

Gravimetric Analysis

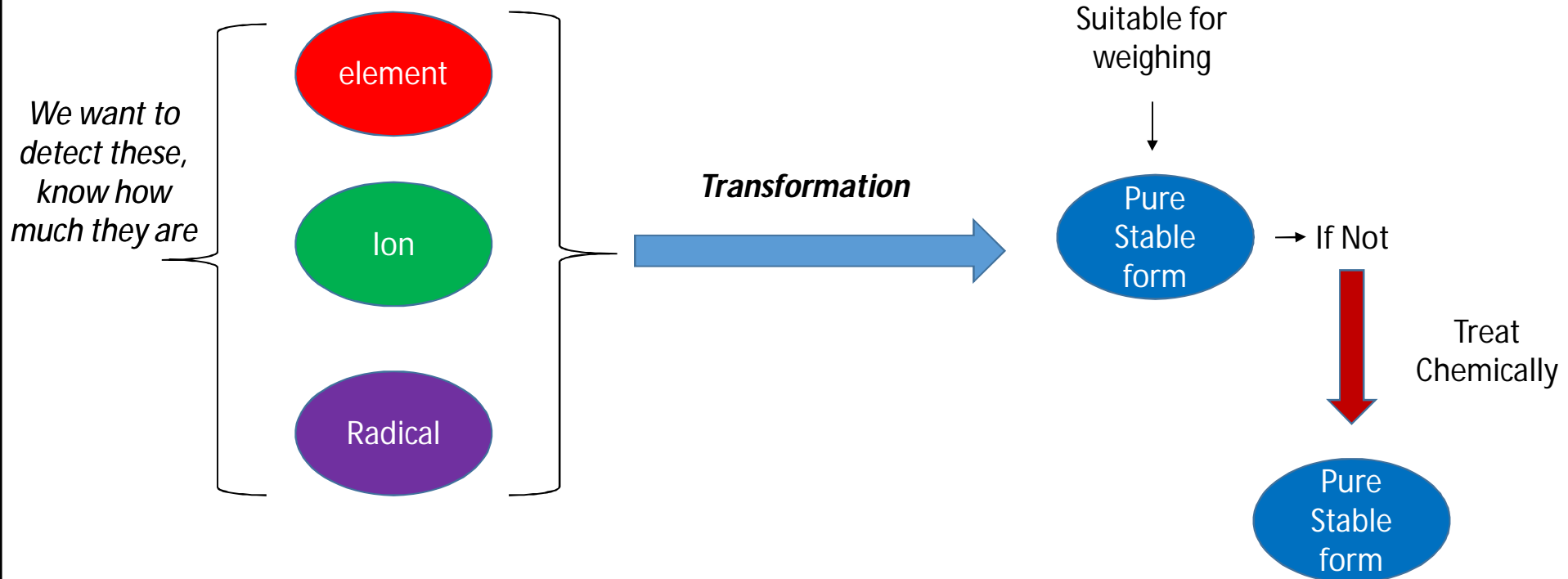
Lecture

By

Dr. Shariq Syed

Introduction to Gravimetry

(Gravi + Metry) = Weigh + measure

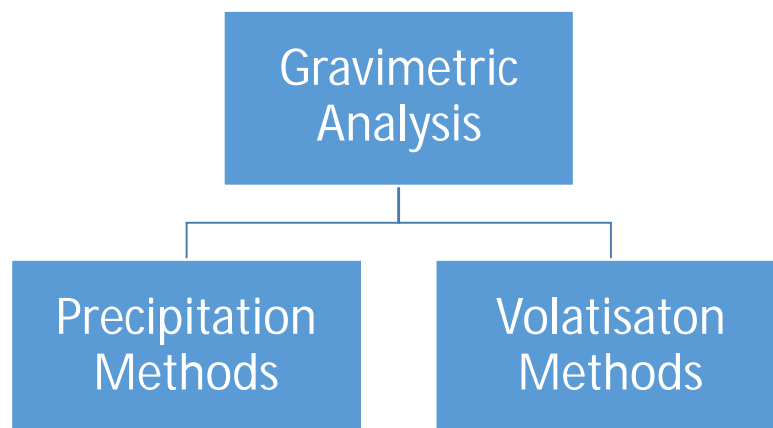


Introduction to Gravimetry

- Process of **producing and weighing** a compound or element in as pure form as possible after some form of chemical reaction is carried out
- Transformation of element, ion or radical into pure stable compound
 - which is suitable for direct weighing or
 - conversion to another form that can readily be quantified

