Faculty of science

Complexometric Titrations

3rd Year Students, General- Science

Course Code: 317 Chem.

Lecture# 7

Date: March 29, 2020

Classification of Quantitative Analysis

- Quantitative analysis
  - Volumetric
    - Acid base Titration ✓
    - Oxidation Reduction ✓
    - Complexometric
    - Precipitation Titration
  - Gravimetric

Analytical Problem

You are an analyst at a company for water purification, and you need to estimate the water hardness (Ca^{2+} & Mg^{2+} amount).

Your job: Plan and design the chemical analysis approach to perform this task.

Type of hardness	limit
Soft water	60-120 mg/L
Hard water	120–180 mg/L
very hard	> 180 mg/L

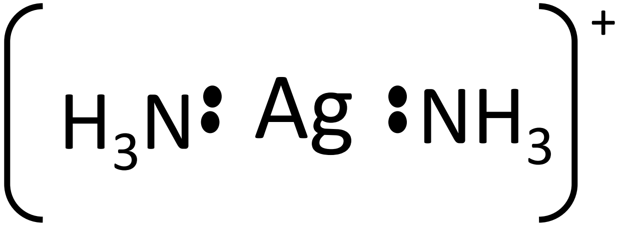
Complex (Coordination Compound)

Compound results from the combination of metal ion as (acceptor) with donor molecules (ligand) through coordinated bonds (**donor→ acceptor**)

Metal ion + Ligand→ Coordination compound (complex)

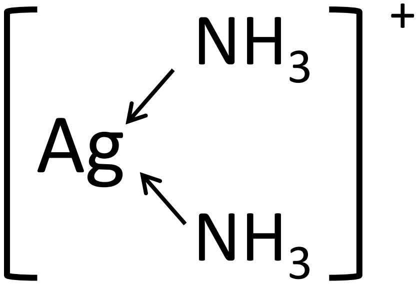
(Lewis acid) (Lewis base)

$M^{n+} + L = (L \longrightarrow M)$



Examples: $[Ag(NH_3)_2]^+$

$[Fe(SCN)_6]^{3-}$



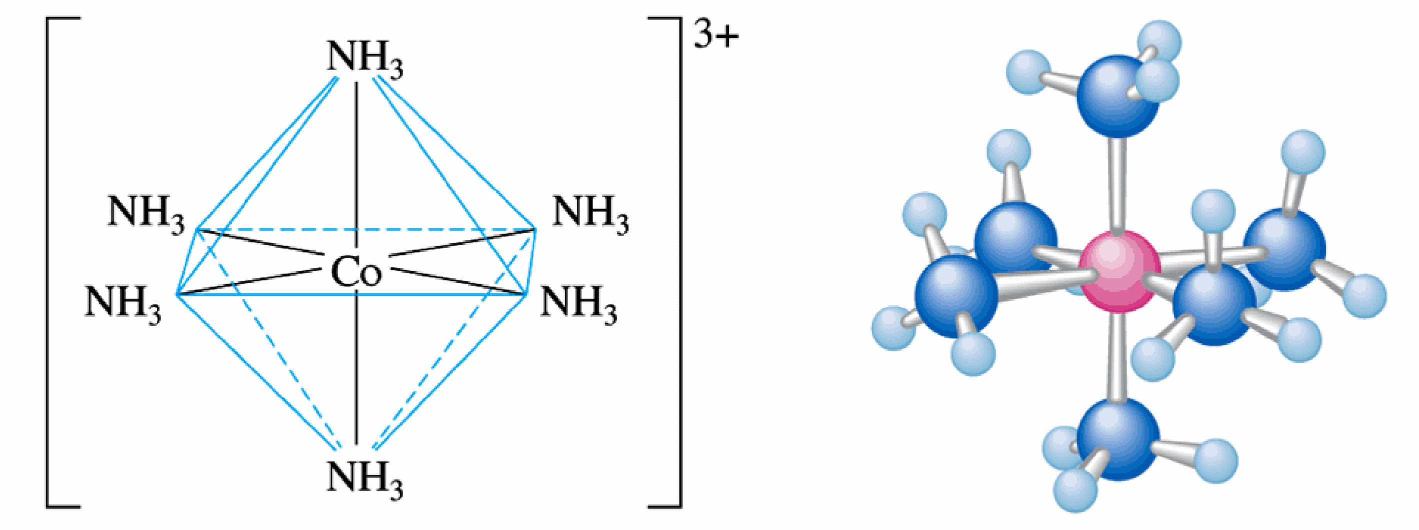
Complex Ion = Transition Metal Cation Surrounded by Ligands

Ligand = Molecule or Ions of Nonbonding Electron Pairs

Bonding is Called “Coordination”

For the complex **$[Co(NH_3)_6]^{3+}$**

Co^{3+} is the electron acceptor and shares a pair of electrons with each of N-atom in NH_3



The $Co(NH_3)_6^{3+}$ ion

Complexometry

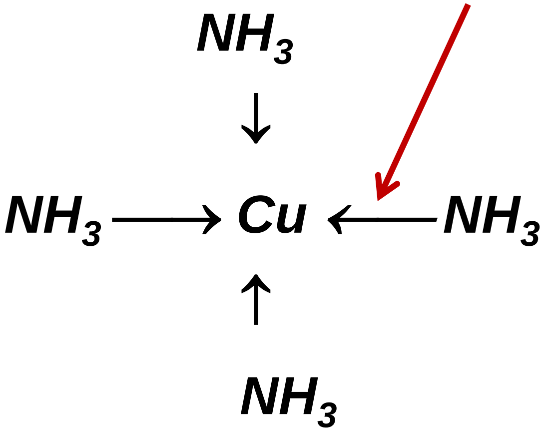
A volumetric titration involves the formation of soluble complex between metal ion (as acceptor) and ligand (as donor) to form coordination bonds.

The metal ion is known as Central metal atom.

