

B pharma 1st year Pharmaceutical analysis

Gravimetry: Principle and Steps

Principle

The principle of gravimetric analysis is based on **Stoichiometry and Mass Conservation**. The analyte is quantitatively separated from the sample, typically via **precipitation**, and converted into a highly pure compound of definite chemical composition. The mass of this final product is then accurately measured. Using the known **chemical formula** and **molar masses**, the original amount (or percentage) of the analyte in the sample is calculated.

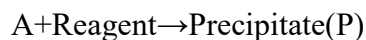
Based on the **conversion of the analyte into an insoluble precipitate** which is then **filtered, washed, dried (or ignited)** and **weighed** accurately

Basic Concept

- A known volume or mass of a sample solution is treated with a suitable reagent to form a **pure, stable, and easily filterable precipitate**.
 - The **mass of this precipitate** is proportional to the amount of the original analyte.
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- Determination of **purity** of chemical substances.
 - **Estimation** of metal ions or anions in inorganic compounds.

$$[\text{Mass of Analyte} = \text{Mass of Precipitate} \times \text{Gravimetric Factor}]$$

If analyte A forms a precipitate P,



Mass of analyte A = $\frac{\text{Mass of P} \times \text{Molecular weight of A}}{\text{Molecular weight of P}}$		
Step	Description	Key Requirements
1. Preparation of Solution	Dissolve the sample in suitable solvent. Conditions like pH and volume are adjusted for optimum precipitation.	Clear and homogeneous solution.
2. Precipitation	Add a precipitating reagent to form insoluble compound. • often to a hot, dilute solution, with constant stirring, to convert the analyte into a sparingly soluble precipitate. This is done to achieve low relative supersaturation , promoting the formation of larger, purer crystals.	Controlled addition, correct temperature & pH.
3. Digestion (Ostwald Ripening)	Heating the precipitate in the mother liquor to form large, pure crystals.	Improves filterability and purity.
4. Filtration	Separate the precipitate using filter paper or sintered crucible.	Avoid loss during transfer.
5. Washing	Remove adhering impurities and electrolytes.	Use wash liquid that does not dissolve the precipitate.
6. Drying/Ignition	Remove water and volatile matter or convert to a constant-weight form. in a muffle furnace at high temperature	Maintain suitable temperature to avoid decomposition. oven

		at 100–130°C
7. Weighing	Cool in a desiccator and weigh accurately.	Repeated weighing till constant weight.

Flow chart of Gravimetric analysis-

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Sample Solution
↓
Addition of Precipitating Agent
↓
Formation of Precipitate
↓
Digestion (Coagulation of Precipitate)
↓
Filtration
↓
Washing of Precipitate
↓
Drying/Ignition
↓
Weighing of Constant Mass
↓
Gravimetric Calculation

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Purity of the Precipitate

The purity of the final precipitate is crucial for accurate gravimetric analysis. Impurities present in the precipitate are primarily due to **co-precipitation** and **post-precipitation**.

A pure precipitate is essential for accurate gravimetric results. Impurities may arise due to:

Co-precipitation

The contamination of the desired precipitate with substances that are normally soluble under the conditions of precipitation.

Co-precipitation is the phenomenon where a normally **soluble** substance is carried down and precipitates along with the desired precipitate **during** the precipitation process. This contamination occurs simultaneously with the formation of the main precipitate.

Type	Mechanism	Example
Surface adsorption	Adsorption of ions on surface of precipitate.	AgCl adsorbs NO_3^- ions.
Occlusion	Impurities trapped inside crystal lattice.	BaSO_4 with trapped Na^+ .
Inclusion	Impurities occupy lattice positions.	K^+ replaces NH_4^+ in $\text{NH}_4\text{MgAsO}_4$.
Mechanical entrapment	Rapid precipitation traps impurities.	Common with colloidal precipitates.

Minimization of Co-precipitation:

Minimization: Can be minimized by digestion (to replace trapped impurities with purer solution), washing, and re-precipitation (dissolving the contaminated precipitate and re-precipitating it).

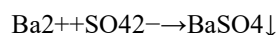
- Slow addition of reagent with stirring.
- Precipitate from hot, dilute solution.
- Digest the precipitate.
- Wash properly.

Minimization: Can be minimized by **immediate filtration** of the desired precipitate after digestion, preventing prolonged contact with the supersaturated mother liquor containing the second substance.

Feature	Co-precipitation	Post-precipitation
Time of Occurrence	During the formation of the main precipitate.	After the main precipitate has formed (requires the mixture to stand).
Contamination	Decreases as digestion time increases (impurities leave the lattice).	Increases with digestion time (more time for the second substance to precipitate).
Nature of Impurity	A normally soluble substance (carried down).	A second sparingly soluble substance that precipitates slowly.
Example	Ba(NO ₃) ₂ trapped inside BaSO ₄ crystals.	ZnS precipitating on CuS when solution is left standing.

Estimation of Barium Sulphate (BaSO₄)

Barium ions react with sulfate ions to form **barium sulfate**, which is **insoluble**, stable, and can be **weighed directly**.



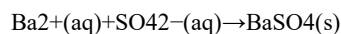
Reagents:

- Barium chloride (BaCl₂) solution
- Dilute sulfuric acid (H₂SO₄) or sodium sulfate solution

This is a classic example of **precipitation gravimetry**, typically used to determine the amount of **sulfate ion (SO₄²⁻)** or **barium ion (Ba²⁺)** in a sample.

Principle

The analyte (e.g., SO₄²⁻ ion) is quantitatively precipitated by the addition of a solution containing an excess of the precipitating reagent (e.g., BaCl₂ for SO₄²⁻), according to the reaction:



The barium sulfate (BaSO₄) precipitate is highly insoluble, making it an excellent choice for gravimetric estimation. The precipitate is filtered, washed, dried, ignited (usually at 800–1000°C for complete water removal and stability), and weighed.

Procedure:

1. Take **known volume of BaCl₂ solution**.
2. Add **dilute H₂SO₄** slowly with stirring → white precipitate of BaSO₄.
3. **Digest** the precipitate on a water bath for 1 hour.
4. **Filter** using ashless filter paper.
5. **Wash** with hot distilled water till chloride-free (test with AgNO₃).
6. **Dry and ignite** at 800°C in a muffle furnace to constant weight.
7. **Weigh** as BaSO₄.

Advantages	Limitations
Highly accurate (0.1% error)	Time-consuming
Simple and inexpensive apparatus	Requires pure reagents
No standard solutions needed	Only suitable for few analytes

Excellent for standardization	Not ideal for colored or complex ions
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Flow chart-

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graph TD
    A[BaCl2 Solution] -- "↓ (Add H2SO4)" --> B[Formation of BaSO4]
    B --> C["Digestion (1 hr, hot)"]
    C --> D["Filtration → Washing"]
    D --> E["Drying → Ignition → Cooling"]
    E --> F[Weighing]
    F --> G["Gravimetric Calculation (Ba or SO4 content)"]
  
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BaCl₂ Solution
 ↓ (Add H₂SO₄)
 Formation of BaSO₄
 ↓
 Digestion (1 hr, hot)
 ↓
 Filtration → Washing
 ↓
 Drying → Ignition → Cooling
 ↓
 Weighing
 ↓
 Gravimetric Calculation (Ba or SO₄ content)