CHAPTER 6

Atomic Absorption Spectrometry

The basis of atomic absorption spectrometry (AAS) is the absorption of discrete wavelengths of light by ground-state, gas-phase free atoms. Free atoms in the gas phase are formed from the sample by an "atomizer" at high temperature. AAS was developed in the 1950s by Alan Walsh and rapidly became a widely used analytical tool. AAS is an **elemental analysis** technique capable of providing quantitative information on ~70 elements in almost any type of sample. As an elemental analysis technique, it has the significant advantage in many (but not all) cases of being practically independent of the chemical form of the element in the sample. A determination of cadmium in a water sample is a determination of the total cadmium concentration. It does not matter whether the cadmium exists as the chloride, sulfate, or nitrate, or even if it exists as a complex or an organometallic compound, if the proper analysis conditions are used. Concentrations as low as ppt levels of some elements in solution can be determined and AAS is used routinely to determine ppb and ppm concentrations of most metal elements. Another principal advantage is that a given element can be determined in the presence of other elements, which do not interfere by absorption of the analyte wavelength. Therefore, it is not necessary to separate the analyte from the rest of the sample (the matrix). This results in rapid analysis times and eliminates some sources of error. This is not to say that AAS measurements are completely free from interferences; both chemical and spectral interferences do occur and must be compensated for, as will be discussed. The major disadvantages of AAS are that no information is obtained on the chemical form of the analyte (no "speciation") and that often only one element can be determined at a time. The latter makes AAS of very limited use for qualitative analysis. AAS is used almost exclusively for quantitative analysis of elements, hence the use of the term "spectrometry" in the name of the technique instead of "spectroscopy."

6.1 ABSORPTION OF RADIANT ENERGY BY ATOMS

AAS is based on the absorption of radiant energy by free gas-phase atoms. In the process of absorption, an atom changes from a low energy state to a higher energy state as discussed in Chapter 2. Gas-phase atoms do not vibrate in the same sense that molecules do. Also, they have virtually no rotational energy. Hence, no vibrational or rotational energy is involved in the electronic excitation of atoms. As a result, atomic absorption spectra consist of a few very narrow absorption lines, in contrast to the wide bands of energy absorbed by molecules in solution.

Each element has a specific number of electrons "located" in an orbital structure that is unique to each element. The lowest energy electronic configuration of an atom is called the ground state. The ground state is the most stable electronic state. If energy ΔE of exactly the right magnitude is applied to a free gas-phase atom, the energy will be absorbed. An outer electron will be promoted to a higher energy, less stable excited state. The frequencies and wavelengths of radiant energy capable of being absorbed by an atom are predicted from $\Delta E = h\nu = hc/\lambda$. The energy absorbed, ΔE, is

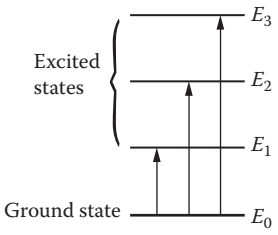


Figure 6.1 Schematic electronic energy levels in a free atom.

the difference between the energy of the higher energy state and the lower energy state. As shown schematically in Figure 6.1, this atom has four electronic energy levels. E_0 is the ground state, and the other levels are higher energy excited states. If the exact energies of each level are known, the three wavelengths capable of being absorbed can be calculated as follows:

$$\Delta E' = \frac{hc}{\lambda_1} = E_1 - E_0$$

$$\Delta E'' = \frac{hc}{\lambda_2} = E_2 - E_0$$

$$\Delta E''' = \frac{hc}{\lambda_3} = E_3 - E_0$$

The calculated wavelengths λ_1, λ_2, and λ_3 all arise from transitions from the ground state to excited states. Absorption lines due to transitions from the ground state are called **resonance lines**. It is possible for an electron in an excited state to absorb radiant energy and move to an even higher excited state; in that case, we use the ΔE values for the appropriate energy levels involved. As we will see, in AAS, most absorptions do arise from the ground state.

Quantum theory defines the electronic orbitals in an atom and predicts the lowest energy configuration (from the order of filling the orbitals). For example, the 11 electrons in sodium have the configuration $1s^2 2s^2 2p^6 3s^1$ in the ground state. The inner shells (principal quantum number, $n = 1$ and 2) are filled and there is one electron in the $n = 3$ shell. It is this outer shell electron that is involved in atomic absorption transitions for sodium. Ultraviolet (UV) and visible (VIS) wavelengths are the range of radiant energies absorbed in AAS. UV/VIS radiation does not have sufficient energy to excite the inner shell electrons, only the electrons in the outermost (valence) shell are excited. This is true of all elements: only the outermost electrons (valence electrons) are excited in AAS.

