# **Atomic Emission Spectrometry**

his 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.

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



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.

<sup>1</sup>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, NI: Prentice-Hall. 1988.

and more expensive optical equipment than is needed for atomic absorption methods with flame or electrothermal

Despite their advantages, it is unlikely that emission methods based on high-energy sources will ever completely displace flame and electrothermal atomic absorption procedures. In fact, atomic emission and absorption methods are complementary. Among the advantages of atomic absorption procedures are simpler and less expensive equipment requirements, lower operating costs, somewhat greater precision (presently, at least), and procedures that require less operator skill to yield satisfactory results.2

### 10A EMISSION SPECTROSCOPY BASED ON PLASMA SOURCES

Plasma sources have become extremely important in analytical spectroscopy. A plasma is an electrically conducting gaseous mixture containing a significant concentration of cations and electrons. (The concentrations of the two are such that the net charge is zero.) In the argon plasma frequently used for emission analyses, argon ions and electrons are the principal conducting species, although cations from the sample are also present in small amounts. Argon ions, once formed in a plasma, can absorb sufficient power from an external source to maintain the temperature at a level where further ionization sustains the plasma indefinitely. Such plasmas achieve temperatures as high as 10,000 K. Several different plasmas have been used in AES.<sup>3</sup> The most important is the *inductively coupled* plasma (ICP), which is discussed in detail in section 10A-1. The microwave-induced plasma (MIP) is also used in some forms of emission spectroscopy. The direct current plasma (DCP) was once widely used in geochemistry, but has largely been supplanted by the ICP and other plasma sources. Microplasmas based on dc, radio-frequency, and microwave radiation have also attracted attention in recent years. Such sources have potential for use as chromatographic detectors, for forming ions in mass spectrometry, and for emission spectroscopy. Finally, the laser-induced plasma, produced by laser breakdown or by laser ablation, is also used for AES (see Section 10A-3).



Exercise: Learn more about ICP torches at www.tinyurl.com/skoogpia7

<sup>3</sup>For reviews of plasma and other atomic spectroscopy sources, see E. H. Evans et al., J. Anal. At. Spectrom., 2015, 30, 1017, DOI: 10.1039/c5ja90017d; J. Anal. At. Spectrom., 2014, 29, 773, DOI: 10.1039/c4ja90019g; N. H. Bings, A. Bogaerts, and J. A. C. Broekaert, Anal. Chem., 2013, 85, 670, DOI: 10.1021/ac3031459; Anal. Chem., 2010, 82, 4653, DOI: 10.1021/ac1010469.

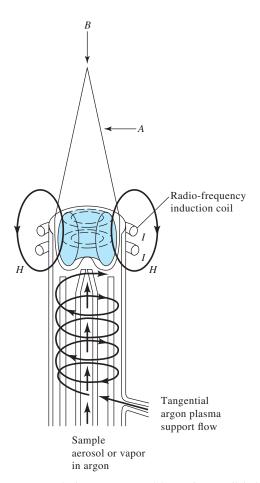


FIGURE 10-1 A typical ICP source. Position A shows radial viewing of the torch, and position B shows axial viewing. (From V. A. Fassel, Science, 1978, 202, 183. With permission. Copyright 1978 by the American Association for the Advancement of Science.)

### 10A-1 The Inductively Coupled **Plasma Source**

Figure 10-1 is a schematic of a typical ICP source called a torch.4 It consists of three concentric quartz tubes through which streams of argon gas flow. Depending on the torch

<sup>4</sup>For a more complete discussion on ICP sources, see V. A. Fassel, Science, 1978, 202, 183; V. A. Fassel, Anal. Chem., 1979, 51, 1290A, DOI: 10.1021/ac50049a717; G. A. Meyer, Anal. Chem., 1987, 59, 1345A, DOI: 10.1021/ac00150a717; Inductively Coupled Plasma Spectrometry and Its Applications, 2nd ed., S. J. Hill, ed., Hoboken, NJ: Wiley-Blackwell, 2007; A. Varma, CRC Handbook of Inductively Coupled Plasma Atomic Emission Spectroscopy, Boca Raton, FL: CRC Press, 1990; Inductively Coupled Plasma Mass Spectrometry, A. E. Montaser, ed., Hoboken, NJ: Wiley-VCH, 1998; Inductively Coupled Plasma in Analytical Atomic Spectroscopy, 2nd ed., A. Montaser and D. W. Golightly, eds., New York: Wiley-VCH, 1992; Inductively Coupled Plasma Atomic Emission Spectrometry: A Model Multi-Elemental Technique for Modern Analytical Laboratory, G. A. Zachariadis, ed., Hauppauge, NY: Nova Science Publishers, Inc., 2012.

<sup>&</sup>lt;sup>2</sup>For an excellent comparison of the advantages and disadvantages of flames, furnaces, and plasmas as sources for emission spectroscopy, see W. Slavin, Anal. Chem., 1986, 58, 589A, DOI: 10.1021/ac00295a803.

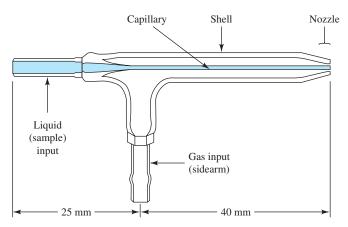


FIGURE 10-2 The Meinhard nebulizer. The nebulizing gas flows through an opening that surrounds the capillary concentrically. This causes a reduced pressure at the tip and aspiration of the sample. The high-velocity gas at the tip breaks up the solution into a mist. (Courtesy of J. Meinhard Associates, Inc.)

design, the total rate of argon consumption is 5 to 20 L/min. The diameter of the largest tube is often about 2.5 cm. Surrounding the top of this tube is a water-cooled induction coil that is powered by an radio-frequency (RF) generator, which radiates 0.5 to 2 kW of power at 27.12 MHz or 40.68 MHz.<sup>5</sup> Ionization of the flowing argon is initiated by a spark from a Tesla coil. The resulting ions, and their associated electrons, then interact with the fluctuating magnetic field (labeled H in Figure 10-1) produced by the induction coil. This interaction causes the ions and electrons within the coil to flow in the closed annular paths shown in Figure 10-1. The resistance of the ions and electrons to this flow of charge causes ohmic heating of the plasma.

The temperature of the plasma formed in this way is high enough to require thermal isolation of the outer quartz cylinder. This isolation is achieved by flowing argon tangentially around the walls of the tube as indicated by the arrows in Figure 10-1. The tangential flow cools the inside walls of the center tube and centers the plasma radially.

A design offered by most manufacturers rotates the torch by 90° so that it is aligned axially with the spectrometer system (B in Figure 10-1). The radiation emitted from the center of the plasma is then used for analyses. This axial arrangement is particularly advantageous for ICP mass spectrometry (ICPMS), which we describe in Section 11C-1 (see Figure 10-6 for a spectrometer with axial viewing geometry and Figure 10-8 for radial geometry).

Note that the argon flow rate through the typical torch is great enough to produce a significant operating cost for an ICP spectrometer (several thousand dollars annually). During the 1980s, low-flow, low-power torches appeared on the market. Typically, these torches require a total argon flow of less than 10 L/min and require less than 800 W of RF power.

#### Sample Introduction

Samples can be introduced into the ICP by argon flowing at about 1 L/min through the central quartz tube. The sample can be an aerosol, a thermally generated vapor, or a fine powder. The most common means of sample introduction is the concentric glass nebulizer shown in Figure 10-2. The sample is transported to the tip by the Bernoulli effect (aspiration). The high-velocity gas breaks up the liquid into fine droplets of various sizes, which are then carried into the plasma.

Another popular type of nebulizer has a cross-flow design (Figure 8-11b). Here, a high-velocity gas flows across a capillary tip at right angles, causing the same Bernoulli effect. Often, in this type of nebulizer, the liquid is pumped through the capillary with a peristaltic pump. Many other types of nebulizers are available for higher-efficiency nebulization, for nebulization of samples with high solids content, and for production of ultrafine mists.6

Another method of introducing liquid and solid samples into a plasma is by electrothermal vaporization. In this technique, the sample is vaporized in a furnace similar to that described in Section 8C-1 for electrothermal atomization. In plasma applications, however, the furnace is used for sample introduction only. Sample atomization occurs in the plasma.

<sup>&</sup>lt;sup>5</sup>Most commercial instruments now operate at 40.68 MHz because better coupling efficiency between the coil and the plasma is achieved at the higher frequency and lower background emission is produced.

<sup>&</sup>lt;sup>6</sup>See J. Sneedon, Sample Introduction in Atomic Spectroscopy, New York: Elsevier, 1990; J. L. Todili and J. M. Mermet, Liquid Sample Introduction in ICP Spectrometry: A Practical Guide, Amsterdam: Elsevier, 2008.

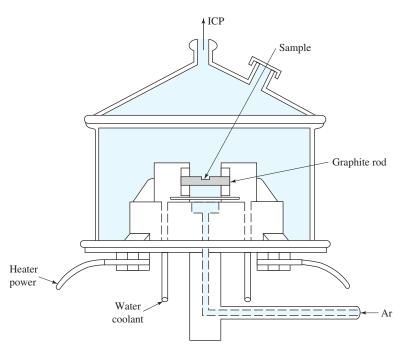


FIGURE 10-3 Device for electrothermal vaporization.

