Ch. 26: Gravimetric Analysis

Outline:

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• 26-2 Precipitation
• 26-3 Examples of G.A. calculations
• 26-4 Combustion Analysis
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• 26-6 Titration of a Mixture
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Note: this is Ch. 27 in the 7th edition.

Updated Dec. 4, 2011: Slide 1 modified
Gravimetric Analysis

In *gravimetric analysis*, the mass of a product from a chemical reaction is used to calculate the quantity of the original *analyte* (the species being analyzed).

*e.g.*, Careful gravimetric analysis by T. W. Richards and his colleagues early in the twentieth century determined the atomic masses of Ag, Cl, and N to six-figure accuracy. This Nobel Prize–winning work allowed the accurate determination of atomic masses of many elements.

An important type of G.A. are *precipitation titrations*, where the quantity of *titrant* (in buret) required for *complete precipitation of analyte* tells us how much analyte was present.

Another important type of G.A. is *combustion analysis*, where a sample is typically burned in excess oxygen and products are measured. Combustion analyses typically provide measures of C, H, N, S and halogens in organic matter.

To measure quantities of other elements, organic matter is burned in a closed system. Products and *ash* (solid residue) are then dissolved in acid or base and measured by *inductively coupled plasma* (ICP) with *atomic emission* (AE) or *mass spectrometry* (MS).

*Gravimetry* was the main form of chemical analysis in the eighteenth and nineteenth centuries, but it is too tedious to be a method of choice today. However, gravimetry remains one of the most accurate methods. Standards used to calibrate instruments are frequently derived from gravimetric or titrimetric procedures.
Geologic Time Scale and G.A.

Since the 1800’s, geologists understood that new layers (strata) of rock were deposited on old layers; however, the ages of these layers was unknown.

Ernest Rutherford, Frederick Soddy, Bertram Boltwood, and Robert Strutt showed in the early 1900s that uranium decays to lead plus eight atoms of helium with a \textit{half-life} of several billion years. From this, Rutherford and Boltwood estimated the age of rocks from U and He content.
In 1910, Arthur Holmes, a 20-year-old student of Strutt at Imperial College, became the first person to assign actual ages to minerals formed in specific geologic periods.

Holmes conjectured that when certain U-containing minerals crystallized from hot magma, the crystals would be relatively free of impurities such as Pb. Once the mineral solidified, Pb would begin to accumulate. The ratio Pb/U would tell how long ago the mineral crystallized.

Holmes measured U by the rate of production of radioactive Rn gas. To measure Pb, he dissolved each mineral in molten borax, dissolved the fused mass in acid, and quantitatively precipitated mg of PbSO₄. The nearly constant ratio Pb/U = 0.045 g/g in 15 minerals was consistent with the hypotheses that Pb is the end product of U decay and that little Pb had been present when the minerals crystallized. The calculated age of the “Devonian-age” minerals was 370 million years—four times older than the most accepted age of Earth at that time.

<table>
<thead>
<tr>
<th>Geologic period</th>
<th>Pb/U (g/g)</th>
<th>Millions of years</th>
<th>Today’s accepted value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboniferous</td>
<td>0.041</td>
<td>340</td>
<td>330–362</td>
</tr>
<tr>
<td>Devonian</td>
<td>0.045</td>
<td>370</td>
<td>362–380</td>
</tr>
<tr>
<td>Silurian</td>
<td>0.053</td>
<td>430</td>
<td>418–443</td>
</tr>
<tr>
<td>Precambrian</td>
<td>0.125–0.20</td>
<td>1 025–1 640</td>
<td>900–2 500</td>
</tr>
</tbody>
</table>

Examples of Gravimetric Analysis

Chloride can be measured by precipitating the anion with Ag\(^+\) and finding the mass of AgCl.

**EXAMPLE**  A Gravimetric Calculation

A 10.00-mL solution containing Cl\(^-\) was treated with excess AgNO\(_3\) to precipitate 0.4368 g of AgCl. What was the molarity of Cl\(^-\) in the unknown?

**Solution**  The formula mass of AgCl is 143.321. Precipitate weighing 0.4368 g contains

\[
\frac{0.4368 \text{ g AgCl}}{143.321 \text{ g AgCl/mol AgCl}} = 3.048 \times 10^{-3} \text{ mol AgCl}
\]

Because 1 mol of AgCl contains 1 mol of Cl\(^-\), there must have been 3.048 \times 10^{-3} mol of Cl\(^-\) in the unknown.

\[
[\text{Cl}^-] = \frac{3.048 \times 10^{-3} \text{ mol}}{0.0100 \text{ L}} = 0.3048 \text{ M}
\]
Examples of Gravimetric Analysis, 2

Marie and Pierre Curie and Henri Becquerel shared the Nobel Prize in physics in 1903 for pioneering investigations of radioactivity. The Curies needed four years to isolate 100 mg of RaCl\(_2\) from several tons of ore. Marie received the Nobel Prize in chemistry in 1911 for her isolation of metallic radium.

**Example:** In her Ph.D. research (*Radioactive Substances*, 1903), Marie Curie measured the atomic mass of the element radium, which she discovered. She knew that radium is in the same family as barium, so the formula of radium chloride is RaCl\(_2\).

