Chelation

(Chemistry-DSE-1002F1: Physical and Inorganic Chemistry, Section-II)

BY

Dr. Sarita D. Shinde

M.Sc., PhD

Assistant Professor in Chemistry

Vivekanand College, Kolhapur (Autonomous)

Syllabus

Unit-1 Corrosion and Passivity **(8)**

Introduction of corrosion, Electrochemical theory of corrosion, Factors affecting on corrosion: i. Position of metals in the electrochemical series on the basis of standard reduction potential ii. Purity of metal iii. Effect of moisture iv. Effect of oxygen (differential aeration principle) v. Hydrogen overvoltage, Methods of protections of metals from corrosion, Passivity: i. Definition ii. Types of passivity iii. Oxide film theory and evidences iv. Applications of passivity.

Unit-2 Chelation **(7)**

A brief introduction with respect to ligands, chelating agent, chelation and metal chelates, Structural requirements of chelate formation, Difference between metal chelate and metal complex, Classification of chelating agents (with specific illustration of bidentate chelating agents), Application of chelation with respect to chelating agents - EDTA and DMG

Unit-3 Nuclear Chemistry **(10)**

Nuclear reactions and energetic of nuclear reactions, Types of nuclear reactions: i) Artificial transmutation ii) Artificial radioactivity iii) Nuclear fission and its application in Heavy water nuclear reactor iv) Nuclear fusion, Applications of radio-isotopes as tracers: i) Chemical investigation – Esterification ii) Structural determination – Phosphorus pentachloride iii) Analytical Chemistry – Isotopic dilution method for determination of volume of blood iv) Age determination-Dating by C^{14}.

Unit-4 Inorganic Reaction mechanism **(6)**

Introduction, Classification of Mechanism Association, dissociation, interchange and the rate determining steps, SN^1 and SN^2 reaction for inert and labile complexes, Mechanism of substitution in cobalt (III) octahedral complexes, Trans effect and its theories, Applications of trans effect in synthesis of Pt (II) complexes.

Unit-5 Nanomaterials **(6)**

Introduction and Importance of nanomaterials, Properties (Comparison between bulk and nanomaterials): i) Optical properties ii) Electrical conductivity and iii) Mechanical properties, Methods of preparation: Top-down, bottom-up fabrication a) Co precipitation method b) Sol-gel method c) Chemical reduction method d) Hydrothermal method, Applications of Nanomaterials.


Chelation
82
Pb
Hg

- **G. D. Morgan & H. D. K. Drew – Describe the term Chelate (Crab's Claw)**

Metal chelate – *The formation of heterocyclic ring by the association of polydentate ligand or ligands with metal atom or ion.*

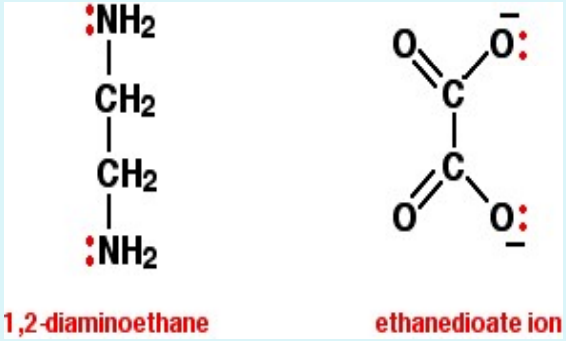
Ligand - Electron pair donor species.

Ligands are two types –

1) Unidentate or monodentate ligand.(are as complexing agent) (Ex. NH_3, H_2O)

2) Polydentate ligand (bi,tri, tetra etc.) (are as chelating agent)

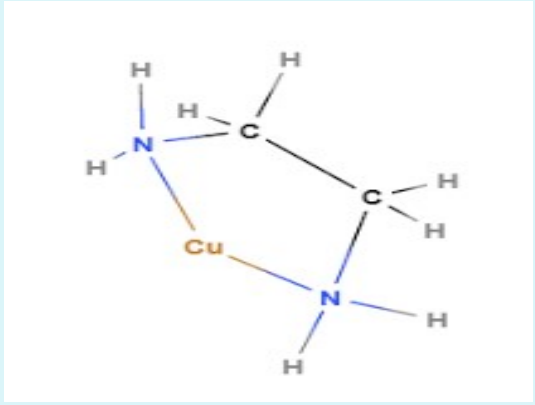
Ex.