Figure 10-3 shows an electrothermal vaporizer in which vapor formation takes place on an open graphite rod. The vapor passes into a plasma torch in a stream of argon. The observed signal is a transient peak similar to the peaks obtained in electrothermal atomic absorption. Electrothermal vaporization coupled with a plasma torch offers the microsampling capabilities ( $\sim$ 5  $\mu$ L) and low absolute detection limits (~1 ng) of electrothermal furnaces while maintaining the wide linear working range, acceptable sample-to-sample precision (5%-10%), freedom from interference, and the multielement capabilities of the ICP.<sup>7</sup>

The ablation devices for solids described in Section 8C-2 are also available from several makers of ICP instruments. With these types of sample-introduction systems, the plume of vapor and particulate matter produced by interaction of the sample with an electric arc or spark or with a laser beam are transported by a flow of argon into the torch where further atomization and excitation occur.

#### Plasma Appearance and Spectra

The typical ICP plasma has a very intense, brilliant white, nontransparent core topped by a flamelike tail. The core, which extends a few millimeters above the tube, produces the atomic spectrum of argon superimposed on a continuum spectrum. The continuum is typical of ion-electron recombination reactions and bremsstrahlung, pronounced 'brem(p)-"shträ-lən, which is continuum radiation produced when charged particles are slowed or stopped. In the region 10 to 30 mm above the core, the continuum fades and the plasma is optically transparent. Spectral observations are generally made at a height of 15 to 20 mm above the induction coil, where the temperature is 6000-6500 K. In this region, the background radiation is remarkably free of argon lines and is well suited for analysis. Many of the most sensitive analyte lines in this region of the plasma are from ions, such as Ca<sup>+</sup>, Cd<sup>+</sup>, Cr<sup>+</sup>, and Mn<sup>+</sup>.

In ICP spectrometers, the torch may be viewed radially, perpendicular to its axis (A in Figure 10-1), or axially (B in the figure) or there may be an optical system that allows viewing of either configuration. Advantages of the axial arrangement over the radial configuration include increased radiation intensity resulting from a longer path length and higher precision, which produce lower detection limits (a factor of 2 to 30 with ultrasonic nebulization). The disadvantages are that the cool plasma tail must be removed from the light path to prevent interference from oxides and that it is more difficult to prevent thermal and contaminant degradation of the spectrometer optics in the axial configuration than in the radial arrangement.8 The cool tail can be removed by blowing a shear gas across the plasma tip or by a conical interface device. The decision as to which viewing arrangement to use depends on the chemical behavior of the analyte in the plasma, the spectral line chosen for the analysis, the quality of the data required, and the detailed nature of the experiment. For example, the axial arrangement is especially useful in ICPMS, which is described in Section 11C.

<sup>&</sup>lt;sup>8</sup>L. H. J. Lajunen and P. Peramaki, Spectrochemical Analysis by Atomic Absorption and Emission, 2nd ed., pp. 253-254, Cambridge: Royal Society of Chemistry, 2004.

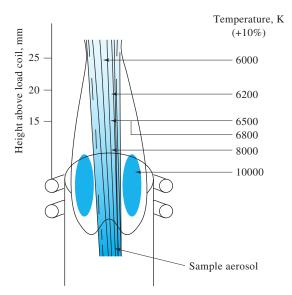


FIGURE 10-4 Temperatures in a typical ICP source. (From V. A. Fassel, Science, 1978, 202, 186. With permission. Copyright 1978 by the American Association for the Advancement of Science.)

#### Analyte Atomization and Ionization

In Figure 10-4, isothermal contours illustrate temperatures in the plasma. Sample atoms reside in the plasma for a few milliseconds before they reach the observation point. During the residence time they experience temperatures ranging from 5500 to 8000 K. The time and temperatures are roughly two to three times greater than those found in the hottest combustion flames (acetylene-nitrous oxide) used in flame spectroscopic methods. As a result, atomization is more complete in plasmas than in flames, and fewer chemical interferences occur. Surprisingly, ionization interference effects are small, probably because the large electron concentration from ionization of the argon maintains a fairly constant electron concentration in the plasma.

Several other advantages are associated with the plasma source. First, atomization occurs in a chemically inert environment, which tends to enhance the lifetime of the analyte by preventing oxide formation. In addition, and in contrast to arcs, sparks, and flames, the temperature cross section of the plasma is relatively uniform, and effects such as self-absorption and self-reversal are not observed as often. Because of this, calibration curves are usually linear over several orders of magnitude of concentration. Finally, the plasma produces significant ionization, which makes it an excellent source for ICPMS.

#### **10A-2 Microwave Plasmas**

Microwave plasmas have been studied for many years. 9 The MIP sustained in a discharge tube by a resonant cavity, such as that developed by Beenakker, 10 has become useful as a gaschromatographic element-selective detector (see Section 27B-4). For AES, however, MIPs have not achieved the low detection limits of ICPs, and the plasmas are not as robust or as stable as ICPs. Introducing liquid samples with conventional nebulizers is particularly problematic.

In the past few years, however, there has been renewed interest in microwave plasmas, especially since the introduction of a commercial system that uses air for plasma operation. 11 The new microwave plasma system sustains the plasma by coupling energy from the magnetic field of the microwave source instead of from the electric field. 12 The magnetically excited plasma is more robust than previous electrically excited MIPs. This allows the plasma to be sustained with nitrogen or air and permits sample introduction with conventional pneumatic nebulizers. The commercial instrument generates nitrogen from an air cylinder, reducing operating costs over the argon-operated ICP. When compared to flames for AA or AES, the lack of dangerous and potentially explosive gases makes the air-operated MIP a safe and efficient source. Detection limits for several elements are comparable to those achieved with a standard ICP source.

#### 10A-3 Other Plasma Sources

Additional plasma sources for AES included microplasmas and laser-induced plasmas. The glow-discharge devices described in Section 9A-3 have also been used successfully for AES.

### Microplasmas<sup>13</sup>

The development of small, miniaturized plasmas is an area of active research. The plasmas described have been based on microwave coupling, radio-frequency coupling, dielectric barrier discharges, and dc discharges such as glow discharges.<sup>14</sup> The microplasmas have the advantages of low power consumption and low gas-flow requirements as well as small sizes. Such devices have been most successfully used with gas-phase sample introduction, such as from gas chromatographic effluents and hydride generators. Discharge devices that utilize solution electrodes have also been described.15



**Exercise:** Learn more about the **ICP** at www.tinyurl .com/skoogpia7

<sup>9</sup>K. J. Jankowski and E. Rezke, Microwave Induced Plasma Analytical Spectrometry, Cambridge, UK: Royal Society of Chemistry Publishing, 2010.

<sup>&</sup>lt;sup>10</sup>C. I. M. Beenakker, Spectrochim. Acta B, 1976, 31, 483, DOI: 10.1016/ 0584-8547(76)80047-X.

<sup>&</sup>lt;sup>11</sup>Agilent Technologies, Santa Clara, CA 95051.

<sup>&</sup>lt;sup>12</sup>M. R. Hammer, Spectrochim. Acta B, 2008, 63, 456, DOI: 10.1016/ j.sab.2007.12.007.

<sup>&</sup>lt;sup>13</sup>N. H. Bings, A. Bogaerts, and J. A. C. Broekaert, Anal. Chem., 2013, 85, 670, DOI: 10.1021/ac3031459.

<sup>&</sup>lt;sup>14</sup>For a review of miniature plasmas, see J. Franzke and M. Miclea, *Appl. Spectrosc.* 2006, 60, 80A, DOI: 10.1366/000370206776342689.

<sup>&</sup>lt;sup>15</sup>M. R. Webb and G. M. Hieftje, Anal. Chem., 2009, 81, 862, DOI: 10.1021/ ac801561t.

#### Laser-Induced Plasmas

Over the past decade, lasers have become very useful for producing plasmas in AES. We consider here laser ablation and laser-induced breakdown spectroscopy (LIBS).

**Laser Ablation.** Ablation is the removal of material from a surface by vaporization or some other process. In laser ablation, the beam irradiates the surface, which is usually a solid but occasionally a liquid, and causes localized heating and vaporization. Usually a high powered, pulsed laser is used, but continuous wave laser beams have also been used. Double pulse ablation is sometimes used. 16 With high enough laser intensity, the material ablated can be converted into a plasma.

The laser plasma can emit radiation that is useful for AES, or it can produce ions that can be analyzed by mass spectrometry. In some techniques, a laser produces only a plume of atoms and ions, while a second device provides excitation. For example, with a laser microprobe, the contents of the plume formed by laser irradiation are excited by a spark discharge between a pair of electrodes located immediately above the surface (see Section 10B-2). The emitted radiation is then focused on a suitable spectrometer system. With a laser microprobe source, the trace element compositions of single blood cells have been determined. With some solids, the laser can be scanned across the surface to obtain a spatial representation of surface composition.

