ANALYTICAL CHEMISTRY

Gravimetric Analysis

by
Wan Norfazilah Wan Ismail
Faculty of Industrial Sciences & Technology
norfazilah@ump.edu.my

Chapter Description

- Expected Outcomes
  - Understand and state the principles of gravimetric analysis
  - Describe the gravimetric analysis involving precipitation reactions
  - State the requirement to remove potentially interfering species prior to the gravimetric measurement

Communitising Technology

Contents

- Steps in Gravimetric Analysis
- Precipitation Agents
- Mechanism of Precipitation
- Impurities of Particles
- Ways to Minimize Impurities
- Gravimetric Calculations
- Volatilization and Particulate Gravimetry

Communitising Technology

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)
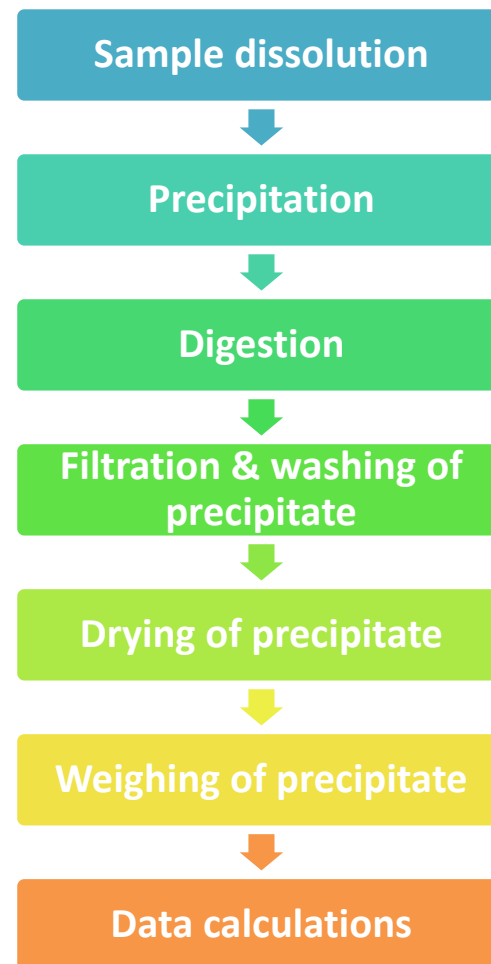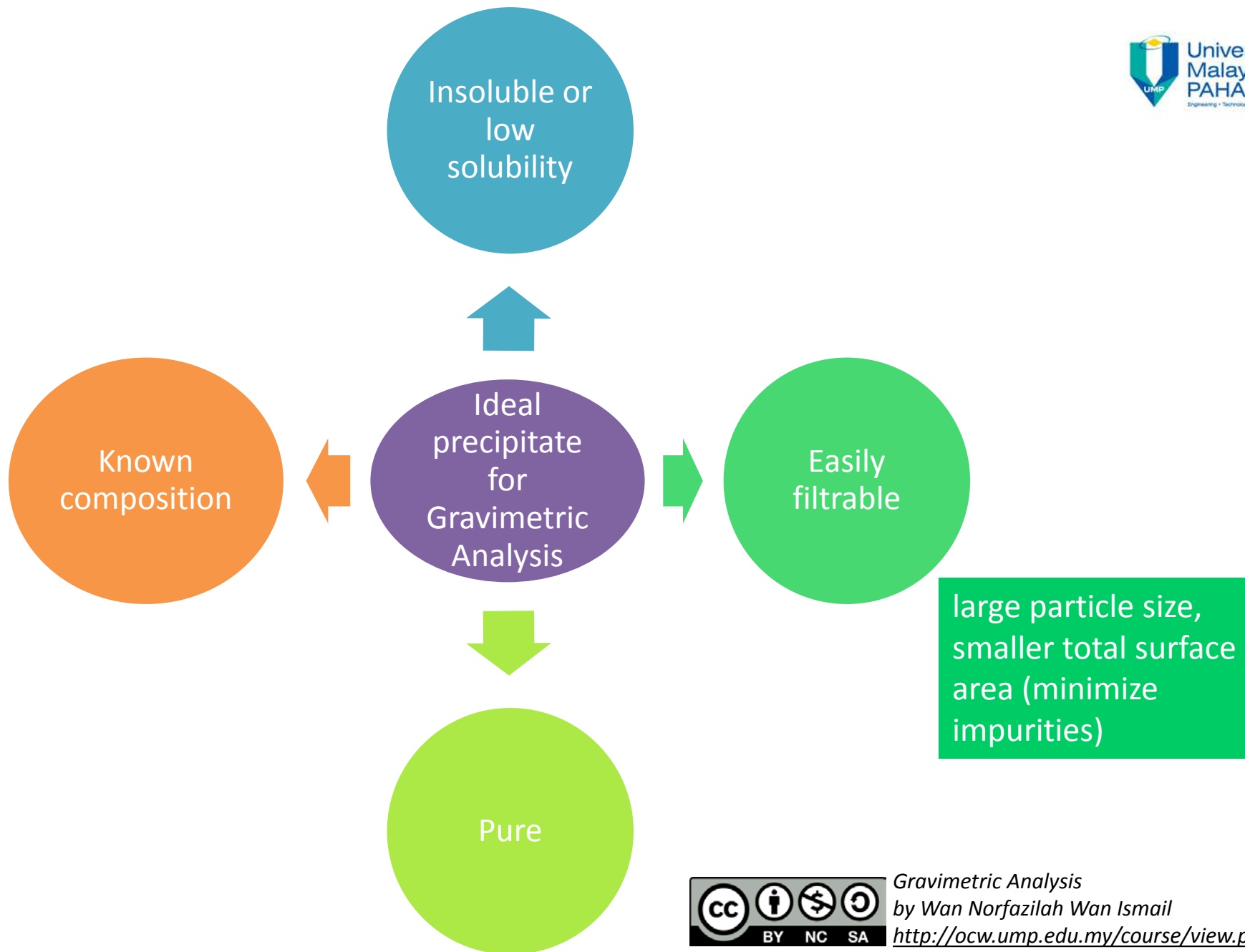
weighed