The anion or neutral molecule is known as Ligand (L)

$$Cu^{2+} + 4NH_3 \leftrightarrow [Cu(NH_3)_4]^{2+}$$

Ligand



Coordination bond

Nature of The Acceptor Atom (Metal Ion)

The metallic ion (atom) has stable electronic configuration
It forms additional completed shells by accepting electron pairs from donor atoms.

Coordination Number:

- The no. of coordinate bonds formed to a metal ion by their ligands.
- The number of electron pairs that metal ion share or accept.
- It could be 2, 4, 6, depending on the metal ion and its oxidation number.
- Independent on the nature of donor atom.

$$Zn(OH)_4^{2-} \qquad \left[Fe(NH_3)_6\right]^{3+}$$

Nature of The Donor Atom

In aqueous solution, donors are nonmetallic elements

N, O, and S.

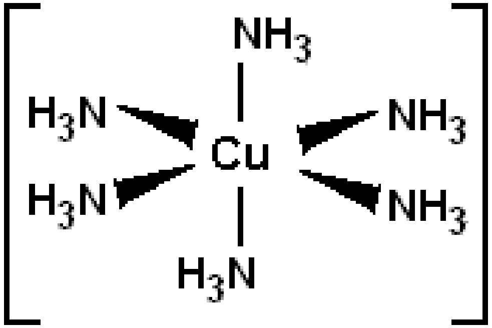
Ion	Coordination number	Typical complex
Ag^{+}	2	$Ag(NH_3)_2^{+}$
Cu^{2+}	4	$Cu(NH_3)_4^{2+}$
Zn^{2+}	4	$Cd(NH_3)_4^{2+}$
Hg^{2+}	4	$Hg(NH_3)_4^{2+}$
Co^{2+}	6	$Co(NH_3)_6^{2+}$
Ni^{2+}	6	$Ni(NH_3)_6^{2+}$
Fe^{3+}	6	$Fe(CN)_6^{3-}$

Type of complexing agents (ligands)

This classification is according to the no. of sites attached to the metal ion

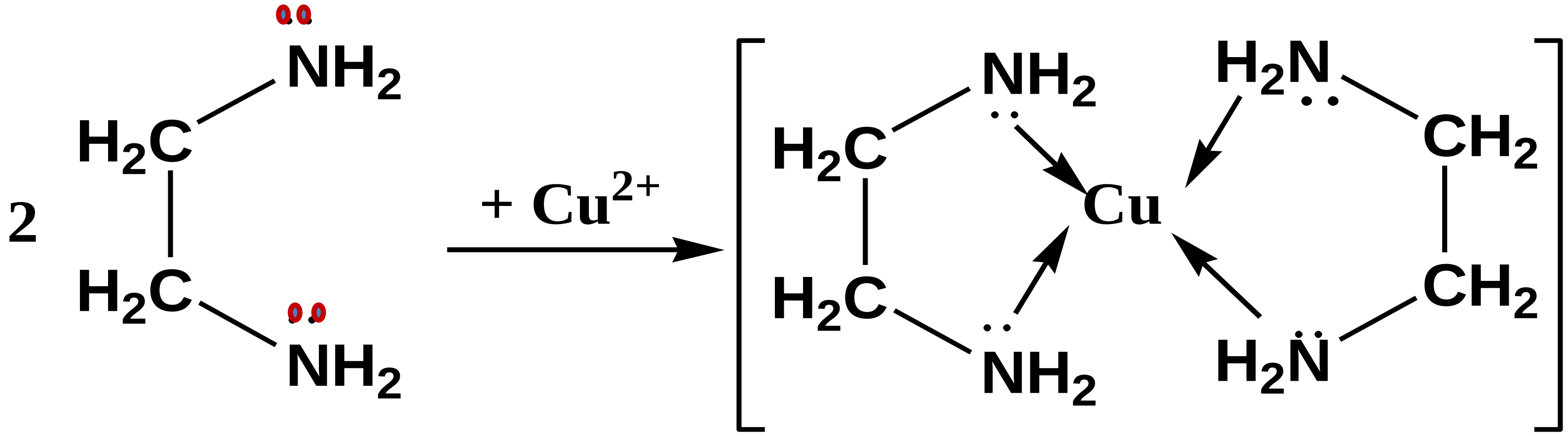
1. Unidentate (Monodentate) Ligand or **"Simple Ligand"**
The ligand attached to metal at one site e.g. H_2O, NH_3, CN^-, Cl^-, I^-, Br^- **(i.e.** forming one coordinate bond, or capable of donating one unshared pair of electrons)

$$H_3N\colon \longrightarrow Ag \longleftarrow \colon NH_3$$



2. Bidentate Ligand

The ligand attached to metal at two sites.

