

Gravimetric methods of analysis

Gravimetry

Gravimetric methods are methods that depend upon measuring mass (i.e., gravity). Several analytical methods are based on mass measurements.

In **precipitation gravimetry**, the analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition that can be weighed.

In **volatilization gravimetry**, the analyte is separated from other constituents of a sample by conversion to a gas of known chemical composition. The weight of this gas then serves as a measure of the analyte concentration. These two types of gravimetry are considered in this chapter.

In **electrogravimetry**, the analyte is separated by deposition on an electrode by an electrical current. The mass of this product then provides a measure of the analyte concentration.

Features of Gravimetric Analysis

- Traditional Method.
- Cheap, easily available apparatus, simple to carry out.
- Slow, especially when accurate results are required.
- Wide range of sample concentrations (ng - kg).
- No calibration required (except for the balance).
- Accurate.

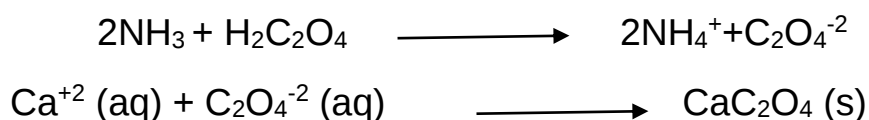
All gravimetric methods usually report the analytes as a weight percent:

$$\%A = \left[\frac{\text{weight A}}{\text{weight of sample}} \right] \cdot 100\%$$

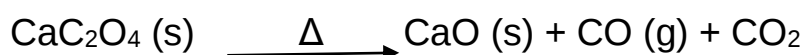
Precipitation Gravimetry

In precipitation gravimetry, the analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, converted to a product of known composition by suitable heat treatment, and weighed. For example, a precipitation method for

determining calcium in natural waters is recommended by the association of official analytical chemists. Here, an excess of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, is added to an aqueous solution of the sample. Ammonia is then added, which neutralizes the acid and causes essentially all of the calcium in the sample to precipitate as calcium oxalate. The reactions are:



The precipitate is filtered using a weighed filtering crucible, then dried and ignited. The process converts the precipitate entirely to calcium oxide. The reaction is:



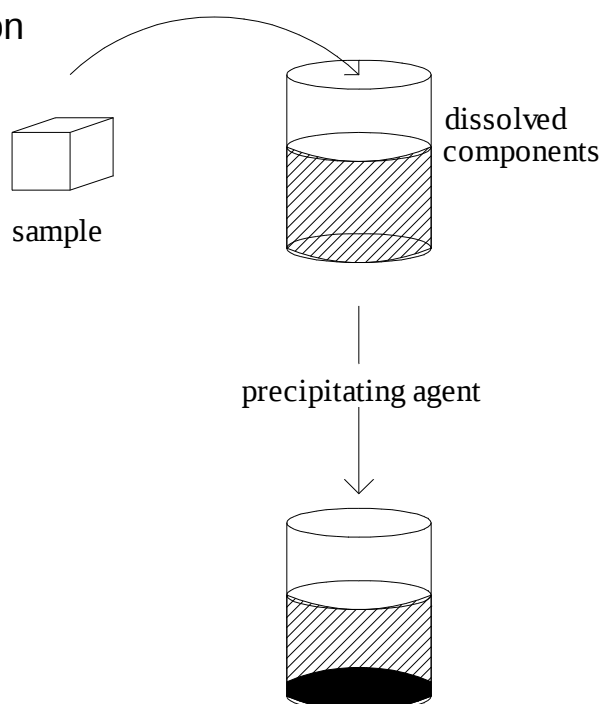
After cooling, the crucible and precipitate are weighed, and the mass of calcium oxide is determined by subtracting the known mass of the crucible. The calcium content of the sample is then computed.

Procedure for gravimetry based on precipitation

What steps are needed?

The steps required in gravimetric analysis, after the sample has been dissolved, can be summarized as follows:

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



Properties of precipitates and precipitating reagents

Ideally, a gravimetric precipitating agent should react specifically or at least selectively with the analyte. Specific reagents, which are rare, react only with a single chemical species. Selective reagents, which are more common, react with a limited number of species. In addition to specificity and selectivity, the ideal precipitating reagent would react with the analyte to give a product that is:

1. Easily filtered 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.

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.

Factors that determine the particle size of precipitates

The particle size of solids formed by precipitation varies enormously. At one extreme are **colloidal suspensions**, whose tiny particles are invisible to the naked eye (10^{-7} – 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 millimeter or greater. The temporary dispersion of such particles of a **crystalline suspension** tend to settle spontaneously and are easily filtered.