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!).

Sample dissolution

↓

Precipitation

↓

Digestion

↓

Filtration & washing of precipitate

↓

Drying of precipitate

↓

Weighing of precipitate

↓

Data calculations

Insoluble or low solubility

Known composition

Ideal precipitate for Gravimetric Analysis

Easily filtrable

large particle size, smaller total surface area (minimize impurities)

Pure

Communitising Technology

TYPES OF PRECIPITATING REAGENTS

1. **<u>Selective</u>** (react with a few analytes)
   - Example: $AgNO_3$
   - $Ag^+ + $ Halides $(X^-) \rightarrow AgX_{(s)}$
   - $Ag^+ + CNS^- \rightarrow AgCNS_{(s)}$

2. **<u>Specific</u>** (react with 1 analyte only)
   - Example: Dimethylglyoxime (DMG) that precipitates only Ni^{2+} from alkaline solutions
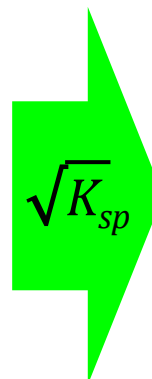   - $2\ DMG + Ni^{2+} \rightarrow Ni(DMG)_{2(s)} + 2\ H^+$

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_2S	2×10^{-49}	4×10^{-17}
HgS	4×10^{-53}	6×10^{-27}

$\sqrt{K_{sp}}$

Communitising Technology

SOLUBILITY RULES

ALMOST (always SOLUBLE)

Nitraes (NO_3^-)

Acetates ($C_2H_3O^-$)

Group 1 (Li^+, Na^+, K^+, etc)

Sulfates (SO_4^{2-})

Ammonium (NH_4^+)

Group 17 (F^-, Cl^-, Br^-, etc)

EXCEPTIONS (2 groups)

1. "PMS"
   - P $\rightarrow$ Pb^{2+} (lead)
   - M $\rightarrow$ Mercury (Hg_2^{2+})
   - S $\rightarrow$ Silver (Ag^+)

2. Castro Bear
   - Ca^{2+}, Sr^{2+}, Ba^{2+}

Communitising Technology

TYPES OF PRECIPITATE FORMED

▸ <u>Colloidal suspensions</u>
- 10^{-7} to 10^{-4} cm diameter
- Normally remain suspended
- Very difficult to filter

▸ <u>Crystalline suspensions</u>
- > tenths of mm diameter
- Normally settle out spontaneously
- Readily filterable

Communitising Technology

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 → Slow addition of the precipitating agent with good stirring

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

Communitising Technology

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
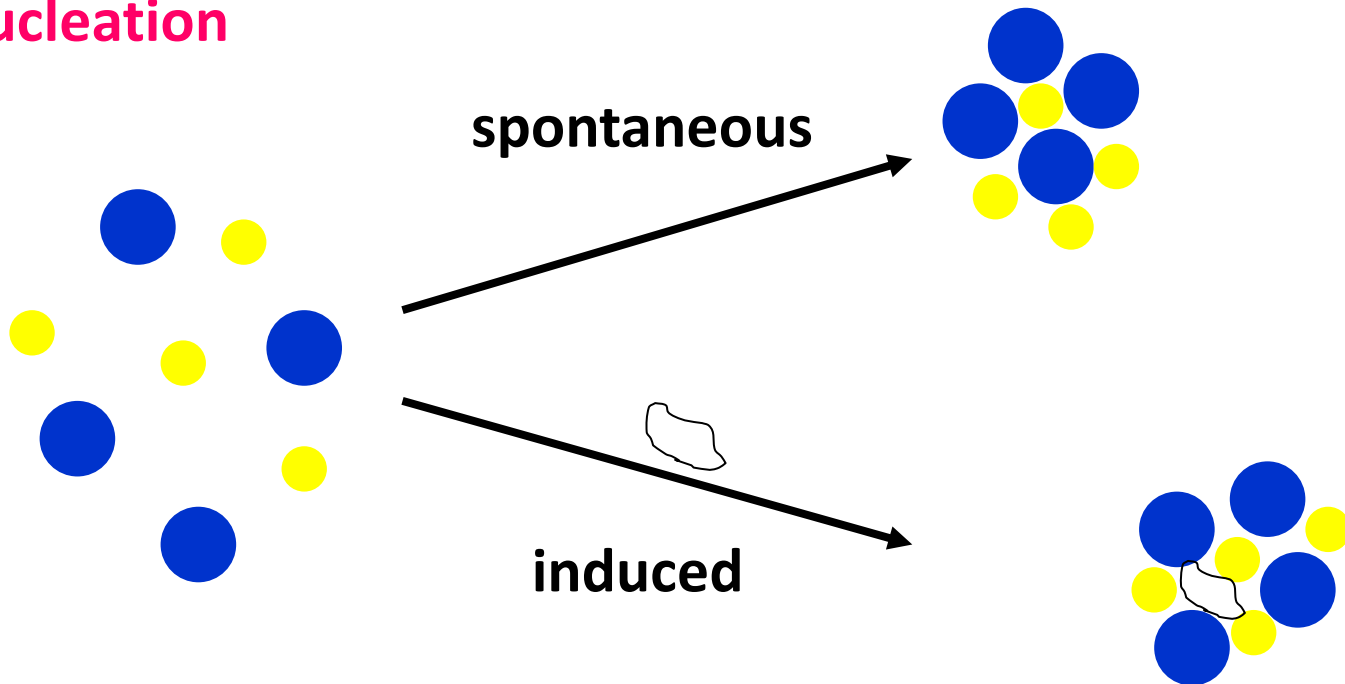
MECHANISM OF PRECIPITATION

