UNIT 3

Introduction to Precipitation Titrations

Precipitation titrations involve the **formation of an insoluble precipitate** during a chemical reaction between the analyte and the titrant. These are mainly used for the **determination of halides (Cl⁻, Br⁻)** and **certain metal ions** using **silver nitrate (AgNO₃)** as a titrant. The common indicators used in such titrations depend on the nature of the precipitate.

Mohr's Method

Definition:
Mohr's method is a **direct precipitation titration** used for the **determination of chloride and bromide ions** by titration with **standard silver nitrate solution**, using **potassium chromate (K_2CrO_4)** as an indicator.

Principle

- When **silver nitrate** is added to a solution containing **chloride ions**, **white precipitate of silver chloride (AgCl)** forms:

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$
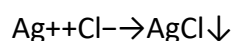
- After all chloride ions are precipitated, **excess silver ions** react with **chromate indicator** to form a **red precipitate of silver chromate (Ag_2CrO_4)**, indicating the end point:

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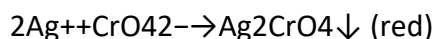
Reagents

- **Titrant:** Standard **silver nitrate (AgNO₃)** solution

- **Indicator: Potassium chromate (K_2CrO_4)** (1% solution)

- **Analyte:** Chloride-containing sample (e.g., NaCl, tap water)

Procedure

1. Pipette a measured volume of chloride solution into a conical flask.

2. Add 1–2 mL of **1% potassium chromate indicator**.

3. Titrate with **0.1 N AgNO₃** from a burette.

4. During titration, a **white precipitate** of AgCl forms.

5. The **end point** is indicated by the **first permanent reddish-brown color** due to the formation of **Ag_2CrO_4**.

Conditions for Accurate Results

- The solution should be **neutral to slightly alkaline** (pH ~7–9); in acidic media, chromate converts to dichromate and in basic media silver hydroxide may precipitate.

- Avoid strong light and temperature changes as silver salts are photosensitive.

Calculations

From the volume of AgNO₃ used and its normality, the amount of **Cl⁻** present can be calculated using:

$$1 \text{ mL of } 0.1 \text{ N AgNO}_3 \equiv 0.003545 \text{ g}$$

Applications

- Estimation of **chloride in drinking water, urine, or pharmaceutical preparations**

- Quality control of **sodium chloride injections**

- Analysis of **brine solutions**

3. Volhard's Method

Definition:
Volhard's method is an **indirect precipitation titration** used to estimate **halide ions (e.g., Cl⁻, Br⁻, I⁻)** by **back titration** with **standard thiocyanate solution** in **acidic medium**, using **ferric ammonium sulfate** as an indicator.

Principle:

- A known excess of **standard silver nitrate (AgNO₃)** is added to the halide-containing solution to precipitate all halide ions as **AgCl, AgBr, or AgI**:

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$
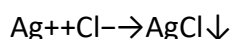
- The excess unreacted **AgNO₃** is back-titrated with **standard ammonium thiocyanate (NH₄SCN)**:

$$Ag^+ + SCN^- \rightarrow AgSCN \downarrow$$
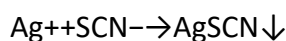
- At the endpoint, **ferric ions (Fe³⁺)** react with the first excess of thiocyanate to form a **blood-red complex**:

$$Fe^{3+} + 3SCN^- \rightarrow Fe(SCN)_3 \text{ (red)}$$
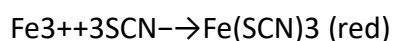
Medium:

- Acidic (usually nitric acid) to prevent precipitation of Fe(OH)₃ and to dissolve any formed Ag₂CrO₄

Indicator:

- Ferric ammonium sulfate (gives red color with SCN⁻)

Applications:

- Estimation of **chloride, bromide, iodide** in **insoluble salts**

- Also used for **silver** determination (by direct titration with SCN⁻)

4'Modified Volhard's Method

Definition:

Modified Volhard's method is an **indirect titration method** used for the estimation of **halide ions (Cl⁻, Br⁻, I⁻)** where the precipitated **silver halide** (AgCl, AgBr, AgI) is **filtered off** before the back titration. This modification is made to avoid **interference** caused by the precipitate during endpoint detection.