Laser-Induced Breakdown Spectroscopy. The LIBS technique is closely related to laser ablation. Lasers used in LIBS are so powerful that dielectric breakdown of the atmosphere surrounding the ablated sample occurs, producing a highly luminous plasma. Typically, a short pulse of perhaps a few nanoseconds duration, such as that from a Nd:YAG laser, produces the plasma. Near the end of the laser pulse, the plasma cools, and radiation from excited atoms and ions can be detected. A spectrometer is used to collect the emission at the appropriate time so that the intense continuum radiation produced by the breakdown dies away before measurement of appropriate atom or ion lines. $^{17}$ 

In addition to single-pulse LIBS, two-laser LIBS has also been successful. In two-laser LIBS, one laser ablates the sample while the second laser produces the plasma. The LIBS technique has been applied in several different areas. Metals, semiconductors, ceramics, coals, polymers, and pharmaceuticals are among these application areas. In addition to solid samples, gaseous and liquid samples have also been investigated. In fact, the first applications of LIBS were for the remote analyses of hazardous gases in industrial environments. Various process liquids, biological

solutions, aqueous environmental solutions, and pharmaceutical preparations have also been analyzed. The success of LIBS has led to commercial instrumentation devoted to the technique. A desktop LIBS analyzer is said to be able to determine trace elements, including light elements such as Al, Mg, and C, in almost any matrix.18

Recent developments have brought about miniaturization of the LIBS instrumentation, initially stimulated by the inclusion of a LIBS instrument package in the Mars Science Laboratory now active on Mars. The LIBS instrument is part of the Chem-Cam package on the rover Curiosity. The ChemCam system consists of a camera with a telephoto lens and the LIBS system. The LIBS laser enables the Martian soil or a rock of interest to be sampled remotely, without contamination from a robotic arm, and analyzed with the on-board spectrometer. Figure 10-5 shows an example of a spectrum obtained from the LIBS instrument. This package has enabled depth profiling by using the laser to tunnel through rock surfaces, a few laser shots at a time. ChemCam has enabled the construction of three-dimensional models of the target surface.

#### **10A-4 Plasma Source Spectrometers**

Table 10-1 lists the most important properties of the ideal instrument for plasma emission spectroscopy. The ideal spectrometer is not available today, partly because some of these properties are mutually exclusive. For example, high resolution requires the use of narrow slits, which usually reduces the signal-to-noise ratio and thus the precision of intensity readings. Nevertheless, instruments developed recently approach many of the ideals listed in the table.

A dozen or more instrument manufacturers currently offer plasma emission spectrometers. The designs, performance characteristics, and wavelength ranges of these instruments vary substantially. Most encompass the entire ultraviolet-visible spectrum, from 170 to 800 nm. A few instruments are equipped for vacuum operation, which extends the ultraviolet to 150 to 160 nm. This short-wavelength region is important because elements such as phosphorus, sulfur, and carbon have emission lines in this range.

Instruments for emission spectroscopy are of three basic types: sequential, simultaneous multichannel, and Fourier transform. Fourier transform instruments have not been widely used in AES. Sequential instruments are usually programmed to move from the line for one element to that of a second, pausing long enough (a few seconds) at each to measure line intensities with a satisfactory signal-to-noise ratio. In contrast, multichannel instruments are designed to measure simultaneously, or nearly so, the intensities of emission lines for a number of elements (sometimes as many as fifty or sixty). When several elements are determined, sequential instruments require significantly greater time for samples to be introduced than is required with the other

<sup>&</sup>lt;sup>16</sup>For more information, see Laser Ablation: Effects and Applications, S. E. Black, ed., Hauppauge, NY: Nova Science Publishers, Inc., 2011; C. Phillips, Laser Ablation and Its Applications, New York: Springer, 2007.

<sup>&</sup>lt;sup>17</sup>See D. A. Cremers and L. J. Radziemski, Handbook of Laser-Induced Breakdown Spectroscopy, Chichester, UK: Wiley, 2013; R. Noll, Laser-Induced Breakdown Spectroscopy: Fundamentals and Applications, Heidelberg: Springer-Verlag, 2012.

<sup>&</sup>lt;sup>18</sup>TSI Incorporated, Shoreview, MN, 55126.

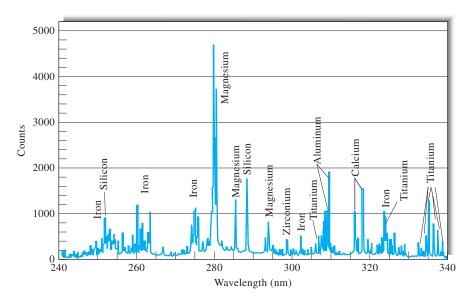


FIGURE 10-5 Spectrum of Martian rock obtained from the ChemCam LIBS system aboard the rover Curiosity. (Courtesy of NASA).

two types. Thus, these instruments, although simpler, are costly in terms of sample consumption and time.

Both sequential and multichannel emission spectrometers are of two general types, one using a classical grating spectrometer and the other an echelle spectrometer, such as that shown in Figure 7-23.

#### Sequential Instruments

Sequential instruments often incorporate a grating monochromator such as that shown in Figure 10-6. Usually, the grating is a holographic type having 2400 or 3600 grooves per millimeter. With some instruments of this type, scanning is accomplished by rotating the grating with a digitally controlled stepper motor so that different wavelengths are sequentially and precisely focused on the exit slit. In some designs, however, the grating is fixed and the slit and photomultiplier tube are moved along

### **TABLE 10-1** Desirable Properties of an Emission Spectrometer

- 1. High resolution (0.01 nm or  $\lambda/\Delta\lambda > 100,000$ )
- 2. Rapid signal acquisition and recovery
- 3. Low stray light
- 4. Wide dynamic range ( $>10^6$ )
- 5. Accurate and precise wavelength identification and selection
- 6. Precise intensity readings (<1% relative standard deviation at  $500 \times$  the detection limit)
- 7. High stability with respect to environmental changes
- 8. Easy background corrections
- 9. Computerized operation: readout, storage data manipulation, etc.

the focal plane or curve. Instruments such as the one shown in Figure 10-6 have two sets of slits and photomultiplier tubes, one for the UV region and one for the visible. In such instruments, at an appropriate wavelength, the exit beam is switched from one photomultiplier to the other by movement of the plane mirror located between the two transducers.

Slew-Scan Spectrometers. With complex spectra made up of hundreds of lines, scanning a significant wavelength region takes too long and is thus impractical. To partially overcome this problem, *slew-scan* spectrometers were developed in which the grating (see Figure 10-6), or the transducer and slit, is driven by a two-speed (or multispeed) motor. In such instruments, the monochromator scans very rapidly, or slews, to a wavelength near a line of interest. The scan rate is then quickly reduced so that the instrument scans across the line in a series of small (0.01 to 0.001 nm) steps. With slew scanning, the time spent in wavelength regions containing no useful data is minimized, but sufficient time is spent at analyte lines to obtain satisfactory signal-to-noise ratios. In spectrometers, such as the one illustrated in Figure 10-6, in which the grating movement is under computer control, slewing can be accomplished very efficiently. For example, the spectrometer shown can slew to lines corresponding to fifteen elements and record their intensities in less than 5 minutes. Generally, however, these instruments are slower and consume more sample than multichannel instruments.

**Scanning Echelle Spectrometers.** Figure 10-7 is a schematic of an echelle spectrometer that can be operated either as a scanning instrument or as a simultaneous multichannel spectrometer. Scanning is accomplished by moving a photomultiplier tube in both x and y directions to scan an aperture plate located on the focal plane of the monochromator. The plate contains as many as 300 photo-etched slits. The time required to move from one

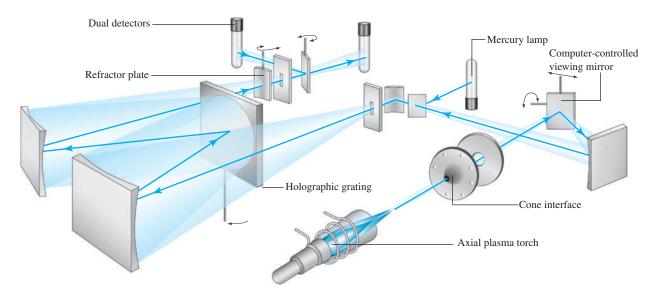


FIGURE 10-6 Optical diagram of a sequential ICP optical emission spectrometer. All moving parts are under computer control, and their modes of motion are indicated by the three-dimensional arrows. Moving parts include the grating, a mirror for transducer selection, a refractor plate for optimizing signal throughput, and a viewing mirror to optimize the plasma viewing position. The spectrometer contains a mercury lamp for automatic wavelength calibration. Notice the axial viewing geometry. (Courtesy of Agilent Technologies, Inc., Santa Clara, CA.)

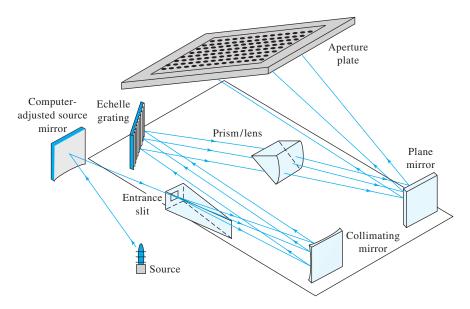


FIGURE 10-7 Schematic of an echelle spectrograph system.

slit to another is typically 1 s. The instrument can be operated in a slew-scan mode. This instrument can also be converted to a multichannel polychromator by mounting several small photomultiplier tubes behind appropriate slits in the aperture plate.