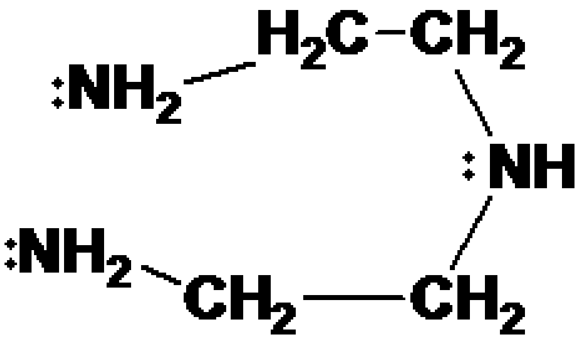


Ethylene diamine

Copper amine complex

3. Tridentate Ligands

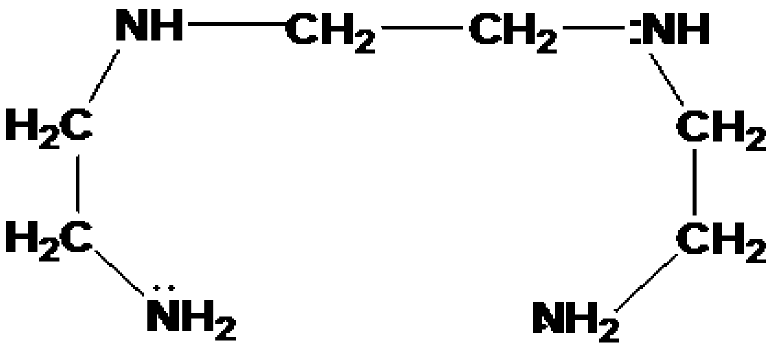
The Ligand attached to metal at 3 sites



Diethylene triamine

4. Tetradentate Ligands

The Ligand attached to metal at 4 sites

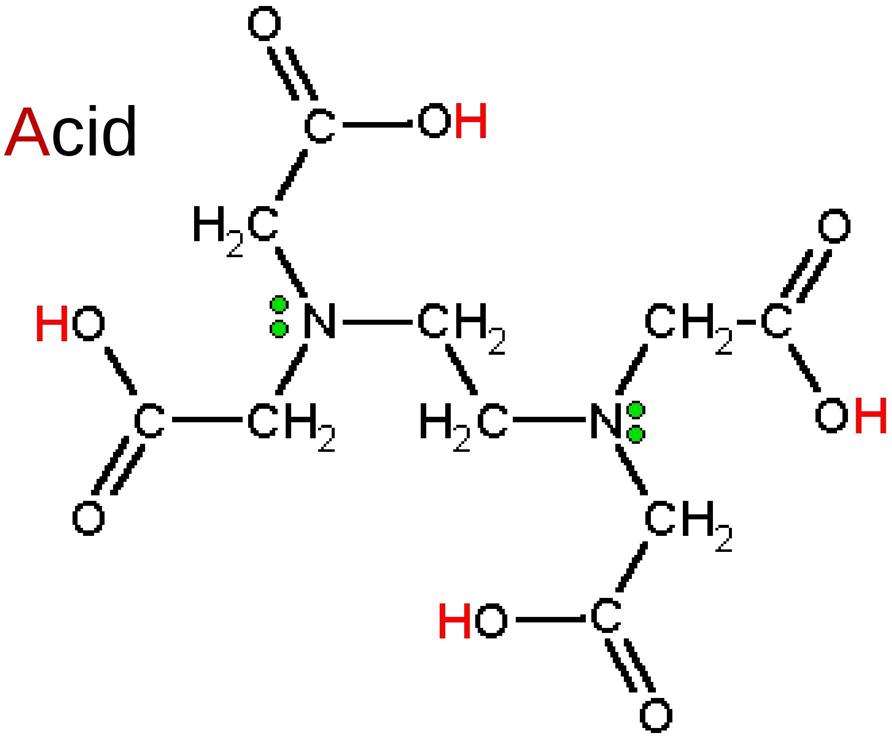


Triethylene tetramine

5. Multidenate Ligands (Chelating Agent)

Substance with multiple sites available for coordination bonding with metal ions. Such bonding typically results in the formation of five or six membered rings.

Ethylene Diamine Tetra acetic Acid



EDTA

EDTA has six sites for complex formation.
The electron pairs on the two nitrogen atoms and the four electron-rich carboxyl groups.

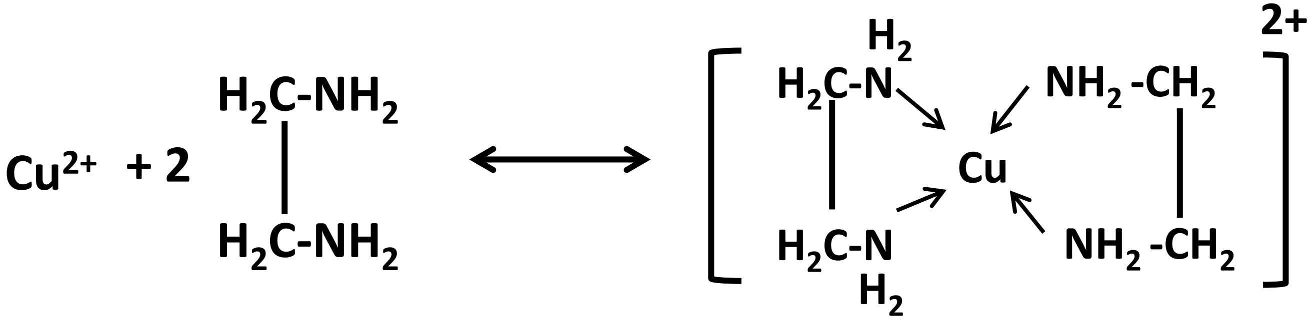
Chelation

Chelate: A complex formed between the ligand containing two or more donor atoms and a metal, forming ring structure (heterocyclic rings or chelate rings).

Chelating agents: organic molecules containing two or more donor groups that combine with metal to form a complex of ring structure.

Examples:

Ethylene diamine
EDTA



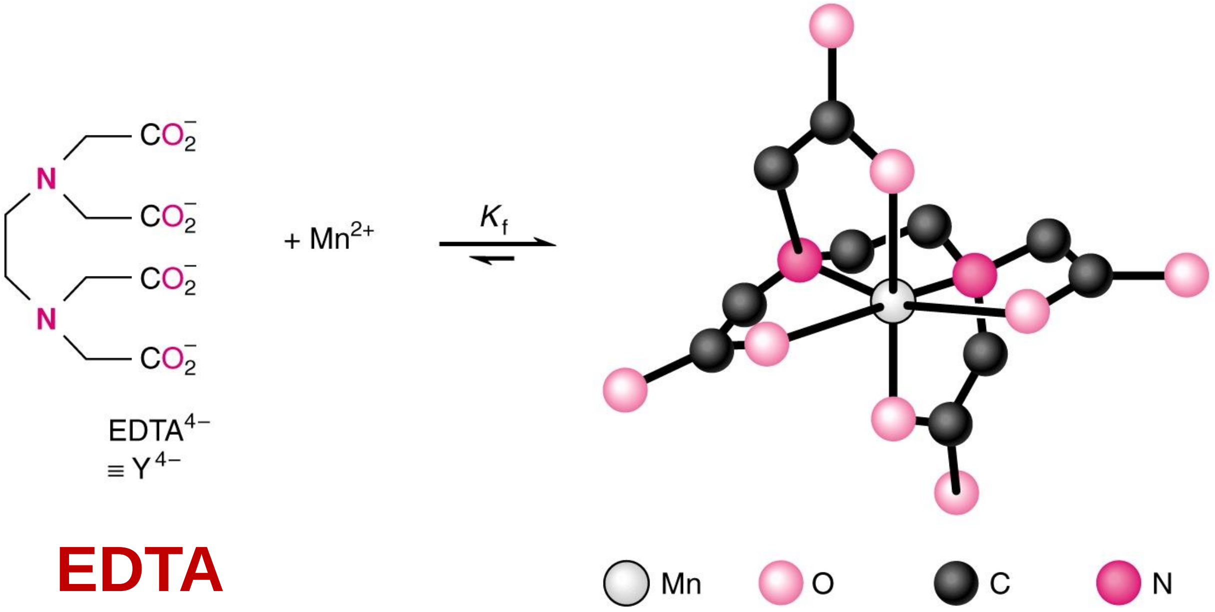
Cu(II) ethylenediamine chelate

Chelate effect

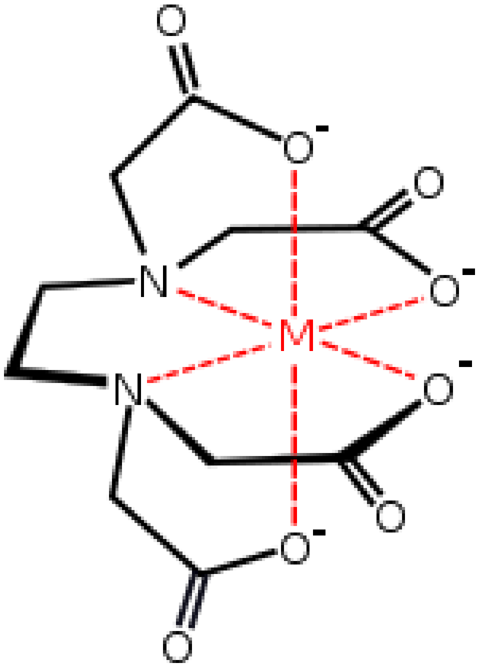
Enhancing the stability of multidentate complexes than unidentate complexes.

Titration With Multidentate Complexers (Chelating Agents)

Chelating agent: Ethylene diamine tetra acetic acid (EDTA) possess enough donor atoms to fill the whole coordination sphere of metal ions in one step.



EDTA



The three-dimensional structure of the 1:1 metal-EDTA chelate with Mn^{2+}.

Advantages of EDTA or H_4Y

1. It forms very stable and soluble stoichiometric, 1:1 complexes with many metal ions.

2. It offers some selectivity against specific metal ions by controlling the pH at which titration is performed.

3. The disodium salt of EDTA ($Na_2H_2Y.\ 2H_2O$) is an acceptable primary standard and commercially available.

4. Since the metal complexes are soluble, coprecipitation errors are absent.

5. The end point could be easily achieved using metal ion indicators.

Factors Affecting the Stability of Metal-EDTA Chelate

1. pH of the solution

$$M^{2+} + H_2Y^{2-} \leftrightarrow MY^{2-} + 2H^{+} \qquad pH = 5$$

$$M^{2+} + HY^{2-} \leftrightarrow MY^{2-} + H^{+} \qquad pH = 8$$

$$M^{n+} + Y^{4-} \leftrightarrow MY^{2-} \qquad pH = 12$$

2. Nature of the metal ion

- Complexes of **divalent** cations: only stable in **basic** medium

- Chelates of **trivalent** cations: stable in **acidic** media (pH 1-2).

- Chelates of **tetravalent** cations: stable at pH values **less than 1**.

For better comparison of chelates, stability constants are used

Stability constants for some metal-EDTA chelates

Metal ion	Log K_{stab}
Mg^{2+}	6.7
Ca^{2+}	10.7
Sr^{2+}	18.7
Ba^{2+}	7.9
Mn^{2+}	13.8
Fe^{2+}	25.1
Zn^{2+}	16.5
Co^{2+}	16.3
Cu^{2+}	18.8

$$M^{n+} + Y^{4-} \leftrightarrow MY^{(n-4)+}$$

$$K_{stab} = \frac{(MY^{(n-4)+})}{(M^{n+})(Y^{4-})}$$

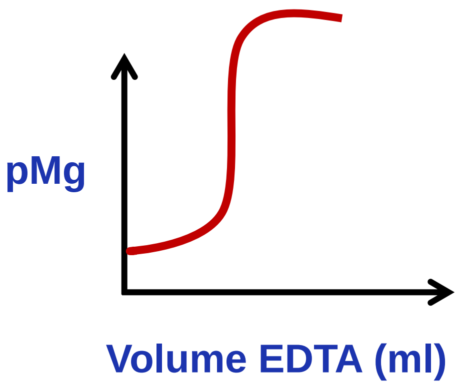
Titration curves

For derivation of the titration curve, consider the titration of 50.0 mL of 0.1 M solution of Mg^{2+} (buffered at pH 10) with 0.1 M EDTA solution.

