# 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:

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

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

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

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

## Procedure:

1. Pipette a known volume of the chloride-containing solution into a flask.
2. Add distilled water to dilute the sample.
3. Add 2-3 drops of potassium chromate indicator (solution turns yellow).
4. Titrate with standardized $AgNO_3$ solution, forming a white AgCl precipitate.
5. 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 (Ksp) compared to silver chromate.
- Once all chloride is consumed, excess silver reacts with chromate to form $Ag_2CrO_4$, signaling the endpoint.

## Calculation:

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

- Where:
  - $C_{Cl^-} = concentration\ of\ chlorideions$
  - $C_{AgNO_3} = concentration\ of\ AgNO^3$
  - $V_{AgNO_3} = volume\ of\ AgNO^3 at\ the\ end\ point$
  - $V_{sample} = volume\ of\ chloride - containing\ sample$

# 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.

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## Principle:

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

$$AgNO^3 + X^- \rightarrow AgX(s) + NO^{3-}$$

$$(X^- = Cl^-, Br^-, I^-, or\ SCN^-)$$

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

$$Ag^+ + SCN^- \rightarrow AgSCN(s)$$

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

$$Fe^{3+} + 3SCN^- \rightarrow Fe(SCN)^3(red - brown)$$

## Procedure:

1. Pipette a known volume of the halide-containing solution into a flask.
2. Add an excess of standardized $AgNO_3$ to precipitate all halide ions.
3. Add nitric acid ($HNO_3$) to maintain an acidic environment and prevent silver hydroxide formation.
4. Add ferric ammonium sulfate as the indicator (solution turns pale yellow).
5. 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:

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

- Where:
  - $C_{X^-}$ = concentration of halide ions,
  - $C_{AgNO_3}$ = concentration of $AgNO_3$,
  - $V_{AgNO3}$ = 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:

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- 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:

$$C_{X^-} = \frac{C_{AgNO_3} \times V_{mixed_titrant}}{V_{sample}}$$

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

# Fajans Method (Adsorption Indicator Method)

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