Principle:

1. A known excess of **standard silver nitrate (AgNO₃)** is added to the halide-containing solution to form a **precipitate of silver halide**:

$$Cl^- + Ag^+ \rightarrow AgCl\downarrow$$
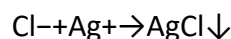
2. The precipitate (AgCl) is **filtered off**, and the **filtrate** (which contains the excess unreacted Ag⁺) is collected.

3. This excess silver nitrate is then titrated with **standard ammonium thiocyanate (NH₄SCN)** solution:

$$Ag^+ + SCN^- \rightarrow AgSCN\downarrow$$
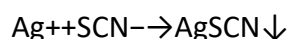
4. The **endpoint** is detected by the formation of a **blood-red complex** between the first excess of thiocyanate and added **ferric ions**:

$$Fe^{3+} + 3SCN^- \rightarrow Fe(SCN)_3 \text{ (red)}$$
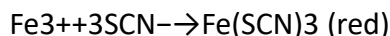
Reagents Required:

- **Standard AgNO₃ solution** (e.g., 0.1 N)

- **Standard NH₄SCN solution** (e.g., 0.1 N)

- **Ferric ammonium sulfate** (Fe³⁺ indicator)

- **Nitric acid** (to maintain acidic medium)

- **Halide-containing sample** (e.g., NaCl solution)

Procedure:

1. Take the halide-containing sample and add a **known excess of standard AgNO₃ solution** in acidic medium (HNO₃).

2. Allow complete precipitation of AgCl.

3. **Filter the precipitate** to remove AgCl and collect the **filtrate**.

4. Add **1–2 mL of ferric ammonium sulfate indicator** to the filtrate.

5. Titrate with **standard NH₄SCN** until a **permanent blood-red color** appears, indicating the endpoint.

Advantages of Modified Volhard's Method:

*   **More accurate** than Mohr's method when interfering substances or colored solutions are present.

*   **Filtration step** removes surface-adsorbed SCN⁻ or Fe³⁺ from AgCl, eliminating endpoint errors.

*   Suitable for **colored, turbid, or complex matrices** where direct titration is difficult.

Applications:

*   Estimation of **chloride** in pharmaceutical and biological samples.

*   Suitable for samples where **silver halide precipitate** may adsorb indicator or SCN⁻, causing inaccurate endpoints.

Limitations:

*   **Filtration step** adds complexity and time.

*   Requires **strict control** of pH and cleanliness to avoid silver ion loss.

Fajans Method

Definition:
Fajans method is a **precipitation titration technique** that uses **adsorption indicators** to detect the **end point** of halide titration with **silver nitrate (AgNO₃)**. It is used primarily for the **direct estimation of halides** like chloride (Cl⁻), using indicators such as **eosin**, **fluorescein**, or **dichlorofluorescein**.

Principle:

*   When AgNO₃ is added to a solution containing Cl⁻, a **white precipitate of silver chloride (AgCl)** forms:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$
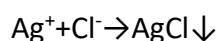
*   Near the end point, after all Cl⁻ is precipitated, **excess Ag⁺** is adsorbed on the surface of the AgCl precipitate, making it **positively charged**.

- The **negatively charged indicator anion** (e.g., fluorescein⁻) is then **adsorbed onto the AgCl surface**, forming a **pink or red layer**, signaling the **end point**.

Key Conditions:

- **pH** should be around **neutral (6–8)** for proper functioning of the indicator.

- **Indicator** must be **adsorbed only after the equivalence point**.

- The titration should be **performed in dim light** to prevent photodecomposition of AgCl.

Indicators Used:

- **Fluorescein**, **eosin**, or **dichlorofluorescein**

- These give a visible **color change** upon adsorption onto AgCl

Estimation of Sodium Chloride

Reagents Required:

- Standard **0.1 N AgNO₃**

- Sample solution containing **NaCl**

- **Eosin Y** or **fluorescein indicator**

- Dilute **nitric acid (HNO₃)** to maintain ionic strength

Procedure:

1. **Pipette** a known volume of sodium chloride solution (e.g., 25 mL) into a conical flask.

2. Add **1–2 drops** of eosin Y or fluorescein indicator.

3. Add a few drops of **dilute HNO₃** to maintain pH and ionic strength.

4. Titrate with **0.1 N AgNO₃** from a burette while swirling the solution.

5. The solution will remain colorless during most of the titration.

6. At the **end point**, the color will change to **pale pink** or **red** due to adsorption of indicator onto excess Ag⁺-covered AgCl precipitate.

