Atomic Absorption and Atomic Fluorescence Spectrometry

I n this chapter we consider two types of optical atomic spectrometric methods that use similar techniques for sample introduction and atomization. The first is **atomic absorption spectrometry** (AAS), which for half a century has been the most widely used method for the determination of single elements in analytical samples. The second is **atomic fluorescence spectrometry** (AFS), which since the mid-1960s has been studied extensively. By contrast to the absorption method, atomic fluorescence has not gained widespread general use for routine elemental analysis. Thus, although several instrument makers have in recent years begun to offer special-purpose atomic fluorescence spectrometers, the vast majority of instruments are still of the atomic absorption type. Because of this difference in usage, we devote the bulk of this chapter to AAS and confine our description of AFS to a brief section at the end.

Throughout this chapter, this logo indicates an opportunity for online self-study at **www.tinyurl.com/skoogpia7**, linking you to interactive tutorials, simulations, and exercises.

Prior to discussing AAS[1] in detail, we first present an overview of the types of atomizers used in both AAS and AFS.

9A   SAMPLE ATOMIZATION TECHNIQUES

We first describe the two most common methods of sample atomization encountered in AAS and AFS, flame atomization, and electrothermal atomization. We then turn to three specialized atomization procedures used in both types of spectrometry.

9A-1 Flame Atomization

In a flame atomizer, a solution of the sample is *nebulized* by a flow of gaseous oxidant, mixed with a gaseous fuel, and carried into a flame where atomization occurs. As shown in Figure 9-1, a complex set of interconnected processes then occur in the flame. The first step is *desolvation*, in which the solvent evaporates to produce a finely divided solid molecular aerosol. The aerosol is then *volatilized* to form gaseous molecules. *Dissociation* of most of these molecules produces an atomic gas. Some of the atoms in the gas ionize to form cations and electrons. Other molecules and atoms are produced in the flame as a result of interactions of the fuel with the oxidant and with the various species in the sample. As indicated in Figure 9-1, a fraction of the molecules, atoms, and ions are also excited by the heat of the flame to yield atomic, ionic, and molecular emission spectra. With so many complex processes occurring, it is not surprising that atomization is the most critical step in flame spectroscopy and the one that limits the precision of such methods. Because of the critical nature of the atomization step, it is important to understand the characteristics of flames and the variables that affect these characteristics.

[1]General references on atomic absorption spectrometry include L. H. J. Lajunen and P. Peramaki, *Spectrochemical Analysis by Atomic Absorption and Emission*, 2nd ed., Cambridge: Royal Society of Chemistry, 2004; J. A. C. Broekaert, *Analytical Atomic Spectrometry with Flames and Plasmas*, Weinheim, Germany: Wiley-VCH, 2002; B. Magyar, *Guide-Lines to Planning Atomic Spectrometric Analysis*, New York: Elsevier, 1982; J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, Chap. 10, Englewood Cliffs, NJ: Prentice Hall, 1988; B. Weiz and M. Sperling, *Atomic Absorption Spectrometry*, 3rd ed., New York: VCH Publishers, 1999; N. H. Bings, A. Bogaerts, and J. A. C. Broekaert, *Anal. Chem.*, **2013**, *85*, 670, **DOI**: 10.1021/ac3031459.
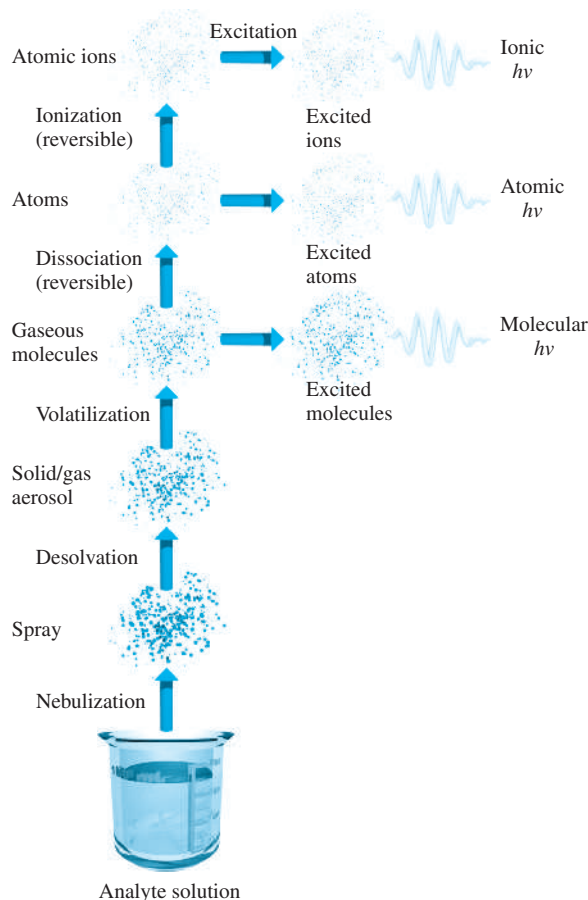
FIGURE 9-1 Processes occurring during atomization.

Types of Flames

Table 9-1 lists the common fuels and oxidants used in flame spectroscopy and the approximate range of temperatures realized with each of these mixtures. Note that temperatures of 1700°C to 2400°C occur with the various fuels when air is the

TABLE 9-1 Properties of Flames

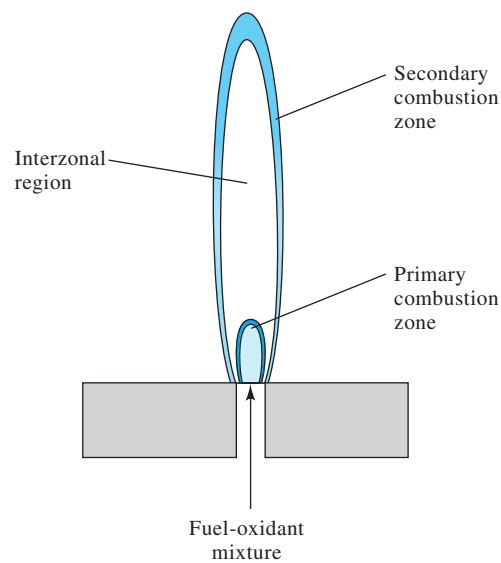| Fuel	Oxidant	Temperature, °C	Maximum Burning Velocity, cm s^{-1}
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	≈285

FIGURE 9-2 Regions in a flame.

oxidant. At these temperatures, only easily decomposed samples are atomized, so oxygen or nitrous oxide must be used as the oxidant for more difficult to atomize samples (refractory samples). These oxidants produce temperatures of 2500°C to 3100°C with the common fuels.

The burning velocities listed in the fourth column of Table 9-1 are important because flames are stable only in certain ranges of gas flow rates. If the gas flow rate does not exceed the burning velocity, the flame propagates back into the burner, giving *flashback*. As the flow rate increases, the flame rises until it reaches a point above the burner where the flow velocity and the burning velocity are equal. This region is where the flame is stable. At higher flow rates, the flame rises and eventually reaches a point where it blows off the burner. With these facts in mind, it is easy to see why it is very important to control the flow rate of the fuel-oxidant mixture. This flow rate very much depends on the type of fuel and oxidant being used.

Flame Structure

As shown in Figure 9-2, important regions of a flame include the primary combustion zone, the interzonal region, and the secondary combustion zone. The appearance and relative size of these regions vary considerably with the fuel-to-oxidant ratio, the type of fuel and oxidant, and the type of burner. The primary combustion zone in a hydrocarbon flame is recognizable by its blue luminescence arising from the band emission of C_2, CH, and other radicals. Thermal equilibrium is usually not achieved in this region, and it is, therefore, rarely used for flame spectroscopy.

The interzonal area, which is relatively narrow in stoichiometric hydrocarbon flames, may reach several centimeters in height in fuel-rich acetylene-oxygen or acetylene–nitrous oxide sources. Because free atoms are prevalent in the interzonal region,

it is the most widely used part of the flame for spectroscopy. In the secondary reaction zone, the products of the inner core are converted to stable molecular oxides that are then dispersed into the surroundings.

A flame profile provides useful information about the processes that go on in different parts of a flame; it is a contour plot that reveals regions of the flame that have similar values for a variable of interest. Some of these variables include temperature, chemical composition, absorbance, and radiant or fluorescence intensity.

Temperature Profiles. Figure 9-3 shows a temperature profile of a typical flame for atomic spectroscopy. The maximum temperature is located in the flame about 2.5 cm above the primary combustion zone. It is important—particularly for emission methods (Section 10C-1)—to focus the same part of the flame on the entrance slit for all calibrations and analytical measurements.

Flame Absorption Profiles. Figure 9-4 shows typical absorption profiles for three elements. Magnesium exhibits a maximum in absorbance at about the middle of the flame because of two opposing effects. The initial increase in absorbance as the distance from the base increases results from an increased number of magnesium atoms produced by the longer exposure to the heat of the flame. As the secondary combustion zone is approached, however, appreciable oxidation of the magnesium begins. This process eventually leads to a decrease in absorbance because the oxide particles formed do not absorb at
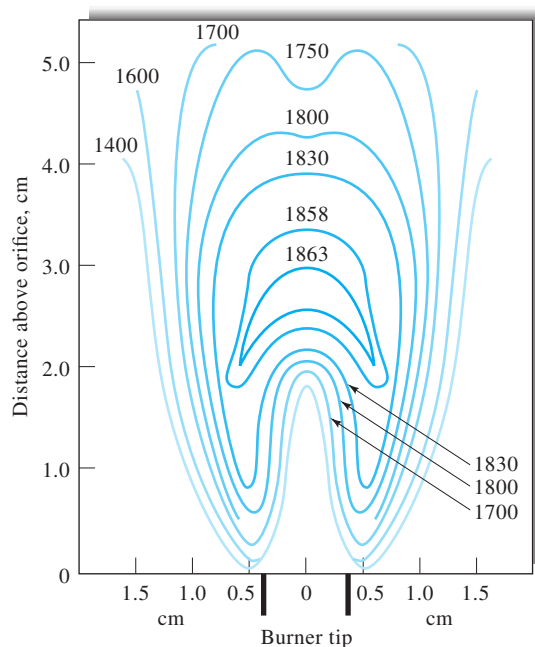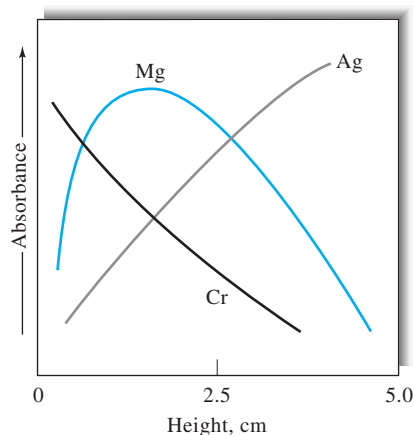

FIGURE 9-4 Flame absorption profiles for three elements.

the observation wavelength. To achieve maximum analytical sensitivity, then, the flame must be adjusted up and down with respect to the beam until the region of maximum absorbance is located.

The behavior of silver, which is not easily oxidized, is quite different. As shown in Figure 9-4, a continuous increase in the number of atoms, and thus the absorbance, is observed from the base to the periphery of the flame. By contrast, chromium, which forms very stable oxides, shows a continuous decrease in absorbance beginning close to the burner tip; this observation suggests that oxide formation predominates from the start. These findings suggest that a different portion of the flame should be used for the determination of each of these elements. The more sophisticated instruments for flame spectroscopy are equipped with monochromators that sample the radiation from a relatively small region of the flame, and so a critical step in the optimization of signal output is the adjustment of the position of the flame with respect to the entrance slit.