#### **Multichannel Spectrometers**

A simultaneous multichannel instrument incorporates either a polychromator or a spectrograph. Polychromators contain a series of photomultiplier tubes for detection, but spectrographs use two-dimensional charge-injection devices (CIDs) or charge-coupled devices (CCDs) as transducers. Older spectrographs used photographic emulsions as transducers.

Polychromators. In some multichannel emission spectrometers, photomultipliers are located behind fixed slits along the focal curve of a grating polychromator such as the Paschen-Runge design shown in Figure 10-8. In these instruments, the entrance slit, the exit slits, and the grating surface are located along the circumference of a Rowland circle, the curvature of which corresponds to the focal curve of the concave grating.

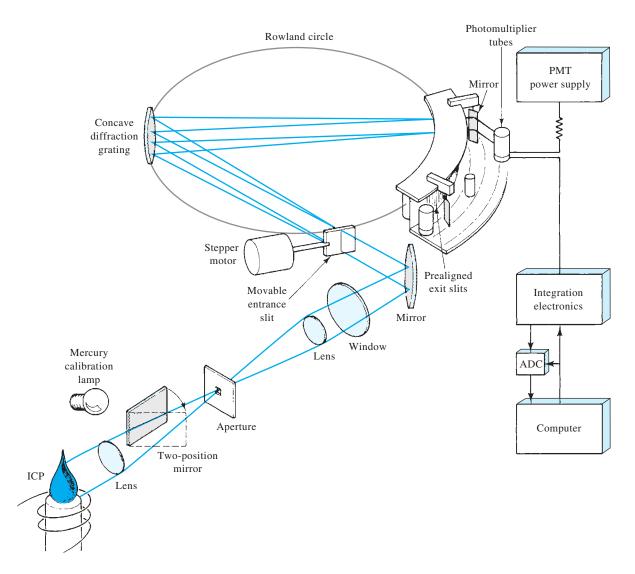


FIGURE 10-8 Direct-reading ICP emission spectrometer. The polychromator is of the Paschen-Runge design. It features a concave grating and produces a spectrum around a Rowland circle. Separate exit slits isolate each spectral line, and a separate photomultiplier tube converts the optical information from each channel into an electrical signal. Notice the radial viewing geometry. PMT = photomultiplier tube; ADC = analog-to-digital converter. (From J. D. Ingle Jr. and S. R. Crouch, Spectrochemical Analysis, p. 241, Upper Saddle River, NJ: Prentice-Hall, 1988, with permission.)

Radiation from each of the fixed slits impinges on the photomultiplier tubes. The slits are factory configured to transmit lines for selected elements. In these polychromators, the pattern of lines can be changed relatively inexpensively to accommodate new elements or to delete others. The signals from the photomultiplier tubes are integrated, and the output voltages are digitized. After converting to concentrations, the results are stored and displayed. The entrance slit can be moved tangentially to the Rowland circle by means of a stepper motor. This device permits scanning through peaks and provides information for background corrections.

Polychromator-based spectrometers with photomultipliers as transducers have been used both with plasma and with older sources such as arcs and sparks. For rapid routine analyses, such instruments can be quite useful. For example, in the production of alloys, quantitative determinations of twenty or more elements can be completed within 5 minutes of receipt of a sample; close control over the composition of a final product is then possible.

In addition to speed, photoelectric multichannel spectrometers often exhibit good analytical precision. Under ideal conditions, reproducibilities of the order of 1% relative to the amount present have been demonstrated. Because other instrument components (such as the source) exhibit lower precision than the spectrometer, such high precision is not often achieved in the overall measurement. Multichannel instruments of this type

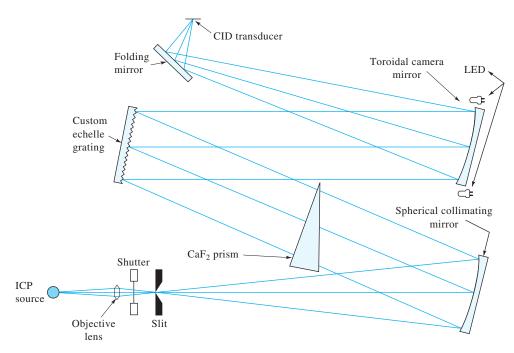


FIGURE 10-9 Optical diagram of an echelle spectrometer with a CID. (From M. J. Pilon, M. B. Denton, R. G. Schleicher, P. M. Moran, and S. B. Smith, Appl. Spectrosc., 1990, 44, 1613, **DOI**: 10.1366/0003702904417490. With permission.)

are generally more expensive than the sequential instruments described in the previous section and not as versatile.

A Charge-Injection Device Instrument. A number of companies offer multichannel simultaneous spectrometers based on echelle spectrometers and two-dimensional array devices. This type of instrument has replaced other types of multichannel emission spectrometers in many applications.

Figure 10-9 is an optical diagram of an echelle spectrometer that has a CID for simultaneous operation. 19 It uses a calcium fluoride prism to sort the spectral orders that are subsequently formed by the echelle grating (see also Figure 7-21). The transducer is a CID (Section 7E-3) 8.7 mm by 6.6 mm and containing 94.672 transducer elements. A toroidal camera mirror focuses the slit images onto the transducer surface. To eliminate dark currents in the transducer elements, the unit is housed in a liquid nitrogen cryostat that maintains a temperature of 135 K.

A set of 39 transducer elements, called a read window, is used to monitor each spectral line as shown in Figure 10-10a. Normally, as shown by the projected image of one of the windows labeled "examination window," the spectral line is focused on the 9 center elements of the window, and the 15 elements on either side of the central set provide background intensity data. Figure 10-10b shows the intensities recorded for the read

window for the iron 297.32 nm line.<sup>20</sup> Note that most of the iron radiation falls on the central elements of the window.

One of the useful features of the CID, in contrast to the CCD discussed next, is that the amount of charge accumulated in an element at any instant can be monitored nondestructively; that is, no charge is lost in the measurement process. To make the measurement of line intensity as rapid and efficient as possible, only the charge accumulated in the 9 central elements of the window are read initially to determine when sufficient charge has accumulated to provide a satisfactory signal-to-noise ratio. Only then are the remaining elements in the two 15-element sets read to correct the observed line intensity for the background radiation. This process goes on simultaneously at the read windows for each element. With an intense line, the time required to accumulate the desired charge is brief. With weak lines, the charge accumulated in a brief period is often used to estimate the integration time required to yield a satisfactory signal-tonoise ratio. In some cases integration times of 100 s or more are required.

Periodic wavelength calibration of the spectrometer just described is maintained through reference to the 253.65 nm mercury line from a small mercury lamp. Data files for line positions for more than 40 elements have been developed. The file for each element contains the wavelengths of up to ten lines and the x

<sup>&</sup>lt;sup>19</sup>See M. J. Pilon, M. B. Denton, R. G. Schleicher, P. M. Moran, and S. B. Smith, Appl. Spectrosc., 1990, 44, 1613, DOI: 10.1366/0003702904417490.

<sup>&</sup>lt;sup>20</sup>R. B. Bilhorn and M. B. Denton, Appl. Spectrosc., 1990, 44, 1538, DOI: 10.1366/0003702904417850.

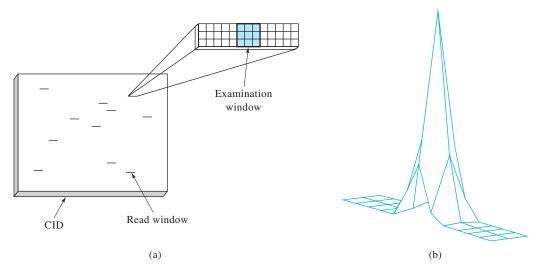


FIGURE 10-10 (a) Schematic representing the surface of a CID. The short horizontal lines represent the read windows. A magnified image of one of the read windows is also shown. The nine central elements form the examination window, where a line is positioned. (b) Intensity profile for an iron line. All of the radiation from the line falls on the 3 imes 3 examination window. (From R. B. Bilhorn and M. B. Denton, Appl. Spectrosc., 1990, 44, 1538. With permission.)

and y coordinates of each of these spectral lines with respect to the coordinates for the mercury line. Database recalibration is seldom necessary unless something perturbs the optics of the system significantly. Identification of elements in samples is done by visual inspection with the use of a video monitor and interactive markers. With an ICP excitation source, detection limits that range from a few tenths of a nanogram to 10 μg/mL have been reported for most elements. For nonmetals such as phosphorus and arsenic, detection limits are larger by a factor of 100.

A Charge-Coupled Device Instrument. Figure 10-11 is an optical diagram of a commercial spectrometer with two echelle systems and two CCDs, one system for the 160-375-nm region and the other for the 375–782-nm range. 21 Radiation from the plasma enters the spectrometer via a slit and is then dispersed by an echelle grating. The radiation falls on a Schmidt crossdisperser element that separates the orders of the ultraviolet radiation and also separates the ultraviolet and visible optical beams. The Schmidt element consists of a grating ruled on a spherical surface with a hole in the center to pass the visible radiation to a prism where order separation takes place as shown in Figure 7-23. The two dispersed beams are then focused onto the surface of transducer elements as shown. Note that a schematic representation of the surface of the ultraviolet transducer is shown as an insert in Figure 10-11.