Gravimetric Analysis

Classification based on how the substance to be measured is created

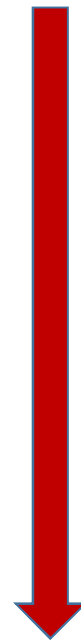


**Substance either
Precipitated from
solution

or volatized and
absorbed**

STEPS INVOLVED IN GRAVIMETRIC *PRECIPITATION*

- Preparation of the sample solution
- Precipitation process
- Digestion (or) Ostwald ripening
- Filtration
- Washing
- Drying
- Igniting
- Weighing
- Calculation



Precipitate Formation Stages

Super-saturation

- First step of precipitation
- Solute/Analyte conc \gg Equilibrium solubility
- Extent of super-saturation determines particle size, filtrability

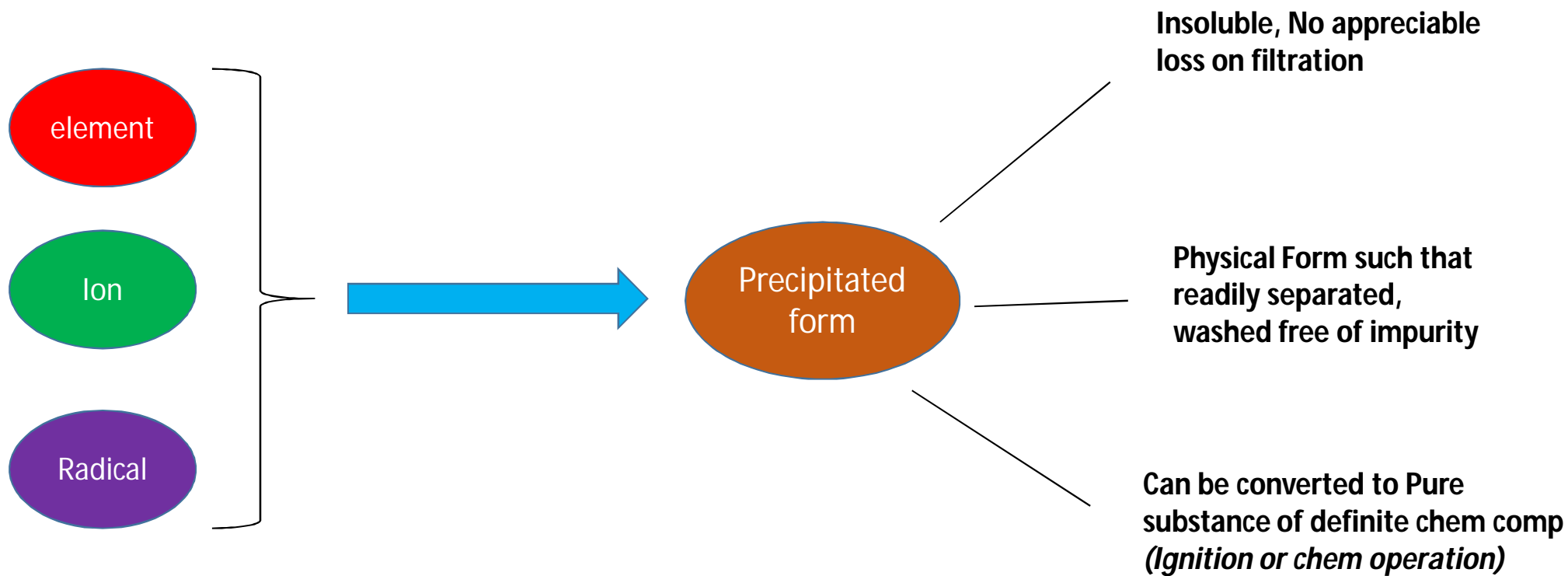
Nucleation

- Formation of more stable phase
- Aggregation of ions/elements to form sub-micro nuclei

