Before we consider specific gravimetric methods, let’s take a moment to develop a broad survey of gravimetry. Later, as you read through the descriptions of specific gravimetric methods, this survey will help you focus on their similarities instead of their differences. It is easier to understand a new analytical method when you can see its relationship to other similar methods.

### Using Mass as an Analytical Signal

Suppose we 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, we pass it through a preweighed filter that retains the suspended solids, and then 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.

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 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 convert the Pb\(^{2+}\) to PbO\(_2\), which deposits on the Pt anode.

\[
\text{Pb}^{2+}(aq) + 4\text{H}_2\text{O}(l) \rightleftharpoons \text{PbO}_2(s) + \text{H}_2(g) + 2\text{H}_3\text{O}^+(aq)
\]

If we weigh the anode before and after we apply the potential, its change in mass gives the mass of PbO\(_2\) and, from the reaction’s stoichiometry, the amount of Pb\(^{2+}\) in the sample. This is a direct analysis because 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 we need to determine a food’s moisture content. One approach is to heat a sample of the food to a temperature that will vaporize water and capture the water vapor using 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 we heat it and use the change in its mass to determine the amount of water originally present. We call this an indirect analysis because we determine the analyte, H\(_2\)O in this case, using a signal that is proportional its disappearance.

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.
The indirect determination of a sample’s moisture content is made by measuring a change in mass. The sample’s initial mass includes the water, but its final mass does not. We can also determine an analyte indirectly without its being weighed. For example, phosphite, \( \text{PO}_3^{3-} \), reduces \( \text{Hg}^{2+} \) to \( \text{Hg}_2^{2+} \), which in the presence of \( \text{Cl}^- \) precipitates as \( \text{Hg}_2\text{Cl}_2 \).

\[
2 \text{HgCl}_2(aq) + \text{PO}_3^{3-}(aq) + 3 \text{H}_2\text{O}(l) \rightleftharpoons \text{Hg}_2\text{Cl}_2(s) + 2 \text{H}_3\text{O}^+(aq) + 2 \text{Cl}^-(aq) + \text{PO}_4^{3-}(aq)
\]

If we add \( \text{HgCl}_2 \) in excess to a sample that contains phosphite, each mole of \( \text{PO}_3^{3-} \) will produce one mole of \( \text{Hg}_2\text{Cl}_2 \). The precipitate’s mass, therefore, provides an indirect measurement of the amount of \( \text{PO}_3^{3-} \) in the original sample.

### Types of Gravimetric Methods

The examples in the previous section illustrate four different ways in which a measurement of mass may serve as an analytical signal. 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 an example, as is the direct determination of \( \text{Cl}^- \) by precipitating \( \text{AgCl} \).

In **electrogravimetry**, we deposit the analyte as a solid film on an electrode in an electrochemical cell. The deposition as \( \text{PbO}_2 \) at a Pt anode is one example of electrogravimetry. The reduction of \( \text{Cu}^{2+} \) to \( \text{Cu} \) at a Pt cathode is another example of electrogravimetry.

We will not consider electrogravimetry in this chapter. See Chapter 11 on electrochemical methods of analysis for a further discussion of electrogravimetry.

When we use thermal or chemical energy to remove a volatile species, we call the method **volatilization gravimetry**. In determining the moisture content of bread, for example, we use thermal energy to vaporize the water in the sample. To determine the amount of carbon in an organic compound, we use the chemical energy of combustion to convert it to \( \text{CO}_2 \).

Finally, in **particulate gravimetry** we determine the analyte by separating it from the sample’s matrix using a filtration or an extraction. The determination of total suspended solids is one example of particulate gravimetry.

### Conservation of Mass

An accurate gravimetric analysis requires that the analytical signal—whether it is a mass or a change in mass—is 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 we must know the stoichiometry of the reactions. In the analysis of \( \text{PO}_3^{3-} \) described earlier, for example, we know that each mole of \( \text{Hg}_2\text{Cl}_2 \) corresponds to a mole of \( \text{PO}_3^{3-} \). 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.

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

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 any analysis to a **definitive technique**, such as gravimetry, that we can relate to fundamental physical properties [Valacárcel, M.; Ríos, A. *Analyst* **1995**, *120*, 2291–2297]. Although most analysts never use gravimetry to validate their results, they often verifying an analytical method by analyzing a standard reference material whose composition is traceable to a definitive technique [{(a) Moody, J. R.; Epstein, M. S. *Spectrochim. Acta* **1991**, *46B*, 1571–1575; (b) Epstein, M. S. *Spectrochim. Acta* **1991**, *46B*, 1583–1591}].

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 this textbook; however, you will find some suggested readings in this chapter’s Additional Resources.