GRAVIMETRIC ANALYSIS

Gravimetric methods – are quantitative methods in which the mass of the analyte or some compound that is chemically related to the analyte is determined.

What are the steps in a gravimetric analysis?
The steps required in a gravimetric analysis, after the sample has been dissolved are summarized below:

1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration
5. Washing
6. Drying or igniting
7. Weighing
8. Calculation

Gravimetric analysis can be generalized into two types:

a) precipitation – based on isolation of an insoluble precipitate of known composition

b) volatilization. – analyte is volatized, weighed and the loss is determined
(only the first of these methods will be discussed)

a) Precipitation Gravimetry

This method of analysis involves isolation of an ion in solution by a precipitation reaction, filtering, washing the precipitate free of contaminants, conversion of the precipitate to a product of known composition, and finally weighing the precipitate and
determining its mass by difference. From the mass and known composition of the precipitate, the amount of the original ion can be determined.

**For successful determinations the following criteria must be met:**

The desired substance must be completely precipitated. The ideal precipitating reagent would react with the analyte to give a product that is:

1. easily filterable and washed free of contaminants;
2. of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washing;
3. unreactive with constituents of the atmosphere;
4. of known chemical composition after it is dried or, if necessary, ignited.

An additional factor is the "common ion" effect, this further reduces the solubility of the precipitate.

Chloride is precipitated from solution as silver chloride by the addition of silver nitrate as shown below:

\[
\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(s)
\]

The (low) solubility of AgCl is reduced still further by the excess of Ag⁺ which is added, pushing the equilibrium to the right. We can further decrease the solubility by decreasing the temperature of the solution by using an ice bath. The weighed form of the product should be of known composition. The product should be "pure" and easily filtered. It is usually difficult to obtain a product which is "pure", i.e. one which is free from impurities but careful precipitation and sufficient washing helps reduce the level of impurity.
**Particle Size and Filterability of Precipitates**

Precipitates consisting of large particles are generally desirable for gravimetric work because these particles are easy to filter and wash free of impurities. In addition, precipitates of this type are usually purer than are precipitates made up of fine particles.

The particle size of solids varies enormously. At one extreme are *colloidal suspensions*, 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 and are not easily filtered.

At the other extreme are particles with dimensions on the order of tenths of a millimetre 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 spontaneously and are easily filtered.

**Factors that Determine the Particle Size of Precipitates**

The particle size of a precipitate is influenced by experimental variables such as, precipitate solubility, temperature, reactant concentrations, and rate at which reactants are mixed. The net effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system called the *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.

Generally, precipitation reactions are slow, so that even when a precipitating reagent is added drop by drop to a solution of an analyte, some supersaturation is likely. An *supersaturated solution* is an unstable solution that contains a higher solute concentration than a saturated solution. With time, supersaturation is relieved by precipitation of the excess solute.
The particle size varies inversely with the average relative supersaturation during the time when the reagent is being introduced. Thus, when \((Q - S)/S\) is large, the precipitate tends to be colloidal; when \((Q - S)/S\) is small, a crystalline solid is more likely.

**The optimum conditions for precipitation which make the supersaturation low are:**

- a. Precipitation using dilute solutions to decrease \(Q\)
- b. Slow addition of precipitating agent to keep \(Q\) as low as possible
- c. Stirring the solution during addition of precipitating agent to avoid concentration sites and keep \(Q\) low
- d. Increase solubility by precipitation from hot solution
- e. Adjust the pH in order to increase \(S\) but not a too much increase as we do not want to loose precipitate by dissolution
- f. Usually add a little excess of the precipitating agent for quantitative precipitation and check for completeness of the precipitation

**Mechanism of Precipitation**

The effect of relative supersaturation on particle size can be explained if we assume that precipitates form in two ways; by **nucleation** and by **particle growth**. The manner in which a precipitate is formed often determines its size, how it can or cannot be isolated and also its purity.

**Nucleation**

**Nucleation** is a process in which a minimum number of atoms, ions, or molecules join together to give a stable solid. i.e. the smallest aggregate of molecules capable of growing into a large precipitate particle.
After the addition of the precipitating agent to the solution of the ion under analysis there is an initial **induction period** before nucleation occurs. The time between mixing and the visual appearance of a precipitate is called the *induction period* and it varies with the nature of the substance being precipitated, the concentration of the reagents being mixed, and even the order of addition of the reagents. When concentrated solutions are mixed, the induction periods are short so that precipitation appears to occur instantly upon mixing. (Induction periods are longer when dilute solutions are mixed).

After induction, **nucleation** occurs, here small aggregates or nuclei of atoms form and it is from these "clumps" of atoms that the crystals which form the filtrate will grow. As these nuclei form, ions from the solution (which at this point are in excess) congregate around them.

For example if hydrochloric acid were added very slowly to a solution of silver nitrate, silver chloride nuclei would form and silver ions (which would be in excess relative to Cl ions) would congregate around them.
Particle Growth

Once a nucleation aggregate has formed, it begins to grow as ions or molecules from the solution deposit on the surface in a regular, geometric pattern. This process helps produce more easily filtered crystals (since it produces larger crystals).
Growth of larger nuclei or crystallites can be encouraged by digestion, a process which involves heating the solid and mother liquor for a certain period of time. During
digestion, small particles dissolve and larger ones grow. Digestion of the product is an important practical process and you will find that most if not all gravimetric analysis involve a digestion period.

**Colloidal Precipitates**

Silver halide precipitates are well known for their tendency to form colloidal suspensions. A **colloid** is a solid made up of particles having diameters less than $10^{-4}$ cm.