When 0.09192 g of pure RaCl\(_2\) was dissolved and treated with excess AgNO\(_3\), 0.08890 g of AgCl precipitated. How many moles of Cl\(^{-}\) were in the RaCl\(_2\)? From this measurement, find the atomic mass of Ra. (*written example*)
<table>
<thead>
<tr>
<th>Species analyzed</th>
<th>Precipitated form</th>
<th>Form weighed</th>
<th>Interfering species</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>KB(C₆H₅)₄</td>
<td>KB(C₆H₅)₄</td>
<td>NH⁺⁺, Ag⁺⁺, Hg²⁺⁺, Tl⁺⁺, Rb⁺⁺, Cs⁺⁺</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Mg(NH₄)PO₄·6H₂O</td>
<td>Mg₂P₂O₇</td>
<td>Many metals except Na⁺⁺ and K⁺</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>CaC₂O₄·H₂O</td>
<td>CaCO₃ or CaO</td>
<td>Many metals except Mg²⁺⁺, Na⁺⁺, K⁺</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>BaSO₄</td>
<td>Same</td>
<td>Na⁺⁺, K⁺⁺, Li⁺⁺, Ca²⁺⁺, Al³⁺⁺, Cr³⁺⁺, Fe³⁺⁺, Sr²⁺⁺, Pb²⁺⁺, NO₃⁻⁻</td>
</tr>
<tr>
<td>Ti⁴⁺</td>
<td>TiO (5,7-dibromo-8- hydroxyquinoline)₂</td>
<td>Same</td>
<td>Fe³⁺⁺, Zr⁴⁺⁺, Cu²⁺⁺, C₂O₄⁻⁻, citrate, HF</td>
</tr>
<tr>
<td>VO₄⁻⁻</td>
<td>H₂₃VO₄</td>
<td>V₂O₅</td>
<td>Cl⁻⁻, Br⁻⁻, I⁻⁻, SO₄⁻⁻, CrO₄⁻⁻, AsO₄⁻⁻, PO₄⁻⁻</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>PbCrO₄</td>
<td>PbCrO₄</td>
<td>Ag⁺⁺, NH₄⁺⁻</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>Mn(NH₄)PO₄·H₂O</td>
<td>Mn₂P₂O₇</td>
<td>Many metals</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>Fe(HCO₃)₃</td>
<td>Fe₂O₃</td>
<td>Many metals</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>Co(1-nitroso-2-naphtholate)₂</td>
<td>CoSO₄ (by reaction with H₂SO₄)</td>
<td>Fe³⁺⁺, Pd²⁺⁺, Zr⁴⁺⁺</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>Ni(dimethylglyoximate)₂</td>
<td>Same</td>
<td>Pd²⁺⁺, Pt²⁺⁺, Bi³⁺⁺, Au³⁺⁺</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>CuSCN (after reduction of Cu²⁺ to Cu⁺ with HSO₃⁻⁻)</td>
<td>CuSCN</td>
<td>NH₄⁺⁻, Pb²⁺⁺, Hg²⁺⁺, Ag⁺⁺</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>Zn(NH₄)PO₄·H₂O</td>
<td>Zn₂P₂O₇</td>
<td>Many metals</td>
</tr>
<tr>
<td>Ce⁴⁺</td>
<td>Ce(IO₃)₄</td>
<td>CeO₂</td>
<td>Th⁴⁺⁺, Tl⁺⁺, Zr⁺⁺</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>Al(8-hydroxyquinolate)₃</td>
<td>Same</td>
<td>Many metals</td>
</tr>
<tr>
<td>Sn⁴⁺</td>
<td>Sn(cupferron)₄</td>
<td>SnO₂</td>
<td>Cu²⁺⁺, Pb²⁺⁺, As(III)</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>PbSO₄</td>
<td>PbSO₄</td>
<td>Ca²⁺⁺, Sr²⁺⁺, Ba²⁺⁺, Hg²⁺⁺, Ag⁺⁺, HCl, HNO₃</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>NH₄B(C₆H₅)₄</td>
<td>NH₄B(C₆H₅)₄</td>
<td>K⁺⁺, Rb⁺⁺, Cs⁺⁺</td>
</tr>
<tr>
<td>Cl⁻⁻</td>
<td>AgCl</td>
<td>AgCl</td>
<td>Br⁻⁻, I⁻⁻, SCN⁻⁻, S₂⁻⁻, S₂O₅⁻⁻, CN⁻⁻</td>
</tr>
<tr>
<td>Br⁻⁻</td>
<td>AgBr</td>
<td>AgBr</td>
<td>Cl⁻⁻, I⁻⁻, SCN⁻⁻, S₂⁻⁻, S₂O₅⁻⁻, CN⁻⁻</td>
</tr>
<tr>
<td>I⁻⁻</td>
<td>AgI</td>
<td>AgI</td>
<td>Cl⁻⁻, Br⁻⁻, SCN⁻⁻, S₂⁻⁻, S₂O₅⁻⁻, CN⁻⁻</td>
</tr>
<tr>
<td>SCN⁻⁻</td>
<td>CuSCN</td>
<td>CuSCN</td>
<td>NH⁺⁺, Pb²⁺⁺, Hg²⁺⁺, Ag⁺⁺</td>
</tr>
<tr>
<td>CN⁻⁻</td>
<td>AgCN</td>
<td>AgCN</td>
<td>Cl⁻⁻, Br⁻⁻, I⁻⁻, SCN⁻⁻, S₂⁻⁻, S₂O₅⁻⁻</td>
</tr>
<tr>
<td>F⁻⁻</td>
<td>(C₆H₅)₃SnF</td>
<td>(C₆H₅)₃SnF</td>
<td>Many metals (except alkali metals), SiO₄⁻⁻, CO₃⁻⁻</td>
</tr>
<tr>
<td>ClO₄⁻⁻</td>
<td>KClO₄</td>
<td>KClO₄</td>
<td>Na⁺⁺, K⁺⁺, Li⁺⁺, Ca²⁺⁺, Al³⁺⁺, Cr³⁺⁺, Fe³⁺⁺, Sr²⁺⁺, Pb²⁺⁺, NO₃⁻⁻</td>
</tr>
<tr>
<td>SO₄²⁻⁻</td>
<td>BaSO₄</td>
<td>BaSO₄</td>
<td>Many metals except Na⁺⁺, K⁺⁺</td>
</tr>
<tr>
<td>PO₄³⁻⁻</td>
<td>Mg(NH₄)PO₄·6H₂O</td>
<td>Mg₃P₂O₇</td>
<td>ClO₄⁻⁻, I⁻⁻, SCN⁻⁻, CrO₄²⁻⁻, ClO₃⁻⁻, NO₂⁻⁻, Br⁻⁻, C₂O₄²⁻⁻</td>
</tr>
<tr>
<td>NO₃⁻⁻</td>
<td>Nitron nitrate</td>
<td>Nitron nitrate</td>
<td>(The liberated CO₂ is trapped with Ascarite and weighed.)</td>
</tr>
<tr>
<td>CO₃²⁻⁻</td>
<td>CO₂ (by acidification)</td>
<td>CO₂</td>
<td></td>
</tr>
</tbody>
</table>

