



Gravimetric Analysis and Precipitation Equilibria

CEB 4032: ANALYTICAL CHEMISTRY
CFB3032: ANALYTICAL INSTRUMENTATION

TS. CHM. DR. MOHD DZUL HAKIM WIRZAL

Chemical
Engineering

Inspiring Potential • Generating Futures

Outline

- Introduction to Gravimetry Analysis
- Properties of Precipitates
- Precipitation Process
 - Colloidal Precipitates
 - Crystalline Precipitates
 - Co-precipitation
 - Homogeneous Solution
 - Precipitate Drying
- Gravimetry Calculations
- Application

Learning Outcomes:

At the end of this chapter:

- (1) The **specific steps** involved in gravimetric analysis.
- (2) **Properties of a successful precipitate.**
- (3) **Calculation procedures** for determining the quantity of analyte from the weight of precipitate.

Outline

- Introduction to Gravimetry Analysis
- Properties of Precipitates
- Precipitation Process
 - Colloidal Precipitates
 - Crystalline Precipitates
 - Co-precipitation
 - Homogeneous Solution
 - Precipitate Drying
- Gravimetry Calculations
- Application

Introduction to Gravimetric Analysis

- Methods of analysis that **are based on the measurement of mass**.
- One of the most accurate and precise methods of macro-quantitative analysis.

Overall gravimetric analysis involved:

1. The analyte/sample is selectively converted to an **insoluble form**.
2. The **separated precipitate is dried or ignited** → to another form and is **accurately weighed**.
3. From the **weight of the precipitate** and a knowledge of its chemical composition, we can **calculate the weight** of analyte in the desired form.

Gravimetric Methods

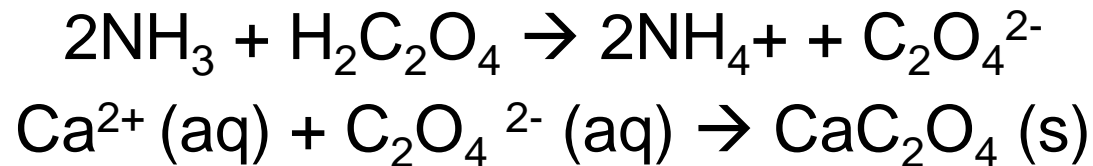
1. Precipitation Method

In precipitation method, the analyte is converted to an **insoluble product**, **filtered**, **washed** and **heated**. The mass of the **resulting residue** is **determined**.

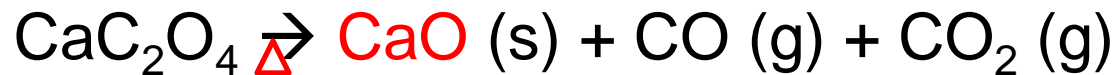


Example of Precipitation Method: Determining Calcium in Natural Waters

- An excess of **oxalic acid**, $\text{H}_2\text{C}_2\text{O}_4$, is added to an aqueous solution of the sample.
- Ammonia is then added, which neutralizes the acid and causes essentially all of the **calcium** in the sample to **precipitate as calcium oxalate**.
- The reactions are:



- The precipitate is **filtered** using a weighed filtering crucible, then **dried and ignited**.
- This process converts the precipitate entirely to calcium oxide:



- After cooling, the **crucible and precipitate are weighed**, and the **mass of calcium oxide** is determined by **subtracting the known mass of the crucible**.

2. Volatilization Method

In volatilization method, **the analyte is heated and the analyte or its decomposition product is collected.**
The resulting **loss of mass is determined.**



Outline

- Introduction to Gravimetry Analysis
- **Properties of Precipitates**
- Precipitation Process
 - Colloidal Precipitates
 - Crystalline Precipitates
 - Co-precipitation
 - Homogeneous Solution
 - Precipitate Drying
- Gravimetry Calculations
- Application

Properties of Precipitate in a Successful Gravimetric Analysis

- Quality of precipitate:
 - i. Easily filtered and washed, free of contaminants.
 - ii. No significant loss of the analyte occurs during filtration and washing.
 - iii. Unreactive with constituents of the atmosphere.

Factors:

- A gravimetric precipitating agent should react specifically or at least selectively with the analyte.
- Accurate gravimetric analysis requires careful manipulation in forming and treating the precipitate.

Outline

- Introduction to Gravimetry Analysis
- Properties of Precipitates
- Precipitation Process
 - Colloidal Precipitates
 - Crystalline Precipitates
 - Co-precipitation
 - Homogeneous Solution
 - Precipitate Drying
- Gravimetry Calculations
- Application

Precipitation Process: What Steps Are Involved ?

Steps involved in a precipitation:

1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration
5. Washing
6. Drying or igniting
7. Weighing

1. Preparation of Analyte Solution

- Preliminary separation may be necessary to eliminate **potential interferences** before precipitating analyte.
- May require **pH and/or other adjustments** to maximize precipitate formation.
- Select **precipitating agents that are selective** (or specific, if possible).

2. Precipitation

- High quality precipitate should
 - Sufficiently insoluble
 - Have large crystals → easier to filter
 - Free of contaminants → large crystal could minimize contamination
- The smaller the solubility,
 - the greater the tendency to form lots of small crystals that trap contaminants and are difficult to filter
- The greater the solubility,
 - the more analyte is left unprecipitated
- Balance is needed.

Precipitation Process

1) Supersaturation



2) Nucleation



3) Precipitation

1) **Supersaturation** occurs

→ the solution phase contains **more of dissolved salt** than at equilibrium.

2) Following by **Nucleation**

→ a **minimum** number of particle must **gather** to produce **microscopic nuclei**.

→ the **higher the degree of supersaturation**, the **greater the rate of nucleation**.

3) Following by **Precipitation**,

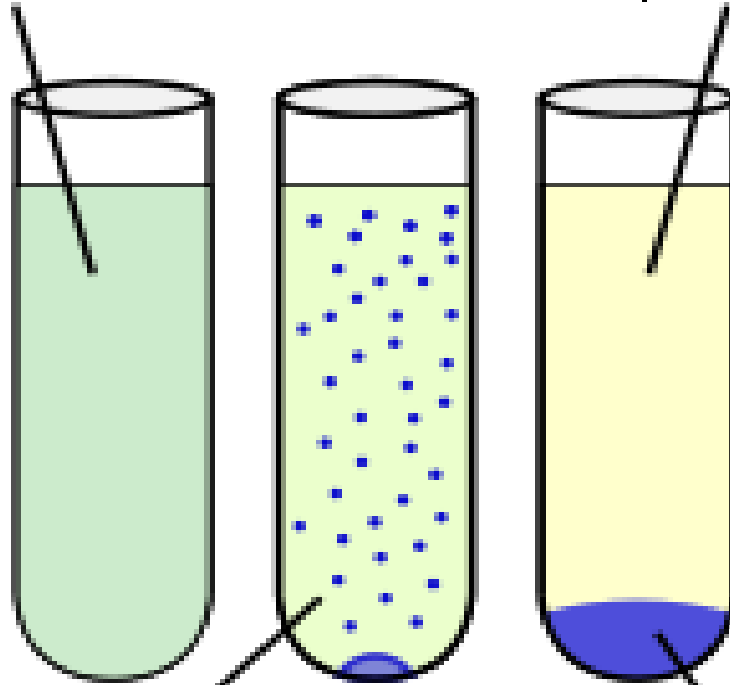
- the initial nucleus, will grow by **depositing other precipitate particles** to form crystal.
- the greater supersaturation, the more rapid the crystal growth rate.
- however, increased of growth rate increases the chances of **imperfections in the crystal** and **trapping of impurities** → balance is needed.