Reaction:

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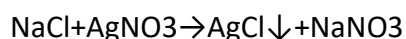
Calculation:

From the volume of AgNO₃ used, the amount of NaCl is calculated using:

1 mL of 0.1 N AgNO₃ ≡ 0.005844 g of NaCl

Advantages of Fajans Method:

- **Sharp and visible end point**

- No need for filtration or heating

- Suitable for **low concentrations of halides**

Limitations:

- The **color change is sometimes subtle**

- **Photodecomposition** of AgCl may cause error
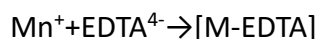
- Not suitable in **colored or turbid solutions**

Complexometric Titration

Definition of Complexometric Titration

Complexometric titration is a type of volumetric titration based on the formation of a stable **complex** between a **metal ion** and a **complexing agent (ligand)**. The most widely used reagent is **EDTA (ethylenediaminetetraacetic acid)**, a hexadentate ligand that forms stable chelates with most metal ions.

Basis of Reaction

The titration involves the reaction:

$$M^{n+} + EDTA^{4-} \rightarrow [M\text{-}EDTA]$$

Where **M^{n+}** is a metal ion and **$EDTA^{4-}$** is the complexing agent.

Classification of Complexometric Titrations

Complexometric titrations can be classified into the following types based on the method of performing the titration:

1. Direct Titration

- **Definition:** Metal ion is directly titrated with standard EDTA solution.

- **Conditions:** pH must be suitably buffered to ensure complete complex formation.

- **Example:** Estimation of calcium or magnesium in water using Eriochrome Black T indicator.

2. Back Titration

- **Definition:** A known excess of EDTA is added to the metal ion solution; the unreacted EDTA is titrated with a standard solution of another metal ion (e.g., Mg^{2+} or Zn^{2+}).

- **Use:** Applied when the direct titration is not feasible due to slow complex formation or precipitation of metal ions.

- **Example:** Estimation of aluminium or bismuth.

3. Replacement (Displacement) Titration

- **Definition:** A less stable metal-EDTA complex is displaced by a more stable metal ion.

- **Process:** EDTA is first added to form a weak complex with the analyte; then a stronger metal ion is added, which displaces the analyte from the complex. The displaced analyte is titrated.

- **Example:** Estimation of Hg^{2+} by replacing it with Mg^{2+} and titrating the released Mg^{2+}.

4. Indirect Titration

- **Definition:** The substance to be estimated is first converted into a form that can react with EDTA, and the metal ion content is determined indirectly.

- **Example:** Estimation of phosphate by precipitating it as $MgNH_4PO_4$, then determining the Mg^{2+} by EDTA titration.

5. Masking and Demasking Titrations

- **Masking:** A process of **preventing a particular ion** from reacting with EDTA by converting it into a non-reactive form.

- **Demasking:** The process of **releasing a masked ion** so it can be titrated.

- **Use:** Useful in selective titration of one metal ion in the presence of others.

- **Example:** Masking of aluminium ions using triethanolamine in the presence of calcium and magnesium.

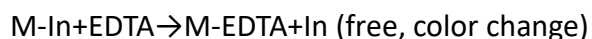# Metal ion indicators

Definition:

Metal ion indicators are **organic dyes** that form **weakly dissociable, colored complexes** with metal ions. In complexometric titrations, they help **visually indicate the endpoint** by undergoing a distinct **color change** when the metal ion is completely complexed by the titrant (usually EDTA).

Principle:

At the start of the titration, the metal ion (M^{n+}) forms a weak, colored complex with the indicator (In):

$M^{n+} + In^{n-} \rightleftharpoons M\text{-}In$ (colored complex)
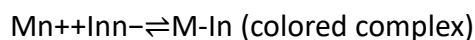
During titration, EDTA (a stronger ligand) displaces the indicator from the metal ion due to its higher stability constant:

$M\text{-}In + EDTA \rightarrow M\text{-}EDTA + In$ (free, color change)

The **color change** of the indicator from metal-complex form to free indicator signals the **endpoint** of the titration.

