PHARMACEUTICAL ANALYTICAL CHEMISTRY

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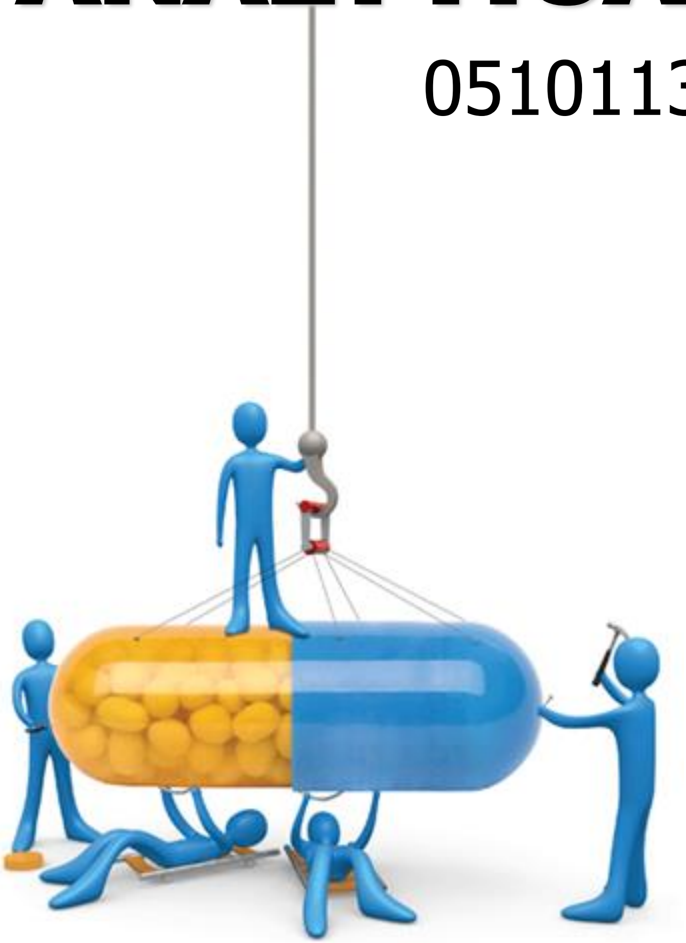

Precipitation Titration

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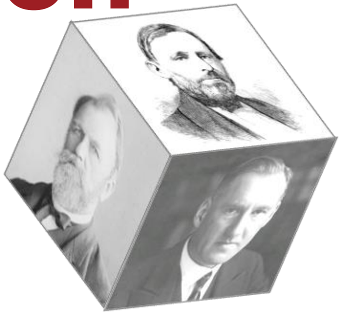
Precipitation Titration

Chapter 11



Learning Objectives

- *To calculate precipitation titration curves*
- *To describe the function of different indicators in precipitation titrations*
- *To explain the principles of adsorption indicators*
- *To use the precipitation volumetric methods in quantitative precipitation determinations*

Precipitation Titration

Key Concepts

- A titration in which the reaction between the analyte and titrant involves a precipitation.
- The solids produced from the titration reactions should have very low K_{sp} values.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \leftrightarrow AgCl_{(s)} \qquad K_{sp} = 1.82\times10^{-10}$$

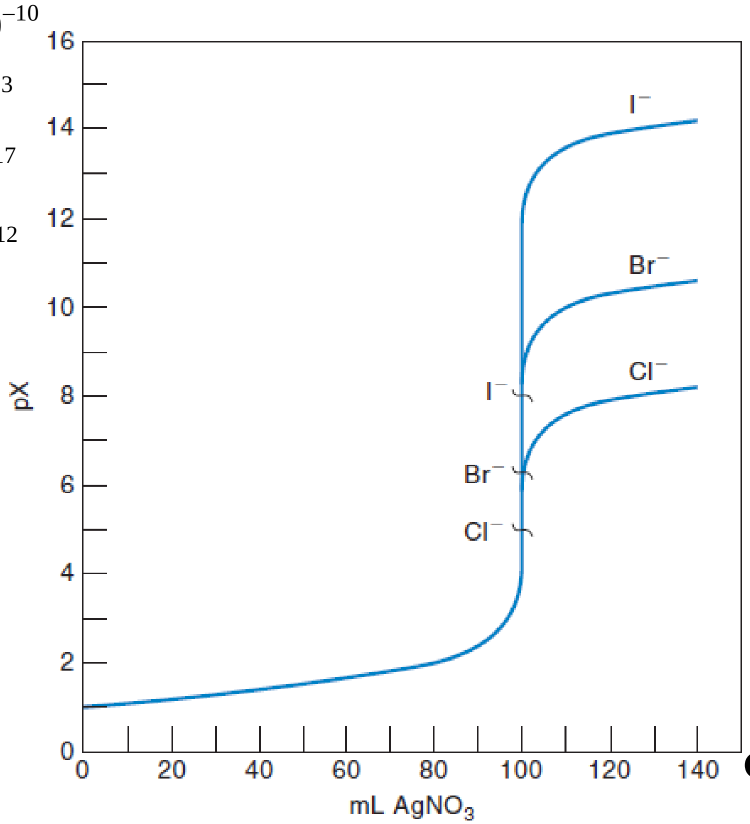
$$Ag^{+}_{(aq)} + Br^{-}_{(aq)} \leftrightarrow AgBr_{(s)} \qquad K_{sp} = 5.0\times10^{-13}$$