Flame Atomizers

Flame atomizers are used for atomic absorption, fluorescence, and emission spectroscopy (see Chapter 10 for flame emission spectroscopy). Figure 9-5 is a diagram of a typical commercial laminar-flow burner that uses a concentric-tube nebulizer, similar to that shown in Figure 8-11a. The aerosol, formed by the flow of oxidant, is mixed with fuel and passes a series of baffles that remove all but the finest solution droplets. The baffles cause most of the sample to collect in the bottom of the mixing chamber where it drains to a waste container. The aerosol, oxidant, and fuel are then burned in a slotted burner to provide a 5- to 10-cm high flame.

Laminar-flow burners produce a relatively quiet flame and a long path length for maximizing absorption. These properties tend to enhance sensitivity and reproducibility in AAS. The mixing chamber in this type of burner contains a potentially explosive mixture that can flash back if the flow rates are too low. Note that the laminar-flow burner in Figure 9-5 is equipped with
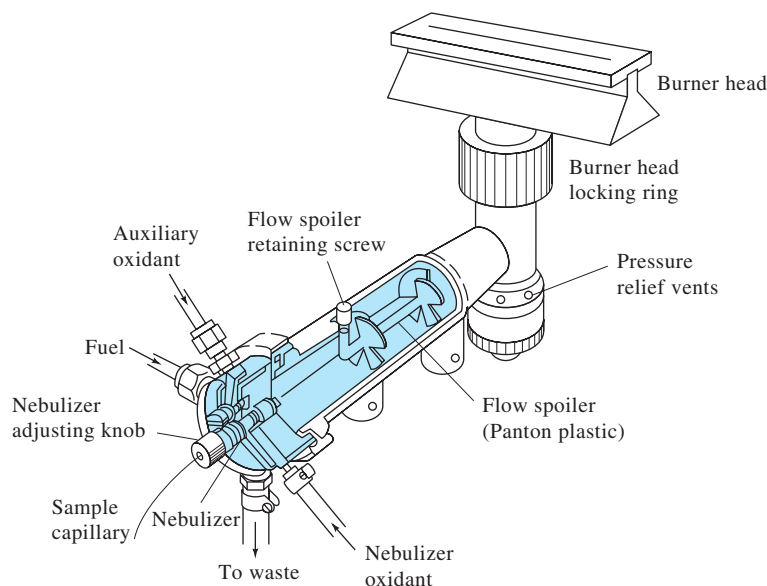

FIGURE 9-3 Temperature profiles in degrees Celsius for a natural gas–air flame. (From B. Lewis and G. van Elbe, *J. Chem. Phys.*, **1943**, *11*, 94, **DOI:** 10.1063/1.1723808. With permission.)

FIGURE 9-5 A laminar-flow burner. (Courtesy of Perkin-Elmer Corporation, Norwalk, CT.)

pressure relief vents for this reason. Other types of laminar-flow burners and turbulent-flow burners are available for atomic emission spectrometry and AFS.

Fuel and Oxidant Regulators. An important variable that requires close control in flame spectroscopy is the flow rate of both oxidant and fuel. It is desirable to be able to vary each over a broad range so that optimal atomization conditions can be determined experimentally. Fuel and oxidant are usually combined in approximately stoichiometric amounts. For the determination of metals that form stable oxides, however, a flame that contains an excess of fuel is often desirable. Flow rates are usually controlled by means of double-diaphragm pressure regulators followed by needle valves in the instrument housing. A widely used device for measuring flow rates is the rotameter, which consists of a tapered, graduated, transparent tube that is mounted vertically with the smaller end down. A lightweight conical or spherical float is lifted by the gas flow; its vertical position is determined by the flow rate. Newer AAS instruments feature computer control over fuel and oxidant flows and flame ignition. In addition, computer control enables many safety features to be implemented such as not allowing ignition under many unsafe conditions.

Performance Characteristics of Flame Atomizers. Flame atomization is the most reproducible of all liquid-sample-introduction methods that have been developed for AAS to date. The sampling efficiency of other atomization methods and thus the sensitivity, however, are markedly better than in flame atomization. There are two primary reasons for the lower sampling efficiency of the flame. First, a large portion of the sample flows down the drain. Second, the residence time of individual atoms in the optical path in the flame is brief ($\sim 10^{-4}$ s).

9A-2 Electrothermal Atomization

Electrothermal atomizers, which first appeared on the market in the early 1970s, generally provide enhanced sensitivity because the entire sample is atomized in a short period, and the average residence time of the atoms in the optical path is a second or more.[2] Electrothermal atomizers are used for atomic absorption and atomic fluorescence measurements but have not been generally applied for direct production of emission spectra. They are also used for vaporizing samples in inductively coupled plasma emission spectroscopy, however.

In electrothermal atomizers, a few microliters of sample is first evaporated at a low temperature and then ashed at a somewhat higher temperature in an electrically heated graphite tube similar to the one in Figure 9-6 or in a graphite cup. After ashing, the current is rapidly increased to several hundred amperes, which causes the temperature to rise to 2000°C to 3000°C; atomization of the sample occurs in a period of a few milliseconds to seconds. The absorption of the atomic vapor is then measured in the region immediately above the heated surface.

[2]For detailed discussions of electrothermal atomizers, see K. W. Jackson, *Electrothermal Atomization for Analytical Atomic Spectrometry*, New York: Wiley, 1999. For recent developments, see N. H. Bings, A. Bogaerts, J. A. C. Broekaert, *Anal. Chem.*, **2013**, *85*, 670, **DOI**: 10.1021/ac3031459; *Anal. Chem.*, **2010**, *82*, 4653, **DOI**: 10.1021/ac1010469; E. H. Evans, J. Pisonero, C. M. M. Smith, R. N. Taylor, *J. Anal. At. Spectrom.*, **2015**, *30*, 779, **DOI**: 10.1039/c5ja90017d; *J. Anal. At. Spectrom.*, **2014**, *29*, 773, **DOI**: 10.1039/c4ja90019g.
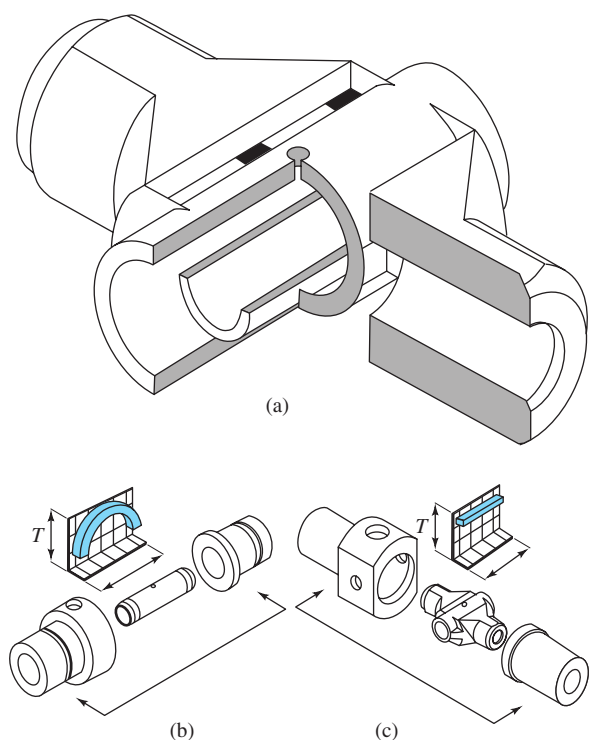
FIGURE 9-6 (a) Cross-sectional view of a graphite furnace with integrated L'vov platform. (b) Longitudinal configuration of the graphite furnace. Note the temperature profile shown in blue along the path of the furnace. In the longitudinal configuration, the temperature varies continuously along the path, reaching a maximum at the center. (c) Transverse configuration of the furnace. The temperature profile is relatively constant along the path. (Courtesy of Perkin-Elmer Life and Analytical Sciences, Shelton, CT.)

Electrothermal Atomizers

Figure 9-6a is a cross-sectional view of a commercial electro-thermal atomizer. In this device, atomization occurs in a cylindrical graphite tube that is open at both ends and that has a central hole for introduction of sample by means of a micropipette. The tube is about 5 cm long and has an internal diameter of somewhat less than 1 cm. The interchangeable graphite tube fits snugly into a pair of cylindrical graphite electrical contacts located at the two ends of the tube. These contacts are held in a water-cooled metal housing. Two inert gas streams are provided. The external stream prevents outside air from entering and incinerating the tube. The internal stream flows into the two ends of the tube and out the central sample port. This stream not only excludes air but also serves to carry away vapors generated from the sample matrix during the first two heating stages.

Figure 9-6a illustrates the so-called L'vov platform, which is often used in graphite furnaces. The platform is also made of graphite and is located beneath the sample entrance port. The sample is evaporated and ashed on this platform. When the tube temperature is increased rapidly, however, atomization is delayed because the sample is no longer directly on the furnace wall. As a result, atomization occurs in an environment in which the temperature is not changing so rapidly, which improves the reproducibility of analytical signals.

Figure 9-6b and c shows the two ways of heating the graphite furnace while it is held in the optical path. Traditionally, the furnace was heated in the longitudinal mode illustrated in Figure 9-6b, which provides a continuously varying temperature profile as shown in the figure. The transverse mode, shown in Figure 9-6c, gives a uniform temperature profile along the entire length of the tube. This arrangement provides optimum conditions for the formation of free atoms throughout the tube. Recombination of atoms to molecules, atom loss, and condensation on the cooler tube ends exhibited in the longitudinal mode are thus minimized in the transverse heating mode.

Experiments show that reducing the natural porosity of the graphite tube minimizes some sample matrix effects and poor reproducibility associated with graphite furnace atomization. During atomization, part of the analyte and matrix apparently diffuse into the surface of the tube, which slows the atomization process, thus giving smaller analyte signals. To overcome this effect, most graphite surfaces are coated with a thin layer of pyrolytic carbon, which seals the pores of the graphite tube. Pyrolytic graphite is a type of graphite that is deposited layer by layer from a highly homogeneous environment. It is formed by passing a mixture of an inert gas and a hydrocarbon such as methane through the tube while it is held at an elevated temperature.

In addition to graphite furnaces, several other electrothermal devices have been proposed and tested. Coils and loops made from platinum and tungsten have been the subject of several studies. The tungsten coil atomizer is perhaps the most successful of these and has the advantages of low power and simplicity.[3] Enclosed furnaces made from tungsten have also been studied.

Output Signal

At a wavelength at which absorption occurs, the transducer output rises to a maximum after a few seconds of ignition followed by a rapid decay back to zero as the atomization products escape into the surroundings. The change is rapid enough (often <1 s) to require a moderately fast data-acquisition system. Quantitative determinations are usually based on peak height, although peak area is also used.

Figure 9-7 shows typical output signals from an atomic absorption spectrophotometer equipped with an electrothermal atomizer. The series of four peaks on the right show the absorbance at the wavelength of a lead peak as a function of time when a 2-μL sample of canned orange juice was atomized. During drying and ashing, three peaks appear that are probably due to molecular evaporation products and particulate ignition products. The three peaks on the left are for lead standards used

[3]S. N. Hanna and B. T. Jones, *Appl. Spectrosc. Rev.*, **2011**, *46*, 624, **DOI**: 10.1080/05704928.2011.582659.
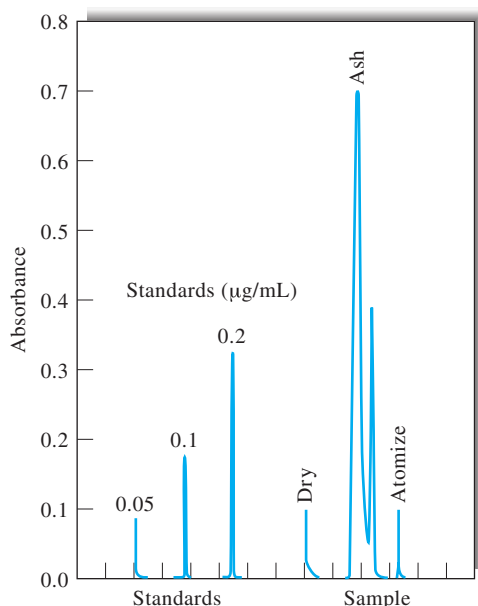
FIGURE 9-7 Typical output for the determination of lead from a spectrophotometer equipped with an electrothermal atomizer. The sample was 2 μL of canned orange juice. The times for drying and ashing are 20 and 60 s, respectively. (Courtesy of Agilent Technologies, Inc., Santa Clara, CA.)

for calibration. The sample peak on the far right indicates a lead concentration of about 0.05 μg/mL of juice.

