Titrimetric Method: analytical procedures in which the amount of analyte is determined from the amount of a standard reagent required to react with the analyte completely.

Three types of quantitative titrimetry
1. Volumetric (the most widely used)
2. Gravimetric
3. Coulometric

13A Some Terms Used in Volumetric Titrimetry

*Standard solution* (standard titrant)
1. Accurate known conc.: 4 significant figures
2. Stable
3. Stoichiometric reaction: whole-number ratio
4. Rapid and quantitatively complete reaction: 99.9%

*Titration*

*Direct titration*

*Back-titration, residual-titration*: when the rate of reaction between the analyte and reagent is slow or when the reagent lacks stability.

*Equivalence point*, theoretical point: the point in a titration when the amount of added standard reagent exactly equivalent to the amount of analyte.

*End point*: the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

*Titration error* $E_t$: the difference in volume or mass between the equivalence point and the end point. $(V_{ep} - V_{eq})$

*Indicator*: large changes in the relative conc. of analyte or titrant occur in the equivalence-point region.
   a. Appearance or disappearance of a color.
   b. Change in color.
   c. Appearance or disappearance of turbidity.

Instruments for detect end point: voltmeters, ammeters, ohmmeters, colorimeters, temperature recorders, refractometers.
Fig. 13-1 The titration process

*Primary standards:
1. high purity
2. stability in air
3. absence of hydrate water
4. ready availability at modest cost
5. reasonable solubility in the titration medium
6. reasonably large formula weight

*Secondary standard

13B Standard Solutions

*Standardization, establishing the conc. of standard soln.
1. Direct method: carefully weighed quantity of a primary standard
   \[ \rightarrow \text{dissolved} \rightarrow \text{diluted to an exactly known volume.} \]
2. Standardized by titrating
   a. a weighed quantity of a primary standard
   b. a weighed quantity of a secondary standard
   c. a measured volume of another standard soln

<table>
<thead>
<tr>
<th>Method</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. a weighed quantity of a primary standard</td>
<td>secondary standard solution</td>
</tr>
<tr>
<td>b. a weighed quantity of a secondary standard</td>
<td></td>
</tr>
<tr>
<td>c. a measured volume of another standard soln</td>
<td></td>
</tr>
</tbody>
</table>

*Methods for expressing the conc. of standard solutions
a. molarity \( C \): no. of moles/L soln
b. normality \( C_N \): no. of equivalent/L soln.

13C Volumetric calculations

\[
\text{amount A (mol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mol)}} = \frac{V(L) \times C_A (\text{mol/L})}{L}
\]

\[
\text{amount A (mmol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mmol)}} = \frac{V(mL) \times C_A (\text{mmol/mL})}{mL}
\]
*Calculation of the Molarity of Standard Solutions (SS)*

Ex. 13-1. Describe the preparation of 2.000 L of 0.0500 M AgNO₃ (169.87 g/mol) from the primary standard-grade solid.

- amount AgNO₃ = 0.050 L × 2.000 mol/L = 0.1000 mol
- mass AgNO₃ = 0.1000 mol × 169.87 g/mol = 16.98 g

dissolving 16.98 g AgNO₃ in water and diluting to 2.000 L.

Ex. 13-2. Describe how 500 mL of standard 0.0100 M Na⁺ solution can be prepared from primary standard Na₂CO₃ (105.99 g/mol).

- amount Na₂CO₃ = 500 mL × 0.0100 mmol/mL × ½ = 2.50 mmol
- mass Na₂CO₃ = 2.50 mmol × 0.10599 g/mmol = 0.265 g

→ dissolving 0.265 g Na₂CO₃ in water and diluting to 500 mL.

Ex. 13-3. How would you prepare 50.0-mL portions of SS that are 0.00500 M, 0.00200 M and 0.00100 M in Na⁺ from the soln in Ex. 2?

\[
V_{\text{conc}} \times C_{\text{conc}} = V_{\text{dil}} \times C_{\text{dil}}
\]

\[
V_{\text{conc}} = \frac{V_{\text{dil}} \times C_{\text{dil}}}{C_{\text{conc}}} = \frac{50.0\text{mL} \times 0.00500\text{mmol Na}^+ / \text{mL}}{0.0100\text{mmol Na}^+ / \text{mL}} = 25.0\text{mL}
\]

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00500 M Na⁺</td>
<td>25.0 mL</td>
</tr>
<tr>
<td>0.00200 M Na⁺</td>
<td>10.0 mL</td>
</tr>
<tr>
<td>0.00100 M Na⁺</td>
<td>5.00 mL</td>
</tr>
</tbody>
</table>

Ex. 13-4. Describe how you would prepare 2.0 L of approximate 0.25 M HClO₄ (100.46 g/mol) from the conc. reagent, which has a specific gravity of 1.67 g/mL and contains 71 % (w/w) HClO₄.