Nucleation

spontaneous

induced

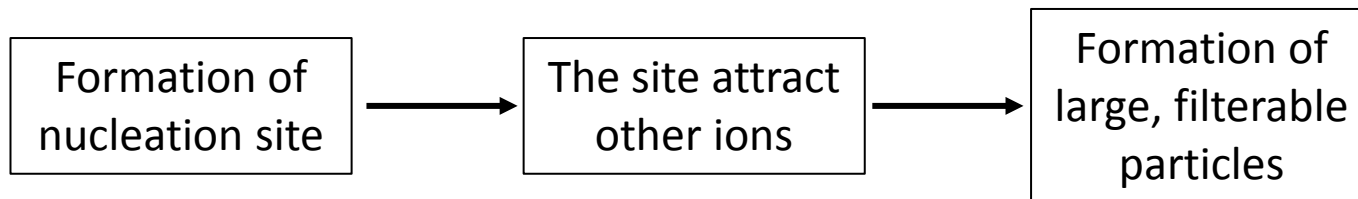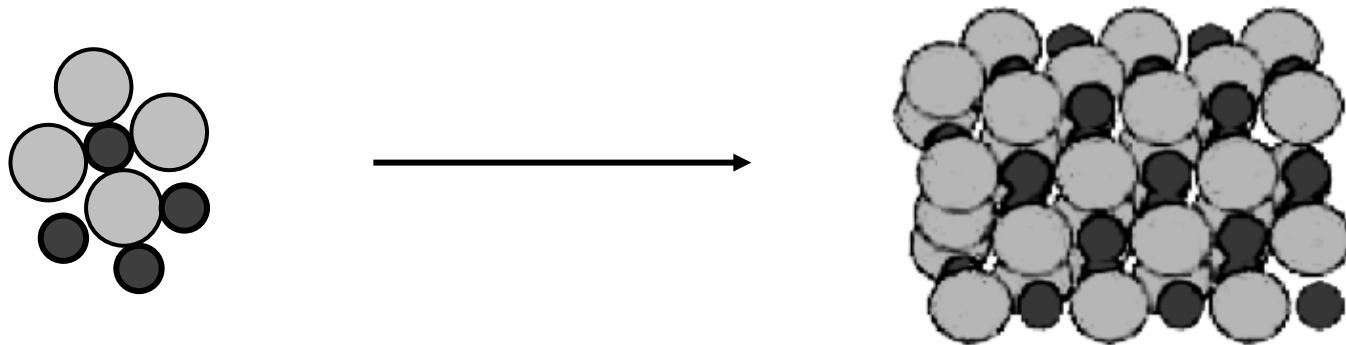**Induced nucleation involves grain growth initiated by 'seed' particles (i.e. dust, glass fragment, other crystals …)**

Gravimetric Analysis
by Wan Norfazilah Wan Ismail
http://ocw.ump.edu.my/course/view.php?id=467

MECHANISM OF PRECIPITATION

Particle growth

| Formation of nucleation site | → | The site attract other ions | → | Formation of large, filterable particles |

