12 Gravimetric Methods of Analysis

Gravimetric analysis: based upon mass measurements highly accurate and precise.
--- Isolation (pure known substance) & weighing

*Advantages
1. accuracy
2. single fundamental chemical precipitation reaction
   
ex: \( \text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl}(s) \)
3. require no accuracy known standard solution

12A Precipitation Gravimetry

1. Precipitation methods
   ex: For Calcium in natural water
   AOAC (Association of Official Analytical Chemists)
   
   \[
   \begin{align*}
   2\text{NH}_3 + \text{H}_2\text{C}_2\text{O}_4 & \rightarrow 2\text{NH}_4^+ + \text{C}_2\text{O}_4^{2-} \\
   \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-} (aq) & \rightarrow \text{CaC}_2\text{O}_4(s) \\
   \text{CaC}_2\text{O}_4 & \xrightarrow{\Delta} \text{CaO(s)} + \text{CO(g)} + \text{CO}_2(g)
   \end{align*}
   \]

2. Volatilization methods
   ex: For NaHCO\(_3\) in antacid tablets
   
   \[
   \begin{align*}
   \text{NaHCO}_3(aq) + \text{H}_2\text{SO}_4(aq) & \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l) + \text{NaHSO}_4(aq) \\
   & \downarrow \\
   & \text{absorption tube}
   \end{align*}
   \]

12A-1 Properties of Precipitates and Precipitating Agents

*specifically* (rare): reactly only with a single chemical species.
   
   \[
   \text{dimethylglyoxime} \rightarrow \text{Ni}^{2+}
   \]

*selectively* (common): react with a limited number of species.
   
   \[
   \text{AgNO}_3 \rightarrow \text{Cl}^-, \text{Br}^-, \text{I}^- & \text{SCN}^-
   \]

1. Readily filtered and washed free of contaminants.
2. Of sufficiently low solubility so that no significant loss of the analyte occurs during filtration and washing.
3. Unreactive with constituents of the atmosphere.
4. Of known composition after it is dried or, if necessary, ignited.
12A-2 Particle size and filterability of precipitates

Particle size: • colloidal suspensions (10^-7 ~ 10^-4 cm or 10^-6 ~ 10^-4 mm)
  - ex: Fe(OH)_3 (gelatinous)
  • curdy: ex: AgCl
  • crystalline (10^-2 ~ 10 mm): ex: BaSO_4

♦ Factors that determine the particle size of precipitates
  1. ppt solubility
  2. temperature
  3. reactant concentrations
  4. rate at which reactants are mixed

♦ relative supersaturation(RS) or Von Weimarn ratio

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

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

Particle size \( \propto \frac{1}{RS} \)

RS ↑ → ppt size ↓ (colloidal)
RS ↓ → ppt size ↑ (crystalline solid)

♦ Mechanism of precipitate formation
  1. supersaturated soln formed
  2. nucleation
  3. particle growth

♦ Experimental Control of Particle Size
  * RS↓, Q↓, S↑ → particle size ↑
  1. dilute sample soln and dilute reagents (Q ↓)
  2. slow addition of precipitating agent with good stirring (Q ↓)
  3. in hot solution (S ↑)
  4. pH control, acidity solution (S ↑)
  - ex: precipitation of calcium oxalate
    - a. in mildly acidic, calcium oxalate → large, easily filtered crystals
       (moderately soluble)
    - b. adding aqueous ammonia → pH ↑ → completed ppt

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

12A-3 Colloidal Precipitates

Coagulation (or agglomeration) of colloids: converting a colloid suspension into a filterable solid.

60
**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.

