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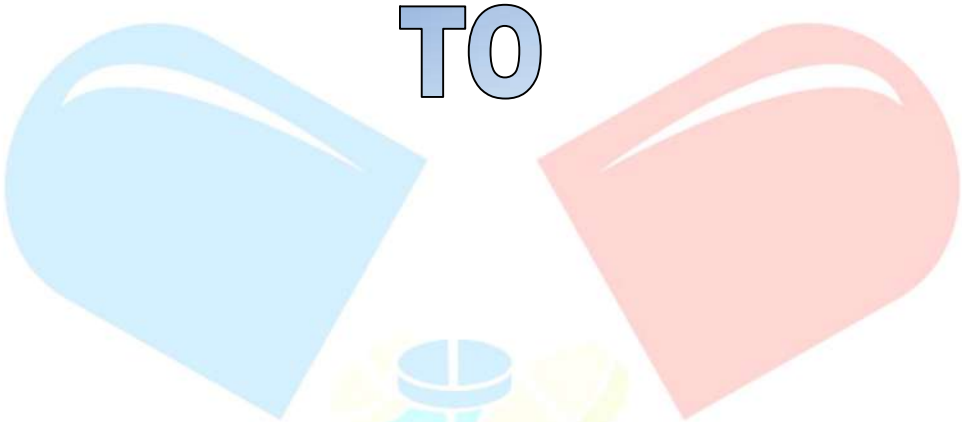
# TO





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# PHARMACEUTICAL ANALYSIS I

## UNIT 3

TOPIC :

- **Precipitation titrations :** Mohr's method, Volhard's, Modified Volhard's, Fajans method, estimation of sodium chloride.

# Precipitation titration

→ Precipitation titration is a type of titration which involves the formation of precipitate during the titration techniques
→ In precipitation titration the titrant reacts with analytic and forms an insoluble substance called precipitate
→ For example $AgNO_3$ is used as a precipitating agent for the determination of cl-

**Principle**

- Formation of an insoluble product by the combination of two ionic species is known as precipitation.
- Precipitation reaction are not frequently used in titration because of the precipitation reaction do not comply with desired specification.

**Indicators used in precipitation**

- The end point in precipitation titration can be marked using a regent known as indicator
- **Adsorption indicators**
- Adsorption indicators are substance that indicates an excess of a reactant in argentometric titration
    - Precipitation becomes coloured when adsorption indicators is adsorbed
    - Eg sodium salt of fluorescein
    - Sodium fluor can be used as an indicator in the titration of chloride with $AgNO_3$ solution in a neutral or slightly basic medium

**Precipitation titration method**

- The precipitation titration silver nitrate with chloride, bromide, iodide, and thiocyanade are most widely used
- These precipitation titration are also known as Argentometric titration

- ♦ Since silver is always involved during the reaction there fore concluding that there titration have limited use

**There procedure are follow in precipitation titration**

I. Mohr s method
II. Volhard s method
III. Modified volhard s method
IV. Farjan s method

## Mohr' s method

- This method is named after Karl friedrich Mohr.
- In this method potassium chromate is used as an indicator which produces Red coloured silver chromate at the end point when all the chloride ions have reached.
- In mohrs method the end point is detected when a coloured precipitate of chloride or bromide is formed.
- A neutral sol of chloride ions is titrated with silver nitrate solution using a small quantity of potassium chromate solution as an indicator.
- The chromate ions combine with silver ions at the end point, forming a red coloured and sparingly soluble silver chromate.

**Principle:**

- Based on precipitation reaction:
  Chloride or bromide ions react with silver nitrate to form white silver halide precipitate (AgCl or AgBr).
- After all halide ions are precipitated, silver ions react with chromate ions to form a brick-red precipitate of silver chromate ($Ag_2CrO_4$).
- This color change signals the end point.

**Chemical Reactions:**

**Main reaction (during titration):**

$$Cl^- + Ag^+ \rightarrow AgCl \downarrow \text{(white precipitate)}\backslash$$

**At end point (excess $Ag^+$):**

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4 \downarrow \text{(brick red)}$$

**Procedure:**

1. Take a measured volume of chloride-containing solution in a conical flask.
2. Add a few drops of potassium chromate indicator (yellow color).
3. Titrate with standard $AgNO_3$ solution.
4. Formation of red precipitate of $Ag_2CrO_4$ indicates end point.
5. Note the volume of titrant used.

