Gravimetric Analysis

Disclaimer

All the content material provided here is only for teaching purpose.

Points to be covered

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

Introduction

- The term gravimetric pertains to a Weight Measurement.
- Gravimetric method is one in which the analysis is completed by a weighing operation.
- Gravimetric Analysis is a group of analytical methods in which the amount of analyte is determined by the measurement of the mass of a pure substance containing the analyte.
- Gravimetric Methods can also be defined as quantitative methods based on the determining the mass of a pure compound to which the analyte is chemically related

Types of Gravimetric Analyses:

- There are two main types of gravimetric analyses:

A) Precipitation

- analyte must first be converted to a solid (precipitate) by precipitation with an appropriate reagent. The precipitates from solution is filtered, washed, purified (if necessary) and weighed.

B) Volatilization

- In this method the analyte or its decomposition products are volatilised (dried) and then collected and weighed, or alternatively, the mass of the volatilised product is determined indirectly by the loss of mass of the sample.

Example for Precipitation

- Calcium can be determined gravimetrically by precipitation of calcium oxalate and ignition of the oxalate ion to calcium oxide.
- $Ca_{2+} + C_2O_{4_{2-}} \rightarrow CaC_2O_4$
- $CaC_2O_4 \rightarrow CaO + CO_2 + CO$
- The precipitate thus obtained are weighed and the mass of calcium oxide is determined.

Example for Volatilisation

- The analyte or its decomposition products are volatilised at a suitable temperature.
- The volatile product is then collected and weighed, i.e. the mass of the product is indirectly determined from the loss in mass of the sample.
- Example
- Water can be separated from most inorganic compounds by ignition, the evolved water can then be absorbed on any one of several solid desiccants.
- The weight of water evolved may be calculated from the gain in weight of the absorbent.
- Not all insoluble precipitates are well suited for gravimetric analysis.

Criteria For a successful determination

- For a successful determination in gravimetric analysis the following criteria should be met

1. The desired substance must be completely precipitated. In most determination the precipitate is of such low solubility that losses from dissolution are negligible. An additional factor is the common ion effect, this further decrease the solubility of the precipitate.
   - E.g. When Ag+ is precipitated out by addition of Cl-
   - $Ag^{+} + Cl^{-} = AgCl$

- The low solubility of AgCl is reduced further by the excess of Cl- which is added force to the reaction to proceed towards right side.

Criteria For a successful determination

2. The weighed form of the product should be of known composition.
3. The product should be pure and easily filtered.
4. Easy in handling i.e. ppt filtering, washing drying and weighing.

- It is usually difficult to obtain a product which is pure or which is free from impurities.
- This could be reduced by careful precipitation and sufficient washing.

Advantages of Gravimetric Analysis

- Accurate and precise: Gravimetric analysis is potentially more accurate and more precise than volumetric analysis
- Possible sources of errors can be checked: Gravimetric analysis avoids problems with temperature fluctuations, calibration errors, and other problems associated with volumetric analysis.
- It is an ABSOLUTE method.
- Relatively inexpensive

Disadvantages

- But there are potential problems with gravimetric analysis that must be avoided to get good results.
- Proper lab technique is critical
- Careful and time consuming.
- Scrupulously clean glassware.
- Very accurate weighing.
- Coprecipitation.

Properties of precipitate

- The ppt should be so insoluble that no significant loss occurs during filtration and washing
- Physical nature of ppt should be such that it cab be easily separated by filtration
- The PPT should be stable to atmospheric cond^{n}.
- The ppt must be convertible to pure compound of definite composition, either by ignition or by simple chemical operations such as evaporations.
- Have large crystals (Easier to filter large crystals)
- Be free of contaminants

Particle Size and Filterability of Precipitates

- Precipitates made up of large particles are generally desirable in gravimetric work because large particles are easy to filter and wash free of impurities. In addition, such precipitates are usually purer than are precipitates made up of fine particles.
- Three types of ppt are produced
  - Crystalline, Curdy and gelatinous etc.

Process of precipitation

- It is a most imp step in gravimetric analysis
- Involves both physical and chemical process
- The physical process consists of three steps

1) Super saturation: the solution phase contains more dissolved salt than at equilibrium. The driving force will be for the system to approach equilibrium (saturation).
2) Nucleation : initial phase of precipitation. A min number of particle will gather together to form a nucleus of particle or precipitate (solid phase). Higher degree of super saturation, the greater rate of nucleation

- nucleation involves the formation of ion pairs and finally a group of ions formed.
- it is of two types 1. Spontaneous and 2. Induced

3) Crystal growth : particle enlargement process. Nucleus will grow by deposition of particles precipitate onto the nucleus and forming a crystal of a specific geometric shape. Involving two steps diffusion of ion to surface of nucleus and Deposition on surface.

