

Analytical Chemistry

PRECIPITATION TITRATION



Sawa University
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First Stage

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المحاضرة الخامسة : الجانب النظري

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Precipitation Titration

Definition of Precipitation Titration

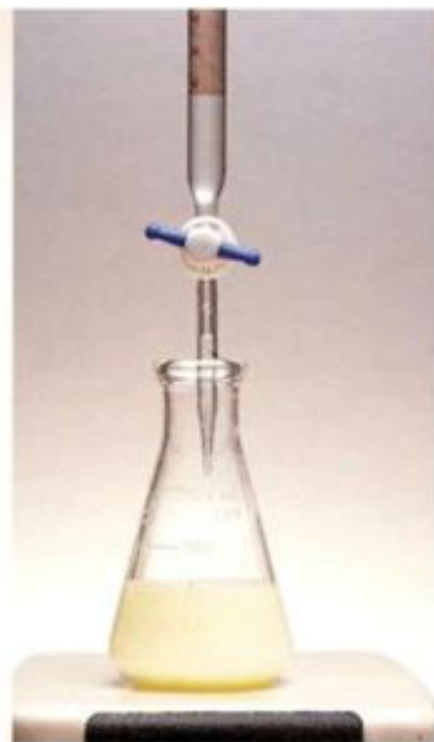
A precipitation titration is a volumetric analytical method based on the formation of a sparingly soluble precipitate when the titrant reacts with the analyte.

The titration proceeds until all analyte ions are completely precipitated.

