Vocabulary of Analytical Chemistry

Analysis, Determination, and Measurement

The first important distinction we will make is among the terms analysis, determination, and measurement. An analysis provides chemical or physical information about a sample. The component of interest in the sample is called the **analyte**, and the remainder of the sample is the **matrix**. In an analysis we determine the identity, concentration, or properties of an analyte. To make this determination we measure one or more of the analyte's chemical or physical properties.

An example helps clarify the difference between an **analysis**, a **determination** and a **measurement**. In 1974 the federal government enacted the Safe Drinking Water Act to ensure the safety of public drinking water supplies. To comply with this act, municipalities regularly monitor their drinking water supply for potentially harmful substances. One such substance is fecal coliform bacteria. Municipal water departments collect and analyze samples from their water supply. They determine the concentration of fecal coliform bacteria by passing a portion of water through a membrane filter, placing the filter in a dish containing a nutrient broth, and incubating for 22–24 hr at 44.5 °C ± 0.2 °C. At the end of the incubation period they count the number of bacterial colonies in the dish and report the result as the number of colonies per 100 mL (Figure 3.1). Thus, municipal water departments analyze samples of water to determine the concentration of fecal coliform bacteria by measuring the number of bacterial colonies that form during a carefully defined incubation period.
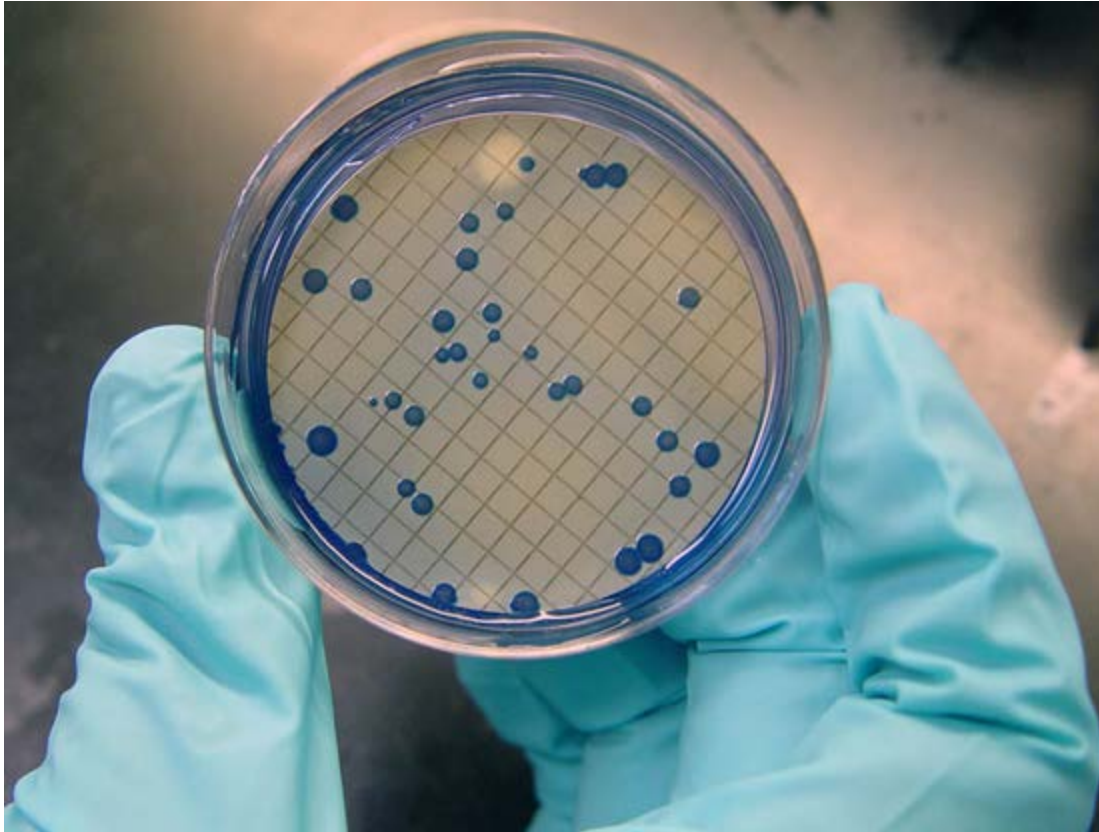
Figure 3.1 Colonies of fecal coliform bacteria from a water supply. Source: Susan Boyer. Photo courtesy of ARS–USDA (www.ars.usda.gov). Fecal coliform counts provide a general measure of the presence of pathogenic organisms in a water supply. For drinking water, the current maximum contaminant level (MCL) for total coliforms, including fecal coliforms is less than 1 colony/100 mL. Municipal water departments must regularly test the water supply and must take action if more than 5% of the samples in any month test positive for coliform bacteria.