**Representative Gravimetric Analyses**
<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Ions precipitated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylglyoxime</td>
<td><img src="image" alt="Structure" /></td>
<td>Ni$^{2+}$, Pd$^{2+}$, Pt$^{2+}$</td>
</tr>
<tr>
<td>Cupferron</td>
<td><img src="image" alt="Structure" /></td>
<td>Fe$^{3+}$, VO$_2^+$, Ti$^{4+}$, Zr$^{4+}$, Ce$^{4+}$, Ga$^{3+}$, Sn$^{4+}$</td>
</tr>
<tr>
<td>8-Hydroxyquinoline (oxine)</td>
<td><img src="image" alt="Structure" /></td>
<td>Mg$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Al$^{3+}$, Fe$^{3+}$, Bi$^{3+}$, Ga$^{3+}$, Th$^{4+}$, Zr$^{4+}$, UO$_2^{2+}$, TiO$_2^{2+}$</td>
</tr>
<tr>
<td>Salicylaldoxime</td>
<td><img src="image" alt="Structure" /></td>
<td>Cu$^{2+}$, Pb$^{2+}$, Bi$^{3+}$, Zn$^{2+}$, Ni$^{2+}$, Pd$^{2+}$</td>
</tr>
<tr>
<td>1-Nitroso-2-naphthol</td>
<td><img src="image" alt="Structure" /></td>
<td>Co$^{2+}$, Fe$^{3+}$, Pd$^{2+}$, Zr$^{4+}$</td>
</tr>
<tr>
<td>Nitron</td>
<td><img src="image" alt="Structure" /></td>
<td>NO$_3^-$, ClO$_4^-$, BF$_4^-$, WO$_4^{2-}$</td>
</tr>
<tr>
<td>Sodium tetraphenylborate</td>
<td>Na$^+$B(C$_6$H$_5$)$_4$</td>
<td>K$^+$, Rb$^+$, Cs$^+$, NH$_4^+$, Ag$^+$, organic ammonium ions</td>
</tr>
<tr>
<td>Tetraphenylarsonium chloride</td>
<td>(C$_6$H$_5$)$_4$As$^+$Cl$^-$</td>
<td>Cr$_2$O$_7^{2-}$, MnO$_4^-$, ReO$_4^-$, MoO$_4^{2-}$, WO$_4^{2-}$, ClO$_4^-$, I$_3^-$</td>
</tr>
</tbody>
</table>
Precipitation

The ideal product of a gravimetric analysis should be pure, insoluble, easily filterable, and should possess a known composition. Few substances meet these requirements, but appropriate techniques can help optimize properties of gravimetric precipitates.

Precipitated particles should not be so small that they clog or pass through the filter, and precipitation conditions determine the particle size:
- Larger crystals have less surface area to which impurities can become attached.
- At the other extreme is a colloidal suspension of particles that have diameters in the approximate range 1 - 500 nm and pass through most filters.

Colloids are particles with diameters of ca. 1 – 100 nm. They are larger than most molecules but too small to precipitate. Hence, they remain in solution, suspended by the Brownian motion (random movement) of the solvent molecules.

To the left: distributions of particle sizes of colloids formed when FeSO$_4$ is oxidized to Fe$^{3+}$ in 10$^{-4}$ M OH$^-$ in the presence of phosphate (PO$_4^{3-}$), silicate (SiO$_4^{4-}$) or no added anions.
Crystallization occurs in two phases:

In *nucleation*, solutes are thought to form a disorganized cluster of sufficient size, which then reorganizes into an ordered structure capable of growing into larger particles (*nucleus*). Nucleation can occur on suspended impurity particles or scratches on a glass surface.

In *particle growth*, molecules or ions condense onto the nucleus to form a larger crystal.

(a) Nucleation of crystals, (b) crystal growth, and (c) irregular grains form as crystals grow together. (d) The grain boundaries between the crystals, as seen under a microscope.

http://www.steelguru.com/article/details/MjU=/Solid_State_Structure.html

e.g., When Fe(III) reacts with 0.1 M Me₄NOH at 25°C, nuclei of hydrated Fe(OH)₃ are 4 nm in diameter and contain ca. 50 Fe atoms. Fe(OH)₃ nuclei grow into plates with lateral dimensions of ca. 30 × 7 nm after 15 min at 60°C.
Crystal Growth, 2

A supersaturated solution contains more solute than should be present at equilibrium. Nucleation proceeds faster than particle growth in a highly supersaturated solution to produce tiny particles or, worse, a colloid. In a less supersaturated solution, nucleation is slower, and nuclei have a chance to grow into larger, more tractable particles. So, supersaturation is undesirable, since this tends to decrease the particle size of the precipitate.

Techniques that promote particle growth include:

1. **Raising the temperature** to increase solubility and thereby decrease supersaturation

2. **Adding precipitant slowly with vigorous mixing**, to prevent a local, highly supersaturated condition where the stream of precipitant first enters the analyte.

3. Using a **large volume of solution** so that concentrations of analyte and precipitant are low

A supersaturated solution will crystallize if a seed crystal is added.

Rapid precipitation from a quickly formed supersaturated solution usually forms small and impure crystals (though there are exceptions).

Slow crystallization from an almost supersaturated solution can produce large, very pure crystals.
Homogeneous Precipitation

In a *homogeneous precipitation*, the precipitant is generated slowly by a chemical reaction. 

**e.g.**, Urea decomposes slowly in boiling water to produce OH⁻:

\[
\text{H}_2\text{N} \quad \text{NH}_2 \quad \frac{\text{O}}{\text{C}} + 3\text{H}_2\text{O} \xrightarrow{\text{heat}} \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^- \\
\text{Urea}
\]

Gradual OH⁻ production enhances the particle size of Fe(III) formate precipitate:

\[
\begin{align*}
\text{O} \\
\text{H} \quad \text{OH} + \text{OH}^- & \rightarrow \text{HCO}_2^- + \text{H}_2\text{O} \\
\text{Formic acid} & \quad \text{Formate}
\end{align*}
\]

\[
3\text{HCO}_2^- + \text{Fe}^{3+} \rightarrow \text{Fe(HCO}_2)_3 \cdot n\text{H}_2\text{O(s)} \downarrow \\
\text{Fe(III) formate}
\]
Homogeneous Precipitation, 2

Some common reagents for homogeneous precipitation:

<table>
<thead>
<tr>
<th>Precipitant</th>
<th>Reagent</th>
<th>Reaction</th>
<th>Some elements precipitated</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH(^-)</td>
<td>Urea</td>
<td>((\text{H}_2\text{N})_2\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^-)</td>
<td>Al, Ga, Th, Bi, Fe, Sn</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>Potassium cyanate</td>
<td>(\text{HOCN} + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{CO}_2 + \text{OH}^-)</td>
<td>Cr, Fe</td>
</tr>
<tr>
<td>S(^2-)</td>
<td>Thioacetamide(^a)</td>
<td>(\text{CH}_3\text{CNH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CNH}_2 + \text{H}_2\text{S})</td>
<td>Sb, Mo, Cu, Cd</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>Sulfamic acid</td>
<td>(\text{H}_3\text{NSO}_5^- + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{SO}_4^{2-} + \text{H}^+)</td>
<td>Ba, Ca, Sr, Pb</td>
</tr>
<tr>
<td>C(_2\text{O}_4^{2-})</td>
<td>Dimethyl oxalate</td>
<td>(\text{CH}_3\text{OCCOCH}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + \text{C}_2\text{O}_4^{2-} + 2\text{H}^+)</td>
<td>Ca, Mg, Zn</td>
</tr>
<tr>
<td>PO(_4^{3-})</td>
<td>Trimethyl phosphate</td>
<td>((\text{CH}_3\text{O})_3\text{P} \rightarrow 3\text{CH}_3\text{OH} + \text{PO}_4^{3-} + 3\text{H}^+)</td>
<td>Zr, Hf</td>
</tr>
<tr>
<td>Cr(_2\text{O}_4^{2-})</td>
<td>Chromic ion plus bromate</td>
<td>(2\text{Cr}^{3+} + \text{BrO}_3^- + 5\text{H}_2\text{O} \rightarrow 2\text{CrO}_4^{2-} + \text{Br}^- + 10\text{H}^+)</td>
<td>Pb</td>
</tr>
</tbody>
</table>

\(^a\) Hydrogen sulfide is volatile and toxic; it should be handled only in a well-ventilated hood. Thioacetamide is a carcinogen that should be handled with gloves. If thioacetamide contacts your skin, wash yourself thoroughly immediately. Leftover reagent is destroyed by heating at 50°C with 5 mol of NaOCl per mole of thioacetamide. [H. Elo, J. Chem. Ed. 1987, 64, A144.]
Precipitation in the Presence of Electrolyte

Ionic compounds are usually precipitated in the presence of an *electrolyte* (compound dissociating into ions). This is because tiny colloidal crystallites coagulate (come together) into larger crystals. Consider the case of AgCl, which is commonly formed in 0.1 M HNO₃.

The surface of the particle has excess positive charge due to the *adsorption* of extra Ag⁺ ions on exposed Cl⁻ ions. (To be *adsorbed* means to be attached to the surface. In contrast, *absorption* means penetration beyond the surface.) The surrounding *ionic atmosphere* has a net negative charge. The positively charged particle and the negatively charged ionic atmosphere together are called the *electric double layer*.

Colloidal particles must collide to coalesce to form larger particles, but the negative charges repel one another. Heating promotes coalescence, as does the increase of electrolyte concentration.
Digestion

Liquid from which a substance precipitates or crystallizes is called the *mother liquor*.

After precipitation, most procedures call for a period of standing in the presence of the hot mother liquor. This treatment, called *digestion*, promotes slow recrystallization of the precipitate. Particle sizes increase and impurities tend to be expelled from the crystal.
Purity

The best place to start discussing purity is to consider the types of impurities that occur during precipitation processes.

*Adsorbed impurities* are bound to the surface of a crystal.

*Absorbed impurities* are within the crystal, and include:

**Inclusions**: Impurity ions that randomly occupy sites in the crystal lattice normally occupied by ions that belong in the crystal. (Very likely when impurity ion has a size and charge similar to those of one of the ions that belongs to the product).

**Occlusions**: Pockets of impurity that are literally trapped inside the growing crystal.

Adsorbed, occluded, and included impurities are said to be *coprecipitated*: i.e., The impurity is precipitated along with the product, even though the solubility of the impurity has not been exceeded.

To the right: Coprecipitation of phosphate with calcium carbonate in coral. Coprecipitated phosphate is proportional to phosphate concentration in seawater. By measuring P/Ca in ancient coral, we can infer that phosphate concentration in the western Mediterranean Sea 11,200 years ago was twice as high as current values.
Purity, 2

Coprecipitation tends to be worst in colloidal precipitates such as BaSO\(_4\), Al(OH)\(_3\) and Fe(OH)\(_3\), which all have large surface areas. Many procedures call for washing away the mother liquor, *redissolving* the precipitate, and *reprecipitating* the product. During the second precipitation, the concentration of impurities in solution is lower than during the first precipitation, and the degree of coprecipitation therefore tends to be lower.

**Some other considerations:**

*Gathering agents:* A trace component is intentionally isolated by coprecipitation with a major component of the solution. e.g., naturally occurring arsenic in drinking water in Bangladesh is isolated by coprecipitation with Fe(OH)\(_3\).

*Masking agents:* Species that are reacted with predicted impurities to prevent them from reacting with the precipitant. e.g., In the gravimetric analysis of Be\(^{2+}\), Mg\(^{2+}\), Ca\(^{2+}\) or Ba\(^{2+}\) with the reagent \(N\)-\(p\)-chlorophenylcinnamohydroxamic acid, impurities such as Ag\(^{+}\), Mn\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\), Fe\(^{2+}\), and Ga\(^{3+}\) are kept in solution by excess KCN.

*Post-precipitation:* Impurities collect on the pure precipitated product while it is standing in the mother liquor - this usually involves a supersaturated impurity that does not readily crystallize. e.g., Crystallization of MgC\(_2\)O\(_4\) on CaC\(_2\)O\(_4\).
Product Composition

The final product must have a known, stable composition. If this is not the case, there are ways of converting this product to something more stable, or at least stabilizing the product.

A **hygroscopic substance** is one that picks up water from the air and is therefore difficult to weigh accurately. Many precipitates contain a variable quantity of water and must be dried under conditions that give a known (possibly zero) stoichiometry of H$_2$O.

**Ignition** (strong heating) is used to change the chemical form of some precipitates. For example, igniting Fe(HCO$_2$)$_3$ · $n$H$_2$O at 850°C for 1 h gives Fe$_2$O$_3$, and igniting Mg(NH$_4$)PO$_4$ · 6H$_2$O at 1100°C gives Mg$_2$P$_2$O$_7$.

In **thermogravimetric analysis**, a substance is heated, and its mass is measured as a function of temperature (product composition depends on temp. and degree of heating).

---

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Examples of Gravimetric Titrations

Let’s look at some examples that illustrate how to relate the mass of a gravimetric precipitate to the quantity of the original analyte. The general approach is to relate the moles of product to the moles of reactant.

**EXAMPLE** Relating Mass of Product to Mass of Reactant

The piperazine content of an impure commercial material can be determined by precipitating and weighing the diacetate:

\[
\text{ Piperazine } \quad + \quad 2\text{CH}_3\text{CO}_2\text{H} \quad \rightarrow \quad \text{H}_2\text{N}^+\text{NH}_2(\text{CH}_3\text{CO}_2)_2
\]

Piperazine    Acetic acid     Piperazine diacetate  
FM 86.136     FM 60.052      FM 206.240

In one experiment, 0.3126 g of sample was dissolved in 25 mL of acetone, and 1 mL of acetic acid was added. After 5 min, the precipitate was filtered, washed with acetone, dried at 110°C, and found to weigh 0.7121 g. Find the wt% of piperazine in the sample.