Ideal Properties of a Metal Ion Indicator:

1. Forms a **weak and reversible complex** with metal ions.

2. Exhibits a **distinct color difference** between the free and complexed form.

3. Must not form a more stable complex than EDTA.

4. The pH range of the indicator must match the titration conditions.

5. Should be highly sensitive to even small changes in metal ion concentration.

Common Metal Ion Indicators:

Indicator	Metal Ion Detected	Color Change (Approx.)	pH Range
Eriochrome Black T	Ca^{2+}, Mg^{2+} (e.g., in water)	Wine red (complex) → Blue (free)	8–10
Murexide	Ca^{2+}	Pink (complex) → Purple (free)	11
Calcon	Ca^{2+}	Red (complex) → Blue (free)	12
Xylenol Orange	Fe^{3+}, Bi^{3+}, Th^{4+}	Red-orange (complex) → Yellow (free)	1–3
PAN (1-(2-Pyridylazo)-2-naphthol)	Zn^{2+}, Cu^{2+}, Co^{2+}	Red (complex) → Yellow (free)	3–5
Patton-Reeder Indicator	Ca^{2+} in presence of Mg^{2+}	Red (complex) → Blue (free)	12

In complexometric titrations, especially when using EDTA to estimate metal ions, **interference** from other metal ions can lead to **inaccurate results**. To overcome this, specific reagents called **masking and demasking agents** are used.

1. Masking Agents

Definition:
Masking agents are chemical substances that **selectively react with interfering metal ions** to form **stable, unreactive complexes**, thereby **preventing** them from reacting with the titrant (EDTA).

Purpose:
To **"hide" interfering metal ions** without removing them physically from the solution, allowing accurate titration of the target metal ion.

Mechanism:
The masking agent forms a complex with the interfering metal ion that is **more stable** than the one formed with EDTA, hence **inhibiting reaction** between the interfering metal ion and EDTA.

Examples of Masking Agents:

Masking Agent	Masked Metal Ion(s)	Remarks
Potassium cyanide (KCN)	Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}	Forms stable cyanide complexes
Triethanolamine (TEA)	Al^{3+}, Fe^{3+}	Used in presence of Ca^{2+} and Mg^{2+}
Sodium thiosulfate ($Na_2S_2O_3$)	Ag^+, Hg^{2+}	Forms soluble thiosulfate complexes
Citric acid	Fe^{3+}, Al^{3+}, Mn^{2+}	Chelating ligand
Oxalate	Ca^{2+}, Sr^{2+}	Forms insoluble calcium oxalate
Ascorbic acid	Fe^{3+}	Reduces to Fe^{2+} which can be masked

2. Demasking Agents

Definition:
Demasking agents are substances that **release a previously masked metal ion** from its masked complex, **restoring its ability** to react with EDTA or be titrated.

Purpose:
To allow **sequential determination** of multiple metal ions in the same solution.

Mechanism:
The demasking reagent **breaks the complex** between the masking agent and metal ion, thereby freeing the metal ion for titration.

Examples of Demasking Agents:

Demasking Agent	Demasked Metal Ion(s)	Mechanism
Formaldehyde	Al^{3+}	Breaks Al–triethanolamine complex
Acetone	Fe^{3+}	Breaks Fe–citric acid complex
8-Hydroxyquinoline	Zn^{2+}, Cu^{2+}	Precipitates metal ions
H_2S (hydrogen sulfide)	Cd^{2+}, Hg^{2+}	Precipitates as metal sulfides

Applications of Masking and Demasking:

1. Estimation of **Ca^{2+}** in presence of **Mg^{2+}** using **Patton-Reeder indicator** after masking **Mg^{2+}**.

2. Estimation of **Zn^{2+}** after masking interfering **Fe^{3+}** using **ascorbic acid**.

3. Sequential analysis of multiple metal ions in **pharmaceutical formulations** or **alloy samples**.

1. Estimation of Magnesium Sulphate ($MgSO_4 \cdot 7H_2O$)

Method Used: Complexometric titration using **EDTA**
Principle: Magnesium ions (Mg^{2+}) form a stable complex with EDTA in a buffered alkaline medium.
**Indicator:** Eriochrome Black T
Buffer: Ammonia-ammonium chloride buffer (pH 10)

Procedure:

1. Accurately weigh a quantity of magnesium sulphate and dissolve it in water.

2. Pipette an aliquot into a conical flask.

3. Add about 10 mL of pH 10 buffer solution.

4. Add 2–3 drops of **Eriochrome Black T** indicator; solution turns **wine red**.

5. Titrate with **0.01 M EDTA** until the color changes from wine red to **blue**.

Reaction:

$$Mg^{2+} + EDTA^{4-} \rightarrow Mg\text{-}EDTA^{2-}$$
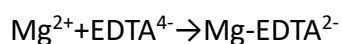
Calculation:
1 mL of 0.01 M EDTA ≡ 0.00247 g of $MgSO_4 \cdot 7H_2O$

2. Estimation of Calcium Gluconate ($C_{12}H_{22}CaO_{14} \cdot H_2O$)

Method Used: Complexometric titration using **EDTA**
**Principle:** Calcium ions (Ca^{2+}) form a stable 1:1 complex with EDTA in alkaline medium.
Indicator: Murexide
Buffer: pH ~12 (NaOH used)

Procedure:

1. Dissolve the accurately weighed calcium gluconate in water.

2. Pipette an aliquot into a conical flask.

3. Add 1 mL of **NaOH** (to maintain pH ~12).

4. Add a small amount of **murexide indicator** (solution turns **pink**).

5. Titrate with **0.01 M EDTA** until the color changes from pink to **purple**.

Reaction:

$Ca^{2-} + EDTA^{4-} \rightarrow Ca\text{-}EDTA2^-$
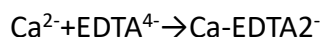
Calculation:
1 mL of 0.01 M EDTA ≡ 0.00427 g of calcium gluconate

Precautions:

• Maintain appropriate **pH** for each titration.

• Avoid contamination with other metal ions.

• Use freshly prepared indicator solutions.

GRAVIMETRY

Definition:

Gravimetry is a **quantitative analytical technique** in which the **amount of an analyte is determined based on the mass** of a solid product that is formed and weighed after chemical transformation and isolation.

Principle of Gravimetric Analysis:

The principle of gravimetry is based on the **measurement of mass**. It involves converting the analyte into a **pure, stable, and insoluble compound** of known composition, isolating it from the reaction mixture, drying (or igniting) it to a constant weight, and then **weighing** it accurately. The **amount of analyte** present in the original sample is calculated from the **mass of the precipitate** using **stoichiometry**.

Key Conditions for Gravimetric Analysis:

1. The precipitate must be **pure**, **stable**, and of **known composition**.

2. The precipitation must be **complete** with minimum solubility of the product.

3. The analyte must be **completely and selectively precipitated**.

4. The product must be **easily filtered, washed, and dried/ignited**.

5. Precipitating agent must react **specifically** or **selectively**.

Steps Involved :

1. Sample Preparation

- The analyte (metal or ion to be estimated) is dissolved in a suitable solvent, usually water or dilute acid/base.

- If necessary, interferences are removed or masked before precipitation.

2. Precipitation

- A **suitable precipitating agent** is added to the solution to form an **insoluble compound** of the analyte.

- Conditions such as **pH, temperature, and concentration** are adjusted to ensure complete and selective precipitation.

- The precipitate should form slowly to produce larger and purer crystals, which are easier to filter.

3. Digestion

- The precipitate is allowed to stand in the hot mother liquor (solution from which it formed) for some time.

- This helps improve crystal size and purity by recrystallization (Ostwald ripening), making it easier to filter and wash.

- Digestion also helps in removing co-precipitated impurities.

4. Filtration

- The precipitate is separated from the mother liquor using **filter paper** or a **porous crucible** (e.g., Gooch or sintered glass crucible).

- Care is taken to avoid loss of precipitate during transfer.

5. Washing

- The precipitate is washed with cold distilled water or a suitable washing liquid to remove soluble impurities like electrolytes and mother liquor.

- The wash liquid should not dissolve or react with the precipitate.

6. Drying or Ignition

- The precipitate is either:
  a) **Dried** at 100–120 °C to remove moisture (for hygroscopic or thermally unstable substances), or
  b) **Ignited** at high temperatures (600–1000 °C) in a furnace to convert it into a stable form (e.g., metal oxide).