$$Ag^{+}_{(aq)} + I^{-}_{(aq)} \leftrightarrow AgI_{(s)} \qquad K_{sp} = 8.3\times10^{-17}$$

$$2Ag^{+}_{(aq)} + CrO_{4\ (aq)}^{2-} \leftrightarrow Ag_{2}CrO_{4(s)} \qquad K_{sp} = 1.2\times10^{-12}$$

- Titration curves

pX vs. volume of titrant



Precipitation Titration

- For the reaction $A^{+}_{(aq)} + B^{-}_{(aq)} \rightleftharpoons AB_{(s)}$

  The concentrations of A^+ and B^- are varying through the titration process. When titrating B^- (analyte) with A^+ (titrant).

a) in the beginning of titration, concentration of A^+ is zero and concentration of B^- is calculated from its salt.

b) After addition of few milliliters of A^+, B^- will react with A^+ forming AB precipitate, concentrations of A^+ will be calculated according to K_{sp}. B^- will be excess.

c) At the end point, concentrations A^+, B^- will be calculated from K_{sp}.

d) After the end point A^+ is the excess and B^- will be calculated from K_{sp}.

Titration curve in the precipitation titration is a plot of

pA and/or pB versus volume of titrant (A)

Precipitation Titration

Example: Calculate pCl for the titration of 100.0mL of 0.1000 M Cl^- with 0.1000 M $AgNO_3$ for the addition of 0.00, 20.00, 99.00, 99.50, 100.00, 100.50, and 110.00mL $AgNO_3$ (assume Ksp = $1.0x10^{-10}$)

a) at 0.0mL addition

$$pCl = -\log(0.1000) = 1.000$$

b) after 20.0mL addition

$$\text{mmol } Cl^- = 100.0 \text{ mL} \times 0.1000 \text{ mmol/mL} = 10.00 \text{ mmol}$$

$$\text{mmol } Ag^+ = 20.00 \text{ mL} \times 0.1000 \text{ mmol/mL} = 2.000 \text{ mmol}$$

$$Cl^- \text{ left} = 10.00 - 2.00 = 8.00 \text{ mmol/120.0 mL} = 0.0667 \text{ M}$$

$$pCl = -\log 0.0667 = 1.18$$

c) after 99.00 mL addition

$$\text{mmol } Ag^+ = 99.00 \text{ mL} \times 0.1000 \text{ mmol/mL} = 9.900 \text{ mmol}$$

$$Cl^- \text{ left} = 10.00 - 9.90 = 0.10 \text{ mmol/199.0 mL} = 5.0\times10^{-4} \text{ M}$$

$$pCl = -\log 5.0\times10^{-4} = 3.26$$

d) After 99.50mL addition

$$\text{mmol } Ag^+ = 99.50 \text{ mL} \times 0.1000 \text{ mmol/mL} = 9.950 \text{ mmol}$$

$$Cl^- \text{ left} = 10.00 - 9.95 = 0.05 \text{ mmol/199.5 mL} = 2.5\times10^{-4}\text{M}$$