(written example)
Examples of Gravimetric Titrations, 2

For a reaction in which the stoichiometric relation between analyte and product is not 1:1, we must use the correct stoichiometry in formulating the gravimetric factor.

**EXAMPLE** Calculating How Much Precipitant to Use

(a) To measure the nickel content in steel, the alloy is dissolved in 12 M HCl and neutralized in the presence of citrate ion, which maintains iron in solution. The slightly basic solution is warmed, and dimethylglyoxime (DMG) is added to precipitate the red DMG-nickel complex quantitatively. The product is filtered, washed with cold water, and dried at 110°C.

\[
\text{Ni}^{2+} + 2 \text{DMG} \rightarrow \text{Bis(dimethylglyoximate)nickel(II)} + 2\text{H}^+ \quad (26-7)
\]

If the nickel content is known to be near 3 wt% and you wish to analyze 1.0 g of steel, what volume of 1.0 wt% alcoholic DMG solution should be used to give a 50% excess of DMG for the analysis? Assume that the density of the alcohol solution is 0.79 g/mL.

*written example*
Combustion Analysis

A historically important form of gravimetric analysis was *combustion analysis* to determine C and H in organic compounds burned in excess O\textsubscript{2}. Modern instruments use thermal conductivity, infrared absorption, *flame photometry* (for S), and *coulometry* (for halogens) to measure products (as opposed to weighing the by-products of combustion).

In *gravimetric combustion analysis*, partially combusted product is passed through catalysts such as Pt gauze, CuO, PbO\textsubscript{2} or MnO\textsubscript{2} at elevated temperature to complete the oxidation to CO\textsubscript{2} and H\textsubscript{2}O. The combustion products are flushed through a chamber containing P\textsubscript{4}O\textsubscript{10} (“phosphorus pentoxide”), which absorbs water, and then through a chamber of *Ascarite* (NaOH on asbestos, nowadays: *Ascarite II*, which is sodium hydroxide-coated silica), which absorbs CO\textsubscript{2}. The increase in mass of each chamber tells how much H and C were initially present. A guard tube prevents atmospheric H\textsubscript{2}O or CO\textsubscript{2} from entering the chambers.
Combustion Analysis Calculations

**Example** Combustion Analysis Calculations

A compound weighing 5.714 mg produced 14.414 mg of CO₂ and 2.529 mg of H₂O upon combustion. Find the wt\% of C and H in the sample.

**Solution** One mole of CO₂ contains 1 mol of carbon. Therefore,

Moles of C in sample = moles of CO₂ produced

\[
\frac{14.414 \times 10^{-3} \text{ g CO}_2}{44.010 \text{ g/mol CO}_2} = 3.275 \times 10^{-4} \text{ mol}
\]

Mass of C in sample = (3.275 × 10⁻⁴ mol C)(12.0107 g/mol C) = 3.934 mg

\[
\text{wt}\% \text{ C} = \frac{3.934 \text{ mg C}}{5.714 \text{ mg sample}} \times 100 = 68.84\%
\]

One mole of H₂O contains 2 mol of H. Therefore,

Moles of H in sample = 2(moles of H₂O produced)

\[
= 2 \left( \frac{2.529 \times 10^{-3} \text{ g H}_2\text{O}}{18.015 \text{ g/mol H}_2\text{O}} \right) = 2.808 \times 10^{-4} \text{ mol}
\]

Mass of H in sample = (2.808 × 10⁻⁴ mol H)(1.0079 g/mol H) = 2.830 × 10⁻⁴ g

\[
\text{wt}\% \text{ H} = \frac{0.2830 \text{ mg H}}{5.714 \text{ mg sample}} \times 100 = 4.95\%
\]
Combustion Analysis Today

An C, H, N, S elemental analyzer uses gas chromatography with thermal conductivity detection to measure N₂, CO₂, H₂O and SO₂ combustion products.
Combustion Analysis Today, 2

1. A ∼2 mg sample is accurately weighed and sealed in a tin or silver capsule.
2. The analyzer is swept with He gas that has been treated to remove traces of O\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2}. At the start of a run, a measured excess of O\textsubscript{2} is added to the He stream.
3. The capsule is dropped into a preheated ceramic crucible, where the capsule melts and sample is rapidly oxidized.

\[
\text{C, H, N, S} \xrightarrow{1050^\circ\text{C}/\text{O}_2} \text{CO}_2(g) + \text{H}_2\text{O}(g) + \text{N}_2(g) + \frac{\text{SO}_2(g) + \text{SO}_3(g)}{95\% \text{SO}_2}
\]

4. Products pass through hot WO\textsubscript{3} oxidation catalyst to complete the combustion of C to CO\textsubscript{2}.
5. In the next zone, metallic Cu at 850°C reduces SO\textsubscript{3} to SO\textsubscript{2} and removes excess O\textsubscript{2}:

\[
\text{Cu} + \text{SO}_3 \xrightarrow{850^\circ\text{C}} \text{SO}_2 + \text{CuO}(s)
\]

\[
\text{Cu} + \frac{1}{2} \text{O}_2 \xrightarrow{850^\circ\text{C}} \text{CuO}(s)
\]

6. The mixture of CO\textsubscript{2}, H\textsubscript{2}O, N\textsubscript{2} and SO\textsubscript{2} is separated by gas chromatography, and each component is measured with a thermal conductivity detector. Alternatively, CO\textsubscript{2}, H\textsubscript{2}O and SO\textsubscript{2} can be measured by infrared absorbance.
A key to elemental analysis is *dynamic flash combustion*, which creates a short burst of gaseous products, instead of slowly bleeding products out over several minutes. Chromatographic analysis requires that the whole sample be injected at once; otherwise, the injection zone is so broad that the products cannot be separated.

In dynamic flash combustion, the tin-encapsulated sample is dropped into the preheated furnace shortly after the flow of a 50/50 vol% O₂/He is started. The Sn capsule melts at 235°C and is instantly oxidized to SnO₂, thereby liberating 594 kJ/mol, and heating the sample to 1 700°–1 800°C. By dropping the sample in before much O₂ is present, decomposition (*cracking*) occurs prior to oxidation, which minimizes formation of nitrogen oxides.