- This step ensures that the final product is in a known, constant composition suitable for weighing.

7. Weighing

- After drying or ignition, the crucible and precipitate are cooled in a **desiccator** to avoid moisture uptake.

- The final weight is accurately recorded using an **analytical balance**.

8. Calculation

- From the known stoichiometry of the precipitate and its mass, the **amount of analyte** in the original sample is calculated.

Purity of the Precipitate: Co-precipitation and Post-precipitation

In gravimetric analysis, the **accuracy** of the result depends on obtaining a precipitate that is **pure and of known composition**. However, during precipitation, the product may contain **impurities** due to phenomena like **co-precipitation** and **post-precipitation**.

1. Co-precipitation

Definition:
Co-precipitation is the process by which **impurities are carried down along with the desired precipitate**, even though the impurity itself does not exceed its solubility limit under the experimental conditions.

Occurs:

- Simultaneously during the formation of the main precipitate

- Most significant in **initial stages of precipitation**

Causes of Co-precipitation:

a) **Surface Adsorption** – Impurities get adsorbed on the surface of the precipitate crystals (e.g., Fe^{3+} adsorbed on $BaSO_4$)
b) **Occlusion** – Trapping of impurities inside growing crystals due to rapid precipitation
c) **Inclusion** – Ions with similar size and charge as the primary ion occupy its position in the crystal lattice (e.g., K^+ replacing NH_4^+)

Prevention/Minimization:

- Use **slow and controlled precipitation**

- Add precipitating reagent slowly with constant stirring

- Digest the precipitate in the mother liquor to promote crystal purity

- Wash the precipitate thoroughly

2. Post-precipitation

Definition:
Post-precipitation occurs when a **second, unwanted precipitate forms after the desired precipitate** has already formed and started to settle. This new precipitate may contaminate the primary product.

Occurs:

- **After** the main precipitation

- Due to **prolonged standing** of the mixture, allowing other ions to slowly form insoluble compounds

Example:

- In estimation of calcium as calcium oxalate, **magnesium oxalate** may form if the solution is left standing too long

Prevention/Minimization:

- **Filter the precipitate promptly** after digestion

- Avoid long standing time after precipitation

- Remove interfering ions beforehand (by masking or proper reagent selection)

Key Differences Between Co-precipitation and Post-precipitation

| Feature	Co-precipitation	Post-precipitation
Time of occurrence	During primary precipitation	After primary precipitation
Type of contamination	Impurities from same solution phase	A different compound precipitating later
Nature	Surface adsorption, inclusion, occlusion	Separate precipitation of another compound
Prevention	Slow precipitation, digestion, washing	Prompt filtration after digestion

Estimation of Barium as Barium Sulphate (BaSO₄)

(Gravimetric Method – As per B.Pharm PCI syllabus, Pharmaceutical Analysis)

Principle:

Barium ions (Ba²⁺) are quantitatively precipitated from an aqueous solution using **dilute sulfuric acid (H₂SO₄)** as **insoluble barium sulfate (BaSO₄)**. The BaSO₄ formed is a white crystalline precipitate which is filtered, washed, ignited to constant weight, and weighed. From the known stoichiometry, the amount of barium (or its salt) in the original sample is calculated.

Ba2++SO42−→BaSO4↓\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4 \downarrowBa2++SO42−→BaSO4↓
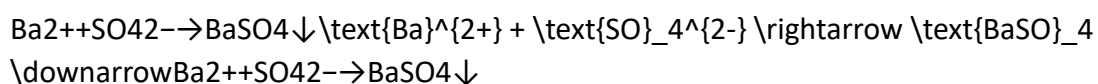
Requirements:

- Standard barium chloride solution (BaCl₂)

- Dilute H₂SO₄

- Beakers, funnel, filter paper or sintered crucible

- Desiccator and analytical balance

- Hot water and wash bottle

Procedure:

1. Weigh accurately a sample containing barium (e.g., BaCl₂·2H₂O) and dissolve in distilled water in a beaker.

2. Heat the solution to about 70–80°C.

3. Add **dilute H₂SO₄ slowly with constant stirring** to precipitate BaSO₄.

4. Digest the mixture (keep hot without boiling) for 30–60 minutes to promote crystal growth and reduce co-precipitation.

