Unit-3 L-3

Precipitation titrations: Mohr's method, Volhard's, Modified Volhard's, Fajans method, estimation of sodium chloride.

-Complexometric titration: Classification, metal ion indicators, masking and demasking reagents, estimation of Magnesium sulphate, and calcium gluconate.

-Gravimetry: Principle and steps involved in gravimetric analysis. Purity of the precipitate: co-precipitation and post precipitation, Estimation of barium sulphate.

-Basic Principles, methods and application of diazotisation titration.



Gravimetry

Gravimetry analysis is a technique used to measure the amount of a substance in a sample (quantity) & purity by determining its mass.

It involves separating the substance (usually by precipitation), isolating it, and then weighing it to calculate its concentration or purity.

It is a quantitative analysis & it is based on precipitation

$$\begin{array}{c} eg \longrightarrow & BaCl_2 + H_2SOy \longrightarrow & BaSOy + HCl. \\ \hline & Analyte & PPt_{\circ} & \\ & Agent & PPt_{\circ} \end{array}$$



Steps involved in Gravimetry Titration

1. Sample Preparation

<u>Weighing the Sample</u>: A known quantity of the sample is accurately weighed using an analytical balance. This is the starting point of the analysis, as it will be used to calculate the final concentration or amount of the substance of interest.

Dissolution of the Sample: The sample may need to be dissolved in an appropriate solvent (such as water, acid, or a mixture) to make it easier to react with reagents. This is done by adding a suitable solvent to the sample.

2. Precipitation of the Analyte

Adding Precipitating Reagents: <u>A reagent is added to the sample solution to react with the</u> <u>substance of interest, forming a precipitate</u>. The precipitate is an insoluble solid that can be separated from the rest of the solution. For example, if you're determining the chloride content, silver nitrate (AgNO₃) could be used to precipitate silver chloride (AgCl).

Conditioning the Solution: Sometimes, the reaction conditions (such as temperature, pH, or concentration) need to be controlled to ensure complete precipitation. It may also involve the addition of a stabilizing agent to form a pure precipitate.

3. Filtration

Separation of Precipitate: After precipitation, the solid precipitate is separated from the solution using filtration. The solution containing the dissolved ions or compounds passes through a filter paper or filtration apparatus, while the precipitate is retained on the paper.

Washing the Precipitate: The precipitate is washed with a solvent (usually distilled water or a specific solvent depending on the precipitate) $\frac{1}{10}$ remove soluble impurities that may have been trapped in or on the precipitate. This ensures the purity of the solid.





4. Drying or Igniting the Precipitate

Drying: The precipitate is carefully dried to remove any water or solvent that may still be attached to it. This is typically done in a drying oven at a controlled temperature.

Ignition (if necessary): For some analyses, the precipitate must be heated to a higher temperature (ignition) to decompose it into a more stable form or to remove volatile components like water. This is done using a furnace or a muffle furnace. For example, in the determination of sulfate content, the precipitate may be heated to convert it to a stable form like barium oxide (BaO).

Cooling: After drying or ignition, the precipitate is allowed to cool in a desiccator to prevent moisture absorption from the air.

5. Weighing the Precipitate

Accurate Weighing: <u>After drying or ignition, the mass of the precipitate is carefully weighed</u> using an analytical balance.^{**}This weight is essential for determining the amount of the analyte in the original sample.

Repetition of Weighing: The weighing process is often repeated to ensure that the weight of the precipitate is constant, indicating that the drying or ignition process is complete, and no further changes in mass are occurring.

Example of Gravimetric Analysis Process

Determination of Chloride Content Using Silver Nitrate:

Sample Preparation: A known mass of the sample (e.g., sodium chloride solution) is measured.

Precipitation: Silver nitrate (AgNO₃) is added to the solution. Silver chloride (AgCl) precipitates out.

Filtration: The AgCl precipitate is filtered out of the solution. Washing: The precipitate is washed with distilled water to remove impurities. Drying/Ignition: The AgCl precipitate is dried to remove moisture.

Weighing: The dried AgCl precipitate is carefully weighed.

Calculation: Using the weight of AgCl, the amount of chloride (Cl⁻) in the sample is calculated based on stoichiometric relationships.

Advantages of Gravimetric Analysis:

High Precision and Accuracy: It provides very accurate results, especially when instruments like analytical balances are used.

No Need for Calibration Curves: Unlike other methods, gravimetry does <u>not require calibration</u> curves, making it simpler in some cases.

Applicable for Pure Samples: It is *particularly useful for determining purity and concentration* in very pure samples.