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

Precipitation Mechanism

- Induction period
  - Precipitating agent added to a solution
  - Period before nucleation occurs – induction period
  - Range between miliseconds - minutes
- Nucleation
  - Formation of precipitate (small, stable aggregates/nuclei)
  - Nuclei size: ~1 nm (few atoms up to 1010 nuclei/mole analyte)
  - Excess ions accumulated around the nuclei
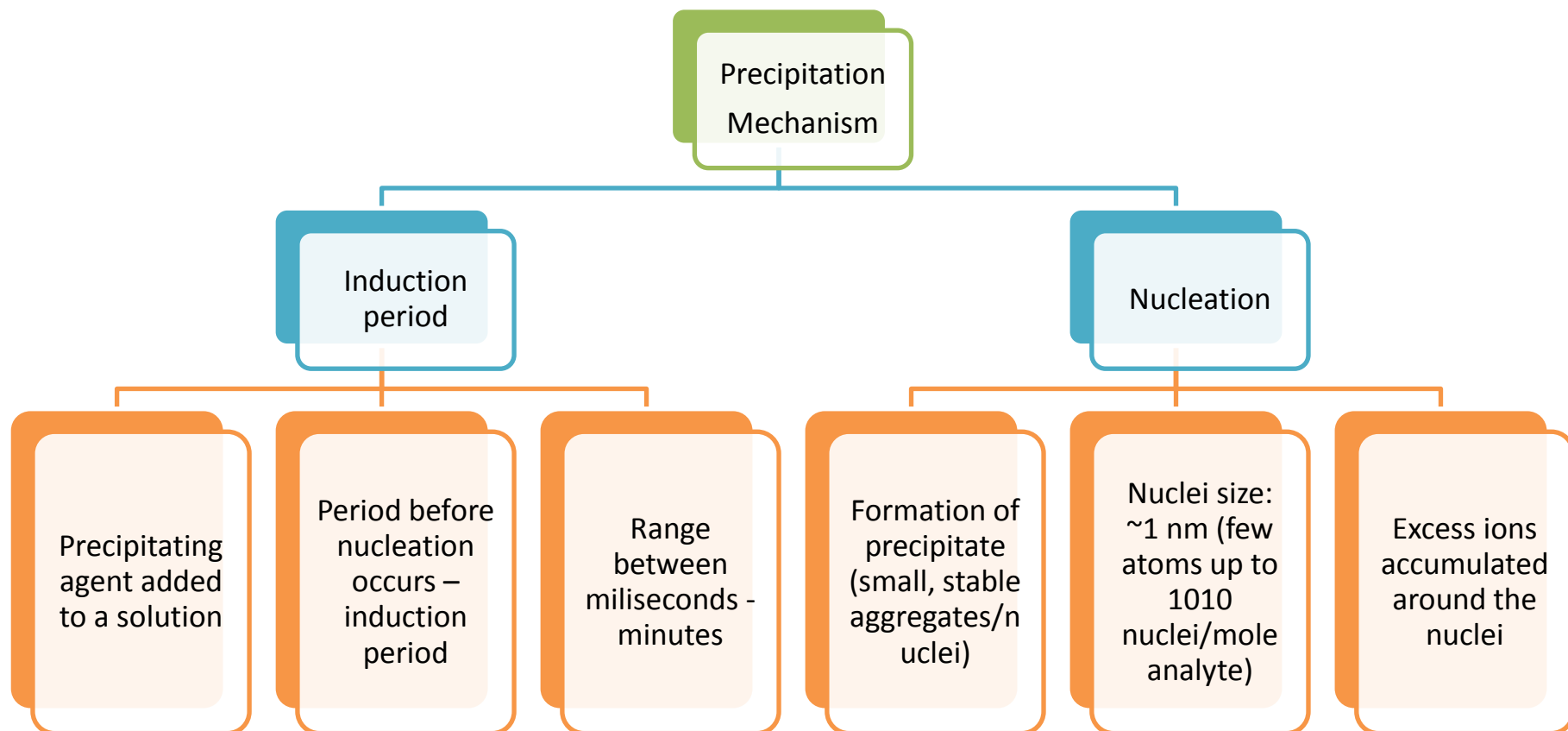
Mechanism of Precipitation

The region surrounding the particle has a net negative charge because the particle attracts anions and repels cations.
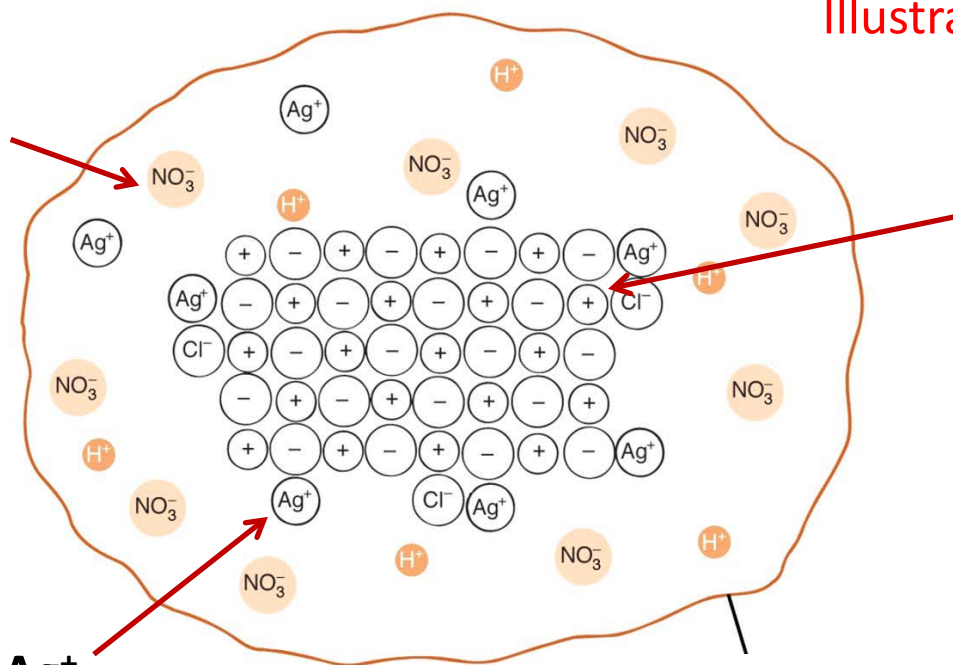
Illustration of an Electrical Double Layer