Analyzers that measure C, H and N, but not S, use better optimized catalysts. The oxidation catalyst is Cr₂O₃. The gas then passes through hot Co₃O₄ coated with Ag to absorb halogens and sulfur. A hot Cu column scavenges excess O₂.
Table 26-4 shows representative results for two of seven compounds sent to more than 35 laboratories to compare their performance in combustion analysis. The accuracy for all seven compounds is excellent: Mean values of wt% C, H, N, and S for ~150 measurements of each compound are almost always within 0.1 wt% of theoretical values. Precision for all seven compounds is summarized at the bottom of the table. The mean 95% confidence interval for C is ±0.47 wt%. For H, N, and S, the 95% confidence intervals are ±0.24, ±0.31, and ±0.76 wt%, respectively. Chemists consider a result within ±0.3 of the theoretical wt% to be good evidence that the compound has the expected formula (which can be difficult to meet for C and S with a single analysis because the 95% confidence intervals are larger than ±0.3 wt%.

<table>
<thead>
<tr>
<th>Substance</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₇H₉NO₂S theoretical wt%</td>
<td>49.10</td>
<td>5.30</td>
<td>8.18</td>
<td>18.73</td>
</tr>
<tr>
<td>Toluene-4-sulfonamide</td>
<td>49.1±0.63</td>
<td>5.3±0.31</td>
<td>8.2±0.38</td>
<td>18.7±0.89</td>
</tr>
<tr>
<td>C₄H₇NO₂S theoretical wt%</td>
<td>36.07</td>
<td>5.30</td>
<td>10.52</td>
<td>24.08</td>
</tr>
<tr>
<td>4-Thiazolidinecarboxylic acid</td>
<td>36.0±0.33</td>
<td>5.3±0.16</td>
<td>10.5±0.16</td>
<td>24.0±0.53</td>
</tr>
<tr>
<td>Mean uncertainty (wt%) for</td>
<td>±0.47</td>
<td>±0.24</td>
<td>±0.31</td>
<td>±0.76</td>
</tr>
<tr>
<td>7 different compounds</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Results for two of seven pure compounds that were analyzed by 33–45 laboratories each year over six years. Each lab analyzed each compound at least five times during at least two days. For each substance, first row gives theoretical wt% and second row gives measured wt%. Uncertainties are 95% confidence intervals computed for all results after rejecting outliers at the 1% significance level.

Precipitation Titration Curves

In a precipitation titration involving the analysis of the concentration of an ionic species, I\(^-\), by titration with an aqueous solution of Ag\(^+\), we monitor the course of the reaction between analyte (I\(^-\)) and titrant (Ag\(^+\)) to locate the equivalence point at which there is exactly enough titrant for stoichiometric reaction with the analyte.

We seek the equivalence point in a titration, but we observe the end point at which there is an abrupt change in a physical property (such as an electrode potential or colour change) that is being measured.

The titration curve is a graph showing how the concentration of a reactant varies as titrant is added. In this section, we derive equations that can be used to predict precipitation titration curves. Titration curves are important:

1. For understanding the chemistry that occurs during titrations.

2. For learning how experimental control can be exerted to influence the quality of an analytical titration.
Precipitation Titration Curves, 2

Concentrations of the analyte and titrant, as well as the $K_{sp}$, influence the sharpness of the endpoint. Since concentrations vary over orders of magnitude, we often plot $pX$:

$$pX = -\log[X]$$

Consider the titration of 25.00 mL of 0.1000 M $\text{I}^-$ with 0.05000 M $\text{Ag}^+$:

$$\text{I}^- + \text{Ag}^+ \rightarrow \text{AgI}(s)$$

Suppose that we monitor $[\text{Ag}^+]$ with an electrode. The reverse of the dissolution of $\text{AgI}(s)$ has a very small $K_{sp}$:

$$\text{AgI}(s) \rightarrow \text{I}^- + \text{Ag}^+ \quad K_{sp} = [\text{Ag}^+][\text{I}^-] = 8.3 \times 10^{-17}$$

The equilibrium constant for the titration reaction above is large ($K = 1/K_{sp} = 1.2 \times 10^{16}$), so the equilibrium lies far to the right. Hence, each aliquot of $\text{Ag}^+$ reacts nearly completely with $\text{I}^-$, leaving only a tiny amount of $\text{Ag}^+$ in solution. Therefore, at the equivalence point, there will be a sudden increase in $[\text{Ag}^+]$ because there is no $\text{I}^-$ left to consume the added $\text{Ag}^+$. The volume of $\text{Ag}^+$ titrant needed to reach the equivalent point is easily calculated (1:1 $\text{Ag}^+:\text{I}^-$):

$$\left(\frac{0.025 \ 00 \ \text{L}}{\text{mol} \ \text{I}^-/\text{L}} \right) \left(0.100 \ 0 \ \text{mol} \ \text{I}^-/\text{L} \right) = \left(\frac{V_e}{\text{mol} \ \text{Ag}^+/\text{L}} \right) \left(0.050 \ 00 \ \text{mol} \ \text{Ag}^+/\text{L} \right)$$

$$\Rightarrow V_e = 0.050 \ 00 \ \text{L} = 50.00 \ \text{mL}$$
Before the Equivalence Point

Suppose that 10.00 mL of Ag\(^+\) have been added. There are more moles of I\(^-\) than Ag\(^+\) at this point, so virtually all Ag\(^+\) is “used up” to make AgI(s). What is the small concentration of Ag\(^+\) remaining in solution after reaction with I\(^-\)? The solubility of Ag\(^+\) is determined by the concentration of free I\(^-\) remaining in the solution:

\[
[Ag^+] = \frac{K_{sp}}{[I^-]}
\]

Free I\(^-\) is overwhelmingly from the I\(^-\) that has not been precipitated by 10.00 mL of Ag\(^+\). By comparison, I\(^-\) from dissolution of AgI(s) is negligible.

Moles of I\(^-\) = original mols of I\(^-\) − moles of Ag\(^+\) added
= (0.025 00 L)(0.100 mol/L) − (0.010 00 L)(0.050 00 mol/L)
= 0.002 000 mol I\(^-\)

The volume is 0.03500 L (25.00 mL + 10.00 mL), so the concentration is

\[
[I^-] = \frac{0.002000 \text{ mol I}^-}{0.03500 \text{ L}} = 0.05714 \text{ M}
\]

The concentration of Ag\(^+\) in equilibrium with this much I\(^-\) is

\[
[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.3 \times 10^{-17}}{0.05714} = 1.45 \times 10^{-15} \text{ M}
\]
Finally, the p is

\[
p_{Ag^+} = -\log[Ag^+] = -\log(1.45 \times 10^{-15}) = 14.84
\]

The preceding step-by-step calculation is tedious. Here is a streamlined procedure that is well worth learning (remember that \( V_e = 50.00 \text{ mL} \)).

