Selectivity Selectivity is rarely a problem in molecular absorption spectrophotometry. In many cases it is possible to find a wavelength at which only the analyte absorbs or to use chemical reactions in a manner such that the analyte is the only species that absorbs at the chosen wavelength. When two or more species contribute to the measured absorbance, a multicomponent analysis is still possible, as shown in Example 10.6.

Time, Cost, and Equipment The analysis of a sample by molecular absorption spectroscopy is relatively rapid, although additional time may be required when it is necessary to use a chemical reaction to transform a nonabsorbing analyte into an absorbing form. The cost of UV/Vis instrumentation ranges from several hundred dollars for a simple, manually operated, single-beam instrument equipped with an inexpensive grating, to as much as $50,000 for a computer-controlled, high-resolution, double-beam instrument equipped with variable slits and operating over an extended range of wavelengths. Fourier transform infrared spectrometers can be obtained for as little as $15,000–$20,000, although more expensive models are available.

Figure 10.37
Photo of a typical atomic absorption spectrophotometer.
Courtesy of Varian, Inc.

atomization
The process of converting an analyte into a free atom.

10E Atomic Absorption Spectroscopy

Atomic absorption, along with atomic emission, was first used by Guystav Kirchhoff and Robert Bunsen in 1859 and 1860, as a means for the qualitative identification of atoms. Although atomic emission continued to develop as an analytical technique, progress in atomic absorption languished for almost a century. Modern atomic absorption spectroscopy was introduced in 1955 as a result of the independent work of A. Walsh and C. T. J. Alkemade.[18] Commercial instruments were in place by the early 1960s, and the importance of atomic absorption as an analytical technique was soon evident.

10E.1 Instrumentation

Atomic absorption spectrophotometers (Figure 10.37) are designed using either the single-beam or double-beam optics described earlier for molecular absorption spectrophotometers (see Figures 10.25 and 10.26). There are, however, several important differences that are considered in this section.

Atomization The most important difference between a spectrophotometer for atomic absorption and one for molecular absorption is the need to convert the analyte into a free atom. The process of converting an analyte in solid, liquid, or solution form to a free gaseous atom is called **atomization.** In most cases the sample containing the analyte undergoes some form of sample preparation that leaves the analyte in an organic or aqueous solution. For this reason, only the introduction of solution samples is considered in this text. Two general methods of atomization are used: flame atomization and electrothermal atomization. A few elements are atomized using other methods.

Flame Atomizers In flame atomization the sample is first converted into a fine mist consisting of small droplets of solution. This is accomplished using a nebulizer assembly similar to that shown in the inset to Figure 10.38. The sample is aspirated into a spray chamber by passing a high-pressure stream consisting of one or more combustion gases, past the end of a capillary tube immersed in the sample. The impact of the sample with the glass impact bead produces an aerosol mist. The aerosol