Limitations of Gravimetric Analysis:

Time-Consuming: The process can be slow, especially when drying or igniting precipitates.

Requires Large Sample Sizes: Gravimetric analysis often requires a reasonably large amount of the sample <u>for accurate results.</u>

Potential for Errors: If the precipitate is not pure or if washing is incomplete, the results can be inaccurate.

The principle of gravimetry is based on the measurement of the mass of a substance after it has been isolated and purified through a chemical process. Typically, this involves the following steps:

Precipitation: The substance of interest is separated from the sample by forming an insoluble precipitate through a chemical reaction.

Filtration and Washing: The precipitate is filtered and washed to remove impurities.

Drying or Heating: The precipitate is dried or heated to remove any remaining solvent or moisture.

Weighing: The dried precipitate is carefully weighed to determine its mass.

Purity of the precipitate

The purity of the precipitate in gravimetric analysis <u>refers to the degree to which the</u> <u>precipitate consists of the desired substance</u>, free from impurities that could affect the <u>results</u>. Achieving a high-purity precipitate is crucial for accurate determination of the analyte's quantity in the sample.

To ensure the purity of the precipitate, the following steps are typically taken:

1. Careful Precipitation

Choosing the Right Reagent: A suitable reagent is selected to form a specific precipitate with the analyte, avoiding reactions with other substances present in the sample. The reagent should selectively precipitate the analyte with minimal interference from other compounds.

Optimizing Reaction Conditions: Conditions such as pH, temperature, and concentration are controlled to promote the formation of a pure precipitate. For instance, adjusting pH can prevent the precipitation of undesired compounds and ensure that only the target substance forms a solid.

Factors Affecting the Purity of the Precipitate:

Incomplete Precipitation: If the precipitation reaction is not complete, unprecipitated analyte may remain in the solution, affecting purity.

<u>Co-precipitation</u>: Sometimes, other substances may form similar precipitates or become trapped in the desired precipitate. This is called co-precipitation and can lower purity.

Impurities in Reagents: <u>If the reagents used are not pure</u>, <u>they can introduce impurities into the</u> precipitate.

Importance of Purity of Precipitate:

Accurate Calculation: The mass of the pure precipitate is used to calculate the amount of the target analyte in the sample. Any impurity in the precipitate will result in an incorrect mass, leading to errors in the final analysis.

Reliability: High-purity precipitates ensure that the gravimetric analysis yields precise and reliable results, which is critical for pharmaceutical, environmental, and chemical analyses.

Co-precipitation & Post precipitation

Co-precipitation and post-precipitation are two phenomena that can occur during gravimetric analysis.

1. Co-precipitation

Co-precipitation occurs when impurities or unwanted substances are trapped within the precipitate of the desired analyte during the formation of the precipitate. <u>These impurities can be present in the solution before precipitation and become part of the solid precipitate</u> because of similar physical or chemical properties (such as size, solubility, or charge).

Causes of Co-precipitation:

Similar Chemical Properties: If the impurity has similar chemical characteristics to the precipitating analyte (e.g., ionic size, charge, or solubility), it may co-precipitate with the analyte.

Over-Saturation: When the solution is too concentrated or supersaturated, leading to the incorporation of unwanted substances into the growing crystals of the desired precipitate.

Rapid Precipitation: If the precipitate forms too quickly, there may not be enough time for the impurities to be excluded from the solid phase.

Example of Co-precipitation:



If you're precipitating calcium carbonate $(CaCO_3)$ from a solution and there are magnesium ions (Mg^{2+}) present, the magnesium ions may co-precipitate with calcium carbonate to form a mixed precipitate. Both calcium and magnesium ions are divalent, and their physical properties can lead to magnesium being trapped within the calcium carbonate crystals.

Mitigating Co-precipitation:

<u>Slow Precipitation</u>: Allowing the precipitate to form slowly under controlled conditions <u>(like</u> * <u>temperature and concentration</u>) can help minimize co-precipitation.

Addition of Solvents: Sometimes, ^{*}adding a solvent can help to selectively precipitate the analyte while leaving impurities behind in the solution.

Purification Steps: Techniques such as washing the precipitate with a suitable solvent or dissolving and re-precipitating the substance can help remove co-precipitated impurities.

2. Post-precipitation

Post-precipitation occurs when a foreign substance that precipitates very slowly (or at a later stage) forms a precipitate on the surface of an already formed precipitate, or as a separate precipitate after the main precipitation has taken place

Causes of Post-precipitation:

Continued Precipitation: After the initial precipitation, some ions may still be in excess in the solution and continue to precipitate over time.