*Let us examine the process that occurs when sodium chloride is treated with an excess of silver nitrate in dilute nitric acid solution.*

As small crystals and aggregates of silver chloride form they attract to their surface, and hold by normal bonding forces, new silver and chloride ions in proportion to their availability in the bulk solution. Since they are not yet part of the regular crystal lattice, these ions are said to be adsorbed on the surface and comprise what is called the **primary adsorption layer**. Adsorption is a process in which a substance (gas, liquid, or solid) is
held on the surface of a solid. In contrast, absorption involves the retention of a substance within the pores of a solid.

Because there are more silver ions than chloride ions in the solution, the primary adsorption layer will contain an excess of silver ions and be positively charged. Had the solution contained an excess of chloride ion, the primary adsorption layer will be negatively charged. The net charge of the primary adsorption layer depends on both the absolute and relative silver-ion and chloride-ion concentrations in the bulk solution.

In addition to the primary adsorbed silver ion, there are some nitrate ions aggregating further from the AgCl nucleus. These are counter ions and tend to aggregate around the [AgCl:Ag]⁻ centre because these centres have a net positive charge (excess Ag⁺) and additional negative charge is required to maintain electrical neutrality. The counter ions are less tightly held than the primary adsorbed ions and the counter ion layer (secondary layer) is somewhat diffuse and contains ions other than those of the counter ions. These layers of charges are known as the electric double layer. The electric double layer of a
colloid consists of a layer of charge absorbed on the surface of the particles and a layer with a net opposite charge in the solution surrounding the particles.

Peptization of Colloids

**Peptization** is a process by which a coagulated colloid returns to its dispersed state.

**Conditions for analytical precipitation**

An analytical precipitate for gravimetric analysis should consist of perfect crystals large enough to be easily washed and filtered. The perfect crystal would be free from impurities and be large enough so that it presented a minimum surface area onto which foreign ions could be adsorbed.
Impurities which may be present in the precipitates.

Impurities can be incorporated into a precipitate during its formation, called coprecipitation, or after its formation while still in contact with the precipitating solution, called postprecipitation.

Coprecipitation

Coprecipitation is a process in which normally soluble compounds are carried out of solution by a precipitate. It occurs to some degree in every gravimetric analysis (especially barium sulfate and those involving hydrous oxides). A diverse substance can be coprecipitated by the process of adsorption (discussed already), inclusion or occlusion. Coprecipitation can be minimized by careful precipitation and thorough washing.

Washing and Filtering

Problems with co-precipitation and surface adsorption may be reduced by careful washing of the precipitate. With many precipitates, peptization (when a coagulated colloid reverts to its dispersed state) occurs during washing. Here part of the precipitate reverts to the colloidal form e.g.

\[ \text{AgCl(colloidal)} \xrightleftharpoons{} \text{AgCl(s)} \]

This results in the loss of part of the precipitate because the colloidal form may pass through on filtration. By washing with ice cold water this can be minimized.

Surface adsorption

Here unwanted material is adsorbed onto the surface of the precipitate. Digestion of a precipitate reduces the amount of surface area and hence the area available for surface adsorption. Washing can also remove surface material.
Oclusion

This is a type of coprecipitation in which impurities are trapped within the growing crystal.

Postprecipitation

Sometimes a precipitate standing in contact with the mother liquor becomes contaminated by the precipitation of an impurity on top of the desired precipitate.

Precipitation from Homogenous Solution

Homogenous precipitation is a process in which a precipitate is formed by slow generation of a precipitating reagent homogenously throughout a solution. Solids formed by homogenous precipitation are generally purer and more easily filtered than precipitates generated by direct addition of a reagent to the analyte solution.

Drying the solid

Generally the solids are dried at about 120°C but conditions for drying can vary considerably. It is heated until it reaches constant weight. During the heating process, moisture and volatile electrolytes are removed.

Cooling and weighing precipitates

After the heating process, the precipitate must be cooled to room temperature before weighing. Since many gravimetric precipitates have a tendency to pick up moisture while cooling, they are cooled and stored in a dessicator. The process of heating, cooling and weighing is generally repeated until a constant weight is achieved. (Usually, this means three successive weights that are the same, within experimental error.)
**Calculating the Results**

Gravimetric analysis is characterised by the fact that only one kind of measurement, that of weight, is made on the sample, its constituent, and reaction products. Only measurements of weight are thus used in the calculation.

The point here is to find the weight of analyte from the weight of precipitate. We can use the concepts discussed previously in stoichiometric calculations. Gravimetric calculations are simply an extension of stoichiometric calculations. The stoichiometric factor is often based on the amount of analyte (in moles) in the material weighed.

The result is reported as a percentage of analyte.

\[
\text{% analyte} = \frac{\text{mass of analyte}}{\text{mass of sample}} \times 100
\]
Calculating the Results using the gravimetric factor

The gravimetric factor - this is the ratio of RMM of substance sought to that of substance weighed.

Assume Cl$_2$ is to be precipitated as AgCl, then we can write a stoichiometric factor reading as follows: one mole of Cl$_2$ gives 2 moles of AgCl. This is in fact what is called the gravimetric factor (GF) where we can substitute for the number of moles by grams

Weight of substance sought = weight of precipitate (or substance known) x GF

We can also write the equation for the percentage of a constituent as follows:

$$\% \text{ constituent} = \frac{\text{weight of precipitate} \times \text{g.f.} \times 100}{\text{Weight of sample}}$$

References

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3. http://ull.chemistry.uakron.edu/analytical/Gravimetry/
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