This is the case for the titration of a halide



Initial



①

AgCl formed



②

Ag₂CrO₄ formed
endpoint

the
, and

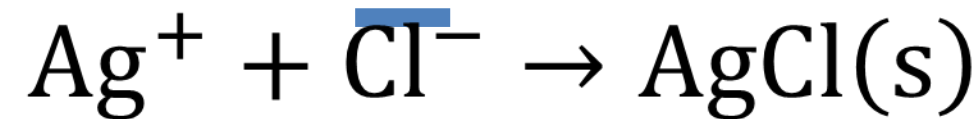


of

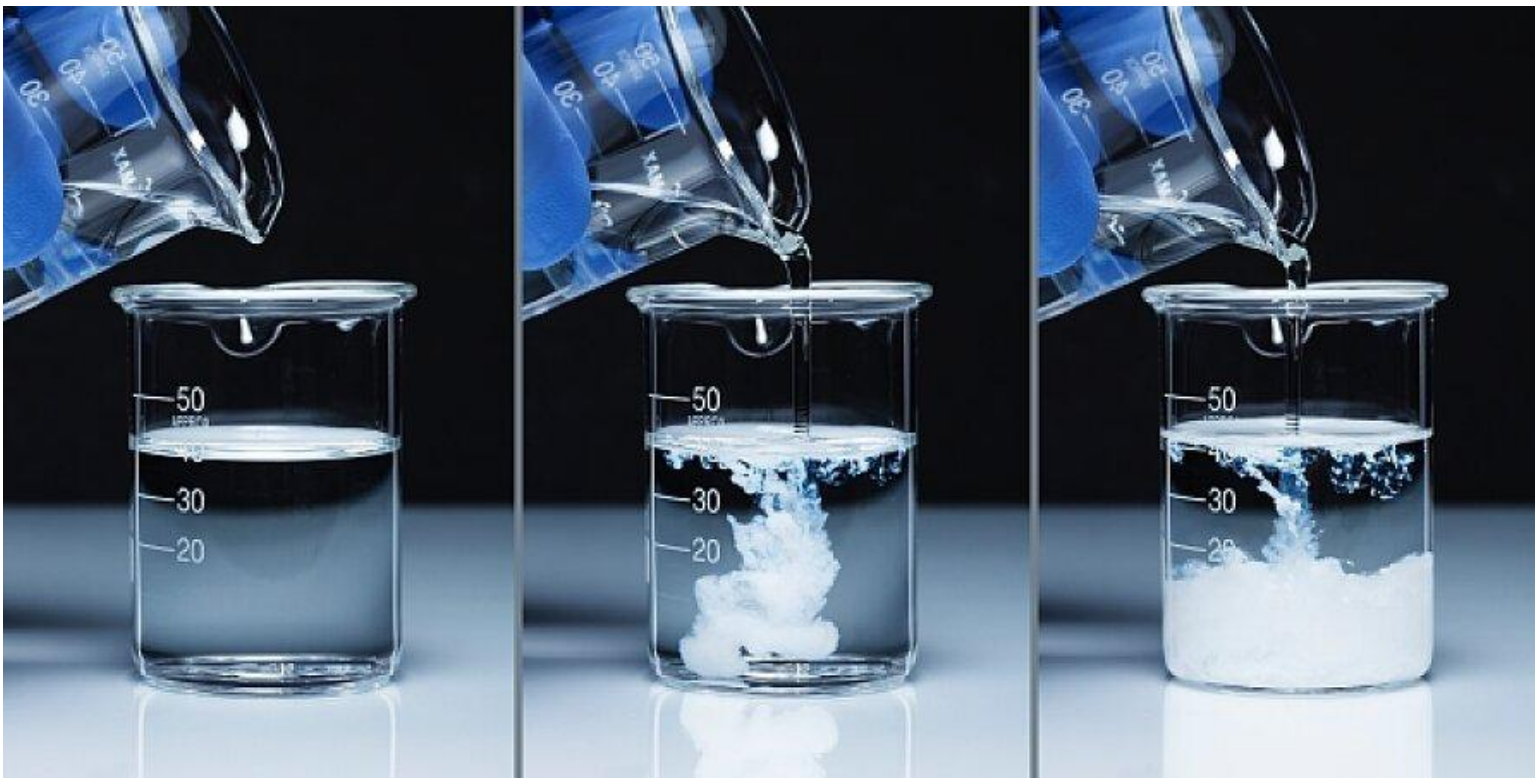
Principle of Precipitation Titration

The principle of precipitation titration depends on the formation of an insoluble salt with a very small solubility product (K_{sp}).

Example reaction:



As long as chloride ions are present, added silver ions are consumed to form the precipitate



Detection of End Point

Explanation:

In precipitation titrations, the equivalence point cannot be detected by pH change.

Instead, the end point is **detected** by a secondary reaction involving an indicator that reacts with excess titrant.

Two classical methods are used:

- Mohr method
- Volhard method

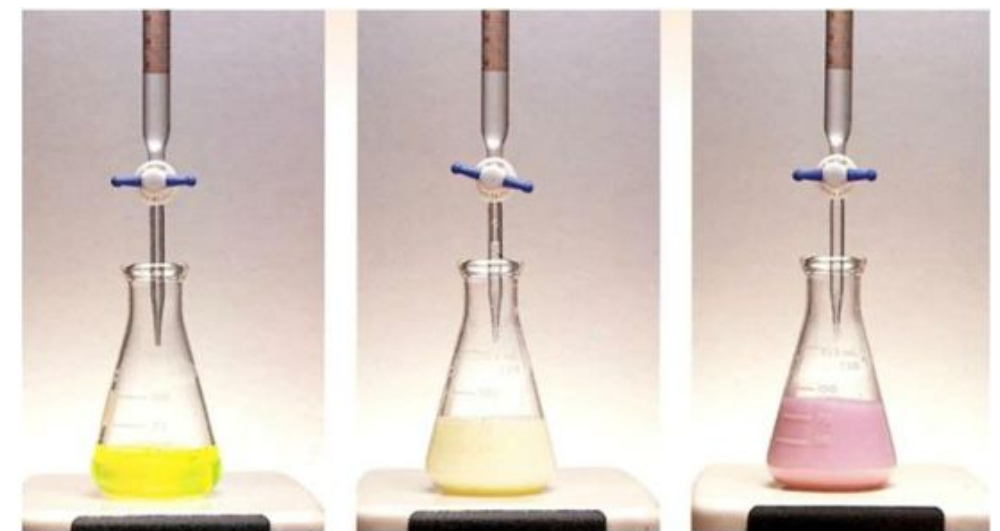
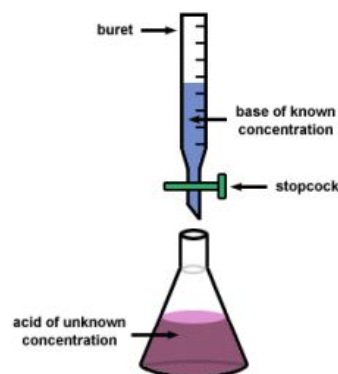
Mohr Method (Definition)

Explanation:

The Mohr method is a direct precipitation titration used for the determination of chloride or bromide ions using silver nitrate as titrant and potassium chromate as indicator.