Solution

Supernate

Suspension

Precipitate



Colloidal Precipitation

- Colloidal → large number of small particles (1 to 100 μ m) and have a very large surface-to-mass ratio which promote surface adsorption.
- Colloidal particles show no tendency to settle from solution
- Cause difficulties in filtering and washing.

Crystalline Precipitation

- Particles with dimensions of a millimeter or greater.
- The particles tend to **settle spontaneously**.
- **Easily filtered.**

Particle Size of Precipitates: The von Weimarn Ratio

- Particle size of precipitates is **inversely proportional to the relative supersaturation** of the solution during precipitation process.
- **Relative Supersaturation (von Weimarn Ratio)**
$$= (Q - S)/S$$
 - Q = concentration of mixed reactants before precipitation
 - S = solubility of precipitate at equilibrium

- The lower the relative supersaturation the better the precipitation:
 - If high, get excessive nucleation, produce lots of small crystals with high surface area.
 - If low, get larger crystals and fewer small crystals with low surface area

Favorable Conditions for Precipitation

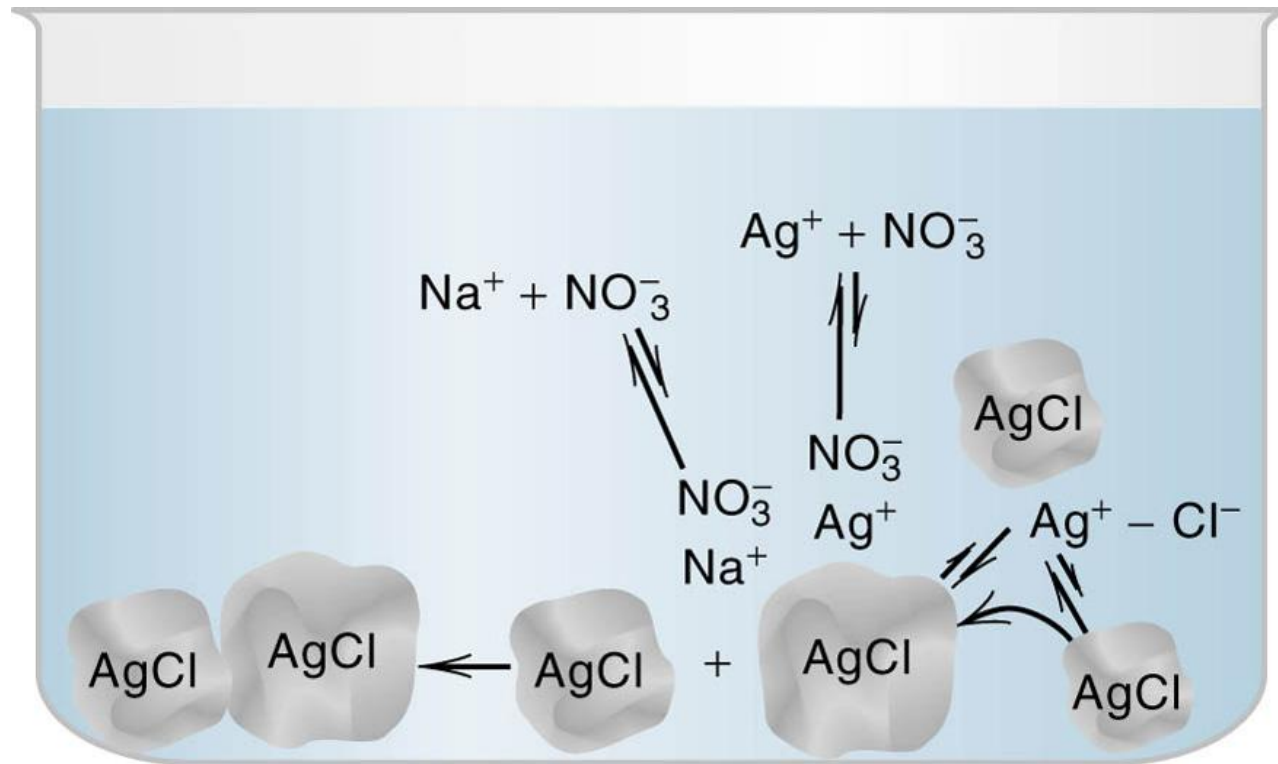
We want to keep Q low and S high during precipitation.
Minimize relative supersaturation and obtain large crystal:

1. Precipitate from **dilute solution**. (Q low)
2. Add dilute precipitating reagents slowly, with **effective stirring** (Q low and prevent excess of reagents)
3. Precipitate from **hot solution**. (High- S)
4. Precipitate at **low pH** as possible (adjust the pH). (High- S)
5. Add a **little excess of the precipitating agent** -check completeness of the precipitation.

3. Digestion (Ostwald Ripening)

- A process in which a precipitate is **heated for an hour or more in the solution** from which it was formed (the mother liquor).
- Digest the precipitate **to make larger and more pure crystal** → the **large crystals grow at the expense of the small one.**

Ostwald Ripening



During digestion at elevated temperature:

- Small particles tend to dissolve and reprecipitate on larger ones.
- Individual particles agglomerate.
- Adsorbed **impurities tend to go into solution** → **imperfection of the crystals tend to disappear.**

Advantages of Digestion

- Digestion makes:
 - i) **larger crystals**
 - ii) **reduces surface contamination**
 - iii) **reduces crystal imperfections**
- Digestion coagulates a colloid (causes the particles to agglomerate, or stick together), but **surface area does not decrease** as much as if larger crystals actually grew.
- Usually done at **elevated temperature to speed** the process.

Impurities in Precipitates

- Precipitates tend to carry down from the solution containing **other constituents that are normally soluble**, causing the **precipitate to become contaminated** → **Co-precipitation**

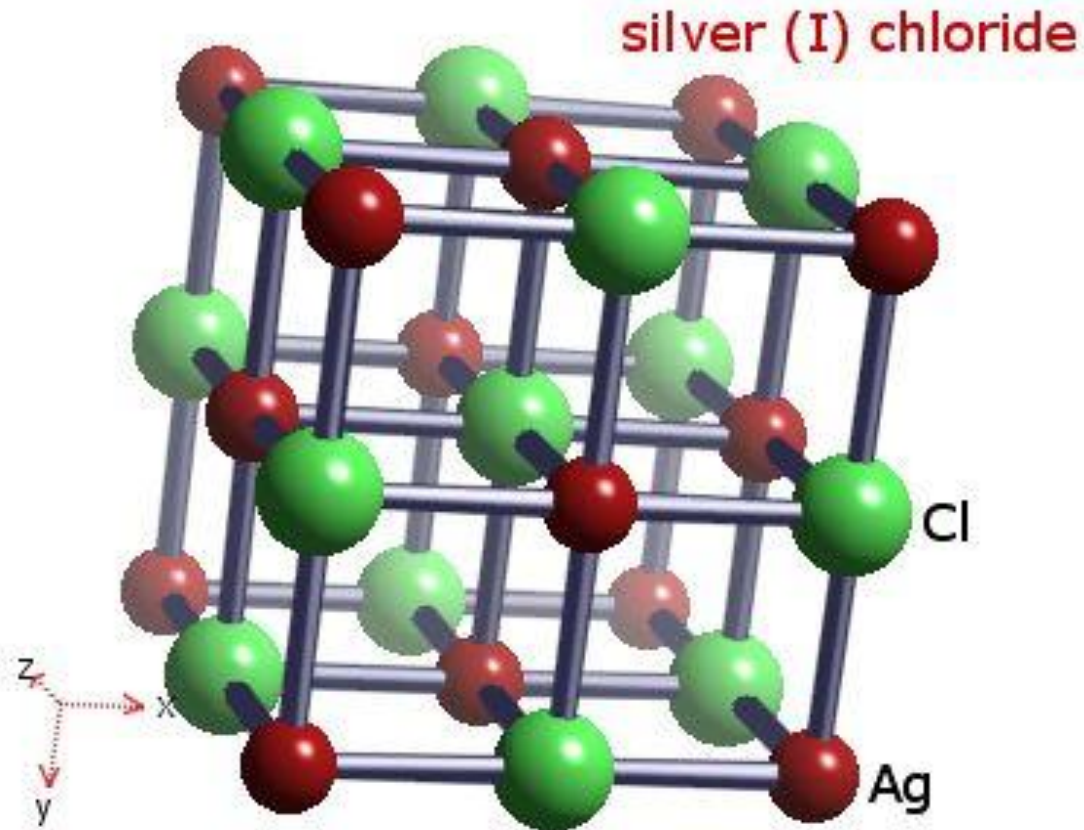
Types of co-precipitation:

- i) Occlusion and Inclusion
- ii) Surface adsorption
- iii) Isomorphous replacement
- iv) Mechanical entrapment

i) Occlusion and Inclusion

- Occlusion → material (e.g. foreign ions, water) that is not part of the crystal structure is **trapped within the growing crystal**.
- Inclusion → when ions are **trapped within the crystal lattice**.
- Occluded and included impurities are difficult to remove.
- **Digestion and purification by dissolving and reprecipitating** may help.
- The impurities **cannot be removed by washing**.

Crystal Lattice for AgCl



ii) Surface Adsorption

- Adsorption is a **common source** of co-precipitation and is likely to cause **significant contamination** of precipitates with **large specific surface areas (coagulated colloids)** .

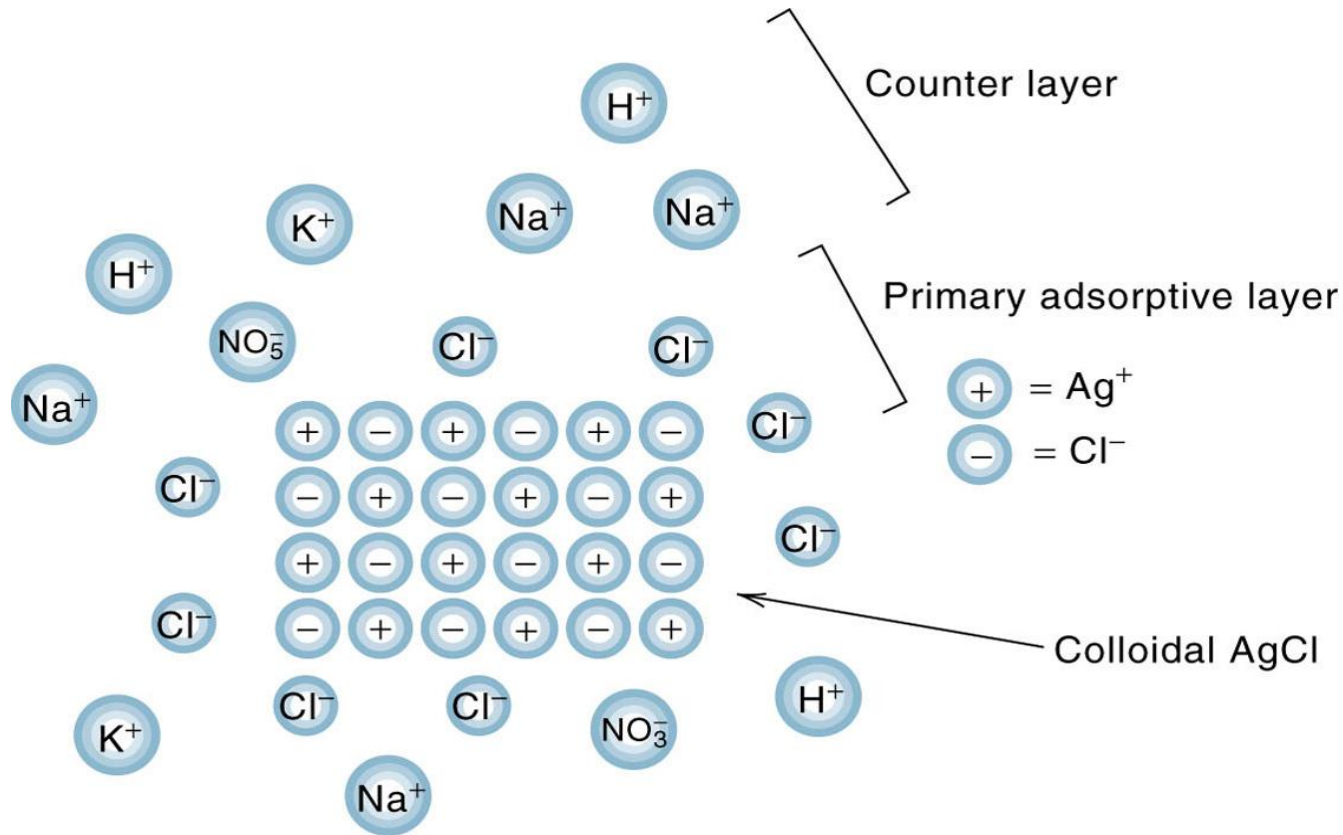
Example: **Precipitation of AgCl**

Primary adsorption layer

- **Ion in excess adsorbs on the surface** of the precipitate
 - Crystal becomes positive if Ag^+ is in excess
 - Crystal becomes negative if Cl^- is in excess

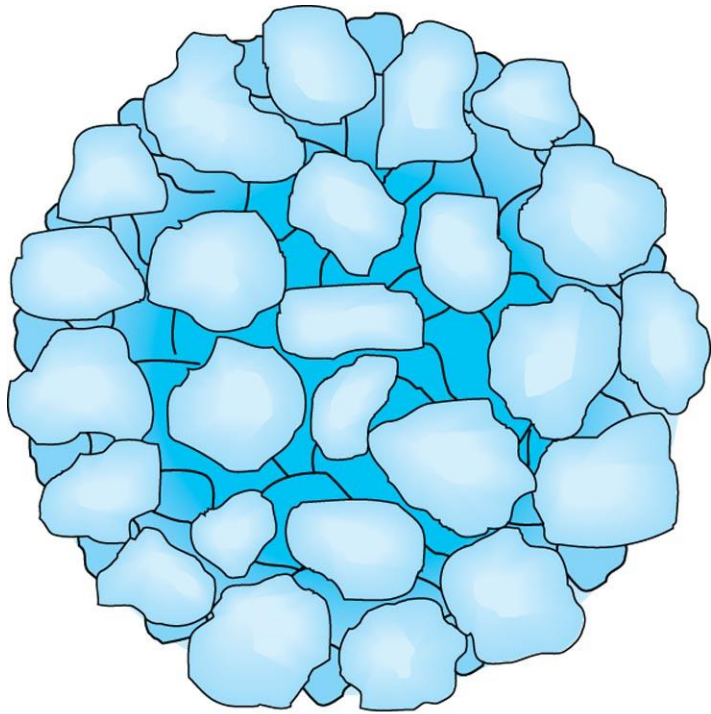
- Counter-ion layer (counterlayer)
 - A layer of solution contains ions of opposite charge to balance the charge on the primary adsorption layer.
 - For example, NO_3^- attracted to positive crystal, Ag^+ and results in a layer of AgNO_3 around the AgCl .
 - For example, Na^+ attracted to negative crystal, Cl^- and results in a layer of NaCl around the AgCl .
- The counter layer completely neutralizes the primary layer → will collect together to form large particles (coagulate).

Representation of silver chloride colloidal particle and adsorptive layers when Cl^- is in excess.



