

GRAVIMETRIC METHOD

- ▶ Gravimetric analysis is a quantitative determination of the amount of analyte through a precipitation process, precipitate isolation, and determination of isolated product weight.
- ▶ Gravimetry = analytical methods that measure the **mass** or mass changes.
- Using an analytical balance (highly accurate instrument with precise data)
- Still being used in industry and environmental research

TYPES OF GRAVIMETRIC METHODS

Gravimetric methods	Definition	Application
Precipitation gravimetry	A gravimetric method in which the signal is the mass of a precipitate	Suspended solid: determination of Cl^- by AgNO_3 precipitating to AgCl (filtration)
Electrogravimetry	A gravimetric method in which the signal is the mass of an electrodeposit on the cathode or anode in an electrochemical cell	Aqueous ion: determination of Pb^{2+} by oxidizes to PbO_2 and deposited on Pt anode (chemical converting)
Volatilization gravimetry	A gravimetric method in which the loss of a volatile species gives rise to the signal (remove the volatile species)	Moisture: determination of water in food content by heat or thermal or chemical energy (heating)
Particulate gravimetry	A gravimetric method in which the mass of a particulate analyte is determined following its separation from its matrix	Suspended solid: determination of solid that can be separated from the sample (filtration or extraction)

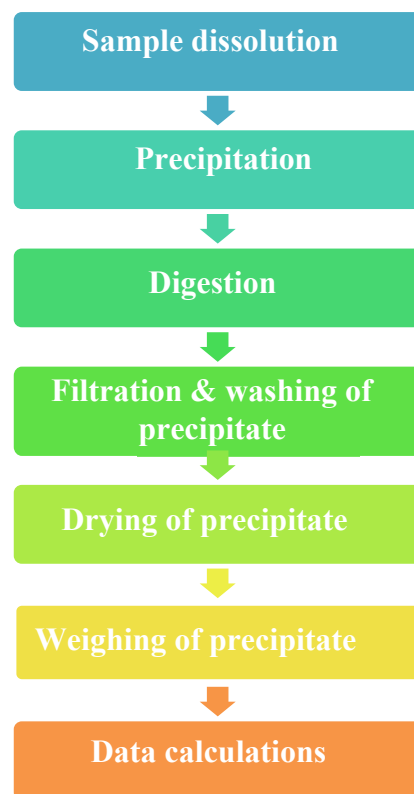
PRECIPITATION GRAVIMETRY

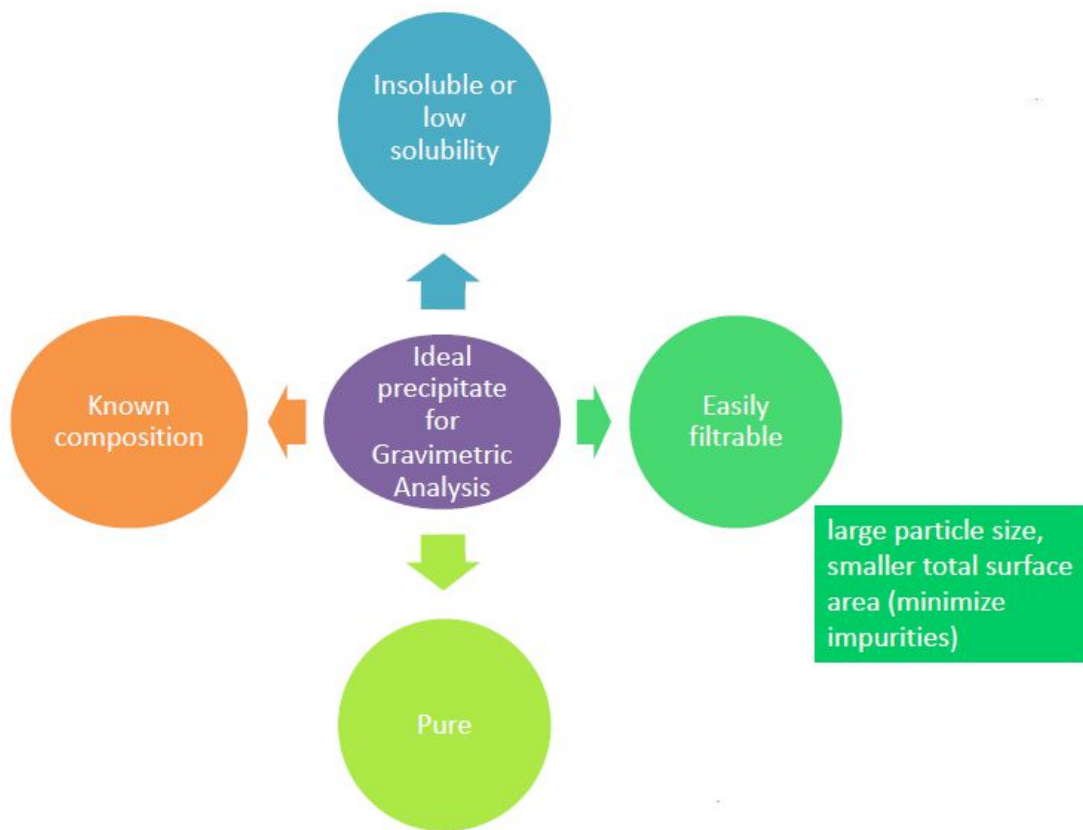
- ▶ Appearance of insoluble compounds in a solution containing our analyte when a precipitating reagent/precipitant is added.
- ▶ The precipitate is then: filtered and washed (impurities removal) converted to a product (known composition) weighed

