

## Lecture - 13

### Gravimetric Methods of Analysis

#### 13.1.1 Using Mass as an Analytical Signal

Suppose you are to determine the total suspended solids in the water released by a sewage-treatment facility. Suspended solids are just that—solid matter that has yet to settle out of its solution matrix. The analysis is easy. After collecting a sample, you pass it through a preweighed filter that retains the suspended solids, and dry the filter and solids to remove any residual moisture. The mass of suspended solids is the difference between the filter's final mass and its original mass. We call this a **direct analysis** because the analyte—the suspended solids in this example—is the species that is weighed.

**Note :** Method 2540D in *Standard Methods for the Examination of Waters and Wastewaters*, 20th Edition (American Public Health Association, 1998) provides an approved method for determining total suspended solids. The method uses a glass-fiber filter to retain the suspended solids. After filtering the sample, the filter is dried to a constant weight at 103–105°C

What if our analyte is an aqueous ion, such as  $\text{Pb}^{2+}$ ? Because the analyte is not a solid, we cannot isolate it by filtration. We can still measure the analyte's mass directly if we first convert it into a solid form. If we suspend a pair of Pt electrodes in the sample and apply a sufficiently positive potential between them for a long enough time, we can force the following reaction to completion.



Oxidizing  $\text{Pb}^{2+}$  deposits  $\text{PbO}_2$  on the Pt anode. If we weigh the anode before and after applying the potential, the change in its mass gives the mass of  $\text{PbO}_2$  and, from the reaction's stoichiometry, the amount of  $\text{Pb}^{2+}$  in the sample. This is a direct analysis because  $\text{PbO}_2$  contains the analyte.

Sometimes it is easier to remove the analyte and let a change in mass serve as the analytical signal. Suppose you need to determine a food's moisture content. One approach is to heat a sample of the food to a temperature that vaporizes the water, capturing it in a preweighed absorbent trap. The change in the absorbent's mass provides a direct determination of the amount of water in the sample. An easier approach is to weigh the sample of food before and after heating, using the change in its mass as an indication of the amount of water originally present. We call this an **indirect analysis** because we determine the analyte using a signal that is proportional its disappearance.

**Note:** Method 925.10 in *Official Methods of Analysis*, 18th Edition (AOAC International, 2007) provides an approved method for determining the moisture content of flour. A preweighed sample is heated for one hour in a 130°C oven and transferred to a desiccator while it cools to room temperature. The loss in mass gives the amount of water in the sample.

### 13.1.2 Types of Gravimetric Methods

In the previous section we used four examples to illustrate the different ways that mass can serve as an analytical signal. These examples also illustrate the four gravimetric methods of analysis.

- 1- When the signal is the mass of a precipitate, we call the method **precipitation gravimetry**. The indirect determination of  $\text{PO}_3^{3-}$  by precipitating  $\text{Hg}_2\text{Cl}_2$  is a representative example, as is the direct determination of  $\text{Cl}^-$  by precipitating  $\text{AgCl}$ .
- 2- In **electrogravimetry** the analyte is deposited as a solid film on one electrode in an electrochemical cell. The oxidation of  $\text{Pb}^{2+}$ , and its deposition as  $\text{PbO}_2$  on a Pt anode is one example of electrogravimetry. Reduction also may be used in electrogravimetry. The electrodeposition of Cu on a Pt cathode, for example, provides a direct analysis for  $\text{Cu}^{2+}$ .
- 3- When thermal or chemical energy is used to remove a volatile species, we call the method **volatilization gravimetry**. In determining the moisture content of food, thermal energy vaporizes the  $\text{H}_2\text{O}$ . The amount of carbon in an organic compound may be determined by using the chemical energy of combustion to convert C to  $\text{CO}_2$ .
- 4- Finally, in **particulate gravimetry** the analyte is determined following its removal from the sample matrix by filtration or extraction. The determination of suspended solids is one example of particulate gravimetry.

### 13.1.3 Conservation of Mass

An accurate gravimetric analysis requires that the analytical signal—whether it is a mass or a change in mass—be proportional to the amount of analyte in our sample. For all gravimetric methods this proportionality involves a **conservation of mass**. If the method relies on one or more chemical reactions, then the stoichiometry of the reactions must be known. Thus, for the analysis of  $\text{PO}_3^{3-}$  described earlier, we know that each mole of  $\text{Hg}_2\text{Cl}_2$  corresponds to a mole of  $\text{PO}_3^{3-}$  in our sample. If we remove the analyte from its matrix, then the separation must be selective for the analyte. When determining the moisture content in bread, for example, we know that the mass of  $\text{H}_2\text{O}$  in the bread is the difference between the sample's final mass and its initial mass.

**Note** : We will return to this concept of applying a conservation of mass later in the chapter when we consider specific examples of gravimetric methods.

### 13.1.4 Why Gravimetry is Important

Except for particulate gravimetry, which is the most trivial form of gravimetry, you probably will not use gravimetry after you complete this course. Why, then, is familiarity with gravimetry still important? The answer is that gravimetry is one of only a small number of **definitive techniques** whose measurements require only base SI units, such as mass or the mole, and defined constants, such as Avogadro's number and the mass of  $^{12}\text{C}$ . Ultimately, we must be able to trace the result of an analysis to a definitive technique, such as gravimetry, that we can relate to fundamental physical properties.<sup>2</sup> Although most analysts never use gravimetry to validate their results, they often verify an analytical method by analyzing a standard reference material whose composition is traceable to a definitive technique.

**Note** : Other examples of definitive techniques are coulometry and isotope-dilution mass spectrometry. Coulometry is discussed in Chapter 11. Isotope-dilution mass spectrometry is beyond the scope of an introductory textbook; however, you will find some suggested readings in this chapter's Additional Resources.

## 13.2: Precipitation Gravimetry

In precipitation gravimetry an insoluble compound forms when we add a precipitating reagent, or **precipitant**, to a solution containing our analyte. In most methods the precipitate is the product of a simple metathesis reaction between the analyte and the precipitant; however, any reaction generating a precipitate can potentially serve as a gravimetric method.

