

# An Introduction to Optical Atomic Spectrometry

**I**n this chapter, we first present a basic discussion of the sources and properties of optical atomic spectra. We then list methods used for producing atoms from samples for elemental analysis. Finally, we describe in some detail the various techniques used for introducing samples into the devices that are used for optical absorption, emission, and fluorescence spectrometry as well as atomic mass spectrometry. Chapter 9 is devoted to atomic absorption methods, the most widely used of all the atomic spectrometric techniques. Chapter 10 deals with several types of atomic emission techniques. Brief chapters on atomic mass spectrometry and atomic X-ray methods follow this discussion.

Three major types of spectrometric methods are used to identify the elements present in samples of matter and determine their concentrations: (1) optical spectrometry, (2) mass spectrometry, and (3) X-ray spectrometry. In optical spectrometry, discussed in this chapter, the elements present in a sample are converted to gaseous atoms or elementary ions by a process called *atomization*. The ultraviolet-visible absorption, emission, or fluorescence of the atomic species in the vapor is then measured. In atomic mass spectrometry (Chapter 11), samples are also atomized, but in this case, the gaseous atoms are converted to positive ions (usually singly charged) and separated according to their mass-to-charge ratios. The separated ions are then counted to provide quantitative data. In X-ray spectrometry (Chapter 12), atomization is not required because X-ray spectra for most elements are largely independent of their chemical composition in a sample. Quantitative results can therefore be based on the direct measurement of the fluorescence, absorption, or emission spectrum of the sample.

## 8A OPTICAL ATOMIC SPECTRA

In this section, we briefly consider the basis of optical atomic spectrometry and some of the important characteristics of optical spectra.

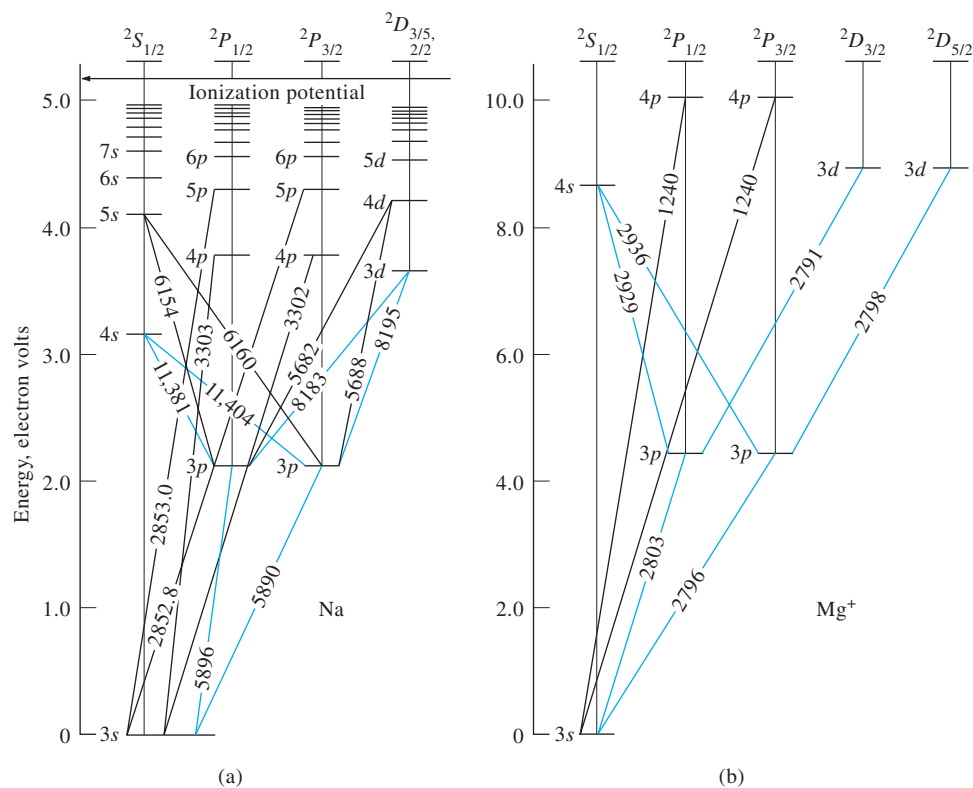
### 8A-1 Energy Level Diagrams

The processes underlying atomic spectroscopic methods can be understood by considering energy level diagrams for the outer electrons of the elements being detected. The diagram for sodium shown in Figure 8-1a is typical. Notice that the energy scale is linear in units of electron volts (eV), with the 3s orbital assigned a value of zero. The scale extends to about 5.14 eV, the energy required to remove the single 3s electron to produce a sodium ion, the *ionization energy*.

Horizontal lines on the diagram indicate the energies of several atomic orbitals. Note that the *p* orbitals are split into two levels that differ only slightly in energy. The classical view rationalizes this difference by invoking the idea that an electron spins on an axis and that the direction of the spin may be in either the same direction as its orbital motion or the opposite direction.



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



**FIGURE 8-1** Energy level diagrams for (a) atomic sodium and (b) magnesium ion. Note the similarity in pattern of lines shown in blue but not in actual wavelengths (Å).

Both the spin and the orbital motions create magnetic fields as a result of the rotation of the charge on the electron. The two fields interact in an attractive sense if these two motions are in the opposite direction; the fields repel one another when the motions are parallel. As a result, the energy of an electron whose spin opposes its orbital motion is slightly smaller than that of an electron with spin parallel to its orbital motion. There are similar differences in the  $d$  and  $f$  orbitals, but their magnitudes are usually so small that they are undetectable; thus, only a single energy level is shown for  $d$  orbitals in Figure 8-1a.

The splitting of higher energy  $p$ ,  $d$ , and  $f$  orbitals into two states is characteristic of all species containing a *single* outer-shell electron. Thus, the energy level diagram for  $\text{Mg}^+$ , shown in Figure 8-1b, has much the same general appearance as that for the uncharged sodium atom. The same is true of the diagrams for  $\text{Al}^{2+}$  and the remainder of the alkali-metal atoms. Even though all these species are isoelectronic, the energy differences between the  $3p$  and  $3s$  states are different in each case as a result of the different nuclear charges. For example, this difference is about twice as great for  $\text{Mg}^+$  as for Na.

By comparing Figure 8-1b with Figure 8-2, we see that the energy levels, and thus the spectrum, of an ion is significantly different from that of its parent atom. For atomic magnesium, with two  $1s$  electrons, there are excited singlet and triplet states with different energies. In the excited singlet state, the spins of the two electrons are opposed and said to be paired; in the triplet

states, the spins are unpaired (parallel) (Section 15A-1). Using arrows to indicate the direction of spin, the ground state and the two excited states can be represented as in Figure 8-3. As is true of molecules, the triplet excited state is lower in energy than the corresponding singlet state.