STEPS IN GRAVIMETRIC ANALYSIS

Gravimetric Analysis

1. Dissolve a sample after weighing.
2. A precipitating agent with excess amount is added to this solution.
3. The resulting precipitate is filtered, dried (or ignited) and weighed.
4. Determine the amount of the original ion from the mass of the precipitate (known composition).
5. Stoichiometry is important (write down the chemical equation!).





TYPES OF PRECIPITATING REAGENTS

Selective (react with a few analytes)

- Example: AgNO_3
- $\text{Ag}^+ + \text{Halides (X}^-) \rightarrow \text{AgX(s)}$, $\text{Ag}^+ + \text{CNS}^- \rightarrow \text{AgCNS(s)}$

Specific (react with 1 analyte only) Example: Dimethylglyoxime (DMG) that precipitates only

Ni^{2+} from alkaline solutions

- $2 \text{ DMG} + \text{Ni}^{2+} \rightarrow \text{Ni(DMG)}_2\text{(s)} + 2\text{H}^+$

SOLUBILITY PRODUCT CONSTANTS OF SELECTED SLIGHTLY SOLUBLE SALTS

Salt	K_{sp}	Solubility, s (mol/L)
PbSO ₄	1.6×10^{-8}	1.3×10^{-4}
AgCl	1.0×10^{-6}	1.0×10^{-5}
AgBr	4×10^{-13}	6×10^{-7}
AgI	1×10^{-16}	1×10^{-8}
Al(OH) ₃	2×10^{-32}	5×10^{-9}
Fe(OH) ₃	4×10^{-38}	2×10^{-10}
Ag ₂ S	2×10^{-49}	4×10^{-17}
HgS	4×10^{-53}	6×10^{-27}

SOLUBILITY RULES

Almost always Soluble

Nitrates (NO₃⁻)

Acetates (C₂H₃O⁻)

Group 1 (Li⁺, Na⁺, K⁺, etc)

Sulfates (SO₄²⁻)

Ammonium (NH₄⁺)

Group 17 (F⁻, Cl⁻, Br⁻, etc)

EXCEPTIONS (2 groups)

“PMS”

P → Pb²⁺ (lead) •

M → Mercury (Hg₂²⁺)

S → Silver (Ag⁺)

Castro Bear

Ca²⁺, Sr²⁺, Ba²⁺

TYPES OF PRECIPITATE FORMED

Colloidal suspensions

- 10⁻⁷ to 10⁻⁴ cm diameter
- Normally remain suspended

- Very difficult to filter

► Crystalline suspensions

- > tenths of mm diameter
- Normally settle out spontaneously
- Readily filterable

