text{Cd-cyanide}]_{\text{complex}} + \text{HCHO} \rightleftharpoons \text{Cd}^{2+} (\text{free})$

➤ $[\text{Cu-cyanide}]_{\text{complex}} + \text{HCHO} \longrightarrow \text{no reaction}$



Oxidation with H_2O_2 releases Cu^{2+} from $[\text{Cu}^+ \text{-Thiourea}]$ complex.