Scientists have studied precipitate formation for many years, but the mechanism of the process is still not fully understood. It is certain, however, that the particle size of a precipitate is influenced by such experimental variables 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 supersaturations**, where:

$$\text{relative supersaturations} = \frac{Q - S}{S}$$

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. Experimental evidence indicated that the particle size of a precipitate 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.

High relative supersaturation	many small crystals (high surface area)
Low relative supersaturation	fewer, larger crystals (low surface area)

Obviously, then, we want to keep Q low and S high during precipitation. Several steps are commonly taken to maintain *favorable conditions for precipitation*:

1. Precipitate from dilute solution. This keeps Q low.
2. Add dilute precipitating reagents *slowly*, with effective *stirring*, this also keeps Q low. Stirring prevents local excesses of the reagent.
3. Precipitate from *hot solution*. This increases S. the solubility should not be too great or the precipitation will not be quantitative (with less than 1 part per thousand remaining). The bulk of the precipitation may be performed in the hot solution, and then the solution may be cooled to make the precipitation quantitative.
4. Precipitate at as *low* a pH as is possible to maintain quantitative precipitation. As we have seen, many precipitates are more soluble in acid medium, and this slows the rate of precipitation. They are more soluble because the anion slows the rate of precipitation. They are more soluble because the anion of the precipitate combines with protons in the solution.

Mechanism of Precipitate Formation

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 particles size of a freshly formed precipitate is determined by the mechanism of predominates.

After the addition of the precipitating agent to the solution of the ion under analysis there is an initial **induction period** before nucleation occurs. This induction period may range from a very short time period to one which is relatively long, ranging from almost instantaneous to several minutes.

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 predominated, a smaller number of larger particles is produced.

The rate of nucleation is believed to increase enormously with increasing relative supersaturation. In contrast, the rate of particle growth is only moderately enhanced by high relative supersaturation. Thus, when a precipitate is formed at *high relative supersaturation, nucleation is the major precipitation mechanism, and a large number of small particles is formed. At low relative supersaturation, on the other hand, the rate of particles growth tends to predominate, and deposition of solid in existing particles occurs to the exclusion of further nucleation; a crystalline suspension results.*

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

Individual colloidal particles are so small that they are not retained by ordinary filters. Moreover, Brownian motion prevents their settling out of solution under the influence of gravity. Fortunately, however, we can coagulate, or agglomerate, the individual particles of most colloids to give a filterable, amorphous mass that will settle out of solution.

Coagulation of colloids

Coagulation can be hastened by heating, by stirring, and by adding an electrolyte to the medium. To understand the effectiveness of these measures, we need to look into why colloidal suspensions are stable and do not coagulate spontaneously.

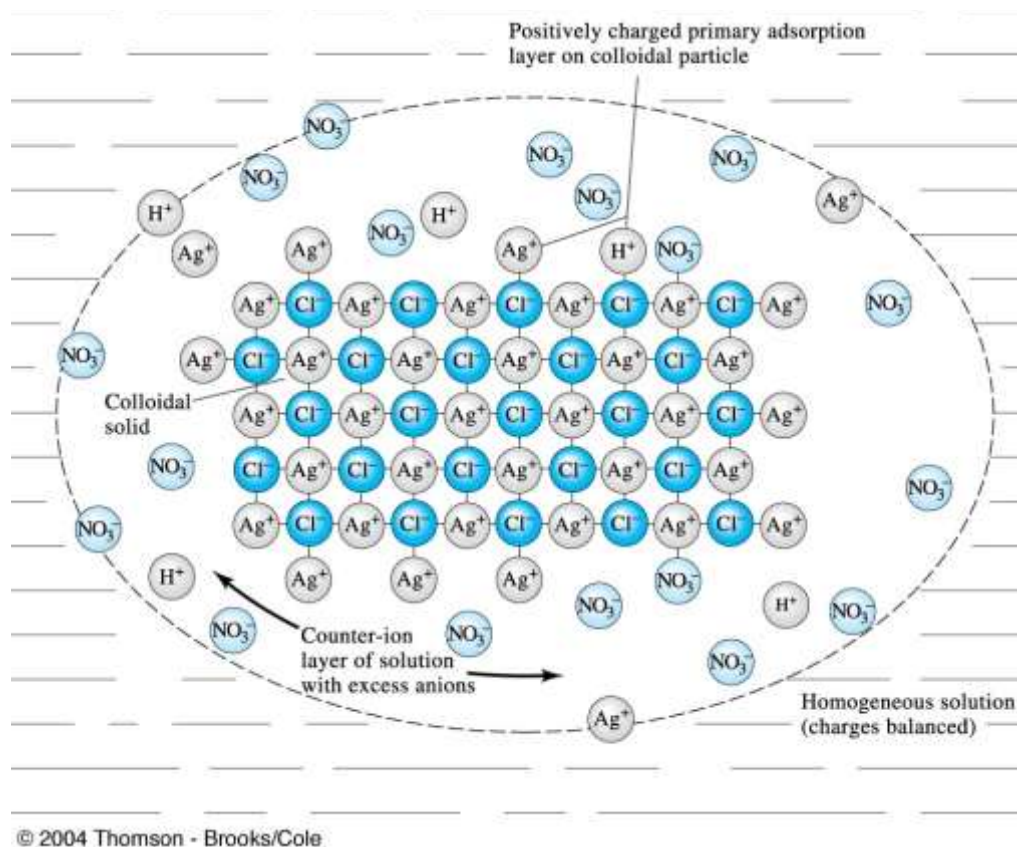
Colloidal suspensions are stable because all of the particles of the colloid are either positively or negatively charged. This charge results from cations or anions that are bound to the surface of the particles. We can easily demonstrate that the colloidal particles are charged by observing their migration when placed in an electrical field. The process by which ions are retained *on the surface of a solid* is known as **adsorption**.

