
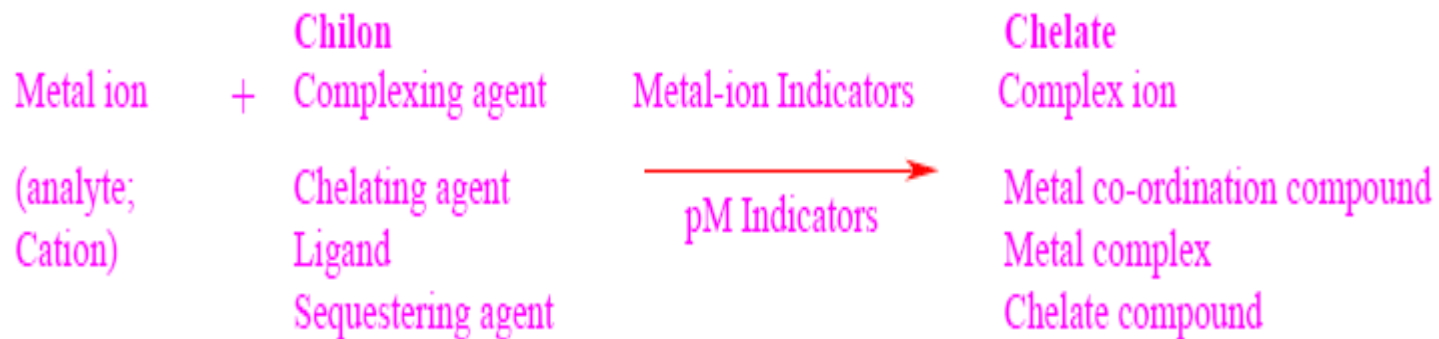




Complexometric Titrations

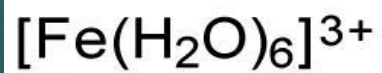
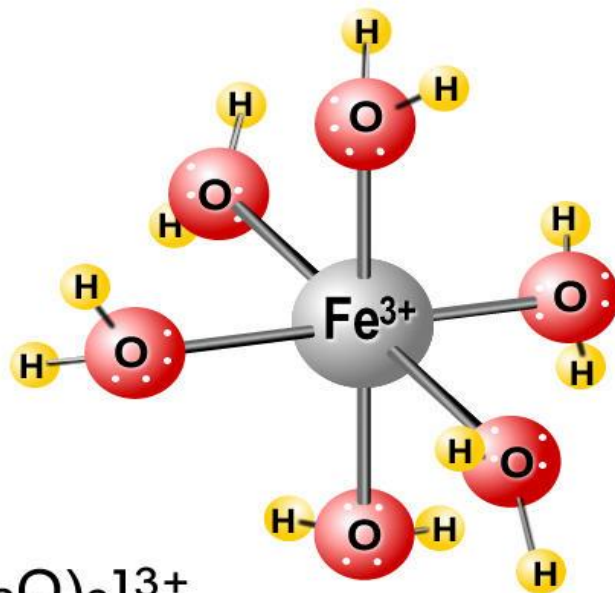
- 
- ▶ The technique involves titrating metal ions with a complexing agent or chelating agent (ligand) and is commonly referred to as complexometric titration
 - ▶ This method represents the analytical application of a complexation reaction
 - ▶ In this method, a simple ion is transformed into a complex ion and the equivalence point is determined by using metal indicators or electrometrically
 - ▶ **Chelometric titrations, chelometry, chelatometric titrations and EDTA titrations**



Metal Center




Ligands




Octahedral

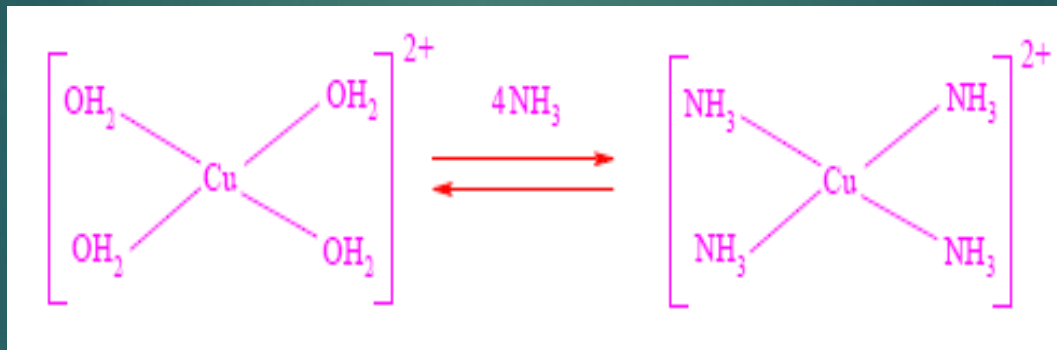
Reactions for Complexometric Titration


- ▶ Any complexation reaction can be used as a volumetric technique provided that:
 - ▶ the reaction reaches equilibrium rapidly after each portion of titrant is added
 - ▶ interfering situations do not arise. For instance, the stepwise formation of several different complexes of the metal ion with the titrant, resulting in the presence of more than one complex in solution during the titration process
 - ▶ a complexometric indicator capable of locating equivalence point with fair accuracy is available