FACTORS THAT DETERMINE THE PARTICLE SIZE OF PRECIPITATES

Particles size of precipitate influenced by:

- Precipitate solubility (S)
- Temperature, Increase temp to increase solubility
- Reactant concentration (Q)
- Rate at which reactant mixed
- pH

Slow
precipitating
good stirring

Large, easily filtered
crystal of calcium
oxalate – mildly acidic
environment

MECHANISM OF PRECIPITATE FORMATION

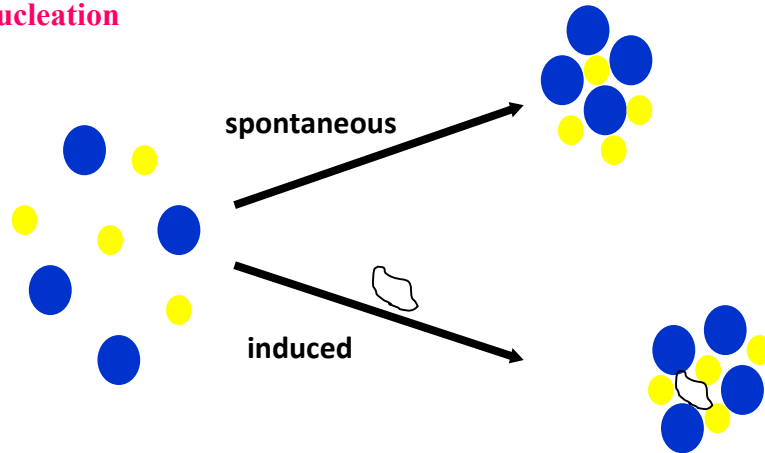
► Nucleation

- Individual ions/atoms/molecules coalesce to form “nuclei” (join together to give a stable solid)
If nucleation predominates, a large number of small particles result

▶ Particle growth

- Ions/atoms/molecules are added to the nucleus to form larger particles
- If particle growth predominates, a smaller number of large particles result

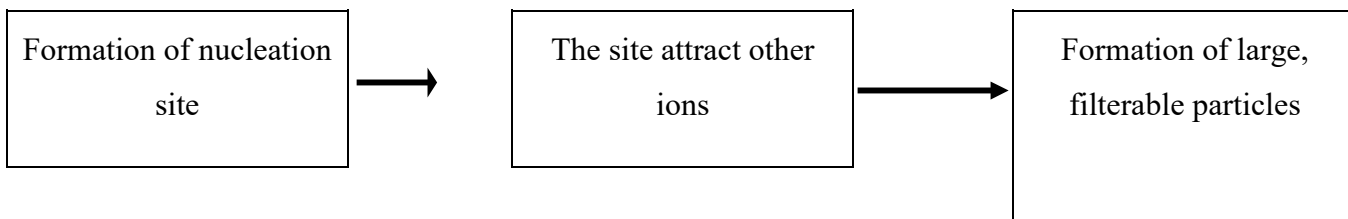
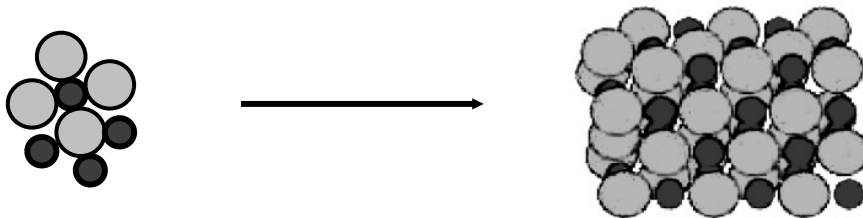
Nucleation



