Chapter 12
Gravimetric Methods of Analysis

[gravi – metric; weighing – measure]

Hydrated and anhydrous copper sulfate
[$CuSO_4 \bullet xH_2O$]

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Features of 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).

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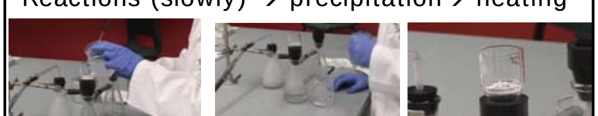
Weighing sample→ dissolving (heating-stirring)

Reactions (slowly) → precipitation→ heating



Filtration → drying → weighing → calculation

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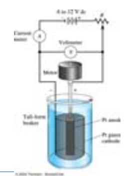
Examples of Isolation of an Analyte

- Precipitating it in an insoluble form.

$$Ag^{+} + X^{-} \rightarrow AgX\downarrow \quad (X = Cl^{-}, Br^{-}, I^{-})$$

- Depositing it as a pure metal by electrolysis.

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$$



- Converting it to a gas which is absorbed in a suitable reagent.

ex: For $NaHCO_3$ in antacid tablets

$$NaHCO_3(aq) + H_2SO_4\,(aq) \rightarrow \underset{\substack{\downarrow \\ \text{absorption tube}}}{CO_2\,(g)} + H_2O\,(l) + NaHSO_4(aq)$$

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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.

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Commonly Employed Gravimetric Analysis

Analyte	Precipitate Formed	Product Weighed	Interferences
Fe	$Fe(OH)_3$	Fe_2O_3	Many, Al, Ti, Cr, etc.
Al	$Al(OH)_3$	Al_2O_3	Many, Al, Ti, Cr, etc.
Ca	CaC_2O_4	$CaCO_3$ CaO	All metals except Alkalis and M
Mg	$MgNH_4PO_4$	MgP_2O_7	All metals except Alkalis.
Zn	$ZnNH_4PO_4$	ZnP_2O_7	All metals except Mg.
Ba	$BaCrO_4$	$BaCrO_4$	Pb
SO_4^{2-}	$BaSO_4$	$BaSO_4$	NO_3^-, PO_4^{3-}, ClO_3^-
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, CN^-, S^{2-}, $S_2O_3^{2-}$
PO_4^{3-}	$MgNH_4PO_4$	MgP_2O_7	MoO_4^{2-}, $C_2O_4^{2-}$, K^+

[Magnesium Pyrophosphate]

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Types of precipitating agents

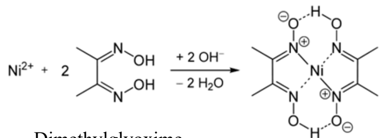
- Inorganic

$2NH_3 + H_2C_2O_4 \rightarrow 2NH_4^+ + C_2O_4^{2-}$

$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)$

$$CaC_2O_4 \xrightarrow{\Delta} CaO(s) + CO(g) + CO_2(g)$$

- Organic (often with functional groups)



Dimethylglyoxime

Bright red ppt

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Properties of precipitates

- Particle size is important

large particles are easier to filter

Colloidal suspensions = very small, does not settle [10^{-7} - 10^{-4} cm diameter (i.e., nm-µm)]

$Fe(OH)_3$ (gelatinous)

Curdy: AgCl → heating to ppt.

Crystalline = larger, settles more easily (0.01-10 mm): $BaSO_4$

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- **Factors that determine the particle size of precipitates**

✓ ppt solubility (K_{sp})
✓ Temperature
✓ Reactant concentrations
✓ Rate at which reactants are mixed

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❑ 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

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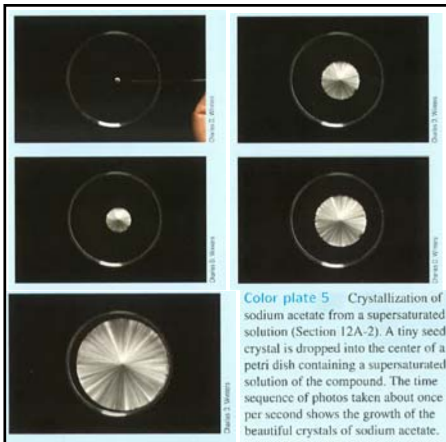

