

Precipitation titrations

Precipitation titrations: Introduction

- Precipitation titrations are a type of volumetric analysis in which a titrant is added to a solution containing an analyte to form a sparingly soluble precipitate.
- The endpoint of the titration is reached when the analyte has completely reacted with the titrant, and no further precipitation occurs.
- Precipitation titrations are often used to determine the concentration of a specific ion in a solution.
- They are particularly useful when the solubility of the precipitate formed is low, and the reaction between the titrant and the analyte is selective.

Argentometric Titrations

- Argentometric titrations are a class of precipitation titrations that use silver ions (Ag^+) as the titrant.
- These titrations are primarily employed for the determination of halide ions (chloride, bromide, and iodide) and other anions, such as thiocyanate, in a solution.
- Silver nitrate (AgNO_3) is the most commonly used titrant in argentometric titrations.

Types of Argentometric Titrations

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

Mohr's method

Introduction:

- Mohr's method is a precipitation titration used to determine chloride ion concentrations in a solution.
- It uses silver nitrate (AgNO_3) as the titrant, forming a white precipitate of silver chloride (AgCl).
- Potassium chromate (K_2CrO_4) is used as the indicator, which forms a red precipitate of silver chromate (Ag_2CrO_4) at the endpoint.

Principle:

- The method is based on the selective precipitation of chloride ions before chromate ions.

Reactions:



- After all chloride has precipitated, excess Ag^+ reacts with chromate ions:



- The appearance of a red precipitate of silver chromate indicates the endpoint.

Procedure:

- Pipette a known volume of the chloride-containing solution into a flask.
- Add distilled water to dilute the sample.
- Add 2-3 drops of potassium chromate indicator (solution turns yellow).
- Titrate with standardized AgNO_3 solution, forming a white AgCl precipitate.
- Continue titrating until a faint reddish-brown precipitate (Ag_2CrO_4) appears, indicating the endpoint.

Theory:

- Silver chloride precipitates first due to its lower solubility product (K_{sp}) compared to silver chromate.
- Once all chloride is consumed, excess silver reacts with chromate to form Ag_2CrO_4 , signaling the endpoint.

Calculation:

$$C_{\text{Cl}^-} = \frac{V_{\text{sample}} C_{\text{AgNO}_3}}{V_{\text{AgNO}_3}}$$

- 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:

- Volhard's method is an indirect precipitation titration used to determine halide ions (Cl^- , Br^- , I^-) and thiocyanate (SCN^-) in solution.
- It involves two steps: adding an excess of silver nitrate to precipitate the halide, followed by a back-titration of unreacted silver ions with a standardized thiocyanate solution.
- The endpoint is indicated by a red-brown ferric thiocyanate complex, using ferric ammonium sulfate as the indicator.

Principle:

- Halide ions react with silver nitrate to form a precipitate:



- The excess Ag^+ is titrated with thiocyanate (SCN^-), forming silver thiocyanate:



- The endpoint occurs when the first excess SCN^- forms a red-brown complex with ferric ions:



Procedure:

- Pipette a known volume of the halide-containing solution into a flask.
- Add an excess of standardized $AgNO_3$ to precipitate all halide ions.
- Add nitric acid (HNO_3) to maintain an acidic environment and prevent silver hydroxide formation.
- Add ferric ammonium sulfate as the indicator (solution turns pale yellow).
- Titrate with standardized thiocyanate (NH_4SCN) until the first permanent red-brown color appears, indicating the endpoint.

Theory:

- Volhard's method relies on the selective precipitation of silver halides and the clear color change when the ferric thiocyanate complex forms.
- The concentration of halide ions is calculated using:

$$C_{X^-} = \frac{V_{\text{sample}}(C_{AgNO_3} V_{AgNO_3} - C_{SCN^-} V_{SCN^-})}{V_{\text{sample}}}$$

- Where:
 - C_{X^-} = concentration of halide ions,
 - C_{AgNO_3} = concentration of $AgNO_3$,
 - V_{AgNO_3} = volume of $AgNO_3$ added,
 - C_{SCN^-} = concentration of SCN^- titrant,
 - V_{SCN^-} = volume of SCN^- used,
 - V_{sample} = volume of the halide-containing sample.

Modified Volhard's Method (Direct Volhard's Method)

Introduction:

- The Modified Volhard's method, also called the "direct Volhard's method," simplifies the original Volhard's method by eliminating the back-titration step.
- It combines the addition of excess silver nitrate and the titration with thiocyanate into a single step, making the procedure faster and more efficient.

Principle:

- Like the original method, this technique relies on the selective precipitation of halide ions with silver ions.
- The key difference is that the titration of unreacted silver ions with thiocyanate occurs simultaneously in one step, rather than separately.

Procedure:

1. Pipette a known volume of the halide-containing solution into an Erlenmeyer flask.
2. Add nitric acid (HNO_3) to maintain an acidic pH and prevent the formation of silver hydroxide.
3. Add ferric ammonium sulfate as the indicator (solution turns yellow/pale brown due to ferric ions).
4. Prepare a burette containing a mixture of standardized silver nitrate and thiocyanate solutions. The ratio of AgNO_3 to SCN^- matches the ratio of halide to silver ions in the sample.
5. Titrate the sample with the mixed titrant until a permanent red-brown color appears, indicating the endpoint.

Theory:

- The modified method simplifies the titration by combining both steps, reducing the time and potential for measurement errors.
- Halide ions react with silver ions, and any excess silver reacts immediately with thiocyanate present in the same titrant.

Calculation:

$$C_{X^-} = \frac{C_{\text{AgNO}_3} \times V_{\text{mixed_titrant}}}{V_{\text{sample}}}$$

- Where:
 - C_{X^-} = concentration of halide ions,
 - C_{AgNO_3} = concentration of AgNO_3 in the mixed titrant,
 - $V_{\text{mixed_titrant}}$ = volume of the mixed titrant used at the endpoint,
 - V_{sample} = volume of the halide-containing sample.

Fajans Method (Adsorption Indicator Method)

Introduction:



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