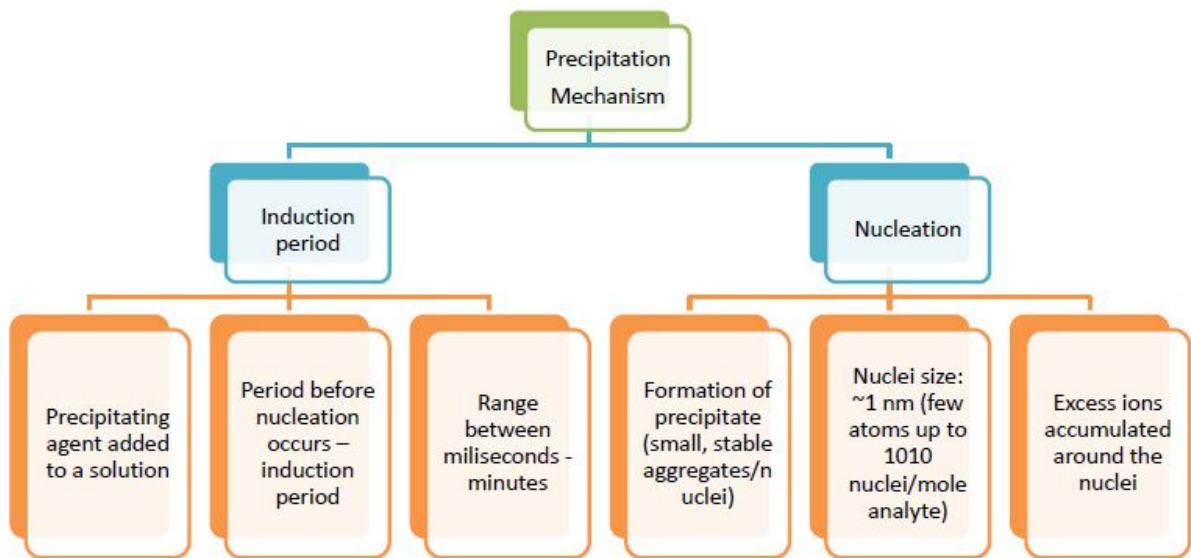
MECHANISM OF PRECIPITATION

Induced nucleation involves grain growth initiated by ‘seed’ particles (i.e. dust, glass fragment, other crystals ...)

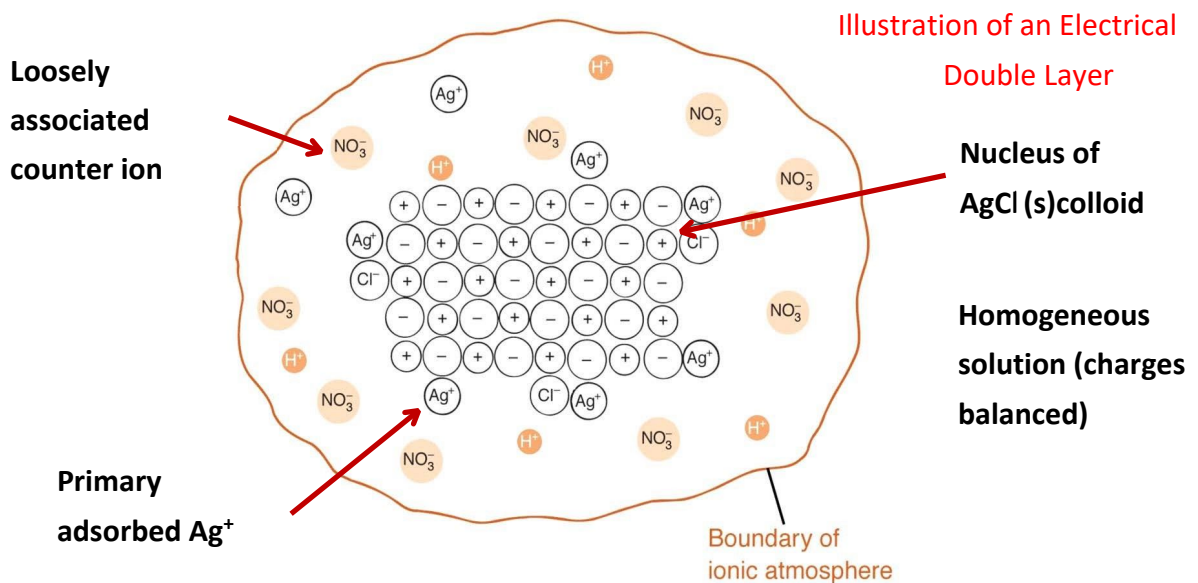
Particle growth



Contaminates are reduced - they don't ‘fit in’ to the crystal structure.