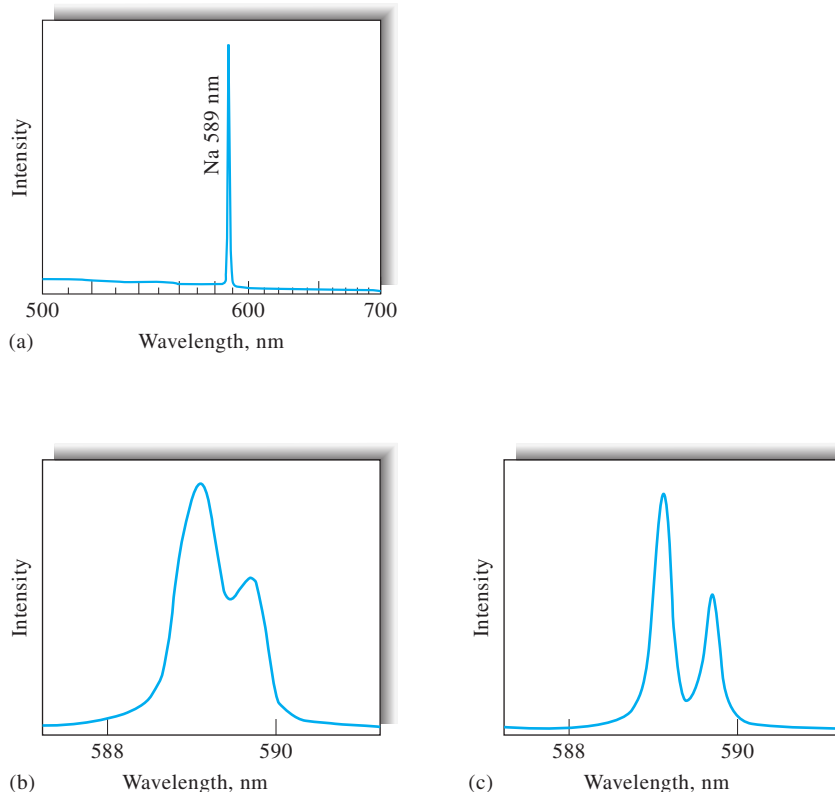
The  $p$ ,  $d$ , and  $f$  orbitals of the triplet state of magnesium ion are split into three levels that differ slightly in energy. We rationalize these splittings by taking into account the interaction between the fields associated with the spins of the two outer electrons and the net field resulting from the orbital motions of all the electrons. In the singlet state, the two spins are paired and their respective magnetic effects cancel; thus, no energy splitting is observed. In the triplet state, however, the two spins are unpaired (that is, their spin moments are in the same direction). The effect of the orbital magnetic moment on the magnetic field of the combined spins produces a splitting of the  $p$  level into a triplet. This behavior is characteristic of all of the alkaline-earth atoms as well as  $\text{B}^+$ ,  $\text{Si}^{2+}$ , and others.

As the number of electrons outside the closed shell becomes larger, the energy level diagrams become increasingly complex. With three outer electrons, a splitting of energy levels into two and four states occurs; with four outer electrons, there are singlet, triplet, and quintet states.



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**FIGURE 8-4** Atomic emission spectra of sodium. (a) Low-resolution spectrum showing unresolved sodium doublet at 589.0 and 589.6 nm. (b) Medium-resolution spectrum showing doublet partially resolved. (c) High-resolution spectrum showing nearly complete resolution. [(a) Modified from C. T. J. Alkemade and R. Herrmann, *Fundamentals of Flame Spectroscopy*, New York: Wiley, 1979; (b) and (c) adapted from B. Kasalica, et al., *J. Anal. At. Spectrom.*, **2013**, *28*, 92, DOI:10.1039/c2ja30239j. With permission.]

*selection rules* permit prediction of which transitions are likely to occur and which are not. These rules are outside the scope of this book.<sup>2</sup>

### Atomic Emission Spectra

At room temperature, essentially all of the atoms of a sample of matter are in the ground state. For example, the single outer electron of a sodium atom occupies the 3s orbital under these circumstances. Excitation of this electron to higher orbitals can be brought about by the heat of a flame, a plasma, or an electric arc or spark. The lifetime of the excited atom is brief, however, and its return to the ground state results in photon emission. The vertical lines in Figure 8-1a indicate some of the common electronic transitions that follow excitation of sodium atoms; the wavelength of the resulting radiation is also shown. The two lines at 589.0 and 589.6 nm (5890 and 5896 Å) are the most intense and are responsible for the yellow color that appears when sodium salts are introduced into a flame.

Figure 8-4a shows a portion of an experimental emission spectrum for sodium. Excitation in this case resulted from spraying an aqueous solution containing sodium chloride into an oxyhydrogen flame. The large peak corresponds to the 3p to 3s transitions at 589.0 and 589.6 nm (5890 and 5896 Å) shown in Figure 8-1a. The resolving power of the monochromator used was insufficient to separate the peaks. Figures 8-4b and c show medium and high-resolution scans of the sodium doublet with modern high-resolution monochromators. Figure 8-4c exhibits almost complete resolution of the doublet. The two lines of the sodium doublet are *resonance lines*, which result from transitions between an excited electronic state and the ground state. As shown in Figure 8-1, other resonance lines occur at 330.2 and 330.3 nm (3302 and 3303 Å) as well as at 285.30 and 285.28 (2853.0 and 2852.8 Å).

### Atomic Absorption Spectra

In a hot gaseous medium, sodium atoms are capable of *absorbing* radiation of wavelengths characteristic of electronic transitions from the 3s state to higher excited states. For example, sharp absorption lines at 589.0, 589.6, 330.2, and 330.3 nm (5890, 5896, 3302, and 3303 Å) appear in the spectrum.

<sup>2</sup>J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, pp. 205–207, Upper Saddle River, NJ: Prentice-Hall, 1988.

We see in Figure 8-1a that each adjacent pair of these peaks corresponds to transitions from the  $3s$  level to the  $3p$  and the  $4p$  levels, respectively. The nonresonance absorption due to the  $3p$  to  $5s$  transition is so weak that it usually goes undetected because the number of sodium atoms in the  $3p$  state is very small at the temperature of a flame. Thus, typically, an atomic absorption spectrum consists predominantly of resonance lines, which are the result of transitions from the ground state to upper levels.

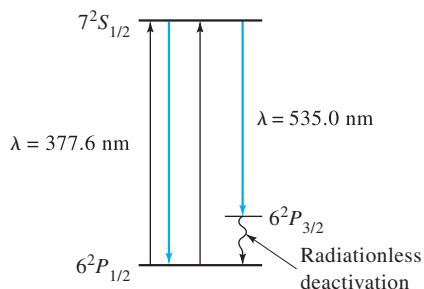
### Atomic Fluorescence Spectra

Atoms or ions in a flame fluoresce when they are irradiated with an intense source containing wavelengths that are absorbed by the element. The fluorescence spectrum is most conveniently measured at  $90^\circ$  to the light path. The observed radiation is quite often the result of resonance fluorescence resulting from absorption of radiation by ground-state atoms and emission by excited-state atoms returning to the ground state. For example, when magnesium atoms are exposed to an ultraviolet source, radiation of 285.2 nm (2852 Å) is absorbed as electrons are promoted from the  $3s$  to the  $3p$  level (see Figure 8-2); the resonance fluorescence emitted at this same wavelength may then be used for analysis. In contrast, when sodium atoms absorb radiation of wavelength 330.3 nm (3303 Å), electrons are promoted to the  $4p$  state (see Figure 8-1a). A radiationless transition to the two  $3p$  states takes place more rapidly than the fluorescence-producing transition to the ground state. As a result, the observed fluorescence occurs at 589.0 and 589.6 nm (5890 and 5896 Å).

