Gravimetric Analysis

- It is quantitative analysis in which the end product is weighed and from that weight composition of analyte is determined.
- Hence gravimetric analysis is based upon the measurement of the weight of a substance of known composition which is chemically related to the analyte.

Types of Gravimetric Analysis:

I. **Precipitation Gravimetry:** This involves chemical precipitation of the constituents.

II. **Volatilization Gravimetry:** In this method, the constituents are decomposed due to volatilization at a suitable temperature.

III. **Electrogravimetry:** This involves electrolysis to deposit the metal from the solution on a solid electrode so that its mass can be determined.

IV. **Thermogravimetry:** In this type, the sample is heated and with the change in temperature changes in mass of the sample are recorded.

Precipitation Gravimetry:

1. **Steps involved in Precipitation Gravimetric Analysis**

i. Preparation of the test solution

ii. Precipitation

iii. Digestion of precipitate

iv. Filtration of precipitate

v. Washing of precipitate

vi. Drying and / or ignition of precipitate

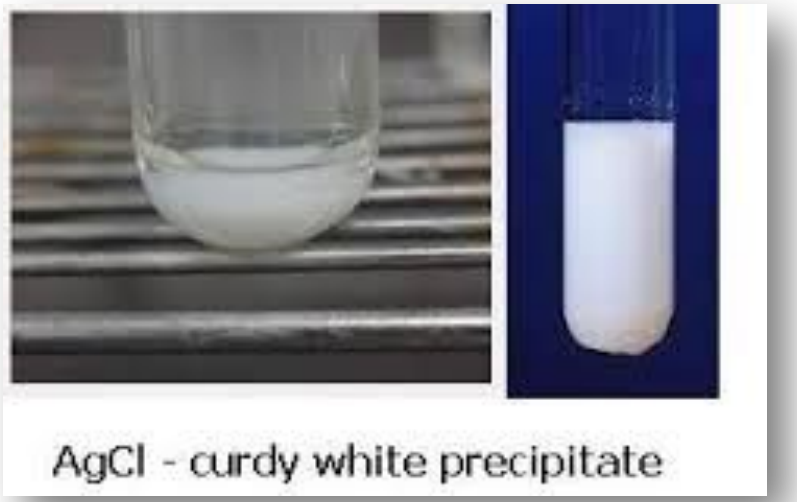
vii. Weighing

viii. Calculation

During this gravimetry precipitate is formed which of mainly three types.

Crystalline Precipitate: This precipitate is relatively pure and easily filterable.

Curdy Precipitate: This precipitate is colloidal particle size but are filterable.



Gelatinous Precipitate: This precipitate is flocculated colloids. The particle size is smaller than curdy precipitate and difficult to filter.

2. Conditions for Precipitation:

- Precipitation is an ionic reaction of mixing of +ve ions of one substance and -ve ions of another substance to from a sparingly soluble substance.
- The completeness of a precipitate depends on equilibrium solubility of a precipitate.
- The **solubility** of any substance is defined as the amount of the substance dissolved in a solvent at a given temperature and is expressed in gram / dm^3 or mol / dm^3.
- **Solubility product** is defined as the product of concentration of the constituent ions raised to the appropriate power depending on the number of ions present in a molecule of the compound. (Saturated solution)

$$aA_{(s)} \rightleftharpoons cC_{(aq)} + dD(aq)$$

$$K_{sp} = [C]^c[D]^d$$

- Both the solubility and solubility product are temperature dependent. If temperature is increases, solubility and solubility product is also increases.

- Most important condition for precipitation is that the **ionic product** ***(product of the concentration of the salt at any concentration)*** **must be greater than the solubility product of the salt.**

  When,

  Ionic product > Solubility product = Precipitate formation

  Ionic product = Solubility product = Saturated solution

  Ionic product < Solubility product = Unsaturated solution

Factors affecting the solubility, solubility products and completeness of a precipitates

- **Common Ion Effect:**

  Presence of an ion common with ions of the salt decreases the solubility of the salt.

  The solubility of the salt is less in presence of a common ion compared to pure water. This effect is known as the common ion effect.