CHClO₄ = 1.67 (g/mL)/0.10046 (g/mmol) × 0.71 = 11.8 M

\[
\text{no. mmol HClO₄ required} = 2000 \text{ mL} \times 0.25 \text{ mmol/mL} = 500 \text{ mmol}
\]

\[
\text{vol conc. reagemnt} = 500 \text{ mmol}/11.8 \text{ (mmol/mL)} = 42.4 \text{ conc. reagent}
\]

→ diluted about 42 mL of 71 % HClO₄ to 2.0 L.

*Calculation of Molarities from Standardization Data*

Ex. 13-5. A 50.00-mL of an HCl solution required 29.71 mL of 0.01963 M Ba(OH)₂ to reach an end point with bromocresol green indicator. Calculate the molarity of the HCl.

\[
\text{Ba(OH)₂} + 2\text{HCl} \rightarrow \text{BaCl}_2 + 2\text{H}_2\text{O}
\]

1 mmol Ba(OH)₂ reacts with 2 mmol of HCl

amount Ba(OH)₂ = 29.71 mL × 0.01963 mmol/mL = 0.5832 mmol

amount HCl = 2 × 0.5832 = 1.1664 mmol

\[
C_{\text{HCl}} = \frac{(29.71 \times 0.01963 \times 2) \text{ mmol HCl}}{50.0 \text{ mL soln}} = 0.023328 \text{ M} = 0.0233 \text{ M}
\]
Ex. 13-6. Titration of 0.2121 g pure Na₂C₂O₄ (134.00 g/mol) required 43.31 mL KMnO₄. What is the molarity of the KMnO₄ soln?

\[
2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}
\]

stoichiometric ratio = \( \frac{2 \text{ mmol KMnO}_4}{5 \text{ mmol Na}_2\text{C}_2\text{O}_4} \)

amount Na₂C₂O₄ = \( \frac{0.2121 \text{ g}}{0.13400 \text{ g/ mmol}} \)

amount KMnO₄ = \( \frac{0.2121}{0.13400} \times \frac{2}{5} \)

\[C_{\text{KMnO}_4} = \frac{(0.2121 \times \frac{2}{5}) \text{ mmol}}{43.31 \text{ mL}} = 0.01462 \text{ M} \]

*Calculation the Quantity of Analyte from Titration Data*

Ex. 13-7. A 0.8040-g sample of an iron ore is dissolved in acid. The iron is then reduced to Fe²⁺ and titrated with 47.22 mL of 0.02242 M KMnO₄ solution. Calculate the results of this analysis in term of (a) % Fe (55.847 g/mol); and (b) % Fe₃O₄ (231.54 g/mol).

\[
\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}
\]

(a). stoichiometric ratio = \( \frac{5 \text{ mmol Fe}^{2+}}{1 \text{ mmol KMnO}_4} \)

amount KMnO₄ = 47.22 mL × 0.02242 mol/L = 1.0587 mmol

amount Fe²⁺ = 47.22 mL × 0.02242 mol/L × 5 = 5.2934 mmol

mass Fe²⁺ = 5.2934 mmol × 0.055847 g/mmol = 0.2956 g

percent Fe²⁺ = \( \frac{(47.22 \times 0.02242 \times 5 \times 0.055847) \text{ g}}{0.8040 \text{ g sample}} \times 100\% = 36.77\% \)

(b). stoichiometric ratio: \( 5 \text{ Fe}_3\text{O}_4 \equiv 1 \text{ MnO}_4^- \)