### 13.2.1 Theory and Practice

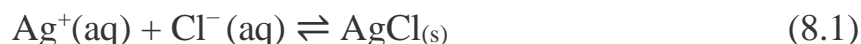
All precipitation gravimetric analysis share two important attributes. First, the precipitate must be of low solubility, of high purity, and of known composition if its mass is to accurately reflect the analyte's mass. Second, the precipitate must be easy to separate from the reaction mixture.

#### Solubility Considerations

To provide accurate results, a precipitate's solubility must be minimal. The accuracy of a total analysis technique typically is better than  $\pm 0.1\%$ , which means that the precipitate must account for at least 99.9% of the analyte. Extending this requirement to 99.99% ensures that the precipitate's solubility does not limit the accuracy of a gravimetric analysis.

**Note** : A total analysis technique is one in which the analytical signal—mass in this case—is proportional to the absolute amount of analyte in the sample.

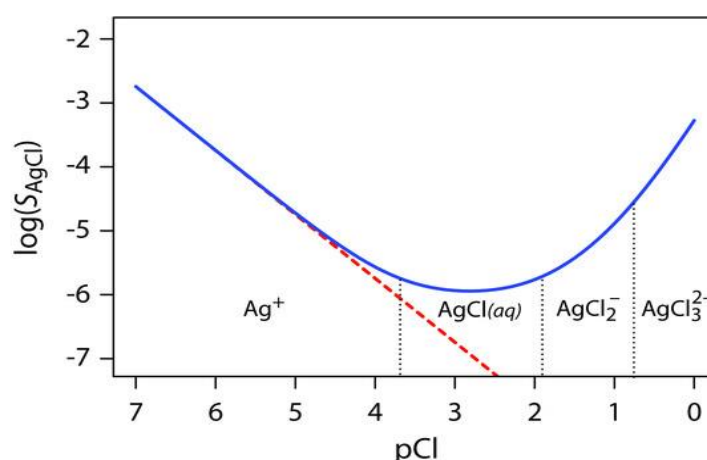
We can minimize solubility losses by carefully controlling the conditions under which the precipitate forms. This, in turn, requires that we account for every equilibrium reaction affecting the precipitate's solubility. For example, we can determine  $\text{Ag}^+$  gravimetrically by adding  $\text{NaCl}$  as a precipitant, forming a precipitate of  $\text{AgCl}$ .



If this is the only reaction we consider, then we predict that the precipitate's

$$S_{\text{AgCl}} = [\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} \quad (8.2)$$

Equation 8.2 suggests that we can minimize solubility losses by adding a large excess of  $\text{Cl}^-$ . In fact, as shown in Figure 8.1, adding a large excess of  $\text{Cl}^-$  increases the precipitate's solubility.



**Figure 13.1** Solubility of  $\text{AgCl}$  as a function of  $\text{pCl}$ . The dashed red line shows our prediction for  $S_{\text{AgCl}}$  if we incorrectly assume that only reaction 8.1 and equation 8.2 affect silver chloride's solubility. The solid blue curve is calculated using equation 8.7, which accounts for reaction 8.1 and reactions 8.3–8.5. Because the solubility of  $\text{AgCl}$  spans several orders of magnitude,  $S_{\text{AgCl}}$  is displayed on the y-axis in logarithmic form.

To understand why the solubility of  $\text{AgCl}$  is more complicated than the relationship suggested by equation 8.2, we must recognize that  $\text{Ag}^+$  also forms a series of soluble silver-chloro metal–ligand complexes.



The actual solubility of  $\text{AgCl}$  is the sum of the equilibrium concentrations for all soluble forms of  $\text{Ag}^+$ , as shown by the following equation.

$$S_{\text{AgCl}} = [\text{Ag}^+] + [\text{AgCl}(\text{aq})] + [\text{AgCl}_2^-] + [\text{AgCl}_3^{2-}] \quad (8.6)$$

By substituting into equation 8.6 the equilibrium constant expressions for reaction 8.1 and reactions 8.3–8.5, we can define the solubility of AgCl as

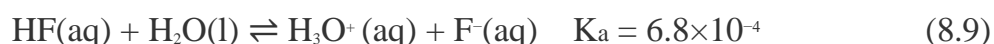
$$S_{\text{AgCl}} = \frac{K_{\text{sp}}}{[\text{Cl}^-]} + K_1K_{\text{sp}} + K_1K_2K_{\text{sp}}[\text{Cl}^-] + K_1K_2K_3K_{\text{sp}}[\text{Cl}^-]^2 \quad (8.7)$$

**Note :** Problem 1 in the end-of-chapter problems asks you to show that equation 8.7 is correct by completing the derivation.

Equation 8.7 explains the solubility curve for AgCl shown in Figure 8.1. As we add NaCl to a solution of Ag<sup>+</sup>, the solubility of AgCl initially decreases because of reaction 8.1. Under these conditions, the final three terms in equation 8.7 are small and equation 8.1 is sufficient to describe AgCl's solubility. At higher concentrations of Cl<sup>-</sup>, reaction 8.4 and reaction 8.5 increase the solubility of AgCl. Clearly the equilibrium concentration of chloride is important if we want to determine the concentration of silver by precipitating AgCl. In particular, we must avoid a large excess of chloride.

**Note :** The predominate silver-chloro complexes for different values of pCl are shown by the ladder diagram along the x-axis in Figure 8.1 Note that the increase in solubility begins when the higher-order soluble complexes, AgCl<sub>2</sub><sup>-</sup> and AgCl<sub>3</sub><sup>2-</sup>, become the predominate species.