→ Cl^- adsorbs on the particles when in excess (**primary layer**).

→ A **counter layer of cations forms**. The neutral double layer causes the colloidal particles to coagulate.



© 2004 Thomson - Brooks/Cole

A **coagulated colloid** → large specific surface area

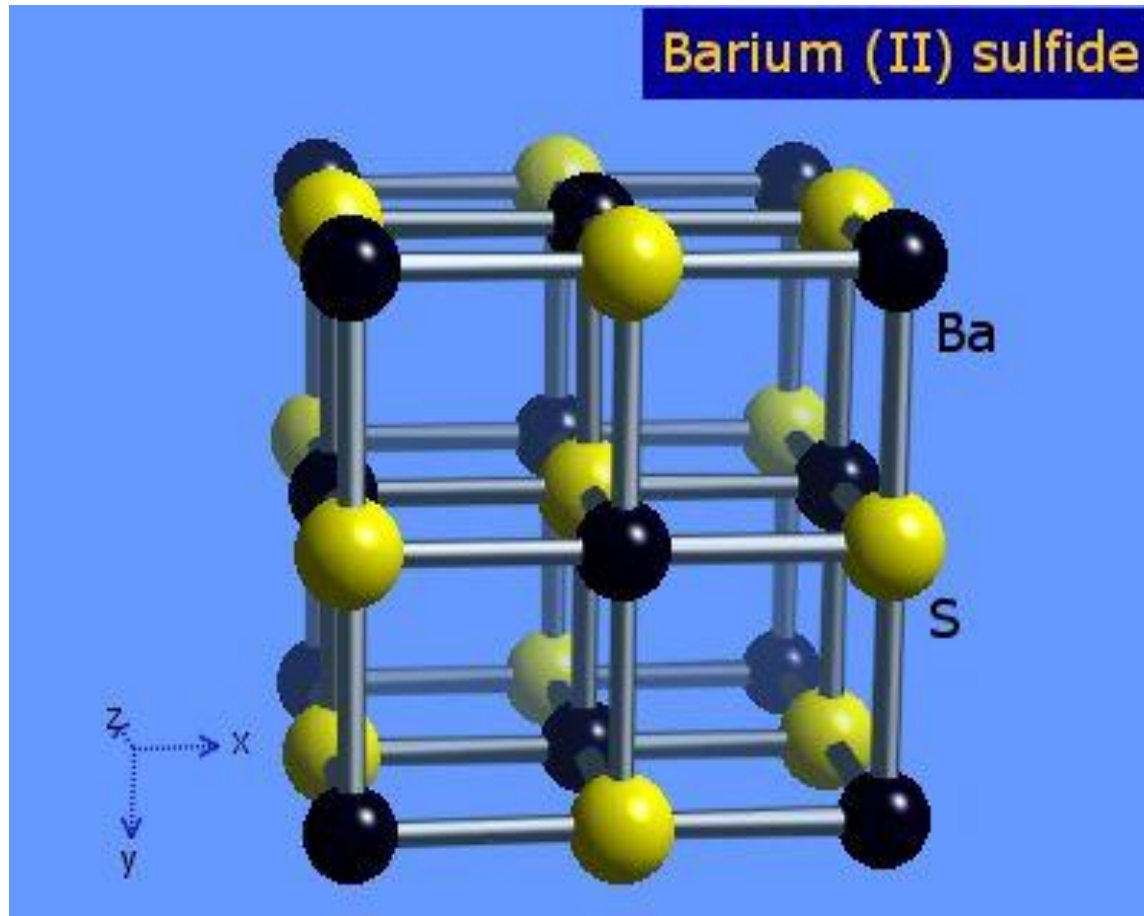
- When colloidal precipitates are filtered, they **retain the adsorbed primary and secondary** ion layers along with the solvent.
- Washing the particles with water causing the secondary layer to be loosely bound, and **the particles revert to the colloidal state (peptization)**
- **Adding electrolytes to promote coagulation.** For example HNO_3 or NH_4NO_3 for AgCl precipitate.

- In order to **minimizing adsorbed impurities** on colloids:
 - Using **digestion** process to improve the purity.
 - **Washing a coagulated colloid** with a solution containing a **volatile electrolyte**.
The adsorbed layers can often be removed by washing.
 - **Reprecipitation** is effective way to minimize the effects of adsorption (precipitate is re-dissolved the reprecipitated)

iii) Isomorphous Replacement (Mixed Crystal Formation)

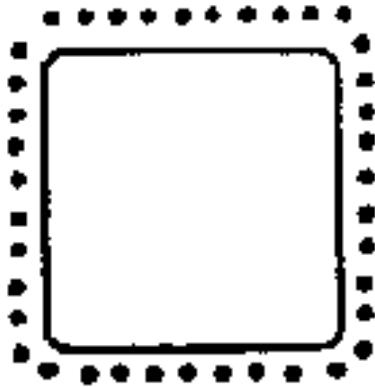
- One of the ions in the crystal lattice of a solid **is replaced by an ion of another element** → **mixed crystal**. Example: Pb ion replace some of the Ba ion (contaminant ion).
- The ions have the **same type of formula** and crystallized in **similar geometric forms** (lattice dimensions are about the same)
- In order to minimizing isomorphous replacement:
 - the interfering ion may have to be **separated** before the final precipitation step.
 - a **different precipitating reagent** that does not give mixed crystals with the ions interested may be used.

Crystal Lattice for BaS

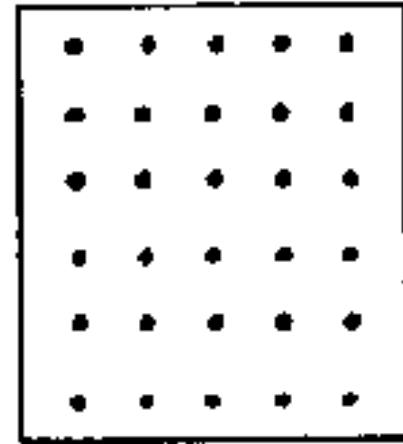


iv) Mechanical Entrapment

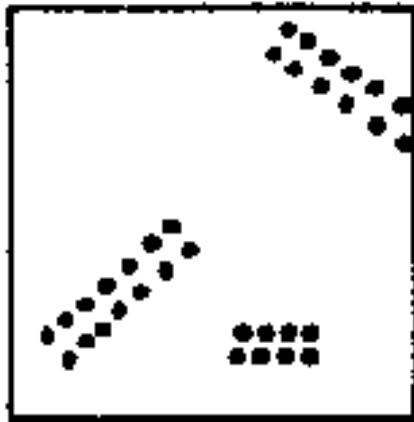
- Mechanical entrapment occurs **when crystals lie close together during growth.**
- Several crystals grow together and in so, doing **trap a portion of the solution** in a tiny pocket.
- Can be minimized when the **rate of precipitate formation is low**—that is under conditions of **low supersaturation.**
- **Digestion** is often remarkably helpful in reducing this types of coprecipitation.