5 Fe₃O₄ ≡ 15 Fe²⁺ ≡ 3 MnO₄⁻

amount KMnO₄ = 47.22 mL × 0.02242 mol/L = 1.0587 mmol

amount Fe₃O₄ = 47.22 mL × 0.02242 mol/L × 5/3 = 1.76445 mmol

mass Fe₃O₄ = 1.76445 mmol × 0.23154 g/mmol = 0.4085 g

percent Fe₃O₄ = \( \frac{(47.22 \times 0.02242 \times \frac{5}{3}) \times 0.23154 \text{ g}}{0.8040 \text{ g sample}} \times 100\% = 50.81\% \)
Ex. 13-8. A 100.0-mL sample of brackish water was made ammonical, and the sulfide it contained was titrated with 16.47 mL of 0.02310 M AgNO₃. The analytical reaction is $2\text{Ag}^+ + \text{S}^{2-} \rightarrow \text{Ag}_2\text{S}(s)$ Calculate $[\text{H}_2\text{S}]$ in the water in ppm.

$$[\text{H}_2\text{S}] = \frac{(16.47 \times 0.02310 \times \frac{1}{2}) \times 0.034802\text{g}}{100.0\text{mL} \times 1.000\text{g/mL}\text{sample}} \times 10^6 \text{ppm} = 66.2 \text{ppm H}_2\text{S}$$

Ex. 13-9. The phosphorus in a 4.258-g sample of a plant food was converted to $\text{PO}_4^{3-}$ and precipitated as $\text{Ag}_3\text{PO}_4$ through the addition of 50.00 mL of 0.0820 M AgNO₃. The excess AgNO₃ was back-titrated with 4.06 mL of 0.0625 M KSCN. Express the results of the analysis in terms of % P₂O₅.

$$\text{P}_2\text{O}_5 + 9\text{H}_2\text{O} \rightarrow 2\text{PO}_4^{3-} + 6\text{H}_3\text{O}^+$$

$$2\text{PO}_4^{3-} + 6\text{Ag}^+_{(\text{excess})} \rightarrow 2\text{Ag}_3\text{PO}_4(s)$$

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

$$\%\text{P}_2\text{O}_5 = \frac{(50.00 \times 0.0820 - 4.06 \times 0.0625) \times \frac{1}{6} \times 0.1419\text{g/mmol}}{4.258\text{g sample}} \times 100\% = 2.14\%$$

Ex. 13-10. The CO in a 20.3-L sample of gas was converted to $\text{CO}_2$ by passing the gas over iodine pentoxide heated to 150°C, and I₂ was distilled and collected to 8.25 mL of 0.01101 M Na₂S₂O₃, then back titration with 2.16 mL of 0.00947 M I₂ solution. Calculate the mg of CO (28.01 g/mol) per liter of sample.

$$\text{I}_2\text{O}_5(s) + 5\text{CO}(g) \rightarrow 5\text{CO}_2(g) + \text{I}_2(g)$$

$$\text{I}_2(aq) + 2\text{S}_2\text{O}_5^{2-}(aq) \rightarrow 2\text{I}^-(aq) + \text{S}_4\text{O}_6^{2-}(aq)$$

$$\%\text{CO} : \text{S}_2\text{O}_5^{2-} = 5 : 2$$

$$\text{Mass CO} = \frac{(8.25 \times 0.01101 - 2.16 \times 0.00947 \times 2) \times \frac{5}{2} \times 28.01}{20.3\text{L}}$$

$$= \frac{0.1248 \text{mmol} \times 28.01}{20.3} = \frac{3.4956}{20.3} = 0.172 \text{mg/L}$$

Ex. 11. The organic matter in a 3.776-g sample of a mercuric ointment is decomposed with HNO₃. After dilution, the Hg²⁺ is titrated with 21.30 mL of a 0.1144 M soln of NH₄SCN. Calculate the percent Hg (200.59 g/mol) in the ointment.