Particles may precipitate after the main event due to size differences or varying charges that affect their precipitation behaviour

Crystallization Changes: Environmental changes, such as temperature or concentration, can lead to the precipitation of new, smaller crystals, which may mix with the primary precipitate.

Example of Post-precipitation:

If you are precipitating barium sulfate (BaSO₄), the primary precipitate may be large crystals, but as the reaction continues or if conditions change, smaller crystals of BaSO₄ may form and be mixed with the larger ones, leading to inaccurate mass measurements.

Mitigating Post-precipitation:

Washing: <u>Washing the precipitate thoroughly with an appropriate solvent can help remove the</u> smaller, newly-formed crystals.

Digestion: Heating the precipitate in the solution (a process called digestion) helping to reduce the effect of post-precipitation.

Controlling Reaction Conditions: Maintaining steady and controlled temperature

Differences Between Co-precipitation and Post-precipitation:

Feature	Co-precipitation	Post-precipitation
Timing	Occurs during the formation of the precipitate.	Occurs after the desired precipitate has been formed.
Cause	Similar solubility properties, rapid precipitation, or physical adsorption.	Changes in solution conditions (e.g., temperature, pH).
Nature of Impurity	The impurity is incorporated into the crystal lattice or adsorbed onto the precipitate.	The impurity forms a separate precipitate after the main one has formed.
Mitigation	Slow precipitation, recrystallization, and thorough washing.	Careful control of solution conditions, frequent washing.

Estimation of BaSO4

The estimation of barium sulfate $(BaSO_4)$ is a common gravimetric analysis procedure used to determine the concentration of barium ions (Ba^{2+}) in a sample. The method is based on the precipitation of barium sulfate from a solution containing barium ions by adding sulfate ions, typically in the form of a soluble salt like sodium sulfate (Na_2SO_4) .

Materials Needed:

Barium-containing sample (e.g., barium chloride solution or any sample with barium ions) Sodium sulfate (Na_2SO_4) solution (precipitating reagent)

Distilled water

Filter paper

Analytical balance

Crucible or drying oven (Heat provide).

Beakers and glassware

Heat source (for drying or igniting)

Desiccator (for cooling)

Steps Involved:

1. Preparation of the Sample

Weigh a known amount of the barium-containing sample. If the sample is in solid form (like barium chloride, $BaCl_2$), dissolve it in distilled water to make an aqueous solution. Make sure the barium ions are completely dissolved.

2. Precipitation of Barium Sulfate

Add an excess of sodium sulfate (Na_2SO_4) solution to the sample solution. This will result in the formation of a white precipitate of barium sulfate $(BaSO_4)$ according to the reaction:

 $\mathrm{Ba}^{2+}(aq) + \mathrm{SO}_4^{2-}(aq) o \mathrm{BaSO}_4(s)$

The precipitation of $BaSO_4$ is almost complete under these conditions, but if necessary, the solution can be heated to ensure full precipitation. Allow the mixture to stand for some time to ensure that precipitation is complete.

3. Filtration

Filter the precipitate using filter paper to separate the barium sulfate $(BaSO_4)$ from the rest of the solution. The filtrate will contain excess sulfate ions and other dissolved substances. Wash the precipitate with small amounts of distilled water to remove any soluble impurities, such as sodium ions or excess sodium sulfate.

4. Drying or Ignition of the Precipitate

After filtration, the barium sulfate precipitate is transferred to a crucible or another suitable container and dried to remove any water content.

Dry the precipitate in an oven at a controlled temperature (around 110°C) to ensure it is completely free of moisture.

After drying, the precipitate is often ignited (heated to a high temperature in a muffle furnace) if required to ensure that the sample is completely pure.

5. Weighing the Precipitate

Once the precipitate is dry or ignited, allow it to cool in a desiccator to prevent moisture absorption from the air.

Weigh the dry or ignited barium sulfate precipitate using an analytical balance. Record the mass accurately.

6. Calculation of the Barium Content

Using the mass of the barium sulfate (BaSO₄) precipitate, calculate the amount of barium (Ba²⁺) in the original sample using stoichiometric calculations

Advantages of this Method:

High Precision: Gravimetric analysis provides a highly accurate method for determining the concentration of a substance.

No Calibration Curve Required: Unlike some other methods, gravimetry does not require a calibration curve, which simplifies the procedure.

Limitations:

Time-Consuming: The process of filtering, drying, and igniting can take time. Potential for Impurities: Co-precipitation or post-precipitation can lead to impurities in the $BaSO_4$ precipitate, which might affect the results.