Another important parameter that may affect a precipitate's solubility is pH. For example, a hydroxide precipitates such as Fe(OH)<sub>3</sub> is more soluble at lower pH levels where the concentration of OH<sup>-</sup> is small. Because fluoride is a weak base, the solubility of calcium fluoride, S<sub>CaF<sub>2</sub></sub>, also is pH-dependent. We can derive an equation for S<sub>CaF<sub>2</sub></sub> by considering the following equilibrium reactions



and the following equation for the solubility of CaF<sub>2</sub>.

$$S_{\text{CaF}_2} = [\text{Ca}^{2+}] = \frac{1}{2} \{[\text{F}^{-}] + [\text{HF}]\} \quad (8.10)$$

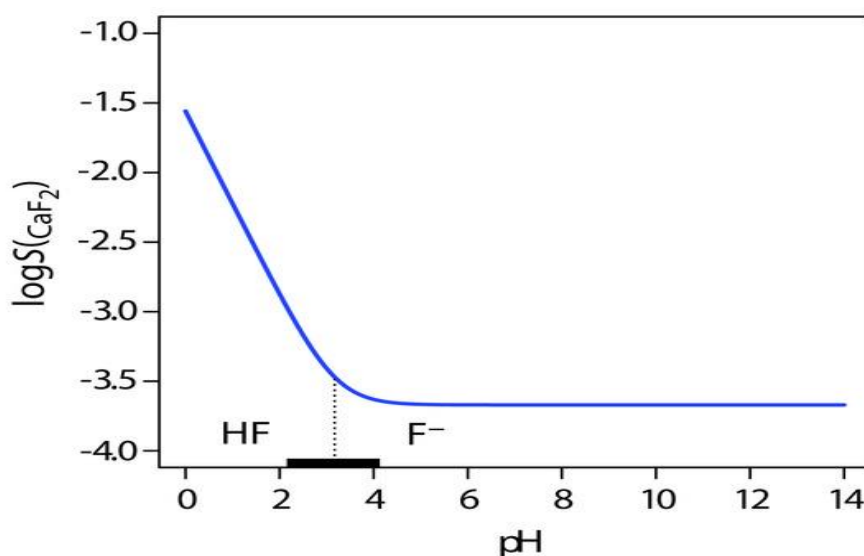
**Note :** Be sure that equation 8.10 makes sense to you. Reaction 8.8 tells us that the dissolution of CaF<sub>2</sub> produces one mole of Ca<sup>2+</sup> for every two moles of F<sup>-</sup>, which explains the term of 1/2 in equation 8.10. Because F<sup>-</sup> is a weak base, we need to account for both of its chemical forms in solution, which explains why we include HF.

Substituting the equilibrium constant expressions for reaction 8.8 and reaction 8.9 into equation 8.10 defines the solubility of CaF<sub>2</sub> in terms of the equilibrium concentration of H<sub>3</sub>O<sup>+</sup>.

$$S_{\text{CaF}_2} = [\text{Ca}^{2+}] = \left\{ \frac{K_{\text{sp}}}{4} \left( 1 + \frac{[\text{H}_3\text{O}^+]}{K_a} \right)^2 \right\}^{1/3} \quad (8.11)$$

**Note :** Problem 4 in the end-of-chapter problems asks you to show that equation 8.11 is correct by completing the derivation.

Figure 8.2 shows how pH affects the solubility of CaF<sub>2</sub>. Depending on the solution's pH, the predominate form of fluoride is either HF or F<sup>-</sup>. When the pH is greater than 4.17, the predominate species is F<sup>-</sup> and the solubility of CaF<sub>2</sub> is independent of pH because only reaction 8.8 occurs to an appreciable extent. At more acidic pH levels, the solubility of CaF<sub>2</sub> increases because of the contribution of reaction 8.9.



**Figure 13.2** Solubility of CaF<sub>2</sub> as a function of pH. The solid blue curve is a plot of equation 8.11. The predominate form of fluoride in solution is shown by the ladder diagram along the x-axis, with the black rectangle showing the region where both HF and F<sup>-</sup> are important species. Note that the solubility of CaF<sub>2</sub> is independent of pH for pH levels greater than 4.17, and that its solubility increases dramatically at lower pH levels where HF is the predominate species. Because the solubility of CaF<sub>2</sub> spans several orders of magnitude, its solubility is shown in logarithmic form.

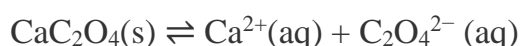
When solubility is a concern, it may be possible to decrease solubility by using a non-aqueous solvent. A precipitate's solubility is generally greater in an aqueous solution because of water's ability to stabilize ions through solvation. The poorer solvating ability of non-aqueous solvents, even those which are polar, leads to a smaller solubility product. For example, the  $K_{\text{sp}}$  of PbSO<sub>4</sub> is  $2 \times 10^{-8}$  in H<sub>2</sub>O and  $2.6 \times 10^{-12}$  in a 50:50 mixture of H<sub>2</sub>O and ethanol.

### Practice Exercise 13.1

You can use a ladder diagram to predict the conditions for minimizing a precipitate's solubility. Draw a ladder diagram for oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , and use it to establish a suitable range of pH values for minimizing the solubility of  $\text{CaC}_2\text{O}_4$ . Relevant equilibrium constants may be found in the appendices.

### Solution

The solubility reaction for  $\text{CaC}_2\text{O}_4$  is



To minimize solubility, the pH needs to be basic enough that oxalate,  $\text{C}_2\text{O}_4^{2-}$ , does not react to form  $\text{HC}_2\text{O}_4^-$  or  $\text{H}_2\text{C}_2\text{O}_4$ . The ladder diagram for oxalic acid, including approximate buffer ranges, is shown in Figure 8.17. Maintaining a pH greater than 5.3 ensures that  $\text{C}_2\text{O}_4^{2-}$  is the only important form of oxalic acid in solution, minimizing the solubility of  $\text{CaC}_2\text{O}_4$ .

