PHARM.D • YEAR 1

Pharmaceutical Inorganic Chemistry

CHAPTER 6

Precipitation Titrations

PPT CHAPTER COVER



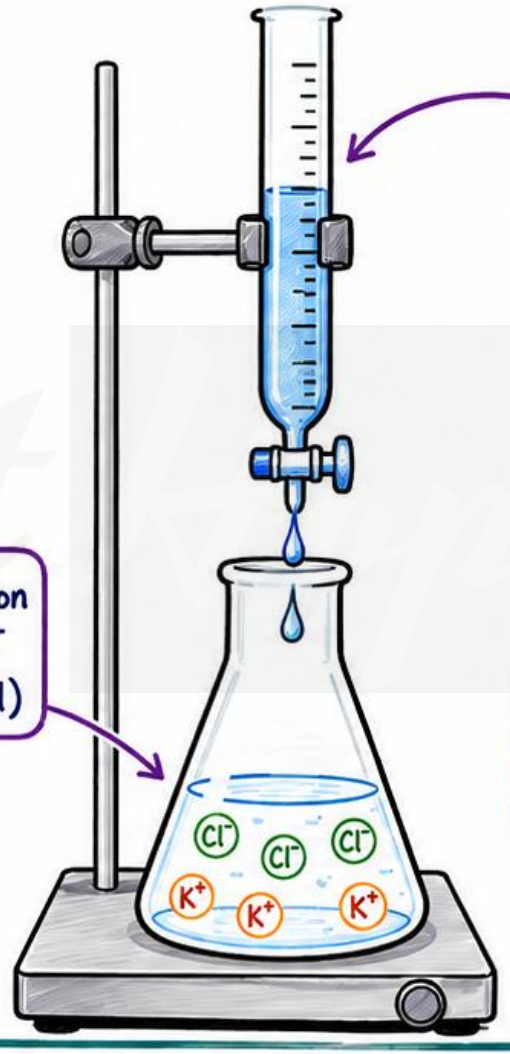
Precipitation Titration and Argentometry

1) Precipitation Titrations

- Volumetric analysis where a titrant reacts with analyte to form a sparingly soluble precipitate.
- Endpoint is reached when analyte is completely reacted and no further precipitation occurs.
- Used to determine concentration of a specific ion in solution.

2) Argentometric Titrations (Mohr's Method)

- Argentometric titrations use Ag^+ as titrant.
- Principle: Selective precipitation of chloride ions before chromate ions.



1) Burette with $AgNO_3$ solution (Ag^+ titrant)

2) Analyte solution containing Cl^- (e.g., NaCl or KCl)

3) Precipitation of chloride before chromate

$$Ag^+ + Cl^- \longrightarrow AgCl_{(s)}\downarrow$$

4) Endpoint (Mohr's indicator)

$$2\,Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_{4(s)}\downarrow$$

Brick-red Ag_2CrO_4 indicates endpoint.

Mohr's Method: Determines chloride ion concentration using Ag^+ titrant.

Cl^- = Chloride ion CrO_4^{2-} = Chromate ion

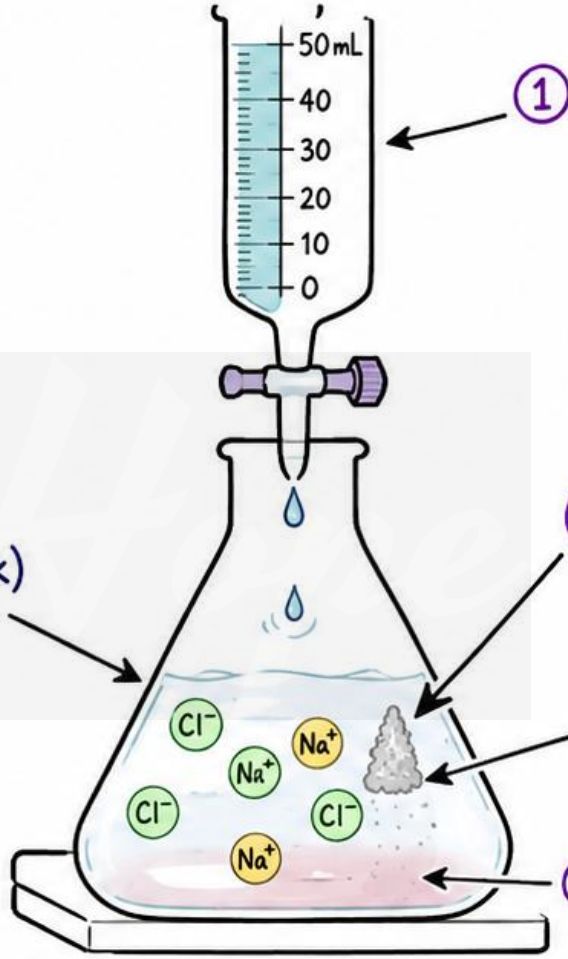
Three Argentometric Methods

What are they?