Example: The solubility product of $BaSO_4$ is $1x10^{-10}$ mol/dm^3

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{-2}(aq)$$

x x

Let 'x' is the solubility of the salt in mol/dm^3

$$K_{sp} = [Ba^{2+}] [SO4^{2-}]$$

$$1x10^{-10} = x^2$$

$$x = 10^{-5} \text{ mol/dm}^3$$

Solubility of $BaSO_4$ in 0.1 M H_2SO_4

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

0.1 M 2 X 0.1 M 0.1 M

Due to presence of H_2SO_4, SO_4^{2-} ions are common ion, therefore

$$K_{sp}[BaSO_4] = [Ba^{2+}] [SO_4^{2-}]$$

x x + 0.1

But $x << 0.1$

$$K_{sp}[BaSO_4] = (x)\ (0.1)$$

$$1x10^{-10} = [Ba^{2+}]\ [0.1]$$

$$[Ba^{2+}] = 1x10^{-10} / 0.1$$

$$[Ba^{2+}] = 1x10^{-9}$$

This shows decrease in solubility due to common ion effect.

- **Diverse Ion Effect:**

If the solubility of sparingly soluble salt increases in presence of foreign ions, that ions are not common to those of the salt. This effect is known as diverse ion effect or salt effect or activity effect.

Example: Solubility of $BaSO_4$ is increased by 70% in 0.1M solution of potassium nitrate than in water.

- **Temperature:**

Solubility of any salt increases with increase in temperature. The increase in solubility of two salts with increase in temperature may be different.

Example: Solubility of AgCl in water increases 12 times when temperature is increases from 273K to 383K. While at the same increase of temperature the solubility of $BaSO_4$ in water is doubled only.

- **pH:**

  The solubility of substance depends on pH of the solution from which that is precipitated.

  The change in pH is brought by addition of strong acid or a base.

  If the salt is of strong acid or strong base type, then addition of acid or base will produce diverse ion effect. This increases the solubility to small extent.

  On the other hand, if the salt is of weak acid or weak base then solubility is increases to high extent.

  Example: Consider a salt of weak acid, a strong acid is added to change pH. The hydrogen ion from the added strong acid react with anion of salt and form the weak undissociated acid, to maintain the solubility equilibrium more and more salt dissolves.

- **Complexation:**

  In many cases precipitating agent itself may act as complexing agent dissolving the precipitate by converting it in to a complex.

Example: The cyanide ions act as precipitating agent for silver ions forming precipitate of AgCN. But the AgCN is dissolved in excess of the cyanide ions forming a complex $[Ag(CN)_2]^{1-}$

$$Ag^{1+}_{(aq)} + CN^{1-}_{(aq)} \rightleftharpoons AgCN_{(s)}$$

$$AgCN_{(aq)} + CN^{1-}_{(aq)} \rightleftharpoons [Ag(CN)_2]^{1-}_{(aq)}$$

- **Nature of the solvent:** Polar solvents like water will always favour dissolution of the polar or ionic solute but nonpolar solvent not favour dissolution.

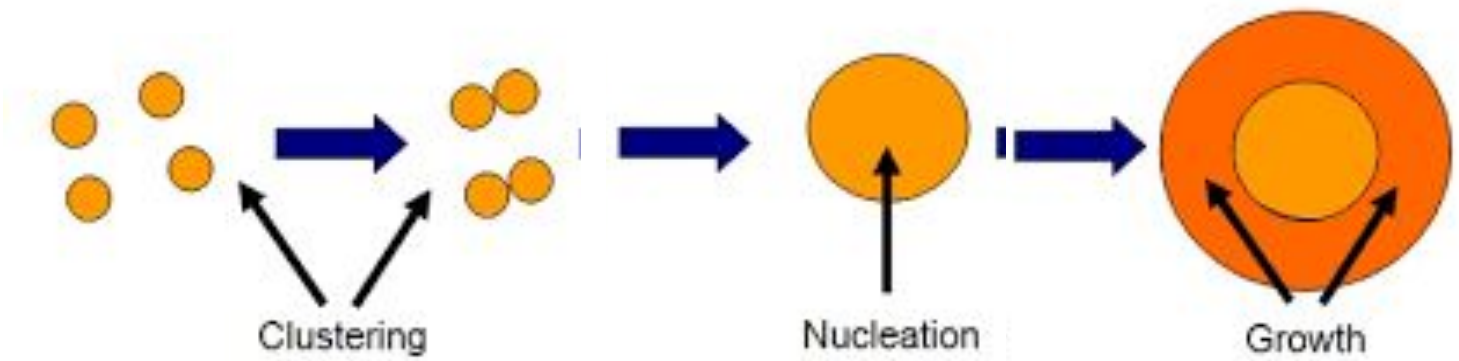
Example: Solubility of a salt like calcium sulphate in water can be decreased by addition of a less polar solvent like ethanol to it.