Figure 8-5 illustrates yet a third mechanism for atomic fluorescence that occurs when thallium atoms are excited in a flame. Some of the atoms return to the ground state in two steps: a fluorescence emission step producing a line at 535.0 nm (5350 Å) and a radiationless deactivation to the ground state that quickly follows. Resonance fluorescence at 377.6 nm (3776 Å) also occurs.

### 8A-2 Atomic Line Widths

The widths of atomic lines are quite important in atomic spectroscopy. For example, narrow lines are highly desirable for both absorption and emission spectra because they reduce the possibility of interference due to overlapping lines. Furthermore,



**FIGURE 8-5** Energy level diagram for thallium showing the source of two fluorescence lines.

as will be shown later, line widths are extremely important in the design of instruments for atomic emission spectroscopy. For these reasons, we now consider some of the variables that influence the width of atomic spectral lines.

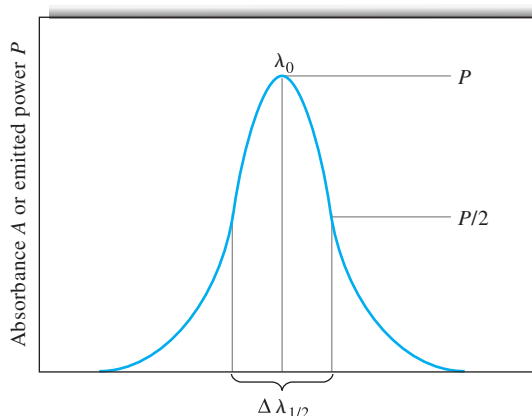
As shown in Figure 8-6, atomic absorption and emission lines are generally found to be made up of a symmetric distribution of wavelengths that centers on a mean wavelength  $\lambda_0$ , which is the wavelength of maximum absorption or maximum intensity for emitted radiation. The energy associated with  $\lambda_0$  is equal to the exact energy difference between the two quantum states responsible for absorption or emission.

Energy level diagrams, such as that shown in Figure 8-1a, suggest that an atomic line contains only a single-wavelength  $\lambda_0$ —that is, because a line results from a transition of an electron between two discrete, single-valued energy states, the line width should be zero. Several phenomena, however, cause line broadening so that all atomic lines have finite widths, as shown in Figure 8-6. Note that the *line width* or *effective line width*  $\Delta\lambda_{1/2}$  of an atomic absorption or emission line is defined as its width in wavelength units when measured at one half the maximum signal. This point is chosen because the measurement can be made more accurately at half-peak intensity than at the base.

There are four sources of line broadening: (1) the uncertainty effect, (2) the Doppler effect, (3) pressure effects due to collisions between atoms of the same kind and with foreign atoms, and (4) electric and magnetic field effects. We consider only the first three of these phenomena here. The magnetic field effect is discussed in Section 9C-1 in connection with the Zeeman effect.

### Line Broadening from the Uncertainty Effect

Spectral lines always have finite widths because the lifetimes of the upper and lower states of the transition are finite, which leads to uncertainties in the energies of the states and to line broadening (see Section 6C-7). In other words, the breadth of an atomic line resulting from a transition between two states would approach zero



**FIGURE 8-6** Profile of an atomic line showing definition of the effective line width  $\Delta\lambda_{1/2}$ .

only if the lifetimes of two states approached infinity. Although the lifetime of a ground-state electron is long, the lifetimes of excited states are generally short, typically  $10^{-7}$  to  $10^{-8}$  s. Example 8-1 illustrates how we can estimate the width of an atomic emission line from its mean lifetime and the uncertainty principle.

### EXAMPLE 8-1

The mean lifetime of the excited state produced by irradiating mercury vapor with a pulse of 253.7 nm radiation is  $2 \times 10^{-8}$  s. Calculate the approximate value for the width of the fluorescence line produced in this way.

#### Solution

According to the uncertainty principle (Equation 6-25),

$$\Delta\nu\Delta t \geq 1$$

Substituting  $2 \times 10^{-8}$  s for  $\Delta t$  and rearranging gives the uncertainty  $\Delta\nu$  in the frequency of the emitted radiation.

$$\Delta\nu = 1/(2 \times 10^{-8}) = 5 \times 10^7 \text{ s}^{-1}$$

To evaluate the relationship between this uncertainty in frequency and the uncertainty in wavelength units, we write Equation 6-2 in the form

$$\nu = c\lambda^{-1}$$

Differentiating with respect to frequency gives

$$d\nu = -c\lambda^{-2} d\lambda$$

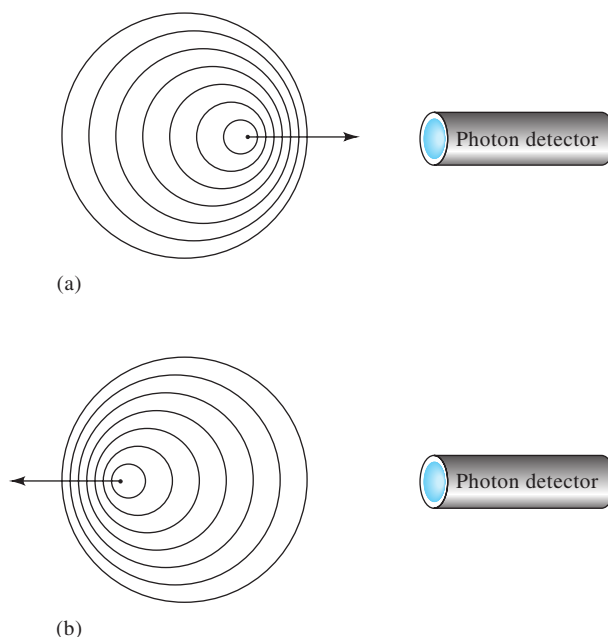
By rearranging and letting  $\Delta\nu$  approximate  $d\nu$  and  $\Delta\lambda_{1/2}$  approximate  $d\lambda$ , we find

$$\begin{aligned} |\Delta\lambda_{1/2}| &= \frac{\lambda^2 \Delta\nu}{c} \\ &= \frac{(253.7 \times 10^{-9} \text{ m})^2 (5 \times 10^7 \text{ s}^{-1})}{3 \times 10^8 \text{ m/s}} \\ &= 1.1 \times 10^{-14} \text{ m} \\ &= 1.1 \times 10^{-14} \text{ m} \times 10^{10} \text{ \AA/m} = 1 \times 10^{-4} \text{ \AA} \end{aligned}$$

Line widths due to uncertainty broadening are sometimes called *natural line widths* and are generally about  $10^{-5}$  nm ( $10^{-4}$  Å), as shown in Example 8-1.