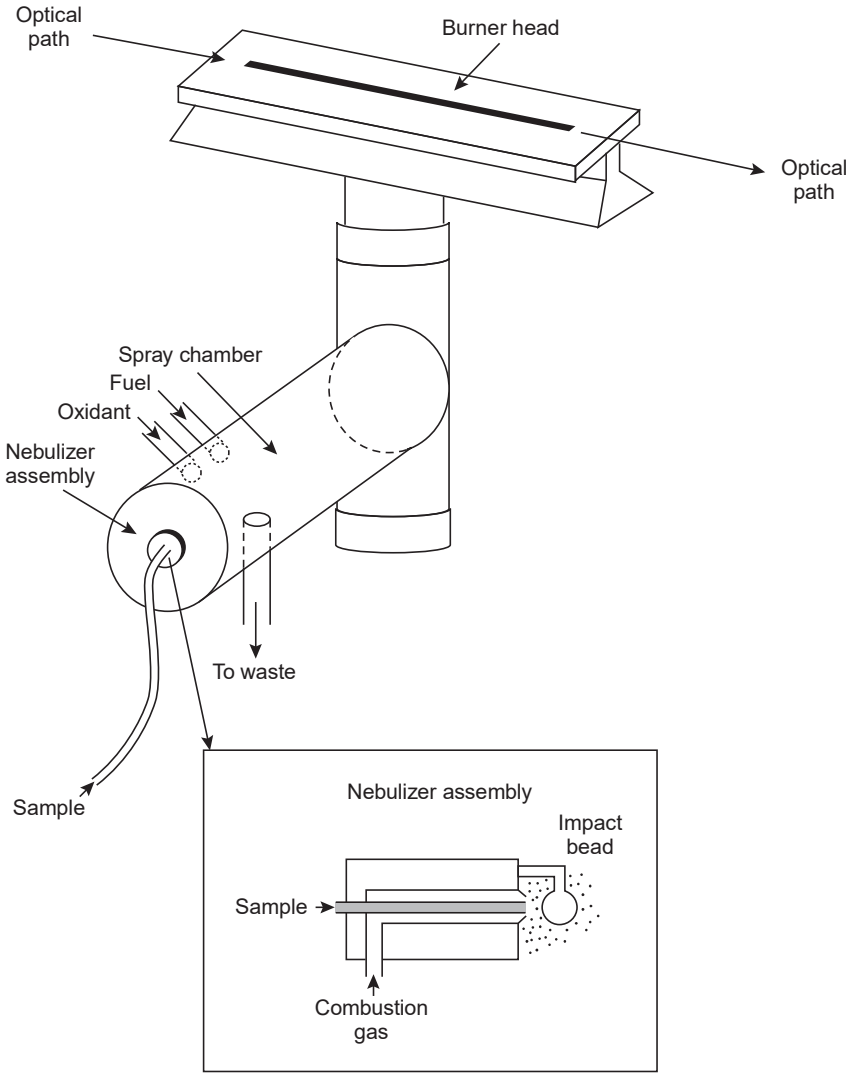

Figure 10.38
Flame atomization assembly equipped with spray chamber and slot burner. The inset shows the nebulizer assembly.

mist mixes with the combustion gases in the spray chamber before passing to the burner where the flame's thermal energy desolvates the aerosol mist to a dry aerosol of small, solid particles. Subsequently, thermal energy volatilizes the particles, producing a vapor consisting of molecular species, ionic species, and free atoms.

Thermal energy in flame atomization is provided by the combustion of a fuel–oxidant mixture. Common fuels and oxidants and their normal temperature ranges are listed in Table 10.9. Of these, the air–acetylene and nitrous oxide-acetylene flames are used most frequently. Normally, the fuel and oxidant are mixed in an approximately stoichiometric ratio; however, a fuel-rich mixture may be desirable for atoms that are easily oxidized. The most common design for the burner is the slot burner shown in Figure 10.38. This burner provides a long path length for monitoring absorbance and a stable flame.

The burner is mounted on an adjustable stage that allows the entire burner assembly to move horizontally and vertically. Horizontal adjustment is necessary to ensure that the flame is aligned with the instrument's optical path. Vertical adjustments are needed to adjust the height within the flame from which absorbance is

Table 10.9 Fuels and Oxidants Used for Flame Combustion

Fuel	Oxidant	Temperature Range (°C)
natural gas	air	1700–1900
hydrogen	air	2000–2100
acetylene	air	2100–2400
acetylene	nitrous oxide	2600–2800
acetylene	oxygen	3050–3150

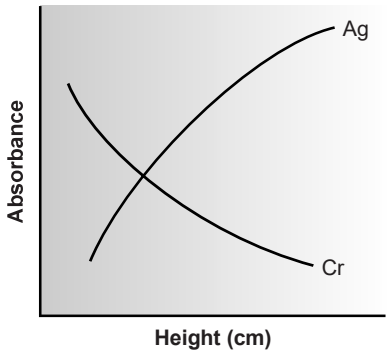

Figure 10.39
Absorbance profile for Ag and Cr in flame atomic absorption spectroscopy.

monitored. This is important because two competing processes affect the concentration of free atoms in the flame. An increased residence time in the flame results in a greater atomization efficiency; thus, the production of free atoms increases with height. On the other hand, longer residence times may lead to the formation of metal oxides that absorb at a wavelength different from that of the atom. For easily oxidized metals, such as Cr, the concentration of free atoms is greatest just above the burner head. For metals, such as Ag, which are difficult to oxidize, the concentration of free atoms increases steadily with height (Figure 10.39). Other atoms show concentration profiles that maximize at a characteristic height.