**Electric double layer:**

- **Primary adsorbed layer**
  - primary adsorbed ion:
    1. lattice ions which in excess.
    2. held by chemical bond
    3. fixed on ppt surface
  - ex: AgCl in excess Ag$^+$
    \[ \rightarrow \text{AgCl:Ag}^+ (s) \]

- **Counter-ion layer**
  - ex: AgCl in excess AgNO$_3$
    \[ \rightarrow \text{AgCl:Ag}^+ \cdots \text{NO}_3^- (s) \]

---

**Coagulation** of a colloidal suspension

1. **heating:** a. ↓ no. of adsorbed ions and the thickness $d_1$ of the double layer.
   b. gain enough kinetic energy to overcome the barrier to close approach posed by the double layer.
2. **stirring**
3. **adding an electrolyte:** conc. of counter ions ↑ → shrinkage of the counter-ion layer (Fig. 12-2b) → particle can then approach one another more closely and agglomerate.
*Peptization of Colloids*
Peptization: a process by which a coagulated colloid returns to its dispersed state.

washing coagulated colloid $\rightarrow$ removal of electrolyte  
$\rightarrow$ volume of the counter-ion layer $\uparrow$

Peptization is prevented by washing ppt with a soln of a volatile electrolyte. ex:  
AgCl, washed with a d-HNO$_3$.

*Treatment of Colloidal Precipitates*

**Digestion**: a process in which a ppt is heated for an hour or more in the soln from which it was formed (the mother liquor)  
$\rightarrow$ $\uparrow$ purity and filterability  
1. colloidal suspension $\rightarrow$ coagulated to curdy ppt  
2. small crystalline particles $\rightarrow$ reprecipitated on the large crystalline particles  
3. impurities tend to dissolve $\rightarrow$ pure crystalline particles

12A-4 Crystalline Precipitates

**Methods of Improving Particle Size and Filterability**: Q $\downarrow$, S $\uparrow$, digestion

12A-5 Coprecipitation:

A process in which normally soluble compounds are carrier out of solution by a precipitate.

**Four types of coprecipitation:**
1. surface adsorption  
2. mixed-crystal formation  
3. occlusion  
4. mechanical entrapment

1, 2 $\rightarrow$ equilibrium processes  
3, 4 $\rightarrow$ arise from the kinetics of crystal growth

1. **Surface adsorption**

specific surface areas(SA) $\uparrow \rightarrow$ adsorption $\uparrow$  
SA = (cm$^2$/mass(g)
Adsorption, a normally soluble compound is carried out of soln on the surface of a coagulated colloid. This compound consists of the primarily adsorbed ion and an ion of opposite charge from the counter-ion layer.

ex: in chloride analysis
   primary adsorbed ion : $\text{Ag}^+$
   counter-ion layer : $\text{NO}_3^-$ or other anions
   $\rightarrow$ $\text{AgNO}_3$ (normally soluble) is coprecipitated with the $\text{AgCl}$.

*Methods for Minimizing Adsorbed Impurities on Colloids
a. Digestion:
   particle size $\uparrow \rightarrow$ specific surface area $\downarrow \rightarrow$ adsorption $\downarrow$

b. Washing with volatile electrolyte soln
   ex: in $\text{Ag}^+$ analysis, primary adsorbed ion : $\text{Cl}^-$
   washing with an acidic soln $\rightarrow$ counter-ion layer : $\text{H}^+$
   $\rightarrow$ $\text{HCl}$ volatilized when ppt is dried

c. Reprecipitation, double precipitation

2. **Mixed-crystal formation**
   a contaminant ion replaces an ion in the lattice of a crystal
   a. the same charge
   b. the size differ $< 5\%$
   c. salt : the same crystal class

ex: (a). $\text{PbSO}_4$ in $\text{BaSO}_4$
   $\text{BaCl}_2$ + soln containing sulfate, lead & acetate
   $\rightarrow$ $\text{BaSO}_4 + \text{PbSO}_4$ (Pb + acetate $\rightarrow$ lead acetate)
(b). MgKPO₄ in MgNH₄PO₄
(c). SrSO₄ in BaSO₄
(d). MnS in CdS

3. Occlusion
A compound is trapped within a pocket formed during rapid crystal growth.

4. Mechanical entrapment
Several crystals grow together & in so doing trap a portion of the solution in a tiny pocket.

3 & 4 : rate of ppt formation ↓ (low supersaturation)
→ occlusion & mechanical entrapment at a minimum

Digestion decrease these coprecipitation.

