Chapter 12
Gravimetric Methods of Analysis

gravimetric
(weighing - measure)

Gravimetric Analysis

• A given analyte is isolated from the sample and weighed in some pure form.
• One of the most accurate and precise methods of macro quantitative analysis.
• One of the oldest methods known (before 1810).
• Absolute analysis (no standard needed).

Weighing sample → dissolving → reactions → precipitation → heating → filtration → drying → weighing → calculation
Isolation of an Analyte

- Precipitating it in an insoluble form.
  \[ \text{Ag}^+ + X^- \rightarrow \text{AgX} \downarrow \quad (X = \text{Cl}^-, \text{Br}^-, \text{I}^-) \]
- Depositing it as a pure metal by electrolysis.
  \[ \text{Cu}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Cu(s)} \]
- Converting it to a gas which is absorbed in a suitable reagent.

\[ \text{ex. For NaHCO}_3 \text{ in antacid tablets} \]
\[ \text{NaHCO}_3(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{NaHSO}_4(\text{aq}) \]
\[ \downarrow \text{absorption tube} \]

Criteria for the precipitate in Gravimetric Analysis

- Very low solubility (very low \( K_{sp} \)).
- Forms a particulate or large crystal solid.
- Be sufficiently pure and in a form suitable for drying and weighing.
- Stoichiometrical reactions.
- Preferably knows its solubility product.

Commonly Employed Gravimetric Analysis

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Precipitate Formed</th>
<th>Product Weighed</th>
<th>Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe(OH)(_3)</td>
<td>FeO(_2)</td>
<td>Many, Al, Ti, Cr, etc.</td>
</tr>
<tr>
<td>Al</td>
<td>Al(OH)(_3)</td>
<td>AlO(_2)</td>
<td>Many, Al, Ti, Cr, etc.</td>
</tr>
<tr>
<td>Ca</td>
<td>CaC(_2)O(_4)</td>
<td>CaCO(_3)</td>
<td>All metals except Alkalis and M</td>
</tr>
<tr>
<td>Cu</td>
<td>CuC(_2)O(_4)</td>
<td>CuO</td>
<td>All metals except Alkalis.</td>
</tr>
<tr>
<td>Mg</td>
<td>MgNH(_4)PO(_4)</td>
<td>MgPO(_4)</td>
<td>All metals except Mg.</td>
</tr>
<tr>
<td>Zn</td>
<td>ZnNH(_4)PO(_4)</td>
<td>ZnPO(_4)</td>
<td>All metals except Mg.</td>
</tr>
<tr>
<td>Ba</td>
<td>BaC(_2)O(_4)</td>
<td>BaSO(_4)</td>
<td>Pb</td>
</tr>
<tr>
<td>SO(_4)(_2)</td>
<td></td>
<td></td>
<td>NO(_3); PO(_4)(_3); OIO(_3)</td>
</tr>
<tr>
<td>Cl</td>
<td>AgCl</td>
<td>AgCl</td>
<td>Br(^-), I(^-), SCN(^-), CN(^-), S(^2)(^-), S(_2)O(_3)(^2)-</td>
</tr>
<tr>
<td>PO(_4)(_3)</td>
<td>M(_2)PO(_4)</td>
<td>M(_2)O(_3)</td>
<td>MoO(_4)(^2)-, C(_2)O(_2)(^2)-, K(^+)</td>
</tr>
</tbody>
</table>
Types of precipitating agents

- Inorganic
  
  \[ 2\text{NH}_3 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{NH}_4^+ + \text{C}_2\text{O}_4^{2-} \]
  
  \[ \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \rightarrow \text{CaC}_2\text{O}_4(s) \]
  
  \[ \text{CaC}_2\text{O}_4 \xrightarrow{\Delta} \text{CaO(s)} + \text{CO(g)} + \text{CO}_2(g) \]

- Organic (often with functional groups)

Properties of precipitates

- Particle size is important
  
  Large particles are easier to filter
  
  Colloidal suspensions = very small, does not settle (10^{-7} - 10^{-4} \text{ cm diameter})
  
  Fe(OH)_3 (gelatinous)
  
  Curdy: \( \text{AgCl} \rightarrow \) heating to ppt.
  
  Crystalline = larger, settles more easily (0.01-10 mm): \( \text{BaSO}_4 \)

Factors that determine the particle size of precipitates

- \( \checkmark \) ppt solubility
- \( \checkmark \) Temperature
- \( \checkmark \) Reactant concentrations
- \( \checkmark \) Rate at which reactants are mixed
How particles are formed (Mechanism)?