Loosely associated counter ion

Nucleus of AgCl (*s*) colloid

Homogeneous solution (charges balanced)

Primary adsorbed Ag⁺

Boundary of ionic atmosphere

Sources: D.C. Harris (2010) Quantitative Chemical Analysis, 8th edition, W. H. Freeman & Company: New York.

Communitising Technology

MECHANISM OF PRECIPITATION

- In addition to the colloidal particles of AgCl formation, they grow in the excess of Ag+, NO3- 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**.

Communitising Technology

MORE TERMINOLOGY

- Adsorption is a process where a substance is attached to the surface of a solid.

  *** While, absorbtion 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

▸ **<u>Colloidal Suspension</u>**
  ◦ Colloidal particles remain suspended due to adsorbed ions giving a net +ve or -ve charge

▸ **<u>Coagulation, agglomeration</u>**
  ◦ Suspended colloidal particles unite to form larger filterable particles - inert electrolyte allows closer approach
    • Can be syncronized by adding an electrolyte to the medium, heating, and stirring.

▸ **<u>Peptization</u>**
  ◦ Re-dissolution of coagulated colloids by washing and removing inert electrolyte

Communitising Technology
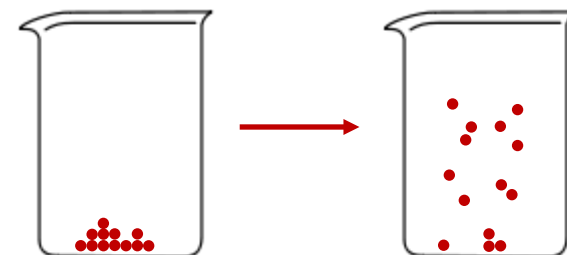
COLLOIDAL PRECIPITATES

- 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 ice-water bath minimizes loss of precipitate due to dissolution

AgCl (s) → AgCl (colloid)

Communitising Technology

CONDITIONS FOR ANALYTICAL PRECIPITATION

- Saturation = Q – S
- Relative supersaturation = (Q – S) / S

      Q: solute concentration

      S: solute solubility

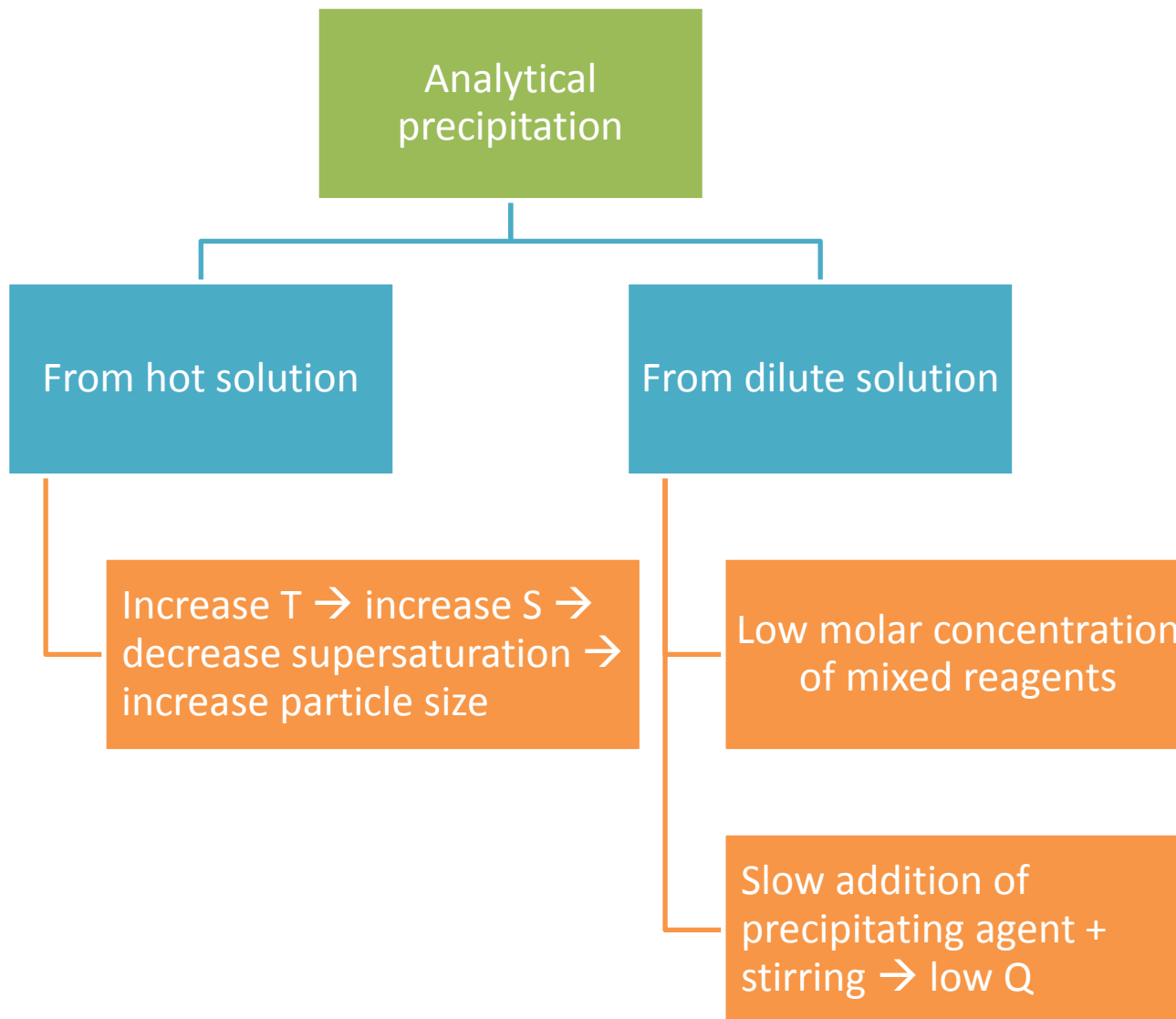For best possible results: Q should be as low as possible and S should be relatively large.