*Coprecipitation error: negative or positive errors
Ex: (a). in Cl analysis, colloidal AgCl + AgNO₃ → (+) error
(b). in Ba²⁺ → BaSO₄ analysis
   if Ba(NO₃)₂ (larger FW than BaSO₄) → (+) error
   if BaCl₂ ( FW: BaCl₂ < BaSO₄) → (-) error

12A-6 Precipitation from Homogeneous Solution (Table 12-1)

Homogeneous precipitation:
a precipitate is formed by slow generation of a precipitating reagent homogeneously throughout a solution.

Solid formed by homogeneous precipitation are generally purer and more easily filtered than precipitate generated by direct addition of a reagent to the analyte solution.

Fig. 12-5 Al(OH)₃ formed by the direct addition of NH₃(left) and the homogeneous production of hydroxide(right).

ex: urea → OH⁻ for Fe(III) & Al

\[
\text{H}_2\text{N}_2\text{CO} + 3\text{H}_2\text{O} \xrightarrow{100^\circ \text{C, } 2 \text{hr}} \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^- 
\]
**Filtration**

1. Sintered-glass filtering crucible: 110 °C ~ 250 °C  
   crystalline or granular type ppt  
   pore: coarse, medium, fine  
2. Gooch crucible with an asbestos mat: 800 °C ~ 1000 °C  
3. Filter paper  
   ashless filter paper: residue < 0.1 mg.

**Washing the Precipitate**

wash soln  
1. Wash out all impurity but leave it unchanged in composition.  
2. Not introduce insoluble product into ppt  
3. completely volatile at drying temp of ppt  
   • pure water → peptization  
   • electrolyte soln

12A-7 Drying and ignition of Precipitates

← Fig. 12-6 Effect of temperature on precipitate mass.

1. oven 110°C ~ 250°C → desiccator, cool → weight  
2. ignite (ashless filter paper)  
   \[ \text{Fe}^{3+} + \text{OH}^- \rightarrow \text{Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 \]  
   weighing form  
3. desiccator or vacuum desiccator

**Constant weight (恆量)**

◆ 依照中華藥典第四版 (CHP IV): 檢品按照規定經乾燥稱量後，再乾燥一小時，或  
   熹灼稱量後，再熹灼十五分鐘，直至前後  
   称量之差，以檢品每 g 不得超過 0.5 mg  
   而言。  
◆ 二次連續稱重不大於 0.2 mg。

65
12B Calculation of Results from Gravimetric Data

\[ \frac{R \times FW_{\text{species}}}{FW_{\text{ppt}}} \]

Gravimetric factor (GF)

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

**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 26.6002 g. The mass of the crucible plus CaO (56.077 g/mol) was 26.7134 g. Calculate the con. of Ca (40.078 g/mol) in the water in units of grams per 100 mL.

\[
\text{mass of CaO} = 26.7134 - 26.6002 = 0.1132 \text{ g}
\]

\[
\text{moles Ca} = \text{moles CaO} = \frac{0.1132 \text{ g}}{56.077 \text{ g/mol}} = 2.0186 \text{ mmol}
\]

\[
\text{mass Ca} = \frac{2.0186 \text{ mmol} \times 40.078 \text{ g/mol}}{200 \text{ mL}} \times 100 \text{ mL} = 0.04045 \text{ g/100 mL}
\]

**Ex. 12-2.** An iron ore was analyzed by dissolving a 1.1324-g sample in c-HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide 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 0.5394 g of pure Fe\(_2\)O\(_3\) (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe\(_3\)O\(_4\) (231.54 g/mol) in the sample.