1,2-diaminoethane ethanedioate ion

Ex. - M + Chelating agent ⟶ Metal Chelate

Cu^{++} + $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$ ⟶



➢Structural Requirements for Chelate Formation -

1) The chelating agents should have donor atoms. Ex. O, N, S, P.

2) The chelating agents must contains donor groups. Ex. $–NH_2$, -COOH, =NOH, -OH, SH.

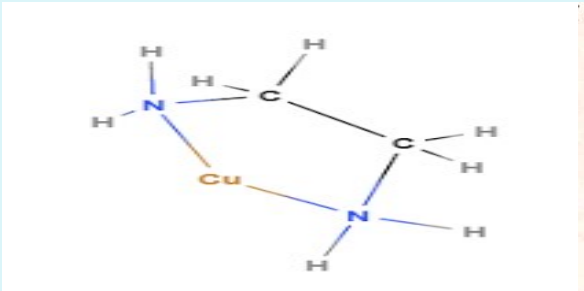
3) Essential to form heterocyclic ring between chelating agents & metal ion.

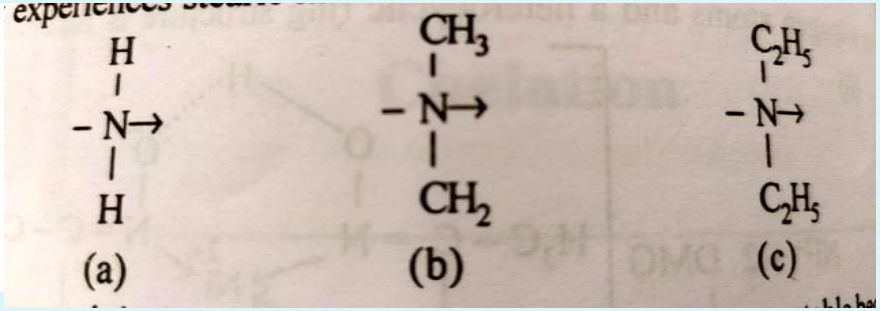
4) Metal chelate should be free from strain.

5) There should not be contain bulky group on donor atoms.

6) Size should be proper to avoids steric hindrance

7) Metal ion should have adequate size, higher charge, & suitable vacant 'd' orbital.





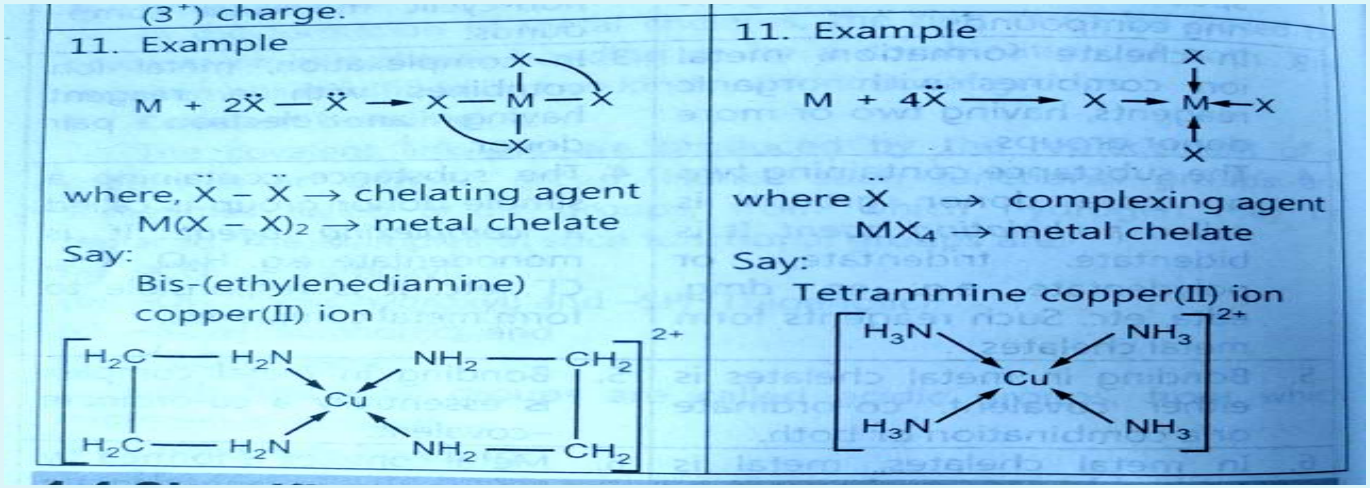
Distinction between Metal Chelate & Metal Complex