The adsorption of ions on an ionic solid originates from the normal bounding forces that are responsible for crystal growth. For example, a silver ion at the surface of a silver chloride particle has a partially unsatisfied bonding capacity for anions because of its surface location. Negative ions are attracted to this site by the same forces that hold chloride ions in the silver chloride lattice. Chloride ions at the surface of the solid exert an analogous attraction for cations dissolved in the solvent.

The kind of ions retained on the surface of a colloidal particle and their number depend, in a complex way, on several variables. For a suspension produced in the course of a gravimetric analysis, however, the species adsorbed, and hence the charge on the particles, can be easily predicated because lattice ions are generally more strongly held than others. For example, when silver nitrate is first added to a solution containing chloride ion, the colloidal particles of the precipitate are negatively charged as a result of adsorption of some of the excess chloride ions. This charge, however, becomes positive when enough silver nitrate has been added to provide an excess of silver ions. The surface charge is at a minimum when the supernatant liquid contains an excess of neither ion.

The extent of adsorption and thus the charge on a given particle increase rapidly as the concentration of a common ion becomes greater. Eventually, however, the surface of the particles becomes covered with the adsorbed ions, and the charge becomes constant and independent of concentration.

The Figure below shows a colloidal silver chloride particle in a solution that contains an excess of silver nitrate. Attached directly to the solid surface is the **primary adsorption layer**, which consists mainly of adsorbed silver ions. Surrounding the charged particle is a layer of solution called the **counter-ion layer**, which contains sufficient excess of negative ions (principally nitrate) to just balance the charge on the surface of the particle. The primarily adsorbed silver ions and the negative counter-ion layer constitute an **electric double layer** that imparts stability to the colloidal suspension. As colloidal particles approach one another, this double layer exerts an electrostatic repulsive force that prevents particles from colliding and adhering.



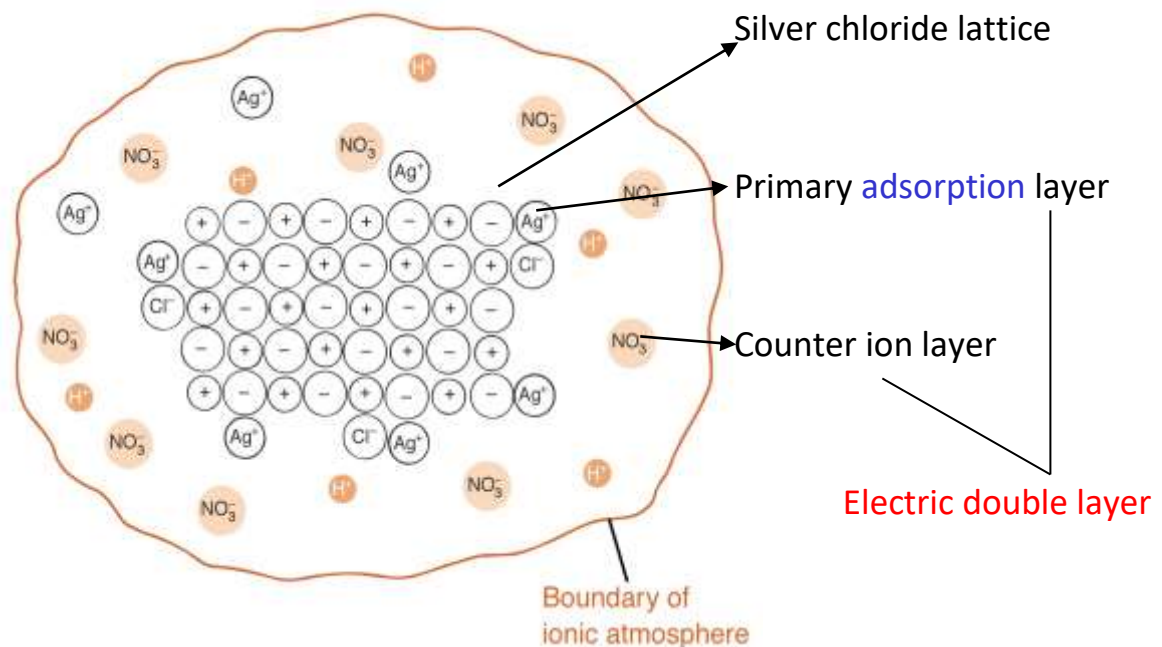
A colloidal silver chloride particle suspended in a solution of silver nitrate.