Argentometric titrations are precipitation titrations that use silver ions (Ag^+) as the titrant.

The Three Methods

1. Mohr's Method
2. Volhard's Method
3. Modified Volhard's Method (Direct Volhard's Method)
4. Fajans Method (Adsorption Indicator Method)



① Titrant (in burette)
Silver nitrate solution ($AgNO_3$)

② Analyte (in flask)
Chloride ion solution

③ Reaction
$Ag^+ + Cl^- \rightarrow AgCl(s) \downarrow$

④ White precipitate ($AgCl$)

⑤ Endpoint (Mohr's Method)
First permanent reddish-brown color from chromate ion (CrO_4^{2-}).

Takeaway

Three argentometric methods are used to determine chloride ions by precipitation with Ag^+.

Principle (Mohr's Method)

Selectively precipitate chloride ions with Ag^+. After Cl^- is precipitated, excess Ag^+ reacts with chromate ion to give a reddish-brown endpoint.

$$Ag^+ + Cl^- \rightarrow AgCl(s) \downarrow$$
$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4(s) \downarrow$$

Mohr Method: Principle

Principle:

Ag^+ first precipitates Cl^- as white AgCl.
After Cl^- is exhausted, excess Ag^+ reacts with chromate to form red Ag_2CrO_4.
The first red precipitate marks the endpoint.

Key Steps:

1. Pipette a known volume of chloride solution.
2. Add distilled water to dilute.
3. Add 2–3 drops of K_2CrO_4 indicator (solution turns yellow).
4. Titrate with standard $AgNO_3$ to form white AgCl.
5. Continue until a faint reddish-brown Ag_2CrO_4 appears (endpoint).

Step 1: Precipitation of chloride

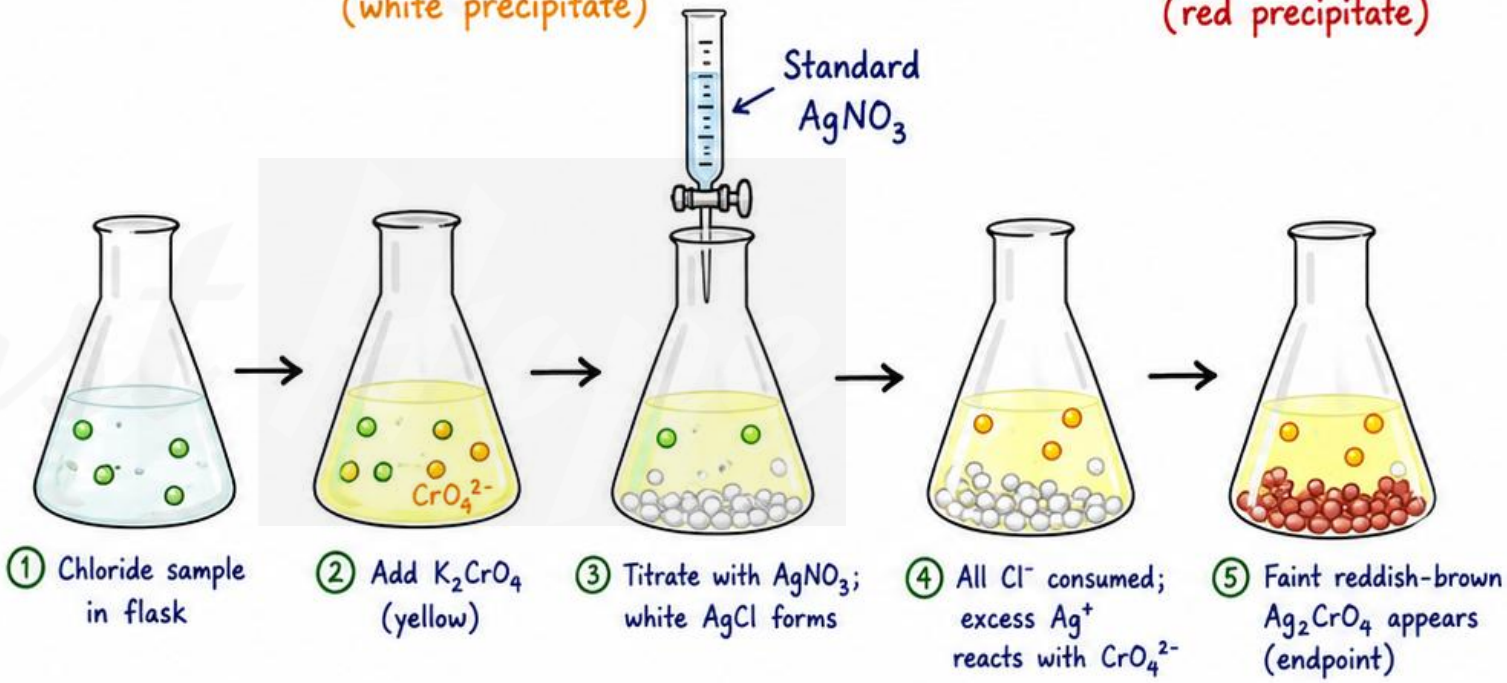
$$Ag^+ + Cl^- \longrightarrow AgCl\ (s)$$