Precipitate Particle Growth

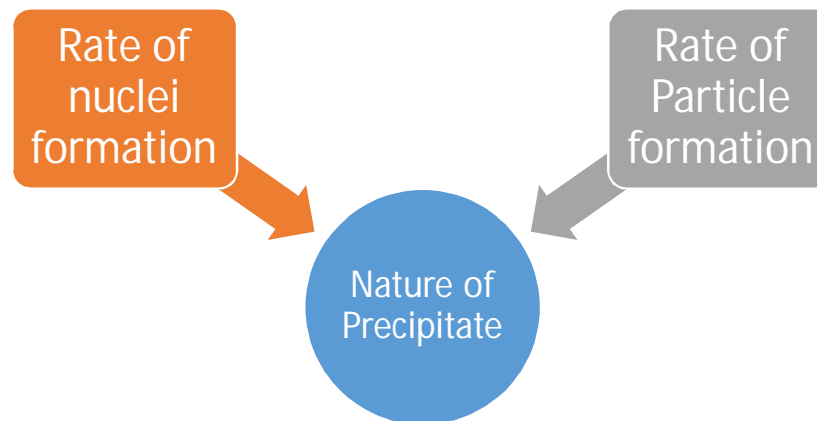
- Precipitation (Ppt) continues
- Ion/elements added to nuclei leading to particle growth

Factors determining successful Precipitation



Nature of Precipitate

Physical nature of Ppt will be determined by relative rates of nucleation and particle growth



Nature of Precipitate

Rate of Nuclei
Formation

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Rate of particle
Formation



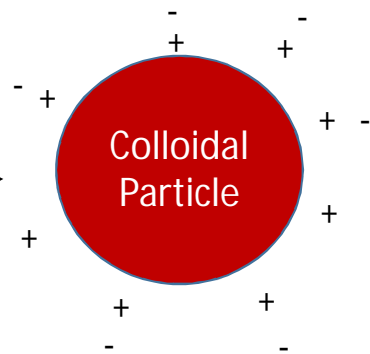
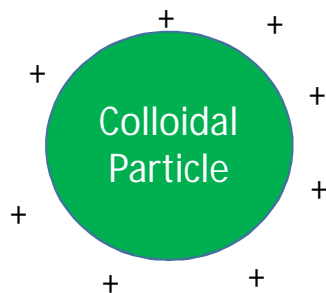
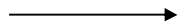
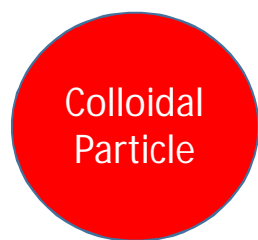
- ***More number of nuclei formed***
- ***Smaller particle produced***
- ***Colloidal PPT formed ($10^{-7} - 10^{-5}$ cm)***
- ***Adsorbs impurity***
- ***Increased chance of imperfection in the crystal & surface area of precipitate increase this leads to easy trapping of impurities***
- ***Not easily filterable, do not settle***

Colloidal Precipitate

Rate of Nuclei Formation

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Rate of particle Formation



Electrovalent colloids attract common ions

Double layer stabilized colloid

• Solution to colloid formation

1. Neutralise electrical double
2. Remove adsorbed ions by heating/stirring
3. Process called coagulation or agglomeration

AgCl surrounded by Ag or Cl ions

Relationship between particle sizes & supersaturation

Von weimarn – discovered that

Particle size of precipitate is inversely proportional to the relative super-saturation of the solution during the precipitation process

$$\text{(Von weimarn ratio) Relative supersaturation} = \frac{(Q-S)}{S}$$

- Q- concentration of mixed reagents before precipitation occurs(Degree of supersaturation)
- S- solubility of precipitate at equilibrium
- **So in order to get particle growth instead of further nucleation we need to make the relative super-saturation ratio as small as possible**

Relationship between super-saturation & Nucleation

High relative supersaturation

- Increase nucleation
- Many small crystals
- Colloidal particles form**
- High surface area
- More adsorption of impurities

Low relative supersaturation

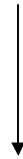
- Less nucleation
- Fewer larger crystals
- Crystalline particles form**
- Low surface area
- Less adsorption of impurities