- **Controlling Particle Size:**
  - The purity and filterability depends upon the particle size of the precipitate.
  - If there are colloidal suspensions (1nm to 10^3nm) which are invisible to naked eye, not easily settled down and not easy to filter.
  - On the other hand if crystalline precipitate is form, it is easily get settled down and easily filtered.
  - During the precipitation process, initially small particles known as nuclei are formed and subsequently the size of these nuclei is increased to large enough to settled down.

  The particle size is therefore determined by the relative rates of **Nucleation** and **Growth of Crystals.**

- **The process of Nucleation:**
  - Precipitation is beginning with the attraction of ions towards each other due to electrostatic forces between them.
  - This results in to formation of ion pairs.
  - These ion pairs grow further by the addition of ions or ions pairs to form ion clusters.

- The ion clusters can be separated easily into ion pairs till they attain some minimum size known as critical size.
- Once the critical size is attained, the ion cluster becomes the nucleus (Nucleation) and continues to grow to form crystals.



There are two types of Nucleation process.

i. **Heterogenous Nucleation Process**: In this process nuclei formed by clustering of ions around another particle.
ii. **Homogenous Nucleation Process**: In this process nuclei formed by clustering of ions, by themselves and arranging in a definite pattern.

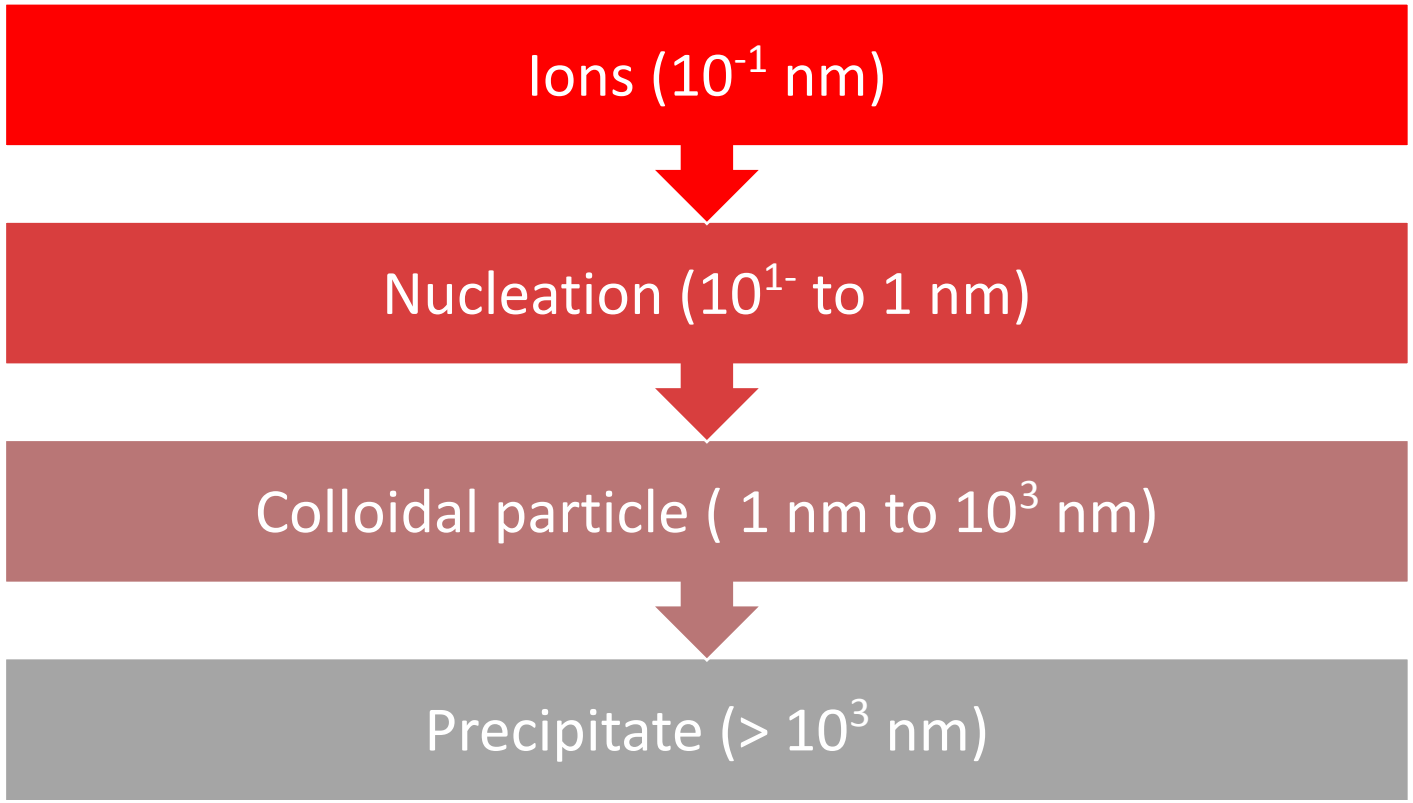
The precipitation process occurs in three stages:

i. **Nucleation:** Collision of ions in supersaturated solution to yield primary nuclei.

ii. **Formation of Colloidal Particles:** Aggregation of ions around primary nuclei forming colloidal particles.

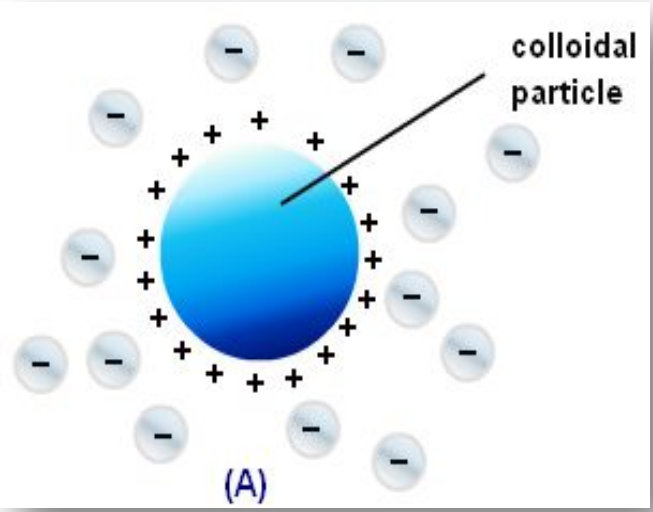
iii. **Growth of Colloidal Particles:** Growth of Colloidal particles to form particles which settle as precipitate.

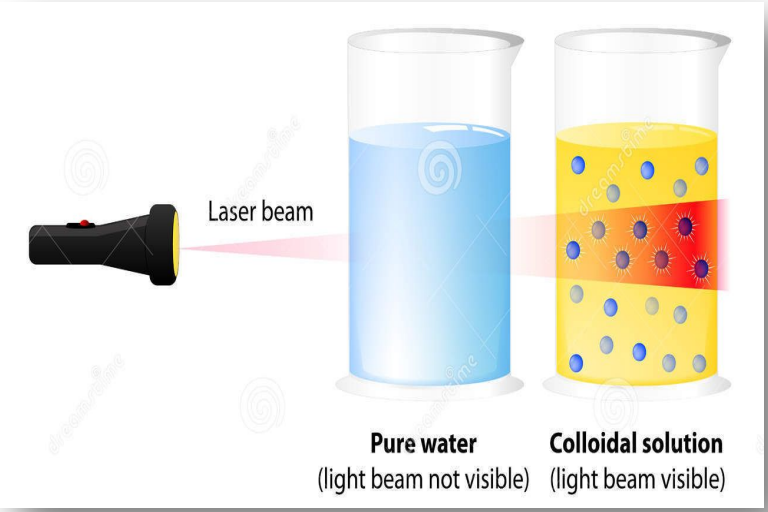
The precipitation process can be represented as,