Precipitation process (Von weimarn eq)

- Von weimarn discover – the particle size of precipitates is inversely proportional to the relative supersaturation of the sol. during the precipitation process.
  - The von Weimarn Ratio (The lower the better)
  - von Weimarn ratio = (Q – S)/S
- A measure of relative supersaturation or supersaturation ratio
- If high, get excessive nucleation, lots of small crystals, large surface area
- If low, get larger, fewer crystals, small surface area
- S = solubility of precipitate at equilibrium, (Keep it high with high temperatures, adjusting pH)
- Q = concentration of reagents before precipitation (Keep it low by using dilute solutions, stir mixture well, add reactants slowly)
- Can lower S later by cooling mixture after crystals have formed

What Factors Determine Particle Size?

The particle size of solids formed by precipitation varies enormously. At one extreme are **colloidal suspension**, whose tiny particles are invisible to the naked eye (10^{-7} to 10^{-4} cm in diameter). Colloidal particles show no tendency to settle from solution, nor are they easily filtered. At the other extreme are particles with dimensions on the order of tenths of millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a **crystalline suspension**. The particles of a crystalline suspension tend to settle

The particle size of a precipitate is influenced by experimental variables as precipitate solubility, temperature, reactant concentrations, and the rate at which reactants are mixed. The particle size is related to a single property of the system called its **relative supersaturation**, where

$$\text{relative supersaturation} = (Q - S) / S$$

In this equation, Q is the concentration of the solute at any instant and S is its equilibrium solubility.

When $(Q - S)/ S$ is large, the precipitate tends to be colloidal.

when $(Q - S) / S$ is small, a crystalline solid is more likely.

- **How do Precipitates Form?** Precipitates form in two ways, by **nucleation** and by **particle growth**. The particle size of a freshly formed precipitate is determined by which way is faster.

In nucleation, a few ions, atoms, or molecules (perhaps as few as four or five) come together to form a stable solid. Often, these nuclei form on the surface of suspended solid contaminants, such as dust particles. Further precipitation then involves a

competition between additional nucleation and growth on existing nuclei (particle growth). If nucleation predominates, a precipitate containing a large number of small particles results; if growth predominates, a smaller number of larger particles is produced.

Controlling Particle Size

Experimental variables that minimize lead supersaturation and thus to crystalline precipitates include elevated temperatures to increase the solubility of the precipitate (S in Equation), dilute solutions (to minimize Q), and slow addition of the precipitating agent with good stirring. The last two measures also minimize the concentration of the solute (Q) at any given instant.

Larger particles can also be obtained by pH control, provided the solubility of the precipitate depends on pH.

Peptization of Colloids

Peptization refers to the process by which a coagulated colloid reverts to its original dispersed state. When a coagulated colloid is washed, some of the electrolyte responsible for its coagulation is leached from the internal liquid in contact with the solid particles. Removal of this electrolyte has the effect of increasing the volume of the counter- ion layer. The repulsive forces responsible for the original colloidal state are then reestablished, and particles detach themselves from the coagulated mass. The washings become cloudy as the freshly

Crystalline Precipitates

Crystalline precipitates are generally more easily filtered and purified than coagulated colloids. In addition, the size of individual crystalline particles, and thus their filterability, can be controlled to a degree.

The particle size of crystalline solids can often be improved significantly by minimizing Q, maximizing S, or both in Equation. Minimization of Q is generally accomplished by using dilute solution and adding the precipitating from hot solution or by adjusting the pH of the precipitation medium.

Digestion of crystalline precipitates (without stirring) for some time after formation frequently yields a purer, more filterable product. The improvement in filterability results from the dissolution and recrystallization.

Purity of precipitate

- When the ppt is separated out from solution it is always not preferably pure and may be contaminated even after washing
- The amount of impurities depends on nature of PPt and condition of pptn
- It may be due to
  - Co-precipitation
  - Post precipitation, Surface adsorption
  - Mixed crystal formation
  - Occlusion and Mechanical Entrapment

Coprecipitation

Coprecipitation is the phenomenon in which soluble compounds are removed from solution during precipitate formation.

There are four types of coprecipitation:

i) surface adsorption, ii) mixed-crystal formation,
iii) occlusion, iv) mechanical entrapment

Surface adsorption and mixed crystal formation are equilibrium processes, whereas occlusion and mechanical entrapment arise from the kinetics of crystal growth.

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