The number of energy levels in an atom can be predicted from quantum theory. The actual energy differences of these levels have been deduced from studies of atomic spectra. These levels have been graphed in *Grotrian diagrams*, which are plots for a given atom showing energy on the *y*-axis and the possible atomic energy levels as horizontal lines. A partial Grotrian diagram for sodium is shown in Figure 6.2. The energy levels are split because the electron itself may spin one way or another, resulting in two similar energy levels and therefore two possible absorption lines rather than a single line (a singlet). For the transition from the ground state to the first excited state of sodium, the electron moves from the 3s orbital to the empty 3p orbital. The latter is split into two levels, designated $^2P_{1/2}$ and $^2P_{3/2}$, by the electron spin, so two transitions are possible. The levels differ very slightly in energy because of the interaction of the electron spin and the orbital motion of the electron. The wavelengths that are associated with these transitions are 589.5 and 589.0 nm, respectively, the well-known sodium D lines that give rise to the yellow color of sodium vapor street lights.

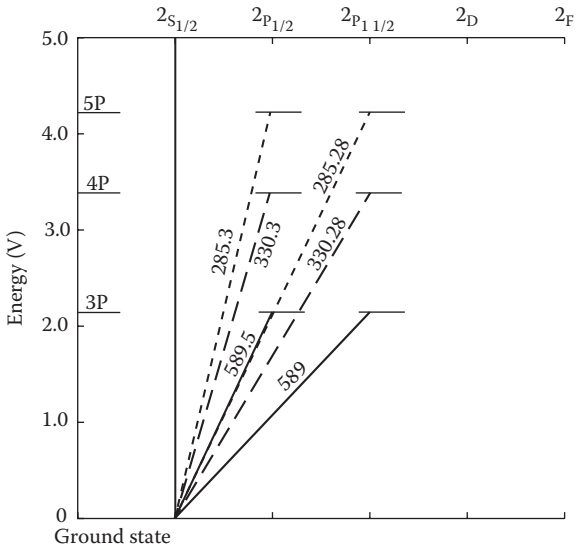


Figure 6.2 Partial Grotrian diagram for sodium.

Under the temperatures encountered in the atomizers used in commercial AAS systems, a large majority of the atoms exist in their lowest possible energy state, the ground state. Very few atoms are normally in the higher energy states. The ratio of atoms in an upper excited state to a lower energy state can be calculated from the Maxwell–Boltzmann equation (also called the Boltzmann distribution):

$$\frac{N_1}{N_0} = \frac{g_1}{g_0} e^{-\Delta E/kT} \tag{6.1}$$

where

N_1 is the number of atoms in the upper state
N_0 is the number of atoms in the lower state
g_1, g_0 are the number of states having equal energy at each level 0, 1, etc. (g is called the degeneracy of the level)
ΔE is the energy difference between the upper and lower states (J)
k is the Boltzmann constant = 1.381×10^{-23} J/K
T is the absolute temperature (K)

For example, it can be calculated from the Boltzmann distribution that if zinc vapor (Zn^0 gas) with resonance absorption at 213.9 nm is heated to 3000 K, there will be only one atom in the first excited state for every 10^{10} atoms in the ground state. Zinc atoms need a considerable amount of energy to become excited. On the other hand, sodium atoms are excited more easily than the atoms of most other elements. Nevertheless, at 3000 K, only 1 sodium atom is excited for every 1000 atoms in the ground state. In a normal atom population, there are very few atoms in states E_1, E_2, E_3, and higher. The total amount of radiation absorbed depends, among other things, on how many atoms are available in the lower energy state to absorb radiation and become excited. Consequently, the total amount of radiation absorbed is greatest for absorptions from the ground state. Excited-to-excited state transitions are very rare, because there are so few excited atoms; only the ground-state resonance lines are useful analytically in AAS.

This greatly restricts the number of absorption lines that can be observed and used for measurement in atomic absorption. Quite frequently only three or four useful lines are available in the UV/VIS spectral region for each element, and in some cases, fewer than that. The wavelengths of these absorption lines can be deduced from the Grotrian diagram of the element being determined but are more readily located in AAS instrument methods manuals (called "AAS cookbooks") available from the major instrument manufacturers. A list of the most intense absorption wavelengths for flame AAS (FAAS) determination of elements is given in Appendix 6.A.