When 10.00 mL of Ag\(^+\) have been added, the reaction is one-fifth complete because 10.00 mL out of the 50.00 mL of Ag\(^+\) needed for complete reaction have been added. Therefore, four-fifths of the I\(^-\) is unreacted. If there were no dilution, \([I^-]\) would be four-fifths of its original value. However, the original volume of 25.00 mL has been increased to 35.00 mL. If no I\(^-\) had been consumed, the concentration would be the original value of \([I^-]\) times (25.00/35.00). Accounting for both the reaction and the dilution, we can write

\[
[I^-] = \left(\frac{4.000}{5.000}\right) \left(0.100 \text{ M}\right) \left(\frac{25.00}{35.00}\right) = 0.057 14 \text{ M}
\]
Before the Equivalence Point, 3

**EXAMPLE** Using the Streamlined Calculation

Let’s calculate pAg$^+$ when $V_{Ag^+}$ (the volume added from the buret) is 49.00 mL.

**Solution** Because $V_e = 50.00$ mL, the fraction of $I^-$ reacted is $49.00/50.00$, and the fraction remaining is $1.00/50.00$. The total volume is $25.00 + 49.00 = 74.00$ mL.

\[
[I^-] = \left( \frac{1.00}{50.00} \right) \left( 0.100 \text{ M} \right) \left( \frac{25.00}{74.00} \right) = 6.76 \times 10^{-4} \text{ M}
\]

\[
[Ag^+] = K_{sp}/[I^-] = (8.3 \times 10^{-17})/(6.76 \times 10^{-4}) = 1.23 \times 10^{-13} \text{ M}
\]

\[
pAg^+ = -\log[Ag^+] = 12.91
\]

The concentration of Ag$^+$ is negligible compared with the concentration of unreacted I$^-$, even though the titration is 98% complete.

**Test Yourself** Find pAg$^+$ at 49.1 mL. *(Answer: 12.86)*
At the Equivalence Point

Enough Ag\(^+\) has been added to react with all of the I\(^-\). AgI precipitates and some redissolves to give equal concentrations of Ag\(^+\) and I\(^-\). The value of pAg\(^+\) is found by setting [Ag\(^+\)] = [I\(^-\)] = x in the solubility product:

\[
[Ag^{+}][I^{-}] = K_{sp}
\]

\[
(x)(x) = 8.3 \times 10^{-17} \implies x = 9.1 \times 10^{-9} \implies pAg^{+} = -\log x = 8.04
\]

This value of pAg\(^+\) is independent of the original concentrations or volumes.
After the Equivalence Point

Virtually all Ag\(^+\) added before the equivalence point has precipitated. The solution contains all of the Ag\(^+\) added after the equivalence point. Suppose that \(V_{Ag^+} = 52.00\) mL. The volume past the equivalence point is 2.00 mL. The calculation proceeds as follows:

\[
\text{Moles of Ag}^+ = (0.002\text{ L})(0.050\text{ mol Ag}^+/\text{L}) = 0.000\text{ 100 mol}
\]

\[
\text{[Ag}^+] = (0.000\text{ 100 mol})/(0.077\text{ 00 L}) = 1.30 \times 10^{-3}\text{ M} \Rightarrow pAg^+ = 2.89
\]

For a streamlined calculation, the concentration of Ag\(^+\) in the buret is 0.05000 M, and 2.00 mL of titrant are being diluted to \((25.00 + 52.00) = 77.00\) mL. Hence, [Ag\(^+\)] is

\[
[Ag^+] = (0.050\text{ 00 M})(\frac{2.00}{77.00}) = 1.30 \times 10^{-3}\text{ M}
\]
Shape of the Titration Curve

The equivalence point is the point of maximum slope (a negative slope in this case) and is therefore an inflection point (at which the second derivative is 0):

\[
\frac{dy}{dx} \text{ reaches its greatest value}
\]

\[
\frac{d^2y}{dx^2} = 0
\]

In titrations involving 1:1 stoichiometry of reactants, the equivalence point is the steepest point of the titration curve. For stoichiometries other than 1:1, the curve is not symmetric, and the equivalence point is not at the centre of the steepest section of the curve, and it is not an inflection point.

In practice, conditions are chosen such that titration curves are steep enough for the steepest point to be a good estimate of the equivalence point, regardless of the stoichiometry.

Titration curves showing the effect of diluting the reactants.
Outer curve: 25.00 mL of 0.1000 M I\(^–\) titrated with 0.05000 M Ag\(^+\)
Middle curve: 25.00 mL of 0.01000 M I\(^–\) titrated with 0.005000 M Ag\(^+\)
Inner curve: 25.00 mL of 0.001000 M I\(^–\) titrated with 0.0005000 M Ag\(^+\)
$K_{sp}$ affects the titration of halide ions. The least soluble product, AgI, gives the sharpest change at the equivalence point. However, even for AgCl, the curve is steep enough to locate the equivalence point accurately. The larger the equilibrium constant for a titration reaction, the more pronounced will be the change in concentration near the equivalence point.

Titration curves showing the effect of $K_{sp}$. Each curve is calculated for 25.00 mL of 0.1000 M halide titrated with 0.05000 M Ag$^+$. Equivalence points are marked by arrows.
Sample Calculation

EXAMPLE

Calculating Concentrations During a Precipitation Titration

25.00 mL of 0.041 32 M Hg₂(NO₃)₂ were titrated with 0.057 89 M KIO₃.

\[
\text{Hg}^2^+ + 2\text{IO}_3^- \rightarrow \text{Hg}_2(\text{IO}_3)_2(s)
\]

Iodate

For Hg₂(IO₃)₂, \(K_{sp} = 1.3 \times 10^{-18}\). Find [Hg₂⁺] in the solution after addition of (a) 34.00 mL of KIO₃; (b) 36.00 mL of KIO₃; and (c) at the equivalence point.

(written example)
Titration of a Mixture

If a mixture of two ions is titrated, the less soluble precipitate forms first. If the solubilities are sufficiently different, the first precipitation is nearly complete before the second commences.

Consider the addition of AgNO₃ to a solution containing KI and KCl. Because $K_{sp}(\text{AgI}) \ll K_{sp}(\text{AgCl})$, AgI precipitates first. When precipitation of I⁻ is almost complete, the concentration of Ag⁺ abruptly increases and AgCl begins to precipitate. When Cl⁻ is consumed, another abrupt increase in [Ag⁺] occurs. There are two breaks in the titration curve, first at $V_e$ for AgI and then at $V_e$ for AgCl.