The most common means for introducing samples into a flame atomizer is continuous aspiration, in which the sample is continuously passed through the burner while monitoring the absorbance. Continuous aspiration is sample-intensive, typically requiring 2–5 mL of sample. Flame microsampling provides a means for introducing a discrete sample of fixed volume and is useful when the volume of sample is limited or when the sample's matrix is incompatible with the flame atomizer. For example, the continuous aspiration of a sample containing a high concentration of dissolved solids, such as sea water, may result in the build-up of solid deposits on the burner head. These deposits partially obstruct the flame, lowering the absorbance. Flame microsampling is accomplished using a micropipet to place 50–250 μL of sample in a Teflon funnel connected to the nebulizer, or by dipping the nebulizer tubing into the sample for a short time. Dip sampling is usually accomplished with an automatic sampler. The signal for flame microsampling is a transitory peak whose height or area is proportional to the amount of analyte that is injected.

The principal advantage of flame atomization is the reproducibility with which the sample is introduced into the spectrophotometer. A significant disadvantage to flame atomizers is that the efficiency of atomization may be quite poor. This may occur for two reasons. First, the majority of the aerosol mist produced during nebulization consists of droplets that are too large to be carried to the flame by the combustion gases. Consequently, as much as 95% of the sample never reaches the flame. A second reason for poor atomization efficiency is that the large volume of combustion gases significantly dilutes the sample. Together, these contributions to the efficiency of atomization reduce sensitivity since the analyte's concentration in the flame may be only 2.5×10^{-6} of that in solution.[19]

graphite furnace
An electrothermal atomizer that relies on resistive heating to atomize samples.

Electrothermal Atomizers A significant improvement in sensitivity is achieved by using resistive heating in place of a flame. A typical electrothermal atomizer, also known as a **graphite furnace,** consists of a cylindrical graphite tube approximately

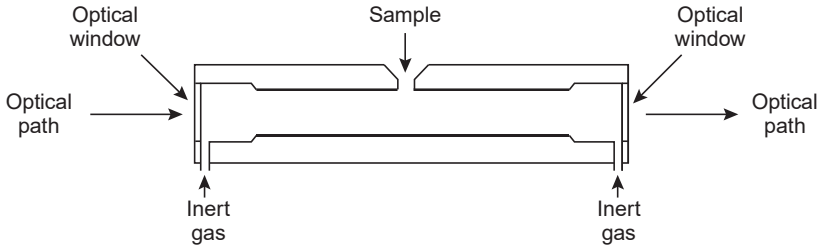

Figure 10.40
Diagram of an electrothermal analyzer.

1–3 cm in length, and 3–8 mm in diameter (Figure 10.40). The graphite tube is housed in an assembly that seals the ends of the tube with optically transparent windows. The assembly also allows for the passage of a continuous stream of inert gas, protecting the graphite tube from oxidation, and removing the gaseous products produced during atomization. A power supply is used to pass a current through the graphite tube, resulting in resistive heating.

Samples between 5 and 50 μL are injected into the graphite tube through a small-diameter hole located at the top of the tube. Atomization is achieved in three stages. In the first stage the sample is dried using a current that raises the temperature of the graphite tube to about 110 °C. Desolvation leaves the sample as a solid residue. In the second stage, which is called ashing, the temperature is increased to 350–1200 °C. At these temperatures, any organic material in the sample is converted to CO_2 and H_2O, and volatile inorganic materials are vaporized. These gases are removed by the inert gas flow. In the final stage the sample is atomized by rapidly increasing the temperature to 2000–3000 °C. The result is a transient absorbance peak whose height or area is proportional to the absolute amount of analyte injected into the graphite tube. The three stages are complete in approximately 45–90 s, with most of this time used for drying and ashing the sample.