Performance Characteristics of Electrothermal Atomizers

Electrothermal atomizers offer the advantage of unusually high sensitivity for small volumes of sample. Typically, sample volumes between 0.5 and 10 μL are used; under these circumstances, absolute detection limits typically lie in the range of 10^{-10} to 10^{-13} g of analyte.

The relative precision of electrothermal methods is generally in the range of 5% to 10% compared with the 1% or better that can be expected for flame or plasma atomization. Furthermore, because of the heating-cooling cycles, furnace methods are slow—typically requiring several minutes per element. A final disadvantage is that the analytical range is relatively narrow, usually less than two orders of magnitude. As a result, electrothermal atomization is the method of choice only when flame or plasma atomization provides inadequate detection limits.

Analysis of Solids with Electrothermal Atomizers

In most methods based on electrothermal atomizers, samples are introduced as solutions. Several reports, however, have described the use of this type of atomizer for the direct analysis of solid samples. One way of performing such measurements is to weigh the finely ground sample into a graphite boat and insert the boat into the furnace manually. A second way is to prepare a slurry of the powdered sample by ultrasonic agitation in an aqueous medium. The slurry is then pipetted into the furnace for atomization.

## 9A-3 Specialized Atomization Techniques

By far, the most common sample-introduction and atomization techniques for atomic absorption analyses are flames or electrothermal vaporizers. Several other atomization methods are used occasionally, however. Three of these are described briefly in this section.

Glow-Discharge Atomization

As described in Section 8C-2, a glow-discharge device produces an atomized vapor that can be swept into a cell for absorption measurements. Figure 9-8a shows a glow-discharge cell that can be used as an accessory to most flame atomic absorption spectrometers. It consists of a cylindrical cell about 17 cm long with a circular hole about 2 cm in diameter cut near the middle of the cylinder. An O-ring surrounds the hole. The sample is pressed against this hole with a torque screw so that it seals the tube. Six fine streams of argon gas from tiny nozzles arranged in a circular pattern above the sample impinge on the sample surface in a hexagonal pattern. The argon is ionized by a current between an anode supporting the nozzles and the sample, which acts as a cathode. As a result of sputtering, six craters quickly form on the sample surface as shown in Figure 9-8b. The sputtered atoms
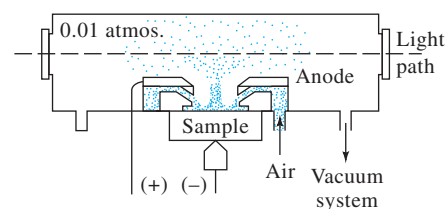
(a)
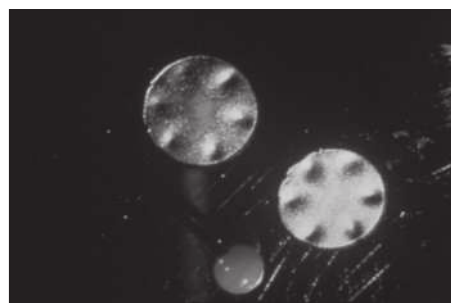
(b)

FIGURE 9-8 (a) Cross section of a cell for glow-discharge atomization of solid samples. (b) Craters formed on sample surface by six jets of ionized argon. (Teledyne Leeman Labs, Hudson, NH.)
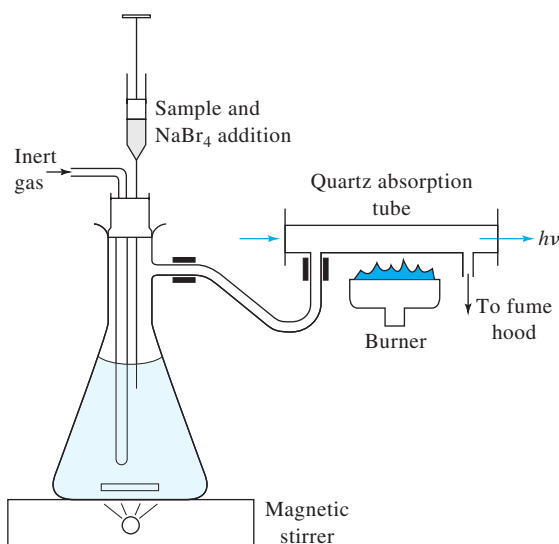
FIGURE 9-9 A hydride generation and atomization system for AAS.

are drawn by a vacuum to the axis of the cell where they absorb radiation from the spectrometer source.[4]

For this technique to be applicable, the sample must be an electrical conductor or must be made into a pellet with a powdered conductor such as finely ground graphite or copper. Solution samples have also been analyzed by deposition on a graphite, aluminum, or copper cathode. Detection limits with this type of device are reported to be in the low parts-per-million range for solid samples.[5]

Glow-discharge devices find many additional applications in atomic emission spectrometry (Chapter 10) and in atomic mass spectrometry (Chapter 11).

Hydride Atomization
In Section 8C-1, we considered methods for introducing solution samples by hydride generation. Atomization of the hydrides requires only that they be heated in a quartz tube, as shown in Figure 9-9.

Cold-Vapor Atomization
The cold-vapor technique is an atomization method applicable only to the determination of mercury because it is the only metallic element that has an appreciable vapor pressure at ambient temperature.[6] The determination of mercury in various types of samples is of vital importance currently because of the toxicity of organic mercury compounds and their widespread distribution in the environment.[7] One popular method for this determination is cold vaporization followed by atomic absorption spectrophotometry. To perform a determination of this type, mercury is converted to Hg^{2+} by treatment of samples with an oxidizing mixture of nitric and sulfuric acids, followed by reduction of the Hg^{2+} to the metal with $SnCl_2$. The elemental mercury is then swept into a long-pass absorption tube similar to the one shown in Figure 9-9 by bubbling a stream of inert gas through the reaction mixture.[8] The determination is completed by measuring the absorbance at 253.7 nm. Detection limits in the parts-per-billion range are achieved. Several manufacturers offer automatic instruments for performing this determination.

9B   ATOMIC ABSORPTION INSTRUMENTATION

Instruments for AAS are similar in general design to that shown in Figure 7-1a and consist of a radiation source, a sample holder, a wavelength selector, a detector, and a signal processor and readout.[9] The sample holder in atomic absorption instruments is the atomizer cell that contains the gaseous atomized sample.

9B-1 Radiation Sources
Atomic absorption methods are potentially highly specific because atomic absorption lines are remarkably narrow (0.002 to 0.005 nm) and because electronic transition energies are unique for each element. On the other hand, narrow line widths create a problem that does not normally occur in molecular absorption spectroscopy. In Section 13B-2, we show that a linear relationship between the analytical signal (absorbance) and concentration—that is, for Beer's law as given by Equation 6-34 to be obeyed—requires a narrow source bandwidth relative to the width of an absorption line or band. Even good-quality monochromators, however, have effective bandwidths significantly greater than the width of atomic absorption lines. As a result, nonlinear calibration curves are inevitable when atomic absorbance measurements are made with an ordinary spectrophotometer equipped with a continuum radiation source. Furthermore, the slopes of calibration curves obtained in these experiments are small because only a small fraction of the radiation from the monochromator slit is absorbed by the sample; the result is poor sensitivity. In recent years, the development

[4]See E. H. Piepmeier in *Glow Discharge Spectroscopies*, pp. 69–71, R. K. Marcus, ed., New York: Plenum Press, 1993.

[5]For a review of pulsed glow-discharge spectroscopy, see W. W. Harrison, C. Yang, and E. Oxley, *Anal. Chem.*, **2001**, *73*, 480A, **DOI**: 10.1021/ac012502g.

[6]See L. H. J. Lajunen and P. Peramaki, *Spectrochemical Analysis by Atomic Absorption and Emission*, 2nd ed., p. 63, Cambridge: Royal Society of Chemistry, 2004.

[7]See, for example, D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, *Fundamentals of Analytical Chemistry*, 9th ed., pp. 797–798, Belmont, CA: Brooks/Cole, 2014.

[8]For a discussion of the importance of determining mercury in the environment, refer to the Instrumental Analysis in Action feature at the end of Section 2.

[9]Reference books on atomic absorption spectroscopy include L. H. J. Lajunen and P. Peramaki, *Spectrochemical Analysis by Atomic Absorption and Emission*, 2nd ed., Cambridge, UK: Royal Society of Chemistry, 2004; B. Welz and M. Sperling, *Atomic Absorption Spectrometry*, 3rd ed., New York: VCH, 1999.

of high-resolution $(R > 10^5)$ continuum-source spectrometers based on the double echelle monochromator coupled with array detection has clouded this issue, and such instruments are beginning to compete with traditional spectrometers equipped with line sources.[10]

The problem created by the limited width of atomic absorption lines has been solved by the use of line sources with bandwidths even narrower than the absorption line width. For example, to use the 422.7-nm line of calcium as the basis for determining the element, a calcium emission line at this same wavelength is isolated to serve as the source. In this instance, a calcium vapor lamp in which calcium atoms are excited by an electrical discharge may be used to produce the line. The other calcium lines emitted from the source are removed with filters or with a relatively inexpensive monochromator. Operating conditions for the source are chosen such that Doppler broadening of the emitted lines is less than the broadening of the absorption line that occurs in the flame or other atomizer. That is, the source temperature and pressure are kept below that of the atomizer. Figure 9-10 illustrates the principle of this procedure. Figure 9-10a shows the emission spectrum of a typical atomic lamp source, which consists of four narrow lines. With a suitable filter or monochromator, all but one of these lines are removed. Figure 9-10b shows the absorption spectrum for the analyte between wavelengths λ_1 and λ_2. Note that the bandwidth is significantly greater than that of the emission line. As shown in Figure 9-10c, passage of the line from the source through the flame reduces its intensity from P_0 to P; the absorbance is then given by $\log(P_0/P)$, which is linearly related to the concentration of the analyte in the sample.

A disadvantage of the procedure just described is that a separate source lamp is needed for each element (or sometimes group of elements).

Hollow-Cathode Lamps

The most common source for atomic absorption measurements is the hollow-cathode lamp, such as the one shown in Figure 9-11.[11] This type of lamp consists of a tungsten anode and a cylindrical cathode sealed in a glass tube filled with neon or argon at a pressure of 1 to 5 torr. The cathode is constructed of the metal whose spectrum is desired or serves to support a layer of that metal.