**Applications:**

- Estimation of chloride in drinking water and saline injections.
- Determination of NaCl in pharmaceutical formulations.
- Estimation of halides in industrial effluents and environmental samples.

## Volhard s method

- This method is named after Jacob Volhard
- In this method a soluble coloured compound forms at the end point
- Thiocyanate is used to titrate silver ions in an acidic solution using ferric ions as an indicator
- In which an excess of a standard solution of silver nitrate is added to a chloride containing sample solution. The excess silver is then back titrated using a standardized Sol of potato or ammonium thiocyanate with ferric ions as an indicator

**Principle:**

- A known excess of standard $AgNO_3$ is added to the solution containing halide ions to precipitate silver halide (AgCl, AgBr, etc.).

- The unreacted $Ag^+$ is then back-titrated with standard $NH_4SCN$.
- At the end point, ferric ions ($Fe^{3+}$) react with $SCN^-$ to form a red complex ($FeSCN^{2+}$), indicating completion.

**Chemical Reactions:**

**Step 1:** Precipitation of halide

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$

**Step 2:** Back titration of excess $Ag^+$

$$Ag^+ + SCN^- \rightarrow AgSCN \downarrow$$

**At End Point:**

$$Fe^{3+} + SCN^- \rightarrow FeSCN^{2+} \text{ (reddish brown complex)}$$

**Procedure :**

1. Add a known excess volume of standard $AgNO_3$ to the chloride-containing solution.
2. Precipitation of AgCl occurs.
3. Filter (if needed) and wash the precipitate with nitric acid.
4. Titrate the remaining $Ag^+$ with standard $NH_4SCN$.
5. Add ferric ammonium sulfate as an indicator.
6. End point: Appearance of reddish-brown color due to $FeSCN^{2+}$.

**Applications:**

- ✓ Estimation of chloride, bromide, and iodide ions.
- ✓ Determination of NaCl in pharmaceutical formulations and infusions.
- ✓ Applicable in food, biological samples, and water testing

## Modified volhard s method I.P 1985

- ❑ The principle of assay by volhard s method is based on indirect volumetric precipitation titration
- ❑ In this method nitric acid solution is used to acidify NaCl solution and then in the presence of nitrobenzene, this solution is treated with measured excess amount of standard solution of silver nitrate
- ❑ Some moles of silver nitrate are consumed in the reaction with NaCl and the remaining unreacted silver nitrate is determined by titration with a standard solution of ammonium thiocyanate. In this titration solution of ferric ammonium sulphate ferric alum is used as an indicator

**Principle:**

- Excess standard $AgNO_3$ is added to precipitate all halide ions as AgX (X = $Cl^-$, $Br^-$).
- The precipitate is filtered off.
- The remaining unreacted $Ag^+$ in the filtrate is titrated with $NH_4SCN$ (ammonium thiocyanate).
- Ferric ion is used as an indicator to detect the endpoint (formation of red ferric thiocyanate complex).

**Chemical Reactions:**

**Step 1: Precipitation of halide**

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$

**Step 2: Back titration of excess $Ag^+$**

$$Ag^+ + SCN^- \rightarrow AgSCN \downarrow$$

**At End Point:**

$$Fe^{3+} + SCN^- \rightarrow FeSCN^{2+} \text{ (reddish brown complex)}$$

**Procedure :**

1. Add known excess standard $AgNO_3$ to the halide solution.
2. Allow precipitation of AgCl (or AgBr).
3. Filter to remove the AgX precipitate.
4. Wash the precipitate with nitric acid to avoid loss of $Ag^+$.
5. Collect the filtrate (contains excess $Ag^+$).
6. Add ferric ammonium sulfate as an indicator.
7. Titrate the filtrate with standard $NH_4SCN$.
8. Endpoint: Appearance of reddish-brown color ($FeSCN^{2+}$ complex).

**Applications:**

- Estimation of chloride in pharmaceuticals (e.g., NaCl in injections).
- Water and food testing (chloride/bromide content).
- Analytical research involving halide salts.