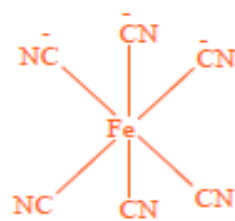
- 
- ▶ Metal ions in solution are always solvated, i.e. a definite number of solvent molecules (usually 2, 4 or 6) are firmly bound to the metal ion
 - ▶ However, these bound solvent molecules are replaced by other solvent molecules or ions during the formation of a metal complex or metal co-ordination compound

- 
- ▶ The molecules or ions which displace the solvent molecules – **ligands**
 - ▶ ***Any electron donating entity which has the ability to bind to the metal ion and produce a complex ion***

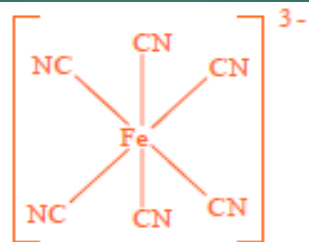
- ▶ An example of a complexation reaction between Cu (II) ion and four ammonia molecules in aqueous solution



- 
- ▶ The bonds are either ordinary covalent bonds in which the metal and the ligand contribute one electron each or co-ordinate bonds in which both electrons are contributed by the ligand
 - ▶ Thus, the hexacyanoferrate ion may be considered to consist of three ordinary covalent bonds and three co-ordinate bonds, although in the complex the bonds are identical hybrid bonds which have been shown to be directed towards the apices of a regular octahedron

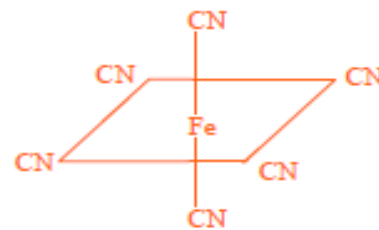


(a)



Hybrid bonds

(b)



(c)


The hexacyanoferrate iron (III) ion

Werner's Co-ordination Number

- ▶ **Alfred Werner** (1891) first noticed that for each atom there were an observed maximum number of small groups which can be accommodated around it. This number, which is called **Werner's co-ordination number**, depends purely upon steric factors and is in no way related to the valency of the ion
- ▶ ***The total number of ligands or atoms which are directly attached to the central metal atom***

- 
- ▶ Steric factors
 - ▶ Nature of the ligand
 - ▶ Number of pairs of electrons accommodated within that metals
 - ▶ Stereochemical environment of the metal ion and the coordination number is in no way related to the valency of the metal ion

Coordination number is a characteristic for each metal ion


- 
- ▶ Within the limits imposed by Werner's coordination number, there is a tendency for the metal to attain or approach inert gas structure, and this is probably the driving force for complex formation

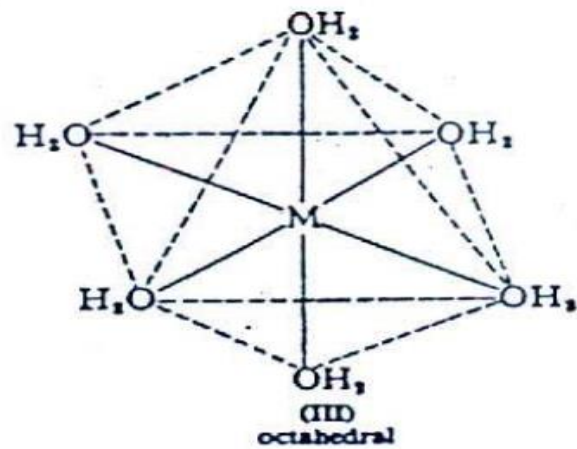
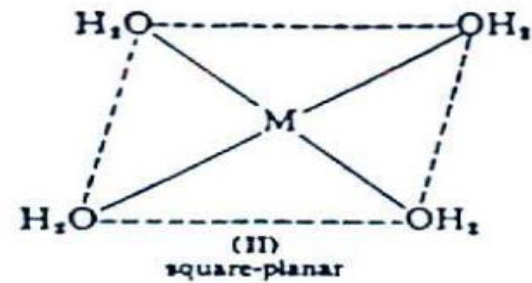
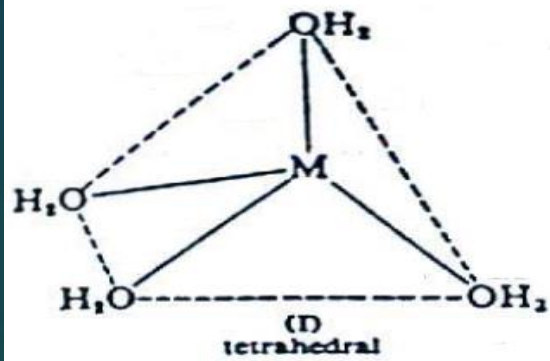
Some Common Coordination Numbers (CN) of Metal Ions