\[
\text{amount Fe}_2\text{O}_3 = \frac{0.5394 \text{ g}}{159.69 \text{ g/mol}} = 3.3778 \text{ mmol}
\]

(a) mass Fe = \(3.3778 \times 10^{-3} \text{ mol} \times 2 \times 55.847 \text{ g/mol} = 0.37728 \text{ g}
\]

\%

\[
\text{Fe} = \frac{0.37728 \text{ g}}{1.1324 \text{ g}} \times 100\% = 33.317 \approx 33.32 \%
\]

(b) \(3 \text{ Fe}_2\text{O}_3 \rightarrow 2 \text{ Fe}_3\text{O}_4 + \frac{1}{2} \text{ O}_2\)

\[
\text{mass Fe}_3\text{O}_4 = 3.3778 \text{ mmol} \times \frac{2}{3} \times 231.54 \text{ g/mol} = 0.52140 \text{ g}
\]

\%

\[
\text{Fe}_3\text{O}_4 = \frac{0.52140 \text{ g}}{1.1324 \text{ g}} \times 100\% = 46.044 \approx 46.04 \%
\]
Ex. 12-3. A 0.2356-g sample containing only NaCl (58.44 g/mol) and BaCl$_2$ (208.25 g/mol) yielded 0.4637 g of dried AgCl (143.32 g/mol). Calculate the percent of each halogen compound in the sample.

let $x$ = mass of NaCl, $y$ = mass of BaCl$_2$ $\rightarrow$ $x + y = 0.2356$ g

mass AgCl from NaCl $= \frac{x \text{ g} \times 143.32 \text{ g/mol}}{58.44 \text{ g/mol}} = 2.4524x \text{ g}$

mass AgCl from BaCl$_2$ $= \frac{y \text{ g} \times 2 \times 143.32 \text{ g/mol}}{208.23 \text{ g/mol}} = 1.3766y \text{ g}$

$2.4524x \text{ g} + 1.3766y \text{ g} = 2.4524x \text{ g} + 1.3766 (0.2356 - x) \text{ g} = 0.4637 \text{ g}$

$1.0758x = 0.13942$

$x =$ mass NaCl $= 0.12960$ g NaCl

$\% \text{ NaCl} = \frac{0.12956 \text{ g NaCl}}{0.2356 \text{ g}} \times 100\% = 55.01\%$

$\% \text{ BaCl}_2 = 100 \% - 55.01\% = 44.99\%$

Ex. 12-4. Sample: NaCl + NaBr + inert $= 1.000$ g

excess AgNO$_3$ $\downarrow$

AgCl(s) + AgBr(s) $= 0.5260$ g

Cl$_2$ treatment $\downarrow$

AgCl(s) + AgCl(s) $= 0.4260$ g

NaCl $= \ ? \ %$; NaBr $= \ ? \ %$

Ans: if NaCl $= x$ g, NaBr $= y$ g

$g$ of AgCl(s) $= \frac{x \times 143.32}{58.44}$; $g$ of AgBr(s) $= \frac{y \times 187.77}{102.89}$

\[
\frac{x \times 143.32}{58.44} + \frac{y \times 187.77}{102.89} = 0.5260 \text{ g}
\]

$\% \text{ NaCl} = \frac{x \times 100}{1.000}$

\[
\frac{x \times 143.32}{58.44} + \frac{y \times 143.32}{102.89} = 0.4260 \text{ g}
\]

$\% \text{ NaBr} = \frac{y \times 100}{1.000}$
12C Applications of Gravimetric Methods
(a). most inorganic anions and cations
(b). neutral species: water, SO₂, CO₂, I₂.
(c). organic substances: lactose in milk products, salicylates in drug preparations, nicotine in pesticides, cholesterol in cereals, benzaldehyde in almond extracts

12C-1 Inorganic precipitating agents (Table 12-2)

