

GRAVIMETRY

- Gravimetric methods are the quantitative methods that are based on measuring the mass of a pure compound to which the sample is chemically related.
- Since weight can be measured with greater accuracy than almost any other fundamental property, gravimetric analysis is one of the most accurate classes of analytical methods. It involves isolation and weighing of an element or a definite compound of the element in as pure a form as possible.
- The steps in gravimetric analysis, can be explained as follows –

1. Preparation of the Solution:

- The first step in performing gravimetric analysis is to dissolve the given sample in suitable solvent to prepare the solution. Some form of preliminary separation may be necessary to eliminate impurities. Also, adjustment of the solution conditions is necessary to maintain low solubility of the precipitate such as pH.

2. Precipitation:

- It is an ionic reaction in which the positive ion of one substance in solution combines with the negative ion of another substance, to form a sparingly soluble substance.
- The factors which determine a successful analysis by precipitation are-
 - 1) Precipitate must be formed quantitatively.
 - 2) Precipitate must be formed within a reasonable time.
 - 3) Its solubility should be low enough for quantitative separation.
 - 4) Particle of the precipitate must be of such size that they do not pass through the filtering medium and is unaffected by the washing process.
 - 6) It should be easily and quickly filterable and it should be possible to remove the soluble contaminations by washing the precipitate.
 - 7) The precipitate must be free of impurities.
- Precipitation mechanism is an important step and the completeness of precipitation of the desired constituent is determined by the solubility of the constituent at equilibrium. Therefore, the precision of the analytical result depends on the factors that affect the solubility of a precipitate namely the **choice of precipitant, the amount of precipitant added, the conditions of precipitation**, etc.
- **Mechanism of precipitate formation:** Upon addition of the first drops of the precipitating agent, **Supersaturation (step 1)** occurs, then **Nucleation (step 2)** starts to occur where every few molecules of precipitate come close together forming a nucleus. At this point, addition of extra precipitating agent will build up on existing nuclei to give a precipitate with large particles called as **Crystal growth (Step 3)**.

3. Digestion:

- It is the process of keeping the precipitate formed in contact with the mother liquor for a specified amount of time.
- The precipitate is kept in hot air oven (below boiling point of the liquid) for 30 min to 1 hour in order for the particles to be digested. Digestion involves dissolution of small particles and re-precipitation on larger ones resulting in particle growth and better precipitate characteristics. This is called as **Ostwald Ripening**. It improves the purity and crystallinity of the precipitate.

4. Filtration and Washing

- Filtration is the separation of the precipitate from the mother liquor. The systems employed are filter papers, Gooch crucibles and sintered-glass crucibles. The choice of the filtering medium will be controlled by the nature of the precipitate and the cost.
- The liquid for washing is generally water. The mode of washing is also equally important.
- The precipitate on the filter paper should be thoroughly stirred using a jet of wash liquid. This should be followed by washing the edges of the filter paper with the jet of wash liquid since the precipitate might spread out during washing. A large number of washes with small volumes of wash liquid are more efficient to remove the impurities.



Fig. Glass crucibles



Fig. Filter papers



Fig. Gooch crucibles

5. Drying and Ignition of precipitate:

- The purpose of drying (heating at about 120-150°C in an oven) is to remove the remaining moisture while the purpose of ignition in a muffle furnace at temperatures ranging from 600-1200°C, to get a material with exactly known chemical structure so that the amount of sample can be accurately determined. The precipitate is converted to a more chemically stable form.
- This is then cooled under proper condition to be weighed accurately. Use of ash-free filter papers has greatly simplified the ignition step.
- The precipitate can be carefully heated in a crucible until the filter paper has burned away; this leaves only the precipitate. (As the name suggests, "ashless" paper is used so that the precipitate is not contaminated with ash).

6. Weighing

- Modern balances can readily weigh samples directly and masses from several grams to a few micrograms can be used accurately and quickly.
- It is essential that the conditions are the same for the initial weighing as for the final weighing. Temperature is especially important and hot samples should never be placed directly onto a balance.