Metal Chelate

- Approaching ligand is polydentate.
- It is formed when metal ion treated with polydentate ligand under specific condition
- Nature of chemical bond is Co-ordinate or covalent or both.
- The formation of heterocyclic ring is essential.
- It has high stability
- Even in solution they dissociate negligibly.
- They may or may not have regular shape

Metal Complex

- Approaching ligand is unidentate
- It is formed when metal ion treated with unidentate ligand under specific condition
- Nature of chemical bond is Co-ordinate.
- The ring system is absent
- Relatively it has low stability
- Comparatively they dissociate more in solution.
- They have generally regular shape



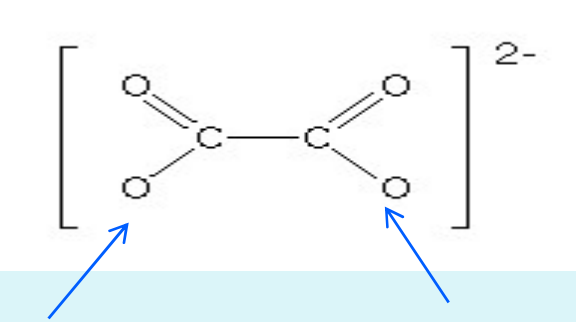
Classification of chelating ligand – Chelating ligand(specially bidentate) are

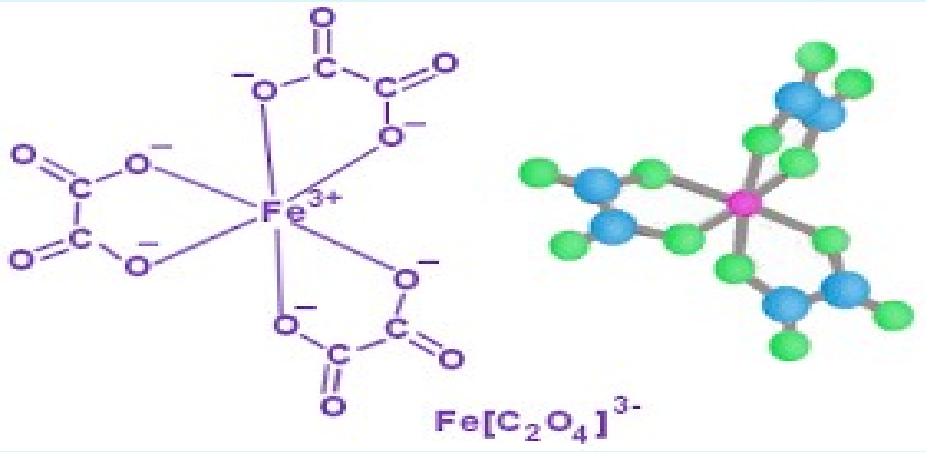
Classified two types – I) On the basis of group

II) On the symmetry of group

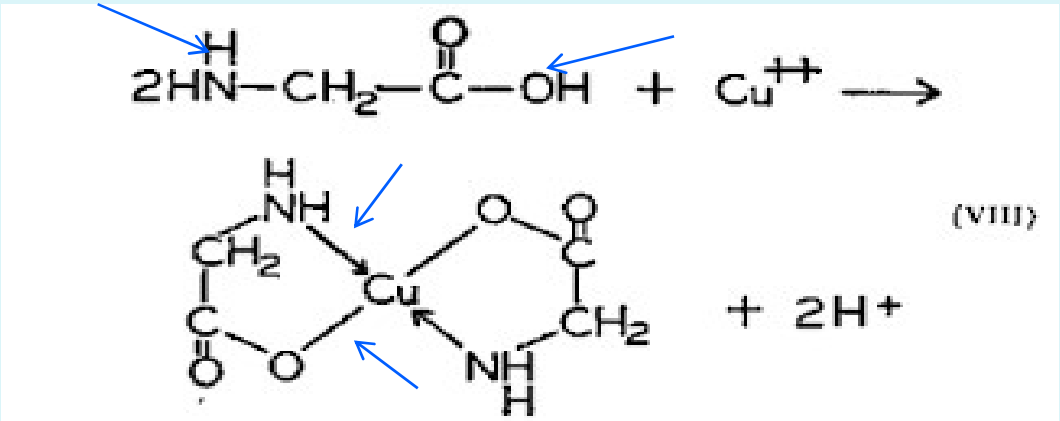
I) On the basis of group – bidentate chelating agents are three types on nature of group