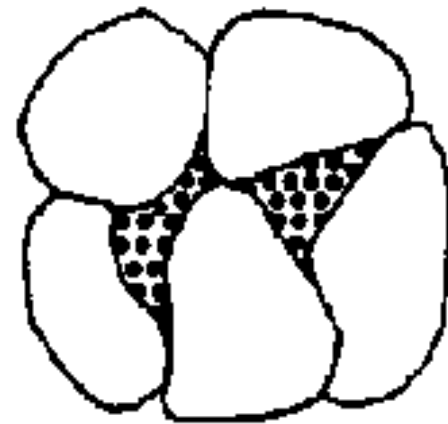
Surface
Adsorption



Isomorphous
Replacement



Occlusion



Mechanical
Entrapment

Outline

- Introduction to Gravimetry Analysis
- Properties of Precipitates
- Precipitation Process
 - Colloidal Precipitates
 - Crystalline Precipitates
 - Co-precipitation
 - Homogeneous Solution
 - Precipitate Drying
- Gravimetry Calculations
- Application

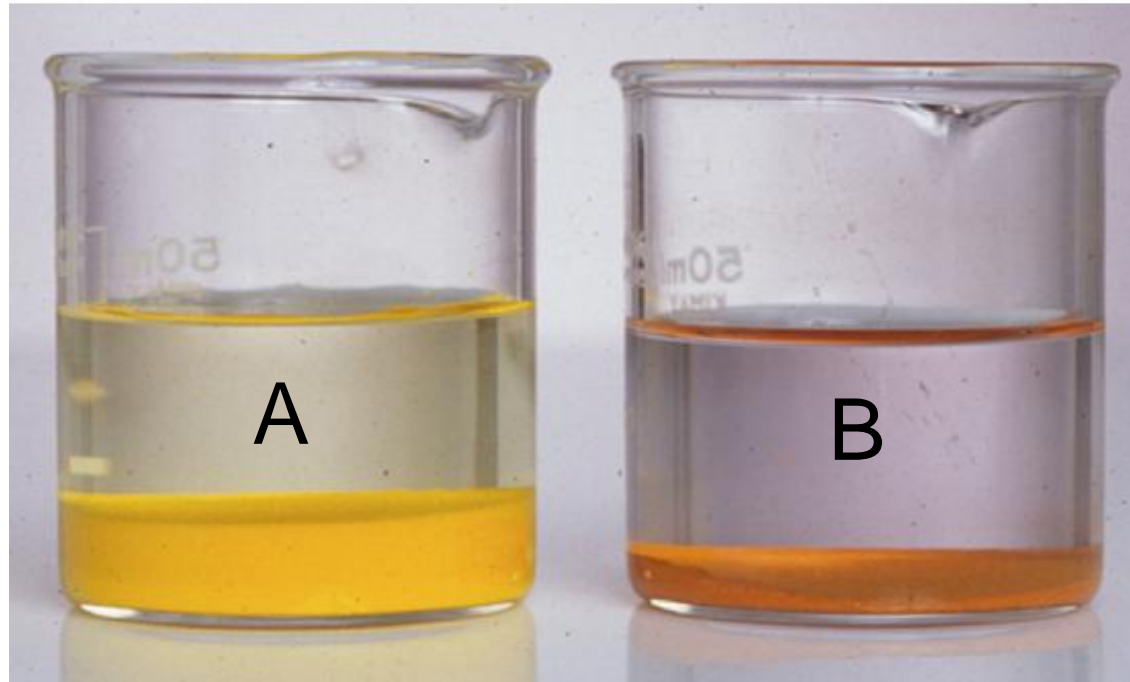
Precipitation from Homogeneous Solution

- A technique in which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction.
- The precipitating agent appears gradually and homogeneously throughout the solution and reacts immediately with the analyte.
- As a result, the relative supersaturation is kept low during the entire precipitation.
- Better suited for analysis than a solid formed by direct addition of a precipitating reagent.

TABLE 12-1
Methods for Homogeneous Generation of Precipitating Agents

Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH^-	Urea	$(\text{NH}_2)_2\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^-$	Al, Ga, Th, Bi, Fe, Sn
PO_4^{3-}	Trimethyl phosphate	$(\text{CH}_3\text{O})_3\text{PO} + 3\text{H}_2\text{O} \rightarrow 3\text{CH}_3\text{OH} + \text{H}_3\text{PO}_4$	Zr, Hf
$\text{C}_2\text{O}_4^{2-}$	Ethyl oxalate	$(\text{C}_2\text{H}_5)_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{C}_2\text{O}_4$	Mg, Zn, Ca
SO_4^{2-}	Dimethyl sulfate	$(\text{CH}_3\text{O})_2\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + \text{SO}_4^{2-} + 2\text{H}_3\text{O}^+$	Ba, Ca, Sr, Pb
CO_3^{2-}	Trichloroacetic acid	$\text{Cl}_3\text{CCOOH} + 2\text{OH}^- \rightarrow \text{CHCl}_3 + \text{CO}_3^{2-} + \text{H}_2\text{O}$	La, Ba, Ra
H_2S	Thioacetamide*	$\text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S}$	Sb, Mo, Cu, Cd
DMG^\dagger	Biacetyl + hydroxylamine	$\text{CH}_3\text{COCOCH}_3 + 2\text{H}_2\text{NOH} \rightarrow \text{DMG} + 2\text{H}_2\text{O}$	Ni
HOQ^\ddagger	8-Acetoxyquinoline§	$\text{CH}_3\text{COOQ} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HOQ}$	Al, U, Mg, Zn

Example: Two precipitates of PbCrO_4

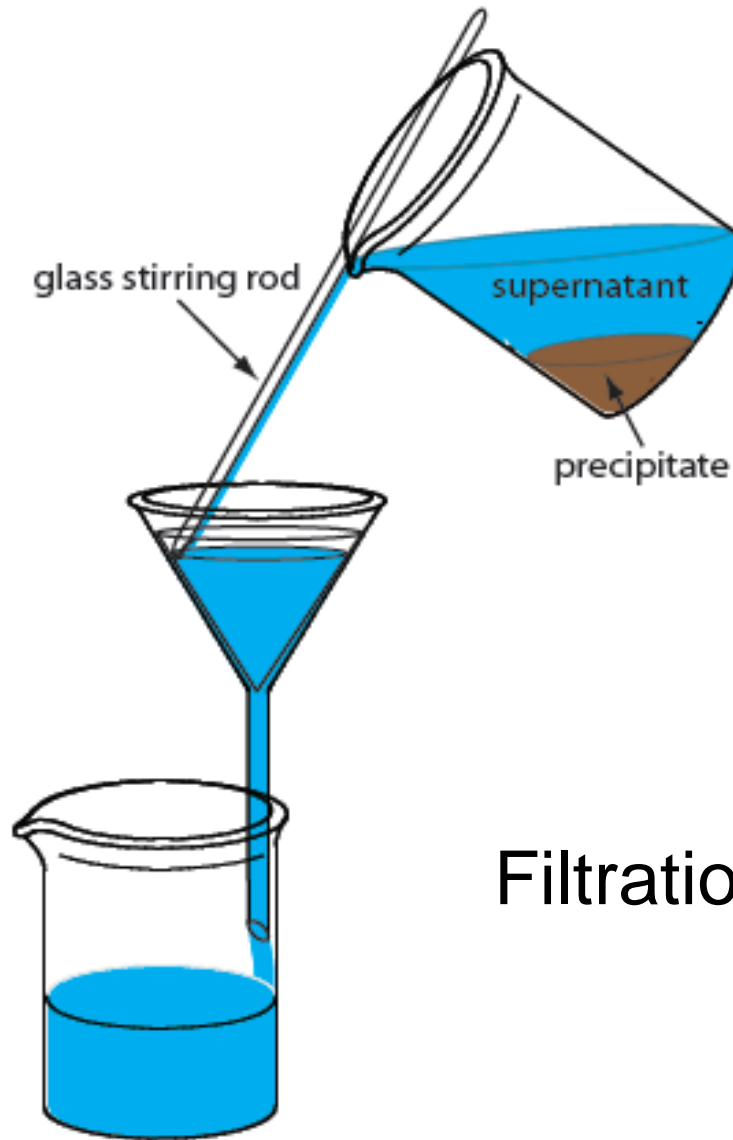


In **Beaker A**, combining 0.1 M $\text{Pb}(\text{NO}_3)_2$ and 0.1 M K_2CrO_4 forms the precipitate (under conditions of **high RSS**). The precipitate forms rapidly and consists of **very small particles**.

