Precipitation titrations

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Precipitation Titrations

Definition:-Precipitation titrations are a type of **volumetric analysis** in which the titration reaction is based on the **formation of a precipitate** when two soluble salts react in solution. These titrations are used to determine the concentration of ions that form insoluble compounds (precipitates).

They are commonly used to determine **halide ions** (like Cl^-, Br^-, I^-) using **silver nitrate ($AgNO_3$)** as the titrant.

Example:- Titration of Sodium Chloride (NaCl) with Silver Nitrate ($AgNO_3$)

- **Reaction:**

  $NaCl + AgNO3 \rightarrow AgCl\downarrow + +NaNO3$

- **Indicator used: Potassium chromate (K_2CrO_4)**
- **Endpoint:** Formation of **red-brown precipitate** of **silver chromate (Ag_2CrO_4)** indicates that all chloride ions have reacted.

Mohr's Method

Discovery:

- Discovered by **Karl Friedrich Mohr** in the **mid-19th century**.

Principle:

- Direct titration of **chloride or bromide ions** with **$AgNO_3$**, using **potassium chromate (K_2CrO_4)** as an indicator.
- **Silver ions** react first with chloride ions to form **AgCl**, and after all Cl^- is consumed, they react with chromate ions to form **red Ag_2CrO_4**, indicating the endpoint.

Reaction:

Main reaction:- $Ag^+ + Cl^- \rightarrow AgCl\downarrow$ **(white ppt)**

At endpoint:- $2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4\downarrow$ **(red ppt)**

Endpoint:

- Appearance of **red-brown precipitate** of **silver chromate (Ag_2CrO_4).**

Limitations:

- pH must be near **neutral (6.5–10)** – too acidic dissolves Ag_2CrO_4; too basic forms AgOH.
- Not suitable for iodide (I^-) titration.
- Cannot be used in colored or turbid solutions.
- CO_2 in water affects pH; must be removed.

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Volhard's Method

Discovery:

- Developed by **Jacob Volhard**, a German chemist, in the **late 19th century**.

Principle:

- **Back titration** method. Excess standard $AgNO_3$ is added to chloride-containing sample to form AgCl. The excess Ag^+ is titrated with **standard thiocyanate (KSCN)**, using **ferric ammonium sulfate** as an indicator.

Reaction:

- **Precipitation of chloride:-** $Ag^+ + Cl^- \rightarrow AgCl\downarrow$
- **Back titration:-** $Ag^+ + SCN^- \rightarrow AgSCN\downarrow$
- **At endpoint:-** $Fe^{3+} + SCN^- \rightarrow FeSCN^{2+}$ **(red complex)**

Endpoint:

- Appearance of **blood red color** due to **ferric thiocyanate complex**.

Limitations:

- AgCl must be filtered before back titration to avoid interference.
- Accurate only in **acidic medium**.
- Interference from other halides and ions that form precipitates with Ag^+ or SCN^-.

Modified Volhard's Method

Principle:

- A **variation** of Volhard's method where the **AgCl precipitate is not filtered**. A **protective agent like nitrobenzene** is added to **coat the AgCl**, preventing reaction with thiocyanate.

Reaction:

- Same as Volhard's, but AgCl remains in solution, and nitrobenzene prevents further reaction.

Endpoint:

- Blood red color from Fe^{3+} + SCN^{-}.

Limitations:

- Addition of nitrobenzene or similar solvent is crucial for accuracy.
- Not suitable for large amounts of precipitate.
- More complex setup than original Volhard's method.

Fajans Method

Discovery:

- Developed by **Kasper Fajans**, a Polish-American chemist, in the **early 20th century**.

Principle:

- Based on **adsorption indicators**. After all chloride has reacted with Ag^+, the excess Ag^+ forms a layer on the precipitate surface (AgCl). An indicator like **fluorescein** adsorbs onto this surface and changes color.

Reaction:

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

At endpoint:-Indicator (e.g., **fluorescein** or eosin) adsorbs on surface of precipitate, changing color due to interaction with surface charge.

Endpoint:

- Color change of indicator adsorbed on AgCl surface (e.g., **pale yellow to pink** with fluorescein).

Limitations:

- Works only in **neutral to slightly acidic pH**.
- Requires **clear solution** and controlled lighting for endpoint visibility.
- Indicator choice is critical and sensitive to pH.
- Not suitable for back titration.

Estimation of Sodium Chloride (NaCl)

Aim:- To estimate the amount of sodium chloride present in a given solution by **Mohr's method** using **silver nitrate** as titrant and **potassium chromate** as indicator.

Principle:-Sodium chloride (NaCl) contains **chloride ions (Cl^-)** which react with **silver nitrate ($AgNO_3$)** to form a **white precipitate** of silver chloride (AgCl). After all Cl^- has reacted, the **next drop of $AgNO_3$** reacts with the indicator (**K_2CrO_4**) to form **red-brown silver chromate (Ag_2CrO_4)**, which marks the **endpoint**.

Chemical Reactions:

Titration reaction:- $AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$

At endpoint:- $2AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4\downarrow + 2KNO_3$

Requirement:

- **Chemical Required:-**Standard $AgNO_3$ solution (e.g., 0.1 N), Sodium chloride solution (unknown concentration), Potassium chromate indicator (5% solution), Distilled water.
- **Glassware Requirement:-** conical flask, burette, Beaker, measuring cylinder.

Procedure:

1. Pipette **25.0 mL** of sodium chloride solution into a clean conical flask.
2. Add **1–2 mL of potassium chromate** indicator (yellow in color).
3. Titrate with **standard $AgNO_3$** solution from a burette.
4. Swirl the flask continuously.
5. Stop titration when a **permanent red-brown color** appears (Ag_2CrO_4), indicating the endpoint.
6. Note the **volume of $AgNO_3$ used**.

📌 **Calculation:**

$$\mathrm{NaCl}\ (\mathrm{g}) = \frac{V_1 \times N_1 \times 58.5}{1000}$$

Where:

- V_1 = Volume of $AgNO_3$ used (in mL)
- N_1 = Normality of $AgNO_3$
- 58.5 = Molar mass of NaCl (g/mol)

Endpoint:

- Appearance of a **permanent brick-red color** due to **Ag_2CrO_4**.

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Thank you

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