## Farjan s method

- This method named after kazimierz fajan
- Dichlorofluorescein uses as an indicator and the end point is observed when the green colour suspension turns pink
- Fajan s method involves the titration of chloride ions with silver ions using adsorption indicators
- These indicator are basically dyes that adsorb or desorb on the surface of the precipitate at the equivalence point and produces the colour change
- The indicator are acid dyes, fluorescein, etc
- Basic dyes rhodamine service

**Principle:**

- ❖ A halide ion (like $Cl^-$) is titrated with $AgNO_3$.
- ❖ A precipitate of AgX (e.g., AgCl) forms during the reaction.
- ❖ Before the equivalence point, AgCl surface is negatively charged (due to $Cl^-$).
- ❖ After the equivalence point, surface becomes positively charged (due to excess $Ag^+$).
- ❖ The adsorption indicator (e.g., fluorescein) gets adsorbed on the surface and causes a visible color change, indicating the end point.

**Chemical Reactions:**

**Main Titration:**

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$

**At End Point:**

- Excess $Ag^+$ → positively charged AgCl particles
- Adsorbs negatively charged indicator → color change

**Procedure :**

- ♦ Take halide-containing solution (e.g., NaCl) in a flask.
- ♦ Add a few drops of adsorption indicator (e.g., fluorescein).
- ♦ Titrate with standard $AgNO_3$.
- ♦ Watch for color change as indicator adsorbs onto precipitate surface.
- ♦ Note volume at sharp end point (color change persists).

**Applications:**

- Estimation of **chloride**, **bromide**, **iodide** in:
  - Pharmaceutical products (e.g., saline solutions)
  - Biological samples
  - Environmental/water analysis

## Application of precipitation titration

- Precipitation reaction are applicable in removal of salts from water during water treatment in qualitative inorganic analysis and also in manufacturing of pigments
- Products of any reaction can also be isolated during work up by the precipitation reaction
- Precipitation reaction are also used in metallurgy

# Estimation of Sodium Chloride (NaCl)

**Principle:**

→ Sodium chloride (NaCl) contains chloride ions ($Cl^-$).

→ These ions react with silver nitrate ($AgNO_3$) to form white silver chloride precipitate (AgCl).

→ After all $Cl^-$ is precipitated, the excess $Ag^+$ reacts with chromate ions ($CrO_4^{2-}$) from the indicator ($K_2CrO_4$), forming red silver chromate ($Ag_2CrO_4$).

→ The appearance of red color indicates the end point.

**Chemical Reactions:**

Main reaction (precipitation):

$$NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3$$

At end point:

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4 \downarrow \text{ (red precipitate)}$$

**Reagents Required:**

- Standard $AgNO_3$ solution (0.1 N)
- Potassium chromate indicator (5% solution)
- Sample containing NaCl
- Distilled water

**Indicator:**

- **Potassium chromate ($K_2CrO_4$)**
  - Color: Yellow → Brick red at end point

**Procedure:**

- ❖ Pipette 25.0 mL of NaCl solution into a clean conical flask.
- ❖ Add 1–2 mL of potassium chromate indicator (yellow color appears).
- ❖ Titrate with 0.1 N $AgNO_3$ from a burette.
- ❖ Initially, white precipitate of AgCl forms.
- ❖ Near the end point, a brick-red color ($Ag_2CrO_4$) appears.
- ❖ Stop titration at the first permanent reddish tint.
- ❖ Note the burette reading (V mL).

**Calculation:**

Use the formula:

$$\text{Weight of NaCl (g)} = V \times N \times 58.44 / 1000$$

Where:

- **V** = Volume of $AgNO_3$ used (mL)
- **N** = Normality of $AgNO_3$
- **58.44** = Molecular weight of NaCl (g/mol)

**Example Calculation:**

If 25.0 mL of NaCl solution required **23.5 mL** of **0.1 N $AgNO_3$**, then:

$$\text{NaCl (g)} = 23.5 \times 0.1 \times 58.44 / 1000 = 0.1374 \text{ g}$$

**Applications:**

- ✓ Estimation of NaCl in 0.9% saline injections
- ✓ Chloride analysis in water and food samples
- ✓ Useful in pharmaceutical quality control