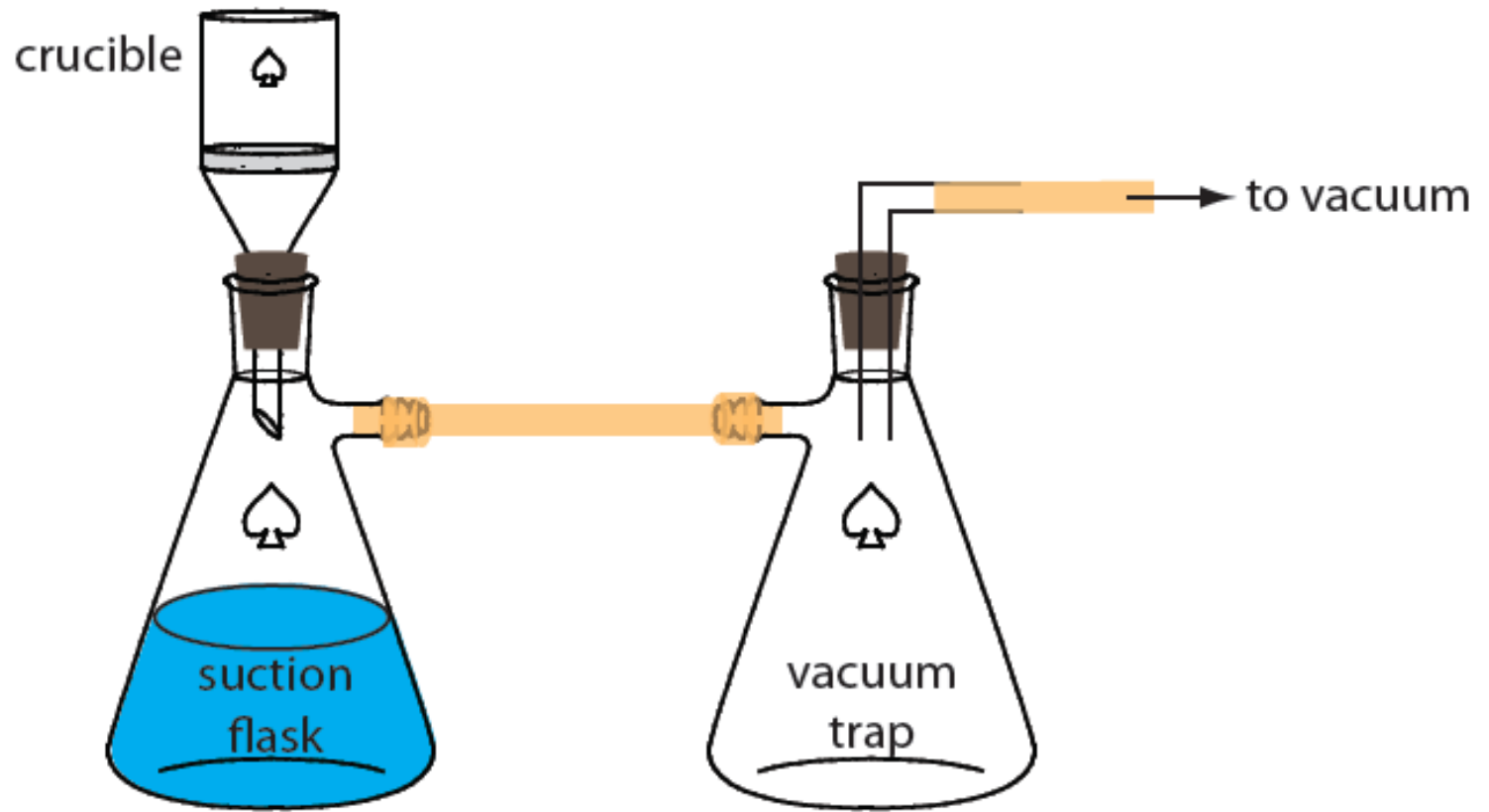
In **Beaker B**, **heating a solution** of 0.1 M $\text{Pb}(\text{NO}_3)_2$, 0.1 M $\text{Cr}(\text{NO}_3)_3$, and 0.1 M KBrO_3 slowly oxidizes Cr^{3+} to CrO_4^{2-} , precipitating PbCrO_4 (under conditions of **low RSS**). The precipitate forms slowly and consists of much **larger particles**.

4. Filtration

- Depend on your ability to decant the solution, transfer the precipitate to the filter correctly and completely.
- Colloidal precipitates present filtering problems if particles are too small.



Filtration through a filtering
paper



Filtration through a filtering crucible
(funnel)

5. Washing

- Removes the **mother liquor** (main solution).
- Remove **coprecipitated compounds**.
- Many precipitates can not be washed with pure water
→ **peptization occurs**.

- Peptization is the reverse of coagulation by which a coagulated colloids reverts to its original dispersed state (the precipitate reverts to a colloidal state and is lost) → avoided by washing with an electrolyte that can be volatilized by heating.
- The electrolyte must be one that is volatile at the temperature to be used for drying or ignition and it must not dissolve the precipitate.

6. Drying or Igniting

- Dry the precipitate to **remove water and volatile electrolytes** from wash solution → Suitable for weighing.
- **Heating** at 110-120 °C for 1-2 h.
- **Ignition** (very high-temperature drying) converts precipitates to compounds more suitable for weighing.



TI
GI
AS

Precipitation Process



7. Weighing

- Properly calibrated analytical balance
- Good weighing technique
- Avoid static electricity
- Review important procedures periodically

Outline

- Introduction to Gravimetry Analysis
- Properties of Precipitates
- Precipitation Process
 - Colloidal Precipitates
 - Crystalline Precipitates
 - Co-precipitation
 - Homogeneous Solution
 - Precipitate Drying
- Gravimetry Calculations
- Application

Gravimetric Calculations

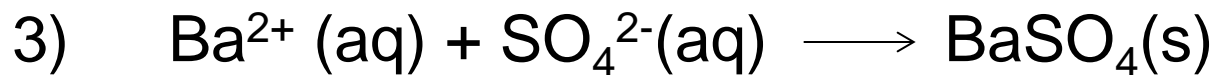
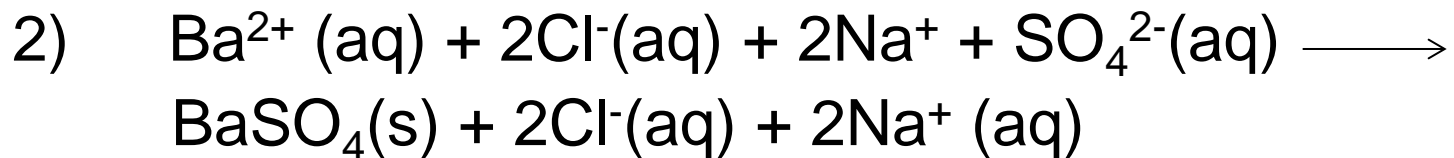
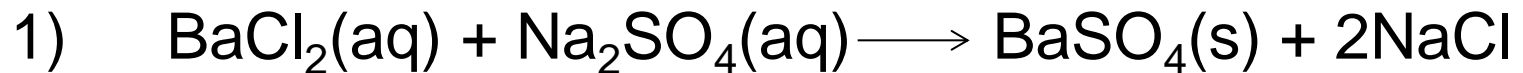
- Precipitate –usually in different form than the analyte whose weight we wish to report.
- Calculations of analyte content requires knowledge of :
 - ✓ Chemistry
 - ✓ Stoichiometry
 - ✓ Composition of precipitate
- Get mole ratio from balanced **reaction equation**.
- Can also get mole ratio from **formulas of analyte and precipitate**.