Ionization of the inert gas occurs when a potential difference on the order of 300 V is applied across the electrodes, which generates a current of about 5 to 15 mA as ions and electrons migrate to the electrodes. If the voltage is sufficiently large, the gaseous cations acquire enough kinetic energy to dislodge some of the metal atoms from the cathode surface and produce
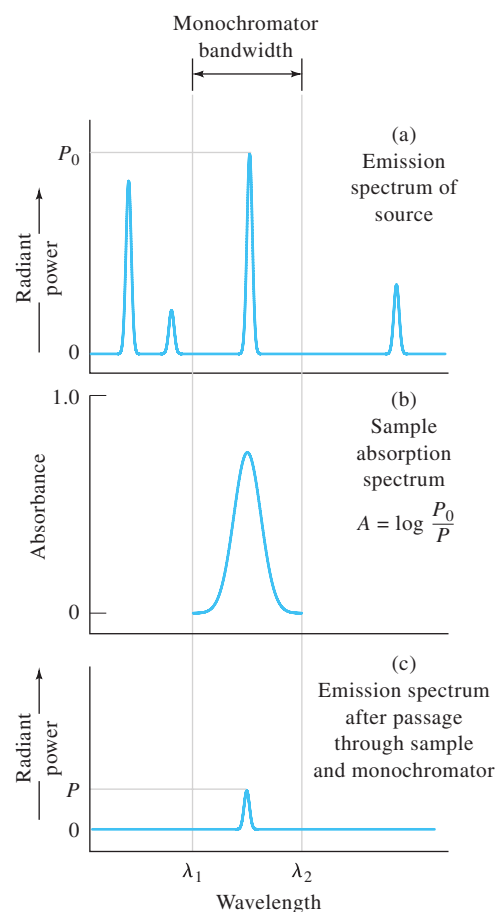

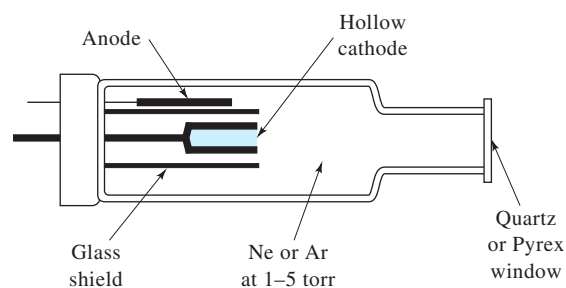**FIGURE 9-10** Absorption of a resonance line by atoms.

FIGURE 9-11 Schematic cross section of a hollow-cathode lamp.

an atomic cloud in a process called *sputtering*. A portion of the sputtered metal atoms are in excited states and thus emit their characteristic radiation as they return to the ground state. Eventually, the metal atoms diffuse back to the cathode surface or to the glass walls of the tube and are redeposited.

The cylindrical configuration of the cathode tends to concentrate the radiation in a limited region of the metal tube; this design also enhances the probability that redeposition will occur at the cathode rather than on the glass walls.

[10]B. Welz, H. Becker-Ross, S. Florek, and U. Heitmann, *High-Resolution Continuum Source AAS*, Hoboken, NJ: Wiley-VCH, 2005.

[11]See S. Caroli, *Improved Hollow Cathode Lamps for Atomic Spectroscopy*, New York: Wiley, 1985.

The efficiency of the hollow-cathode lamp depends on its geometry and the operating voltage. High voltages, and thus high currents, lead to greater intensities. This advantage is offset somewhat by an increase in Doppler broadening of the emission lines from the lamp. Furthermore, the greater currents produce an increased number of unexcited atoms in the cloud. The unexcited atoms, in turn, are capable of absorbing the radiation emitted by the excited ones. This *self-absorption* leads to lowered intensities, particularly at the center of the emission band.

Hollow-cathode lamps can also be used as sources in AFS, as discussed in Section 9E-1. In this application, the lamps are pulsed with a duty cycle of 1% to 10% and a peak current of 0.1 to 1 A, which increases their peak radiance by a factor of 10 to 100 relative to the steady-state radiance of dc operation.[12]

Many different hollow-cathode lamps are available commercially. The cathodes of some consist of a mixture of several metals. These multi-element lamps permit the determination of more than a single element.

Electrodeless Discharge Lamps

Electrodeless discharge lamps (EDLs) are useful sources of atomic line spectra and provide radiant intensities usually one to two orders of magnitude greater than hollow-cathode lamps.[13] A typical lamp is constructed from a sealed quartz tube containing a few torr of an inert gas such as argon and a small quantity of the metal (or its salt) whose spectrum is of interest. The lamp contains no electrode but instead is energized by an intense field of radio-frequency or microwave radiation. Ionization of the argon occurs to give ions that are accelerated by the high-frequency component of the field until they gain sufficient energy to excite the atoms of the metal whose spectrum is sought.

EDLs are available commercially for fifteen or more elements. Because of their high radiant intensities, EDLs were initially investigated as sources for AFS. Although the high intensities of EDLs are not needed for most AAS applications, for some elements, such as Se, As, and Sb, EDLs exhibit better detection limits than do hollow-cathode lamps. This occurs because hollow-cathode lamps for these elements are of low intensity or low stability, and thus EDLs provide better sensitivity and precision. Figure 9-12 is a schematic of a commercial EDL, which is powered by a 27-MHz radio-frequency source.

Source Modulation

In the typical atomic absorption instrument, it is necessary to eliminate interferences caused by emission of radiation by the flame. The emitted radiation at wavelengths outside of the monochromator bandpass is, of course, removed by the monochromator. However, emitted radiation corresponding in
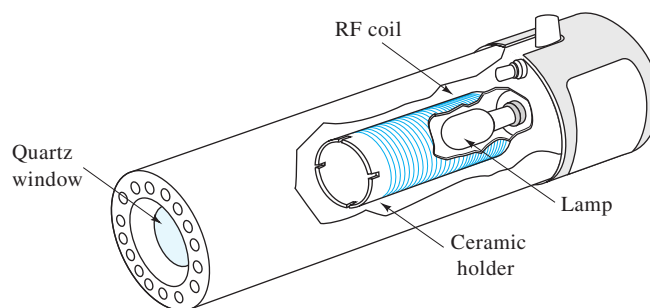

FIGURE 9-12 Cutaway of an EDL. (Courtesy of Perkin-Elmer Corp, Norwalk, CT. With permission.)

wavelength to the monochromator setting is inevitably present in the flame because of excitation and emission of analyte atoms and flame gas species. To eliminate the effects of flame emission, it is necessary to modulate the output of the source so that its intensity fluctuates at a constant frequency. The detector then receives two types of signal, an alternating one from the source and a continuous one from the flame. These signals are converted to the corresponding types of electrical response. A simple high-pass *RC* filter (Section 2B-5) can then be used to remove the unmodulated dc signal and pass the ac signal for amplification. Alternatively, a tuned or lock-in amplifier can be used.

A simple way of modulating the emission from the source is to interpose a circular metal disk, or chopper, in the beam between the source and the flame. Rotating disk and rotating vane choppers are common (see Figure 5-7a and b). Rotation of the disk or vane at a constant known rate provides a beam that is chopped to the desired frequency. Other types of electromechanical modulators include tuning forks with vanes attached to alternately block and transmit the beam (see Figure 5-7c) and devices that rotate a vane through a fixed arc to perform the same function.[14] As another alternative, the power supply for the source can be designed for intermittent or ac operation so that the source is switched on and off at the desired constant frequency.

9B-2 Spectrophotometers

Instruments for atomic absorption measurements are offered by numerous manufacturers; both single- and double-beam designs are available. The range of sophistication and cost (upward of a few thousand dollars) is substantial.

In general, the instrument must be capable of providing a sufficiently narrow bandwidth to isolate the line chosen for the measurement from other lines that may interfere with or diminish the sensitivity of the determination. An interference filter

[12]J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, p. 310, Englewood Cliffs, NJ: Prentice Hall, 1988.

[13]L. H. J. Lahunen and P. Peramki, *Spectrochemical Analysis by Atomic Absorption and Emission*, 2nd ed., pp. 43–44, Cambridge: Royal Society of Chemistry, 2004.

[14]J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, p. 44, Englewood Cliffs, NJ: Prentice Hall, 1988.

suffices for some of the alkali metals, which have only a few widely spaced resonance lines in the visible region. An instrument equipped with easily interchangeable interference filters is available commercially. A separate filter and light source are used for each element. Satisfactory results for the determination of twenty-two metals are claimed. Most instruments, however, incorporate good-quality ultraviolet-visible monochromators, many of which are capable of achieving a bandwidth on the order of 1 Å.

Most atomic absorption instruments use photomultiplier tubes, which were described in Section 7E-2, as transducers. As pointed out earlier, electronic systems that are capable of discriminating between the modulated signal from the source and the continuous signal from the flame are required. Most instruments currently on the market are equipped with computer systems that are used to control instrument parameters and to control and manipulate data.

Exercise: Learn more about **single-beam and double-beam spectrophotometers** at www.tinyurl.com/skoogpia7

Single-Beam Instruments

A typical single-beam instrument, such as that shown in Figure 9-13a, consists of several hollow-cathode sources (only one of which is shown), a chopper or a pulsed power supply, an atomizer, and a simple grating spectrophotometer with a photomultiplier transducer. In use, the dark current is first nulled with a shutter in front of the transducer. The 100% transmittance adjustment is then made while a blank is aspirated into the flame or ignited in an electrothermal atomizer. Finally, the sample transmittance is obtained with the sample being atomized.

Double-Beam Instruments

Figure 9-13b is a schematic of a typical double-beam-in-time instrument. The beam from the hollow-cathode source is split by a mirrored chopper, one half passing through the flame and the other half around it. The two beams are then recombined by a half-silvered mirror and passed into a grating monochromator; a photomultiplier tube serves as the transducer. The output from the latter is the input to a lock-in amplifier that is synchronized with the chopper drive. The ratio between the reference and sample signal is then amplified and sent to the readout, which is typically a digital meter or a computer.
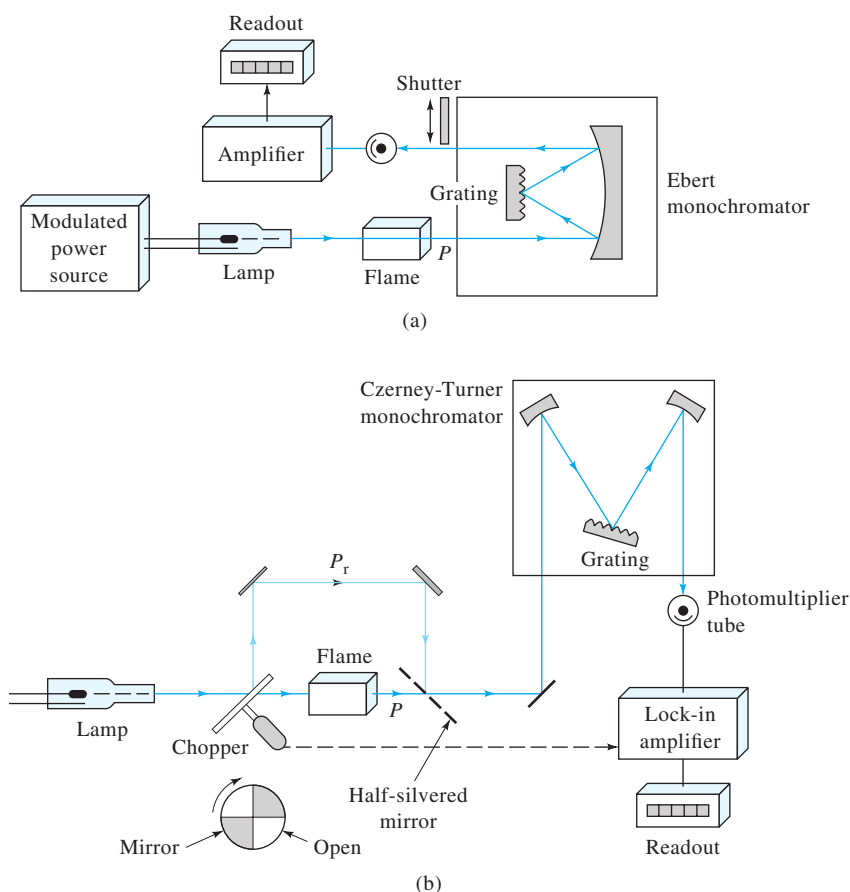

FIGURE 9-13 Typical flame atomic absorption spectrophotometers: (a) single-beam design and (b) double-beam design.

It should be noted that the reference beam in atomic double-beam instruments does not pass through the flame and thus does not correct for loss of radiant power due to absorption or scattering by the flame itself. Methods of correcting for these losses are discussed in the next section.

9C   INTERFERENCES IN ATOMIC ABSORPTION SPECTROSCOPY

Interferences of two types are encountered in atomic absorption methods. Spectral interferences arise when the absorption or emission of an interfering species either overlaps or lies so close to the analyte absorption or emission that the monochromator cannot resolve them. Chemical interferences result from various chemical processes occurring during atomization that alter the absorption characteristics of the analyte.