AAS is useful for the analysis of approximately 70 elements, almost all of them metal or metalloid elements. Grotrian diagrams correctly predict that the energy required to reach even the first excited state of *nonmetals* is so great that they cannot be excited by normal UV radiation (>190 nm). The resonance lines of nonmetals lie in the vacuum UV region. Commercial AAS systems generally have air in the optical path, and the most common atomizer, the flame, must operate in air. Consequently, using flame atomizers, atomic absorption cannot be used for the direct determination of nonmetals. However, nonmetals have been determined by indirect methods, as will be discussed in the applications section.

6.1.1 Spectral Linewidth

According to the Bohr model of the atom, atomic absorption and emission linewidths should be infinitely narrow, because there is only one discrete value for the energy of a given transition. However, there are several factors that contribute to line broadening. The natural width of a spectral line is determined by the Heisenberg uncertainty principle and the lifetime of the excited state. Most excited states have lifetimes of 10^{-8}–10^{-10} s, so the uncertainty in the energy of the electron slightly broadens the spectral line. This is called the *natural* linewidth and is on the order of 10^{-4} Å (1.0 Å = 1.0×10^{-10} m).

Collisions with other atoms in the atomizer lead to *pressure* (*Lorentz*) *broadening*, on the order of 0.05 Å. *Doppler broadening*, due to random kinetic motion toward and away from the detector, results in broadening of the spectral line on the order of 0.01–0.05 Å. Doppler and collisional broadening are temperature dependent. In an atomization source with high concentrations of ions and electrons (such as in a plasma, discussed in Chapter 7), *Stark broadening* occurs as a result of atoms encountering strong local electrical fields. In the presence of a magnetic field, *Zeeman splitting* of the electronic energy levels also occurs. Localized magnetic fields within atomizers from moving ions and electrons are negligibly small and their effects are generally not seen. However, by adding an external magnetic field, we can use Zeeman splitting to assist in the correction of background absorption. The width of atomic absorption lines is on the order of 0.002 nm. These are very narrow lines, but not infinitely narrow.

6.1.2 Degree of Radiant Energy Absorption

The fraction of incident light absorbed by atoms at a particular wavelength is proportional to the number of atoms, *N*, that can absorb the wavelength and to a quantity called the oscillator strength *f*. The oscillator strength *f* is a dimensionless quantity whose magnitude expresses the transition probability for a specific transition. The **oscillator strength** is a constant for a particular transition; it is an indicator of the probability of absorbing the photon that will cause the transition. *N* is the number of ground-state atoms in the light path, since most atoms are in the ground state at normal atomizer temperatures.

As discussed in Chapter 2, the fraction of incident light absorbed by a species can be expressed as the absorbance, *A*. The relationship between absorbance and the amount of analyte, in this case, atoms, in the light path is given by Beer's law:

$$A = abc = (\text{constant} \times f)\,(b)\,(\text{N/cm}^3) \tag{6.2}$$

The proportionality constant a is called the absorptivity and includes the oscillator strength f. The term b is the length of the light path and c is the concentration of ground-state atoms in the light path (i.e., atoms/cm^3).

The amount of radiation absorbed is only slightly dependent on temperature as shown by Equation 6.1. This is an advantage for AAS over atomic emission spectrometry and flame photometry (Chapter 7) where the signal intensity is highly temperature dependent. Although the temperature does not affect the *process* of absorption by atoms, it does affect the efficiency with which free atoms are produced from a sample and therefore indirectly affects the atomic absorption signal. This effect can sometimes be significant. Some atoms, particularly those of the alkali metals, easily ionize. Low ionization energies and high temperatures result in the formation of ions rather than atoms. Ions do not absorb at atomic absorption wavelengths. Atoms that become ionized are effectively removed from the absorbing population, resulting in a loss of signal.

6.2 INSTRUMENTATION

A schematic block diagram of the instrumentation used for AAS is shown in Figure 6.3. The components are similar to those used in other spectroscopic absorption methods as discussed in Chapters 2 and 5. Light from a suitable source is directed through the **atomizer**, which serves as the sample cell, into a wavelength selector and then to a detector. The detector measures how much light is absorbed by the sample. The sample, usually in solution form, is introduced into the atomizer by some type of introduction device. The atomizer converts the sample to gas-phase ground-state atoms that can absorb the incident radiation.