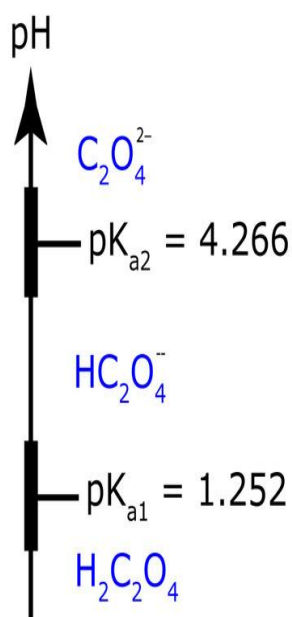
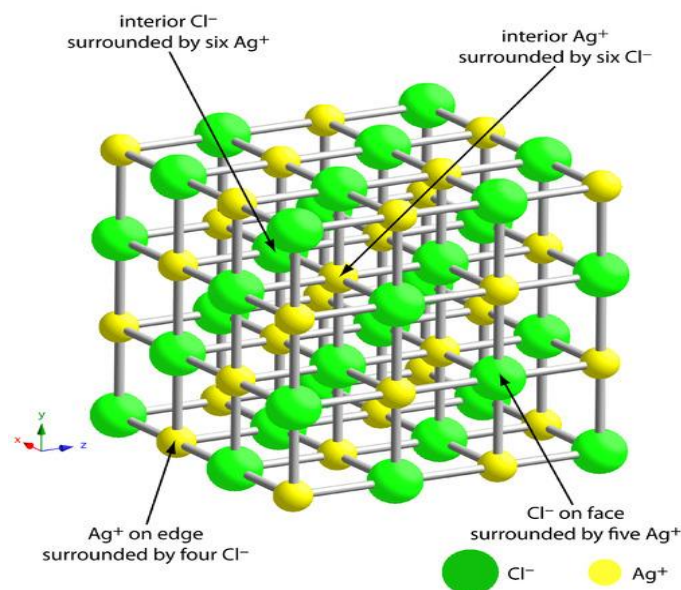


Figure 13.17 pH ladder diagram for oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ .

### Avoiding Impurities

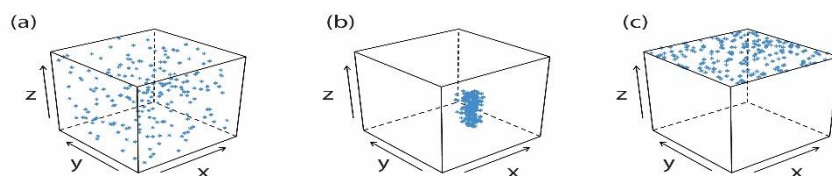
In addition to having a low solubility, the precipitate must be free from impurities. Because precipitation usually occurs in a solution that is rich in dissolved solids, the initial precipitate is often impure. We must remove these impurities before determining the precipitate's mass.

The greatest source of impurities is the result of chemical and physical interactions occurring at the precipitate's surface. A precipitate is generally crystalline—even if only on a microscopic scale—with a well-defined lattice of cations and anions. Those cations and anions at the precipitate's surface carry, respectively, a positive or a negative charge because they have incomplete coordination spheres. In a precipitate of AgCl, for example, each silver ion in the precipitate's interior is bound to six chloride ions. A silver ion at the surface, however, is bound to no more than five chloride ions and carries a partial positive charge (Figure 8.3). The presence of these partial charges makes the precipitate's surface an active site for the chemical and physical interactions that produce impurities.



**Figure 13.3** Ball-and-stick diagram showing the lattice structure of AgCl. Each silver ion in the lattice's interior binds with six chloride ions, and each chloride ion in the interior binds with six silver ions. Those ions on the lattice's surface or edges bind to fewer than six ions and carry a partial charge. A silver ion on the surface, for example, carries a partial positive charge. These charges make the surface of a precipitate an active site for chemical and physical interactions.

One common impurity is an **inclusion**. A potential interfering ion whose size and charge is similar to a lattice ion, may substitute into the lattice structure, provided that the interferent precipitates with the same crystal structure (Figure 8.4a). The probability of forming an inclusion is greatest when the concentration of the interfering ion is substantially greater than the lattice ion's concentration. An inclusion does not decrease the amount of analyte that precipitates, provided that the precipitant is present in sufficient excess. Thus, the precipitate's mass is always larger than expected.





**Figure 13.4** Three examples of impurities that may form during precipitation. The cubic frame represents the precipitate and the blue marks are impurities: (a) inclusions, (b) occlusions, and (c) surface adsorbates. Inclusions are randomly distributed throughout the precipitate. Occlusions are localized within the interior of the precipitate and surface adsorbates are localized on the precipitate's exterior. For ease of viewing, in (c) adsorption is shown on only one surface.

An inclusion is difficult to remove since it is chemically part of the precipitate's lattice. The only way to remove an inclusion is through **reprecipitation**. After isolating the precipitate from its supernatant solution, we dissolve it by heating in a small portion of a suitable solvent. We then allow the solution to cool, reforming the precipitate. Because the interferent's concentration is less than that in the original solution, the amount of included material is smaller. We can repeat the process of reprecipitation until the inclusion's mass is insignificant. The loss of analyte during reprecipitation, however, can be a significant source of error.

**Note :** Suppose that 10% of an interferent forms an inclusion during each precipitation. When we initially form the precipitate, 10% of the original interferent is present as an inclusion. After the first reprecipitation, 10% of the included interferent remains, which is 1% of the original interferent. A second reprecipitation decreases the interferent to 0.1% of the original amount.

**Occlusions** form when interfering ions become trapped within the growing precipitate. Unlike inclusions, which are randomly dispersed within the precipitate, an occlusion is localized, either along flaws within the precipitate's lattice structure or within aggregates of individual precipitate particles (Figure 8.4b). An occlusion usually increases a precipitate's mass; however, the mass is smaller if the occlusion includes the analyte in a lower molecular weight form than that of the precipitate.

We can minimize occlusions by maintaining the precipitate in equilibrium with its supernatant solution for an extended time. This process is called a **digestion**. During digestion, the dynamic nature of the solubility–precipitation equilibrium, in which the precipitate dissolves and reforms, ensures that the occlusion is reexposed to the supernatant solution. Because the rates of dissolution and reprecipitation are slow, there is less opportunity for forming new occlusions.

After precipitation is complete the surface continues to attract ions from solution (Figure 8.4c). These **surface adsorbates** comprise a third type of impurity. We can minimize surface adsorption by decreasing the precipitate's available surface area. One benefit of digesting a precipitate is that it increases the average particle size. Because the probability of a particle completely dissolving is inversely proportional to its size, during digestion larger particles increase in size at the expense of smaller particles. One consequence of forming a smaller number of larger particles is an overall decrease in the precipitate's surface area. We also can remove surface adsorbates by washing the precipitate, although the potential loss of analyte can not be ignored.