Nature of Precipitate

Rate of Nuclei
Formation

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Rate of particle
Formation



- **Coarse PPT formed**
- **Particle diameter $>10^{-3}$ cm)**
- **easily filterable**

Contamination of Precipitates

- Post Precipitation:
 - Deposition of impurity after ppt
 - Ex. Ca-oxalate ppt in presence of Mg ions
 - After some time, Mg-oxalate formed, deposits on Ca-oxalate surface
 - *Can be avoided by filtering within 1 – 2 hrs after ppt*

Contamination of Precipitates

- Co-precipitation:
 - Inclusion of impurity during ppt formation
- Adsorption:
 - Adsorption of impurities at surface
 - More for colloidal particles
 - *Ppt have to be washed to remove adsorbed impurity*

Contamination of Precipitates

- Co-precipitation:
 - Inclusion of impurity during ppt formation

- Mixed crystal contamination:
 - Substitution of impurity ions in cryst lattice
 - Impurity ions have similar crystallinity
 - Ex, Ppt of Ba as BaSO_4 in presence of Pb ions

- *Separate analyte from contaminating ions before ppt*

Contamination of Precipitates

- Co-precipitation:
 - Occlusion occurs when foreign ions get trapped in growing crystal
 - Mechanical Entrapment:
 - several crystals growing together come close
 - Traps portion of solution between pockets
 - *Both occlusion and entrapment are at minimum when rate of ppt is low*

Solutions to problems in gravimetry

- Process carried out in dilute solution
- Reagents mixed slowly with constant stirring
- Ppt carried in hot solutions if stability permits
 - Advantages of heating
 - Solubility increased, reduction in degree of supersat
 - Coagulation occurs
 - Velocity of crystallization increased
- Crystalline ppt digested as long as possible

Solutions to problems in gravimetry

- PPT should be washed with dilute solution of electrolyte
- If contamination high, re-dissolve in appropriate solvent & then rePPT for purity

Solutions to problems in gravimetry:

Digestion of precipitate

- Digestion is a process keeping the precipitate within the mother liquor (or solution from which it precipitated) for a certain period of time to encourage densification of nuclei.
- During digestion, small particles dissolve and larger ones grow (Ostwald ripening).
- This process helps produce larger crystals that are more easily filtered from solution

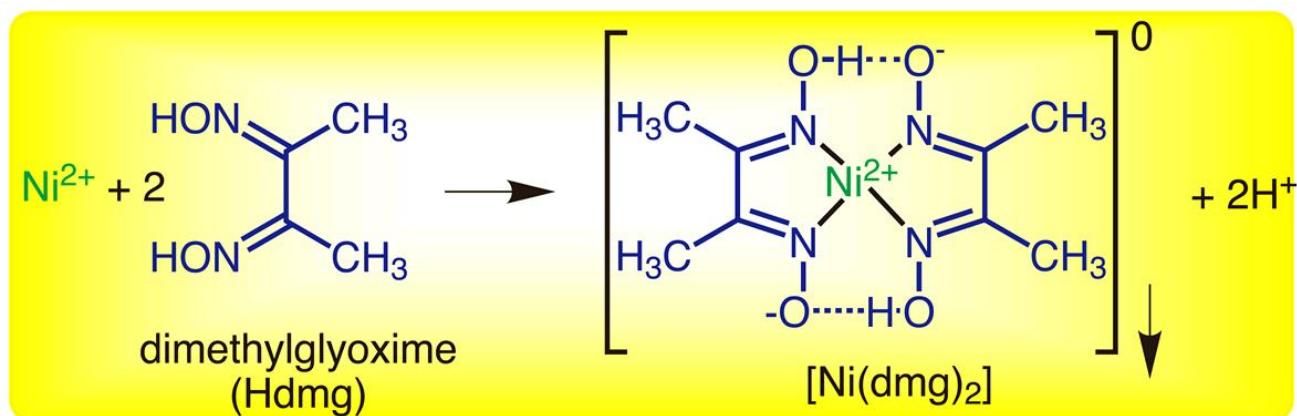
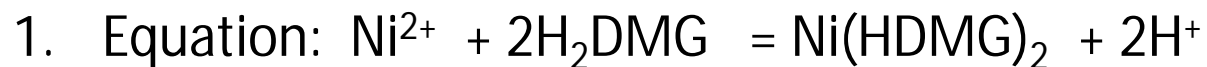
Ostwald ripening improves the purity and crystallinity of the precipitate