The region surrounding the particle has a net negative charge because the particle attracts anions and repels cations.



- In addition to the colloidal particles of AgCl formation, they grow in the excess of Ag^+ , NO_3^- and H^+ .
- The surface of the particle now has an excess of positive charge – adsorption of extra Ag^+
- Then, the surface attracts anions and repels cations.

- Both layers of positively charged particles and negatively charged ionic atmosphere are known as the **ELECTRIC DOUBLE LAYER**.

MORE TERMINOLOGY

- **Adsorption** is a process where a substance is attached to the surface of a solid.
While, **absorption** is a process where a substance is held within the pores.
- **electric double layer**: a layer of charge absorbed on the particles' surface together with a layer of net opposite charge surrounding the particles in the solution.

COLLOIDAL PRECIPITATES

- ▶ **Colloidal Suspension**
 - Colloidal particles remain suspended due to adsorbed ions giving a net +ve or -ve charge
- ▶ **Coagulation, agglomeration**
 - Suspended colloidal particles unite to form larger filterable particles - inert electrolyte allows closer approach. Can be synchronized by adding an electrolyte to the medium, heating, and stirring.
- ▶ **Peptization**
 - Re-dissolution of coagulated colloids by washing and removing inert electrolyte.

COLLOIDAL PRECIPITATES

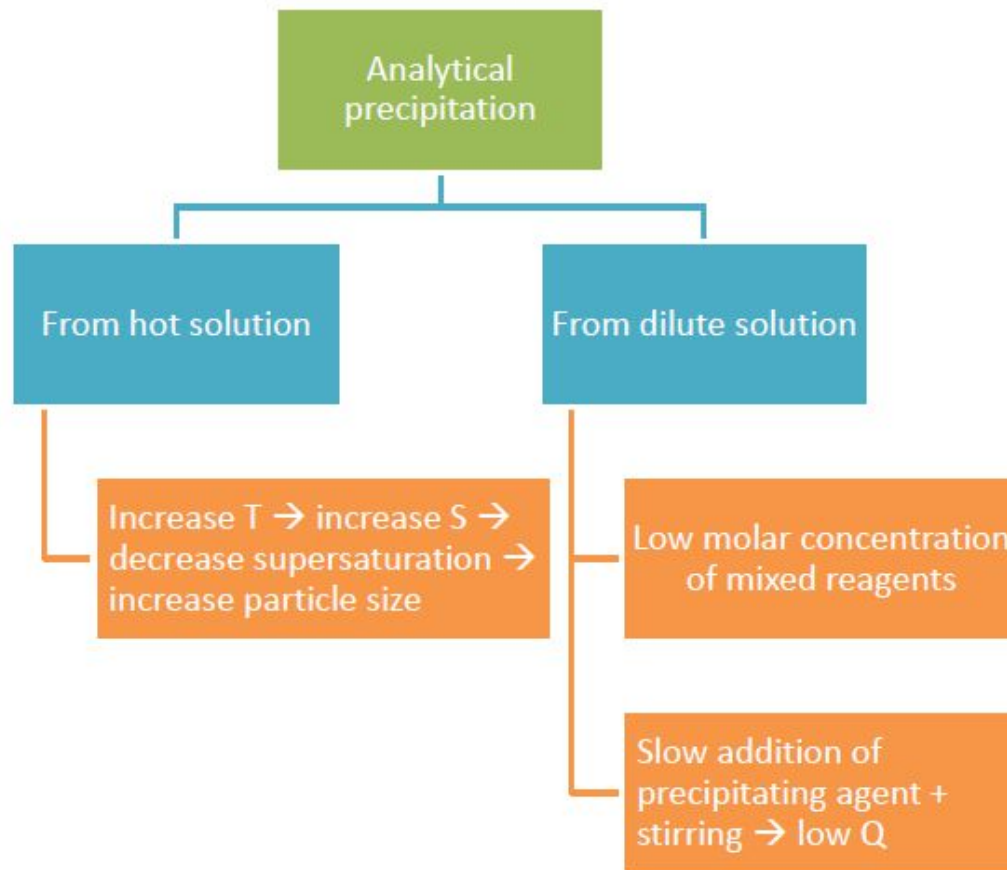
- Peptidization
A procedure where the precipitate is washed and filtered but part of the precipitate reverts to the colloidal form because supporting electrolyte is gone.
- Cooling the system with an icewater bath minimizes loss of precipitate due to dissolution