6.2.1 Radiation Sources

Two radiation sources are commonly used in commercial AAS instruments, the hollow cathode lamp (HCL) and the electrodeless discharge lamp (EDL). Both types of lamps are operated to provide as much intensity as possible while avoiding line-broadening problems caused by the collision processes described earlier.

6.2.1.1 Hollow Cathode Lamp

As we have already mentioned, atomic absorption lines are very narrow (about 0.002 nm). They are so narrow that if we were to use a continuous source of radiation, such as a hydrogen or deuterium lamp, it would be very difficult to detect any absorption of the incident radiation at all. Absorption of a narrow band from a continuum is illustrated in Figure 6.4, which shows the absorption of energy from a deuterium lamp by zinc atoms absorbing at 213.9 nm. The width of the zinc absorption line is exaggerated for illustration purposes. The wavelength scale for the deuterium lamp in Figure 6.4 is 50 nm wide and is controlled by the monochromator bandpass. If the absorption line of Zn were 0.002 nm wide, its width would be $0.002 \times 1/50 = 1/25{,}000$ of the scale shown.

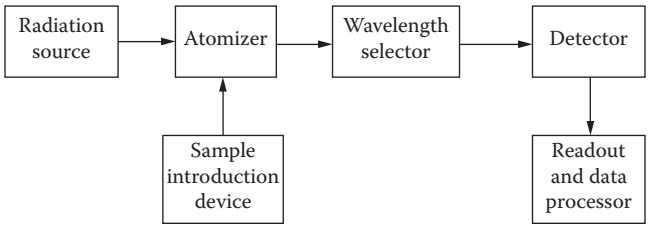


Figure 6.3 Block diagram of the components of an AAS.

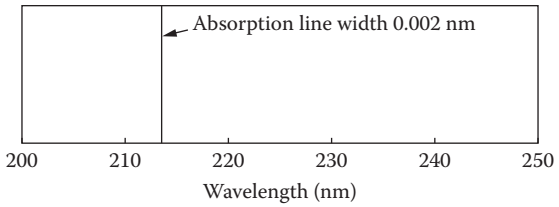


Figure 6.4 Width of an atomic absorption line (Zn 213.9 nm line), greatly exaggerated, compared with the emission bandwidth from a continuum source such as a deuterium lamp.

Such a narrow line would be detectable only under extremely high resolution (i.e., very narrow bandpass), which is not encountered in commercial AAS equipment.

With the use of slits and a good monochromator, the bandwidth falling on the detector can be reduced to about 0.2 nm (much less than the earlier 50 nm example). If the light source is continuous, the entire 0.2 nm bandwidth contributes to the signal falling on the detector. If an absorption line 0.002 nm wide were absorbed from this light source, the signal reaching the detector would be reduced by only 1% from the original signal. Since this is about the absorption linewidth of atoms, even with complete absorption of the radiation at 213.9 nm by Zn atoms, the total signal from a continuous light source would change by only 1%. This would result in an insensitive analytical procedure of little practical use.

What is needed for a light source in AAS is a source that produces very narrow emission lines at the exact wavelengths capable of being absorbed by analyte atoms. The problem was solved by the development of the HCL, shown schematically in Figure 6.5. The cathode is often formed by hollowing out a cylinder of pure metal or making an open cylinder from pure metal foil. The metal used for the cathode is the metal whose spectrum will be emitted by the lamp. If we want to determine Cu in our AAS experiment, the lamp cathode must be a copper cylinder; if we want to determine gold, the cathode must be a gold cylinder, and so on. The cathode and an inert anode are sealed in a glass cylinder filled with Ar or Ne at low pressure (the "filler gas"). A window of quartz or glass is sealed onto the end of the lamp; a quartz window is used if UV wavelengths must be transmitted. Most HCLs have quartz windows, because most elements have emission and absorption lines in the UV. Glass can be used for some elements, such as sodium, where all the strong absorption lines are in the visible region of the spectrum.