We calculate the concentration of Mg^{2+} (as pMg= -log(Mg) and plotted versus the volume added from ETDA

1) pMg before the addition of EDTA

Mg^{2+} = 0.1 M , so, pMg=-log (0.1)=1.0



2) pMg after adding 10.0 mL EDTA, we will calculate the remaining unchelated Mg solution in the whole solution (60 ml)

$$MV_{Mg^{2+}} = MV_{EDTA}$$

$$M_{Mg^{2+}} unreacted = \frac{(50*0.1)-(10*0.1)}{50+10} = 0.067M$$

$$P_{Mg} = -\log(0.067) = ...$$

3) pMg after adding 25.0 mL EDTA, we will calculate the remaining unchelated Mg solution in the whole solution (75 ml)

$$M_{Mg^{2+}} unreacted = \frac{(50*0.1)-(25*0.1)}{50+25} = 0.067M$$

$$P_{Mg} = -\log(0.067) = ...$$

4) pMg at the equivalence point

At this Point, 50 mL of EDTA have been added to completely react with Mg solution

We will use the stability constant to calculate the pMg

$$Mg^{2+} + Y^{4-} \leftrightarrow MgY^{2-} \qquad K_{stab} = \frac{(MgY^{2-})}{(Mg^{2+})(Y^{4-})} = 5.0x10^8$$

a a 0.05-a

Concentration of MgY^{2-} is calculated as follows

$$M_{Mg^{2+}} = \frac{(50*0.1)}{50+50} = 0.05M$$

$$M_{MgY^{2-}} = \frac{(50*0.1)}{50+50} = 0.05-a$$

Substitute at equation K_{stab} $K_{stab} = \frac{(0.05-a)}{a^2} = 5.0x10^8$

Substitute at equation K$_{stab}$ $$K_{stab} = \frac{(0.05-a)}{a^2} = 5.0x10^8$$

a, is neglected because it is very small relative to 0.05

So, $$\frac{(0.05)}{a^2} = 5.0x10^8$$ $$a = (Mg^{2+}) = 1.0x10^{-5}, P_{Mg} = 5.0$$

5) pMg, beyond the equivalence point:

By adding 60 mL of the 0.1 M EDTA

$$M_{MgY^{2-}} = \frac{(50*0.1)}{50+60} - a$$

Neglect the term a
and then substitute (MgY^{2-}) of 5/110 M in K_{stab} equation

There will be an excess from EDTA $Y^{4-} = \frac{(60x0.1)-(50x0.1)}{(50+60)} = 1/110$

$$\frac{(5/110)}{(1/110)(a)} = 5.0x10^8$$

$a = 1x10^{-8} M$ And pMg=8.0

The titration curve is plotted by using the previous data

Volume added (ml)EDTA	pMg
0	
5	
10	
25	
50	
51	
55	
60	

Please complete this table and plot the titration curve!!!

Detection of End Point: use Metal Ion Indicators

- Organic dyes with acid-base properties that undergoes a color change upon proton transfer to/from the dye molecule.

- In addition, the dye molecules contains a chelating group that is joined to the conjugated system responsible to for the color.

- These indicators responds to a change in pM and thereby convert the break in pM into the color changes.

- The success of an EDTA titration depends on the precise determination of the end point.

- The most common procedures uses the metal ion indictors.

Characteristics of Metal Ion Indicators

1. Form colored chelates (complexes) and exhibit a different color in the free form than in the complex form.

2. The reaction between metal and indicator must be reversible.

3. The metal-indicator complex should be less stable than the metal-EDTA complex.

Metal-indictor +EDTA ⟶ Metal-EDTA+ free indicator

4. The color reaction should be specific or at least selective.

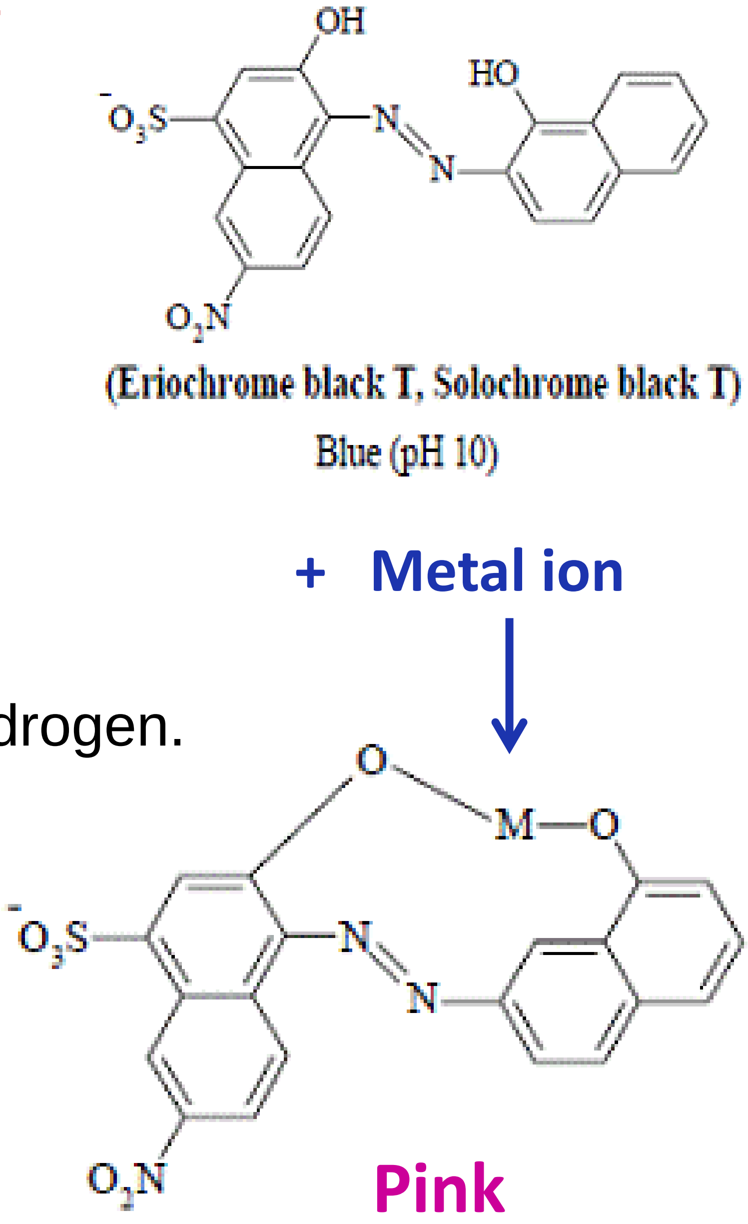
5. Changes its color according to the pH of the medium.

Examples of Metal Ion Indicators

1. Eriochrome black T (EBT)

It can be represented by H_2In^-
The color of Indicator change with the change of pH.