**Inclusions, occlusions, and surface adsorbates** are examples of **coprecipitates**—otherwise soluble forms an independent precipitate under the conditions of the analysis. For example, the species that form within the precipitate

containing the analyte. Another type of impurity is an interferent that precipitation of nickel dimethylglyoxime requires a slightly basic pH. Under these conditions, any  $\text{Fe}^{3+}$  in the sample precipitates as  $\text{Fe}(\text{OH})_3$ . In addition, because most precipitants are rarely selective toward a single analyte, there is always a risk that the precipitant will react with both the analyte and an interferent.

**Note** : In addition to forming a precipitate with  $\text{Ni}^{2+}$ , dimethylglyoxime also forms precipitates with  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$ . These cations are potential interferents in an analysis for nickel.

We can minimize the formation of additional precipitates by carefully controlling solution conditions. If an interferent forms a precipitate that is less soluble than the analyte's precipitate, we can precipitate the interferent and remove it by filtration, leaving the analyte behind in solution. Alternatively, we can mask the analyte or the interferent to prevent its precipitation.

Both of the above-mentioned approaches are illustrated in Fresenius' analytical method for determining Ni in ores containing  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$  (see Figure 1.1). Dissolving the ore in the presence of  $\text{H}_2\text{SO}_4$  selectively precipitates  $\text{Pb}^{2+}$  as  $\text{PbSO}_4$ . Treating the supernatant with  $\text{H}_2\text{S}$  precipitates the  $\text{Cu}^{2+}$  as  $\text{CuS}$ . After removing the  $\text{CuS}$  by filtration, adding ammonia precipitates  $\text{Fe}^{3+}$  as  $\text{Fe}(\text{OH})_3$ . Nickel, which forms a soluble amine complex, remains in solution.

### Controlling Particle Size

Size matters when it comes to forming a precipitate. Larger particles are easier to filter, and, as noted earlier, a smaller surface area means there is less opportunity for surface adsorbates to form. By carefully controlling the reaction conditions we can significantly increase a precipitate's average particle size.

Precipitation consists of two distinct events: nucleation, the initial formation of smaller stable particles of precipitate, and particle growth. Larger particles form when the rate of particle growth exceeds the rate of nucleation. Understanding the conditions favoring particle growth is important when designing a gravimetric method of analysis.

We define a solute's **relative supersaturation**,  $RSS$ , as

$$RSS = \frac{Q - S}{S} \quad 8.12$$

where  $Q$  is the solute's actual concentration and  $S$  is the solute's concentration at equilibrium.<sup>4</sup> The numerator of equation 8.12,  $Q - S$ , is a measure of the solute's supersaturation. A solution with a large, positive value of  $RSS$  has a high rate of nucleation, producing a precipitate with many small particles. When the  $RSS$  is small, precipitation is more likely to occur by particle growth than by nucleation.

**Note** : A supersaturated solution is one that contains more dissolved solute than that predicted by equilibrium chemistry. The solution is inherently unstable and

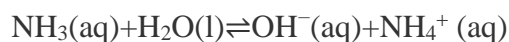
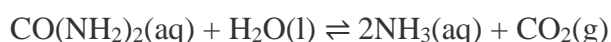
precipitates solute to reach its equilibrium position. How quickly this process occurs depends, in part, on the value of  $RSS$ .

Examining equation 8.12 shows that we can minimize  $RSS$  by decreasing the solute's concentration,  $Q$ , or by increasing the precipitate's solubility,  $S$ . A precipitate's solubility usually increases at higher temperatures, and adjusting pH may affect a precipitate's solubility if it contains an acidic or a basic ion. Temperature and pH, therefore, are useful ways to increase the value of  $S$ . Conducting the precipitation in a dilute solution of analyte, or adding the precipitant slowly and with vigorous stirring are ways to decrease the value of  $Q$ .

There are practical limitations to minimizing  $RSS$ . Some precipitates, such as  $Fe(OH)_3$  and  $PbS$ , are so insoluble that  $S$  is very small and a large  $RSS$  is unavoidable. Such solutes inevitably form small particles. In addition, conditions favoring a small  $RSS$  may lead to a relatively stable supersaturated solution that requires a long time to fully precipitate. For example, almost a month is required to form a visible precipitate of  $BaSO_4$  under conditions in which the initial  $RSS$  is 5.

A visible precipitate takes longer to form when  $RSS$  is small both because there is a slow rate of nucleation and because there is a steady decrease in  $RSS$  as the precipitate forms. One solution to the latter problem is to generate the precipitant in situ as the product of a slow chemical reaction. This maintains the  $RSS$  at an effectively constant level. Because the precipitate forms under conditions of low  $RSS$ , initial nucleation produces a small number of particles. As additional precipitant forms, particle growth supersedes nucleation, resulting in larger precipitate particles. This process is called **homogeneous precipitation**.

Two general methods are used for homogeneous precipitation. If the precipitate's solubility is pH-dependent, then we can mix the analyte and the precipitant under conditions where precipitation does not occur, and then increase or decrease the pH by chemically generating  $OH^-$  or  $H_3O^+$ . For example, the hydrolysis of urea is a source of  $OH^-$ .



Because the hydrolysis of urea is temperature-dependent—it is negligible at room temperature—we can use temperature to control the rate of hydrolysis and the rate of precipitate formation. Precipitates of  $CaC_2O_4$ , for example, have been produced by this method. After dissolving the sample containing  $Ca^{2+}$ , the solution is made acidic with HCl before adding a solution of 5% w/v  $(NH_4)_2C_2O_4$ . Because the solution is acidic, a precipitate of  $CaC_2O_4$  does not form. The solution is heated to approximately 50°C and urea is added. After several minutes, a precipitate of  $CaC_2O_4$  begins to form, with precipitation reaching completion in about 30 min.