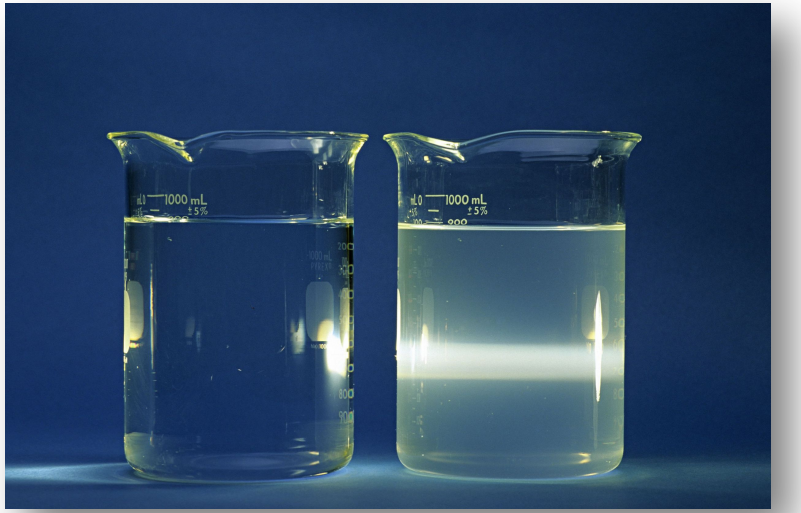


Colloidal State:

- The colloidal state has particle size ranging from 1 nm to 10^3 nm.
- Charge on colloidal particles arises due to adsorption of ions on the surface of the catalyst.
- Due to charge, these particles migrate in an applied electrical filed, and colloidal particles scatter light. The scattering effect is known as the Tyndall effect.
- Colloidal particles are involved in the random motion which is known as Brownian movement.
- These particles absorb ions from the solution which are present in large concentration in the solution.







Impurities in the Analytical Precipitate:

Once the precipitate is formed, it has to be treated as it can be contaminated. The contamination of a precipitate is due to two reasons.

i. **Co-precipitation**:
   - The phenomenon in which the impurity is soluble and it is precipitated along with the main precipitate causes the contamination of precipitate is known as co-precipitation.
   - Co-precipitation may be due to surface phenomenon (adsorption), occlusion (trapping of impurity during crystal growth) and mechanical entrapment (The process of random incorporation of comparatively small quantities of other phases (e.g. water, dust, particles, etc.) in the bulk of a precipitate during its formation).

ii. **Post-precipitation:**
   - The phenomenon in which an impurity which occurs on the surface of the first precipitate after appreciable time is known as post-precipitation.
   - The contamination of precipitate is removed by digestion, filtration and washing.

Completion of Precipitation:

- When the beaker containing the precipitate is allowed to stand in water bath for digestion, after some time the precipitate settles down and the clear solution is obtained above the settled precipitate.
- Completion of precipitation is confirmed by adding little volume of precipitating agent from the walls of beaker, if there is no more precipitate form, indicates the completion of precipitation.

Role of different steps:

a. Digestion: (Ageing or Ostwald Ripening)

- When the precipitation is carried out from the concentrated solution, the particles of precipitate (colloids) obtained have imperfect structure and size.
- Such crystals are difficult to filter. This can be resolved by keeping such precipitate for digestion.
- **Digestion** is the process in which the precipitate is allowed to stand for an hour or more in contact with hot solution from which it is formed.

Before Digestion

Digestion

After Digestion

- During this process, smaller particles dissolves and the solution becomes saturated with larger particles.
- The dissolved particles get redeposited on larger particles. This increases the average particle size. This process is called digestion or ageing or Ostwald's ripening.
- As the particle size is increased, the surface area is decreased and hence the concentration of co-precipitated impurities adsorbed on precipitate is also decreased.
- The occluded impurities are also exposed to the solution during digestion and they pass into the solution.

b. Filtration:

Filtration is the separation of precipitate from the mother liquor. The main object of this is to obtain the precipitate free from solution.