1. Supersaturated solution formed
2. Nucleation: formation of a solid particle with a minimum number of atoms or molecules
3. Particle growth: enlargement of existing particle with new atoms or molecules

- More nucleation yields large number of small particles
- More growth yields small number of large particles

Relative Supersaturation (RS)

\[ RS = \frac{Q - S}{S} \]

\[ \text{Particle size } \propto \frac{1}{RS} \]

Q: conc. of the solute at any instant
S: equilibrium solubility

RS ↑ → ppt size ↓ (colloidal)
RS ↓ → ppt size ↑ (crystalline solid)
**Experimental Control of Particle Size**

*RS↓, Q↓, S↑ → particle size ↑

1. Dilute sample solution and dilute reagents (Q↓)
2. Slow addition of precipitating agent with good stirring (Q↓)
3. In hot solution (S↑)
4. pH control (in acidic solution Q↓ and S↑)

* Precipitates with very low solubilities, such as many sulfides and hydrous oxides, generally form colloids.

**pH control of precipitation**

\[
\begin{align*}
\text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} & \rightleftharpoons \text{CaC}_2\text{O}_4 (s) \\
\text{H}_2\text{C}_2\text{O}_4 & \rightleftharpoons 2 \text{H}^+ + \text{C}_2\text{O}_4^{2-}
\end{align*}
\]

(Feeder Reaction)

a. In mildly acidic, CaC₂O₄ (s) → large, easily filtered crystals (moderately soluble)
b. Adding aqueous ammonia → pH↑ → completed precipitation

**Colloidal Precipitates**

- **Coagulation** (or agglomeration) of colloids: converting a colloid suspension into a filterable solid.
- **Adsorption**: a process in which a substance (gas, liquid or solid) is held on the surface of a solid. In contrast, absorption, involves retention of a substance within the pores of a solid.
A colloidal silver chloride particle
Suspended in a solution of silver nitrate

**Electric double layer:**

*Primary adsorbed layer*
Primary adsorbed ion:
1. lattice ions which in excess
2. held by chemical bound
3. fixed on precipitate surface
AgCl in excess Ag⁺ → AgCl:Ag⁺ (s)

*Counter-ion layer*

Counter-ions
1. opposite charge of primary adsorbed ion
2. held by electrostatic attraction
3. loosely held in soln surrounding the ppt
AgCl in excess AgNO₃ → AgCl:Ag⁺ · · · NO₃⁻ (s)
**Coprecipitation**
(process by which soluble compounds are carried out with insoluble analyte)

1. **Surface adsorption**
   - decreased by washing or by reprecipitating product
2. **Mixed-crystal formation**: spectator ions may be incorporated into ppt’s crystal lattice if size, charge, or crystal class are the same
   - eliminate spectator ion or choose different counterion
3. **Oclusion/mechanical entrapment**
   - decreased by low relative supersaturation or digestion

---

**Homogeneous Precipitation**
- Precipitate is generated slowly, often a chelating agent is slowly formed, which reacts with analyte of interest

Al(OH)₃ formed by the direct addition of NH₃ (left) and the homogeneous production of hydroxide (right).

---

**Homogeneous Precipitation**

urea → OH⁻ for Fe(III) & Al

\[(H₂N₂)₂CO + 3H₂O \rightarrow \text{CO}_₂ + 2NH₄⁺ + 2OH⁻\]
Drying and ignition of precipitates

- Drying drives off water.
- Ignition can convert analyte from one form to another.

**Effect of temperature on precipitate mass**

---

**Calculation of Results from Gravimetric Data**

\[
\frac{R \times F_{W\text{species}}}{F_{W\text{pet}}} = \frac{g\text{ ppt \times GF}}{g\text{ impure sample}} = \% \text{ species sought}
\]

**Ex. 12.1**: The Ca in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC$_2$O$_4$. The ppt was filtered, washed, and ignited in a crucible with an empty mass of 26.6092 g. The mass of the crucible plus CaC$_2$O$_4$ (89.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g/mol) in the water in units of grams per 100 mL.

- Mass of CaC$_2$O$_4$ = 26.7134 - 26.6092 = 0.1042 g
- Moles Ca = \( \frac{0.1042}{89.077} \) mmol
- Amount of Ca = \( \frac{0.1042}{56.077} \) mmol = 2.2518 mmol

**Ex. 12.2**: An iron ore was analyzed by dissolving a 1.132-g sample in c-HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydroxide Fe$_2$O$_3$ \( \cdot \) xH$_2$O by the addition of NH$_3$. After filtration and washing, the residue was ignited at a high temp. to give 0.5250 g of pure Fe$_2$O$_3$ (149.99 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe$_2$O$_3$ (231.54 g/mol) in the sample.

- Amount Fe$_2$O$_3$ = \( \frac{0.5250}{159.99} \) mmol
- Mass Fe = \( \frac{0.5250 \times 10^{-3} \text{ mol} \times 2 \times 55.847 \text{ g/mol}}{1.1324 \text{ g}} \) = 0.37728 g
- \% Fe = \( \frac{0.37728}{1.1324} \times 100\% = 33.32\% \)

- Mass Fe$_2$O$_3$ = \( \frac{0.5250 \times 10^{-3} \text{ mmol} \times 231.54 \text{ g/mol}}{1.1324 \text{ g}} \) = 1.1324 g
- % Fe$_2$O$_3$ = \( \frac{1.1324}{1.1324} \times 100\% = 46.04\% \)