In the second method of homogeneous precipitation, the precipitant is generated by a chemical reaction. For example,  $Pb^{2+}$  is precipitated homogeneously as  $PbCrO_4$  by using bromate,  $BrO_3^-$ , to oxidize  $Cr^{3+}$  to  $CrO_4^{2-}$ .

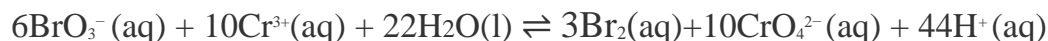


Figure 8.5 shows the result of preparing  $\text{PbCrO}_4$  by the direct addition of  $\text{KCrO}_4$  (Beaker A) and by homogenous precipitation (Beaker B). Both beakers contain the same amount of  $\text{PbCrO}_4$ . Because the direct addition of  $\text{KCrO}_4$  leads to rapid precipitation and the formation of smaller particles, the precipitate remains less settled than the precipitate prepared homogeneously. Note, as well, the difference in the color of the two precipitates.



**Figure 13.5** Two precipitates of  $\text{PbCrO}_4$ . In Beaker A, combining 0.1 M  $\text{Pb}(\text{NO}_3)_2$  and 0.1 M  $\text{K}_2\text{CrO}_4$  forms the precipitate under conditions of high *RSS*. The precipitate forms rapidly and consists of very small particles. In Beaker B, heating a solution of 0.1 M  $\text{Pb}(\text{NO}_3)_2$ , 0.1 M  $\text{Cr}(\text{NO}_3)_3$ , and 0.1 M  $\text{KBrO}_3$  slowly oxidizes  $\text{Cr}^{3+}$  to  $\text{CrO}_4^{2-}$ , precipitating  $\text{PbCrO}_4$  under conditions of low *RSS*. The precipitate forms slowly and consists of much larger particles.

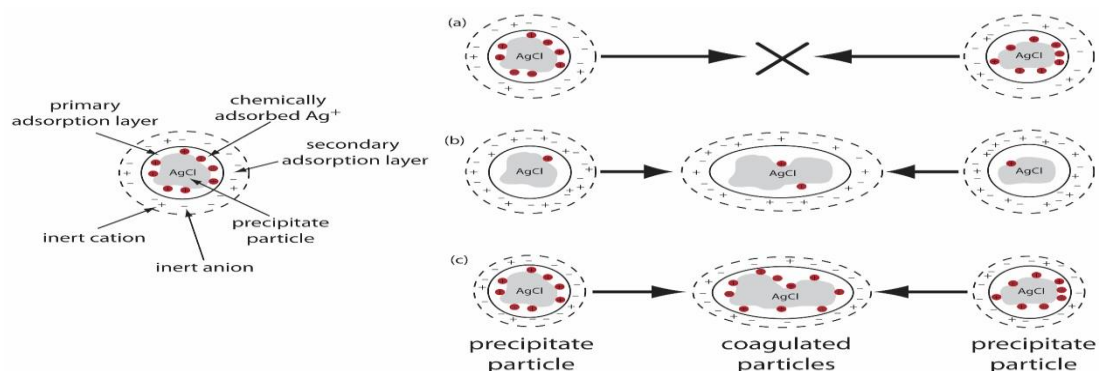
**Note:** The effect of particle size on color is well-known to geologists, who use a streak test to help identify minerals. The color of a bulk mineral and its color when powdered are often different. Rubbing a mineral across an unglazed porcelain plate leaves behind a small streak of the powdered mineral. Bulk samples of hematite,  $\text{Fe}_2\text{O}_3$ , are black in color, but its streak is a familiar rust-red. Crocote, the mineral  $\text{PbCrO}_4$ , is red-orange in color; its streak is orange-yellow.

A homogeneous precipitation produces large particles of precipitate that are relatively free from impurities. These advantages, however, are offset by requiring more time to produce the precipitate and a tendency for the precipitate to deposit as a thin film on the container's walls. The latter problem is particularly severe for hydroxide precipitates generated using urea.

An additional method for increasing particle size deserves mention. When a precipitate's particles are electrically neutral they tend to coagulate into larger particles that are easier to filter. Surface adsorption of excess lattice ions, however, provides the precipitate's particles with a net positive or a net negative surface charge. Electrostatic repulsion between the particles prevents them from coagulating into larger particles.

Let's use the precipitation of  $\text{AgCl}$  from a solution of  $\text{AgNO}_3$  using  $\text{NaCl}$  as a precipitant to illustrate this effect. Early in the precipitation, when  $\text{NaCl}$  is the limiting reagent, excess  $\text{Ag}^+$  ions chemically adsorb to the  $\text{AgCl}$  particles, forming a

positively charged primary adsorption layer (Figure 8.6a). The solution in contact with this layer contains more inert anions,  $\text{NO}_3^-$  in this case, than inert cations,  $\text{Na}^+$ , giving a secondary adsorption layer with a negative charge that balances the primary adsorption layer's positive charge. The solution outside the secondary adsorption layer remains electrically neutral. **Coagulation** cannot occur if the secondary adsorption layer is too thick because the individual particles of AgCl are unable to approach each other closely enough.



**Figure 8.6** Two methods for coagulating a precipitate of AgCl. (a) Coagulation does not happen due to the electrostatic repulsion between the two positively charged particles. (b) Decreasing the charge within the primary adsorption layer, by adding additional NaCl, decreases the electrostatic repulsion, allowing the particles to coagulate. (c) Adding additional inert ions decreases the thickness of the secondary adsorption layer. Because the particles can approach each other more closely, they are able to coagulate.

We can induce coagulation in three ways: by decreasing the number of chemically adsorbed  $\text{Ag}^+$  ions, by increasing the concentration of inert ions, or by heating the solution. As we add additional NaCl, precipitating more of the excess  $\text{Ag}^+$ , the number of chemically adsorbed silver ions decreases and coagulation occurs (Figure 8.6b). Adding too much NaCl, however, creates a primary adsorption layer of excess  $\text{Cl}^-$  with a loss of coagulation.

**Note:** The coagulation and decoagulation of AgCl as we add NaCl to a solution of  $\text{AgNO}_3$  can serve as an endpoint for a titration. See [Chapter 9](#) for additional details.