$$\text{Hg}^{2+} + 2\text{SCN}^- \rightarrow \text{Hg}({\text{SCN}})_2(\text{aq})$$

stoichiometric ratio = 1 mmol Hg²⁺/2 mmol NH₄SCN
amount NH₄SCN = 21.30 mL × 0.1144 mmol/mL = 2.4367 mmol
amount Hg²⁺ = 2.4367 mmol × 1/2 = 1.2184 mmol
mass Hg²⁺ = 1.2184 mmol × 0.20059 g/mmol = 0.2444 g

$$\%\text{Hg} = \frac{(21.30 \times 0.1144 \times \frac{1}{2}) \times 0.20059\text{g}}{3.776\text{g sample}} \times 100\% = 6.472\%$$
Ex. 13-12 A 0.4755-g sample [(NH₄)₂C₂O₄ and inert ]/ H₂O, added KOH to alkaline [NH₄⁺ → NH₃], distilled into 50.00 mL of 0.05035 M H₂SO₄. Then back titration with 11.13 mL of 0.1214 M NaOH. Calculate (a) the % N (14.007 g/mol) and (b) the % (NH₄)₂C₂O₄ (124.10 g/mol) in the sample.

(a) \[ \% \text{N} = \left( \frac{50.00 \times 0.05035 \times 2 - 11.13 \times 0.1214}{0.4755 \times 1000} \right) \times 100\% \]

\[ = \left( \frac{3.6838 \times 14.007}{475.5} \right) \times 100\% = 10.85\% \]

(b) \[ \% (\text{NH}_4)_2\text{C}_2\text{O}_4 = \left( \frac{3.6838 \times 124.10}{0.4755 \times 1000} \right) \times 100\% = \left( \frac{228.58}{475.5} \right) \times 100\% \]

\[ = 48.07\% \]

13D Gravimetric Titrimetry

13 E Titration curves in Titrimetric Methods

Table 13-1 Concentration changes during a titration of 50.00 mL of 0.1000M AgNO₃ with 0.1000M KSCN

<table>
<thead>
<tr>
<th>0.1000M KSCN, mL</th>
<th>[Ag⁺] mmol/L</th>
<th>mL of KSCN to cause a tenfold decrease in [Ag⁺]</th>
<th>pAg</th>
<th>pSCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.000 × 10⁻¹</td>
<td>1.00</td>
<td>1.00</td>
<td>10.00</td>
</tr>
<tr>
<td>40.91</td>
<td>1.000 × 10⁻²</td>
<td>40.91</td>
<td>2.00</td>
<td>10.00</td>
</tr>
<tr>
<td>49.01</td>
<td>1.000 × 10⁻³</td>
<td>8.10</td>
<td>3.00</td>
<td>9.00</td>
</tr>
<tr>
<td>49.90</td>
<td>1.000 × 10⁻⁴</td>
<td>0.89</td>
<td>4.00</td>
<td>8.00</td>
</tr>
<tr>
<td>49.99</td>
<td>1.000 × 10⁻⁵</td>
<td>0.09</td>
<td>5.00</td>
<td>7.00</td>
</tr>
<tr>
<td>50.00</td>
<td>1.000 × 10⁻⁶</td>
<td>0.01</td>
<td>6.00</td>
<td>6.00</td>
</tr>
<tr>
<td>50.01</td>
<td>1.000 × 10⁻⁷</td>
<td>0.01</td>
<td>7.00</td>
<td>5.00</td>
</tr>
<tr>
<td>50.10</td>
<td>1.000 × 10⁻⁸</td>
<td>0.09</td>
<td>8.00</td>
<td>4.00</td>
</tr>
<tr>
<td>51.01</td>
<td>1.000 × 10⁻⁹</td>
<td>0.91</td>
<td>9.00</td>
<td>3.00</td>
</tr>
<tr>
<td>61.11</td>
<td>1.000 × 10⁻¹⁰</td>
<td>10.10</td>
<td>10.00</td>
<td>2.00</td>
</tr>
</tbody>
</table>
13F Precipitation Titrimetry

Silver nitrate titrations: Argentometric methods
for halides, halide-like anion (SCN⁻, CN⁻, CNO⁻) several divalent anions, mercaptans, fatty acids and several divalent and trivalent inorganic anions.

**End point:**
1. A change in color due to the reagent, the analyte or an indicator.
2. A change in potential of an electrode that responds to the conc. of one of the reactants.

Titration curves: plots of a conc.-related variable as a function of reagent volume.