Electrothermal atomization provides a significant improvement in sensitivity by trapping the gaseous analyte in the small volume of the graphite tube. The analyte's concentration in the resulting vapor phase may be as much as 1000 times greater than that produced by flame atomization.[20] The improvement in sensitivity, and the resulting improvement in detection limits, is offset by a significant decrease in precision. Atomization efficiency is strongly influenced by the sample's contact with the graphite tube, which is difficult to control reproducibly.

Miscellaneous Atomization Methods A few elements may be atomized by a chemical reaction that produces a volatile product. Elements such as As, Se, Sb, Bi, Ge, Sn, Te, and Pb form volatile hydrides when reacted with $NaBH_4$ in acid. An inert gas carries the volatile hydrides to either a flame or to a heated quartz observation tube situated in the optical path. Mercury is determined by the cold-vapor method in which it is reduced to elemental mercury with $SnCl_2$. The volatile Hg is carried by an inert gas to an unheated observation tube situated in the instrument's optical path.

10E.2 Quantitative Applications

Atomic absorption using either flame or electrothermal atomization is widely used for the analysis of trace metals in a variety of sample matrices. Using the atomic absorption analysis for zinc as an example, procedures have been developed for its determination in samples as diverse as water and wastewater, air, blood, urine, muscle

tissue, hair, milk, breakfast cereals, shampoos, alloys, industrial plating baths, gasoline, oil, sediments, and rocks.

Developing a quantitative atomic absorption method requires several considerations, including choosing a method of atomization, selecting the wavelength and slit width, preparing the sample for analysis, minimizing spectral and chemical interferences, and selecting a method of standardization. Each of these topics is considered in this section.

Flame Versus Electrothermal Atomization The choice of atomization method is determined primarily by the analyte's concentration in the samples being analyzed. Because of its greater sensitivity, detection limits for most elements are significantly lower when using electrothermal atomization (Table 10.10). A better precision when using flame atomization makes it the method of choice when the analyte's concentration is significantly greater than the detection limit for flame atomization. In addition, flame atomization is subject to fewer interferences, allows for a greater throughput of samples, and requires less expertise from the operator. Electrothermal atomization is the method of choice when the analyte's concentration is lower than the detection limit for flame atomization. Electrothermal atomization is also useful when the volume of sample is limited.

Selecting the Wavelength and Slit Width The source for atomic absorption is a hollow cathode lamp consisting of a cathode and anode enclosed within a glass tube filled with a low pressure of Ne or Ar (Figure 10.41). When a potential is applied across the electrodes, the filler gas is ionized. The positively charged ions collide with the negatively charged cathode, dislodging, or "sputtering," atoms from the cathode's surface. Some of the sputtered atoms are in the excited state and emit radiation characteristic of the metal from which the cathode was manufactured. By fashioning the cathode from the metallic analyte, a hollow cathode lamp provides emission lines that correspond to the analyte's absorption spectrum.

characteristic concentration
The concentration of analyte giving an absorbance of 0.00436.

The sensitivity of an atomic absorption line is often described by its **characteristic concentration,** which is the concentration of analyte giving an absorbance of 0.00436 (corresponding to a percent transmittance of 99%). For example, Table 10.11 shows a list of wavelengths and characteristic concentrations for copper.

Usually the wavelength providing the best sensitivity is used, although a less sensitive wavelength may be more appropriate for a high concentration of analyte. A less sensitive wavelength also may be appropriate when significant interferences occur at the most sensitive wavelength. For example, atomizing a sample produces atoms of not only the analyte, but also of other components present in the sample's matrix. The presence of other atoms in the flame does not result in an interference unless the absorbance lines for the analyte and the potential interferant are within approximately 0.01 nm. When this is a problem, an interference may be

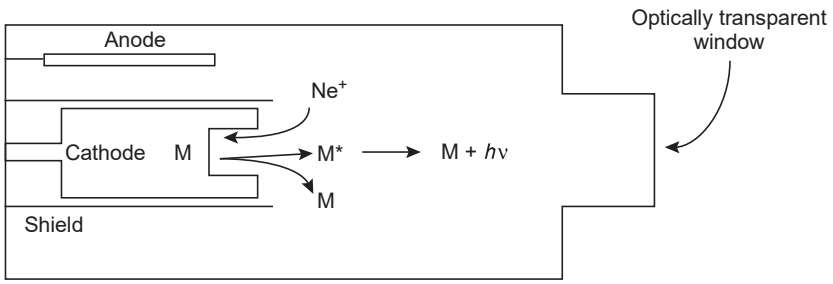

Figure 10.41
Schematic diagram of a hollow cathode lamp showing mechanism by which atomic emission is obtained.