EBT contains 2 replaceable phenolic hydrogen.



(Eriochrome black T, Solochrome black T)

Blue (pH 10)

+ Metal ion

Pink

EBT is a tribasic acid at pH 10, exists as blue HIn^{2-}

$$H_3In \leftrightarrow HIn^{2-} \leftrightarrow In^{3-}$$

Red	**Blue**	**Orange**
pH below 7	**pH 7-11**	**pH above 11**

The blue form of the indicator reacts with metal ions, to give a wine red chelate

$$Mg^{2+} + HIn^{2-} \xleftrightarrow{pH10} MgIn^{-} + H^{+}$$

Analyte
colorless

Free indicator
Blue

Metal –indicator
complex
Wine red

By the titration with EDTA, it initially chelates the free Mg^{2+} ion, then displaces the chelated Mg from the indicator.

$$MgIn^{-} + HY^{3-} \xleftrightarrow{pH\,10} MgY^{2-} + HIn^{2-}$$

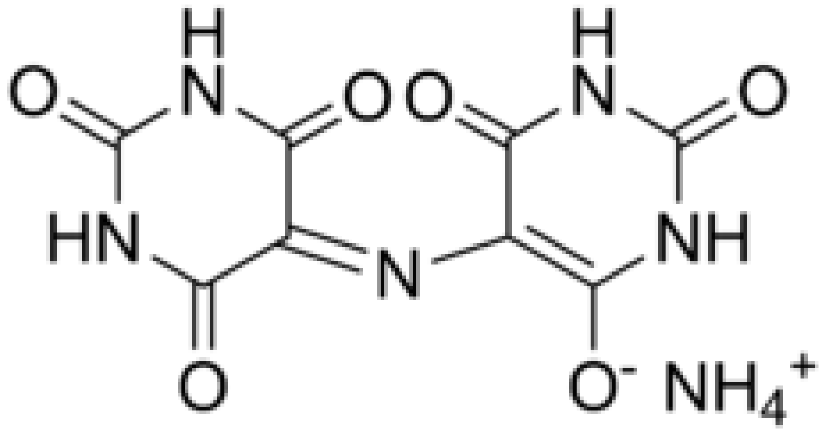
Metal –ind. complex **Wine red**	Titrant EDTA colorless	Metal–EDTA complex colorless	Free indicator **Blue**

EBT is used for the determination of
Mg^{2+}, Zn^{2+}, Cd^{2+}, pb^{2+}, Hg^{2+} & Mn^{2+} salt at pH 7 – 11 using ammonia buffer (pH = 10)

EBT cannot be used for the determination of
Cu^{2+}, Fe^{3+}, Al^{3+}, Co^{2+} and Ni^{2+}

2. Murexide

Ammonium salt of purpuric acid and its anion has the following structure



$$H_4Ind^- \xleftrightarrow{OH^-} H_3Ind^{2-} \xleftrightarrow{OH^-} H_2Ind^{3-}$$

Reddish violet	**Violet**	**Blue**
pH < 9	**9-11**	**> 11**

- Murexide is used for the direct titration of calcium at pH=12, the end point changes from red to blue violet.
- At pH=12, Mg-murexide is less stable than the Ca-complex, so Ca^{2+} ion can be titrated in the presence of Mg at this pH.
- Murexide gives yellow chelates with **Cu, Co, Ni** metals ions.

It is used for the determination of
Ca^{2+}, Co^{2+}, Ni^{2+}, & Cu^{2+} salts at pH 9-11

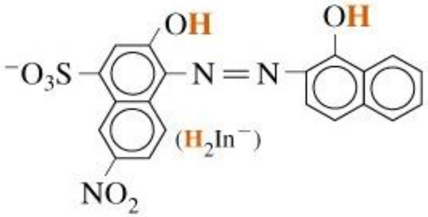
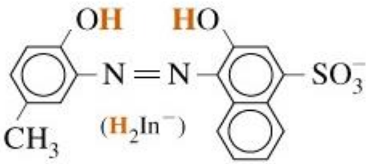
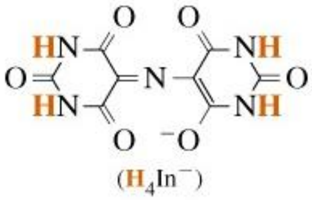
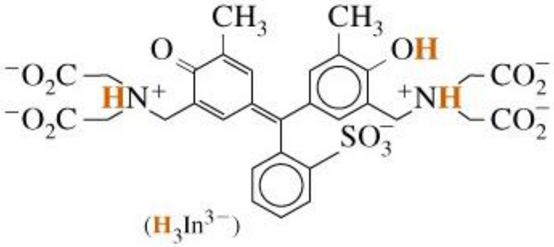
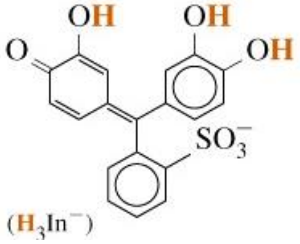
$Ca^{2+} + H_3In^{2-} \longrightarrow Ca\,H_2In^- + H^+$

$Ca\,H_2In^- + H_2Y^{2-} + OH^- \longrightarrow CaY^{2-} + H_3In^{2-} + H_2O$

Pink Violet

Metal	Color of complex	Color of indicator
Ca^{2+}	Pink	violet
Cu^{2+}	Orange	Violet
Co^{2+}	Yellow	violet
Ni^{2+}	yellow	violet

Common Metal Ion Indicators

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Eriochrome black T	 (H_2In^-)	$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Calmagite	 (H_2In^-)	$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide	 (H_4In^-)	$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}
Xylenol orange	 (H_3In^{3-})	$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$	H_5In^- yellow H_4In^{2-} yellow H_3In^{3-} yellow H_2In^{4-} violet HIn^{5-} violet In^{6-} violet	Red
Pyrocatechol violet	 (H_3In^-)	$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	H_4In red H_3In^- yellow H_2In^{2-} violet HIn^{3-} red-purple	Blue

Complexometric Titrations: Types

1. Direct titration

The solution of the metal ion to be determined is buffered to the desired pH(e.g. to pH=10 with NH_4^+, NH_4OH) and titrated directly with the standard EDTA solution.