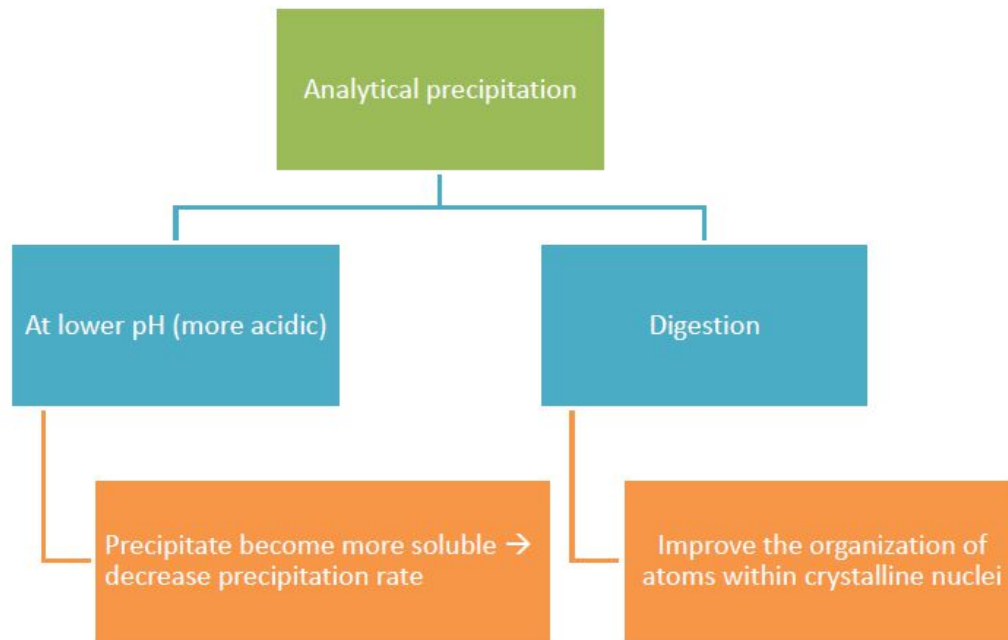
CONDITIONS FOR ANALYTICAL PRECIPITATION

- Saturation = $Q - S$
- Relative supersaturation = $(Q - S) / S$, where Q: solute concentration, S: solute solubility

For best possible results: Q should be as low as possible and S should be relatively large.

- $Q \uparrow, S \downarrow$: high supersaturation \rightarrow fine particles
- $Q \downarrow, S \uparrow$: low supersaturation \rightarrow large particles





OPTIMUM PRECIPITATION CONDITIONS WITH LOW SUPERSATURATION

1. Use dilute solutions - decrease Q
2. Add precipitating agent slowly - keep Q low
3. Stirring during the above addition - keep Q low
4. Use hot solution - increase solubility
5. Adjust the pH - increase S
6. Add precipitating agent with excess amount

CO-PRECIPITATION: IMPURITIES IN PRECIPITATES

- ▶ Co-precipitation is a process where the impurity is precipitated along with the desired precipitate.
- ▶ Example: barium sulfate, hydrous oxides compounds.
- ▶ Normally soluble compounds carried down with insoluble precipitate

CO-PRECIPITATION: IMPURITIES IN PRECIPITATES

4 types:

1. surface adsorption
2. Occlusion (pockets of impurities that are trapped inside the rapidly growing crystal)
3. Inclusion (impurity ions replace an ion in the crystal lattice)
4. mechanical entrapment (crystals lie close together during growth)