Table 10.10 Atomic Absorption Detection Limits for Selected Elements

	Detection Limits (ppb)	
Element	Flame Atomization	Electrothermal Atomization
Ag	0.9	0.001
Al	20	0.01
As[a]	20	0.08
Au	6	0.01
B	700	15
Ba	8	0.04
Be	1	0.003
Bi[a]	20	0.1
Ca	0.5	0.01
Cd	0.5	0.0002
Co	2	0.008
Cr	2	0.004
Cs	8	0.04
Fe	3	0.01
Ga	50	0.01
Ge	50	0.1
Hg[b]	200	0.2
K	1	0.004
Li	0.3	0.01
Mg	0.1	0.0002
Mn	0.8	0.0006
Mo	10	0.02
Na	0.2	0.004
Ni	2	0.05
Pb	10	0.007
Pd	10	0.05
Pt	40	0.2
Sb[a]	30	0.08
Se[a]	100	0.05
Si	20	0.005
Sn	10	0.03
Sr	2	0.01
Ti	10	0.3
V	20	0.1
Zn	0.8	0.0006

Source: Compiled from Parson, M. L.; Major, S.; Forster, A. R. *Appl. Spectrosc.* **1983,** *37,* 411–418; Weltz, B. *Atomic Absorption Spectrometry,* VCH: Deerfield Beach, FL, 1985.

[a]Detection limit by hydride vaporization method:
As 0.02 ppb
Bi 0.02 ppb
Sb 0.1 ppb
Se 0.02 ppb

[b]Detection limit by cold-vapor method:
Hg 0.001 ppb

Table 10.11 Absorption Lines and Characteristic Concentrations for Copper

Wavelength (nm)	Characteristic Concentration (ppm)
324.8	0.04
327.4	0.1
217.9	0.6
222.6	2.0
249.2	10
244.2	40

avoided by selecting another wavelength at which the analyte, but not the interferant, absorbs.

The emission spectrum from a hollow cathode lamp includes, besides emission lines for the analyte, additional emission lines for impurities present in the metallic cathode and the filler gas. These additional lines serve as a potential source of stray radiation that may lead to an instrumental deviation from Beer's law. Normally the monochromator's slit width is set as wide as possible, improving the throughput of radiation, while being narrow enough to eliminate this source of stray radiation.

Preparing the Sample Flame and electrothermal atomization require that the sample be in a liquid or solution form. Samples in solid form are prepared for analysis by dissolving in an appropriate solvent. When the sample is not soluble, it may be digested, either on a hot plate or by microwave, using HNO_3, H_2SO_4, or $HClO_4$. Alternatively, the analyte may be extracted via a Soxhlet extraction. Liquid samples may be analyzed directly or may be diluted or extracted if the matrix is incompatible with the method of atomization. Serum samples, for instance, may be difficult to aspirate when using flame atomization and may produce unacceptably high background absorbances when using electrothermal atomization. A liquid–liquid extraction using an organic solvent containing a chelating agent is frequently used to concentrate analytes. Dilute solutions of Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, and Zn^{2+}, for example, can be concentrated by extracting with a solution of ammonium pyrrolidine dithiocarbamate in methyl isobutyl ketone.

Minimizing Spectral Interference A spectral interference occurs when an analyte's absorption line overlaps with an interferant's absorption line or band. As noted previously, the overlap of two atomic absorption lines is seldom a problem. On the other hand, a molecule's broad absorption band or the scattering of source radiation is a potentially serious spectral interference.