A) Two acidic groups – Ex. Oxalate ion

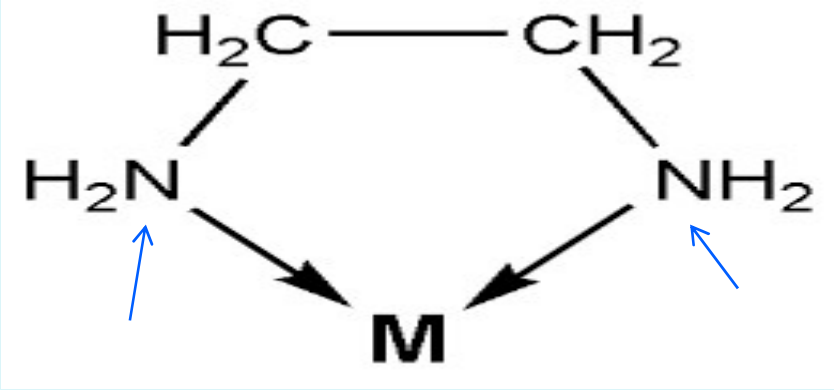




B) One acidic & One Co-ordinating groups – Ex. Glycine

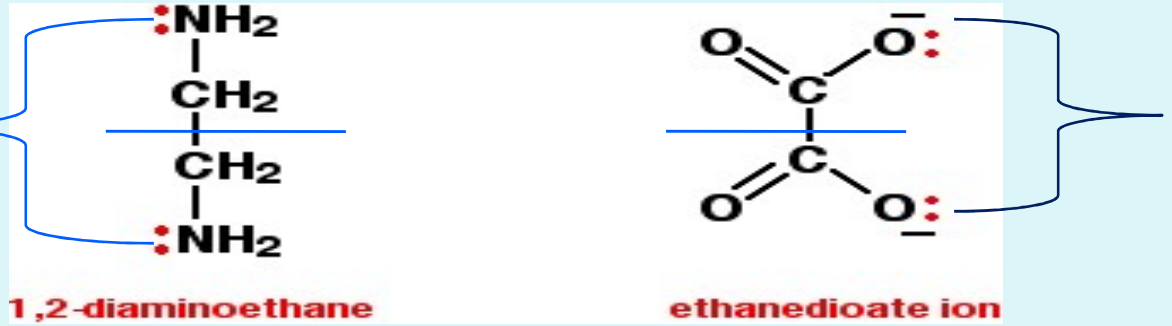


C) Two Co-ordinating groups.- Ex. Ethylene diamine



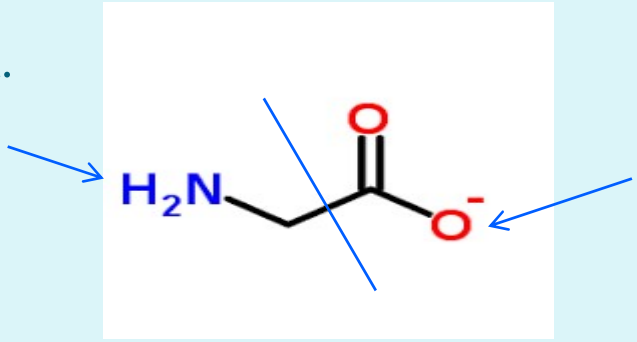
II) On the symmetry of group – bidentate chelating agents classified on symmetry are two types

A) Symmetrical Chelating agents – both donor groups are same i.e. (AA) type ligand



B) Asymmetrical Chelating agents- both donor groups are different i.e. (AB) type ligand

Ex. Glycinate ion.



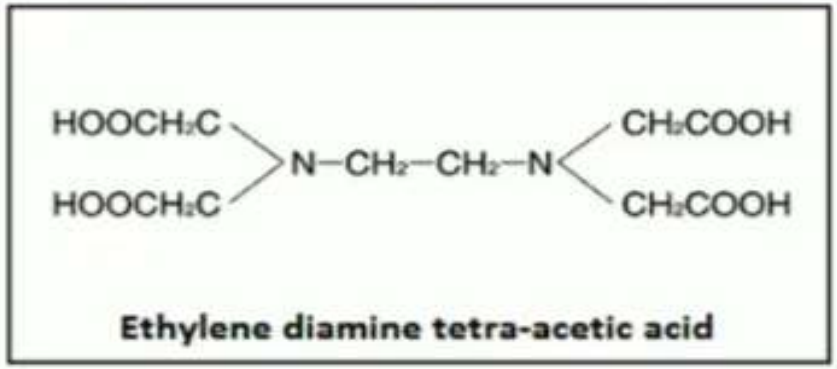
Applications of Chelation

- **Chelation** means "to grab" or "to bind."