Precipitation Reagents

- Mostly precipitation reagents are organic
- Advantages of organic reagents
 - PPT products sparingly soluble
 - Colored
 - High molecular masses, so more ppt
- Ideal reagent for precipitation should be specific, only ppt a specific ion
- Precipitation product dried, weighed
- If composition not definite then oxidised

Applications

- Assay of Nickel by Dimethylglyoximate (DMG):



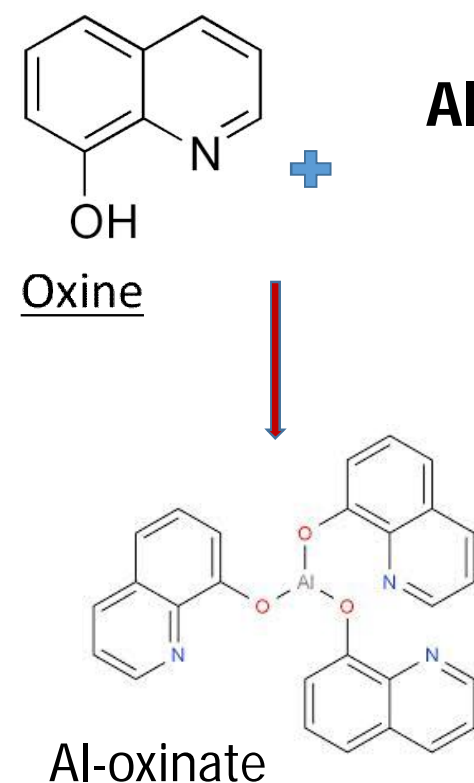
Characteristic bright red ppt

Applications

- **Assay of Nickel by Dimethylglyoximate (DMG):**
 1. DMG insoluble in water, added as 1% solution in 90% ethanol
 2. 1 ml ppt 0.0025g of nickel
 3. Reagent added to hot acidic solution of nickel salt
 4. Only slight excess of reagent should be used
 5. PPT washed with cold water, dried at 110-120 °C
 6. Equation: $\text{Ni}^{2+} + 2\text{H}_2\text{DMG} = \text{Ni}(\text{HDMG})_2 + 2\text{H}^+$
- *For detailed process please refer to Vogel, pp 408*

Applications

- Assay of Aluminium by Oxine (8-hydroxyquinoline):
 - Separates Al from beryllium & other earth metals
 - 2 or 5 % solution of Oxime in 2M Ethanoic acid
 - 1 ml sol can ppt 3 mg of aluminium
- Procedure
 1. Dissolve 0.4 g of Al ammonium sulphate in 100 ml of water
 2. Heat to 70 – 80 °C
 3. Add appropriate volume of oxime reagent
 4. Keep adding reagent to ensure complete ppt
 5. Allow to cool, collect Al-oxinate
 6. Wash with water, dry to constant weight at 110 °C



Applications

- Assay of Barium as Barium sulphate:
 - Slow addition of dilute solution of BaCl to hot solution of sulphate
 - $Ba^{2+} + SO_4^{2-} = BaSO_4$
 - Acidic solution prevent other salts formation (Chromate, carbonate, phosphate)
 - Process carried out at boiling temp for lower supersat
 - Ba has strong tendency to carry down other salts
 - Barium chloride, Barium nitrate are co-precipitated
 - *Nitrate can be converted to oxide by ignition*
 - *Slow addition of Ba to SO_4 solution lowers formation of BaCl*

Advantages & Disadvantages

- **Advantages**

- Extensive numbers of inorganic ions are determined with excellent precision and accuracy.
- Routine assays of metallurgical samples
- Relative precision 0.1 to 1%
- Good accuracy, relatively in-expensive

- **Disadvantages**

- Careful and time consuming
- Scrupulously clean glassware
- Very accurate weighing
- Co-precipitation