Table 22.2 Some Common Coordination Numbers of Metal Ions

Metal Ion	Coordination Number	Metal Ion	Coordination Number
Al^{3+}	4, 6	Ni^{2+}	4, 6
Sc^{3+}	6	Cu^+	2, 4
Ti^{4+}	6	Cu^{2+}	4, 6
V^{3+}	6	Zn^{2+}	4
Cr^{3+}	6	Pd^{2+}	4
Mn^{2+}	6	Ag^+	2
Fe^{2+}	6	Pt^{2+}	4
Fe^{3+}	6	Pt^{4+}	6
Co^{2+}	4, 6	Au^+	2, 4
Co^{3+}	6	Au^{3+}	4

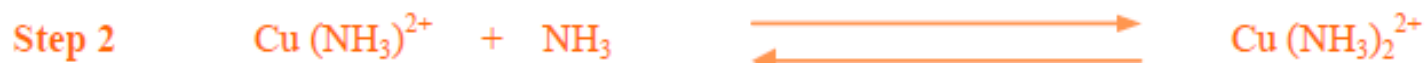
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- 
- ▶ Ligand molecules are bound to the metal ion in a specific pattern which is characteristic of the metal
 - ▶ Metals with a coordination number of four bind ligand molecules in such a way as to produce either a tetrahedral or square-planar structure
 - ▶ These structures arise from the spatial arrangement of the ligand molecules about the metal ion
 - ▶ An octahedral structure is usually formed by metal ions with a coordination number of six




Classification of Ligands

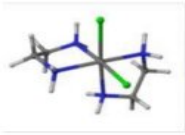
- ▶ **Unidentate Ligands:** Ligands that are bound to metal ion only at one place
- ▶ NH_3 is a unidentate ligand capable of complexing with cupric ions
- ▶ Halide ions, cyanide ions



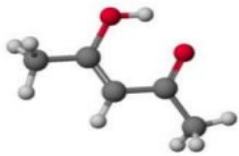
Considering the overall reaction:



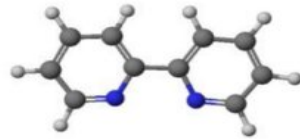
- 
- ▶ **Multidentate Ligands:** Many ligands are known that contain more than one group, capable of binding with metal ions
 - ▶ Such ligands are known as multidentate ligands or chelating agents
 - ▶ Molecules or ions that contain two or more donor groups that attach to a metallic ion
 - ▶ They include bidentate ligands (2 donor atoms), tridentate ligands (3 donor atoms), quadridentate ligands, etc.



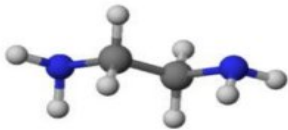
Common Bidentate Ligands



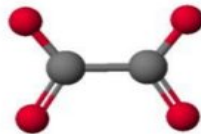
Acetylacetonone (acac)



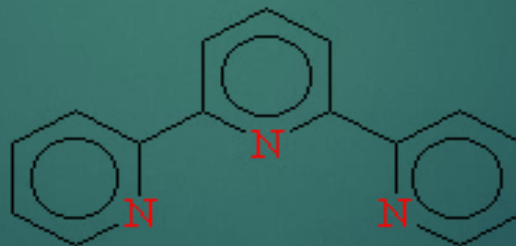
Bipyridine (bipy)



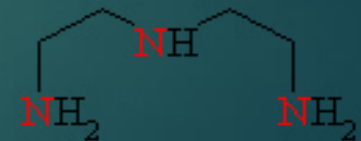
Ethylenediamine (en)