Techniques, Methods, Procedures, and Protocols

Suppose you are asked to develop an analytical method to determine the concentration of lead in drinking water. How would you approach this problem? To provide a structure for answering this question let's draw a distinction among four levels of analytical methodology: techniques, methods, procedures, and protocols.[1]

- A **technique** is any chemical or physical principle we can use to study an analyte. There are many techniques for determining the concentration of lead in drinking water.[2] In graphite furnace atomic absorption spectroscopy (GFAAS), for example, we first convert aqueous lead ions into a free atom state—a process we call atomization. We then measure the amount of light absorbed by the free atoms. Thus, GFAAS uses both a chemical principle (atomization) and a physical principle (absorption of light).
- A **method** is the application of a technique for a specific analyte in a specific matrix. As shown in Figure 3.2, the GFAAS method for determining lead in water is different from that for lead in soil or blood.
- A **procedure** is a set of written directions telling us how to apply a method to a particular sample, including information on obtaining samples, handling interferents, and validating results. A method may have several

procedures as each analyst or agency adapts it to a specific need. As shown in Figure 3.2, the American Public Health Agency and the American Society for Testing Materials publish separate procedures for determining the concentration of lead in water.

- A **protocol** is a set of stringent guidelines specifying a procedure that must be followed if an agency is to accept the results. Protocols are common when the result of an analysis supports or defines public policy. When determining the concentration of lead in water under the Safe Drinking Water Act, for example, labs must use a protocol specified by the Environmental Protection Agency.

There is an obvious order to these four levels of analytical methodology. Ideally, a protocol uses a previously validated procedure. Before developing and validating a procedure, a method of analysis must be selected. This requires, in turn, an initial screening of available techniques to determine those that have the potential for monitoring the analyte.
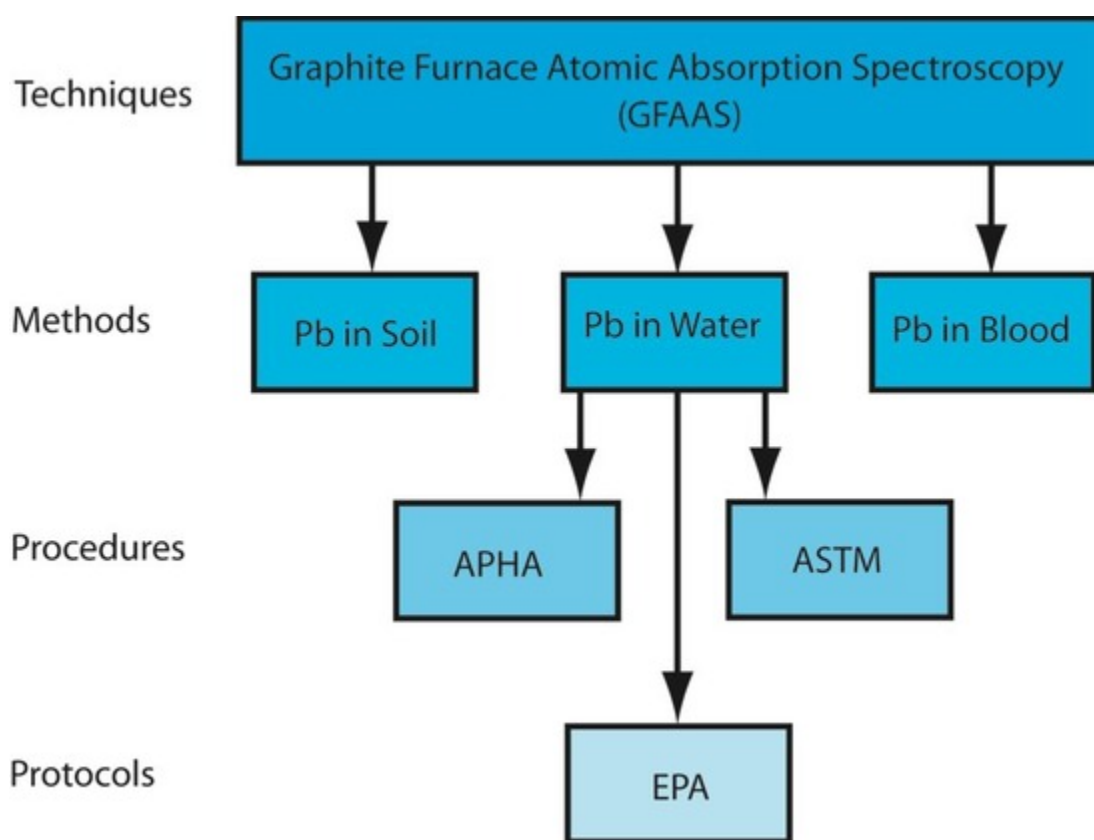