**13F-1 Precipitation titration curves involving silver ion**
- preequivalence points
- equivalence point
- post equivalence points

---

Ex. 13-13. Perform calculations needed to generate a titration curve for 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO₃.

\[ \text{Ag}^+(aq) + \text{Cl}^-(aq) \leftrightarrow \text{AgCl}(s), \quad K_{SP} = [\text{Ag}^+][\text{Cl}^-] = 1.82 \times 10^{-10} \]

**Initial point:** 0.000 M in Ag, and pAg is indeterminate.

**preequivalence points, At 10.00 mL**

\[
[\text{Cl}^-] = C_{\text{NaCl}} = \frac{\text{original no. mmol Cl}^- - \text{no. mol AgNO}_3}{\text{total volume of solution}} = \frac{50.00 \times 0.0500 - 10.00 \times 0.100}{50.00 + 10.0} = 0.02500 \text{ M}
\]

\[
[\text{Ag}^+] = \frac{K_{SP}}{0.02500} = \frac{1.82 \times 10^{-10}}{0.02500} = 7.28 \times 10^{-9}, \quad \text{pAg} = \log (7.28 \times 10^{-9}) = 8.14
\]
Equivalence point

\[
[\text{Ag}^+] = \sqrt[3]{K_{sp}} = \sqrt[3]{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}, \quad p\text{Ag} = -\log (1.35 \times 10^{-5}) = 4.87
\]

Post equivalence point,

\[
[\text{Ag}^+] \approx C_{\text{AgNO}_3} = \frac{(26.00 \times 0.1000 - 50.00 \times 0.0500)}{76.00} = 1.316 \times 10^{-3}
\]

\[
p\text{Ag} = -\log (1.316 \times 10^{-3}) = 2.88
\]

Tab. 13-2 Changes in pAg in the titration of Cl⁻ with AgNO₃.

<table>
<thead>
<tr>
<th>AgNO₃, mL</th>
<th>50.00 mL of 0.0500 M NaCl with 0.1000M AgNO₃</th>
<th>50.00 mL of 0.00500 M NaCl with 0.01000M AgNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.00</td>
<td>8.04</td>
<td>7.14</td>
</tr>
<tr>
<td>20.00</td>
<td>7.59</td>
<td>6.59</td>
</tr>
<tr>
<td>24.00</td>
<td>6.87</td>
<td>5.87</td>
</tr>
<tr>
<td>25.00</td>
<td>4.87</td>
<td>4.87</td>
</tr>
<tr>
<td>26.00</td>
<td>2.88</td>
<td>3.88</td>
</tr>
<tr>
<td>30.00</td>
<td>2.20</td>
<td>3.20</td>
</tr>
<tr>
<td>40.00</td>
<td>1.78</td>
<td>2.78</td>
</tr>
</tbody>
</table>

The shapes of titration curves

Fig. 13-4 Titration curve for A, 50.00 mL of 0.0500 M NaCl with 0.1000 M AgNO₃, and B, 50.00 mL of 0.00500 M NaCl with 0.01000 M AgNO₃.

Fig. 13-5 Effect of reaction completeness on precipitation titration curve, 50.00 mL of a 0.0500 M solution of the anion was titrated with 0.1000 M AgNO₃.

Factors influencing end-point sharpness

Satisfactory end points require a change of 2 in p-function within ±0.1 mL of the equivalence point
a. reagent conc. : conc. ↑ → sharpness ↑
b. reaction completeness : product ppt Ksp ↓ → sharpness ↑

*Chemical indicators for precipitation titration
A + R → AR(s) analyze A with titrant R,
In + R → InR indicator In
For a color change to be seen, [InR]/[In] must change by a factor of 10 to 100.

13F-2 Titration curves for mixtures of anions

Titration of 50.00 mL of a solution ([I⁻] = 0.0500M and [Cl⁻]=0.0800 M) with 0.1000 M AgNO₃.

\[
\frac{[Ag^+][I^-]}{[Ag^+][Cl^-]} = \frac{8.3 \times 10^{-17}}{1.82 \times 10^{-10}} = 4.56 \times 10^{-7} \Rightarrow [I^-] = (4.56 \times 10^{-7})[Cl^-]
\]

after added 25.00 mL AgNO₃,

\[
c_{Cl^-} = \frac{50.00 \times 0.0800}{50.00 + 25.00} = 0.0533 \text{ M, } [I^-] = 4.56 \times 10^{-7} \times 0.0533 = 2.43 \times 10^{-8} \text{ M}
\]

no. mmol I⁻ = 75.00 mL \times (2.43 \times 10^{-8} \text{ mmol I⁻/mL}) = 1.82 \times 10^{-6}