Mole Ratio From Balanced Equation

Example:

A typical precipitation reaction occurs when an aqueous solution of **barium chloride** is mixed with one containing **sodium sulfate**;

The equations:



Gravimetric Factor (GF)

- GF – represents the **weight of analyte (or substance sought) per unit weight of precipitate**.
- Obtained from the **ratio of the formula weight of the analyte to that of the precipitate**, multiplied by the **moles of analyte per mole of precipitate** obtained from each mole of analyte.

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

$$= \text{g analyte/g precipitate}$$

- uses “f wt” and “at wt” to symbolize **formula weight** and **atomic weight**, sometimes called molar mass

Examples GF

Precipitate, ppt

Analyte	ppt	G.F.
CaO	CaCO ₃	CaO/CaCO ₃ x 1/1
FeS	BaSO ₄	FeS/BaSO ₄ x 1/1
PbCl ₂	PbCrO ₄	PbCl ₂ /PbCrO ₄ x 1/1

Example 1

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

<i>Analyte</i>	<i>Precipitate</i>
P	Ag₃PO₄
K ₂ HPO ₄	Ag ₃ PO ₄
Bi ₂ S ₃	BaSO ₄

Solution

$$\text{g P/g Ag}_3\text{PO}_4 = \frac{30.97 \text{ (g P/mol)}}{418.58 \text{ (g Ag}_3\text{PO}_4\text{/mol)}} \times \frac{1}{1} = 0.07399 \text{ g P/g Ag}_3\text{PO}_4 = \text{GF}$$

$$\begin{aligned} \text{g K}_2\text{HPO}_4\text{/g Ag}_3\text{PO}_4 &= \frac{174.18 \text{ (g K}_2\text{HPO}_4\text{/mol)}}{418.58 \text{ (g Ag}_3\text{PO}_4\text{/mol)}} \times \frac{1}{1} = 0.41612 \text{ g K}_2\text{HPO}_4\text{/g Ag}_3\text{PO}_4 \\ &= \text{GF} \end{aligned}$$

$$\begin{aligned} \text{g Bi}_2\text{S}_3\text{/g BaSO}_4 &= \frac{514.15 \text{ (g Bi}_2\text{S}_3\text{/mol)}}{233.40 \text{ (g BaSO}_4\text{/mol)}} \times \frac{1}{3} = 0.73429 \text{ g Bi}_2\text{S}_3\text{/g BaSO}_4 \\ &= \text{GF} \end{aligned}$$

- In gravimetric analysis, we generally interested in the **% composition by weight** of the analyte in the sample:

$$\% \text{ substance sought} = \frac{\text{weight of substance sought (g)}}{\text{weight of sample (g)}} \times 100\%$$

Weight of substance sought (g) = weight of precipitate (g)

$$\times \frac{f \text{ wt substance sought (g/mol)}}{f \text{ wt precipitate (g/mol)}} \\ \times \frac{a}{b} \text{ (mol substance sought/mol precipitate)}$$

= weight of precipitate (g)

$$\times \text{GF (g sought/g precipitate)}$$

- In % basis:

$$\% A = \frac{g_A}{g_{sample}} \times 100\%$$

- Where g_A represents the grams of analyte (the desired test substance or substance sought) and g_{sample} represents the grams of sample taken for analysis
- General formula for calculating the % composition of the substance sought:

$$\% \text{ sought} = \frac{\text{weight of precipitate (g)} \times \text{GF (g sought/g precipitate)}}{\text{weight of sample (g)}} \times 100\%$$

Example 2

Orthophosphate (PO_4^{3-}) is determined by weighing as ammonium phosphomolybdate, $(\text{NH}_4)\text{PO}_4 \cdot 12\text{MoO}_3$. Calculate the percent P in the sample and the percent P_2O_5 if 1.1682 g precipitate (ppt) were obtained from a 0.2711-g sample. Perform the % P calculation using the gravimetric factor.

Given: Molar mass of P = 30.97 g/mol

Molar Mass of $(\text{NH}_4)\text{PO}_4 \cdot 12\text{MoO}_3 = 1876.5 \text{ g/mol}$

Molar Mass of $\text{P}_2\text{O}_5 = 141.95 \text{ g/mol}$

Solution

$$\% \text{ P} = \frac{1.1682 \text{ g ppt} \times \frac{\text{P}}{(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3} (\text{g P/g ppt})}{0.2711 \text{ g sample}} \times 100\%$$

$$= \frac{1.1682 \text{ g} \times (30.97/1876.5)}{0.2711 \text{ g}} \times 100\% = 7.111\%$$

$$\% \text{ P}_2\text{O}_5 = \frac{1.1682 \text{ g ppt} \times \frac{\text{P}_2\text{O}_5}{2(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3} (\text{g P}_2\text{O}_5/\text{g ppt})}{0.2711 \text{ g sample}} \times 100\%$$

$$= \frac{1.1682 \text{ g} \times [141.95/(2 \times 1876.5)]}{0.2711 \text{ g}} \times 100\%$$


$$= 16.30\%$$

Example 3

An ore is analyzed for the manganese content by converting the manganese to Mn_3O_4 and weighing it. If a 1.52 g sample yields Mn_3O_4 weighing 0.126 g, what would be the percent Mn_2O_3 in the sample? The percent Mn?

Given molar masses of Mn, Mn_3O_4 and Mn_2O_3 are 54.94 g/mol, 228.8 g/mol and 157.9 g/mol, respectively.

Solution


$$\begin{aligned}\% \text{ Mn}_2\text{O}_3 &= \frac{0.126 \text{ g Mn}_3\text{O}_4 \times \frac{3\text{Mn}_2\text{O}_3}{2\text{Mn}_3\text{O}_4} (\text{g Mn}_2\text{O}_3/\text{g Mn}_3\text{O}_4)}{1.52 \text{ g sample}} \times 100\% \\ &= \frac{0.126 \text{ g} \times [3(157.9)/2(228.8)]}{1.52 \text{ g}} \times 100\% = 8.58\%\end{aligned}$$

$$\begin{aligned}\% \text{ Mn} &= \frac{0.126 \text{ g Mn}_3\text{O}_4 \times \frac{3\text{Mn}}{\text{Mn}_3\text{O}_4} (\text{g Mn/g Mn}_3\text{O}_4)}{1.52 \text{ g sample}} \times 100\% \\ &= \frac{0.126 \text{ g} \times [3(54.94)/228.8]}{1.52 \text{ g}} \times 100\% = 5.97\%\end{aligned}$$

Example 4

An iron ore was analyzed by dissolving a 1.1324 g sample in concentrated HCl. The resulting solution was diluted with water, and the iron (III) was precipitated as the hydrous oxide $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ by the addition of NH_3 . After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate:

- (a) The % Fe (55.847 g/mol) and
- (b) The % Fe_3O_4 (231.54 g/mol) in the sample

Outline

- Introduction to Gravimetry Analysis
- Properties of Precipitates
- Precipitation Process
 - Colloidal Precipitates
 - Crystalline Precipitates
 - Co-precipitation
 - Homogeneous Solution
 - Precipitate Drying
- Gravimetry Calculations
- Application

Application of Gravimetric Methods

- Has been developed for most inorganic anions and cations, as well as for such neutral species as water, sulfur dioxide, carbon dioxide, and iodine.
- A variety of organic substances can also be easily determined gravimetrically.
- Examples:
 - lactose in milk products
 - salicylates in drug preparations
 - phenolphthalein in laxatives
 - nicotine in pesticides
 - cholesterol in cereals
 - benzaldehyde in almond extracts.