The HCL emits narrow, intense lines from the element that forms the cathode. Applying a high voltage across the anode and cathode creates this emission spectrum. Atoms of the filler gas become ionized at the anode and are attracted and accelerated toward the cathode. The fast-moving ions strike the surface of the cathode and physically dislodge some of the surface metal atoms (a process called "sputtering"). The displaced atoms are excited by collision with electrons and emit the characteristic atomic emission spectrum of the metal used to make the cathode. The process is

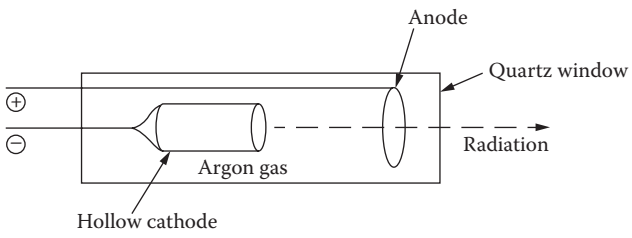


Figure 6.5 Schematic diagram of an HCL. The anode and cathode are sealed in a glass cylinder filled with argon or neon gas at low pressure. The window must be transparent to the emitted radiation.

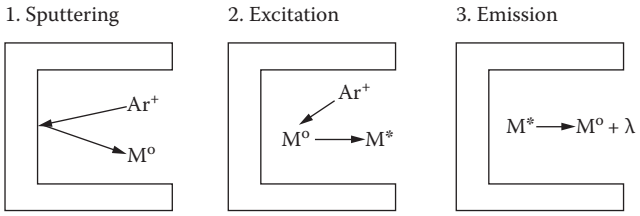


Figure 6.6 The HCL process, where Ar^+ is a positively charged argon ion, M^0 is a sputtered ground-state metal atom, M* is an excited-state metal atom, and λ is emitted radiation at a wavelength characteristic for the sputtered metal. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

shown in Figure 6.6. The emitted atomic lines are extremely narrow. Unlike continuum radiation, the narrow emission lines from the HCL can be absorbed almost completely by unexcited atoms. Using this light source, atomic absorption is easily detected and measured. Narrow line sources such as the HCL provide not only high sensitivity but also specificity. If only Cu atomic emission lines are produced by the Cu HCL, there are few species other than Cu atoms that can absorb these lines. Therefore, there is little spectral interference in AAS. The emitted spectrum consists of all the emission lines of the metal cathode, including many lines that are not resonance absorption lines, but these other lines do not interfere in the analysis.

Each hollow cathode emits the spectrum of metal used in the cathode. For this reason, a different HCL must be used for each different element to be determined. This is an inconvenience in practice and is the primary factor that makes AAS a technique for determining only one element at a time. The handicap is more than offset, however, by the advantage of the narrowness of the spectral lines and the specificity that results from these narrow lines.

It is possible to construct a cathode from more than one element. These are called "multielement" HCLs and can be used for the determination of all the elements in the cathode. This can be done sequentially but without having to change the lamp, which saves some time. In general, multielement cathodes do not perform as well for all of the elements in the cathode as do single HCLs for each element. The multielement cathode may have reduced intensity for one or more of the elements. Each of the elements present will emit its atomic emission spectrum, resulting in a more complex emission than from a single-element lamp. This may require that a less-sensitive absorption line be chosen to avoid a spectral interference. The obvious reason to use a multielement lamp is in the hope that more than one element can be measured simultaneously, making AAS a multielement technique. In fact, there are a few commercial simultaneous multielement AAS systems available for measuring up to eight elements or so. Most use a bank of single-element lamps all focused on the atomizer rather than multielement cathodes. The disadvantage with this approach is that only one set of conditions in the atomizer can be used, and this set of atomization conditions may not be optimum for each element.

HCLs have a limited lifetime, usually due to loss of filler gas atoms through several processes. Adsorption of filler gas atoms onto the lamp surfaces causes decreased sputtering and decreased intensity of emission; eventually, the number of filler gas atoms becomes so low that the lamp will not "light." The sputtering process causes atoms to be removed from the cathode; these metal atoms often condense elsewhere inside the lamp, trapping filler gas atoms in the process and decreasing lamp life. This is particularly a problem for HCLs of volatile metals like Cd and As. HCLs operated at currents higher than recommended will have shorter lifetimes than those operated according to the manufacturer's recommendation. Operating at higher currents results in more intensity in the lamp output but also may increase noise, which impacts both precision and limit of detection (LOD). Since we are measuring the *ratio* of light absorbed to incident light, there is little to be gained by increasing the lamp current.

Single-element HCLs cost between $400 and $700 per lamp, while multielement lamps cost between $500 and $700 each for most elements. Particularly rare elements like Rh, Ir, and Os may cost $1000–$2000 per lamp.