$$pCl = -\log 2.5\times10^{-4} = 3.60$$

Precipitation Titration

e) after 100.00 mL addition

at 100.00 mL, all the Cl^- is reacted with Ag^+

$$[Cl^-] = \sqrt{K_{sp}} = \sqrt{1\times10^{-10}} = 1\times10^{-5}$$

$$pCl = -\log 1.0\times10^{-5} = 5.00$$

f) after 100.50 mL addition

mmol Ag^+ = 100.50 mL × 0.1000 mmol/mL = 10.05 mmol

Ag^+ left = 10.05 − 10.00 = 0.05 mmol/200.5 mL = 2.5×10^{-4} M

$[Cl^-] = Ksp/[Ag^+] = 1.0\times10^{-10}/2.5\times10^{-4} = 4.0\times10^{-7}$ M

$pCl = -\log 4.0\times10^{-7} = 6.40$

g) after 110.00 mL addition

mmol Ag^+ = 110.00 mL × 0.1000 mmol/mL = 11.00 mmol

Ag^+ left = 11.00 − 10.00 = 1.00 mmol/210 mL = 4.76×10^{-3} M

$[Cl^-] = Ksp/[Ag^+] = 1.0\times10^{-10}/4.76\times10^{-3} = 2.1\times10^{-8}$ M

$pCl = -\log 2.1\times10^{-8} = 7.67$

Precipitation Titration

Example: **20 mL of 0.05M $CaCl_2$ was titrated with 0.10M $AgNO_3$. Calculate the concentration of Cl^- and Ag^+ in the solution after addition of 0.0mL $AgNO_3$, 5.0mL $AgNO_3$, at the equivalence point and after addition of 30mL $AgNO_3$. (assume Ksp = 1.82×10^{-10})**

a) at 0.0mL addition

$$[Ag^+] = 0.0 \text{ in the beginning of titration}$$

$$[Cl^-] = 2 \times M_{CaCl_2} = 2 \times 0.05 = 0.10M$$

b) after 5.0mL addition

Firstly, calculate the new rough concentrations after addition

	$Ag^+_{(aq)}$	$+$	$Cl^-_{(aq)}$	$\leftrightarrow$	$AgCl_{(s)}$
mmoles	$5x0.1 = 0.5$		$2x20x0.05 = 2$		
change	-0.5		-0.5		
net mmols	0		$2 - 0.5 = 1.5$		
concentration	$0/25 = 0$		$1.5/25 = 0.075M$		

Precipitation Titration

Secondly, calculate the exact concentrations from K_{sp}

	$AgCl_{(s)}$	$\leftrightarrow$	$Ag^{+}_{(aq)}$	$+$	$Cl^{-}_{(aq)}$
start concentration	solid		0		0.075
change	- x		+ x		+ x
net			x		0.075 + x

$$K_{sp} = 1.82x10^{-10} = [Ag^{+}][Cl^{-}] = x.(0.075 + x) \cong 0.075x \Rightarrow x = \frac{1.82x10^{-10}}{0.075} = 2.4x10^{-9}$$

$$[Ag^{+}] = 2.4x10^{-9}M \quad , \quad [Cl^{-}] \cong 0.075M$$

c) at the equivalence point.

at the equivalence point, volume of titrant will be calculated as following

mole Ag = mole Cl ⇨ $(M.V)_{Ag} = (M.V)_{Cl}$ ⇨ $0.1xV_{Ag} = 0.1x20$ ⇨ $V_{ag} = 20mL$

at this point $[Ag^{+}]$ and $[Cl^{-}]$ only comes from dissociation of AgCl

	$AgCl_{(s)}$	$\leftrightarrow$	$Ag^{+}_{(aq)}$	$+$	$Cl^{-}_{(aq)}$
concentration	- x		+ x		+ x

$$K_{sp} = 1.82x10^{-10} = [Ag^{+}][Cl^{-}] = x.x \Rightarrow x = \sqrt{1.82x10^{-10}} = 1.35x10^{-5}$$

$$[Ag^{+}] = [Cl^{-}] = 1.35x10^{-5}M$$

Precipitation Titration

d) after addition of 30mL $AgNO_3$, Ag is excess now

Firstly, calculate the new rough concentrations after addition

	$Ag^+_{(aq)}$	$+$	$Cl^-_{(aq)}$	$\leftrightarrow$	$AgCl_{(s)}$
mmoles	$30x0.1 = 3$		$2x20x0.05 = 2$		
change	-2		-2		
net mmols	1		0		
concentration	$1/50 = 0.02M$		0		

Secondly, calculate the exact concentrations from K_{sp}

	$AgCl_{(s)}$	$\leftrightarrow$	$Ag^+_{(aq)}$	$+$	$Cl^-_{(aq)}$
concentration	$-x$		$0.02 + x$		$+x$

$$K_{sp} = 1.82x10^{-10} = \left[Ag^+\right]\left[Cl^-\right] = (0.02 + x).x \cong 0.02x \Rightarrow x = \frac{1.82x10^{-10}}{0.02} = 9.1x10^{-9}$$

$$\left[Ag^+\right] \cong 0.02M \quad , \qquad \left[Cl^-\right] = 9.1x10^{-9}M$$