- **Chelation** is the formation of multiple coordination bonds between organic molecules and a transition metal ion leading to sequestration of the metal.

* sequestration: the act of removing or separating.

Use of EDTA as chelating agent



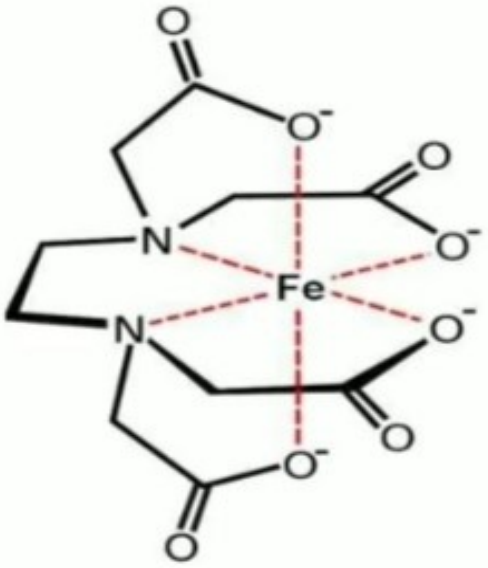
Ethylene diamine tetra-acetic acid

1.Water Softening: Softening is the process of removing the dissolved **calcium** and **magnesium** salts that cause hardness in water.

Hard Water	Soft Water
1) Contains dissolved salts of Ca^{2+} and Mg^{2+}	Does not contain such dissolved salts.
2) Does not forms lather with soap.	Forms lather with soap.
3) Large quantity of soap is required during washing.	Soap is not wasted at all.

2. Removal of dissolved salts of iron from water supply

- The presence of iron in water decolourises wash basin, linens and forms sediments on standing.
- Use of EDTA prevents ill effects of iron. The dissolved disodium salt of EDTA in water forms very stable metal chelate with ferric ion containing five membered rings.



3.Food preservation

- **It is our common observation that:**
  1. cut apples become brown in colour
  2. fats and oils become rancid (smelling or tasting unpleasant)
  3. orange juice loses its flavour on keeping
- Its due to traces of metal ions present in them.
- The addition of EDTA forms metal chelates preventing the damage and it improves the keeping qualities of such food to a very great extent.
- EDTA preserves the food and promote its color, texture and flavor.

4. To evaluate total hardness of water

The known volume of hard water sample (i.e. Ca^{+2} and Mg^{+2} ions) is titrated against standard EDTA solution using Eriochrome black T indicator and hardness of water can be determined.

5.In medical field

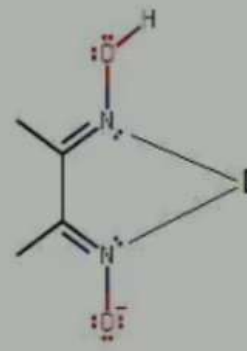
- It can be used as a medicine to treat copper and lead poisoning.
- Removal of radioactive metals from the body fluids.
- Creams containing EDTA are used to treat skin diseases like dermatitis.

6. Titrimetric estimation

EDTA is widely used for the estimation of:

- Almost all metals titrimetrically, e.g. Al, Fe, Cd, Zn, Cu, Co, Hg, Pb, Ca, Mg, Th, U etc.
- Certain anions such as SO_4^{-2}, AsO_4^{-3}, F^- $[Fe(CN)_6]^{-4}$. PO_4^{-3}, CrO_4^- .
- Most of the commercial materials like alloys, ores, rocks, petrol, leathers, cements, minerals, oils, paints etc. can be analysed by EDTA.

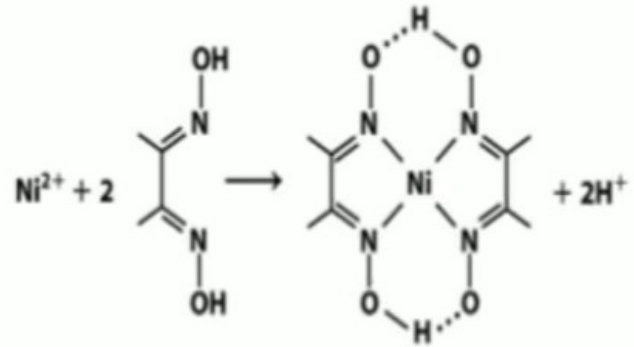
Use of DMG as chelating agent



Structure of dimethylglyoximato ligand

- **DMG was discovered by L. Tschugaeff in 1905.**
- **Used by Brunke in 1907 for the determination of nickel in steel**

- To measure Ni in steel, the alloy is dissolved in 12 M HCl and neutralised in the presence of citrate ion, which maintains iron in solution.
- The slightly basic solution is warmed and dimethylglyoxime (DMG) is added to precipitate the red DMG-nickel complex quantitatively.
- The product is filtered, washed with cold water, and dried at 110 °C.