Color plate 5 Crystallization of sodium acetate from a supersaturated solution (Section 12A-2). A tiny seed crystal is dropped into the center of a petri dish containing a supersaturated solution of the compound. The time sequence of photos taken about once per second shows the growth of the beautiful crystals of sodium acetate.

https://www.youtube.com/watch?v=Jd9C40Svt5g

K_2CrO_4

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Relative Supersaturation (RSS or RS)

$$RS = \frac{Q - S}{S} \qquad (Q \geq S)$$

$$\textbf{Particle size} \propto \frac{1}{RS}$$

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

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

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❑ **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

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

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Two Precipitates of PbCrO4

Beaker A Beaker B

A: $Pb(NO_3)_2$ (0.1 M) + K_2CrO_4 (0.1 M) $\xrightarrow{R.T.}$ $PbCrO_4 \downarrow$
(high RSS, rapid, small particles)
B: $Pb(NO_3)_2$ (0.1 M) + [$Cr(NO_3)_3$ (0.1 M) + K_2BrO_3 (0.1 M)] $\xrightarrow{\Delta}$ $PbCrO_4 \downarrow$
(*slowly* oxidizes Cr^{3+} to CrO_4^{2-}, low RSS, larger particles)

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pH control of precipitation

$$Ca^{2+} + C_2O_4^{2-} \leftrightarrows CaC_2O_4\,(s)$$

$$H_2C_2O_4 \leftrightarrows 2\,H^+ + C_2O_4^{2-}$$

(Feeder Reaction)
(in acidic solution Q↓ and S↑)

a. In mildly acidic,
CaC_2O_4 (s) → large, easily filtered crystals (moderately soluble)
b. Adding aqueous ammonia
→ pH↑ → completed precipitation

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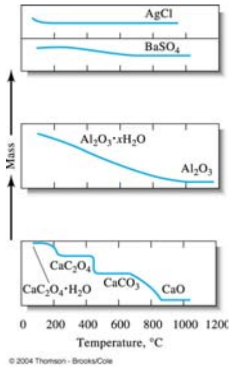
Drying and ignition of precipitates

- drying drives off water.
- ignition can convert analyte from one form to another.

Effect of temperature on precipitate mass →



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Calculation of Results from Gravimetric Data

$$\frac{R \times FW_{species}}{FW_{ppt}}$$

Gravimetric factor (GF)

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

Ex. 12-1. The Ca in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC_2O_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.

mass of CaO = 26.7134 - 26.6002 = 0.1132 g

moles Ca = moles CaO

$$\text{amount of Ca} = \frac{0.1132\text{ g}}{56.077\text{ g/mol}} = 2.0186\text{ mmol}$$

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

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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 $Fe_2O_3 \cdot xH_2O$ 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_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.

$$\text{amount } Fe_2O_3 = \frac{0.5394\text{ g}}{159.69\text{ g/mol}} = 3.3778\text{ mmol}$$

(a) mass Fe = 3.3778×10^{-3} mol × 2 × 55.847 g/mol = 0.37728 g

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

(b) $3\,Fe_2O_3 \rightarrow 2\,Fe_3O_4 + \tfrac{1}{2}\,O_2$

mass Fe_3O_4 = 3.3778 mmol × ⅔ × 231.54 g/mol = 0.52140 g

$$\%\,Fe_3O_4 = \frac{0.52140\text{g}}{1.1324\text{g}} \times 100\% = 46.044 \approx 46.04\,\%$$

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Chapter 12 Summary

- Precipitation gravimetry
- Precipitate particle size
- Colloidal suspensions
- Crystalline precipitates
- Relative Supersaturation (RSS)
- Applications of gravimetry

$$RS = \frac{Q - S}{S} \qquad (Q \geq S)$$

$$\textbf{Particle size} \propto \frac{1}{RS}$$

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