Coagulation of a colloidal suspension can often be brought

1. by short period of heating heating decreases the number of adsorbed ions and the thickness. The particles may gain enough kinetic energy at the higher temper.

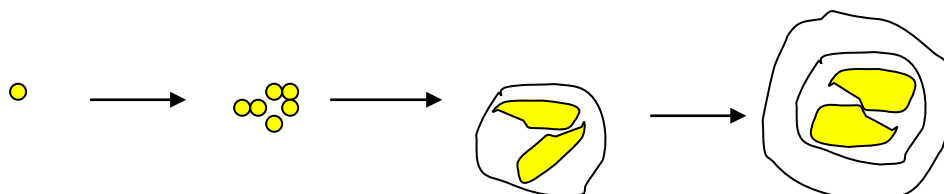
2. Increase the electrolyte concentration of the solution.

If we add ionic compound to a colloidal suspension. The concentration of counter – ions increases in the vicinity of each to balance the charge of the primary adsorption layer decreases. The net effect of adding an electrolyte is thus a shrinkage of the counter-ions layer



We can summarize the precipitation mechanism

- 1) Induction period.
- 2) Nucleation.
- 3) Particle growth to form larger crystal
- 4) Adsorption.
- 5) Electrostatic.



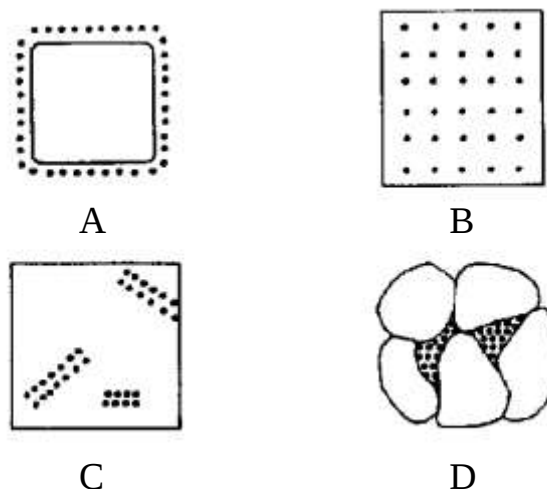
Coprecipitation

Coprecipitation is a phenomenon in which *otherwise soluble* compounds are removed from solution during precipitate formation. It is important to understand that contamination of a precipitate by a second substance whose solubility product has been exceeded does not constitute coprecipitation.

There are four types of coprecipitation:

1. surface adsorption,
2. mixed-crystal formation,
3. occlusion,
4. mechanical entrapment.

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



Types of coprecipitation:

A: surface adsorption

B: inclusion-isomorphic carrying

C: inclusion-mechanical entrapment in crystals

D: occlusion-mechanical entrapment in colloidal aggregate.

1- Surface adsorption

Adsorption is often the major source of contamination in coagulated colloids but is of no significance in crystalline precipitates. The net effect of surface adsorption is therefore the carrying down of an otherwise soluble compound as a surface contaminant.

(1) Minimizing Adsorbed Impurities on Colloids

(A) coagulated colloids is improved by digestion

(B) Washing a coagulated colloid containing a volatile electrolyte.

(2) Reprecipitation : A drastic but effective way to minimize the effects of adsorption is Preprecipitation.

2- Mixed-crystal formation

Mixed-crystal formation ,one of the ions in the crystal lattice of a solid is replaced by an ion of another element. It is necessary that the two ions have the same charge and that their sizes differ by no more than about 5%. The same crystal class.

Ex (Pb ion replace some of the barium ion)

The interfering ion may have to be separated before the final precipitation step.

3- Occlusion

Occlusion is a type of coprecipitation in which a compound is trapped within a pocket formed during rapid crystal growth.

4- Mechanical entrapment

Mechanical entrapment occurs when crystals lie close together during growth. Here, several crystals grow together and in so doing trap a portion of the solution in a tiny pocket.