- Titrant: AgNO_3
- Indicator: K_2CrO_4
- Medium: Neutral or slightly alkaline

Mohr Titration for Sodium Quantification



Initial

①

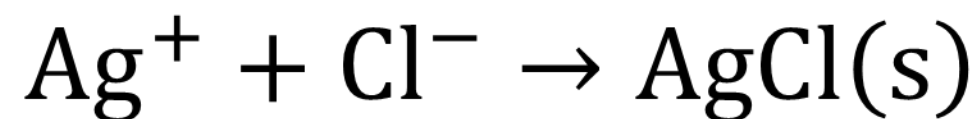
AgCl formed

②

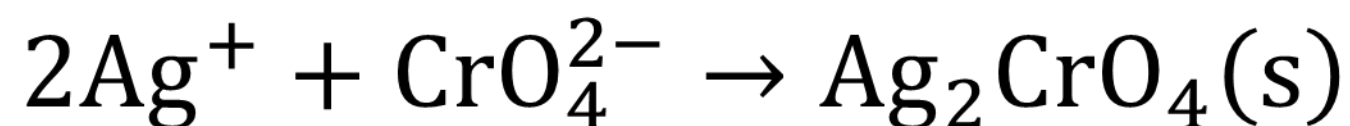
Ag_2CrO_4 formed
endpoint

Mohr Method (Reaction Mechanism)

Main reaction:



Indicator reaction (end point):



Explanation:

As long as Cl^- is present, Ag^+ reacts only with chloride.

After all chloride is precipitated, excess Ag^+ reacts with chromate ions to form a red precipitate of Ag_2CrO_4 .



Mohr Method



Add AgNO_3

Add Chromate indicator



Colorless solution



Titrate with SCN^-



Red-orange silver chromate precipitate

In the Mohr Method, AgNO_3 is added to precipitate Cl^- as AgCl , and potassium chromate is used as an indicator. At the endpoint, all Cl^- is precipitated and a red-orange precipitate of Ag_2CrO_4 .

Volhard Method (Definition)

The Volhard method is an **indirect precipitation** titration used mainly for chloride determination.

It is based on back titration.

Steps:

1. Excess AgNO_3 is added to precipitate chloride
2. Excess Ag^+ is titrated with thiocyanate solution

a)



white precipitate of AgCl

b)



endpoint

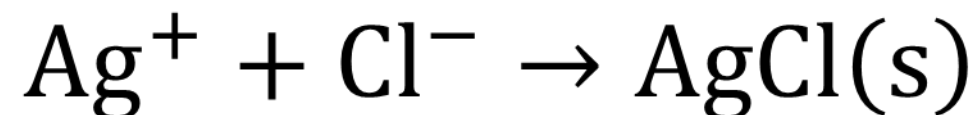
c)



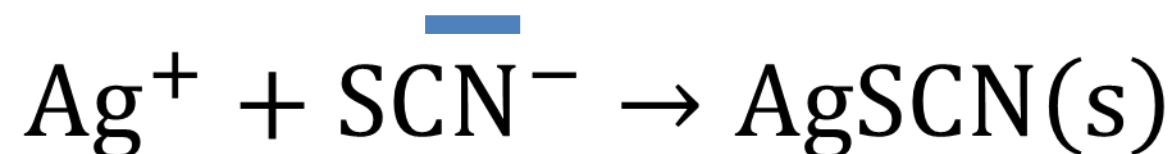
dark red precipitate of AgSCN

Volhard Method (Reaction Mechanism)

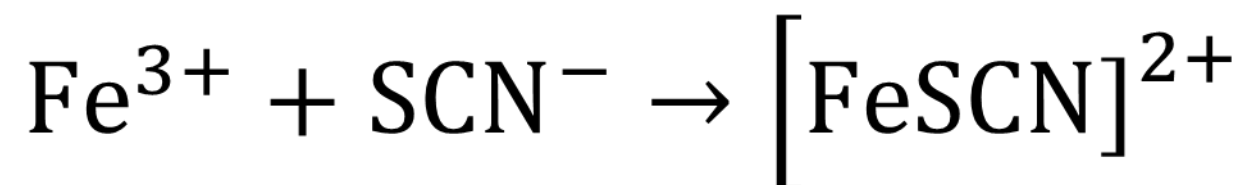
Precipitation reaction:



Back titration reaction:



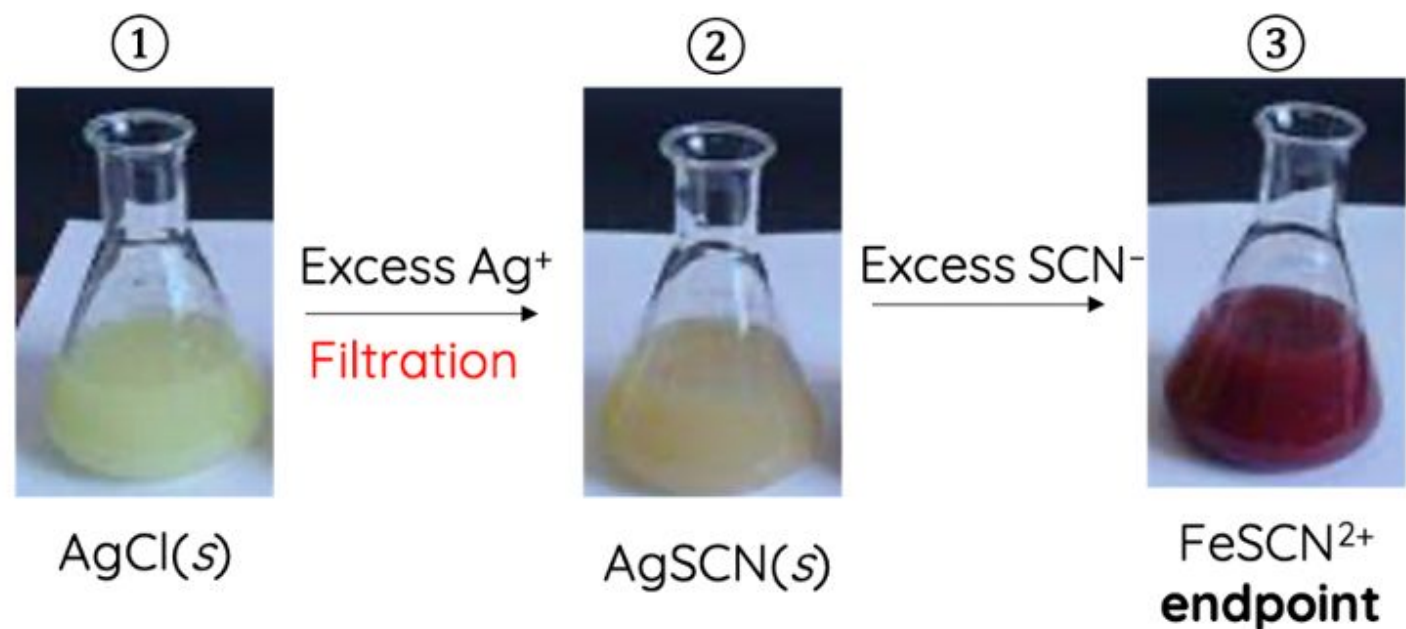
Indicator reaction:



Explanation:

The end point is detected by the appearance of a reddish-brown complex of iron(III)

thiocya:



Volhard Method



Add AgNO_3

Add Fe^{3+} indicator



Colorless solution



Titrate with SCN^-

In the Volhard Method, AgNO_3 is first added to precipitate Cl^- as AgCl , followed by Fe^{3+} indicator and titration with ammonium thiocyanate (NH_4SCN). When an excess of SCN^- is present, a red complex forms with Fe^{3+} indicating the end point.



Red complex indicates end point

Comparison: Mohr vs Volhard Methods

Volhard Method	Mohr Method	Feature
Back titration	Direct titration	Type
Fe^{3+}	K_2CrO_4	Indicator
Red FeSCN^{2+}	Red Ag_2CrO_4	End point
Acidic	Neutral	Medium
Very high	Good	Accuracy