### Doppler Broadening

The wavelength of radiation emitted or absorbed by a rapidly moving atom decreases if the motion is toward a transducer and increases if the atom is receding from the transducer (see Figure 8-7). This phenomenon is known as the *Doppler shift* and is observed not only with electromagnetic radiation but



**FIGURE 8-7** Cause of Doppler broadening. (a) When an atom moves toward a photon detector and emits radiation, the detector sees wave crests more often and detects radiation of higher frequency. (b) When an atom moves away from a photon detector and emits radiation, the detector sees crests less frequently and detects radiation of lower frequency. The result in an energetic medium is a statistical distribution of frequencies and thus a broadening of the spectral lines.

also sound waves. For example, the Doppler shift occurs when an automobile blows its horn while it passes a pedestrian. As the auto approaches the observer, the horn emits each successive sound vibration from a distance that is increasingly closer to the observer. Thus, each sound wave reaches the pedestrian slightly sooner than would be expected if the auto were standing still. The result is a higher frequency, or pitch, for the horn. When the auto is even with the observer, the waves come directly to the ear of the observer along a line perpendicular to the path of the auto, so there is no shift in the frequency. When the car recedes from the pedestrian, each wave leaves the source at a distance that is larger than that for the previous wave; as a result, the frequency is smaller, and this results in a lower pitch.

The magnitude of the Doppler shift increases with the velocity at which the emitting or absorbing species approaches or recedes from the observer. For relatively low velocities, the relationship between the Doppler shift  $\Delta\lambda$  and the velocity  $v$  of an approaching or receding atom is

$$\frac{\Delta\lambda}{\lambda_0} = \frac{v}{c}$$

where  $\lambda_0$  is the wavelength of an unshifted line of a sample of an element at rest relative to the transducer, and  $c$  is the velocity of light.



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In a collection of atoms in a hot environment, such as a flame or plasma, atomic motion occurs in every direction. Individual atoms exhibit a Maxwell-Boltzmann velocity distribution, in which the average velocity of a particular atomic species increases as the square root of the absolute temperature. The Doppler shifts of such an ensemble result in broadening of the spectral lines.<sup>3</sup> The maximum Doppler shifts occur for atoms moving with the highest velocities either directly toward or away from the transducer. No shift is associated with atoms moving perpendicular to the path to the transducer. Intermediate shifts occur for the remaining atoms, and these shifts are a function of their speed and direction. Thus, the transducer encounters an approximately symmetrical distribution of wavelengths. In flames and plasmas, Doppler broadening causes spectral lines to be about two orders of magnitude wider than the natural line width.

### Pressure Broadening

Pressure, or collisional, broadening is caused by collisions of the emitting or absorbing species with other atoms or ions in the heated medium. These collisions produce small changes in energy levels and hence a range of absorbed or emitted wavelengths. In a flame, the collisions are largely between the analyte atoms and the various combustion products of the fuel. These collisions produce broadening that is two or three orders of magnitude greater than the natural line widths. Broadening in the hollow cathode lamps and discharge lamps used as sources in atomic absorption spectroscopy results mainly from collisions between the emitting atoms and other atoms of the same kind. In high-pressure mercury and xenon lamps, pressure broadening of this type is so extensive that continuum radiation is produced throughout the ultraviolet and visible region.

## 8A-3 The Effect of Temperature on Atomic Spectra

Temperature has a profound effect on the ratio between the number of excited and unexcited atomic particles in an atomizer. We calculate the magnitude of this effect from the Boltzmann equation, which takes the form

$$\frac{N_j}{N_0} = \frac{g_j}{g_0} \exp\left(\frac{-E_j}{kT}\right) \quad (8-1)$$

Here,  $N_j$  and  $N_0$  are the number of atoms in an excited state and the ground state, respectively,  $k$  is Boltzmann's constant ( $1.38 \times 10^{-23}$  J/K),  $T$  is the absolute temperature, and  $E_j$  is the energy difference between the excited state and the ground state.



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The quantities  $g_j$  and  $g_0$  are statistical factors called *statistical weights* determined by the number of states having equal energy at each quantum level. Example 8-2 illustrates a calculation of  $N_j/N_0$ .

### EXAMPLE 8-2

Calculate the ratio of sodium atoms in the  $3p$  excited states to the number in the ground state at 2500 and 2600 K.

#### Solution

We calculate  $E_j$  in Equation 8-1 by using an average wavelength of 589.3 nm (5893 Å) for the two sodium emission lines corresponding to the  $3p \rightarrow 3s$  transitions. We compute the energy in joules using the constants found inside the front cover.

$$\begin{aligned} E_j &= h\nu = h \frac{c}{\lambda} \\ &= 6.6261 \times 10^{-34} \text{ J s} \times \frac{2.998 \times 10^8 \text{ m s}^{-1}}{589.3 \text{ nm} \times 10^{-9} \text{ m/nm}} \\ &= 3.37 \times 10^{-19} \text{ J} \end{aligned}$$

The statistical weights for the  $3s$  and  $3p$  quantum states are 2 and 6, respectively, so

$$\frac{g_j}{g_0} = \frac{6}{2} = 3$$

Substituting into Equation 8-1 yields

$$\begin{aligned} \frac{N_j}{N_0} &= 3 \exp\left(\frac{-3.37 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \text{ J K}^{-1} \times 2500 \text{ K}}\right) \\ &= 3 \times 5.725 \times 10^{-5} = 1.72 \times 10^{-4} \end{aligned}$$

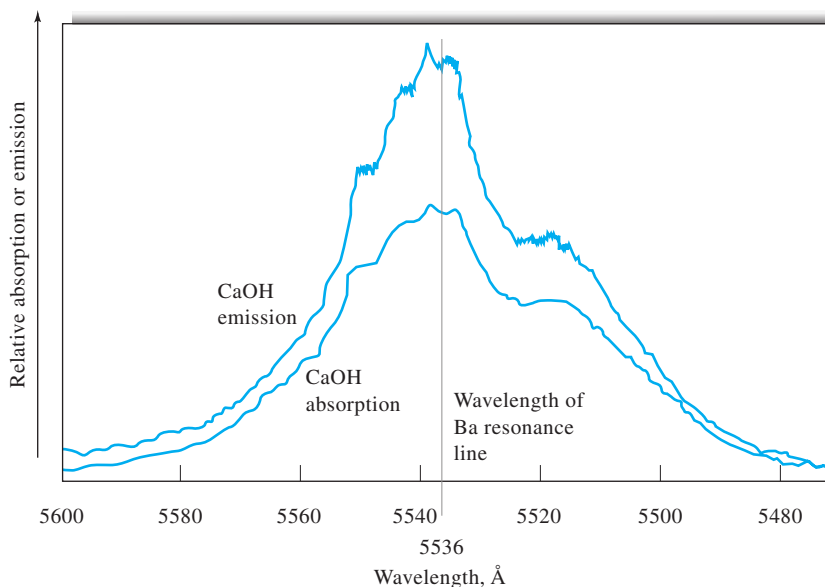
Replacing 2500 with 2600 in the previous equations yields

$$\frac{N_j}{N_0} = 2.50 \times 10^{-4}$$

Example 8-2 demonstrates that a temperature fluctuation of only 100 K results in a 45% increase in the number of excited sodium atoms. A corresponding increase in emitted power by the two lines would result. Thus, an analytical method based on the measurement of atomic emission requires close control of atomization temperature.