6.2.1.2 Electrodeless Discharge Lamp

It is difficult to make stable hollow cathodes from certain elements, particularly those that are volatile, such as arsenic, germanium, or selenium. The HCLs of these elements have short lifetimes and low intensities. An alternative light source has been developed in the EDL. A commercial EDL design is shown in Figure 6.7. A small amount of metal or a salt of the element whose spectrum is desired is sealed into a quartz bulb with a low pressure of Ar gas. The bulb is shown centered inside the coils in Figure 6.7. The coils are part of a self-contained radio-frequency (RF) generator. When power is applied to the coils, the RF field generated will "couple" with the metal or salt in the quartz bulb. The coupled energy will vaporize and excite the metal atoms in the bulb. The characteristic emission spectrum of the metal will be produced.

EDLs are very intense, stable emission sources. They provide better detection limits (DLs) than HCLs for those elements that are intensity limited either because they are volatile or because their primary resonance lines are in the low-UV region. Some elements like As, Se, and Cd suffer from both problems. For these types of elements, the use of an EDL can result in a LOD that is two to three times lower than that obtained with an HCL. EDLs are available for many elements, including antimony, arsenic, bismuth, cadmium, germanium, lead, mercury, phosphorus, selenium, thallium, tin, and zinc. Older EDLs required a separate power supply to operate the lamp. Modern systems are self-contained. EDLs cost more than the comparable HCLs.

Most modern AAS systems have "coded" lamps that are recognized by the spectrometer software, which can then set up the analysis parameters automatically. The instrument "knows" that a copper lamp or a calcium lamp has been inserted and can apply the default analytical conditions without analyst intervention.

Having explained why narrow line sources are needed for AAS, in Section 6.2.6, a new high-resolution AAS using a continuum source will be introduced.

6.2.2 Atomizers

The atomizer is the sample cell of the AAS system. The atomizer must produce the ground-state free gas-phase atoms necessary for the AAS process to occur. The analyte atoms are generally

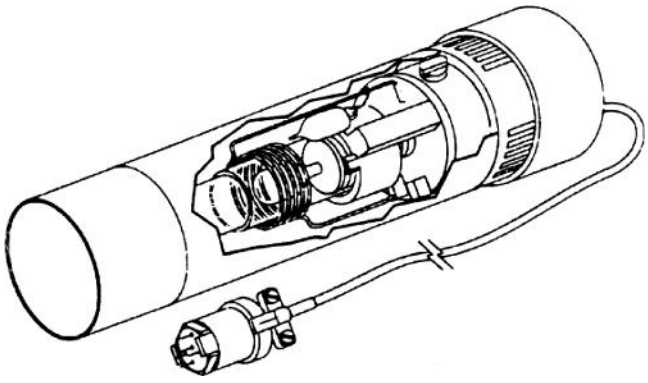


Figure 6.7 EDL. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

present in the sample as salts, molecular compounds, or complexes. The atomizer must convert these species to the reduced, free gas-phase atomic state. The atomizer generally does this via thermal energy and some chemistry. The two most common atomizers are flame atomizers and electrothermal (furnace) atomizers.

6.2.2.1 Flame Atomizers

To create a flame, we need to mix an oxidant gas and a fuel gas and light the mixture. In modern commercial FAAS, two types of flames are used. The first is the air–acetylene flame, where air is the oxidant and acetylene is the fuel. The second type of flame is the nitrous oxide–acetylene flame, where nitrous oxide is the oxidant and acetylene is again the fuel. The fuel and oxidant gases are mixed in a burner system, called a premix burner. An exploded view of one type of commercial flame atomic absorption burner is shown in Figure 6.8a. In this design, the fuel gas is introduced into the mixing chamber through one inlet (not shown), while the oxidant gas is introduced through the sidearm on the *nebulizer*. The premix burner design generates laminar gas flow and this results in a very steady flame. The steady flame generates less noise due to "flame flicker"; this improves precision. Mixing the gases in the mixing chamber eliminates the safety hazard of having a combustible gas mixture piped through the laboratory. The flame burns just above the burner head, along the slot shown in the figure.

The sample is introduced into the burner in the form of a solution. The solution is aspirated into the nebulizer, which is basically a capillary tube. The nebulizer sprays the solution into the mixing chamber in the form of a fine aerosol. Three nebulizer designs are shown schematically in Figure 6.8b. The term "to nebulize" means to convert to a fine mist, like a cloud. The solution exits the capillary tube at high velocity and breaks into tiny droplets as a result of the pressure drop created. Kinetic energy transfer from the nebulizer gas overcomes the surface tension and cohesive forces holding the liquid together. The fuel and oxidant gases carry the sample aerosol to the base of the flame. In the flame, the sample aerosol is desolvated, vaporized, and atomized to form free gas-phase atoms of the analyte. The process will be discussed in detail later.