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

Analytical precipitation

From hot solution

Increase T → increase S → decrease supersaturation → increase particle size

From dilute solution

Low molar concentration of mixed reagents

Slow addition of precipitating agent + stirring → low Q

Communitising Technology

Analytical precipitation

At lower pH (more acidic)

Digestion

Precipitate become more soluble → decrease precipitation rate

Improve the organization of atoms within crystalline nuclei

Communitising Technology
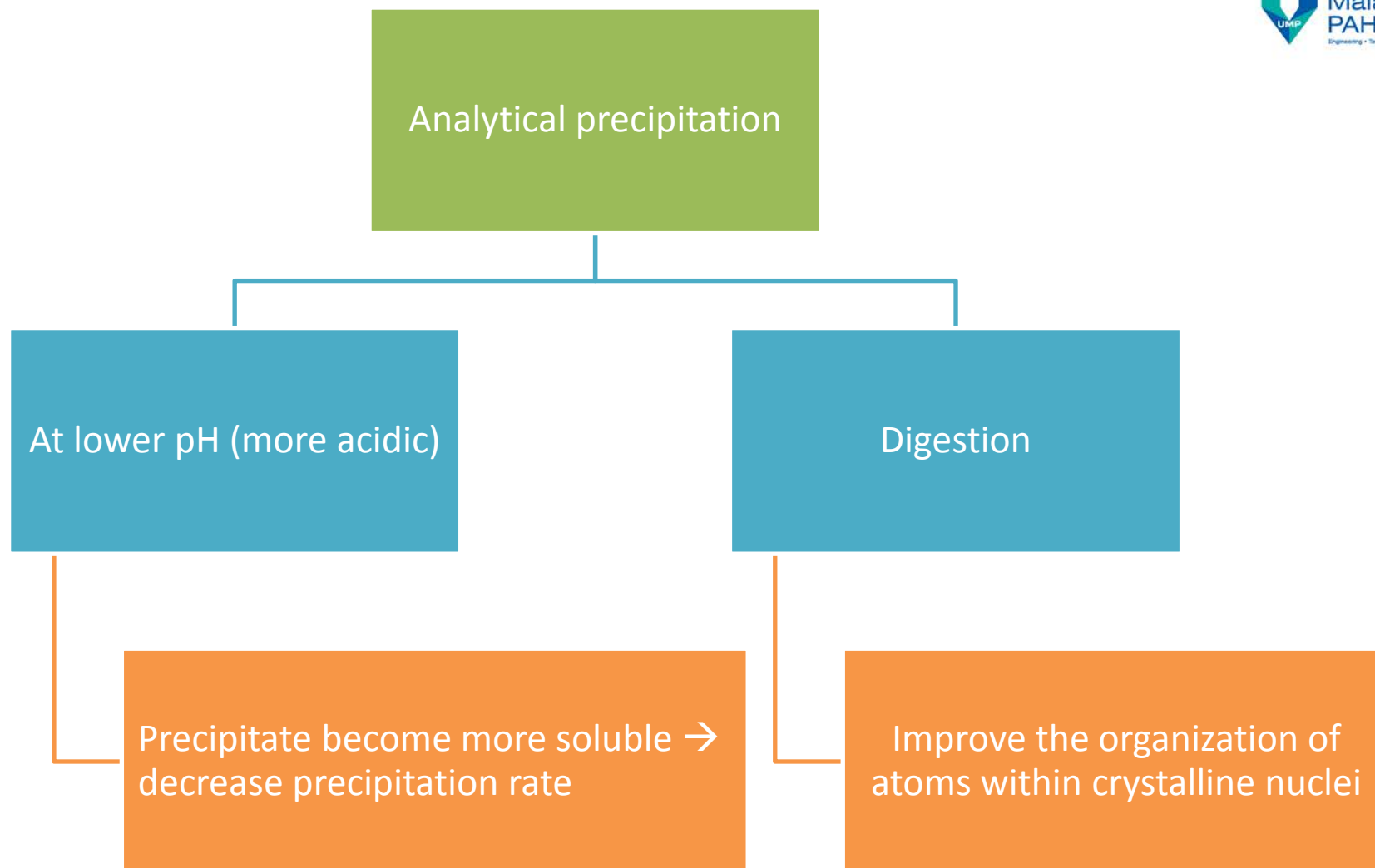
OPTIMUM PRECIPITATION CONDITIONS WITH LOW SUPERSATURATION