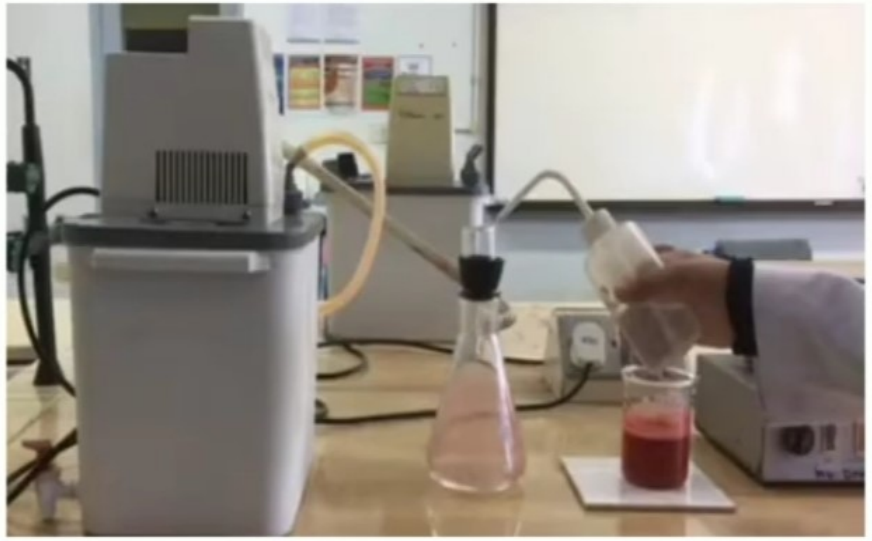
Harris 8th ed., pg 681.

1.Estimation of nickel

- *Gravimetric estimation of nickel*
- *Volumetric estimation of nickel*
- *Colorimetric estimation of nickel*
- **DMG as spot test reagent**

➢ ***Gravimetric estimation of nickel:*** Nickel solution is first acidified, boiled and 1% alcoholic DMG in excess is added to precipitate nickel as scarlet red precipitate in presence of ammonia. The solution is heated for some time and cooled. After an hour it is filtered, washed, dried (at 100^0 – 120^0 C), weighed and the amount of nickel is calculated.

Gravimetric estimation : A method of quantitative chemical analysis in which the constituent wanted is converted into a substance (of known composition) that can be separated from the sample and weighed.



- ***Volumetric estimation of nickel :*** The precipitate of Ni as a Ni DMG chelate is washed and then dissolved in 12N H_2SO_4 solution. The solution is boiled and treated with 50 ml. of 4% ferric sulphate solution. Then it is heated, cooled, diluted by water and 3 ml H_3PO_4. and then titrated against 0.1N $KMnO_4$ solution and amount of nickel is calculated.

Volumetric *estimation*, any method of quantitative chemical analysis in which the amount of a substance is determined by measuring the volume of a second substance that combines with the first in known proportions

- ***Colorimetric estimation of nickel :*** Here Ni (II) is oxidised to Ni (IV) by bromine water. Then it is treated with DMG in ammoniacal medium, so as to produce intense red colour which is measured colorimetrically. DMG *is sensitive, selective and special reagent for nickel.*

Colorimetric analysis is a method of determining the concentration of a chemical element or chemical compound in a solution with the aid of a color reagent.

- **DMG as spot test reagent :** As it is specific reagent for nickel, it is used in the qualitative analysis as a spot test reagent. Here sample solution is treated with drop of 1% alcoholic DMG on spot paper and the paper is exposed to ammonia vapours. Appearance of red spot indicates the presence of nickel.

Spot test: A **test** for the identification of an element or compound by means of a reagent that produces a characteristic color change or precipitate.

2.Estimation of *palladium*

- ***Gravimetric estimation of palladium :*** Palladium is precipitated as a yellow coloured complex by DMG from dilute mineral acid solution and estimated.





THANK YOU