9C-1 Spectral Interferences

Because the emission lines of hollow-cathode sources are so very narrow, interference because of overlapping lines is rare. For such an interference to occur, the separation between the two lines would have to be less than about 0.1 Å. For example, a vanadium line at 3082.11 Å interferes in the determination of aluminum based on its absorption line at 3082.15 Å. The interference is easily avoided, however, by using the aluminum line at 3092.7 Å instead.

Spectral interferences also result from the presence of combustion products that exhibit broadband absorption or particulate products that scatter radiation. Both reduce the power of the transmitted beam and lead to positive analytical errors. When the source of these products is the fuel and oxidant mixture alone, the analytical data can be corrected by making absorption measurements while a blank is aspirated into the flame. Note that this correction must be used with both double-beam and single-beam instruments because the reference beam of a double-beam instrument does not pass through the flame (see Figure 9-13b).

A much more troublesome problem occurs when the source of absorption or scattering originates in the sample matrix. In this instance, the power of the transmitted beam P is reduced by the matrix components, but the incident beam power P_0 is not. The result is a positive error in absorbance and thus concentration. An example of a potential matrix interference because of absorption occurs in the determination of barium in alkaline-earth mixtures. As shown by the solid line in Figure 8-8, the wavelength of the barium line used for atomic absorption analysis appears in the center of a broad absorption band for CaOH. We therefore anticipate that calcium will interfere in barium determinations, but the effect is easily eliminated by substituting nitrous oxide for air as the oxidant. The higher temperature of the nitrous oxide flame decomposes the CaOH and eliminates the absorption band.

Spectral interference because of scattering by products of atomization is most often encountered when concentrated solutions containing elements such as Ti, Zr, and W—which form refractory oxides—are aspirated into the flame. Metal oxide particles with diameters greater than the wavelength of light appear to be formed, and scattering of the incident beam results.

Interference caused by scattering may also be a problem when the sample contains organic species or when organic solvents are used to dissolve the sample. Here, incomplete combustion of the organic matrix leaves carbonaceous particles that are capable of scattering light.

Fortunately, with flame atomization, spectral interferences by matrix products are not widely encountered and often can be avoided by variations in the analytical variables, such as flame temperature and fuel-to-oxidant ratio. Alternatively, if the source of interference is known, an excess of the interfering substance can be added to both sample and standards. Provided the excess added to the standard sample is large with respect to the concentration from the sample matrix, the contribution from the sample matrix will become insignificant. The added substance is sometimes called a *radiation buffer*. The method of standard additions can also be used advantageously in some cases.

In the early days of electrothermal atomization, matrix interference problems were severe. As platform technology, new high-quality graphite materials, fast photometric instrumentation, and Zeeman background correction have developed, matrix interference problems have decreased to the level encountered with flames. Several methods have been developed for correcting for spectral interferences caused by matrix products.[15]

The Two-Line Correction Method
The two-line correction procedure uses a second line from the source as a reference. The wavelength of the reference line should be as close as possible to that of the analyte line but must not be absorbed by the analyte. If these conditions are met, it is assumed that any decrease in power of the reference line from that observed during calibration arises from absorption or scattering by the matrix products of the sample. This decrease in power is then used to correct the absorbance of the analyte line.

The reference line may be from an impurity in the hollow cathode, a neon or argon line from the gas contained in the lamp, or a nonresonant emission line of the element that is being determined. Unfortunately, a suitable reference line is often not available.

The Continuum-Source Correction Method
Figure 9-14 illustrates a second method for background correction that is widely used. In this technique, a deuterium lamp provides a source of continuum radiation throughout the ultraviolet region. The configuration of the chopper is such that radiation from the continuum source and the hollow-cathode lamp are passed alternately through the electrothermal atomizer. The slit width is kept sufficiently wide so that the fraction of the continuum source that is absorbed by the analyte atoms in the sample is negligible. Therefore, the attenuation of the continuum

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[15]For a comparison of the various methods for background correction, see D. J. Butcher and J. Sneddon, *A Practical Guide to Graphite Furnace Atomic Absorption Spectrometry*, New York: Wiley, 1998, pp. 84–89.
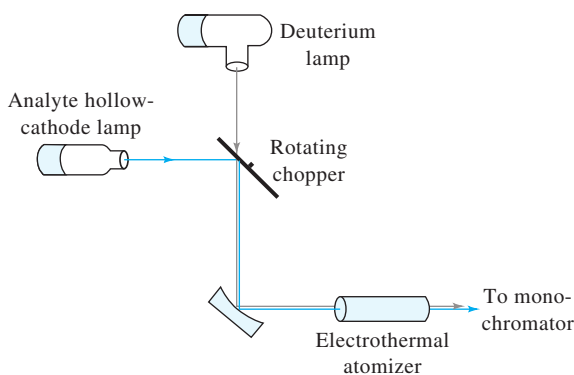
FIGURE 9-14 Schematic of a continuum-source background correction system. Note that the chopper can be eliminated by alternately pulsing each lamp.

source as it passes through the atomized sample reflects only the broadband absorption or scattering by the sample matrix components. A background correction is achieved by subtracting the absorbance of the deuterium lamp from that of the analyte lamp.

Unfortunately, although most instrument manufacturers offer continuum-source background correction systems, the performance of these devices is often less than ideal, which leads to undercorrection in some systems and overcorrection in others. One of the sources of error is the inevitable degradation of signal-to-noise ratio that accompanies the addition of the correction system. Another is that hot gaseous media are usually highly inhomogeneous both in chemical composition and in particulate distribution; thus if the two lamps are not in perfect alignment, an erroneous correction will result that can cause either a positive or a negative error. Finally, the radiant output of the deuterium lamp in the visible region is low enough to preclude the use of this correction procedure for wavelengths longer than about 350 nm.

Background Correction Based on the Zeeman Effect

When an atomic vapor is exposed to a strong magnetic field ($\sim$10 kG), a splitting of electronic energy levels of the atoms takes place that leads to formation of several absorption lines for each electronic transition. These lines are separated from one another by about 0.01 nm, with the sum of the absorbances for the lines being exactly equal to that of the original line from which they were formed. This phenomenon, which is termed the Zeeman effect,[16] is general for all atomic spectra. The splitting patterns that arise depend on the type of electronic transition in the absorption process. The simplest splitting pattern, which is observed with singlet (Section 8A-1) transitions, leads to a central, or π, line and two equally spaced satellite σ lines. The central line, which is at the original wavelength, has an absorbance that is twice that of each σ line. For more complex transitions, further splitting of the π and σ lines occurs.

Application of the Zeeman effect to atomic absorption instruments is based on the differing response of the two types of absorption lines to polarized radiation. The π line absorbs only that radiation that is plane polarized in a direction parallel to the external magnetic field; the σ lines, in contrast, absorb only radiation polarized perpendicular to the field.

Figure 9-15 shows details of an electrothermal atomic absorption instrument, which uses the Zeeman effect for background correction. Unpolarized radiation from an ordinary hollow-cathode source A is passed through a rotating polarizer B, which separates the beam into two components that are plane-polarized at 90° to one another C. These beams pass into a tube-type graphite furnace similar to the one shown in Figure 9-6a. A permanent 11-kG magnet surrounds the furnace and splits the energy levels into the three absorption peaks shown in D. Note that the central peak absorbs only radiation that is plane polarized with the field. During that part of the cycle when the source radiation is polarized similarly, absorption of radiation by the analyte takes place as shown in E. During the other half cycle, no analyte absorption can occur. Broadband molecular absorption and scattering by the matrix products occur during both half cycles, which leads to the cyclical absorbance pattern shown in F. The data-acquisition system is programmed to subtract the absorbance during the perpendicular half cycle from that for the parallel half cycle, thus giving a background corrected value.

A second type of Zeeman effect instrument has been designed in which a magnet surrounds the hollow-cathode source. Here, it is the emission spectrum of the source that is split rather than the absorption spectrum of the sample. This instrument configuration provides an analogous correction. To date, most instruments are of the type illustrated in Figure 9-15.

Zeeman effect instruments provide a more accurate correction for background than the methods described earlier. These instruments are particularly useful for electrothermal atomizers and permit the direct determination of elements in samples such as urine and blood. The decomposition of organic material in these samples leads to large background corrections (background $A > 1$) and, as a result, susceptibility to significant error.

Background Correction Based on Source Self-Reversal

A remarkably simple means of background correction offers most of the advantages of a Zeeman effect instrument.[17] This method, which is sometimes called the Smith-Hieftje background correction method, is based on the self-reversal or self-absorption behavior of radiation emitted from hollow-cathode lamps when

> **Tutorial:** Learn more about the **Zeeman effect** at www.tinyurl.com/skoogpia7

[16]For a detailed discussion of the application of the Zeeman effect to atomic absorption, see D. J. Butcher and J. Sneddon, *A Practical Guide to Graphite Furnace Atomic Absorption Spectrometry*, New York: Wiley, 1998, pp. 73–84; F. J. Fernandez, S. A. Myers, and W. Slavin, *Anal. Chem.*, **1980**, *52*, 741.

[17]See S. B. Smith Jr. and G. M. Hieftje, *Appl. Spectrosc.*, **1983**, *37*, 419, **DOI**: 10.1366/0003702834634893.
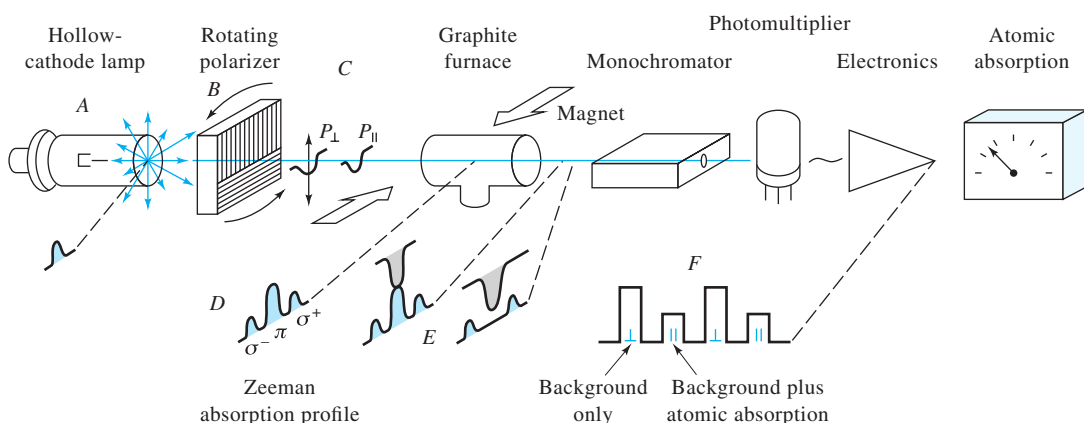
FIGURE 9-15 Schematic of an electrothermal atomic absorption instrument that provides a background correction based on the Zeeman effect. (Courtesy of Hitachi Scientific Instruments, Mountain View, CA.)

they are operated at high currents. High currents produce large concentrations of nonexcited atoms, which are capable of absorbing the radiation produced from the excited species. An additional effect of high currents is to significantly broaden the emission line of the excited species. The net effect is to produce a line that has a minimum in its center, which corresponds exactly in wavelength to that of the absorption line (see Figure 9-16).