a. Use dilute solutions - decrease Q

b. Add precipitating agent slowly - keep Q low

c. Stirring during the above addition - keep Q low

d. Use hot solution - increase solubility

e. Adjust the pH - increase S

f. Add precipitating agent with excess amount

Communitising Technology

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

Communitising Technology

CO-PRECIPITATION: IMPURITIES IN PRECIPITATES

4 types:

i.   surface adsorption
ii. Occlusion (pockets of impurities that are trapped inside the rapidly growing cryctal)
iii. Inclusion (impurity ions replaces an ion in the crystal lattice)
iv. mechanical entrapment (crystals lie close together during growth)

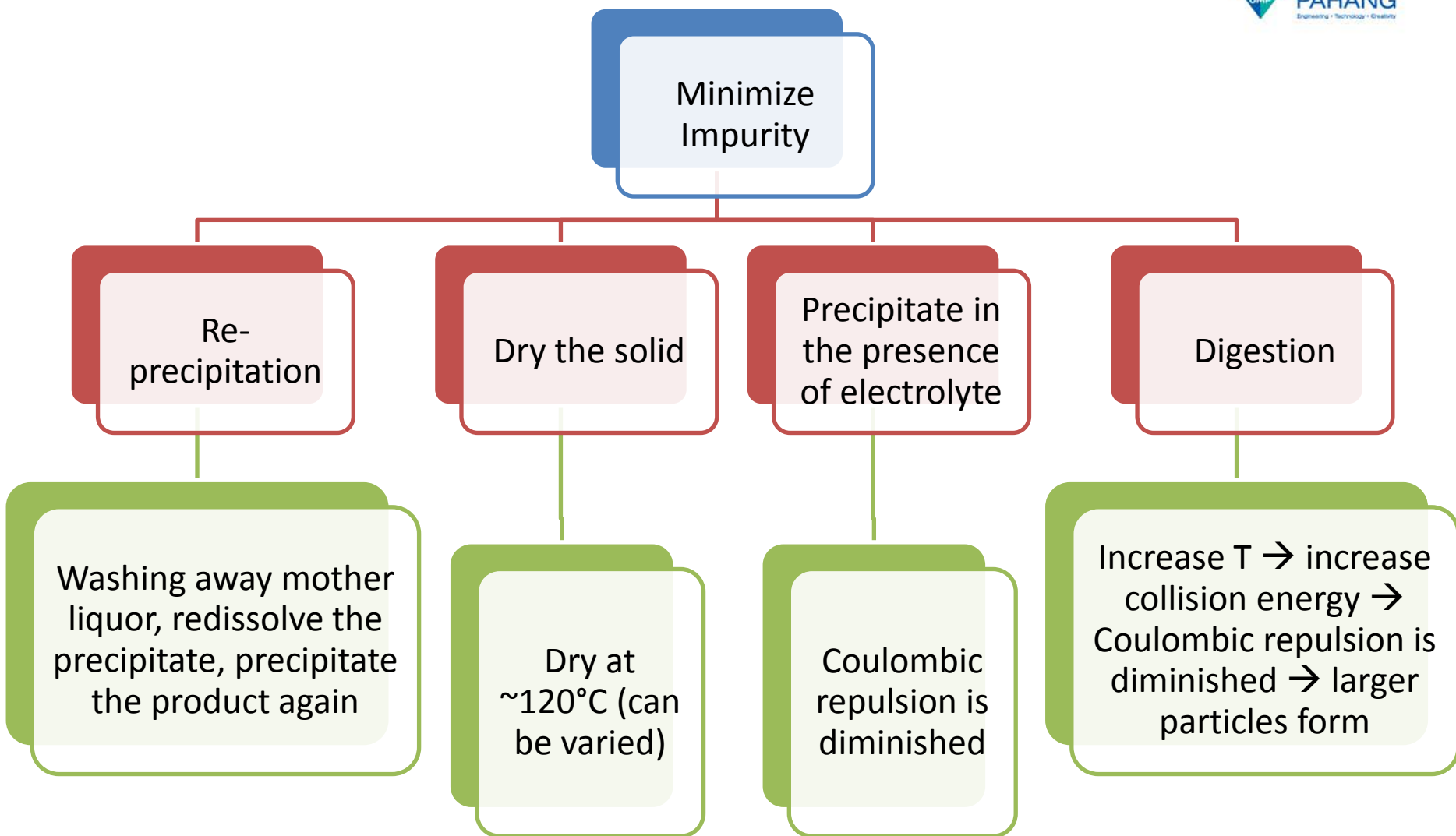*** *Minimizing coprecipitation: careful precipitation & thorough washing.*