When the sample solution passes through the nebulizer, an aerosol is formed, but the droplets are of different sizes. As a droplet enters the flame, the solvent (water or organic solvent) must be vaporized, the residue must vaporize, and the sample molecules must dissociate into atoms. The larger the droplet, the more inefficient this process is. The two devices shown in Figure 6.8a are used to overcome this problem. The impact bead is made of glass, quartz, Teflon, or ceramic and is placed directly in front of the nebulizer spray inside the mixing chamber. The impact bead improves nebulization efficiency by breaking larger droplets into smaller ones through collision of the spray with the bead. The flow spoiler is a piece of polymer or other corrosion-resistant material machined into three or more vanes. The flow spoiler is placed in the mixing chamber, about midway between the end cap and the burner. It physically removes larger droplets from the aerosol through collision, while smaller droplets pass through the openings between the vanes. The larger droplets drain from the mixing chamber through a drain opening (not shown). The aim of this system is to produce an aerosol with droplets about 4 μm in diameter. The two devices may be used alone or in combination. The drain opening is connected to a liquid waste container with a length of polymer tubing. It is extremely important that there be a trap between the drain opening and the waste container to prevent the free flow of flame gases out of the burner assembly. The presence of the trap helps to eliminate "flashback," discussed subsequently. The trap is often a simple water-filled loop in the drain tubing itself.

The nebulizer described is a self-aspirating, pneumatic nebulizer and is the one shown schematically on the lower left of Figure 6.8b. The nebulizer capillary is usually made of stainless steel, but other materials such as Pt, Ta, and polymers may be used for corrosive solvents when contamination from the elements in steel must be avoided. Other nebulizer designs have been developed for specific applications but are not commonly used in AAS. These other nebulizers are often used in atomic emission spectrometry and will be described in Chapter 7.

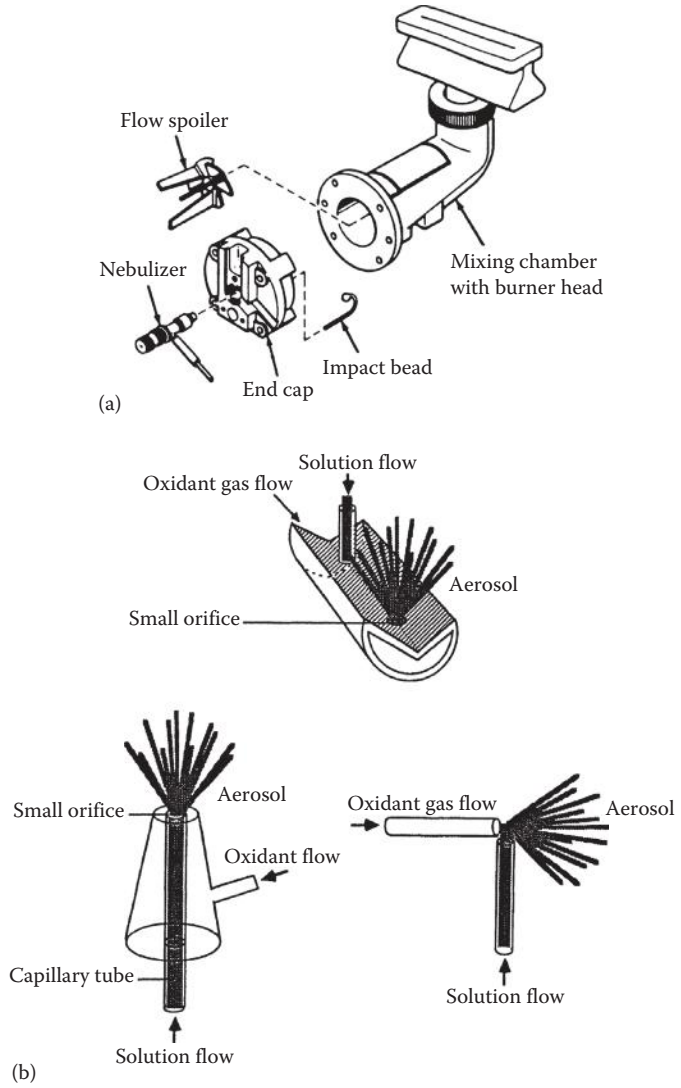


Figure 6.8 (a) Premix burner system. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]** (b) Schematic nebulizer designs. (Top), modified Babington type; (left), concentric (the most common in FAAS); (right) cross-flow type. (From Parsons, M.L., Atomic absorption and flame emission, in Ewing, G.A., ed., *Analytical Instrumentation Handbook*, 2nd edn., Marcel Dekker, Inc., New York, 1997. Used with permission.)