To obtain corrected absorbances, the lamp is programmed to run alternately at low and high currents. The total absorbance is obtained during the low-current operation and the background absorbance is provided by measurements during the second part of the cycle when radiation at the absorption peak is at a minimum. The data-acquisition system then subtracts the background absorbance from the total to give a corrected value. Recovery of the source to its low-current output takes place in milliseconds when the current is reduced. The measurement cycle can be repeated often enough to give satisfactory signal-to-noise ratios. Instrumentation for this type of correction is available from commercial sources.
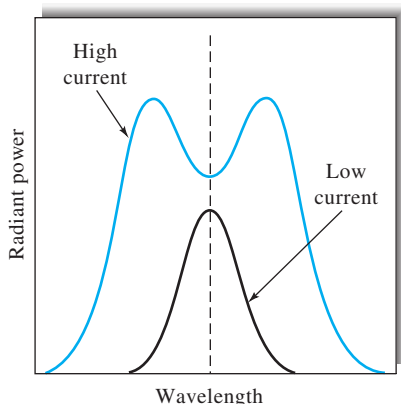

FIGURE 9-16 Emission line profiles for a hollow-cathode lamp operated at high and low currents.

9C-2 Chemical Interferences

Chemical interferences are more common than spectral interferences in ASS. Their effects can frequently be minimized by a suitable choice of operating conditions.

Both theoretical and experimental evidence suggest that many of the processes occurring in the mantle of a flame are in approximate equilibrium. Therefore, it becomes possible to regard the burned gases as a solvent medium to which thermodynamic calculations can be applied. The equilibria of principal interest include formation of compounds of low volatility, dissociation reactions, and ionization.

Formation of Compounds of Low Volatility

Perhaps the most common type of interference is by anions that form compounds of low volatility with the analyte and thus reduce the fraction of the analyte that is atomized. Low results are the outcome. An example is the decrease in calcium absorbance observed with increasing concentrations of sulfate or phosphate. These anions form compounds with calcium that are difficult to volatilize. For example, at a fixed calcium concentration, the absorbance falls off nearly linearly with increasing sulfate or phosphate concentrations until the anion-to-calcium ratio is about 0.5; the absorbance then levels off at about 30% to 50% of its original value and becomes independent of anion concentration.

Cation interference has been observed as well. For example, aluminum causes low results in the determination of magnesium, apparently as a result of the formation of a heat-stable aluminum-magnesium compound (perhaps an oxide).

Interferences caused by formation of species of low volatility can often be eliminated or moderated by use of higher temperatures. Alternatively, *releasing agents*, which are cations that react preferentially with the interferant and prevent its interaction with the analyte, can be used. For example, addition of an excess of strontium or lanthanum ion minimizes the interference of phosphate in the determination of calcium. The same

two species have also been used as releasing agents for the determination of magnesium in the presence of aluminum. In both instances, the strontium or lanthanum replaces the analyte in the compound formed with the interfering species.

Protective agents prevent interference by forming stable but volatile species with the analyte. Three common reagents for this purpose are ethylenediaminetetraacetic acid (EDTA), 8-hydroxyquinoline, and APCD, which is the ammonium salt of 1-pyrrolidinecarbodithioic acid. The presence of EDTA has been shown to nearly eliminate the interference of aluminum, silicon, phosphate, and sulfate in the determination of calcium. Similarly, 8-hydroxyquinoline suppresses the interference of aluminum in the determination of calcium and magnesium.

Dissociation Equilibria

In the hot, gaseous environment of a flame or a furnace, numerous dissociation and association reactions lead to conversion of the metallic constituents to the elemental state. Some of these reactions are reversible and can be treated by the laws of thermodynamics. Thus, equilibria such as

$$MO \rightleftharpoons M + O$$

$$M(OH)_2 \rightleftharpoons M + 2OH$$
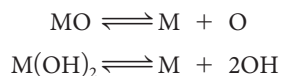
are thought to exist in flames, where M is the analyte atom and OH is the hydroxyl radical.

In practice, not enough is known about the nature of the chemical reactions in a flame to permit a quantitative treatment such as that for an aqueous solution. Instead, we must rely on empirical observations.

Dissociation reactions involving metal oxides and hydroxides play an important part in determining the nature of the emission or absorption spectra for an element. For example, the alkaline-earth oxides are relatively stable, with dissociation energies in excess of 5 eV. Molecular bands arising from the presence of metal oxides or hydroxides in the flame thus constitute a prominent feature of their spectra (see Figure 8-8). Except at very high temperatures, these bands are more intense than the lines for the atoms or ions. In contrast, the oxides and hydroxides of the alkali metals are much more easily dissociated so that line intensities for these elements are high, even at relatively low temperatures.

Dissociation equilibria that involve anions other than oxygen may also influence flame emission and absorption. For example, the line intensity for sodium is markedly decreased by the presence of HCl. A likely explanation is the mass-action effect on the equilibrium

$$NaCl \rightleftharpoons Na + Cl$$
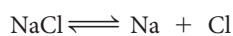
Chlorine atoms formed from the added HCl decrease the atomic sodium concentration and thereby lower the line intensity.

Another example of this type of interference is the enhancement of vanadium absorption when aluminum or titanium is present. The interference is significantly more pronounced in fuel-rich flames than in lean flames. These effects can be explained by assuming that the three metals interact with such species as O and OH, which are always present in flames. If the oxygen-bearing species are given the general formula Ox, a series of equilibrium reactions can be postulated. Thus,

$$VOx \rightleftharpoons V + Ox$$

$$AlOx \rightleftharpoons Al + Ox$$

$$TiOx \rightleftharpoons Ti + Ox$$
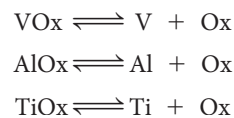
In fuel-rich combustion mixtures, the concentration of Ox is sufficiently small that its concentration is lowered significantly when aluminum or titanium is present in the sample. This decrease causes the first equilibrium to shift to the right with an accompanying increase in the vanadium concentration and absorbance. In lean mixtures, on the other hand, the concentration of Ox is apparently high relative to the total concentration of metal atoms. In this case, addition of aluminum or titanium scarcely changes the concentration of Ox, and the position of the first equilibrium is relatively undisturbed. Therefore, the position of the first equilibrium is not disturbed significantly.

Ionization Equilibria

Ionization of atoms and molecules is small in combustion mixtures with air as the oxidant, and can often be neglected. In higher temperature flames where oxygen or nitrous oxide serves as the oxidant, however, ionization becomes important, and there is a significant concentration of free electrons produced by the equilibrium

$$M \rightleftharpoons M^+ + e^- \tag{9-1}$$

where M represents a neutral atom or molecule and M^+ is its ion. We will focus on equilibria in which M is a metal atom.

The equilibrium constant K for this reaction takes the form

$$K = \frac{[M^+][e^-]}{[M]} \tag{9-2}$$

If no other source of electrons is present in the flame, this equation can be written in the form

$$K = \left(\frac{\alpha^2}{1 - \alpha}\right)P$$

where α is the fraction of M that is ionized, and P is the partial pressure of the metal in the gaseous solvent before ionization.

Table 9-2 shows the calculated fraction ionized for several common metals under conditions that approximate those used in flame spectroscopy. The temperatures correspond roughly to those in air-acetylene and oxygen-acetylene flames, respectively.

TABLE 9-2 Degree of Ionization of Metals at Flame Temperatures

Element	Ionization Potential, eV	Fraction Ionized at the Indicated Pressure and Temperature			
		$P = 10^{-4}$ atm		$P = 10^{-6}$ atm	
		2000 K	3500 K	2000 K	3500 K
Cs	3.893	0.01	0.86	0.11	>0.99
Rb	4.176	0.004	0.74	0.04	>0.99
K	4.339	0.003	0.66	0.03	0.99
Na	5.138	0.0003	0.26	0.003	0.90
Li	5.390	0.0001	0.18	0.001	0.82
Ba	5.210	0.0006	0.41	0.006	0.95
Sr	5.692	0.0001	0.21	0.001	0.87
Ca	6.111	3×10^{-5}	0.11	0.0003	0.67
Mg	7.644	4×10^{-7}	0.01	4×10^{-6}	0.09

Data from B. L. Vallee and R. E. Thiers, in *Treatise on Analytical Chemistry,* I. M. Kolthoff and P. J. Elving, eds., Part I, Vol. 6, p. 3500, New York: Interscience, 1965. Reprinted with permission of John Wiley & Sons, Inc.

It is important to appreciate that treatment of the ionization process as an equilibrium—with free electrons as one of the products—immediately implies that the degree of ionization of a metal will be strongly influenced by the presence of other ionizable metals in the flame. Thus, if the medium contains not only species M but species B as well, and if B ionizes according to the equation

$$B \rightleftharpoons B^+ + e^-$$

then the degree of ionization of M will be decreased by the mass-action effect of the electrons formed from B. Determination of the degree of ionization under these conditions requires a calculation involving the dissociation constant for B and the mass-balance expression

$$[e^-] = [B^+] + [M^+]$$

Atom-ion equilibria in flames create a number of important consequences in flame spectroscopy. For example, intensities of atomic emission or absorption lines for the alkali metals, particularly potassium, rubidium, and cesium, are affected by temperature in a complex way. Increased temperatures cause an increase in the population of excited atoms, according to the Boltzmann relationship (Equation 8-1). Counteracting this effect, however, is a decrease in concentration of atoms resulting from ionization. Thus, under some circumstances a decrease in emission or absorption may be observed in hotter flames. It is for this reason that lower excitation temperatures are usually specified for the determination of alkali metals.

The effects of shifts in ionization equilibria can usually be eliminated by addition of an *ionization suppressor*, which provides a relatively high concentration of electrons to the flame;

suppression of ionization of the analyte results. The effect of a suppressor appears in the calibration curves for strontium shown in Figure 9-17. Note the significant increase in slope of these curves as strontium ionization is repressed by the increasing concentration of potassium ions and electrons. Note also the enhanced sensitivity produced by using nitrous oxide instead of air as the oxidant. The higher temperature achieved with nitrous oxide undoubtedly enhances the degree of decomposition and volatilization of the strontium compounds in the plasma.
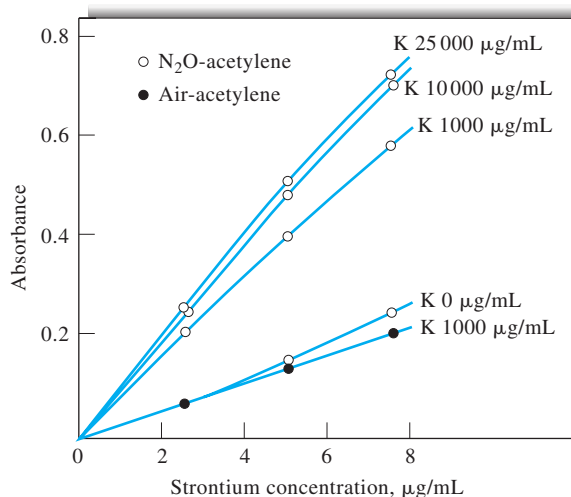

FIGURE 9-17 Effect of potassium concentration on the calibration curve for strontium. (Reprinted with permission from J. A. Bowman and J. B. Willis, *Anal. Chem.*, **1967**, *39*, 1210, **DOI:** 10.1021/ac60255a014. Copyright 1967 American Chemical Society.)

9D ATOMIC ABSORPTION ANALYTICAL TECHNIQUES

There are a number of practical details that must be considered in flame or electrothermal atomic absorption analysis.

9D-1 Sample Preparation

A disadvantage of flame spectroscopic methods is the requirement that the sample be introduced into the excitation source in the form of a solution, most commonly an aqueous one. Unfortunately, many materials of interest, such as soils, animal tissues, plants, petroleum products, and minerals are not directly soluble in common solvents, and extensive preliminary treatment is often required to obtain a solution of the analyte in a form ready for atomization. Indeed, the decomposition and solution steps are often more time-consuming and introduce more error than the spectroscopic measurement itself.

Decomposition of materials such as those just cited usually require rigorous treatment of the sample at high temperatures accompanied by a risk of losing the analyte by volatilization or as particulates in smoke. Furthermore, the reagents used in decomposing a sample often introduce the kinds of chemical and spectral interferences that were discussed earlier. Additionally, the analyte may be present in these reagents as an impurity. In fact, unless considerable care is taken, it is not uncommon in trace analyses to find that the concentration of analyte in the reagents is higher than in the samples—a situation that can lead to serious error even with blank corrections.