A second way to induce coagulation is to add an inert electrolyte, which increases the concentration of ions in the secondary adsorption layer. With more ions available, the thickness of the secondary adsorption layer decreases. Particles of precipitate may now approach each other more closely, allowing the precipitate to coagulate. The amount of electrolyte needed to cause spontaneous coagulation is called the critical coagulation concentration.

Heating the solution and precipitate provides a third way to induce coagulation. As the temperature increases, the number of ions in the primary adsorption layer decreases, lowering the precipitate's surface charge. In addition, heating increases the particles' kinetic energy, allowing them to overcome the electrostatic repulsion that prevents coagulation at lower temperatures.

## Filtering the Precipitate

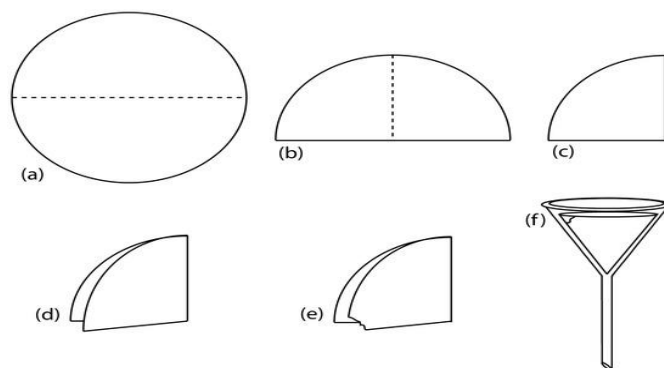
After precipitating and digesting the precipitate, we separate it from solution by filtering. The most common filtration method uses filter paper, which is classified according to its speed, its size, and its ash content on ignition. Speed, or how quickly the supernatant passes through the filter paper, is a function of the paper's pore size. A larger pore allows the supernatant to pass more quickly through the filter paper, but does not retain small particles of precipitate. Filter paper is rated as fast (retains particles larger than 20–25  $\mu\text{m}$ ), medium–fast (retains particles larger than 16  $\mu\text{m}$ ), medium (retains particles larger than 8  $\mu\text{m}$ ), and slow (retains particles larger than 2–3  $\mu\text{m}$ ). The proper choice of filtering speed is important. If the filtering speed is too fast, we may fail to retain some of the precipitate, causing a negative determinate error. On the other hand, the precipitate may clog the pores if we use a filter paper that is too slow.

**Note:** A filter paper's size is just its diameter. Filter paper comes in many sizes, including 4.25 cm, 7.0 cm, 11.0 cm, 12.5 cm, 15.0 cm, and 27.0 cm. Choose a size that fits comfortably into your funnel. For a typical 65-mm long-stem funnel, 11.0 cm and 12.5 cm filter paper are good choices.

Because filter paper is hygroscopic, it is not easy to dry it to a constant weight. When accuracy is important, the filter paper is removed before determining the precipitate's mass. After transferring the precipitate and filter paper to a covered crucible, we heat the crucible to a temperature that converts the paper to  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$ , a process called **ignition**.

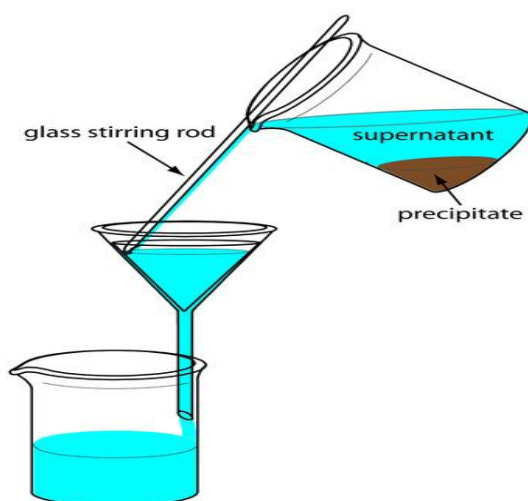
**Note:** Igniting a poor quality filter paper leaves behind a residue of inorganic ash. For quantitative work, use a low-ash filter paper. This grade of filter paper is pretreated with a mixture of HCl and HF to remove inorganic materials. Quantitative filter paper typically has an ash content of less than 0.010% w/w.

Gravity filtering is accomplished by folding the filter paper into a cone and placing it in a long-stem funnel (Figure 8.7). A seal between the filter cone and the funnel is formed by dampening the paper with water or supernatant, and pressing the paper to the wall of the funnel. When properly prepared, the funnel's stem fills with the supernatant, increasing the rate of filtration.



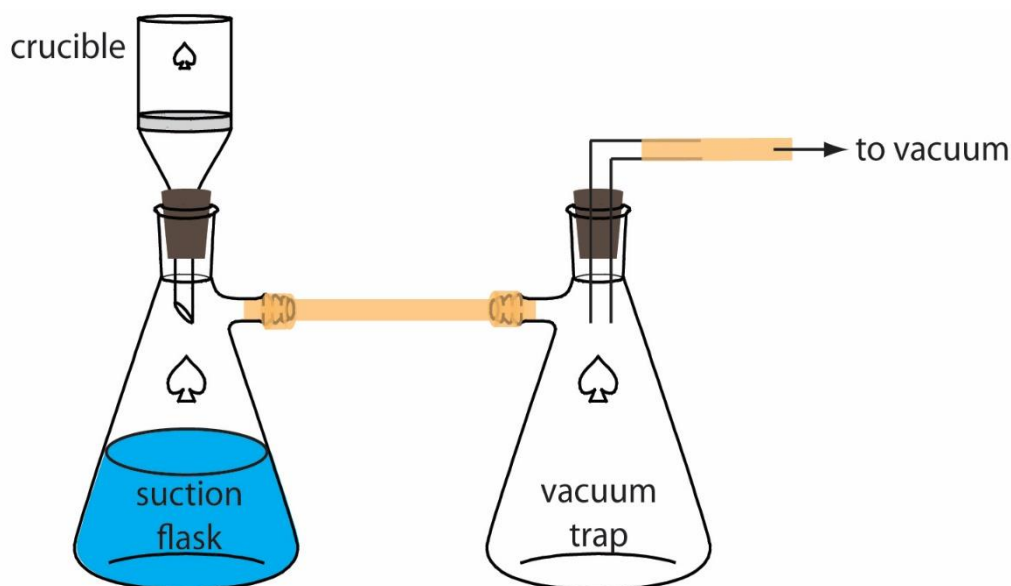
**Figure 13.7** Preparing a filter paper cone. The filter paper circle in (a) is folded in half (b), and folded in half again (c). The folded filter paper is parted (d) and a small corner is torn off (e). The filter paper is opened up into a cone and placed in the funnel (f).