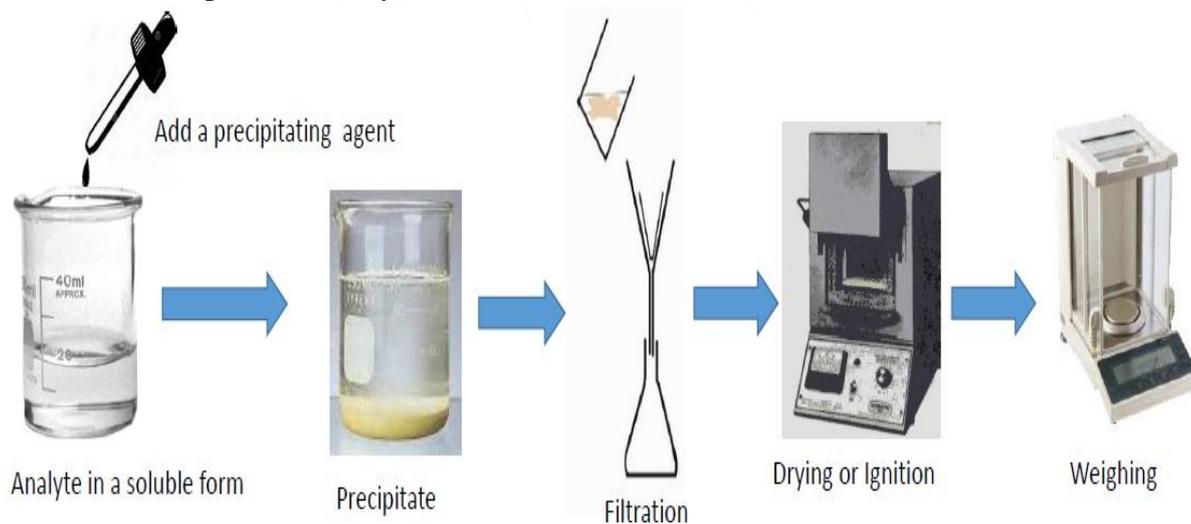


Fig. Summary of Gravimetric analysis

Purity of the precipitate: When a precipitate separates from a solution, it is not always perfectly pure. It may contain varying amounts of impurities due to:

1. **Co-precipitation:** If a precipitate is contaminated by substances which are normally soluble in the solution under the condition of precipitation, then co-precipitation is said to have taken place. Co-precipitation occurs by the adsorption or occlusion.
 - **Occlusion:** It is the trapping of impurities inside the precipitate. In the process of **occlusion**, material that is not part of the crystal structure is trapped within a crystal. For example, water may be trapped in pockets when AgNO_3 crystals are formed. If such mechanical trapping occurs during a precipitation process, the water will contain dissolved impurities. Occluded or included impurities are difficult to remove. Digestion may help some but is not completely effective. The impurities cannot be removed by washing.
 - **Surface Adsorption:** The surface of the precipitate will have a primary adsorbed layer of the lattice ions in excess. This results in surface adsorption.
2. **Post-precipitation:** The process by which an impurity is deposited after precipitation of the desired substance is called as post-precipitation. When there is a possibility that post-precipitation may occur, filtration to be made immediately after the precipitate is formed. For example, Ca-oxalate precipitates in presence of Mg ions. After some time, Mg-oxalate formed which deposits on Ca-oxalate surface.

Estimation/ Assay of Barium as Barium sulphate

- 0.5g of Sodium sulphate was weighed accurately and dissolved in 100ml water in a volumetric flask. About 5ml 2N HCl was added.
- The solution is heated to boiling and a hot solution of BaCl₂ was added drop by drop with constant stirring, till the precipitation is complete.
- The solution containing the precipitate is heated in a water bath for 5 minutes. The precipitate is allowed to stand for an hour.



- The clear solution is decanted through an ashless filter paper (whatman No. 40).
- The precipitate is washed with hot distilled water to free sulphate ions. The particles adhering to the sides of the beaker and glass rod are removed by a policeman.
- Finally the precipitate is washed once again. The dried filter paper is folded and placed in a crucible which has been previously weighed.
- The filter paper with the precipitate is first incinerated on a Bunsen burner by a low flame and then transferred to an electric burner.
- The crucible is then transferred to a desiccator and cooled. When cold, the crucible is weighed.

Calculation:

Mass of crucible + lid = 23 g

Mass of crucible + lid + Barium sulphate = 24 g

Mass of Barium sulphate = (b-a) = 1 g.

233.36 of barium sulphate contain 137.36 g of barium.

Mass of barium in 1 g of Barium sulphate = $(137.36 * 1)/233.36$

Therefore, Mass of Barium in the whole of the given solution = 0.58g

Result:

Mass of Barium in the whole of the given solution = 0.58 g.