

## GRAVIMETRIC METHODS OF ANALYSIS

**Gravimetric methods** are quantitative methods that are based on determining the mass of a pure compound to which the analyte is chemically related.

Gravimetric methods of analysis are based on mass measurements with an analytical balance, an instrument that yields highly accurate and precise data.

### **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.

### **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 ( $10^{-7}$  to  $10^{-4}$  cm in

diameter). Colloidal particles show no tendency to settle from solution and are difficult to filter. At the other extreme are particles with dimensions on the order of tenths of a 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 spontaneously and are easily filtered. The particle size of a precipitate is influenced by

- Precipitate solubility
- Temperature
- Reactant concentrations
- The 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 **relative supersaturation**.

$$RSS = (Q-S) / S$$

*Q*: The concentration of the solute at any instant

*S*: 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 indicates 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, and when (Q-S)/S is small, a crystalline solid is more likely.**

### *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 particle size of a freshly formed precipitate is determined by the mechanism that predominates.

In **nucleation**, a few ions, atoms, or molecules (perhaps as few as four or five) come together to form a stable solid. Further precipitation then is governed by the competition between additional nucleation and growth of existing nuclei (particle growth). **If nucleation predominates, a precipitate containing a large number of small particles results, and if growth predominates, a smaller number of larger particles is produced.**

- At **high relative supersaturations**, the rate of **nucleation** tends to predominate.
  - High relative supersaturation produces colloidal suspensions.
- At **low relative supersaturations**, the rate of **particle growth** tends to predominate.
  - Low relative supersaturation produces crystalline suspensions.

### *Experimental Control of Particle Size*

Experimental variables that minimize supersaturation and thus produce crystalline precipitates include

- Elevated temperatures (increase S)
- Dilute solutions (minimize Q)
- Slow addition of the precipitating agent (minimize Q)
- Good stirring (minimize Q)

### **Colloidal Precipitates**

Individual colloidal particles are so small that they are not retained by ordinary filters. 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:** Colloids come together to form a filterable solid

Coagulation can be hastened by heating, by stirring, and by adding an electrolyte to the medium.

Colloidal suspensions are stable because all of the particles of the colloid are either positively or negatively charged and thus repel one another. The charge results from cations or anions that are bound to the surface of the particles. The process by which ions are retained *on the surface of a solid* is known as **adsorption**.

- **Adsorption** is a process in which a substance (gas, liquid, or solid) is held on the surface of a solid.
- **Absorption** is retention of a substance within the pores of a solid.

Figure 1 shows a colloidal barium sulfate particle in a solution that contains an excess of  $\text{BaCl}_2$ .

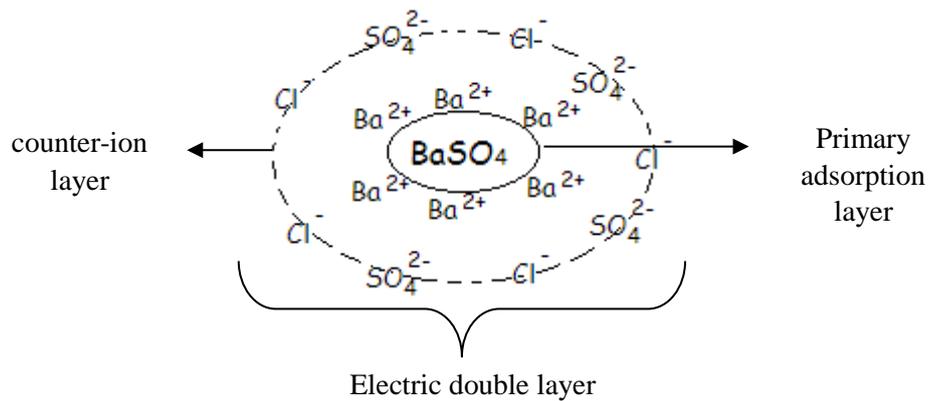


Figure 1

Attached directly to the solid surface is the **primary adsorption layer**, which consists mainly of adsorbed barium ions. Surrounding the charged particle is a layer of solution, called the **counter-ion layer**, which contains sufficient excess of negative ions to just balance the charge on the surface of the particle. The primarily adsorbed barium 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.
- Coagulation of a colloidal suspension can often be brought about by a short period of heating, particularly if accompanied by stirring.
- Heating decreases the number of adsorbed ions and the thickness of the double layer. The particles may also gain enough kinetic energy at the higher temperature to overcome the barrier to close approach imposed by the double layer.

An even more effective way to coagulate a colloid is to increase the electrolyte concentration of the solution. If we add a suitable ionic compound to a colloidal suspension, the concentration of counter-ions increases in the vicinity of each particle. As a result, the volume of solution that contains sufficient counter-ions to balance the charge of the primary adsorption layer decreases. The net effect of adding an electrolyte is thus a shrinkage of the counter-ion layer. The particles can then approach one another more closely and agglomerate.

### ***Peptization of Colloids***

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

Washing the precipitate with pure water causes peptization. The problem is usually solved by washing the precipitate with a solution containing an electrolyte that volatilizes when the precipitate is dried or ignited.

### ***Practical Treatment of Colloidal Precipitates***

Colloids are best precipitated from hot, stirred solutions containing sufficient electrolyte to ensure coagulation.

**Digestion** is a process in which a precipitate is heated in the solution from which it was formed (the mother liquor) and allowed to stand in contact with the solution.

During this process, weakly bound water appears to be lost from the precipitate. The result is a denser mass that is easier to filter.