An important question to consider when using a flame as an atomization source, is how to correct for the absorption of radiation by the flame. The products of combustion consist of molecular species that may exhibit broad-band absorption, as well as particulate material that may scatter radiation from the source. If this spectral interference is not corrected, then the intensity of the transmitted radiation decreases. The result is an apparent increase in the sam-

ple's absorbance. Fortunately, absorption and scattering of radiation by the flame are corrected by analyzing a blank.

Spectral interferences also occur when components of the sample's matrix react in the flame to form molecular species, such as oxides and hydroxides. Absorption and scattering due to components in the sample matrix other than the analyte constitute the sample's background and may present a significant problem, particularly at wavelengths below 300 nm, at which the scattering of radiation becomes more important. If the composition of the sample's matrix is known, then standards can be prepared with an identical matrix. In this case the background absorption is the same for both the samples and standards. Alternatively, if the background is due to a known matrix component, then that component can be added in excess to all samples and standards so that the contribution of the naturally occurring interferant is insignificant. Finally, many interferences due to the sample's matrix can be eliminated by adjusting the flame's composition. For example, by switching to a higher temperature flame it may be possible to prevent the formation of interfering oxides and hydroxides.

When the identity of the matrix interference is unknown, or when it is impossible to adjust the flame to eliminate the interference, then other means must be used to compensate for the background interference. Several methods have been developed to compensate for matrix interferences, and most atomic absorption spectrophotometers include one or more of these methods.

One of the most common methods for **background correction** is the use of a continuum source, such as a D_2 lamp. Since the D_2 lamp is a continuum source, the absorbance of its radiation by the analyte's narrow absorption line is negligible. Any absorbance of radiation from the D_2 lamp, therefore, is due to the background. Absorbance of radiation from the hollow cathode lamp, however, is due to both the analyte and the background. Subtracting the absorbance for the D_2 lamp from that for the hollow cathode lamp gives an absorbance that has been corrected for the background interference. Although this method of background correction may be quite effective, it assumes that the background absorbance is constant over the range of wavelengths passed by the monochromator. When this is untrue, subtracting the two absorbances may under- or over-correct for the background.

background correction
In atomic absorption spectroscopy, the correction of the net absorbance from that due to the sample matrix.

Other methods of background correction have been developed, including Zeeman effect background correction and Smith–Hieftje background correction, both of which are included in some commercially available atomic absorption spectrophotometers. Further details about these methods can be found in several of the suggested readings listed at the end of the chapter.

Minimizing Chemical Interferences The quantitative analysis of some elements is complicated by chemical interferences occurring during atomization. The two most common chemical interferences are the formation of nonvolatile compounds containing the analyte and ionization of the analyte. One example of a chemical interference due to the formation of nonvolatile compounds is observed when PO_4^{3-} or Al^{3+} is added to solutions of Ca^{2+}. In one study, for example, adding 100 ppm Al^{3+} to a solution of 5 ppm Ca^{2+} decreased the calcium ion's absorbance from 0.50 to 0.14, whereas adding 500 ppm PO_4^{3-} to a similar solution of Ca^{2+} decreased the absorbance from 0.50 to 0.38.[21] These interferences were attributed to the formation of refractory particles of $Ca_3(PO_4)_2$ and an Al–Ca–O oxide.

releasing agent
A reagent whose reaction with an interferant is more favorable than the interferant's reaction with the analyte.

protecting agent
A reagent that reacts with the analyte, preventing it from transforming into a nonanalyzable form.

The formation of nonvolatile compounds often can be minimized by increasing the temperature of the flame, either by changing the fuel-to-oxidant ratio or by switching to a different combination of fuel and oxidant. Another approach is to add a releasing agent or protecting agent to solutions containing the analyte. A **releasing agent** is a species whose reaction with the interferent is more favorable than that of the analyte. Adding Sr^{2+} or La^{3+} to solutions of Ca^{2+}, for example, minimizes the effect of PO_4^{3-} and Al^{3+} by reacting in place of the analyte. Thus, adding 2000 ppm $SrCl_2$ to the Ca^{2+}/PO_4^{3-} and Ca^{2+}/Al^{3+} mixtures discussed in the preceding paragraph gave absorbances for each of 0.48, whereas a solution of 2000 ppm $SrCl_2$ and Ca^{2+} alone gave an absorbance of 0.49. **Protecting agents** react with the analyte to form a stable volatile complex. Adding 1% w/w EDTA to the Ca^{2+}/PO_4^{3-} solution discussed in the preceding paragraph gave an absorbance of 0.52, compared with an absorbance of 0.55 for just the Ca^{2+} and EDTA. On the other hand, EDTA does not serve as a protecting agent for solutions of Ca^{2+} and Al^{3+}.