\[
[I^-]_{\text{unprecipitated}} = \frac{1.82 \times 10^{-6}}{50.00 \times 0.0500} \times 100\% = 7.3 \times 10^{-5} \%
\]

\[
[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0533} = 3.41 \times 10^{-9} \Rightarrow pAg = -\log(3.41 \times 10^{-9}) = 8.47
\]

after added 30.00 mL AgNO₃,

\[
c_{Cl^-} = [Cl^-] = \frac{50.00 \times 0.0800 - (30.00 \times 0.100 - 50.00 \times 0.0500)}{50.00 + 30.00} = 0.0438 \text{ M}
\]

\[
[Ag^+] = \frac{1.82 \times 10^{-10}}{0.0438} = 4.16 \times 10^{-9} ,
\]

\[
pAg = 8.38
\]

Fig. 13-6 Titration curves for 50.00 mL of a solution 0.0800 M in Cl⁻ and 0.0500 M in I⁻ or Br⁻.

AgI: Ksp = 8.3 \times 10^{-17}

AgBr: Ksp = 5.2 \times 10^{-13}

AgCl: Ksp = 1.8 \times 10^{-10}
13F-3 Indicators for Argentometric Titrations

*AgNO₃ titrations

<table>
<thead>
<tr>
<th>Method</th>
<th>Mohr (Direct)</th>
<th>Fajans (Direct)</th>
<th>Volhard (Residual)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titrant</td>
<td>AgNO₃</td>
<td>AgNO₃</td>
<td>AgNO₃-KSCN</td>
</tr>
<tr>
<td>Indicator</td>
<td>Na₂CrO₄</td>
<td>Fluorescein</td>
<td>Fe³⁺</td>
</tr>
<tr>
<td>End point</td>
<td>Ag₂CrO₄ (s) red ppt</td>
<td>AgX:Ag⁺⁺ Fl(s) red ppt</td>
<td>Fe(SCN)²⁺ red solution</td>
</tr>
<tr>
<td>Titration pH</td>
<td>6.5 ~ 10.3</td>
<td>≥7</td>
<td>Acidic</td>
</tr>
</tbody>
</table>

1. Chromate Ion; The Mohr method

1865 K. F. Mohr, a German pharmaceutical chemist

sample: Cl⁻, Br⁻, CN⁻

\[ \text{AgNO}_3 + X^- \rightleftharpoons \text{AgX(s) + NO}_3^- \]
white

\[ \text{AgNO}_3 + \text{CN}^- \rightleftharpoons \text{Ag(CN)}_2^-(aq) + \text{NO}_3^- \]

End point: \( 2\text{AgNO}_3 + \text{CrO}_4^{2-} \rightleftharpoons \text{Ag}_2\text{CrO}_4(s) + 2 \text{NO}_3^- \)
yellow \( \text{red (Ksp = 1.1 \times 10^{-12} M^3)} \)

not for arsenate, I⁻, SCN⁻

Solubility: \( \text{Ag}_2\text{CrO}_4 > \text{AgX} \)

*Choice of indicator:

if indicator- I⁻ anion (AgI Ksp = 8.3 \times 10^{-17} M²)

\[ \text{AgCl Ksp = 1.82 \times 10^{-10} M^2} \]

\[ [\text{Ag}^+]_{\text{ep}} = (\text{Ksp})^{1/2} = (1.82 \times 10^{-10} M^2)^{1/2} = 1.35 \times 10^{-5} M \]

if indicator- I⁻ anion conc. = 0.0025 M

AgI ppt formation

\[ [\text{Ag}^+]_{\text{min}} = 8.3 \times 10^{-17} M^2/0.0025 M, \Gamma = 3.3 \times 10^{-14} M \]

pre-equivalence point: \( \text{Ag}^+ \rightarrow \text{AgI}(s) \)

*Concentration of indicator [CrO₄²⁻]

equivalence point: \( [\text{Ag}^+] = [\text{Cl}^-] = 1.35 \times 10^{-5} M \)

\[ [\text{CrO}_4^{2-}] = \text{Ksp}/[\text{Ag}^+]^2 = 1.2 \times 10^{-12}/(1.35 \times 10^{-5})^2 = 6.6 \times 10^{-3} M \]