Filtration is carried out by two ways.

i. **Filtration by using Filter Paper**: Whatman filter paper which is ash less is used for the filtration.

Three qualities of filter papers are generally made,

one for **fine particles**,

second for **average precipitate of medium sized particles** and

third for **gelatinous and coarse particles**.

The precipitate collected on filter paper is further dried and ignited to a constant weight.

ii. Filtration by Counterpoise method:

In this method, sintered glass crucible is used for the filtration.

The sintered glass crucibles are made up of resistance glass and have a porous disc of sintered ground glass fused at the bottom of the crucible.

During the filtration, a previously weighed sintered crucible is connected to vacuum pump and filtration is carried, precipitate is washed with appropriate wash solution. After filtration, the crucible with precipitate is dried in an electric oven at a constant temperature. Finally, the weight of crucible with precipitate is recorded from which weight of precipitate is obtained which used for further calculation.

c. Washing:

Most of precipitates are obtained in presence of one or more soluble compound or contaminants. As these are non-volatile at the temperature at which the precipitated is dried, it is necessary to wash the precipitate to remove such substance completely.

Characteristics of washing solution:

i. It should have no action on the precipitate but capacity to dissolve the impurity.

ii. It should not form any volatile or insoluble substance with precipitate

iii. It should be volatile at the temperature of drying of precipitate

Water is mostly used as a wash solution if precipitate is insoluble in water. If precipitate is soluble in water then an electrolyte containing common ion is added in water and then it is used as wash solution.

d. Drying and Ignition of Precipitate:

Heating of precipitate below 250^{o}C is referred as drying. The purpose of drying and ignition of precipitate is to obtain a compound of known and constant composition. During this drying, the water associated with the precipitate is also get remove.

The drying is depending on the way in which he filtration is carried out. If the filtration is carried out.

i. If the filtration is carried out in a sintered glass crucible then the drying will be done in an oven with the temperature range of 100 to 150^{o}C and weighed to a constant weight.

ii. If the filtration is carried out with Whatman Filter paper then the filter paper along with the precipitate is dried on a cone with care that the filter paper does not charred in the process.

The precipitate along with the filter paper is ignited to white ash in a crucible.

The crucible is cooled to room temperature and then transferred to a desiccator and finally weighed to a constant weight.

Applications of Gravimetric Analysis:

1. Determination of Sulphur in Organic Compounds

Sulphur present in an organic compound can be estimated gravimetrically by the **Carius Method**.

Principal:

Sulphur present in the given organic compound is oxidised to sulphuric acid by digesting with fuming nitric acid. Sulphuric acid so formed is then quantitatively precipitated as barium sulphate by addition of excess barium chloride. The precipitate of barium sulphate is suitable treated and weighed.

Procedure:

- A known mass of the organic compound is heated strongly with fuming nitric acid in a sealed tube, known as Carius tube, for about 2 hours.
- The contents of Calcium tube are cooled and treated with excess barium chloride solution to precipitate SO_4^{2-} ions present in the solution as $BaSO_4$.
- The precipitate of barium sulphate is filtered, washed, dried and then weighed.

Calculation:

Mass of organic compound = W_1 g

Mass of precipitated $BaSO_4$ = W_2 g

From stoichiometry,

1 $BaSO_4$ ≡ 1 S

1 mol $BaSO_4$ ≡ 1 mol S

i.e. Molar mass $BaSO_4$ ≡ Atomic Mass of S

i.e. 233 g ≡ 32 g

Mass of S in W_2 g of $BaSO_4$ = $\frac{W_2 \times 32}{233}$

≡ W_3 g

and % S in compound = $\frac{W_3}{W_1} \times 100$

2. Estimation of Nickel in Cu-Ni alloy using dimethyl glyoxime

Principal:

The amount of nickel can be determined by precipitation with dimethyl glyoxime from slightly ammoniacal solution.