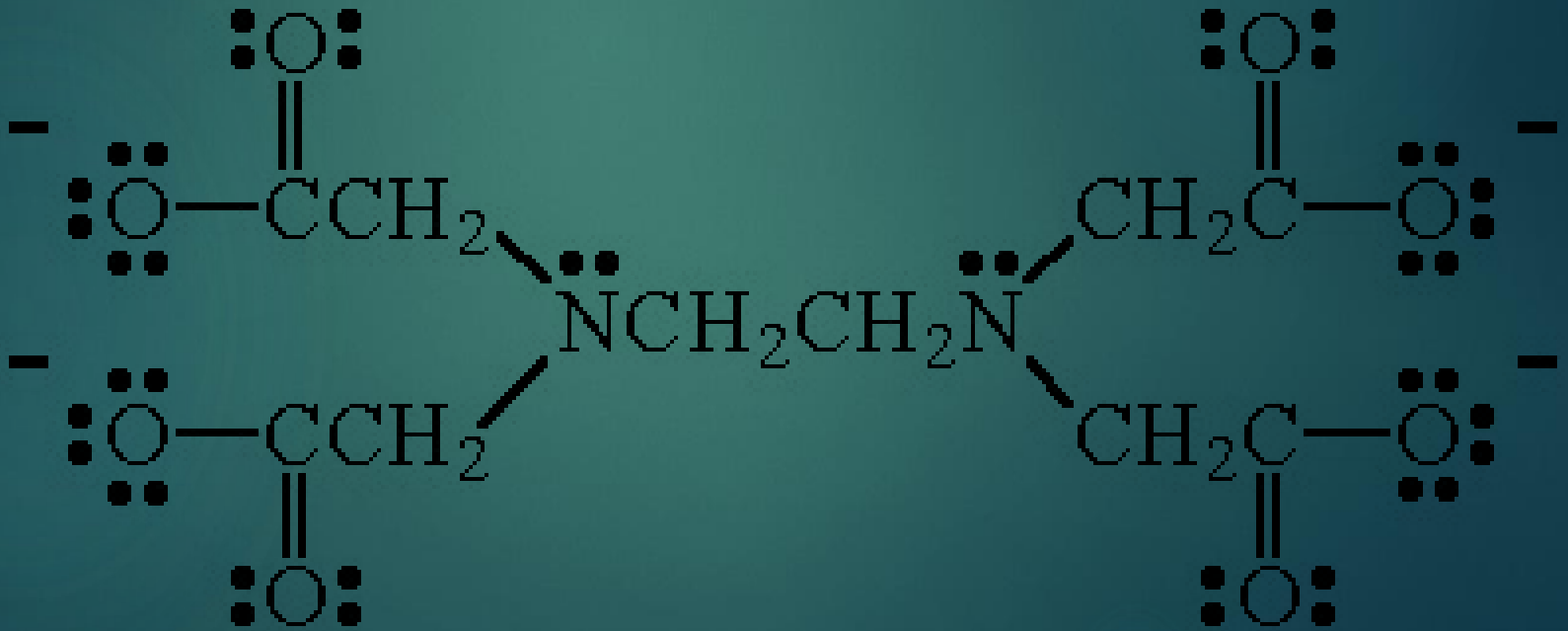
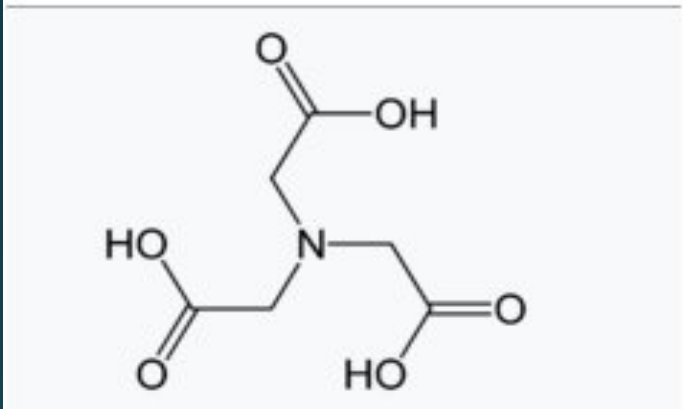
Oxalate (ox)



**Terpyridyl
(terpy)**



**Bisethylenetriamine
(tris)**






▶ **Chelate Compound or Chelate**

- ▶ Complexes involving simple ligands, i.e., those forming only one bond are described as co-ordination compound
- ▶ When a multidentate ligand attaches to a metal at more than one site, a ring structure is formed
- ▶ These ring compounds are called **chelates**
- ▶ *A chelate can be described as a heterocyclic ring structure in which a metal atom is a member of the ring*
- ▶ There is no fundamental difference between co-ordination compound and a chelate compound except that in a chelate compound, ring influence the stability of compound
- ▶ The stability of a chelate is usually much greater than that of corresponding unidentate metal complex

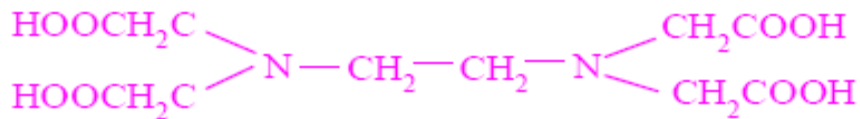


▶ **Chelating agent**

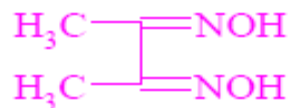
- ▶ Ligands having more than one electron donating groups are called ***chelating agents***
- ▶ The most effective complexing agent in ligands are amino and carboxylate ions

- 
- ▶ The solubility of metal chelates in water depends upon the presence of hydrophilic groups such as COOH , SO_3H , NH_2 and OH
 - ▶ When both acidic and basic groups are present, the complex will be soluble over a wide range of pH
 - ▶ When hydrophilic groups are absent, the solubilities of both the chelating agent and the metal chelate will be low, but they will be soluble in organic solvents
 - ▶ The term **sequestering agent** is generally applied to chelating agents that form water-soluble complexes with bi- or poly-valent metal ions
 - ▶ Thus, although the metals remain in solution, they fail to give normal ionic reactions

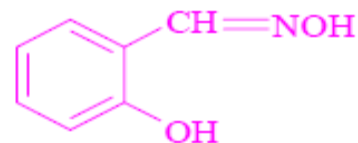
- ▶ Ethylene diamine tetraacetic acid is a typical sequestering agent, whereas, dimethylglyoxime and salicylaldoxime are chelating agents, forming insoluble complexes



EDTA



Dimethylglyoxime



Salicylaldoxime


Types of Complexometric Titrations

- ▶ Direct titration
- ▶ Back titration
- ▶ Replacement titration or substitution titration
- ▶ Alkalimetric titration of metals
- ▶ Indirect titration