Summary Of Calculations

- **For the reaction** $A^+_{(aq)} + B^-_{(aq)} \rightleftharpoons AB_{(s)}$

  When titrating B^- (analyte) with A^+ (titrant).

a) **In the <u>beginning of titration</u>, concentration of A^+ is zero and concentration of B^- is calculated from its salt.**

b) **<u>Before the equivalence point</u>**

   C_B= (original moles of B – moles of A) / total volume

   $C_A = K_{sp}/C_B$

c) **<u>At the equivalence point</u>, $C_B = C_A = \sqrt{K_{sp}}$**

d) **<u>After the equivalence point</u>**

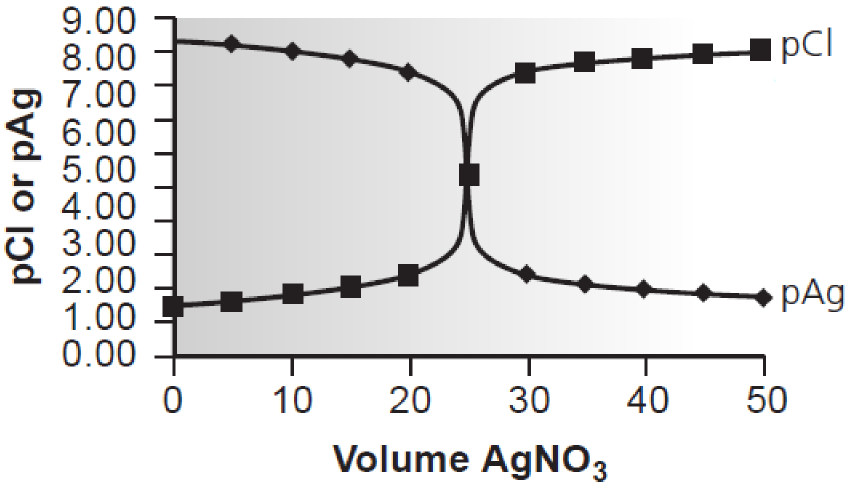
   C_A= (moles of A added – original moles of B) / total volume

   $C_B = K_{sp}/C_A$

Titration Curve

Data for Titration of 50.0 mL of 0.0500 M Cl^- with 0.100 M Ag^+

Volume $AgNO_3$ (mL)	pCl	pAg
0.00	1.30	—
5.00	1.44	8.31
10.00	1.60	8.14
15.00	1.81	7.93
20.00	2.15	7.60
25.00	4.89	4.89
30.00	7.54	2.20
35.00	7.82	1.93
40.00	7.97	1.78
45.00	8.07	1.68
50.00	8.14	1.60

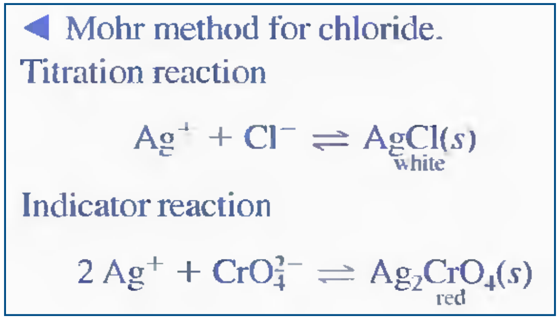


End Point and Indicators

Three methods are well known for precipitation titrations involving Ag^+ as titrant (Argentometry). These are:

- **Mohr method (direct method)**
  in this method, excess Ag cations after the equivalence point will react with the indicator (CrO_4^{2-}) forming red precipitate. This method carried at pH 7-10, to prevent formation of chromic acid (H_2CrO_4).

Example (MOHR)



◀ Mohr method for chloride.

Titration reaction

$$Ag^+ + Cl^- \rightleftharpoons \underset{\text{white}}{AgCl(s)}$$

Indicator reaction

$$2\,Ag^+ + CrO_4^{2-} \rightleftharpoons \underset{\text{red}}{Ag_2CrO_4(s)}$$

35.7mL of 0.10M $AgNO_3$ were needed to reach the end point for titration of 75.0mL of unknown chloride solution using mohr method. Calculate the concentration of Cl^- in the unknown solution.