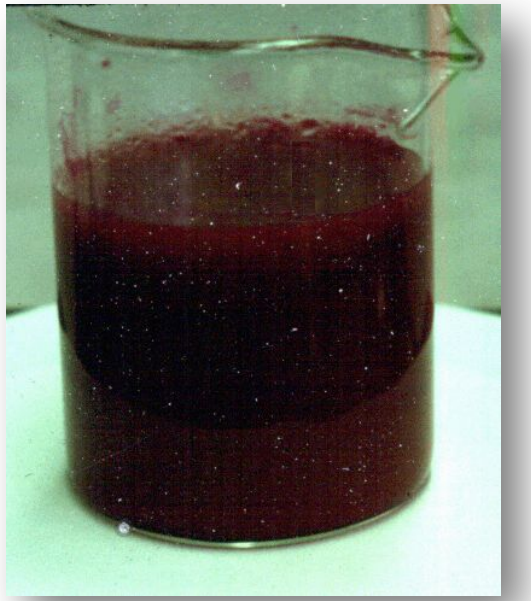
Procedure:

a. Removal of Copper:

- Known weight Cupronickel alloy added in concentrated nitric acid and heat till dissolves and sample is nearly reduced to dryness.
- Then the solution is extracted with dilute sulphuric acid and diluted with distilled water in a standard measuring flask.
- A definite volume of solution is pipette out and sufficient volume of hydrogen gas (H_2S) is passes to precipitate all Cu^{2+} ions present as CuS.
- Filter the solution, wash the precipitate and carefully collect the filtrate and washing in a beaker.

b. Ni^{2+} Estimated as Ni-DMG complex:

- Heat the solution to about 70-80^{o}C to remove H_2S and add about 20 cm^3 of 1% ethanolic solution of dimethyl glyoxime (DMG) followed by adding dilute ammonia with constant stirring until the smell of ammonia persists.
- Digest the precipitate about 30 minutes or till the precipitate is settles.
- A drop of DMG is add to test for complete precipitation.
- Filter through a weighed Gooch crucible and wash with cold water until free from chloride.
- Dry in an oven at 110^{O}C for about 30 minutes, cool in a desiccator and weigh.



Calculation:

Weight of Gooch Crucible	=	W_1 g
Weight of Gooch Crucible + Ni-DMG Complex	=	W_2 g
Weight of Ni-DMG complex	=	$W_2 - W_1 = W_3$ g
$Ni(C_4H_7O_2N_2)_2$	≡	Ni
i.e. 288.69 g Ni-DMG	≡	48.69 g Ni
W_3 g	=	$\frac{W_3 \times 53.69}{288.69}$
Weight of Nickel	≡	W_4 g

3. Determination of Aluminium by converting it to its oxide

Principle:

Aluminium is precipitated as its hydroxide (gelatinous in nature) and ignited to the oxide. Aluminium hydroxide is amphoteric and hence pH range during precipitation must be controlled.

Procedure for Aluminium estimation as Al_2O_3

Pipette out a definite amount of the acidified solution containing Al^{3+} and heat the solution for about 2-3 minutes.

Add about 2 g of NH_4Cl with stirring and then 6N Ammonia solution till the smell of ammonium persists and a gelatinous white precipitate of $Al(OH)_3$ is obtained.

Digest the precipitate for a short period.

The solution with precipitate is filtered through Whatman Filter Paper No. 42 and tested for complete precipitation.

The precipitate is then washed with 1% NH_4NO_3 solution.

- Washing is done till all chloride ions have been removed.
- The precipitate is dried, ignited in a previously weighed silica crucible.
- After heating for about 30 minutes, the crucible is cooled and kept in a desiccator (due hygroscopic nature of Al_2O_3) and then weighed.

Calculation:

Weight of Silica crucible + lid	=	W_1 g
Weight of Gooch Crucible + lid + Al_2O_3	=	W_2 g
Weight of Al_2O_3	=	$W_2 - W_1 = W_3$ g
Now, 1 Al_2O_3	≡	2 Al
i.e. 102 g Al_2O_3	≡	54 g Al
W_3 g	=	$\frac{W_3 \times 54}{102}$
Weight of Al	≡	W_4 g