Absorption and fluorescence methods are theoretically less dependent on temperature because both measurements are made on initially *unexcited* atoms rather than thermally excited ones. In the example just considered, only about 0.017% of the sodium atoms were thermally excited at 2500 K. Emission measurements are made on this tiny fraction of the analyte. On the other hand, absorption and fluorescence measurements use the 99.98% of the analyte present as unexcited sodium atoms to produce the analytical signals. Note also that although a 100-K temperature change causes a 45% increase in excited atoms, the

<sup>3</sup>For a quantitative treatment of Doppler broadening and pressure broadening, see J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, pp. 210–212, Upper Saddle River, NJ: Prentice-Hall, 1988.



**FIGURE 8-8** Molecular flame emission and flame absorption spectra for CaOH. Atomic emission wavelength of barium is also indicated. (Adapted from L. Capacho-Delgado and S. Sprague, *Atomic Absorption Newsletter*, **1965**, 4, 363. Courtesy of Perkin-Elmer Corporation, Norwalk, CT.)

corresponding *relative* change in fraction of unexcited atoms is negligible.

Temperature fluctuations actually do exert an indirect influence on atomic absorption and fluorescence measurements in several ways. An increase in temperature usually increases the efficiency of the atomization process and hence increases the total number of atoms in the vapor. In addition, line broadening and a decrease in peak height occur because the atomic particles travel at greater rates, which enhances the Doppler effect. Finally, temperature variations influence the degree of ionization of the analyte and thus the concentration of nonionized analyte on which the analysis is usually based (see page 223). Because of these effects, reasonable control of the flame temperature is also required for quantitative absorption and fluorescence measurements.

The large ratio of unexcited to excited atoms in atomization media leads to another interesting comparison of the three atomic methods. Because atomic absorption and atomic fluorescence measurements are made on a much larger population of atoms, these two procedures might be expected to be more sensitive than the emission procedure. This apparent advantage is offset in the absorption method, however, because an absorbance measurement calculates a ratio ( $A = \log P_0/P$ ). When  $P$  and  $P_0$  are nearly equal, we expect larger relative errors in the ratio. Therefore, emission and absorption procedures tend to be complementary in sensitivity, one technique being advantageous for one group of elements and the other for a different group. Based on active atom population, atomic fluorescence methods should be the most sensitive of the three, at least in principle.

### 8A-4 Band and Continuum Spectra Associated with Atomic Spectra

Generally, when atomic line spectra are generated, both band and continuum radiation are produced as well. For example, Figure 6-19 (page 136) shows the presence of both molecular bands and a continuum, the latter resulting from the thermal radiation from hot particulate matter in the atomization medium. As we show later, plasmas, arcs, and sparks also produce both bands and continuum radiation.

Band spectra often appear while determining elements by atomic absorption and emission spectrometry. For example, when solutions of calcium ion are atomized in a low-temperature flame, molecular absorption and emission bands for CaOH appear in the region of 554 nm (see Figure 8-8). In this case, the band can be used for the determination of calcium. More often, however, molecular bands and continuum radiation are a potential source of interference that must be minimized by proper choice of wavelength, by background correction, or by a change in atomization conditions. Figure 8-8 shows that determination of barium at the Ba resonance line wavelength would show significant interference from CaOH emission in flame emission or CaOH absorption in atomic absorption spectrometry.

## 8B ATOMIZATION METHODS

To obtain both atomic optical and atomic mass spectra, the constituents of a sample must be converted to gaseous atoms or ions, which can then be determined by emission, absorption,



**TABLE 8-1** Types of Atomizers Used for Atomic Spectroscopy

Type of Atomizer	Typical Atomization Temperature, °C
Flame	1700–3150
Electrothermal vaporization (ETV)	1200–3000
Inductively coupled argon plasma (ICP)	4000–6000
Direct current argon plasma (DCP)	4000–6000
Microwave-induced argon plasma (MIP)	2000–3000
Laser-induced plasma	8000–15,000
Glow-discharge (GD) plasma	Nonthermal
Electric arc	4000–5000
Electric spark	40,000 (?)

fluorescence, or mass spectral measurements. The precision and accuracy of atomic spectrometric methods depend critically on the atomization step and the method of introduction of the sample into the atomization region. The common types of atomizers are listed in Table 8-1. We describe several of these devices in detail in Chapters 9, 10, and 11.

## 8C SAMPLE-INTRODUCTION METHODS

Sample introduction has been called the Achilles' heel of atomic spectroscopy because in many cases this step limits the accuracy, the precision, and the detection limits of atomic spectrometric measurements.<sup>4</sup> The primary purpose of the sample-introduction system in atomic spectrometry is to transfer a reproducible and representative portion of a sample into one of the atomizers listed in Table 8-1 with high efficiency and with no adverse interference effects. Whether it is possible to accomplish this goal easily very much depends on the physical and chemical state of the analyte and the sample matrix. For solid samples of refractory materials, sample introduction is



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usually a major problem; for solutions and gaseous samples, the introduction step is often trivial. For this reason, most atomic spectroscopic studies are performed on solutions.

For the first five atomization sources listed in Table 8-1, samples are usually introduced in the form of aqueous solutions (occasionally, nonaqueous solutions are used) or less often as slurries (a *slurry* is a suspension of a finely divided powder in a liquid). For samples that are difficult to dissolve, however, several methods have been used to introduce samples into the atomizer in the form of solids or finely dispersed powders. Generally, solid sample-introduction techniques are less reproducible and more subject to various errors and as a result are not nearly as widely applied as aqueous solution techniques. Table 8-2 lists the common sample-introduction methods for atomic spectroscopy and the type of samples to which each method is applicable.

### 8C-1 Introduction of Solution Samples

Atomization devices fall into two classes: *continuous atomizers* and *discrete atomizers*. With continuous atomizers, such as plasmas and flames, samples are introduced in a steady manner. With discrete atomizers, samples are introduced in a discontinuous manner with a device such as a syringe or an autosampler. The most common discrete atomizer is the *electrothermal atomizer*.

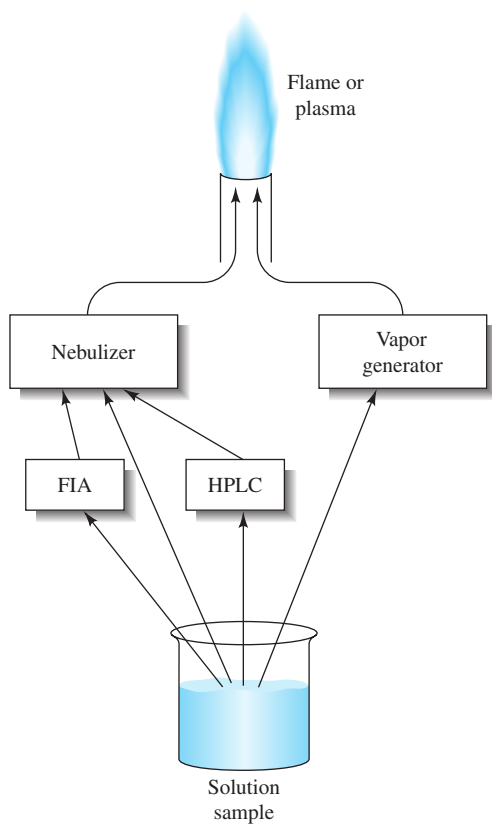
The general methods for introducing solution samples into plasmas and flames<sup>5</sup> are illustrated in Figure 8-9. Direct *nebulization* is most often used. In this case, the *nebulizer* constantly introduces the sample in the form of a fine spray of droplets, called an *aerosol*. Continuous sample introduction into a flame or plasma produces a steady-state population of atoms, molecules, and ions. When flow injection or liquid chromatography