Some of the common methods used for decomposing and dissolving samples for atomic absorption methods include treatment with hot mineral acids; oxidation with liquid reagents, such as sulfuric, nitric, or perchloric acids (wet ashing); combustion in an oxygen bomb or other closed container to avoid loss of analyte; ashing at a high temperature; and high-temperature fusion with reagents such as boric oxide, sodium carbonate, sodium peroxide, or potassium pyrosulfate.[18]

One of the advantages of electrothermal atomization is that some materials can be atomized directly, thus avoiding the solution step. For example, liquid samples such as blood, petroleum products, and organic solvents can be pipetted directly into the furnace for ashing and atomization. Solid samples, such as plant leaves, animal tissues, and some inorganic substances, can be weighed directly into cup-type atomizers or into tantalum boats

Tutorial: Learn more about **atomic absorption spectroscopy** at www.tinyurl.com/skoogpia7

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[18]B. Kebbekus in *Sample Preparation Techniques in Analytical Chemistry*, S. Mitra, ed., Ch. 5. New York: Wiley, 2003; J. A. Dean, *Analytical Chemistry Handbook*, Section 1.7, New York: McGraw-Hill, 1995; R. Bock, *A Handbook of Decomposition Methods in Analytical Chemistry*, New York: Wiley, 1979.

for introduction into tube-type furnaces. Calibration is, however, usually difficult and requires standards that approximate the sample in composition.

9D-2 Sample Introduction by Flow Injection

In Section 33B, we describe the methods and instrumentation for flow injection analysis (FIA). FIA methodology serves as an excellent means of introducing samples into a flame atomic absorption spectrometer. Alternatively, we may think of an atomic absorption spectrometer as a useful detector for an FIA system. From any perspective, the peristaltic pump and valve arrangements of FIA described in Chapter 33 are a convenient means to sample analyte solutions reproducibly and efficiently, especially when it is important to conserve sample. The carrier stream of the FIA system consisting of deionized water or dilute electrolyte provides continuous flushing of the flame atomizer, which is particularly advantageous for samples containing high levels of salts or suspended solids.

9D-3 Organic Solvents

Early in the development of atomic absorption spectroscopy it was recognized that enhanced absorbances could be obtained if the solutions contained low-molecular mass alcohols, esters, or ketones. The effect of organic solvents is largely attributable to increased nebulizer efficiency; the lower surface tension of such solutions leads to smaller drop sizes and a resulting increase in the amount of sample that reaches the flame. In addition, more rapid solvent evaporation may also contribute to the effect. Leaner fuel-oxidant ratios must be used with organic solvents to offset the presence of the added organic material. Unfortunately, however, the leaner mixture produces lower flame temperatures and an increased potential for chemical interferences.

A most important analytical application of organic solvents to flame spectroscopy is the use of immiscible solvents such as methyl isobutyl ketone to extract chelates of metallic ions. The extract is then nebulized directly into the flame. The sensitivity is increased not only by the enhancement of absorption lines because of the solvent but also because for many systems only small volumes of the organic liquid are required to remove metal ions quantitatively from relatively large volumes of aqueous solution. This concentrating procedure has the added advantage that at least part of the matrix components are likely to remain in the aqueous phase, resulting in a reduction of interferences. Common chelating agents include ammonium pyrrolidinedithiocarbamate, diphenylthiocarbazone (dithizone), 8-hydroxyquinoline, and acetylacetone.

9D-4 Calibration Curves

In theory, atomic absorption should follow Beer's law (Equation 6-34) with absorbance being directly proportional to concentration. Unfortunately, plots of absorbance versus

TABLE 9-3 Detection Limits (ng/mL)[a] for Selected Elements

Element	AAS Flame	AAS Electro-thermal	AES Flame	AES ICP	AFS ICP
Al	30	0.1	5	0.2	5
As	200	0.5	—	2	15
Ca	1	0.25	0.1	0.0001	0.4
Cd	1	0.01	2000	0.07	0.1
Cr	4	0.03	5	0.08	0.6
Cu	2	0.05	10	0.04	0.2
Fe	6	0.25	50	0.09	0.3
Hg	500	5	—	—	5
Mg	0.2	0.002	5	0.003	0.3
Mn	2	0.01	—	0.01	1
Mo	5	0.5	100	0.2	8
Na	0.2	0.02	0.1	0.1	0.3
Ni	3	0.5	600	0.2	0.4
Pb	8	0.1	200	1	5
Sn	15	5	300	—	200
V	25	1	200	0.06	25
Zn	1	0.005	50000	0.1	0.1

From J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, pp. 250–251, 300, 321, Englewood Cliffs, NJ: Prentice Hall, 1988.

Note: For AFS, pulsed hollow-cathode-lamp excitation source used with ICP atomization.

[a] $1 \text{ ng/mL} = 10^{-3} \text{ μg/mL} = 10^{-3} \text{ ppm}$.

AAS = atomic absorption spectroscopy; AES = atomic emission spectroscopy; AFS = atomic fluorescence spectroscopy; ICP = inductively coupled plasma.

concentration are often nonlinear. Thus, a calibration curve that covers the range of concentrations found in the sample is almost always needed and should be prepared periodically. In addition, the number of uncontrolled variables in atomization and absorbance measurements is sufficiently large to warrant measurement of at least one standard solution each time an analysis is performed. An even better practice is to use two standards that bracket the analyte concentration. Any deviation of the standard from the original calibration curve can then be used to correct the analytical result.

9D-5 Standard-Addition Method

The standard-addition method, which was described in Section 1D-3, is widely used in atomic absorption spectroscopy to partially or completely compensate for the chemical and spectral interferences introduced by the sample matrix.

9D-6 Applications of AAS

AAS is a sensitive method to determine more than sixty metals or metalloid elements. The resonance lines for the nonmetallic elements are generally located at wavelengths shorter than 200 nm, which can prevent their determination by convenient, nonvacuum spectrophotometers.

Detection Limits

Columns two and three of Table 9-3 present detection limits for a number of common elements by flame and electrothermal atomic absorption. For comparison, detection limits for some of the other atomic procedures are also included. Small differences among the quoted values are not significant. Thus, an order of magnitude is probably meaningful, but a factor of 2 or 3 certainly is not.

For many elements, detection limits for atomic absorption spectroscopy with flame atomization lie in the range of 1 to 20 ng/mL, or 0.001 to 0.020 ppm; for electrothermal atomization, the corresponding figures are 0.002 to 0.01 ng/mL, or 2×10^{-6} to 1×10^{-5} ppm. In a few cases, detection limits well outside these ranges are encountered.

Accuracy

Under the usual conditions, the relative error associated with a flame atomic absorption analysis is of the order of a few percent. With special precautions, this figure can be lowered to a few tenths of a percent. Errors encountered with electrothermal atomization usually exceed those for flame atomization by a factor of 5 to 10.

9E ATOMIC FLUORESCENCE SPECTROSCOPY

Over the years, significant research effort has been devoted to the development of analytical methods based on atomic fluorescence.[19] This research has demonstrated that AFS is useful and convenient for the quantitative determination of several elements. To date, however, AFS has not been used widely because of the overwhelming successes of atomic emission and atomic absorption methods, which were developed prior to atomic fluorescence by more than a decade. As mentioned earlier, these successes have led to the availability of absorption and emission instruments from numerous commercial sources. In recent years, a number of manufacturers have introduced atomic

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[19] For further information on AFS, see L. H. J. Lajunen and P. Peramaki, *Spectrochemical Analysis by Atomic Absorption and Emission*, 2nd ed., pp. 276–285, Cambridge: Royal Society of Chemistry, 2004; J. A. C. Broekaert, *Analytical Atomic Spectrometry with Flames and Plasmas*, pp. 290–296, Weinheim, Germany: Wiley-VCH, 2002; D. J. Butcher in *Handbook of Instrumental Techniques for Analytical Chemistry*, F. A. Settle, ed., Upper Saddle River, NJ, 1997, pp. 441–458.

fluorescence spectrometers useful for determining elements that form vapors and hydrides, such as Pb, Hg, Cd, Zn, As, Sb, Bi, Ge, and Se.[20]

The limited use of atomic fluorescence has not arisen so much from any inherent weakness of the procedure but rather because the advantages of atomic fluorescence have been small relative to the well-established absorption and emission methods. Thus, although fluorescence methods, particularly those based on electrothermal atomization, are somewhat more sensitive for several elements, the procedure is also less sensitive and appears to have a smaller useful concentration range for several others. These disadvantages have been largely overcome in some special-purpose instruments such as those for determining mercury by cold-vapor techniques. This method is further discussed in the Instrumental Analysis in Action feature at the end of Section 2.

9E-1 Instrumentation

The components of instruments for atomic fluorescence measurements are generally arranged as shown in Figure 7-1b. The sample container is most commonly a flame but may also be an electrothermal atomization cell, a glow discharge, a vapor cell, or an inductively coupled plasma, as described in Section 10A-1.

Sources

A continuum source would be desirable for atomic fluorescence measurements. Unfortunately, however, the output power of most continuum sources over a region as narrow as an atomic absorption line is too low to provide sufficient sensitivity for atomic fluorescence.

The earliest work on AFS was done using metal vapor lamps.[21] These lamps are not as stable as many other line sources and are only available for a few elements. Conventional hollow-cathode lamps were also used in early work. However, these were usually not intense enough to achieve low detection limits with AFS. In later work, pulsed hollow-cathode lamps (see Section 9B-1) were used to achieve high intensities. The detection system was gated to observe the fluorescence signal only during the ON time of the pulsed lamp.[22]

Perhaps the most widely used sources for atomic fluorescence have been the EDLs (Section 9B-1), which usually produce radiant intensities greater than those of hollow-cathode lamps by an order of magnitude or two. EDLs have been operated in both the continuous and pulsed modes. Unfortunately, this type of lamp is only available for a few elements.

Lasers, with their high intensities and narrow bandwidths, would appear to be the ideal source for atomic fluorescence measurements. Their high cost and operational complexities, however, have discouraged their widespread application to routine atomic fluorescence methods.

Dispersive Instruments

A dispersive system for atomic fluorescence measurements consists of a modulated source, an atomizer (flame or electrothermal), a monochromator or an interference filter system, a detector, and a signal processor and readout. With the exception of the source, most of these components are similar to those discussed in earlier parts of this chapter.

Nondispersive Instruments

In theory, no monochromator or filter should be necessary for atomic fluorescence measurements when an EDL or hollow-cathode lamp serves as the excitation source because the emitted radiation is, in principle, that of a single element and will thus excite only atoms of that element. A nondispersive system then could be made up of only a source, an atomizer, and a detector. There are several advantages of such a system: (1) simplicity and low-cost instrumentation, (2) adaptability to multielement analysis, (3) high-energy throughput and thus high sensitivity, and (4) simultaneous collection of energy from multiple lines, which also enhances sensitivity.

To realize these important advantages, it is necessary that the output of the source be free of contaminating lines from other elements; in addition, the atomizer should emit no significant background radiation. In some instances with electrothermal atomizers, background radiation is minimal, but certainly, it is not with typical flames. To overcome this problem, filters, located between the source and detector, have often been used to remove most of the background radiation. Alternatively, solar-blind photomultipliers, which respond only to radiation of wavelengths shorter than 320 nm, have been applied. For these devices to be used effectively, analyte emission must be below 320 nm.

9E-2 Interferences

Interferences in atomic fluorescence spectroscopy are generally of the same type and of about the same magnitude as those in atomic absorption spectroscopy.

9E-3 Applications

Atomic fluorescence methods have been applied to the determination of metals in such materials as lubricating oils, seawater, geological samples, metallurgical samples, clinical samples, environmental samples, and agricultural samples. Table 9-3 lists detection limits for atomic fluorescence procedures.