5. Filter the precipitate through a **pre-weighed sintered glass crucible** or filter paper.

6. Wash the precipitate with hot water to remove Cl⁻ and SO₄²⁻ impurities (test washings with AgNO₃ and BaCl₂).

7. Dry the crucible in an oven at 110–120°C or **ignite** in a muffle furnace at 600–800°C to constant weight.

8. Cool in a **desiccator** and weigh.

Calculations:

- Molar mass of $BaSO_4$ = **233.39 g/mol**

- From the mass of $BaSO_4$ obtained, calculate the amount of Ba^{2+} or $BaCl_2$ present.

Amount of Ba^{2+}=(137.33/233.39)×Weight of BaSO4

Amount of BaCl2·2H2O=(244.26/233.39)×Weight of BaSO4

Precautions:

- Avoid excess H_2SO_4 to prevent supersaturation and fine precipitate formation.

- Always wash until sulfate and chloride ions are absent in the filtrate.

- Ensure complete drying or ignition before weighing.

- Do not overheat the precipitate to prevent decomposition.

Diazotisation Titration

Basic Principles of Diazotisation Titration

Diazotisation titration is a **redox volumetric titration** method used primarily for the estimation of **primary aromatic amines**. In this method, the amine group ($-NH_2$) is **converted into a diazonium salt** using **nitrous acid (HNO_2)** under cold acidic conditions.

The reaction proceeds as:

$$Ar\text{-}NH2+HNO2+HCl{\rightarrow}Ar\text{-}N2+Cl^-+2H2O$$
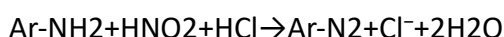
Where:

- $Ar–NH_2$ = Aromatic primary amine

- HNO_2 = Nitrous acid (generated in situ from sodium nitrite and HCl)

- $Ar–N_2^+Cl^-$ = Diazonium chloride (stable at low temperature)

Reagents Used

1. **Sodium nitrite ($NaNO_2$)** – Titrant

2. **Dilute hydrochloric acid (HCl)** – Acidic medium

3. **Potassium iodide and starch** – For iodometric end-point detection

4. **Primary aromatic amine solution** – Analyte

Conditions for Diazotisation

- The reaction is performed at a **temperature of 0–5°C**, since diazonium salts are unstable at higher temperatures.

- Acidic medium (HCl) is essential for the formation of nitrous acid (HNO$_2$) from sodium nitrite.
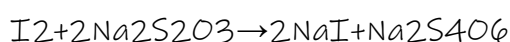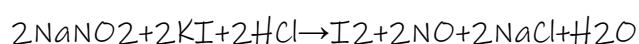
Methods of Diazotisation Titration

1. Direct Method

- A known volume of the **aromatic primary amine** is taken in a flask.

- The solution is cooled in an ice bath (0–5°C).

- Sodium nitrite is titrated into the cold amine solution containing HCl.

- **End-point** is detected by adding starch-iodide paper or by external iodometric detection:

    o A drop of the reaction mixture is placed on starch-iodide paper.

    o The appearance of **blue color** (due to iodine-starch complex) indicates the end-point (excess nitrite oxidizes iodide to iodine).

2. Back Titration Method

- An excess of standard sodium nitrite solution is added to the cold acidified amine solution.

- After completion of reaction, the **excess nitrite** is determined by **iodometric titration** with **standard sodium thiosulphate**.

$2NaNO2+2KI+2HCl \rightarrow I2+2NO+2NaCl+H2O$

$I2+2Na2S2O3 \rightarrow 2NaI+Na2S4O6$

Applications of Diazotisation Titration

- **Estimation of primary aromatic amines** like:

    o **Aniline**

    o **Sulphanilamide**

    o **Sulphadiazine**

    o **Sulphamethoxazole**

- Used in quality control of drugs containing aromatic amine groups.

- Official method in various pharmacopoeias for estimation of sulpha drugs.

Advantages

- Highly **specific** for primary aromatic amines.

- Simple, sensitive, and does not require sophisticated instrumentation.

- Suitable for **bulk drug analysis** and routine quality control.

Precautions

- Strict temperature control (0–5°C) is essential to prevent decomposition of diazonium salts.

- Freshly prepared sodium nitrite solution should be used.

- Use accurate timing and indicators for end-point detection.