<table>
<thead>
<tr>
<th>Precipitating Agent</th>
<th>Element Precipitated</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃(aq)</td>
<td>Be(BeO), Al(Al₂O₃), Sc(Sc₂O₃), Cr(Cr₂O₃), Fe(Fe₂O₃), Ga(Ga₂O₃), Zr(ZrO₂), In(In₂O₃), Sn(SnO₂), U(U₃O₈)</td>
</tr>
<tr>
<td>H₂S</td>
<td>Cu(CuO), Zn(ZnO or ZnSO₄), Ge(GeO₂), As(As₂O₃ or As₂O₅), Mo(MoO₃), Sn(SnO₂), Sb(Sb₂O₃ or Sb₂O₅), Bi(Bi₂S₃)</td>
</tr>
<tr>
<td>(NH₄)₂S</td>
<td>Hg(HgS), Co(Co₃O₄)</td>
</tr>
<tr>
<td>(NH₄)₂HPO₄</td>
<td>Mg(MgP₂O₇), Al(AlPO₄), Mn(Mn₃P₂O₇), Zn(Zn₂P₂O₇), Zr(Zr₂P₂O₇), Cd(Cd₃P₂O₇), Bi(BiPO₄)</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Li, Mn, Sr, Cd, Pb, Ba (all as sulfates)</td>
</tr>
<tr>
<td>H₂PtCl₆</td>
<td>K(K₂PtCl₆ or Pt), Rb(Rb₂PtCl₆), Cs(Cs₂PtCl₆)</td>
</tr>
<tr>
<td>H₂C₂O₄</td>
<td>Ca(CaO), Sr(SrO), Th(ThO₂)</td>
</tr>
<tr>
<td>(NH₄)₂MoO₄</td>
<td>Cd(CdMoO₄), Pb(PbMoO₄)</td>
</tr>
<tr>
<td>HCl</td>
<td>Ag(AgCl), Hg(Hg₂Cl₂), Na(as NaCl from butyl alcohol), Si(SiO₂)</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>Cl(AgCl), Br(AgBr), I(AgI)</td>
</tr>
<tr>
<td>(NH₄)₂CO₃</td>
<td>Bi(Bi₂O₃)</td>
</tr>
<tr>
<td>NH₄SCN</td>
<td>Cu[Cu₂(SCN)₂]</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Ru, Os, Ir (precipitated as hydrous oxides; reduced with H₂ to metallic state)</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Sn(SnO₂)</td>
</tr>
<tr>
<td>H₂IO₆</td>
<td>Hg[Hgs(IO₆)₂]</td>
</tr>
<tr>
<td>NaCl, Pb(NO₃)₂</td>
<td>F(PbClF)</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>SO₄²⁻(BaSO₄)</td>
</tr>
<tr>
<td>MgCl₂, NH₄Cl</td>
<td>PO₄³⁻(MgP₂O₇)</td>
</tr>
</tbody>
</table>

12C-2 Reducing agents (Table 12-3)

<table>
<thead>
<tr>
<th>Reducing agents</th>
<th>Analyte</th>
<th>Reducing agents</th>
<th>Analyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>Se, Au</td>
<td>HCOOH</td>
<td>Pt</td>
</tr>
<tr>
<td>SO₂ + H₂NOH</td>
<td>Te</td>
<td>NaNO₂</td>
<td>Au</td>
</tr>
<tr>
<td>H₂NOH</td>
<td>Se</td>
<td>SnCl₂</td>
<td>Hg</td>
</tr>
<tr>
<td>H₂C₂O₄</td>
<td>Au</td>
<td>Electrolytic reduction</td>
<td>In, Sn, Sb, Cd, Re, Bi</td>
</tr>
<tr>
<td>H₂</td>
<td>Re, Ir</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
12C-3 Organic precipitating agents