These unique detector systems consist of numerous subarrays, or array segments, fabricated on silicon chips, with each subarray being custom positioned so that three to four major emission lines for each of 72 elements fall on its surface. Each array segment consists of a *linear* (rather than two-dimensional) CCD that is made up of twenty to eighty pixels. Figure 10-12 is a schematic of one of these array segments, which is made up of the individual photosensitive registers, storage and output registers, and output electronics. Because each array segment can be addressed separately, charge-integration times can be varied over a wide enough range to provide dynamic ranges of 10<sup>5</sup> or greater. Although there are only 224 (235 in the current production version) of these array segments in the system, multiple lines fall on many of the subarrays so that about 6000 lines can be monitored simultaneously.

In the production version of this spectrometer, one of the mirrors that guides the radiation into the optical system is under computer control so that plasma viewing may be axial, radial, or mixed. This arrangement also permits optimization of the spectrometer signal. The entire optical system is contained within a purged temperature-controlled enclosure and is protected from the intense UV radiation of the plasma between samples by a pneumatically operated shutter to extend the life of the input mirror. In addition, a mercury lamp is built into the shutter mechanism to calibrate the spectrometer periodically. Different models of the spectrometer are available that cover the spectral range of 163-782 nm or segments thereof, depending on whether one or both arrays are installed.

A Combination Instrument. An interesting and useful application of both the Paschen-Runge polychromator and modular array detectors is the spectrometer shown in the photo of Figure 10-13a. Fifteen or sixteen linear CCD array modules (eight

 $<sup>^{21}\</sup>mbox{For a detailed description of this instrument, see T. W. Barnard et al., Anal.$ Chem., 1993, 65, 1225, DOI: 10.1021/ac00057a020; T. W. Barnard, et al., Anal. Chem., 1993, 65, 1231, DOI: 10.1021/ac00057a021.

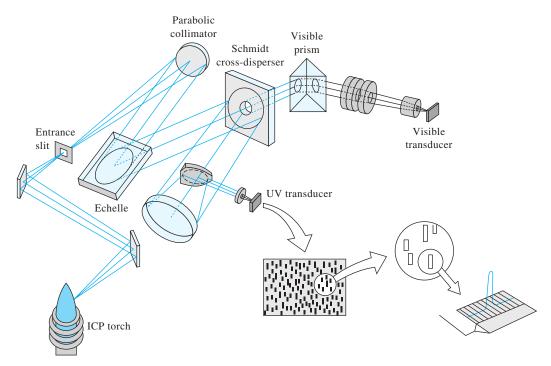


FIGURE 10-11 An echelle spectrometer with segmented array of CCDs. (From T. W. Barnard et al., Anal. Chem., 1993, 65, 1231. Figure 1, p. 1232. Copyright 1993 American Chemical Society.)

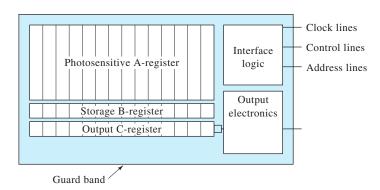


FIGURE 10-12 Schematic of an array segment showing phototransducers, storage and output registers, and readout circuitry. (From T. W. Barnard et al., Anal. Chem., 1993, 65, 1231. Copyright 1993 American Chemical Society.)

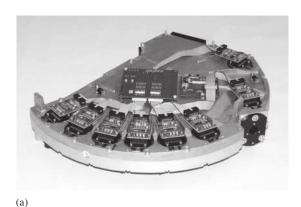
are visible) are arranged along the circumference of the Rowland circle to provide nearly complete coverage of the range from 140 to 670 nm. Each detector module (see Figure 10-13b) contains a mirror to reflect the radiation to the CCD array, which is arranged parallel to the plane of the Rowland circle. The modules are easily exchanged and positioned in the optical path. Because of its relatively compact design (115 cm wide  $\times$  70 cm deep), this spectrometer is particularly well suited to benchtop operation and routine use in industrial and environmental laboratories.



### Tutorial: Learn more about ICP spectrometers at www.tinyurl.com/skoogpia7

#### Fourier Transform Spectrometers

Since the early 1980s, several workers have described applications of Fourier transform instruments to the ultraviolet-visible region of the spectrum by using instruments that are similar in design to the infrared instruments discussed in detail in Section 16B-1.<sup>22</sup> Much of this work has been devoted to the use of such instruments for multielement analyses with ICP sources. The advantages of Fourier transform instruments



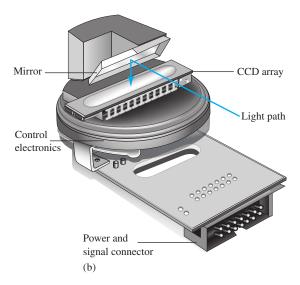


FIGURE 10-13 Components of a simultaneous CCD-ICP spectrometer: (a) Photo of the optical system. Note the Rowland circle with the grating in the rear, the slit in the front, and the detector array modules along the circle. (b) Array detector module containing a 1024-pixel linear CCD. (Courtesy of Spectro Analytical Instruments, Inc., Mahwah, NJ.)

include their wide wavelength coverage (170 nm to > 1000 nm), speed, high resolution, highly accurate wavelength measurements, large dynamic range, compact size, and large optical throughput. In contrast to Fourier transform infrared instruments, however, ultraviolet-visible instruments of this type often exhibit no multiplex advantage and indeed under some circumstances show a multiplex disadvantage (see Section 7I-1). The reason for this difference is that the performance of infrared instruments is usually limited by transducer noise, while ultraviolet-visible spectrometers are limited by shot and flicker noise associated with the source.

### 10A-4 Applications of Plasma Sources

Plasma sources produce spectra rich in characteristic emission lines, which makes them useful for both qualitative and quantitative elemental analysis.<sup>23</sup> The ICP yields significantly better quantitative analytical data than other emission sources. The quality of these results stems from its high stability, low noise, low background, and freedom from interferences when operated under appropriate experimental conditions. The newer air-operated microwave sources have substantial promise and should be less expensive to operate than the conventional ICP.

#### Sample Preparation

ICP emission spectroscopy is used primarily for the qualitative and quantitative analysis of samples that are dissolved or suspended in aqueous or organic liquids. The techniques for preparation of such solutions are similar to those described in Section 9D-1 for flame absorption methods. With plasma emission, however, it is possible to analyze solid samples directly. These procedures include incorporating electrothermal vaporization, laser and spark ablation, and glow-discharge vaporization, all of which were described in Section 8C-2. Suspensions of solids in solutions can also be handled with a Babington nebulizer, such as that shown in Figure 8-11d.

#### **Elements Determined**

In principle, all metallic elements can be determined by plasma emission spectrometry. A vacuum spectrometer is necessary for the determination of boron, phosphorus, nitrogen, sulfur, and carbon because the emission lines for these elements lie at wavelengths less than 180 nm, where components of the atmosphere absorb radiation. The usefulness for the alkali metals is limited by two difficulties: (1) the compromise operating conditions that can be used to accommodate most other elements are unsuited for the alkalis, and (2) the most prominent lines of Li, K, Rb, and Cs are located at near-infrared wavelengths, which lead to detection problems with many plasma spectrometers that are designed primarily for ultraviolet radiation. Because of problems of this sort, plasma emission spectroscopy is generally limited to the determination of about 60 elements.

The periodic table of Figure 10-14 shows the applicability of ICP emission spectrometry to various elements. The detection limits for the best lines for each of the elements are indicated by the color and degree of shading. The areas of shading indicate the number of lines for each element that yields a detection limit within a factor of 3 of the best line. The more such lines that are available, the greater the chance that a usable line can be found that is free from interference when the matrix yields a line-rich spectrum.

<sup>&</sup>lt;sup>23</sup>For useful discussions of the applications of plasma emission sources, see Inductively Coupled Plasma Spectrometry and Its Applications, 2nd ed., S. J. Hill, ed., Hoboken, NJ: Wiley-Blackwell, 2007; Inductively Coupled Plasma Atomic Emission Spectrometry: A Model Multi-Elemental Technique for Modern Analytical Laboratory, G. A. Zachariadis, ed., Hauppauge, NY: Nova Science Publishers, Inc.,

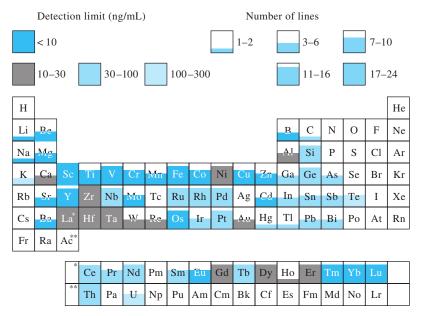


FIGURE 10-14 Periodic table characterizing the detection power and number of useful emission lines of ICP by using a pneumatic nebulizer. The color and degree of shading indicate the range of detection limits for the useful lines. The area of shading indicates the number of useful lines. (Adapted from Inductively Coupled Plasma Emission Spectroscopy, Part 1, p. 143, P. W. J. M. Boumans, ed., New York: Wiley, 1987. With permission.)

#### Line Selection

Figure 10-14 shows that most elements have several prominent lines that can be used for identification and determination purposes. Wavelength data recorded to three decimal places with appropriate intensity information for prominent lines for more than 70 elements can be found in several publications. <sup>24</sup> Thus, a suitable line for the determination of any element can usually be found. Selection depends on a consideration of what elements other than the analyte may be present in the sample and whether there is any likelihood that lines of these elements will overlap analyte lines.