The end point is determined by the change in color of a metal indicator that responds to changes in pM.

$$Mg^{2+} + EBT \xrightarrow{pH10} Mg - EBT \xrightarrow{EDTA} Mg - EDTA + EBT$$

Blue Wine red Colorless Blue

Requirements for Direct EDTA Titrations

1.M-EDTA complex must be more stable than M-Ind. complex in buffered medium.

2. The compound to be determined is water soluble.

3.The reaction between EDTA and metal must be rapid. If not, it must be catalyzed.

4. M^{n+} should not be precipitated at the pH of titration. If M^{n+} is precipitated as MOH, auxiliary reagent must be added to prevent pptn. of M^{n+}.

Examples

1- pb^{2+} ion forms precipitate of $pb(OH)_2$ at the pH 10.

So, tartaric acid (auxiliary reagent) is added to convert $pb(OH)_2$ to soluble lead tartarate complex.

2-Sometimes buffer acts as auxiliary reagent

During titration of Cu^{2+} salt in **alkaline medium**, $Cu(OH)_2$ is ppt. and the reaction with EDTA becomes slow.

So, by using ammonia instead of **alkali hydroxides**, the soluble $[Cu(NH_3)_4]^{2+}$ is formed which is less stable than Cu-EDTA and hence the reaction forward rapidly.

Direct Determination of Water Hardness

- Water hardness is due to the presence of Ca^{2+} & Mg^{2+} salts.
- EDTA forms complex with Ca^{2+} & Mg^{2+}
- Ca-EDTA complex is more stable than Mg-EDTA complex.
- At pH 12 EDTA forms complex with Ca^{2+} only.

Total Ca^{2+} & Mg^{2+}

- Total Ca^{2+} and Mg^{2+} determined by titration with EDTA at pH 10 using ammonia buffer and EBT as indicator

Upon titration with EDTA, Ca^{2+} will be chelated first, then Mg^{2+}.

For Ca^{2+} only

Direct titration with EDTA at pH 12 using 8% NaOH and Murexide. Mg^{2+} is precipitated as $Mg(OH)_2$ leaving Ca^{2+} to be titrated with EDTA

For Mg^{2+}

Total – Ca^{2+} = Mg^{2+}

2. Back Titration

This procedure involves:

1. Addition of known excess of standard *EDTA* solution to the sample

2. The medium is buffered.

3.Titrate excess *EDTA* with standard metal ion solution such as Mg^{2+} or Zn^{2+}

$$M^{n+} + excessEDTA \xrightarrow{pH-acidic} M - EDTA + unreacted - EDTA$$

The color change at the end point:

From free ind. colour $\longrightarrow$ to *M-Ind*. complex (opposite that direct titration)

Why do we use Back Titration?

1. Detection of some insoluble substances such as $BaSO_4$, $Ca(C_2O_4)_2$, $PbSO_4$, $Mg_3(PO_4)_2$, which soluble in hot EDTA.

2. When the reaction between M^{n+} & EDTA is slow (incomplete) e.g. Fe^{3+}, Al^{3+}, Cr^{3+}, Th^{4+}.

3. The precipitation of metal at the pH suitable for titration e.g. $Al(OH)_3$.

4. The suitable indicators are not available

Example #1: Determination of Aluminium salts

- Sample of Al^{3+} is heated with known excess of standard EDTA at pH 7-8.

- The solution is then adjusted to pH=10 using ammonia buffer.

- The residual EDTA is titrated against standardZn^{2+} using EBT indicator.

- The color change from blue to wine red.

$$Al^{3+} + H_2Y^{2-} \xrightarrow{\text{pH 7-8}} AlY^{-} + 2\,H^{+}$$

Boil

$$Zn^{2+} + H_2Y^{2-} \xrightarrow{\text{pH 10}} ZnY^{2-} + 2\,H^{+}$$

$$Zn^{2+} + H\,Ind^{2-} \longrightarrow Zn\text{-}Ind^{-} + H^{+}$$

Blue **wine red**

Example #2: Determination of Mn salts

Mn can not be directly titrated with EDTA in alkaline solution due to the precipitation of the $Mn(OH)_2$.

1. An excess of EDTA is added to an acidic solution of the Mn salt.
2. Ammonia buffer is used to adjust the pH to 10.
3. The excess EDTA (unreacted) after chelation is titrated with standard Zn^{2+} solution.

$$Mn^{2+} + excessEDTA \xrightarrow{pH-acidic} Mn - EDTA + unreacted - EDTA$$

$$unreacted - EDTA + Std.Metal \xrightarrow{pH10}$$

3. Replacement or substitution titration

1.Used for metal ions that does not react (or react unsatisfactorily) with a metal indicator.

2. When metal ions form unstable EDTA complexes.

The metal ion M^{n+} to be determined is treated with Mg-EDTA complex.

$$M^{n+} + Mg - EDTA \leftrightarrow M^{n+} - EDTA + Mg^{2+}$$

The amount of Mg ion librated is equivalent to the cation present and can be titrated with standard solution of EDTA and a suitable metal indicator.

4. Alkalimetric Titration

- When a solution of disodium EDTA, Na_2H_2Y is added to a solution containing metallic ions
- Complexes are formed with the liberation of two equivalents of hydrogen ion:
- Therefore, the hydrogen ions liberated can be titrated with a standard solution of sodium hydroxide using an acid-base indicator.

$$M^{n+} + H_2Y^{2-} \leftrightarrow (MY)^{(n-4)+} + 2H^+$$

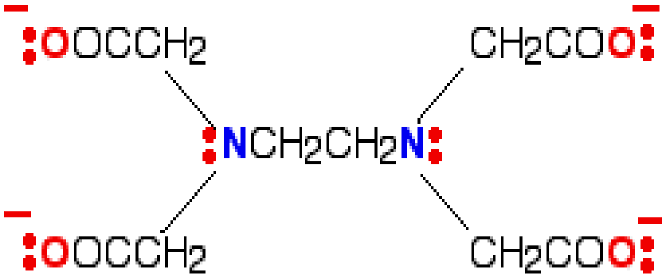
$2H^+ + 2NaOH \rightarrow$

Analysis of Metal Ion Mixtures

EDTA is a very unselective reagent because it complexes di, tri, and tetra- valent cations.

