

# B pharma 1<sup>st</sup> 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.

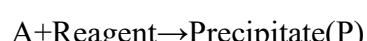
Based on the **conversion of the analyte into an insoluble precipitate** which is then **filtered, washed, dried (or ignited)** and **weighed accurately**

### 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.

[Mass of Analyte=Mass of Precipitate×Gravimetric Factor]

If analyte A forms a precipitate P,



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

		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 $\text{NO}_3^-$ ions.
Oclusion	Impurities trapped inside crystal lattice.	$\text{BaSO}_4$ with trapped $\text{Na}^+$ .
Inclusion	Impurities occupy lattice positions.	$\text{K}^+$ replaces $\text{NH}_4^+$ 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).*

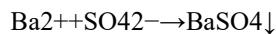
- Slow addition of reagent with stirring.
- Precipitate from hot, dilute solution.
- Digest the precipitate.
- Wash properly.

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

## Estimation of Barium Sulphate (BaSO<sub>4</sub>)

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



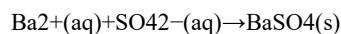
### Reagents:

- Barium chloride (BaCl<sub>2</sub>) solution
- Dilute sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) or sodium sulfate solution

This is a classic example of **precipitation gravimetry**, typically used to determine the amount of **sulfate ion (SO<sub>4</sub><sup>2-</sup>) or barium ion (Ba<sup>2+</sup>)** in a sample.

### Principle

The analyte (e.g., SO<sub>4</sub><sup>2-</sup> ion) is quantitatively precipitated by the addition of a solution containing an excess of the precipitating reagent (e.g., BaCl<sub>2</sub> for SO<sub>4</sub><sup>2-</sup>), according to the reaction:



The barium sulfate (BaSO<sub>4</sub>) 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 BaCl<sub>2</sub> solution**.
2. Add **dilute H<sub>2</sub>SO<sub>4</sub>** slowly with stirring → white precipitate of BaSO<sub>4</sub>.
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 AgNO<sub>3</sub>).
6. **Dry and ignite** at 800°C in a muffle furnace to constant weight.
7. **Weigh** as BaSO<sub>4</sub>.

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-

BaCl<sub>2</sub> Solution  
↓ (Add H<sub>2</sub>SO<sub>4</sub>)  
Formation of BaSO<sub>4</sub>  
↓  
Digestion (1 hr, hot)  
↓  
Filtration → Washing  
↓  
Drying → Ignition → Cooling  
↓  
Weighing  
↓  
Gravimetric Calculation (Ba or SO<sub>4</sub> content)