#### Calibration Curves

Calibration curves for plasma emission spectrometry most often consist of a plot of an electrical signal proportional to line intensity versus analyte concentration. When the range of concentrations is large, log-log plots may be used instead. Figure 10-15 shows typical calibration curves for four trace elements present in steel samples. Often, calibration plots are linear, as are the central two curves in the figure. Departures from linearity often occur, however, when large concentration ranges are covered (see the outer two lines in Figure 10-15). A major cause of nonlinearity is self-absorption, in which the output signal is reduced because of absorption by ground-state atoms in the medium. Self-absorption becomes evident only at high analyte concentrations and causes the calibration curve to bend toward the horizontal axis. None of the plots in Figure 10-15 show evidence of self-absorption. Nonlinearity also arises from erroneous background corrections, from ionization, and from nonlinear responses of the detection systems. The nonlinearities in the curves for niobium and thallium at low concentrations are probably a result of incorrect background corrections. Note that the departures from linearity are away from the concentration axis.

An internal standard is often used in emission spectrometry. In this case, the vertical axis of the calibration curve is the ratio or the log ratio of the detector signal for the analyte to the detector signal for the internal standard. Figure 10-16 shows calibration curves for several elements. In these experiments a fixed amount of yttrium was incorporated in all of the standards, and the relative intensity of the analyte line to that of an yttrium line at 242.2 nm served as the analytical variable. Note that all the curves are linear and cover a concentration range of nearly three orders of magnitude. Note also that some of the

<sup>&</sup>lt;sup>24</sup>See R. K. Winge, V. A. Fassel, V. J. Peterson, and M. A. Floyd, *Inductively* Coupled Plasma Emission Spectroscopy: An Atlas of Spectral Information, New York: Elsevier, 1985; P. W. J. M. Boumans, Line Coincidence Tables for Inductively Coupled Plasma Spectrometry, 2nd ed., Oxford: Pergamon, 1984; C. C. Wohlers, ICP Information Newslett., 1985, 10, 601.

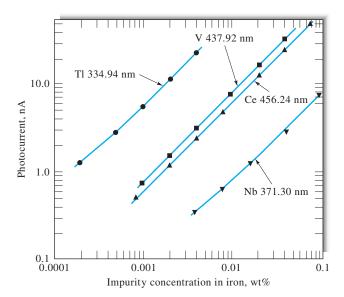


FIGURE 10-15 Typical calibration curves in ICP emission spectrometry. (From V. A. Fassel and R. N. Kniseley, Anal. Chem., 1974, 46, 1110A, DOI: 10.1021/ac60349a023. Copyright 1974 American Chemical Society.)

data were obtained by introducing various amounts of the analyte and internal standard into pure water. Other data are for solutions that contained relatively high concentrations of different salts, thus demonstrating a freedom from interelement interference.

As in atomic absorption spectroscopy, one or more standards should be introduced periodically to correct for the effects of instrument drift. The improvement in precision that results from this procedure is illustrated by the data in Table 10-2. Note also the improved precision when higher concentrations of analyte are measured.

#### **Interferences**

As was noted previously, chemical interferences and matrix effects are significantly lower with plasma sources than with other

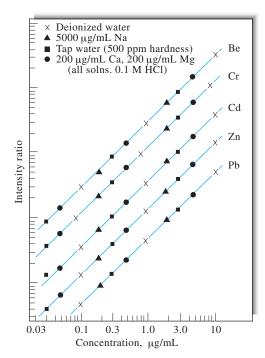


FIGURE 10-16 Internal standard calibration curves with an ICP source. Here, an yttrium line at 242.2 nm served as an internal standard. Notice the lack of interelement interference. (From V. A. Fassel, Science, 1978, 202, 183. With permission. Copyright 1978 by the American Association for the Advancement of Science.)

atomizers. At low analyte concentrations, however, the background emission due to recombination of argon ions with electrons is large enough to require careful corrections. For both single-channel and multichannel instruments, this correction is made by taking background readings on either side of the line of interest. State-of-theart instruments include software designed to make background corrections automatically or under operator control.

Because ICP spectra for many elements are so rich in lines, spectral interferences are always possible. To avoid this type of error requires knowledge of all of the components likely to be

TABLE 10-2 Effect of Standardization Frequency on Precision of ICP Data

	Relative Standard Deviation, %					
Frequency of Recalibration, hours	Concentration Multiple above Detection Limit $10^1 \ \text{to} \ 10^2 \qquad \qquad 10^2 \ \text{to} \ 10^3 \qquad \qquad 10^3 \ \text{to} \ 10^4 \qquad \qquad 10^4 \ \text{to} \ 10^4 \ $					
0.5	3–7	1–3	1–2	1.5-2		
2	5–10	2-6	1.5-2.5	2–3		
8	8–15	3-10	3–7	4-8		

Data from R. M. Barnes, in Applications of Inductively Coupled Plasmas to Emission Spectroscopy, R. M. Barnes, ed., p. 16, Philadelphia: The Franklin Institute Press, 1978. With permission.

	Number of Elements Detected at Concentrations of					
Method	<1 ppb	1–10 ppb	11–100 ppb	101–500 ppb	>500 ppb	
ICP emission	9	32	14	6	0	
Flame atomic emission	4	12	19	6	19	
Flame atomic fluorescence	4	14	16	4	6	
Flame atomic absorption	1	14	25	3	14	

TABLE 10-3 Comparison of Detection Limits for Several Atomic Spectral Methods

Data abstracted with permission from V. A. Fassel and R. N. Kniseley, Anal. Chem., 1974, 46 (13), 1110A. Copyright 1974 American Chemical Society.

Detection limits correspond to a signal that is twice as great as the standard deviation for the background noise.

present in the sample and a careful study of the information in the reference works listed in note 23. The software for modern computerized instruments has powerful routines for wavelength and concentration calibration, spectral analysis, and deconvolution of overlapping lines. These features coupled with integrated databases of spectral lines make spotting and correcting for interferences an integral part of the analytical process.

#### **Detection Limits**

In general, detection limits with the ICP source are comparable to or better than other atomic spectral procedures. Table 10-3 compares detection limits for several of these methods. Note that more elements can be detected at levels of 10 ppb or less with plasma excitation than with other emission or absorption methods. As we shall see in Chapter 11, the ICP coupled with mass spectrometric detection improves detection limits by two to five orders of magnitude for many elements and is thus strong competition for ICP optical emission spectroscopy.

### 10B EMISSION SPECTROSCOPY BASED ON ARC AND SPARK SOURCES

Arc and spark source spectroscopies were the first instrumental methods to become widely used for analysis. These techniques, which began to replace the classical gravimetric and volumetric methods for elemental analysis in the 1920s, were based on excitation of emission spectra of elements with electric arcs or high-voltage sparks. These spectra permitted the qualitative and quantitative determination of metallic elements in a variety of sample types, including metals and alloys, soils, minerals, and rocks.<sup>25</sup> Arc and spark sources are still used in some

situations for qualitative and semiquantitative analysis, particularly in the metals industries. Arcs and sparks are gradually being displaced by plasma sources, and it appears likely that this trend will continue.

In arc and spark sources, sample excitation occurs in the gap between a pair of electrodes. Passage of electricity from the electrodes through the gap provides the necessary energy to atomize the sample and produce atoms or ions in electronic excited states.

### 10B-1 Characteristics of DC Arcs and **High-Voltage Sparks**

Arc and spark source methods are currently limited to the elemental analysis of solids because liquids and gaseous samples are handled much more conveniently by plasma emission methods. If the sample is a metal, electrodes can be formed from the sample by milling, by turning, or by casting the molten metal in a mold. For nonmetallic solids, the sample is often supported on an electrode. Carbon is an ideal electrode for many applications. It can be obtained in a highly pure form, is a good conductor, has good heat resistance, and is easily shaped.

Because of their instabilities, it is necessary to integrate the emission signals from arc and spark sources for at least 20 s and often for a minute or more. This requirement makes the sequential spectrometers, such as those described in section 10A-4, impractical for most applications. Simultaneous multichannel instruments are most often used. Spectrographs, polychromators, and array detector-based multichannel instruments are used.

Direct-current arc sources produce spectra that are rich in intense lines for atoms and contain a lesser number for ionic species. Direct-current arcs produced from a carbon or graphite electrode in air emit intense bands due to the presence of cyanogen radicals (CN). As a result, most of the region between 350 to 420 nm is useless for elemental analysis. High-voltage sparks are much more energetic than typical direct-current arcs. Because

<sup>&</sup>lt;sup>25</sup>For additional details, see J. D. Ingle Jr. and S. R. Crouch, Spectrochemical Analysis, Chap. 9, Upper Saddle River, NJ: Prentice-Hall, 1988; R. D. Sacks, in Treatise on Analytical Chemistry, 2nd ed., P. J. Elving, E. J. Meehan, and I. M. Kolthoff, eds., Part I, Vol. 7, Chap. 6, New York: Wiley, 1981; P. W. J. M. Boumans in Analytical Emission Spectroscopy, Vol. 1, Part I, E. L. Grove, ed., New York: Marcel Dekker, 1972.

of this, ionic spectra are much more pronounced in a highvoltage spark than in a direct-current arc. In fact, lines emitted by ions are often termed "spark lines" by spectroscopists, while atom lines are sometimes called "arc lines."