To increase the selectivity of EDTA, some procedures could be followed:

- Control of pH of the medium
- Adjustment of oxidation number of metal ion
- Using masking and demasking agent



Control of pH of the medium

1. **First group:** Trivalent & tetravalent cations **(Bi^{3+} , Fe^{3+} , Th^{4+})** and **Hg^{2+}** titrated (form stable complex) at pH 1-3 using conc. **HNO_3.**

2. **Second group:** Divalent metals **(Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , pb^{2+}** and **Cd^{2+})** titrated (form stable complex) at pH 4-6 using acetate buffer.

3. **Third group:** Alkaline earth metal **(Ba^{2+} , Sr^{2+} , Ca^{2+})** and **Mg^{2+}** titrated (form stable complex) at pH=10 using ammonia buffer or 8% **NaOH.**

- **At pH** 1-3, metal ion from first group could be titrated without interference of the second and third groups.

- At pH 4-6, **M^{n+}** of the second group without interference of the third group.

Analysis a mixture of *Bi^{3+} & pb^{2+}*

1. First titrate **Bi^{3+}** at pH = 2 using xylenol orange as indicator.
2. Then increased pH to 5 by adding hexamine and titrating **pb^{2+}.**

Adjustment of Oxidation Number of Metal Ion

This procedure remove the interferences between metal ions of the same group of pH.

Examples

1. Ascorbic acid 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^{o}** (ppt.)
- Removal of interference of **Cu^{2+}** in second group (pH 4-6) → reduced to **Cu^{+}**.

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

3. Fe^{2+} , Hg^{o}, Cu^{+}, CrO_4^{2-} do not react with EDTA

Masking and Demasking Agents

Masking agents: A reagent added to prevent reaction of some metal ion with EDTA (block metal ions)

These reagents form complexes with interfering ions which are more stable than complexes formed with indicator & ***EDTA***.

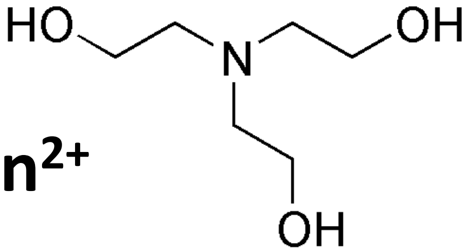
Masking and demasking agents

(A) Cyanide (KCN)

Used as a masking agent for Ag^+, Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}.

$$M^+ + 4\,CN^- \longrightarrow [M(CN)_4]^{2-}$$

(B)- Triethanolamine:



Used as a masking agent for **Fe^{3+} , Al^{3+}** and **Sn^{2+}**

(C) Fluoride (NH_4F):

Used as a masking agent for **Fe^{3+}** and **Al^{3+}** to give hexafluoro complex **$[FeF_6]^{3-}$** and **$[AlF_6]^{3-}$**

(D)- Iodide (KI):

Used as a masking agent for **Hg^{2+}** to give tetraiodo complex **(HgI_4)**

Demasking Agent

Reagents that release of a metal ion from a masking agent

Example

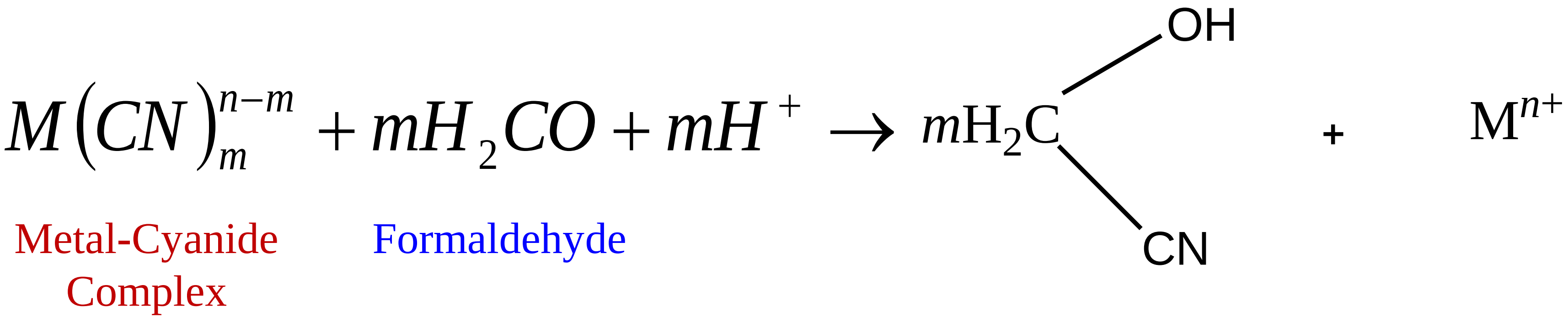
The masking by **CN^-** can be removed by (mixture of formaldehyde – acetic acid)

- on addition of demasking agent to **$[Zn(CN)_4]^{2-}$, Zn** is liberated and titrated.

$$[Zn(CN)_4]^{2-} + 4H^+ + HCHO \leftrightarrow Zn^{2+} + 4HO - CH_2 - CN$$

$$[Zn(CN)_4]^{2-} + 4CH_3COOH + 4HCHO \leftrightarrow Zn^{2+} + 4HO - CH_2 - CN + 4CH_3COO^-$$

(less stable) (more stable) Cyanohydrin



Metal-Cyanide Complex

Formaldehyde

Oxidation with H_2O_2 releases Cu^{2+} from Cu^{+}-Thiourea complex.

Reference

Daniel Harris,(2007), “Quantitative Chemical Analysis” 7th Edition, New York.