Ionization interferences occur when thermal energy from the flame or electrothermal atomizer is sufficient to ionize the analyte

$$M \rightleftharpoons M^+ + e^- \qquad \textbf{10.28}$$

where M is the analyte in atomic form, and M^+ is the cation of the analyte formed by ionization. Since the absorption spectra for M and M^+ are different, the position of the equilibrium in reaction 10.28 affects absorbance at wavelengths where M absorbs. If another species is present that ionizes more easily than M, then the equilibrium in reaction 10.28 shifts to the left. Variations in the concentration of easily ionized species, therefore, may have a significant effect on a sample's absorbance, resulting in a determinate error. The effect of ionization can be minimized by adding a high concentration of an **ionization suppressor,** which is simply another species that ionizes more easily than the analyte. If the concentration of the ionization suppressor is sufficient, then the increased concentration of electrons in the flame pushes reaction 10.28 to the left, preventing the analyte's ionization. Potassium and cesium are frequently used as ionization suppressors because of their low ionization energy.

ionization suppressor
A reagent that is more easily ionizable than the analyte.

Standardizing the Method Because Beer's law also applies to atomic absorption, we might expect atomic absorption calibration curves to be linear. In practice, however, most atomic absorption calibration curves are nonlinear, or linear for only a limited range of concentrations. Nonlinearity in atomic absorption is a consequence of instrumental limitations, including stray radiation from the hollow cathode lamp and a nonconstant molar absorptivity due to the narrow width of the absorption line. Accurate quantitative work, therefore, often requires a suitable means for computing the calibration curve from a set of standards. Nonlinear calibration curves may be fit using quadratic and cubic equations, although neither works well over a broad range of concentrations. More accurate results may be obtained using some of the methods mentioned in Section 5C.5 in Chapter 5.

When possible, a quantitative analysis is best conducted using external standards. Unfortunately, matrix interferences are a frequent problem, particularly when using electrothermal atomization. For this reason the method of standard additions is often used. One limitation to this method of standardization, however, is the requirement that there be a linear relationship between absorbance and concentration.

Representative Methods

Method 10.2 Determination of Cu and Zn in Tissue Samples[22]

Description of Method. Copper and zinc are isolated by digesting tissue samples after extracting any fatty tissue. The concentration of copper and zinc in the supernatant are determined by atomic absorption using an air–acetylene flame.

Procedure. Tissue samples are obtained by a muscle needle biopsy and are dried for 24–30 hours at 105 °C to remove all traces of moisture. The fatty tissue in the dried samples is removed by extracting overnight with anhydrous ether. After removing the ether, the sample is dried to obtain the fat-free dry tissue weight (FFDT). The sample is digested at 68 °C for 20–24 h using 3 mL of 0.75 M HNO_3. After centrifuging at 2500 rpm for 10 min, the supernatant is transferred to a 5-mL volumetric flask. The digestion is repeated two more times, for 2–4 h each, using 0.9-mL aliquots of 0.75 M HNO_3. These supernatants are added to the 5-mL volumetric flask, which is diluted to volume with 0.75 M HNO_3. The concentration of Cu and Zn in the diluted supernatant is determined by atomic absorption spectroscopy using an air–acetylene flame and external standards. Copper is analyzed at a wavelength of 324.8 nm with a slit width of 0.5 nm, and zinc is analyzed at 213.9 nm with a slit width of 1.0 nm. Background correction is used for zinc. Results are reported as micrograms of Cu or Zn per gram of FFDT.