### 10B-2 Applications of Arc and **Spark Emission**

Arc sources are particularly useful for qualitative and semiquantitative analysis of nonmetallic samples, such as soils, plant materials, rocks, and minerals. The precision obtainable with an arc source is usually poorer than that with a spark source and generally much poorer than that with a plasma source. Currently, the primary use for spark emission spectroscopy is for the identification and analysis of metals and other conducting materials. High-voltage sparks have also become important devices for ablating solid samples prior to introduction into plasma excitation sources.

An important use for spark and arc spectrometers is in foundry and shop floors, scrapyards, and metal-casting facilities. The instruments for these are often mobile and may be equipped with a handheld spark or arc gun that the operator can touch to the metal surface to excite atoms of the sample. These devices can be used for the rapid identification of alloy types and for sorting metals by type in scrapyards and recycling centers.

### **10C** OTHER SOURCES FOR OPTICAL **EMISSION SPECTROSCOPY**

In addition to plasma, arc, and spark sources, two additional sources are also used: flame emission sources and the glowdischarge source.

#### **10C-1 Flame Emission Sources**

For many years, flames have been used to excite emission spectra for various elements, and most modern atomic absorption spectrometers may be adapted for flame emission measurements. Flames are not widely used for this purpose, however, because for most single-element determinations, absorption methods provide as good or better accuracy, convenience, and detection limits. For multielement analyses, plasma sources are far superior to flames in most regards. For these reasons flame emission spectrometry is little used except for the determination of the alkali metals and occasionally calcium. These elements are excited at the relatively low temperatures of flames to give spectra that are remarkably simple and free of interference from other metallic species. Alkali-metal spectra generally consist of a relatively few intense lines, many of which are in the visible region and are well suited to quantitative emission measurements.

Because these spectra are simple, basic filter photometers can be quite adequate for routine determinations of the alkali and alkaline-earth metals. A low-temperature flame is used to avoid excitation of most other metals. As a result, interference filters can isolate the appropriate emission line.

Several instrument manufacturers supply flame photometers designed specifically for the determination of sodium, potassium, lithium, and sometimes calcium in blood serum, urine, and other biological fluids. Single-channel and multichannel (two to four channels) instruments are available for these determinations. In the multichannel instruments, each channel can be used to determine a separate element without an internal standard, or one of the channels can be reserved for an internal standard such as lithium. The ratios of the signals from the other channels to the signal of the lithium channel are then taken to compensate for flame noise and noise from fluctuations in reagent flow rate. Flame photometers such as these have been coupled with flow injection systems to automate the sample-introduction process (see Section 33B-3). Typically, relative standard deviations for flow-injectionanalysis-based flame photometric determinations of lithium, sodium, and potassium in serum are on the order of a few percent or less. Automated flow injection procedures require 1/100 the amount of sample and 1/10 the time of batch procedures.26

Although the alkali metals are determined daily in a huge number of samples throughout the world, most are clinical samples that are analyzed potentiometrically (see Chapter 23). Flame photometry is currently used for only a fraction of these samples.

### **10C-2 Glow-Discharge Sources**

The glow discharge, which is described in Section 8C-2 and Section 9A-3, has proven to be a useful source for exciting emission spectra of metals, alloys, and other solid materials.<sup>27</sup> Glowdischarge optical emission spectroscopy (GDOES) has become a mature technique in recent years, and several instrument manufacturers offer glow-discharge sources as well as complete spectrometers configured for this type of analysis. Glow-discharge spectroscopy is a versatile technique in that it is capable of bulk analysis and depth profiling of solids.

Figure 10-17 shows a typical cell for GDOES, and it is similar in many respects to the absorption cells described in Sections 8C-2 and 9A-3. A dc voltage of up to 1 kV applied between the electrodes produces sputtering of the solid sample

<sup>&</sup>lt;sup>26</sup>G. N. Doku and V. P. Y. Gadzekpo, Talanta, 1996, 43, 735, DOI: 10.1016/0039-9140(95)01808-5.

<sup>&</sup>lt;sup>27</sup>Glow Discharge Plasmas in Analytical Spectroscopy, R. K. E. Marcus and J. A. C. E. Broekaert, eds., Hoboken, NJ: Wiley, 2003.

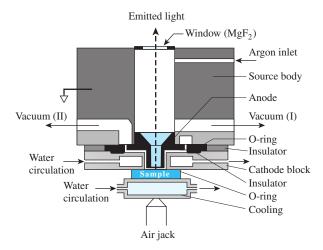


FIGURE 10-17 Diagram of a Grimm-type glow-discharge source. (From M. Boucharcourt and F. Schwoehrer, in Glow Discharge Optical Emission Spectrometry, R. Payling, D. G. Jones, and A. Bengtson, eds., p. 54, New York: Wiley, 1997, with permission.)

at a current of 40-200 mA. In the glow discharge, at the cathode surface, ground-state analyte atoms become excited by collision with high-energy electrons, relax, and emit their characteristic radiation. Radio-frequency (RF) excitation, which permits nonconducting materials to be analyzed by GDOES, is available in some commercial instruments, and pulsed dc and pulsed RF modes have been explored to increase line intensities.<sup>28</sup>

GDOES depth profiling is illustrated in the curves of Figure 10-18 for a sample of brass. The plots show profiles for seven monitored elements as a function of time from the initiation of the glow discharge. During the pre-integration period, surface contaminants volatilize, and over a period of 60 s, the signals reach a relatively constant level corresponding to the composition of the bulk material. The length of the preintegration period is best determined by the precision of the signal at various times during the sputtering process. For the sample illustrated, the precision was optimal at about 3% relative over the period indicated by  $I_1$ . This period was thus chosen for the determination of the composition of similar samples. Depending on the nature of the analysis, the power, the pressure, and the pre-integration and integration periods can be selected to optimize results.<sup>29</sup> The relatively constant signal levels for all of the elements indicate uniform composition throughout the

<sup>&</sup>lt;sup>29</sup>T. A. Nelis and R. A. Payling, Glow Discharge Optical Emission Spectroscopy, pp. 23-24, New York: Springer, 2004.

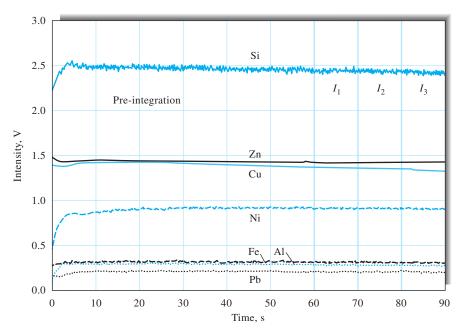


FIGURE 10-18 Qualitative depth profile of a brass sample, showing major and minor elements, indicating the time regions to be used for pre-integration (60 s) and three 10-s integration periods  $I_1$ ,  $I_2$ , and  $I_3$ . (From T. A. Nelis and R. A. Payling, Glow Discharge Optical Emission Spectroscopy, p. 23, New York: Springer, 2004. With permission.)

<sup>&</sup>lt;sup>28</sup>N. Jakubowski, A. Bogaerts, and V. Hoffmann, Atomic Spectroscopy in Elemental Analysis, M. Cullen, ed., p. 120, Boca Raton, FL: CRC Press, 2004.

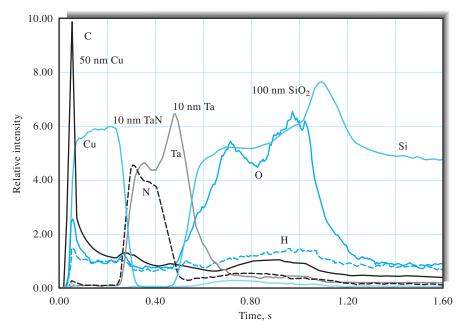


FIGURE 10-19 RF-GDOES depth profile of a microelectronic multilayer system. Note the thickness and composition of each layer shown above each peak or band and the elemental composition indicated by the curves. (From N. Jakubowski, A. Bogaerts, and V. Hoffmann, Atomic Spectroscopy in Elemental Analysis, M. Cullen, ed., p. 129, Boca Raton, FL: CRC Press, 2004. With permission.)

sample. In Figure 10-19, we see a depth profile of an electronic integrated circuit obtained using GDOES with RF excitation. The emergence with time of a peak or a band indicates the appearance of the elements contained in each successive layer of the circuit materials. Labels above each curve indicate the identity and thickness of each layer.<sup>30</sup>

Because of the low background levels of GDOES, detection limits on the order of parts per million are typical using the

Grimm source of Figure 10-17. The dynamic range is relatively large compared to arc and spark sources, and relative standard deviations of 1% or lower are common with these devices.<sup>31</sup>

Recent work with glow discharges has developed the solution-cathode technique that has several advantages.<sup>32</sup> Unlike plasma sources, the solution-cathode glow discharge requires no gas or fuel and can sample analytes directly without a nebulizer.

# **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.
- **10-1** What is an internal standard and why is it used?
- 10-2 Why are atomic emission methods with an ICP source better suited for multielement analysis than are flame atomic absorption methods?
- **10-3** Why do ion lines predominate in spark spectra and atom lines in arc spectra?
- \* 10-4 Calculate the theoretical reciprocal linear dispersion of an echelle grating with a focal length of 0.85 m, a groove density of 120 grooves/mm, and a diffraction angle of 61°16' when the diffraction order is (a) 30 and (b) 90.