(a). Hydroxyquinoline (oxine):
24 cations

(b) Dimethylglyoxime:
specific for Ni$^{2+}$

2. Sodium tetraphenylboron, (C$_6$H$_5$)$_2$B·Na : for K$^+$ & NH$_4^+$
$\rightarrow$ form ionic, saltlike ppts
ppt : dry at 105 °C ~ 120 °C $\rightarrow$ constant weight
interference: mercury(II), rubidium & cesium

12C-4 Organic Functional Group Analysis (Table 12-4)

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Basis for Method</th>
<th>Reaction and product Weighed*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl</td>
<td>Mass of precipitate with 2,4-dinitrophenylhydrazine</td>
<td>RCHO + H$_2$NNHC$_6$H$_5$(NO$_2$)$_2$ $\rightarrow$ R-CH=NNHC$_6$H$_5$(NO$_2$)$_2$(s) + H$_2$O (RCOR’ reacts similarly)</td>
</tr>
<tr>
<td>Aromatic Carboxyl</td>
<td>Mass of CO$_2$ formed at 230°C in quinoline; CO$_2$ distilled, absorbed and weighed</td>
<td>ArCHO $\xrightarrow{230 ^\circ C}$ CuCO$_3$ Ar + CO$_2$(g)</td>
</tr>
<tr>
<td>Methoxyl and ethoxyl</td>
<td>Mass of AgI formed after distillation and decomposition of CH$_3$I or C$_2$H$_5$I</td>
<td>ROCH$_3$ + HI $\rightarrow$ ROH + RCOOCH$_3$ + HI $\rightarrow$ RCOOH + CH$_3$I ROC$_2$H$_5$ + HI $\rightarrow$ ROH + C$_2$H$_5$I CH$_3$I+Ag$^+$+H$_2$O$\rightarrow$AgI(s)+ CH$_3$OH</td>
</tr>
<tr>
<td>Aromatic nitro</td>
<td>Mass loss of Sn RNO₂ + 1.5Sn(s) + 6H⁺ → RNH₂ + 1.5Sn⁴⁺ + 2H₂O</td>
<td></td>
</tr>
<tr>
<td>Azo</td>
<td>Mass loss of Cu RN=NR’ + 2Cu(s) + 4H⁺ → RNH₂ + R’NH₂ + 2Cu²⁺</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>Mass of Ba salt ROPO(OH)₂ + Ba²⁺ → ROPOO₂Ba(s) + 2H⁺</td>
<td></td>
</tr>
<tr>
<td>Sulfamic acid</td>
<td>Mass of BaSO₄ after oxidation with HNO₂ RNHSO₃H + HNO₂ + Ba²⁺ → ROH + BaSO₄(s) + N₂ + 2H⁺</td>
<td></td>
</tr>
<tr>
<td>Sulfinic acid</td>
<td>Mass of Fe₂O₃ after ignition of Fe(III) sulfinate 3ROSOH + Fe³⁺ → (ROSO)₃Fe(s) + 3H⁺ (ROSO)₃Fe → CO₂ + H₂O + SO₂ + Fe₂O₃(s)</td>
<td></td>
</tr>
</tbody>
</table>

12C-5 Volatilization Gravimetry

1. For water
   (a). Direct method: solid desiccant collection
   (b). Indirect method: heating → loss of weight
      • water is not the only compound volatilized)
      • decomposition & change in water

2. For carbonate: carbon dioxide
   Solid adsorbent: Ascarite II - NaOH on a nonfibrous silicate

   ex: For NaHCO₃ in antacid tablets
      NaHCO₃(aq) + H₂SO₄ (aq) → CO₂ (g) + H₂O(l) + NaHSO₄(aq)
      ↓ absorption tube
      2NaOH + CO₂ → Na₂CO₃ + H₂O

3. For sulfides & sulfites: H₂S or SO₂

4. For carbon & hydrogen in organic compound
   → combustion product : H₂O & CO₂