*pH : 6.5 ~ 10.3 (7~10)

\( \text{pH} < 6.5 \quad \text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-} \)

\( \text{CrO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \)

\( \text{pH} > 10.3 \quad \text{Ag}^+ + \text{OH}^- \rightleftharpoons \text{AgOH(s)} \)
2. Adsorption indicators: The Fajans method

1926, Polish chemist, K. Fajans
Advantages: rapid, accurate and reliable

\[
\text{AgNO}_3 + X^- \rightleftharpoons \text{AgX(s) + NO}_3^-
\]

End point: \( \text{Ag}^+ + \text{AgX(s) + Fl}^- \rightleftharpoons \text{AgX:Ag}^+ \cdot \cdot \text{Fl}^-(s) \)

Yellow-green \hspace{1cm} \text{red}

Indicator: Fluorescein anion

* avoid ppt coagulation \( \rightarrow \) ppt surface \( \uparrow \)
  a. adding dextrin or polyethylene glycol
  b. quick titration and avoid excessive stirring
  c. halide ion conc. : 0.005 \( \sim \) 0.025 M

*Fluorescein dyes: weak ionized acids
  \( \text{pH} \downarrow \rightarrow [\text{Fl}^-] \downarrow \rightarrow \text{weak end point} \)
  \( \text{pH} \geq 7, \) (dichlorofluorescein: \( \text{pH} \geq 4 \))

*Photochemical decomposition : ppt \( \rightarrow \) black

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescein</td>
<td>( \geq 7 )</td>
<td>Cl(^-), Br(^-), I(^-), SCN(^-)</td>
</tr>
<tr>
<td>Dichlorofluorescein</td>
<td>( \geq 4 )</td>
<td>Cl(^-), Br(^-), I(^-), SCN(^-)</td>
</tr>
<tr>
<td>Eosin</td>
<td>( \geq 2 )</td>
<td>Br(^-), I(^-), SCN(^-)</td>
</tr>
</tbody>
</table>

3. Iron(III) Ion; The Volhard method

1874 Jacob Volhard, a German chemist, (back titration): Iron(III) ion as indicator

sample: halide ion, \( C_2O_4^{2-}, \text{AsO}_4^{3-}, \text{SCN}^- \)

\( \text{nAgNO}_3 \) (excess) + \( Bn^- \rightleftharpoons \text{Ag}_nB(s) + \text{nNO}_3^- \)

\( \text{KSCN} + \text{unreacted AgNO}_3 \rightleftharpoons \text{AgSCN(s) + K}^+ + \text{NO}_3^- \)

End point: \( \text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons \text{Fe(SCN)}^{2+} \hspace{1cm} \text{red} \)

\( K_r = \frac{[\text{Fe(SCN)}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} = 1050 \)

*pH : in acidic soln to prevent Fe(III) \( \rightarrow \) Fe(OH)\(_3\) (s)
*advantage: carbonate, oxalate & arsenate do not interfere.
*For Cl\(^-\) ion in blood serum, urine. (sample: HNO\(_3\) digestion)

*Quantitativeness of the back titration

\( \text{n SCN}^- + \text{Ag}_nB(s) \rightleftharpoons \text{n AgSCN(s) + B}^{n-} \)

a. compare \( \text{AgSCN and Ag}_nB : \) molar solubility \hspace{1cm} \text{AgSCN:} \( 1.0 \times 10^{-6} \text{ M} \)
b. Calculate $K_{rxn}$

$$K_{rxn} = \frac{[B^{n-}]}{[SCN^{-}]^n} = \frac{K_{sp \ of \ Ag_nB}}{(K_{sp \ of \ AgSCN})^n}$$