<sup>&</sup>lt;sup>30</sup>N. Jakubowski, A. Bogaerts, and V. Hoffmann, Atomic Spectroscopy in Elemental Analysis, M. Cullen, ed., p. 120, Boca Raton, FL: CRC Press, 2004.

<sup>&</sup>lt;sup>31</sup>J. A. C. Broekaert, Analytical Atomic Spectrometry with Flames and Plasmas, pp. 244-246. Hoboken, NJ: Wiley-VCH, 2002.

<sup>&</sup>lt;sup>32</sup>Wang, Zheng, A. J. Schwartz, S. J. Ray, and G. M. Hieftje, *J. Anal. Atom.* Spectrosc., 2013, 28, 234, DOI: 10.1039/c2ja30253e.

# >> QUESTIONS AND PROBLEMS (continued)

- **10-5** Why are arc sources often blanketed with a stream of an inert gas?
- **10-6** Describe three ways of introducing a sample into an ICP torch.
- **10-7** What are the relative advantages and disadvantages of ICP plasmas compared to microwave plasmas?
- **10-8** Why are ionization interferences less severe in ICP than in flame emission spectroscopy?
- **10-9** What are some of the advantages of plasma sources compared with flame sources for emission spectrometry?
- **10-10** Discuss the advantages and disadvantages of sequential versus simultaneous multichannel ICP spectrometers.



**10-11** Gold can be determined in solutions containing high concentrations of diverse ions by ICP-AES. <sup>33</sup> Aliquots of 5.00 mL of the sample solution were transferred to each of four 50.0 mL volumetric flasks. A standard solution was prepared containing 10.0 mg/L Au in  $20\% \text{ H}_2\text{SO}_4$ , and the following quantities of this solution were added to the sample solutions: 0.00, 0.00, 0.00, 0.00, 0.00, and 0.00 mL added Au in each of the flasks. The solutions were made up to a total volume of 0.00 mL, mixed, and analyzed by ICP-AES. The resulting data are presented in the following table.

Volume of	<b>Emission Intensity,</b>			
Standard, mL	Counts			
0.00	12,568			
2.50	19,324			
5.00	26,622			
10.00	40,021			

- **(a)** Use a spreadsheet to perform a least-squares analysis to determine the slope, intercept, and regression statistics, including the standard deviation about regression.
- **(b)** Use your results to find the concentration of gold in the sample solution in mg/L.
- (c) The known concentration of gold in the sample is 8.51 mg/L. Test the hypothesis that your result is equal to this value at the 95% confidence level.

## **X** Challenge Problem

- **10-12** Watters et al. have discussed uncertainties associated with calibration curves for ICP-OES and procedures for optimizing the results of least-squares analysis of such data.<sup>34</sup>
  - (a) The central issue addressed by these workers is whether a weighted or an unweighted least-squares procedure is appropriate for ICP calibration. What is the primary criterion for deciding which procedure to use?
  - **(b)** What do the terms *homoscedasticity* and *heteroscedasticity* mean?
  - (c) The model used by these workers for the ICP curves is represented by the following equation:

$$Y_{ii} = a + bx_i + error_{ii}$$

Define each variable in the equation, and describe the significance of the relationship embodied in it.

**(d)** Watters et al. chose to model the error in ICP working curves in terms of concentration rather than intensity. What is their rationale for this choice?

<sup>&</sup>lt;sup>33</sup>J. A. Whitehead, G. A. Lawrance, and A. McCluskey, *Aust. J. Chem.*, **2004**, *57*, 151, **DOI**: 10.1071/CH03198.

<sup>&</sup>lt;sup>34</sup>R. L. Watters Jr., R. J. Carroll, and C. H. Spiegelman, *Anal. Chem.*, **1987**, 59, 1639, **DOI**: 10.1021/ac00140a013.

$$\sigma(x) = c + dx + ex^2$$

Describe the significance of each variable, and characterize the nature of the model.

- **(f)** How is  $\sigma(x)$  determined in practice?
- (g) Shot noise and source flicker noise correspond to which variables in the expression shown in (e)?
- **(h)** What experimental noise sources are constant? Which variable in the expression shown in (e) corresponds to these sources (or source)?
- (i) What is the relationship of the following alternative model to the model in (e)?

$$\sigma^2(x) = g + hx + kx^2$$

- (j) What is the purpose of the models in (e) and (i)?
- (k) What is the significance of each of the variables  $\hat{a}$  and  $\hat{b}$ ?
- (l) The authors conclude that "if heteroscedasticity is ignored, confidence intervals will be too narrow at the high end and too wide at the low end of the ICP calibration curve. The magnitude of these effects will depend on the particular dilution scheme used to make the calibration standard solutions." How does the dilution scheme for standards affect the results of least-squares analysis on ICP calibration curves?
- (m) Create an Excel spreadsheet similar to the one shown next containing data from Table I of the paper by Watters et al., and perform both unweighted and weighted least-squares analysis of the data. First use LINEST to perform the unweighted analysis, and then perform an unweighted analysis using Solver to minimize cell C25 by varying B14 and C14. Compare the results obtained by both methods. Compare and contrast advantages of each method.<sup>35</sup>

	Α	В	С	D	Е	F	G	Н	I		
1	Concn,	Intensity	si	s	s						
2	μg/μL	(counts)	(obsd)	(10 reps)	(4 reps)			LINEST			
3	0.00	11.33	8.54	7.88	6.97			b	а		
4	0.0101	16.60	7.88	7.98	7.03		Value				
5	0.0251	37.92	9.06	8.12	7.12		Uncertainty				
6	0.0503	57.00	8.46	8.36	7.28		R / Sy				
7	0.101	149.88	6.13	8.84	7.58		F/dF				
8	0.251	369.24	11.57	10.25	8.50 SSreg/SSres						
9	0.503	763.36	11.94	12.48	10.02						
10	2.51	3688.46	26.24	25.42	22.25						
11	5.03	7431.08	29.12	29.30	37.55						
12											
13	Unweighted	b	a	Weighted(10)	b	а	Weighted(4)	b	a		
14											
15	bx + a	Resid	Resid <sup>2</sup>	bx + a	Resid	Resid <sup>2</sup> /s <sup>2</sup>	bx + a	Resid	Resid <sup>2</sup> /s <sup>2</sup>		
16											
17	Cell A16=\$B\$14*A3+\$C\$14				Cell B14=Initial estimate of slope				pe		
18	Cell B16=B3-A16					Cell C1	4=Initial esti	4=Initial estimate of intercept			
19	Cell C16=B16^2										
20	Cell D16=\$E\$14*A3+\$F\$14										
21	Cell F16+E16^2*(1/D3^2)										
22	Cell C25=SU	M(C16:C24)									
23	Cell C26=SQRT(C25/(COUNT(C16:C24)			)-2))							
24											
25		SS	0.0000		SS	0.0000		SS	0.000		
26		<b>S</b> <sub>r</sub>	0.0000		S <sub>r</sub>	0.0000		S <sub>r</sub>	0.0000		

<sup>&</sup>lt;sup>35</sup>S. R. Crouch and F. J. Holler, *Applications of Microsoft*\* Excel in Analytical Chemistry, 3rd ed., pp. 95, 131–138, Belmont, CA: Cengage Learning, 2017.

# >>> QUESTIONS AND PROBLEMS (continued)

Repeat the analysis for the ten-replicate data using the formulas provided in the spreadsheet documentation. Formulas entered in row 16 must be copied into rows 17-24. Minimize cell F25 by varying cells E14 and F14 using Solver to obtain estimates of the slope and intercept. Repeat the analysis for the four-replicate data using Solver to minimize cell I25 by varying cells H14 and I14. Compare your procedures and results to those of Watters et al. and comment on any differences. What advantage does weighted least-squares analysis have over unweighted analysis?

- (n) Add a section to your Excel spreadsheet to compute the mean and standard deviation of the concentration of an analyte given a number of measurements of sample ICP emission intensity.<sup>36</sup>
- There are a number of commercial and noncommercial sources on the Internet for Excel add-ins, which are programs or function packs that supplement the built-in functions of Excel. For example, Solver is actually an add-in that is produced by an independent contractor and that is available from the vendor in an enhanced version. Use a search engine such as Google to locate the websites of programmers and vendors that offer add-ins to perform weighted least-squares analysis. One such vendor is XLSTAT (www.xlstat.com). Download the demonstration version of XLSTAT, install it on your computer, and use it to perform weighted and unweighted least-squares analysis on the data of (n). Note that you must calculate the weighting factors from the standard deviations given in the paper and that you may need to scale them. You should calculate columns in your spreadsheet containing 1/s<sup>2</sup>, and then divide each cell by the largest value in the column. Weighting factors need be only proportional to the variance, so you can scale them in any convenient way. Compare the results from XLSTAT with the results from your spreadsheet, and comment on the ease of use and functionality of XLSTAT. XLSTAT contains many other useful statistics and numerical analysis functions and is available at modest cost to students who desire permanent use of the add-in.

<sup>&</sup>lt;sup>36</sup>D. A. Skoog, D. M. West, F. J. Holler, and S. R. Crouch, Fundamentals of Analytical Chemistry, 9th ed., pp. 173-174, Belmont, CA: Brooks/Cole, 2014.