**TABLE 8-2** Methods of Sample Introduction in Atomic Spectroscopy

Method	Type of Sample
Pneumatic nebulization	Solution or slurry
Ultrasonic nebulization	Solution
Electrothermal vaporization	Solid, liquid, or solution
Hydride generation	Solution of certain elements
Direct insertion	Solid, powder
Laser ablation	Solid, metal
Spark or arc ablation	Conducting solid
Glow-discharge sputtering	Conducting solid

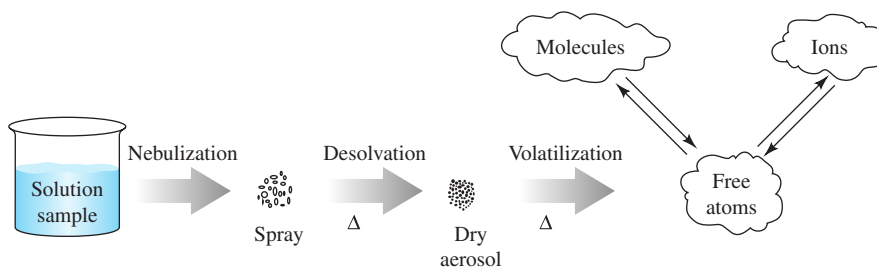
<sup>4</sup>R. F. Browner and A. W. Boorn, *Anal. Chem.*, **1984**, 56, 786A, DOI: 10.1021/ac00271a718, 875A, DOI: 10.1021/ac00271a799; *Sample Introduction in Atomic Spectroscopy*, J. Sneddon, ed., New York: Elsevier, 1990; J. Todoli and J. Mermet, *Liquid Sample Introduction in ICP Spectrometry: A Practical Guide*, Amsterdam: Elsevier, 2008.

<sup>5</sup>For an excellent discussion of liquid introduction methods, see A. Montaser, *Inductively Coupled Mass Spectrometry*, Chaps. 3 & 5, Hoboken, NJ: Wiley, 1998; A. G. T. Gustavsson, in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, 2nd ed., A. Montaser and D. W. Golightly, eds., Chap. 15. New York: Wiley-VCH, 1992.



**FIGURE 8-9** Continuous sample-introduction methods. Samples are frequently introduced into plasmas or flames by means of a nebulizer, which produces a mist or spray. Samples can be introduced directly to the nebulizer or by means of flow injection analysis (FIA; Chapter 33) or high-performance liquid chromatography (HPLC; Chapter 28). In some cases, samples are separately converted to a vapor by a vapor generator, such as a hydride generator or an electrothermal vaporizer.

is used, a time-varying plug of sample is nebulized, producing a time-dependent vapor population. The complex processes that must occur to produce free atoms or elementary ions are illustrated in Figure 8-10.



**FIGURE 8-10** Processes leading to atoms, molecules, and ions with continuous sample introduction into a plasma or flame. The solution sample is converted into a spray by the nebulizer. The high temperature of the flame or plasma causes the solvent to evaporate, leaving dry aerosol particles. Further heating volatilizes the particles, producing atomic, molecular, and ionic species. These species are often in equilibrium, at least in localized regions.

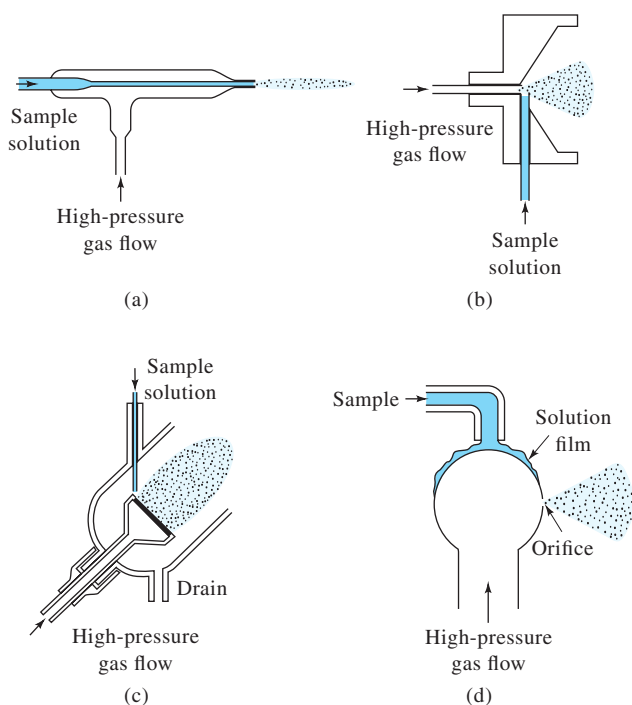
Discrete solution samples are introduced by transferring an aliquot of the sample to the atomizer. The vapor cloud produced with electrothermal atomizers is transient because of the limited amount of sample available. Solid samples can be introduced into plasmas by vaporizing them with an electric spark or with a laser beam. Solutions are generally introduced into the atomizer by one of the first three methods listed in Table 8-2.

### Pneumatic Nebulizers

The most common kind of nebulizer is the concentric tube pneumatic type, shown in Figure 8-11a, in which the liquid sample is drawn through a capillary tube by a high-pressure stream of gas flowing around the tip of the tube (the Bernoulli effect). This process of liquid transport is called *aspiration*. The high-velocity gas breaks up the liquid into droplets of various sizes, which are then carried into the atomizer. Cross-flow nebulizers, in which the high-pressure gas flows across a capillary tip at right angles, are illustrated in Figure 8-11b. Figure 8-11c is a schematic of a fritted-disk nebulizer in which the sample solution is pumped onto a fritted surface through which a carrier gas flows. This type of nebulizer produces a much finer aerosol than do the first two. Figure 8-11d shows a Babington nebulizer, which consists of a hollow sphere in which a high-pressure gas is pumped through a small orifice in the sphere's surface. The expanding jet of gas nebulizes the liquid sample flowing in a thin film over the surface of the sphere. This type of nebulizer is less subject to clogging than other devices, and it is therefore useful for samples that have a high salt content or for slurries with a significant particulate content.

### Ultrasonic Nebulizers

Several instrument manufacturers also offer ultrasonic nebulizers in which the sample is pumped onto the surface of a piezoelectric crystal that vibrates at a frequency of 20 kHz to several megahertz. Ultrasonic nebulizers produce more dense and more homogeneous aerosols than pneumatic nebulizers do. These devices have low efficiencies with viscous solutions and solutions containing particulates, however.