$$\mathbf{mole_{Ag} = mole_{Cl}}$$

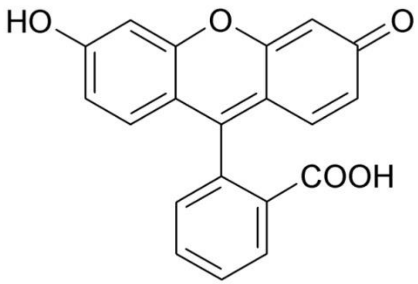
$$\mathbf{(M.V)_{Ag} = (M.V)_{Cl}}$$

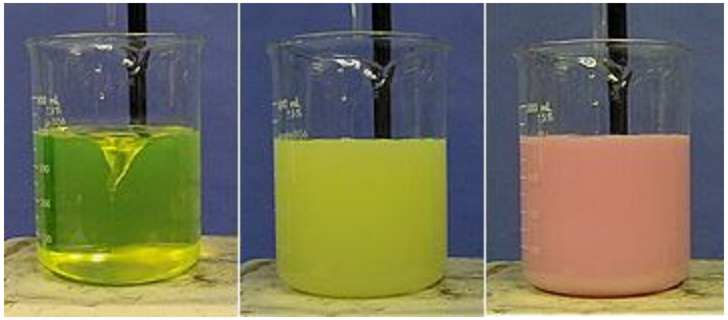
$$\mathbf{35.7x0.1 = M_{Cl}x75}$$

$$\mathbf{3.57 = M_{Cl}x75} \Rightarrow M_{Cl} = 0.0467M$$

End Point and Indicators

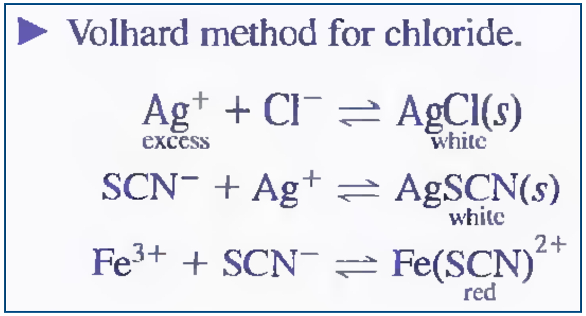
- **Fajans method (direct method)**
  in this method, the indicator (Fluorescein) adsorbed on the surface of the colloidal particles of the precipitate. This will change its color from yellow-green to red. The use of this method is limited because of the relatively few precipitation reactions in which a colloidal precipitate is formed rapidly.





- **Volhard method (back titration method)**
  in this method, the analyte is treated with excess amount of $AgNO_3$, and the remaining $AgNO_3$ is titrated then with SCN^-. At the end point, the titrant SCN^- will react with the indicator Fe^{3+} forming red color complex. pH in this method should be acidic to prevent the formation of $Fe(OH)_3$.

Example (VOLHARD)



▶ Volhard method for chloride.

$$\underset{\text{excess}}{Ag^+} + Cl^- \rightleftharpoons \underset{\text{white}}{AgCl(s)}$$

$$SCN^- + Ag^+ \rightleftharpoons \underset{\text{white}}{AgSCN(s)}$$

$$Fe^{3+} + SCN^- \rightleftharpoons \underset{\text{red}}{Fe(SCN)^{2+}}$$

25.0mL of 0.10M $AgNO_3$ were added to 30 mL of unknown chloride solution. The resulted mixture was then titrated with 19.2mL of 0.10M thiocyanate solution (SCN^-). Calculate the concentration of Cl^- in the unknown solution.

$$\textbf{mole}_{Ag} = \textbf{mole}_{Cl} + \textbf{mole}_{SCN}$$

$$(M.V)_{Ag} = (M.V)_{Cl} + (M.V)_{SCN}$$

$$25 \times 0.1 = M_{Cl} \times 30 + 19.2 \times 0.1$$

$$2.5 - 1.92 = M_{Cl} \times 30 \Rightarrow M_{Cl} = 0.0193M$$

End Point and Indicators

Another Precipitation Titration Methods

1. Barium determination with sulphate:

$$BaCl_2 + H_2SO_4 \rightleftharpoons BaSO_{4(s)} + 2HCl$$

Indicator is sodium rhodizonate, which disappearance red colour of solution.

2. Lead determination with chromate:

$$Pb(NO_3)_2 + K_2CrO_4 \rightleftharpoons PbCrO_{4(s)} + 2KNO_3$$

Indicator is $AgNO_3$ solution. At equivalence point forms red precipitate.

3. Zinc determination with $K_4[Fe(CN)_6]$:

$$3ZnCl_2 + K_4[Fe(CN)_6] \rightleftharpoons Zn_3K_2[Fe(CN)_6]_{(s)} + 2KCl$$

Indicator is $UO_2(NO_3)_2$, which forms brown precipitate with $K_4[Fe(CN)_6]$.

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Thank You!