Type of Precipitating Agent

- **Inorganic Precipitating Agents**
 - These reagents typically form **slightly soluble salts** or **hydrous oxides** with the analyte.

- **Reducing Agents**
 - This type of reagents convert an analyte to its **elemental form** for weighing.

- **Organic Precipitating Agents**
 - i) forms slightly **soluble non-ionic** products
 - ii) forms **largely ionic** products.

TABLE 12-2

Some Inorganic Precipitating Agents

UNIVERSITI
TEKNOLOGI
PETRONAS

Precipitating Agent	Element Precipitated*
$\text{NH}_3(aq)$	Be (BeO), Al (Al_2O_3), Sc (Sc_2O_3), Cr (Cr_2O_3) [†] , Fe (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), In (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO) [†] , Zn (ZnO , or ZnSO_4), Ge (GeO_2), As (<u>As_2O_3</u> , or As_2O_5), Mo (MoO_3), Sn (SnO_2) [†] , Sb (<u>Sb_2O_3</u> , or Sb_2O_5), Bi (Bi_2S_3)
$(\text{NH}_4)_2\text{S}$	Hg (<u>HgS</u>), Co (Co_3O_4)
$(\text{NH}_4)_2\text{HPO}_4$	Mg ($\text{Mg}_2\text{P}_2\text{O}_7$), Al (AlPO_4), Mn ($\text{Mn}_2\text{P}_2\text{O}_7$), Zn ($\text{Zn}_2\text{P}_2\text{O}_7$), Zr ($\text{Zr}_2\text{P}_2\text{O}_7$), Cd ($\text{Cd}_2\text{P}_2\text{O}_7$), Bi (BiPO_4)
H_2SO_4	Li, Mn, Sr, Cd, Pb, Ba (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6 , or Pt), Rb (<u>Rb_2PtCl_6</u>), Cs (<u>Cs_2PtCl_6</u>)
$\text{H}_2\text{C}_2\text{O}_4$	Ca (CaO), Sr (SrO), Th (ThO_2)
$(\text{NH}_4)_2\text{MoO}_4$	Cd (CdMoO_4) [†] , Pb (<u>PbMoO_4</u>)
HCl	Ag (AgCl), Hg (Hg_2Cl_2), Na (as NaCl from butyl alcohol), Si (SiO_2)
AgNO_3	Cl (AgCl), Br (<u>AgBr</u>), I (<u>AgI</u>)
$(\text{NH}_4)_2\text{CO}_3$	Bi (Bi_2O_3)
NH_4SCN	Cu [$\text{Cu}_2(\text{SCN})_2$]
NaHCO_3	Ru, Os, Ir (precipitated as hydrous oxides; reduced with H_2 to metallic state)
HNO_3	Sn (SnO_2)
H_5IO_6	Hg [$\text{Hg}_5(\text{IO}_6)_2$]
NaCl , $\text{Pb}(\text{NO}_3)_2$	F (PbClF)
BaCl_2	SO_4^{2-} (BaSO_4)
MgCl_2 , NH_4Cl	PO_4^{3-} ($\text{Mg}_2\text{P}_2\text{O}_7$)

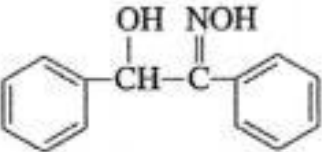
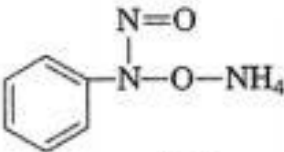
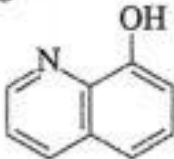
TABLE 12-3

Some Reducing Agents Employed in Gravimetric Methods

Reducing Agent	Analyte
SO ₂	Se, Au
SO ₂ + H ₂ NOH	Te
H ₂ NOH	Se
H ₂ C ₂ O ₄	Au
H ₂	Re, Ir
HCOOH	Pt
NaNO ₂	Au
SnCl ₂	Hg
Electrolytic reduction	Co, Ni, Cu, Zn Ag, In, Sn, Sb, Cd, Re, Bi

Table 10.2

Some Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime	$\begin{array}{c} \text{CH}_3 - \text{C} = \text{NOH} \\ \\ \text{CH}_3 - \text{C} = \text{NOH} \end{array}$	Ni(II) in NH_3 or buffered HOAc; Pd(II) in HCl $(\text{M}^{2+} + 2\text{HR} \rightarrow \underline{\text{MR}_2} + 2\text{H}^+)$
α -Benzoinoxime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ $(\text{M}^{2+} + \text{H}_2\text{R} \rightarrow \underline{\text{MR}} + 2\text{H}^+; \text{M}^{2+} = \text{Cu}^{2+}, \text{MoO}_2^{2+}, \text{WO}_2^{2+})$ Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) $(\text{M}^{n+} + n\text{NH}_4\text{R} \rightarrow \underline{\text{MR}_n} + n\text{NH}_4^+)$ Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) $(\text{M}^{n+} + n\text{HR} \rightarrow \underline{\text{MR}_n} + n\text{H}^+)$
Sodium diethyldithiocarbamate	$(\text{C}_2\text{H}_5)_2\text{N} - \text{C} \begin{array}{c} \text{S} \\ \\ \text{S}^- \text{Na}^+ \end{array}$	Many metals from acid solution $(\text{M}^{n+} + n\text{NaR} \rightarrow \underline{\text{MR}_n} + n\text{Na}^+)$
Sodium tetraphenylboron	$\text{NaB}(\text{C}_6\text{H}_5)_4$	$\text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Tl}^+, \text{Ag}^+, \text{Hg(I)}, \text{Cu(I)}, \text{NH}_4^+, \text{RNH}_3^+, \text{R}_2\text{NH}_2^+, \text{R}_3\text{NH}^+, \text{R}_4\text{N}^+$. Acidic solution $(\text{M}^+ + \text{NaR} \rightarrow \underline{\text{MR}} + \text{Na}^+)$
Tetraphenylarsonium chloride	$(\text{C}_6\text{H}_5)_4\text{AsCl}$	$\text{Cr}_2\text{O}_7^{2-}, \text{MnO}_4^-, \text{ReO}_4^-, \text{MoO}_4^{2-}, \text{WO}_4^{2-}, \text{ClO}_4^-, \text{I}_3^-$. Acidic solution $(\text{A}^{n-} + n\text{RCl} \rightarrow \underline{\text{R}_n\text{A}} + n\text{Cl}^-)$

Gravimetric methods **do not require a calibration or standardization step** because the results are **calculated directly** from the experimental data and atomic masses.

Thus, when only **one or two samples** are to be analyzed, a **gravimetric procedure may be the method of choice** because it **requires less time** and **effort** than a procedure that requires preparation of standards and calibration.

Recap: Topics under Gravimetric Analysis

- Introduction to Gravimetry Analysis
- Properties of Precipitates
- Precipitation Process
 - Colloidal Precipitates
 - Crystalline Precipitates
 - Co-precipitation
 - Homogeneous Solution
 - Precipitate Drying
- Gravimetry Calculations
- Application

End of the Chapter

Exercise

Q1:

Calculate the gravimetric factors for:

Substance Sought (molar mass, g/mol)	Substance Weight (molar mass, g/mol)
As_2O_3 (197.84)	Ag_3AsO_4 (462.53)
FeSO_4 (151.91)	Fe_2O_3 (159.70)

Q2:

Calculate the weight of sodium present in 50.0 g of Na_2SO_4 . Given the molar mass of Na = 23.0 g/mol and molar mass of Na_2SO_4 = 142 g/mol.