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[20]Examples include Teledyne/Leeman Labs (Hudson, NH), Aurora Biomed (Vancouver, BC), PS Analytical (Deerfield Beach, FL), Arizona Instruments (Chandler, AZ), and Skyray Instruments (Japan).

[21]J. D. Winefordner and T. J. Vickers, *Anal. Chem.*, **1964**, *36*, 161, **DOI**: 10.1021/ac60207a052; J. D. Winefordner and R. A. Staab, *Anal. Chem.*, **1964**, *36*, 165, **DOI**: 10.1021/ac60207a053.

[22]E. Cordos and H. V. Malmstadt, *Anal. Chem.*, **1973**, *45*, 27, **DOI**: 10.1021/ac60323a006; *Anal. Chem.*, **1972**, *44*, 2277, **DOI**: 10.1021/ac60322a004.

≫ QUESTIONS AND PROBLEMS

*Answers are provided at the end of the book for problems marked with an asterisk.

X⊞ Problems with this icon are best solved using spreadsheets.

9-1 Define the following terms: (a) releasing agent, (b) protective agent, (c) ionization suppressor, (d) atomization, (e) pressure broadening, (f) hollow-cathode lamp, (g) sputtering, (h) self-absorption, (i) spectral interference, (j) chemical interference, (k) radiation buffer, (l) solute volatilization interference.

9-2 Describe the effects that are responsible for the three different absorbance profiles in Figure 9-4 and select three additional elements you would expect to have similar profiles.

9-3 Why is an electrothermal atomizer more sensitive than a flame atomizer?

9-4 Describe how a deuterium lamp can be used to provide a background correction for an atomic absorption spectrum.

9-5 Why is source modulation used in atomic absorption spectroscopy?

9-6 For two solutions containing the same concentration of nickel, the atomic absorption at 352.4 nm was about 30% greater for a solution that contained 50% ethanol than for an aqueous solution that contained no ethanol. Explain.

9-7 The emission spectrum of a hollow-cathode lamp for molybdenum has a sharp line at 313.3 nm as long as the lamp current is less than 50 mA. At higher currents, however, the emission line develops a cuplike crater at its maximum. Explain.

9-8 An analyst attempts to determine strontium with an atomic absorption instrument equipped with a nitrous oxide–acetylene burner, but the sensitivity associated with the 460.7-nm atomic resonance line is not satisfactory. Suggest at least three things that might be tried to increase sensitivity.

9-9 Why is atomic emission more sensitive to flame instability than atomic absorption or fluorescence?

9-10 Figure 9-1 summarizes many of the processes that take place in a laminar-flow burner. With specific reference to the analysis of an aqueous $CaCl_2$ solution, describe the processes that are likely to occur.

***9-11** Use Equation 7-13 for the resolving power of a grating monochromator to estimate the theoretical minimum size of a diffraction grating that would provide a profile of an atomic absorption line at 500 nm having a line width of 0.002 nm. Assume that the grating is to be used in the first order and that it has been ruled at 2400 grooves/mm.

***9-12** For the flame shown in Figure 9-3, calculate the relative intensity of the 766.5-nm emission line for potassium in the flame center and at the following heights above the orifice (assume no ionization and use the 2.0 cm for comparison).

(a) 2.0 cm   (b) 3.0 cm   (c) 4.0 cm   (d) 5.0 cm

9-13 In a hydrogen-oxygen flame, the atomic absorption signal for iron decreases in the presence of large concentrations of sulfate ion.

(a) Suggest an explanation for this observation.

(b) Suggest three possible methods for overcoming the potential interference of sulfate in a quantitative determination of iron.

***9-14** For Na atoms and Mg^+ ions, compare the ratios of the number of particles in the $3p$ excited state to the number in the ground state in

(a) a natural gas–air flame (2100 K).

(b) a hydrogen-oxygen flame (2900 K).

(c) an inductively coupled plasma source (6000 K).

*9-15 In higher-temperature sources, sodium atoms emit a doublet with an average wavelength of 1139 nm. The transition responsible is from the 4*s* to 3*p* state. Calculate the ratio of the number of excited atoms in the 4*s* level to the number in the ground 3*s* level in

(a) an acetylene-oxygen flame (3000°C).

(b) the hottest part of an inductively coupled plasma source ($\sim$9000°C).

*9-16 Assume that the absorption signal shown in Figure 9-7 were obtained for 2-μL aliquots of standards and sample. Calculate the concentration in parts per million of lead in the sample of canned orange juice.

9-17 Suggest sources of the two signals in Figure 9-7 that appear during the drying and ashing processes.

9-18 In the concentration range of 1 to 100 μg/mL P, phosphate suppresses the atomic absorption of Ca in a linear manner. The absorbance levels off, however, between 100 and 300 μg/mL P. Explain. How can this effect be reduced?

9-19 Describe the physical effects and interferences that the method of standard additions would correct or compensate for in AAS.

*9-20 A 5.00-mL sample of blood was treated with trichloroacetic acid to precipitate proteins. After centrifugation, the resulting solution was brought to a pH of 3 and was extracted with two 5-mL portions of methyl isobutyl ketone containing the organic lead complexing agent APCD. The extract was aspirated directly into an air-acetylene flame yielding an absorbance of 0.454 at 283.3 nm. Five-milliliter aliquots of standard solutions containing 0.240 and 0.475 ppm Pb were treated in the same way and yielded absorbances of 0.412 and 0.642. Calculate the concentration Pb (ppm) in the sample assuming that Beer's law is followed.

9-21 The sodium in a series of cement samples was determined by flame emission spectroscopy. The flame photometer was calibrated with a series of NaCl standards that contained sodium equivalent to 0, 20.0, 40.0, 60.0, and 80.0 μg Na_2O per mL. The instrument readings R for these solutions were 3.1, 21.5, 40.9, 57.1, and 77.3.

(a) Plot the data using a spreadsheet.

(b) Obtain a least-squares equation for the data.

(c) Calculate the statistics for the line in (b).

(d) The following data were obtained for replicate 1.000-g samples of cement that were dissolved in HCl and diluted to 100.0 mL after neutralization.

		Emission Reading		
	Blank	**Sample A**	**Sample B**	**Sample C**
Replicate 1	5.1	28.6	40.7	73.1
Replicate 2	4.8	28.2	41.2	72.1
Replicate 3	4.9	28.9	40.2	Spilled

Calculate the percentage of Na_2O in each sample. What are the absolute and relative standard deviations for the average of each determination?

9-22 The chromium in an aqueous sample was determined by pipetting 10.0 mL of the unknown into each of five 50.0-mL volumetric flasks. Various volumes of a standard containing 12.2 ppm Cr were added to the flasks, following which the solutions were diluted to volume.

≫ QUESTIONS AND PROBLEMS (continued)

Unknown, mL	Standard, mL	Absorbance
10.0	0.0	0.201
10.0	10.0	0.292
10.0	20.0	0.378
10.0	30.0	0.467
10.0	40.0	0.554

(a) Plot the data using a spreadsheet.

(b) Determine an equation for the relationship between absorbance and volume of standard.

(c) Calculate the statistics for the least-squares relationship in (b).

(d) Determine the concentration of Cr in ppm in the sample.

(e) Find the standard deviation of the result in (d).

Challenge Problem

9-23 (a) In an investigation of the influence of experimental variables on detection limits in electrothermal AAS, Cabon and Bihan found several factors to be significant in the optimization of the method.[23] List six of these factors, describe in detail the physical basis for each factor, and discuss why each is important.

(b) These workers describe an a priori method for determining the limit of detection (LOD). Compare and contrast this method with the method described in Section 1E-2. How does this method improve on the method as defined by the International Union of Pure and Applied Chemistry (IUPAC) in the ″Orange Book″? See http://www.iupac.org/publications/analytical_compendium/. Describe any disadvantages of the method.

(c) The investigations described by Cabon and Bihan treated the data using least-squares polynomial smoothing (see Section 5C-2) prior to determining the LOD. Describe precisely how the data were smoothed. What experimental variable was optimized in the smoothing procedure? How was the width of the smoothing window defined? What effect, if any, did the smoothing procedure have on the LOD as determined by these workers? What effect did smoothing have on the determination of the integration window for the instrumental signal?

(d) These workers compared the determination of the signal magnitude by integration and by measuring peak signals. What was the outcome of this comparison? Explain why these results were obtained by using your understanding of signal-to-noise enhancement procedures.

(e) How were instrument signals integrated? What alternative numerical procedures are available for integrating digital signals? What procedural variable or variables influenced the quality of the integrated signal data? Describe the effect of signal integration on working curves for Pb.

(f) What is *dosing volume*, and what effect did it appear to have on the quality of the results in these procedures?

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[23]J. Y. Cabon and A. Le Bihan, *Analyst*, **1997**, *122*, 1335, **DOI**: 10.1039/a701308f.

Atomic Emission Spectrometry

This chapter covers optical **atomic emission spectrometry** (AES). Generally, the atomizers listed in Table 8-1 not only convert the components of samples to atoms or elementary ions but, in the process, excite a fraction of these species to higher electronic states. As the excited species rapidly relax back to lower states, ultraviolet and visible line spectra arise that are useful for qualitative and quantitative elemental analysis. Plasma sources have become the most important and most widely used sources for AES. These devices, including the popular inductively coupled plasma source, are discussed first. Then, emission spectroscopy based on electric arc and electric spark atomization and excitation is described. Historically, arc and spark sources were quite important in emission spectrometry, and they are still useful for the determination of some metallic elements. Finally several miscellaneous atomic emission sources, including flames, glow discharges, and lasers are presented.

Throughout this chapter, this logo indicates an opportunity for online self-study at **www.tinyurl.com/skoogpia7**, linking you to interactive tutorials, simulations, and exercises.

Atomic emission spectrometry (AES) offers several advantages when compared with the flame and electrothermal absorption methods considered in Chapter 9.[1] Emission methods often show lower susceptibility to chemical interferences, which is a direct result of their higher temperatures. Second, good emission spectra result for most elements under a single set of excitation conditions. Consequently, spectra for many elements can be recorded simultaneously. This property is of particular importance for the multielement analysis of very small samples. A major advantage of the more energetic plasma sources is that they permit the determination of low concentrations of elements that tend to form refractory compounds (that is, compounds that are highly resistant to thermal decomposition, such as the oxides of boron, phosphorus, tungsten, uranium, zirconium, and niobium). In addition, plasma sources permit the determination of nonmetals such as chlorine, bromine, iodine, and sulfur. Finally, plasma emission methods usually have concentration ranges of several orders of magnitude, in contrast to a two- or three-decade range for the absorption methods described in the previous chapter. Flames are less satisfactory as atomic emission sources because optimum excitation conditions vary widely from element to element; high temperatures are needed for excitation of some elements and low temperatures for others; and finally, the region of the flame that gives rise to optimum line intensities varies from element to element.

Emission spectra from high-temperature sources, such as plasmas, arcs, and sparks, are often complex and frequently comprise hundreds, or even thousands, of lines. This large number of lines, although advantageous when seeking qualitative information, increases the probability of spectral interferences in quantitative analysis. As a result, emission spectroscopy based on plasmas, arcs, and sparks requires higher resolution

[1]For more extensive treatment of atomic emission spectroscopy, see J. A. C. Broekhaert, *Analytical Atomic Spectrometry with Flames and Plasmas*, 2nd ed., Chap. 5, Hoboken, NJ: Wiley-VCH, 2005; *Atomic Spectroscopy in Elemental Analysis*, M. Cullen, ed., Chaps. 3–5, Boca Raton, FL: CRC Press, 2004; L. H. J. Lajunen and P. Peramaki, *Spectrochemical Analysis by Atomic Absorption and Emission*, 2nd ed., Chaps. 4–6, Royal Society of Chemistry: Cambridge, 2004; J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, Chaps. 7–9, 11, Upper Saddle River, NJ: Prentice-Hall, 1988.