▶ Direct titration

- ▶ Simplest and most convenient method used in chelometry
- ▶ In this procedure the standard chelon solution is added to the metal ion solution until the end point is detected by a suitable method
- ▶ This procedure is analogous to a simple acid-base titration
- ▶ A blank titration may be performed
- ▶ **Ca²⁺, Mg²⁺, Zn²⁺** (direct titration with EDTA)
- ▶ **Assay of calcium gluconate, zinc stearate, magnesium hydroxide**

- 
- ▶ Numerous problems may be encountered with direct titration of some metals, such as precipitation of the metal as a result of side reactions, a slow complexation or interferences of various types caused by the presence of other ions
 - ▶ Many of these problems can be overcome by alternate titration procedures

▶ **Back titration or Residual titration**

- ▶ Back titration involves addition of an excess of a standard chelon to the metal being determined, and the excess is back titrated with a **standard solution of a second metal ion** to a suitable end point
- ▶ A solution of **zinc chloride or sulphate** or of **magnesium chloride or sulphate** or **lead nitrate** is often used
- ▶ Mostly applied to the analysis of **Aluminium** and **Bismuth** compounds
- ▶ An example of this procedure is the determination of Mn(II).
- ▶ This metal cannot be directly titrated with EDTA in alkaline solution, owing to precipitation of the manganese hydroxide
- ▶ An excess of EDTA is added to an acidic solution of the manganese salt, an ammonia buffer is used to adjust the solution pH to 10, and the excess EDTA remaining after chelation is titrated with a standard Zn(II) solution using Eriochrome Black T as the indicator



▶ **Assays**

- ▶ Aluminium hydroxide gel
- ▶ Alumina and magnesia tablets
- ▶ Alumina and magnesia oral suspension
- ▶ Alum

▶ Replacement or substitution titration

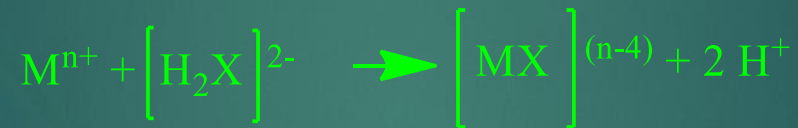
- ▶ The method of replacement titration involves the quantitative displacement of a second metal (M_{II}) from a complex by the metal (M_I) being determined
- ▶ The freed second metal is then directly titrated by a standard chelon solution
- ▶ From these data, one can calculate the concentration of M_I in the system
- ▶ An example of this type of analysis is determination of manganese(II)
- ▶ This ion cannot be satisfactorily titrated directly with an EDTA solution, when Eriochrome Black T is used as the indicator
- ▶ However, if an excess quantity of a Mg-EDTA chelate is added to the manganese solution, the magnesium is quantitatively displaced from the EDTA chelate.
- ▶ This displacement takes place because manganese forms a more stable complex with EDTA
- ▶ The freed Mg ions are then directly titrated with a standard EDTA solution and are equivalent to the amount of Mn(II) originally in the solution



- ▶ These titrations may be used for metal ions that do not react or react unsatisfactorily with a metal indicator or for metal ions which form more stable EDTA complexes than other metals

▶ Alkalimetric titration of metals

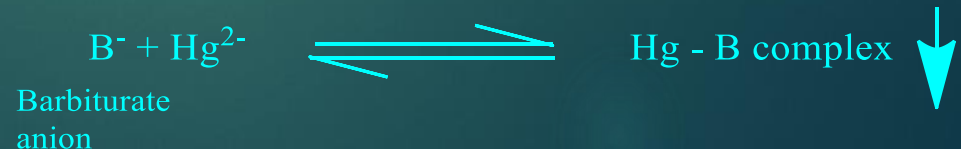
- ▶ Protons from disodium edetate are displaced by a heavy metal and titrated with a standard alkali



- ▶ When a solution of disodium ethylene diamine tetra acetate is added to a solution containing metallic ions, complexes are formed with the liberation of 2 equivalents of hydrogen ions
- ▶ The hydrogen ions can then be titrated with a standard solution of an alkali using an acid/base indicator
- ▶ The solution of the metal to be determined must be accurately neutralised before titration
- ▶ The titration is carried out in **unbuffered solutions**

▶ Indirect titration

- ▶ Determination of ions, such as **anions** which do not react with a chelon (chelating agent)
- ▶ Barbiturates do not react with EDTA but are quantitatively precipitated from alkaline solution by mercuric ion as 1:1 complexes
- ▶ After precipitation with an excess of Hg(II), the complex is removed by filtration and redissolved in an excess of a standard EDTA solution
- ▶ A standardized Zn(II) solution can be employed as the titrant for the excess EDTA using an appropriate method for the detection of the end point
- ▶ This procedure determines the Hg(II) concentration by a back titration and the barbiturate concentration is found by an indirect method since it is equivalent to the Hg(II)




Methods of End Point Detection

- ▶ Visual methods
- ▶ Physical methods



▶ Indicators

- ▶ The end point in complexometric titrations is shown by means of pM indicators
- ▶ The pM 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