The precipitate is transferred to the filter in several steps. The first step is to decant the majority of the **supernatant** through the filter paper without transferring the precipitate (Figure 8.8). This prevents the filter paper from clogging at the beginning of the filtration process. The precipitate is rinsed while it remains in its beaker, with the rinsings decanted through the filter paper. Finally, the precipitate is transferred onto the filter paper using a stream of rinse solution. Any precipitate clinging to the walls of the beaker is transferred using a rubber policeman (a flexible rubber spatula attached to the end of a glass stirring rod).



**Figure 8.8** Proper procedure for transferring the supernatant to the filter paper cone.

An alternative method for filtering a precipitate is a filtering crucible. The most common is a fritted-glass crucible containing a porous glass disk filter. Fritted-glass crucibles are classified by their porosity: coarse (retaining particles larger than 40–60  $\mu\text{m}$ ), medium (retaining particles greater than 10–15  $\mu\text{m}$ ), and fine (retaining particles greater than 4–5.5  $\mu\text{m}$ ). Another type of filtering crucible is the Gooch crucible, which is a porcelain crucible with a perforated bottom. A glass fiber mat is placed in the crucible to retain the precipitate. For both types of crucibles, the precipitate is transferred in the same manner described earlier for filter paper. Instead of using gravity, the supernatant is drawn through the crucible with the assistance of suction from a vacuum aspirator or pump (Figure 8.9).



**Figure 8.9** Procedure for filtering a precipitate through a filtering crucible. The trap prevents water from an aspirator from back-washing into the suction flask.

### Rinsing the Precipitate

Because the supernatant is rich with dissolved inert ions, we must remove any residual traces of supernatant to avoid a positive determinate error without incurring solubility losses. In many cases this simply involves the use of cold solvents or rinse solutions containing organic solvents such as ethanol. The pH of the rinse solution is critical if the precipitate contains an acidic or basic ion. When coagulation plays an important role in determining particle size, adding a volatile inert electrolyte to the rinse solution prevents the precipitate from reverting into smaller particles that might pass through the filter. This process of reverting to smaller particles is called **peptization**. The volatile electrolyte is removed when drying the precipitate.

In general, we can minimize the loss of analyte by using several small portions of rinse solution instead of a single large volume. Testing the used rinse solution for the presence of impurities is another way to guard against over rinsing the precipitate. For example, if  $\text{Cl}^-$  is a residual ion in the supernatant, we can test for its presence using  $\text{AgNO}_3$ . After collecting a small portion of the rinse solution, we add a few drops of  $\text{AgNO}_3$  and look for the presence or absence of a precipitate of  $\text{AgCl}$ . If a precipitate forms, then we know that  $\text{Cl}^-$  is present and continue to rinse the precipitate. Additional rinsing is not needed if the  $\text{AgNO}_3$  does not produce a precipitate.

### Drying the Precipitate



After separating the precipitate from its supernatant solution, the precipitate is dried to remove residual traces of rinse solution and any volatile impurities. The temperature and method of drying depend on the method of filtration and the precipitate's desired chemical form. Placing the precipitate in a laboratory oven and heating to a temperature of 110°C is sufficient when removing water and other easily volatilized impurities. Higher temperatures require a muffle furnace, a Bunsen burner, or a Meker burner, and are necessary if we need to thermally decompose the precipitate before weighing.

Because filter paper absorbs moisture, we must remove it before weighing the precipitate. This is accomplished by folding the filter paper over the precipitate and transferring both the filter paper and the precipitate to a porcelain or platinum crucible. Gentle heating first dries and then chars the filter paper. Once the paper begins to char, we slowly increase the temperature until all traces of the filter paper are gone and any remaining carbon is oxidized to CO<sub>2</sub>.

Fritted-glass crucibles can not withstand high temperatures and must be dried in an oven at temperatures below 200°C. The glass fiber mats used in Gooch crucibles can be heated to a maximum temperature of approximately 500°C.

### **Composition of the Final Precipitate**

For a quantitative application, the final precipitate must have a well-defined composition. Precipitates containing volatile ions or substantial amounts of hydrated water, are usually dried at a temperature that completely removes these volatile species. For example, one standard gravimetric method for the determination of magnesium involves its precipitation as MgNH<sub>4</sub>PO<sub>4</sub>•6H<sub>2</sub>O. Unfortunately, this precipitate is difficult to dry at lower temperatures without losing an inconsistent amount of hydrated water and ammonia. Instead, the precipitate is dried at temperatures above 1000°C where it decomposes to magnesium pyrophosphate, Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

An additional problem is encountered if the isolated solid is nonstoichiometric. For example, precipitating Mn<sup>2+</sup> as Mn(OH)<sub>2</sub> and heating frequently produces a nonstoichiometric manganese oxide, MnO<sub>x</sub>, where x varies between one and two. In this case the nonstoichiometric product is the result of forming of a mixture of oxides with different oxidation state of manganese. Other nonstoichiometric compounds form as a result of lattice defects in the crystal structure.

**Note :** The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical precipitation gravimetric method. Although each method is unique, the determination of Mg<sup>2+</sup> in water and wastewater by precipitating MgNH<sub>4</sub>PO<sub>4</sub> • 6H<sub>2</sub>O and isolating Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> provides an instructive example of a typical procedure. The description here is based on Method 3500-Mg D in *Standard Methods for the Examination of Water and Wastewater*, 19th Ed., American Public Health Association: Washington, D. C., 1995. With the publication of the 20th Edition in 1998, this method is no longer listed as an approved method.