### **Coprecipitation**

**Coprecipitation** is a process in which normally soluble compounds are carried out of solution by a precipitate. There are four types of coprecipitation;

1. Surface adsorption
2. Mixed-crystal formation
3. Occlusion
4. Mechanical entrapment

**Surface Adsorption:** A normally soluble compound is carried out of solution on the surface of a coagulated colloid. This compound consists of the primarily adsorbed ion and an ion of opposite charge from the counter-ion layer. For example, the coagulated barium sulfate formed in the gravimetric determination of barium ion is contaminated with primarily adsorbed barium ions with chloride or other anions in the counter-ion layer. The result is that barium chloride, a normally soluble compound, is coprecipitated with the barium sulfate.

Minimizing Adsorbed Impurities on Colloids:

- Digestion
- Washing a coagulated colloid with a solution containing a volatile electrolyte
- Reprecipitation

**Mixed-Crystal Formation:** A type of coprecipitation in which a contaminant ion replaces an ion in the lattice of a crystal.

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

**Mechanical Entrapment:** A type of coprecipitation which occurs when crystals lie close together during growth. Several crystals grow together and in so doing trap a portion of the solution in a tiny pocket.

### **Precipitation from Homogeneous Solution**

**Homogeneous precipitation** is a process in which a precipitate is formed by slow generation of a precipitating reagent homogeneously throughout a solution.

Solids formed by homogeneous precipitation are generally purer and more easily filtered than precipitates generated by direct addition of a reagent to the analyte solution.

### **Drying and Ignition of Precipitates**

After filtration, a gravimetric precipitate is heated until its mass becomes constant. Heating removes the solvent and any volatile species carried down with the precipitate. Some precipitates are also ignited to decompose the solid and form a compound of known composition. This new compound is often called the **weighing form**.

## **Equipment and Manipulations Associated with Weighing**

The mass of many solids changes with humidity because they tend to absorb weighable amounts of moisture. In the first step in a typical analysis, then, the sample is dried so that the results will not be affected by the humidity of the surrounding atmosphere.

A sample, a precipitate, or a container is brought to **constant mass** by a cycle of heating (usually for one hour or more) at an appropriate temperature, cooling and weighing. This cycle is repeated as many times as needed to obtain successive masses that agree within 0.2 to 0.3 mg of one another.

### **Desiccators and Desiccants**

To minimize the uptake of moisture, dried materials are stored in **desiccators** while they cool.

The base section contains a chemical drying agent, such as anhydrous calcium chloride, calcium sulfate (Drierite), anhydrous magnesium perchlorate (Anhydron or Dehydrite), or phosphorus pentoxide.

- When removing or replacing the lid of a desiccator, use a sliding motion to minimize the likelihood of disturbing the sample.
- Hot materials should not be put directly into the desiccator.
- When placing a heated object in a desiccator, the cooling of heated objects can cause a partial vacuum to develop. It is helpful to break the seal once or twice during cooling to relieve any excessive vacuum that develops.
- The lid must never be left completely open.
- Lock the lid in place with your thumbs while moving the desiccator from one place to another.

## **Filtration and Ignition of Solids**

### ***Simple Crucibles***

Simple crucibles serve only as containers. Porcelain, aluminum oxide, silica, and platinum crucibles maintain constant mass—within the limits of experimental error—and are used principally to convert a precipitate into a suitable weighing form. The solid is first collected on a filter paper. The filter and contents are then transferred to a weighed crucible, and the paper is ignited.

### ***Filtering Precipitates***

The steps in filtering an analytical precipitate are **decantation, washing** and **transfer**.

In decantation, as much supernatant liquid as possible is passed through the filter while the precipitated solid is kept essentially undisturbed in the beaker where it was formed. This procedure speeds the overall filtration rate by delaying the time at which the pores of the filtering medium become clogged with precipitate. A stirring rod is used to direct the flow of the decanted liquid.

Filters are never filled to more than three quarters of capacity to prevent the possible loss of precipitate.

## Experimental Procedure

- Dilute the samples to 100 mL with distilled water.
- Heat the solutions in the water bath for ~5 minutes.
- The diluted  $\text{H}_2\text{SO}_4$  solution is added dropwise (~2 mL) to the warmed solution until the precipitation is complete. When this is done, the solution should be mixed continuously to minimize RSS.
- After the precipitation is complete, the solutions are placed in the water bath with a stirring rod and 10 minutes later 2-3 drops of diluted  $\text{H}_2\text{SO}_4$  solution is added to the solution to check that the settling is definitely complete.
- If the precipitation is complete, the solutions are left to digestion in the water bath for a total of 1 hour.
- After the digestion is completed, the blue band filter paper is used to separate the  $\text{BaSO}_4$  precipitate. Filtration should be done while the solution is warm.
- The inside of the beaker and the precipitate can be washed with diluted HCl solution. The solution prepared by diluting 1:10 of the precipitating reagent can also be used as the washing solution.
- Add 10 drops of diluted  $\text{H}_2\text{SO}_4$  solution on the remaining filtrate and let it stay in the hot water bath for 5 minutes and check last time whether the precipitation is complete or not.
- The filter paper is folded and placed between 2 watch glasses and allowed to dry.
- The dried filter paper is burnt in a crucible that is brought to constant mass. At first, the burner must be very low and the flame must be close to the mouth of the crucible. After 5-10 minutes the flame can be increased a bit and shifted to the center of the crucible. During the burning, the crucibles should be turned at regular intervals with the tweezers. The pens must be cleaned and heated in the flame.
- This process continues until the filter paper is completely ignited and the inside of the crucible turns to white.
- The crucibles are placed in a  $600^\circ\text{C}$  oven for half an hour, cooled for half an hour and weighed. This is done 2 times.

(Ba: 137.327 g/mol,  $\text{BaSO}_4$ : 233.390 g/mol)