**FIGURE 8-11** Types of pneumatic nebulizers: (a) concentric tube, (b) cross-flow, (c) fritted disk, (d) Babington.

### Electrothermal Vaporizers

An electrothermal vaporizer (ETV) is an evaporator located in a chamber through which an inert gas such as argon flows to carry the vaporized sample into the atomizer. A small liquid or solid sample is placed on a conductor, such as a carbon tube or tantalum filament. An electric current then evaporates the sample rapidly and completely into the argon flow. In contrast to the nebulizer arrangements we have just considered, an electrothermal atomization system produces a discrete signal rather than a continuous one. That is, the signal from the atomized sample increases to a maximum and then decreases to zero as the sample is swept through the observation region or dissipates by diffusion. Peak heights or areas then provide the desired quantitative information.

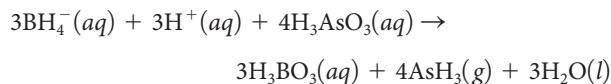
### Hydride Generation Techniques

Hydride generation techniques<sup>6</sup> provide a method for introducing samples containing arsenic, antimony, tin, selenium, bismuth, and lead into an atomizer as a gas. Such a procedure enhances the detection limits for these elements by a factor of 10 to 100. Because several of these species are highly toxic, determining them at low concentration levels is quite important. This toxicity

<sup>6</sup>For a detailed discussion of these methods, see T. Nakahara, in *Sample Introduction in Atomic Spectroscopy*, J. Sneddon, ed., Chap. 10, New York: Elsevier, 1990; J. Didina and D. L. Tsalev, *Hydride Generation Atomic Absorption Spectrometry*, Chichester, England: Wiley, 1995; for a review of vapor generation techniques, see R. A. Gil, P. H. Pacheco, S. Cerutti, and L. D. Martinez, *Anal. Chim. Acta*, **2015**, *875*, 7, DOI: 10.1016/j.aca.2014.12.040.

also dictates that gases from atomization must be disposed of in a safe and efficient manner.

Volatile hydrides can usually be generated by adding an acidified aqueous solution of the sample to a small volume of a 1% aqueous solution of sodium borohydride contained in a glass vessel. A typical reaction is



The volatile hydride—in this case, arsine ( $\text{AsH}_3$ )—is swept into the atomization chamber by an inert gas. The chamber is usually a silica tube heated to several hundred degrees in a tube furnace or in a flame where decomposition of the hydride takes place, leading to formation of atoms of the analyte. The concentration of the analyte is then measured by absorption or emission. The signal has a peak shape similar to that obtained with electrothermal atomization.

## 8C-2 Introduction of Solid Samples

The introduction of solids<sup>7</sup> in the form of powders, metals, or particulates into plasma and flame atomizers has the advantage of avoiding the often tedious and time-consuming step of sample decomposition and dissolution. Such procedures, however, often suffer from severe difficulties with calibration, sample conditioning, precision, and accuracy.

Several techniques have been used for the direct introduction of solids into atomizers. These techniques include (1) direct manual insertion of the solid into the atomization device, (2) electrothermal vaporization of the sample and transfer of the vapor into the atomization region, (3) arc, spark, or laser ablation of the solid to produce a vapor that is then swept into the atomizer, (4) slurry nebulization in which the finely divided solid sample is carried into the atomizer as an aerosol consisting of a suspension of the solid in a liquid medium, and (5) sputtering in a glow-discharge device. None of these procedures yields results as satisfactory as those obtained by introducing sample solutions by nebulization. Most of these techniques lead to a discrete analytical signal rather than a continuous one.

### Direct Sample Insertion

In the direct sample-insertion technique, the sample is physically placed in the atomizer. For solids, the sample may be ground into a powder, which is then placed on or in a probe that is inserted directly into the atomizer. With electric arc and spark atomizers, metal samples are frequently introduced as one or both electrodes that are used to form the arc or spark.

<sup>7</sup>For a description of solid-introduction techniques, see C. M. McLeod, M. W. Routh, and M. W. Tikkanen, in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, 2nd ed., A. Montaser and D. W. Golightly, eds., Chap. 16, New York: Wiley-VCH, 1992.

### Electrothermal Vaporizers

Electrothermal vaporizers, which were described briefly in the previous section, are also used for various types of solid samples. The sample is heated conductively on or in a graphite or tantalum rod or boat. The vaporized sample is then carried into the atomizer by an inert carrier gas.

### Arc and Spark Ablation

Electrical discharges of various types are often used to introduce solid samples into atomizers. The discharge interacts with the surface of a solid sample and creates a plume of a particulate and vaporized sample. The vaporization of a solid by interaction with an electrical discharge or laser beam is called *ablation*. The vaporized sample is then transported into the atomizer by the flow of an inert gas.

For arc or spark ablation to be successful, the sample must be electrically conducting or it must be mixed with a conductor. Ablation is normally carried out in an inert atmosphere such as an argon gas stream. Depending on the nature of the sample, the resulting analytical signal may be discrete or continuous. Several instrument manufacturers market accessories for electric arc and spark ablation and sample transport.

Note that arcs and sparks also atomize samples and excite the resulting atoms to generate emission spectra that are useful for analysis. A spark also produces a significant number of ions that can be separated and analyzed by mass spectrometry (see Section 11D).

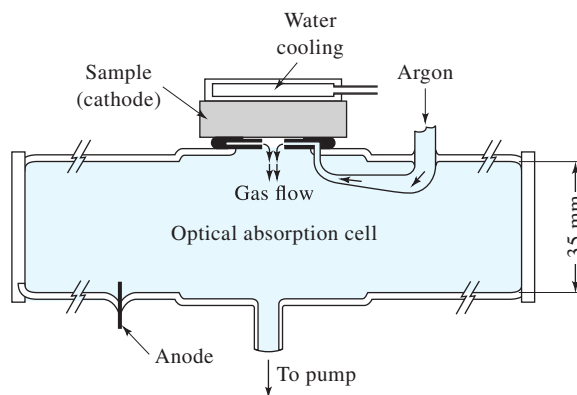
### Laser Ablation

Laser ablation is a versatile method of introducing solid samples into atomizers. This method is similar to arc and spark ablation; a sufficiently energetic focused laser beam, typically from a Nd-YAG or an excimer laser, impinges on the surface of the solid sample, where ablation takes place to convert the sample into a plume of vapor and particulate matter that is then swept into the atomizer.

Laser ablation is applicable to both conducting and non-conducting solids, inorganic and organic samples, and powder and metallic materials. In addition to bulk analysis, a focused laser beam permits analysis of small areas on the surface of solids. Several instrument makers offer laser samplers.

### The Glow-Discharge Technique

A glow-discharge (GD)<sup>8</sup> device is a versatile source that performs both sample introduction and sample atomization simultaneously (see Figure 8-12). A glow discharge takes place



**FIGURE 8-12** A glow-discharge atomizer. (From D. S. Gough, P. Hannaford, and R. M. Lowe, *Anal. Chem.*, **1989**, *61*, 1652, DOI: 10.1021/ac00190a013. Copyright 1989 American Chemical Society.)

in a low-pressure atmosphere (1 to 10 torr) of argon gas between a pair of electrodes maintained at a dc voltage of 250 to 1000 V. The applied voltage causes the argon gas to break down into positively charged argon ions and electrons. The electric field accelerates the argon ions to the cathode surface that contains the sample. Neutral sample atoms are then ejected by a process called *sputtering*. The rate of sputtering may be as high as 100  $\mu\text{g}/\text{min}$ .