- 
- ▶ **pM indicators** or **metal ion indicators** are organic compounds which form coloured complex ions with the metal ion in high dilution
 - ▶ Many of these indicators also have the typical properties of acid-base indicators and the colour changes are the result of the displacement of the H^+ by a metal ions
 - ▶ Metal indicators must comply with the following requirements
 - ▶ Compound must be chemically stable throughout the titration
 - ▶ It should form 1:1 complex which must be weaker than the metal chelate complex
 - ▶ Colour of the indicator and the metal complexed indicator must be sufficiently different
 - ▶ Colour reaction should be selective for the metal being titrated
 - ▶ The indicator should not compete with the EDTA



▶ **Mechanism of action of indicator**

- ▶ Let the metal be denoted by M , indicator by I and chelate by EDTA
- ▶ At the onset of the titration, the reaction medium contains the metal-indicator complex (MI) and excess of metal ion
- ▶ When EDTA titrant is added to the system, a competitive reaction takes place between the free metal ions and EDTA
- ▶ Since the metal-indicator complex (MI) is weaker than the metal-EDTA chelate, the EDTA which is being added during the course of the titration is chelating the free metal ions in solution at the expense of the MI complex
- ▶ Finally, at the end point, EDTA removes the last traces of the metal from the indicator and the indicator changes from its complexed colour to its metal free colour


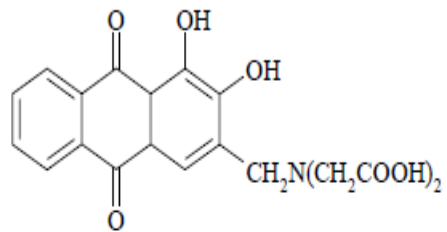
- 
- ▶ Classified according to the chromophore groups responsible for the colour
 - ▶ Hydroxy azo compounds
 - ▶ Mordant black II
 - ▶ Solochrome dark blue(calcon)
 - ▶ Phenolic compounds and hydroxy substituted triphenyl methane compounds
 - ▶ Xylenol orange
 - ▶ catechol violet
 - ▶ Compounds containing an amino methyl dicarboxy methyl group (also triphenyl methane compounds); anthraquinone dyes
 - ▶ Alizarin fluorine blue
 - ▶ Sodium alizarin sulphonate
 - ▶ Miscellaneous
 - ▶ Diphenyl carbazone
 - ▶ Variamine blue
 - ▶ Murexide

Table-1: Indicators used in complexometric titrations

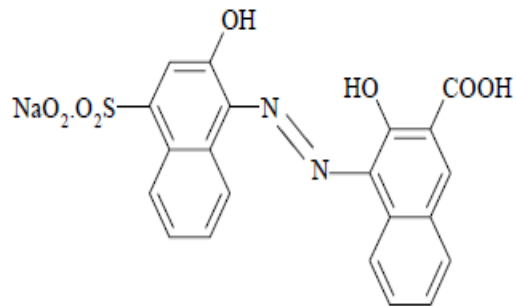
S.No.	Name of the Indicator	Colour change	pH range	Metals detected
1.	Mordant black II	Red to Blue	6-7	Ca, Ba, Mg, Zn, Cd, Mn, Pb, Hg
	Eriochrome blackT			
	Solochrome blackT			
2.	Murexide or Ammonium purpurate	Violet to Blue	12	Ca, Cu, Co
3.	Catechol-violet	Violet to Red	8-10	Mn, Mg, Fe, Co, Pb
4.	Methyl Blue	Blue to Yellow	4-5	Pb, Zn, Cd, Hg
	Thymol Blue	Blue to Grey	10-12	
5.	Alizarin	Red to Yellow	4.3	Pb, Zn, Co, Mg, Cu
6.	Sodium Alizarin sulphonate	Blue to Red	4	Al, Thorium
7.	Xylenol range	Lemon to Yellow	1-3	Bi, Thorium
			4-5	Pb, Zn
			5-6	Cd, Hg

1)



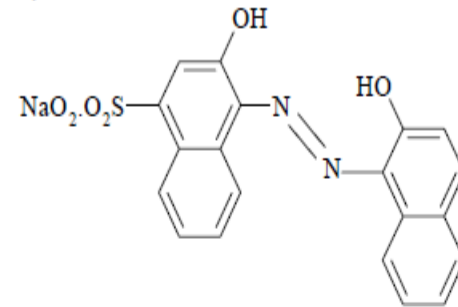
Alizarin fluorine blue (alizarin complexone)

3)