Figure 3.2 Chart showing the hierarchical relationship among a technique, methods using that technique, and procedures and protocols for one method. The abbreviations are APHA: American Public Health Association, ASTM: American Society for Testing Materials, EPA: Environmental Protection Agency.

Classifying Analytical Techniques

Analyzing a sample generates a chemical or physical **signal** that is proportional to the amount of analyte in the sample. This signal may be anything we can measure, such as mass or absorbance. It is convenient to divide analytical techniques into two general classes depending on whether the signal is proportional to the mass or moles of analyte, or to the analyte's concentration.

Consider the two graduated cylinders in Figure 3.3, each containing a solution of 0.010 M $Cu(NO_3)_2$. Cylinder 1 contains 10 mL, or 1.0×10^{-4} moles of Cu^{2+}, and cylinder 2 contains 20 mL, or 2.0×10^{-4} moles of Cu^{2+}. If a technique responds to the absolute amount of analyte in the sample, then the signal due to the analyte, SA, is

$$S_A = k_A n_A$$

where n_A is the moles or grams of analyte in the sample, and k_A is a proportionality constant. Since cylinder 2 contains twice as many moles of Cu^{2+} as cylinder 1, analyzing the contents of cylinder 2 gives a signal that is twice that of cylinder 1.

A second class of analytical techniques are those that respond to the analyte's concentration, C_A

$$S_A = k_A C_A$$

Since the solutions in both cylinders have the same concentration of Cu^{2+}, their analysis yields identical signals.

Figure 3.3 Graduated cylinders containing 0.10 M $Cu(NO_3)_2$. Although the cylinders contain the same concentration of Cu^{2+}, the cylinder on the left contains 1.0×10^{-4} mol Cu^{2+} and the cylinder on the right contains 2.0×10^{-4} mol Cu^{2+}.

A technique responding to the absolute amount of analyte is a **total analysis technique**. Mass and volume are the most common signals for a total analysis technique, and the corresponding techniques are gravimetry and titrimetry. With a few exceptions, the signal for a total analysis technique is the result of one or more chemical reactions involving the analyte. These reactions may involve any combination of precipitation, acid–base, complexation, or redox chemistry. The stoichiometry of the reactions determines the value of k_A in equation 3.1. Historically, most early analytical methods used a total analysis technique. For this reason, total analysis techniques are often called "classical" techniques.

Spectroscopy and electrochemistry, in which an optical or electrical signal is proportional to the relative amount of analyte in a sample, are examples of **concentration techniques**. The relationship between the signal and the analyte's concentration is a theoretical function that depends on experimental conditions and the instrumentation

used to measure the signal. For this reason the value of k_A in equation 3.2 must be determined experimentally. Since most concentration techniques rely on measuring an optical or electrical signal, they also are known as "instrumental" techniques.