The atomic vapor produced in a glow discharge consists of a mixture of atoms and ions that can be determined by atomic absorption or fluorescence or by mass spectrometry. In addition, a fraction of the atomized species present in the vapor is in an excited state. When the excited species relax to their ground states, they produce a low-intensity glow (thus, the name) that can be used for optical emission measurements.

The most important applications of the glow-discharge atomizer have been to the analysis of metals and other conducting samples, although with modification, the device has also been used with liquid samples and nonconducting materials by mixing them with a conductor such as graphite or pure copper powders. A recent advance has been the use of glow-discharge emission spectroscopy for surface imaging and elemental mapping applications.<sup>9</sup>

Glow-discharge sources of various kinds are available from several instrument manufacturers.

<sup>8</sup>See *Glow Discharge Optical Emission Spectrometry*, R. Payling, D. Jones, and A. Bengston, eds., Chichester, England: Wiley, 1997; *Glow Discharge Plasmas in Analytical Spectroscopy*, R. K. Marcus and J. A. C. Broekhaert, eds., Chichester: Wiley, 2003.

<sup>9</sup>See, G. Gamez, M. Voronov, S. J. Ray, V. Hoffman, G. M. Hieftje, and J. Michler, *Spectrochim. Acta B*, **2012**, *70*, 1, DOI: 10.1016/j.sab.2012.04.007; M. Voronov, et al., *J. Anal. At. Spec.*, **2012**, *27*, 419, DOI: 10.1039/c2ja10325g.

## » QUESTIONS AND PROBLEMS

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



Problems with this icon are best solved using spreadsheets.

- 8-1** Why is the CaOH spectrum in Figure 8-8 so much broader than the sodium emission line shown in Figure 8-4?
- 8-2** What is resonance fluorescence?
- 8-3** Under what conditions can a Stokes shift (see Section 6C-6) occur in atomic spectroscopy?
- 8-4** What determines natural line widths for atomic emission and absorption lines? About how broad are these widths, typically?
- 8-5** In a hot flame, the emission intensities of the sodium lines at 589.0 and 589.6 nm are greater in a sample solution that contains KCl than when this compound is absent. Suggest an explanation.
- 8-6** The intensity of a line for atomic Li is much lower in a natural gas flame, which operates at 1800°C, than in a hydrogen-oxygen flame, whose temperature is 2700°C. Explain.
- 8-7** Name a continuous type and a discrete type of atomizer that are used in atomic spectrometry. How do the output signals from a spectrometer differ for each?
- \*8-8** The Doppler effect is one of the sources of the line broadening in atomic absorption spectroscopy. Atoms moving toward the light source encounter higher-frequency radiation than atoms moving away from the source. The difference in wavelength  $\Delta\lambda$  experienced by an atom moving at speed  $v$  (compared to one at rest) is  $\Delta\lambda/\lambda = v/c$ , where  $c$  is the velocity of light. Estimate the line width (in nanometers) of the lithium line at 670.776 (6707.76 Å) when the absorbing atoms are at a temperature of (a) 2000 K and (b) 3120 K. The average speed of an atom is given by  $v = \sqrt{8kT/\pi m}$ , where  $k$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $m$  is its mass.
- \*8-9** For Na atoms and  $Mg^+$  ions, compare the ratios of the number of atoms or ions in the  $3p$  excited state to the number in the ground state in
- a natural gas-air flame (1800 K).
  - a hydrogen-oxygen flame (2950 K).
  - an inductively coupled plasma source (7250 K).
- 8-10** In high-temperature sources, sodium atoms emit a doublet with an average wavelength of 1139 nm. The transition responsible is from the  $4s$  to  $3p$  state. Set up a spreadsheet to calculate the ratio of the number of excited atoms in the  $4s$  state to the number in the ground  $3s$  state over the temperature range from an acetylene-oxygen flame (3000°C) to the hottest part of an inductively coupled plasma source (8750°C).
- 8-11** In the concentration range of 500 to 2000 ppm of U, there is a linear relationship between absorbance at 351.5 nm and concentration. At lower concentrations the relationship is nonlinear unless about 2000 ppm of an alkali metal salt is introduced into the sample. Explain.



### Challenge Problem

- 8-12** In a study of line broadening mechanisms in low-pressure laser-induced plasmas, Gornushkina et al.<sup>10</sup> present the following expression for the half width for Doppler broadening  $\Delta\lambda_D$  of an atomic line.

$$\Delta\lambda_D(T) = \lambda_0 \sqrt{\frac{8kT \ln 2}{\mathcal{M}c^2}}$$

<sup>10</sup>I. B. Gornushkin, L. A. King, B. W. Smith, N. Omenetto, and J. D. Winefordner, *Spectrochim. Acta B*, **1999**, *54*, 1207, DOI: 10.1016/S0584-8547(99)00064-6.

where  $\lambda_0$  is the wavelength at the center of the emission line,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $\mathcal{M}$  is the atomic mass, and  $c$  is the velocity of light. Ingle and Crouch<sup>11</sup> present a similar equation in terms of frequencies.

$$\Delta\nu_D = 2 \left[ \frac{2(\ln 2)kT}{\mathcal{M}} \right]^{1/2} \frac{\nu_m}{c}$$

where  $\Delta\nu_D$  is the Doppler half width and  $\nu_m$  is the frequency at the line maximum.

- (a) Show that the two expressions are equivalent.
- (b) Calculate the half width in nanometers for Doppler broadening of the  $4s \rightarrow 4p$  transition for atomic nickel at 361.939 nm (3619.39 Å) at a temperature of 20,000 K in both wavelength and frequency units.
- (c) Estimate the natural line width for the transition in (b) assuming that the lifetime of the excited state is  $5 \times 10^{-8}$  s.
- (d) The expression for the Doppler shift given in the chapter and in Problem 8-8 is an approximation that works at relatively low speeds. The relativistic expression for the Doppler shift is

$$\frac{\Delta\lambda}{\lambda} = \frac{1}{\sqrt{\frac{c - \nu}{c + \nu}}} - 1$$

Show that the relativistic expression is consistent with the equation given in the chapter for low atomic speeds.

- (e) Calculate the speed that an iron atom undergoing the  $4s \rightarrow 4p$  transition at 385.9911 nm (3859.911 Å) would have if the resulting line appeared at the rest wavelength for the same transition in nickel.
- (f) Compute the fraction of a sample of iron atoms at 10,000 K that would have the velocity calculated in (e).
- (g) Create a spreadsheet to calculate the Doppler half width  $\Delta\lambda_D$  in nanometers for the nickel and iron lines cited in (b) and (e) from 3000–10,000 K.
- (h) Consult the paper by Gornushkin et al. (note 10) and list the four sources of pressure broadening that they describe. Explain in detail how two of these sources originate in sample atoms.

<sup>11</sup>J. D. Ingle Jr. and S. R. Crouch, *Spectrochemical Analysis*, p. 212, Upper Saddle River, NJ: Prentice Hall, 1988.