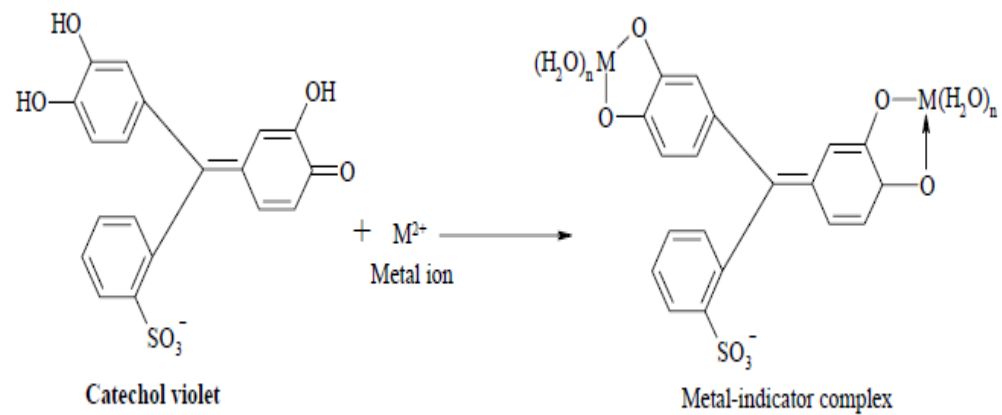
Calcon carboxylic acid

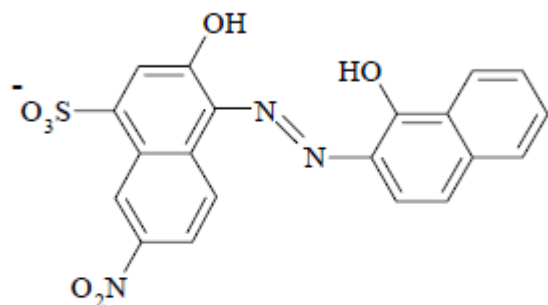
2)



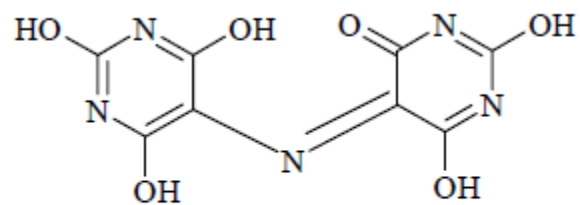
Calcone (mordant black 17)

4)

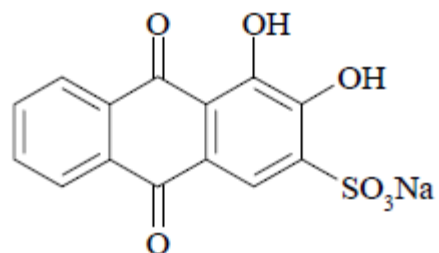




Mordant black II
(Eriochrome black T, Solochrome black T)
Blue (pH 10)



Murexide (violet at pH 10)



Sodium Alizarine sulphonate



▶ Instrumental methods of End point detection

- ▶ Spectrophotometric detection
- ▶ The change in absorption spectrum when a metal ion of a complexing agent is converted to the metal complex, or when one complex is converted to another can usually be detected more accurately and in more dilute solution by spectrophotometric than by visual methods
- ▶ Thus, in disodium EDTA titrations an accurate end point can be obtained using 0.001M solutions



▶ **Amperometric titration:**

- ▶ The effect of complex formation on the half-wave potential of an ion is to render it more negative
- ▶ If the electrode potential is adjusted to a value between that of the half-wave potential of the free cation and that of the complex, and disodium EDTA solution is added slowly, the diffusion current will fall steadily until it equals the residual current, that is, until the last trace of free cation has been complexed
- ▶ This is the end point and the amount of standard disodium EDTA solution added is equivalent to the amount of metal present

▶ Potentiometric titration

- ▶ Since disodium EDTA reacts preferentially with the higher valency state of an ion, it will reduce the redox potential according to the equation,
 - ▶ **$E = E^0 + \log^e [\text{Ox}]/[\text{Red}]$**
 - ▶ where, E = the potential of the electrode
 - ▶ E^0 = the standard electrode potential
 - ▶ [Ox] = activity of the ions in the oxidized state
 - ▶ [Red] = activity of the ions in the reduced state
 - ▶ This method is of limited application owing to the lack of suitable indicator electrodes




▶ **High frequency titrator**

- ▶ This method is particularly suitable for dilute solutions, in some cases with concentrations as low as 0.0002M
- ▶ The ions may be titrated directly in buffered solution or excess reagent can be added to the unbuffered solution and the liberated protons titrated with standard alkali
- ▶ Since buffer solution and other extraneous electrolytes reduce the sensitivity of the titration, their concentration must be kept to a minimum



▶ **Titration Selectivity, Masking and Demasking Agents**

- ▶ EDTA is a very unselective reagent because it complexes with numerous doubly, triply and quadruply charged cations
- ▶ The following procedures will help to increase the selectivity:
 - ▶ Use of masking and demasking agents
 - ▶ pH control
 - ▶ Use of selective metal indicators
 - ▶ Classical separation
 - ▶ Solvent extraction
 - ▶ Removal of anions
 - ▶ Kinetic masking

- 
- ▶ **Use of masking and demasking agents:**
 - ▶ Masking agents act either by precipitation or by formation of complexes more stable than the interfering ion-EDTA complex
 - ▶ **Masking** may be defined as the process in which a substance, without physical separation of it or its reaction products, is so transformed that it does not enter into a particular reaction