If $AgSCN$ solubility < $Ag_nB$ or $K_{rxn} > 1$

→ filter $Ag_nB$ ppt or adding liquid nitrobenzene

Table 13-3 Typical Argentometric Precipitation Methods

<table>
<thead>
<tr>
<th>Analyte</th>
<th>End point</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsO$_4^{3-}$, Br$^-$, I$^-$, CNO$^-$, SCN$^-$</td>
<td>Volhard</td>
<td>Removal of Ag salt not required</td>
</tr>
<tr>
<td>CO$_3^{2-}$, CrO$_4^{2-}$, CN$^-$, Volhard</td>
<td></td>
<td>Removal of Ag salt required before back-titration of excess Ag$^+$</td>
</tr>
<tr>
<td>Cl$^-$, C$_2$O$_4^{2-}$, PO$_4^{3-}$, S$^{2-}$, NCN$^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH$_4^-$</td>
<td>Modified Volhard</td>
<td>Titration of excess Ag$^+$ following $BH_4^- + 8Ag^+ + 8OH^- \to 8Ag(s) + H_2BO_3^- + 5H_2O$</td>
</tr>
<tr>
<td>Epoxide</td>
<td>Volhard</td>
<td>Titration of excess Cl$^-$ following hydrohalogenation</td>
</tr>
<tr>
<td>K$^+$</td>
<td>Modified Volhard</td>
<td>Precipitation of K$^+$ with known excess of B(C$_6$H$_5$)$_4^-$, addition of excess Ag$^+$ giving AgB(C$_6$H$_5$)$_4$(s), and back-titration of the excess</td>
</tr>
<tr>
<td>Br$^-$, Cl$^-$</td>
<td>Mohr method</td>
<td>In neutral solution</td>
</tr>
<tr>
<td>Br$^-$, Cl$^-$, I$^-$, SeO$_3^{2-}$</td>
<td>Adsorption indicator</td>
<td></td>
</tr>
<tr>
<td>V(OH)$_4$$^+$, fatty acids, mercaptans</td>
<td>Electroanalytical</td>
<td>Direct titration with Ag$^+$</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>Modified Volhard</td>
<td>Precipitation as ZnHg(SCN)$_4$, filtration, dissolution in acid, addition of excess Ag$^+$, back-titration of excess Ag$^+$</td>
</tr>
<tr>
<td>F$^-$</td>
<td>Modified Volhard</td>
<td>Precipitation as PbCIF, filtration, dissolution in acid, addition of excess Ag$^+$, back-titration of excess Ag$^+$</td>
</tr>
</tbody>
</table>

Ex. The As in a 9.13-g sample of pesticide was converted to AsO$_4^{3-}$ and precipitated as $Ag_3AsO_4$ with 50.00 mL of 0.02015 M AgNO$_3$. The excess Ag$^+$ was then titrated with 4.75 mL of 0.04321 M KSCN. Calculate the % of As$_2O_3$ in the sample.

no. mmol AgNO$_3$ = 50.00 mL × 0.02015 mmol = 1.0075
no. mmol KSCN = 4.75 mL × 0.04321 mmol = 0.2052
no. mmol AgNO$_3$ consumed by AsO$_4^{3-}$ = 0.8023
$As_2O_3 \equiv 2 \ AsO_4^{3-} \equiv 6 \ AgNO_3$
% As$_2O_3$ = 0.8023 × (1/6) × 0.1978/9.13 × 100 % = 0.2987 %
*Quantitiveness of AgNO₃ titration*

\[ \text{Ag}^+ + \text{X}^- \iff \text{AgX(s)} \quad \text{Krxn} = \frac{1}{K_{sp}} = \frac{1}{[\text{Ag}^+][\text{X}^-]} \]

a. **99.9 % reaction**: at equivalence point, max % Cl⁻ : 0.1 %

ex: AgCl, Ksp = 1.8 \times 10^{-10}; \quad [\text{Cl}^-] = \sqrt{K_{sp}} = 1.34 \times 10^{-5} \text{ M}

\[
\%\text{dissolved} = \frac{\sqrt{K_{sp}} \text{ of AgCl} \times 100}{\text{M of initial Cl}^-} = \frac{1.34 \times 10^{-5} \times 100}{0.010 \text{ M}} = 0.13\%
\]

b. min. theo. Krxn ↔ Krxn

Krxn = 1/Ksp

0.10 M sample [X⁻] \rightarrow 0.1 %

upper limit of [X⁻] = (0.10 M)(0.1 %) = 10^{-4} \text{ M}

equivalence point : [Ag⁺] = [X⁻]

min theo. K_{rxn} = \frac{1}{(10^{-4} \text{ M Ag}^+)(10^{-4} \text{ M X}^-)} = 10^8

for 0.1 M X⁻, actual Krxn \geq 10^8

for 0.01 M X⁻, actual Krxn \geq 10^{10}