(white precipitate)

Step 2: Endpoint reaction

$$2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4\ (s)$$

(red precipitate)



Calculation:

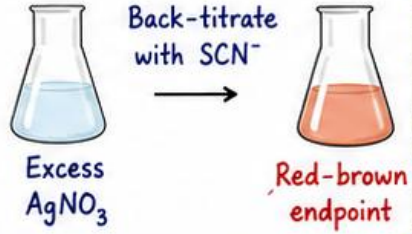
$$C_{Cl^-} = \frac{V_{sample}\ C_{AgNO_3}}{V_{AgNO_3}}$$

Where:

- C_{Cl^-} = concentration of chloride ions
- C_{AgNO_3} = concentration of $AgNO_3$
- V_{AgNO_3} = volume of $AgNO_3$ at the end point
- V_{sample} = volume of chloride-containing sample

Volhard's Method (Introduction)

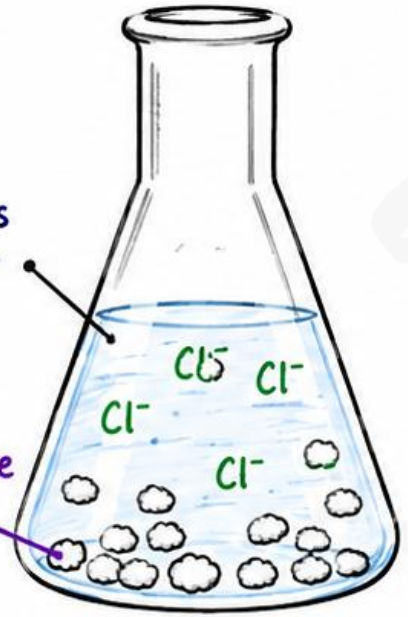
Indirect titration for halides (Cl^-, Br^-, I^-) and SCN^-. Excess $AgNO_3$ precipitates the halide, then unreacted Ag^+ is back-titrated with SCN^-. Endpoint is the red-brown ferric thiocyanate complex using ferric ammonium sulfate indicator.



Mohr Method: End Point and Conditions

BEFORE END POINT

All Cl^- still present

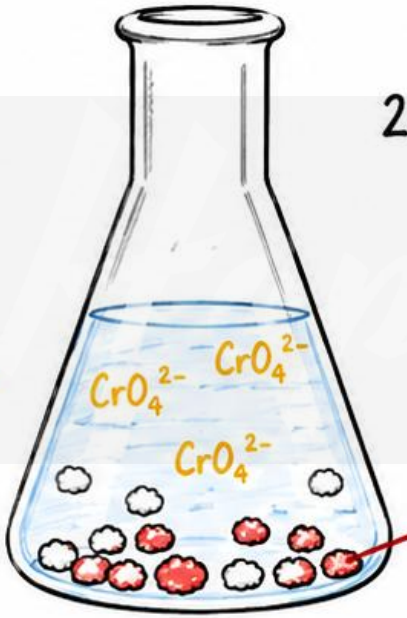


$$Ag^+ + Cl^- \rightarrow AgCl\,(s)$$

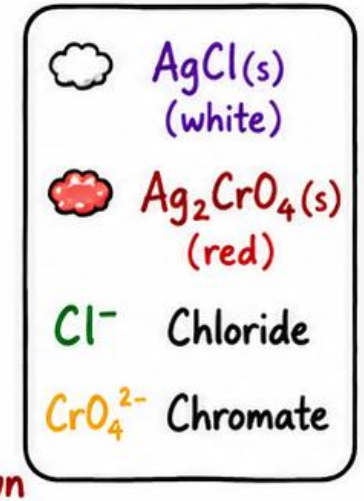
Add Ag^+ (Titrant)

AT END POINT

All Cl^- consumed; excess Ag^+ present



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



- Before endpoint: Ag^+ reacts with Cl^- to form white $AgCl(s)$; chromate remains in solution.
- At endpoint: Excess Ag^+ reacts with chromate to form red $Ag_2CrO_4(s)$. The first faint reddish-brown precipitate. the endpoint.
- Indicator system: Ferric ammonium sulfate; endpoint indicated by red-brown ferric thiocyanate complex.

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