▶ Masking by Precipitation


- ▶ Many heavy metals e.g.- Co, Cu and Pb, can be separated either in the form of insoluble sulphides using sodium sulphide, or as insoluble complexes using thioacetamide
- ▶ These are filtered, decomposed and titrated with disodium EDTA
- ▶ Other common precipitating agents are sulphate for Pb and Ba, oxalate for Ca and Pb, fluoride for Ca, Mg and Pb, ferrocyanide for Zn and Cu, and 8-hydroxy quinoline for many heavy metals
- ▶ Thioglycerol ($\text{CH}_2\text{SH}.\text{CHOH}.\text{CH}_2\text{OH}$) is used to mask Cu by precipitation in the assay of lotions containing Cu and Zn




▶ **Masking by Complex formation**

- ▶ Masking agents form more stable complexes with the interfering metal ions
- ▶ The most important aspect is that the masking agent must not form complexes with the metal ion under analysis

- 
- ▶ **Ammonium fluoride** will mask aluminium, iron and titanium by complex formation
 - ▶ **Ascorbic acid** is a convenient reducing agent for iron(III) which is then masked by complexing as the very stable hexacyanoferrate(II) complex. This latter is more stable and less intensely coloured than the hexacyanoferrate(III) complex
 - ▶ **Dimercaprol (2,3-Dimercaptopropanol); (CH₂SH.CHSH.CH₂OH):** Cations of mercury, cadmium, zinc, arsenic, tin, lead and bismuth react with dimercaprol in weakly acidic solution to form precipitates which are soluble in alkaline solution

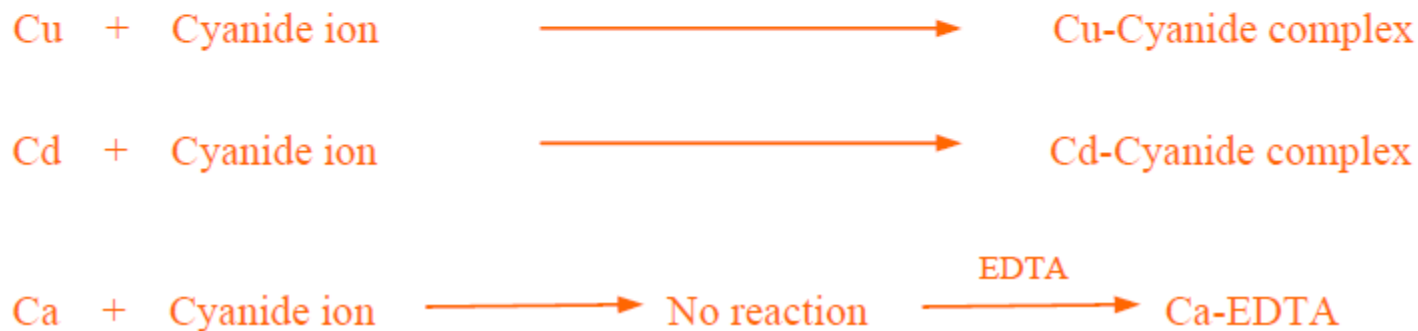
- 
- ▶ **Demasking** is the process by which a masked substance regains its ability to enter into a particular reaction
 - ▶ Formaldehyde
 - ▶ Chloralhydrate
 - ▶ This enables to determine a series of metal ions in one solution containing many cations

- 
- ▶ Decomposition of the masking agent
 - ▶ Replacement of the masked ion in a complex by another ion by which the masking agent forms a stronger complex
 - ▶ Change of pH to alter stability of complex
 - ▶ Changing oxidation state
 - ▶ Volatilization of one of the components of the masked system

Step 1. All three metals are titrated.



Step 2. Only Ca is titrated.



Step 3. Cd and Ca are titrated.





▶ **Preparation of M/20 Disodium EDTA**

- ▶ Dissolve 18.6 gm of disodium EDTA in water and make the volume upto 1000 ml and standardize the prepared solution

▶ **Standardization of Disodium EDTA**

- ▶ Weigh accurately about 200 mg of CaCO_3 in a titration flask. Add 50 ml of water and minimum quantity of dil. HCl to dissolve CaCO_3 . Adjust the pH of the solution to 12 by adding NaOH. Add 300 mg of hydroxyl naphthol blue indicator and titrate with the prepared M/20 disodium EDTA solution, until the solution is deep blue in colour

Estimation of Magnesium Sulphate

- ▶ Dissolve 0.3 g in 50 ml of water, add 10 ml of strong ammonia-ammonium chloride solution and titrate with 0.05 M disodium edetate using 0.1 g of mordant black II mixture as indicator, until a blue colour is obtained

1 ml of 0.05 M disodium edetate \equiv 0.00602 g of MgSO_4

Estimation of Calcium Gluconate

- ▶ Weigh 0.5 g and dissolve in 50 ml of warm water, cool, add 5 ml of 0.05 M magnesium sulphate and 10 ml of strong ammonia solution and titrate with 0.05 M disodium edetate using mordant black II mixture as indicator
- ▶ Carry out a blank titration

1 ml of 0.05 M disodium edetate \equiv 0.02242 g of $C_{12}H_{22}CaO_{14}, H_2O$



THANK
YOU