The I⁻ end point is taken as the intersection of the steep and nearly horizontal curves. Precipitation of I⁻ is not quite complete when Cl⁻ begins to precipitate. The end of the steep portion is a better approximation of the equivalence point than is the middle of the steep section. The Cl⁻ end point is taken as the midpoint of the second steep section, at 47.41 mL.

Experimental titration curves. (a) 40.00 mL of 0.0502 M KI plus 0.0500 M KCl titrated with 0.0845 M AgNO₃. Inset expands the region near the first equivalence point. (b) 20.00 mL of 0.1004 M I⁻ titrated with 0.0845 M Ag⁺.
Titration of a Mixture, 2

If a mixture of two ions is titrated, the less soluble precipitate forms first. If the solubilities are sufficiently different, the first precipitation is nearly complete before the second commences.

Apparatus for measuring the titration curves. The silver electrode responds to changes in Ag\(^+\) concentration, and the glass electrode provides a constant reference potential in this experiment. The measured voltage changes by approximately 59 mV for each factor-of-10 change in [Ag\(^+\)]. All solutions, including AgNO\(_3\), were maintained at pH 2.0 by using 0.010 M sulfate buffer prepared from H\(_2\)SO\(_4\) and KOH.
Endpoint Detection

One can use electrodes to detect the endpoints (as shown in the previous example), or coloured indicators can be used.

*Volhard titration*: formation of a soluble, coloured complex at the end point.  
*Fajans titration*: adsorption of a coloured indicator on the precipitate at the end point.

The **Volhard titration** is a titration of Ag$^+$ in HNO$_3$ solution. For Cl$^-$, a back titration is necessary. First, Cl$^-$ is precipitated by a known, excess quantity of standard AgNO$_3$.

\[
\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(s)
\]

The AgCl is filtered and washed, and excess Ag$^+$ in the combined filtrate is titrated with standard KSCN (potassium thiocyanate) in the presence of Fe$^{3+}$.

\[
\text{Ag}^+ + \text{SCN}^- \rightarrow \text{AgSCN}(s)
\]

When all Ag$^+$ has been consumed, SCN$^-$ reacts with Fe$^{3+}$ to form a red complex.

\[
\text{Fe}^{3+} + \text{SCN}^- \rightarrow \text{FeSCN}^{2+}
\]

The appearance of red colour is the end point. Knowing how much SCN$^-$ was required for the back titration tells us how much Ag$^+$ was left over from the reaction with Cl$^-$. The total amount of Ag$^+$ is known, so the amount consumed by Cl$^-$ can be calculated.
The **Fajans titration** uses an *adsorption indicator*. When Ag⁺ is added to Cl⁻, there is excess Cl⁻ in solution prior to the EP. Some Cl⁻ is adsorbed onto the AgCl surface, imparting a negative charge to the crystal. After the EP, there is excess Ag⁺ in solution, which adsorbs onto the AgCl surface, resulting in a positive charge on the precipitate. The abrupt change from negative to positive occurs at the EP.

Common adsorption indicators are *anionic dyes*, which are attracted to positively charged particles produced immediately after the equivalence point. Adsorption of the negatively charged dye onto the positively charged surface *changes the color of the dye*, signifying the end point in the titration.

Because the indicator reacts with the precipitate surface, we want as much surface area as possible. To attain maximum surface area, we use conditions that keep the particles as small as possible. Low electrolyte concentration helps prevent precipitate coagulation and maintains small particle sizes.

The most common indicator for AgCl is *dichlorofluorescein*. This dye is greenish yellow in solution but turns pink when adsorbed onto AgCl. The pH of the reaction must be controlled because the indicator is a weak acid and must be present in its anionic form.
### TABLE 26-5 Applications of precipitation titrations

<table>
<thead>
<tr>
<th>Species analyzed</th>
<th>Notes</th>
</tr>
</thead>
</table>
| $\text{Br}^-$, $\text{I}^-$, $\text{SCN}^-$, $\text{CNO}^-$, $\text{AsO}_4^{3-}$, $\text{Cl}^-$, $\text{PO}_4^{3-}$, $\text{CN}^-$, $\text{C}_2\text{O}_4^{2-}$, $\text{CO}_3^{2-}$, $\text{S}^2$-, $\text{CrO}_4^{2-}$ | *Volhard Method*  
Precipitate removal is unnecessary. |
| $\text{BH}_4^-$ | Back titration of $\text{Ag}^+$ left after reaction with $\text{BH}_4^-$:  
$\text{BH}_4^- + 8\text{Ag}^+ + 8\text{OH}^- \rightarrow 8\text{Ag}(s) + \text{H}_2\text{BO}_3^- + 5\text{H}_2\text{O}$  
$\text{K}^+$  
$\text{K}^+$ is first precipitated with a known excess of (C$_6$H$_5$)$_4\text{B}^-$.  
Remaining (C$_6$H$_5$)$_4\text{B}^-$ is precipitated with a known excess of $\text{Ag}^+$. Unreacted $\text{Ag}^+$ is then titrated with $\text{SCN}^-$. |
| $\text{Cl}^-$, $\text{Br}^-$, $\text{I}^-$, $\text{SCN}^-$, $\text{Fe(CN)}_6^{4-}$, $\text{Zn}^{2+}$ | *Fajans Method*  
Titration with $\text{Ag}^+$. Detection with dyes such as fluorescein, dichlorofluorescein, eosin, bromphenol blue.  
Titration with $\text{K}_4\text{Fe(CN)}_6$ to produce $\text{K}_2\text{Zn}_3[\text{Fe(CN)}_6]_2$.  
End-point detection with diphenylamine. |
| $\text{SO}_4^{2-}$ | Titration with $\text{Ba(OH)}_2$ in 50 vol% aqueous methanol using alizarin red S as indicator. |
| $\text{Hg}_2^{2+}$ | Titration with $\text{NaCl}$ to produce $\text{Hg}_2\text{Cl}_2$. End point detected with bromphenol blue. |
| $\text{PO}_4^{3-}$, $\text{C}_2\text{O}_4^{2-}$ | Titration with $\text{Pb(CH}_3\text{CO}_2)_2$ to give $\text{Pb}_3(\text{PO}_4)_2$ or $\text{PbC}_2\text{O}_4$. End point detected with dibromofluorescein ($\text{PO}_4^{3-}$) or fluorescein ($\text{C}_2\text{O}_4^{2-}$). |

*Harris, Quantitative Chemical Analysis, 8e  
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