Questions

1. **What is the proper matrix for the external standards and the blank?**

   The matrix for the standards and the blank should match that of the samples; thus, an appropriate matrix is 0.75 M HNO_3. Any interferences from other components of the sample matrix are minimized by background correction.

2. **Why is background correction necessary for the analysis of Zn, but not for the analysis of Cu?**

   Background correction is used to compensate for background absorption and scattering due to interferents in the sample. Such interferences are most severe for analytes, such as Zn, that absorb at wavelengths of less than 300 nm.

3. **The following absorbances were obtained for a set of Cu calibration standards**

ppm Cu	Absorbance
0.000	0.000
0.100	0.006
0.200	0.013
0.300	0.020
0.400	0.026
0.500	0.033
0.600	0.039
0.700	0.046
1.000	0.066

   What is the concentration of copper, in micrograms per gram FFDT, for a 11.23-mg FFDT tissue sample that yields an absorbance of 0.023?

   Linear regression of the calibration standards gives the relationship between absorbance and concentration as

$$A = -0.0002 + 0.0661(\text{ppm Cu})$$

   Substituting the sample's absorbance into the preceding equation gives the concentration of copper in solution as 0.351 ppm. The concentration in the tissue sample, therefore, is

$$\frac{(0.351\ \mu\text{g/mL})(5\ \text{mL})}{0.01123\ \text{g}} = 156\ \mu\text{g Cu/g FFDT}$$

10E.3 Evaluation

Scale of Operation Atomic absorption spectroscopy is ideally suited for the analysis of trace and ultratrace analytes, particularly when using electrothermal atomization. By diluting samples, atomic absorption also can be applied to minor and major analytes. Most analyses use macro or meso samples. The small volume requirement for electrothermal atomization or flame microsampling, however, allows the use of micro, or even ultramicro samples.

Accuracy When spectral and chemical interferences are minimized, accuracies of 0.5–5% are routinely possible. With nonlinear calibration curves, higher accuracy is obtained by using a pair of standards whose absorbances closely bracket the sample's absorbance and assuming that the change in absorbance is linear over the limited concentration range. Determinate errors for electrothermal atomization are frequently greater than that obtained with flame atomization due to more serious matrix interferences.

Precision For absorbances greater than 0.1–0.2, the relative standard deviation for atomic absorption is 0.3–1% for flame atomization, and 1–5% for electrothermal atomization. The principal limitation is the variation in the concentration of free-analyte atoms resulting from a nonuniform rate of aspiration, nebulization, and atomization in flame atomizers, and the consistency with which the sample is heated during electrothermal atomization.

Sensitivity The sensitivity of an atomic absorption analysis with flame atomization is influenced strongly by the flame's composition and the position in the flame from which absorption is monitored. Normally the sensitivity for an analysis is optimized by aspirating a standard and adjusting operating conditions, such as the fuel-to-oxidant ratio, the nebulizer flow rate, and the height of the burner, to give the greatest absorbance. With electrothermal atomization, sensitivity is influenced by the drying and ashing stages that precede atomization. The temperature and time used for each stage must be worked out for each type of sample.

Sensitivity is also influenced by the sample's matrix. We have already noted, for example, that sensitivity can be decreased by chemical interferences. An increase in sensitivity can often be realized by adding a low-molecular-weight alcohol, ester, or ketone to the solution or by using an organic solvent.

Selectivity Due to the narrow width of absorption lines, atomic absorption provides excellent selectivity. Atomic absorption can be used for the analysis of over 60 elements at concentrations at or below the level of parts per million.

Time, Cost, and Equipment The analysis time when using flame atomization is rapid, with sample throughputs of 250–350 determinations per hour when using a fully automated system. Electrothermal atomization requires substantially more time per analysis, with maximum sample throughputs of 20–30 determinations per hour. The cost of a new instrument ranges from $10,000 to $50,000 for flame atomization and $18,000 to $70,000 for electrothermal atomization. The more expensive instruments in each price range include double-beam optics and automatic samplers, are computer controlled, and can be programmed for multielemental analysis by allowing the wavelength and hollow cathode lamp to be changed automatically.