Minimize Impurity

Re-precipitation
Washing away mother liquor, redissolve the precipitate, precipitate the product again

Dry the solid
Dry at ~120°C (can be varied)

Precipitate in the presence of electrolyte
Coulombic repulsion is diminished

Digestion
Increase T → increase collision energy → Coulombic repulsion is diminished → larger particles form

GRAVIMETRIC ANALYSIS

▸ Calculations of analyte content requires knowledge of :

◦ Chemistry

◦ Stoichiometry

◦ Composition of precipitate

Communitising Technology

GRAVIMETRIC ANALYSIS

- For example: determination of silver or chloride by the formation of AgCl (s).

$$Ag^+ + Cl^- \rightarrow AgCl \text{ (s)}$$
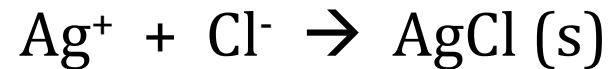
- Precipitation occurs when the value of $[Ag^+][Cl^-]$ exceeds the solubility product K_{sp} of AgCl (1.8×10^{-10}).

Communitising Technology

GRAVIMETRIC FACTOR

- The precipitate obtained is usually different from the weight of the analyte we want to report.

- The gravimetric factor (GF): weight of analyte per unit weight of precipitate.

$$GF = \frac{FW\ analyte\ (g/mol)}{FW\ precipitate\ (g/mol)} \times \frac{a}{b}\ (mol\ analyte/mol\ precipitate)$$

Communitising Technology

GRAVIMETRIC CALCULATION

▸ Gravimetric Factor (GF):

a = moles of analyte
b = moles of precipitate

$$GF = \frac{a}{b} * \frac{fwt\ analyte\ \text{(g/mol)}}{fwt\ precipitate\ \text{(g/mol)}}$$

▸ GF = g analyte / g precipitate

▸ % analyte = (weight analyte (g)/ weight sample (g)) x 100%

▸ % (w/w) analyte (g) = ((wt precipitate (g) x GF)/wt sample) x 100%

EXAMPLE 1:

Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte:	Precipitate:
NaCl	AgCl

$$g \ \frac{NaCl}{AgCl} = \frac{FW \ NaCl \ (g/mol)}{FW \ AgCl \ (g/mol)} \ x \ \frac{1}{1} \ (mol \ NaCl/mol \ AgCl)$$

$$GF = \frac{1}{1} \ x \ \frac{58.44 \ g/mol}{143.32 \ g/mol} = 0.4078 \ g \ NaCl/mol \ AgCl$$

Communitising Technology

EXAMPLE 2:

Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte:	Precipitate:
$2K_2HPO_4$	$Mg_2P_2O_7$

$$g \; \frac{K_2HPO_4}{Mg_2P_2O_7} = \frac{FW \; K_2HPO_4 \; (g/mol)}{FW \; Mg_2P_2O_7 \; (g/mol)} \; x \; \frac{2}{1} \; (mol \; _2HPO_4 / mol \; Mg_2P_2O_7)$$

$$GF \quad = \frac{2}{1} \; x \; \frac{174.2 \; g/mol}{222.6 \, g/mol} = 1.565 \; g \; _2HPO_4 / mol \; Mg_2P_2O_7$$

EXAMPLE 3:

Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte:	Precipitate:
Bi_2S_3	$3BaSO_4$

$$g \frac{Bi_2S_3}{BaSO_4} = \frac{FW\,Bi_2S_3\,(g/mol)}{FW\,BaSO_4\,(g/mol)} \; x \; \frac{1}{3} \; (mol\,Bi_2S_3 / mol\,BaSO_4)$$

$$GF = \frac{1}{3} \; x \; \frac{514.16\ g/mol}{233.43\,g/mol} = 0.734\ g\ Bi_2S_3 / mol\,BaSO_4$$

VOLATILIZATION GRAVIMETRY

▸ Mostly use for determining water and carbon dioxide

▸ For water:

- DIRECT METHOD: Water vapor is collected on any of several solid desiccants, and its mass is determined from the mass gain of desiccants

- INDIRECT METHOD: Amount of water is determined by the loss of mass of the sample during heating, is less satisfactory because it must assumed that the water is the only component volatilized.

PARTICULATE GRAVIMETRY

- Two approaches :

- filtration – solid particulates are separated from their gas, liquid or solid matrix

- Extraction – can be extracted from its matrix with a suitable solvent

APPLICATION OF PARTICULATE GRAVIMETRY

▸ Microbiological testing of water

▸ Determination of suspended solid in river water

▸ Total airborne particulates by using high-volume air sampler

▸ Grain size distributions for sediments and soils

Communitising Technology

Editor: Wan Norfazilah Wan Ismail

Author: Siti Maznah Kabeb

Industrial Chemistry Programme
Faculty of Industrial Sciences & Technology
Universiti Malaysia Pahang

Communitising Technology