The burner head is constructed either of stainless steel or titanium. Different sizes and geometries of burner heads are used for various flames. The single-slot burner head shown in Figure 6.8a with a 10 cm long slot is used for air–acetylene flames. The 10 cm long flame is the sample path length for the AA spectrometer in this case. A smaller 5 cm long single-slot burner head with a narrower slot is used for nitrous oxide–acetylene flames. Some burner head designs use Ti and multiple fins for both flames. Usually, the slot is oriented parallel to the light beam from the radiation source, so the path length is as long as possible to achieve the highest sensitivity (remember Beer's law), as shown in the AAS layout in Figure 6.9. The modern burner head design coupled with the use of a liquid-filled trap between the mixing chamber drain and the waste container prevents the possibility of a flashback. The gas mixture is ignited above the burner head and the flame, a highly energetic chemical reaction

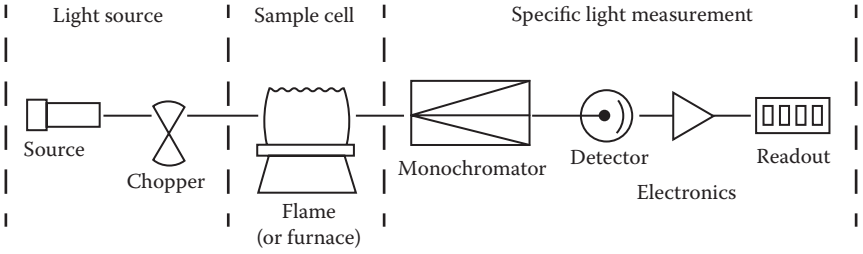


Figure 6.9 Basic AAS system. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission. (www.perkinelmer.com).]**

between the fuel and oxidant, propagates rapidly. The flame is supposed to propagate up from the burner head. It will do so if the linear gas flow rate through the burner slot is higher than the **burning velocity** of the flame. Burning velocity is a characteristic of the flame type; both nitrous oxide–acetylene and air–acetylene flames have low burning velocities. If the premixed gas flow rate is less than the burning velocity, a flashback can occur when the gas mixture is ignited. Flashback is the very undesirable and extremely hazardous propagation of the flame below the burner head slot and back into the mixing chamber. A flashback results in an explosion in the mixing chamber; it can destroy the burner assembly, create flying debris, rupture the fuel and oxidant lines thereby releasing combustible gases into the laboratory, and cause injury to the analyst or other people in the laboratory. Early burner designs and high-burning-velocity flames such as those using pure oxygen as oxidant were often prone to flashback. It is imperative that AAS systems be operated according to the manufacturer's directions, that only the correct gases, properly regulated, and the correct burner head be used, and that the trap and all safety interlocks be in place and functioning.

One reason for the long path length used in FAAS (compared with the typical 1 cm path length in UV/VIS or infrared (IR) absorption spectrometry) is that the premix burner and nebulizer system used is very inefficient and wasteful of sample. Sample solution is aspirated into the nebulizer at ~5 mL/min but only a small amount (<5%) of that solution reaches the burner. The path length has to be as long as possible to compensate for the loss of sample in the mixing chamber. FAAS is very popular because it is fast, has high element selectivity, and the instruments are easy to operate, but the inefficiency of the sample introduction system combined with noise inherent in the system restricts DLs in flames to the ppm range for most elements.

6.2.2.2 Electrothermal Atomizers

In order to measure ppb concentrations of metals, a different type of atomizer is needed. A furnace or electrothermal atomizer (ETA) was developed less than 10 years after the technique of AAS was developed. In 1961, B.V. L'vov built a heated carbon tube atomizer, illustrated in Figure 6.10. The system used a carbon tube heated by electrical resistance. The tube was lined with Ta foil and purged with argon gas. After the tube or furnace reached an elevated temperature, the sample, on a carbon electrode, was inserted at the bottom, as shown in the figure. Atomization took place and the analyte atoms absorbed the light beam passing through the carbon tube. His system was orders of magnitude more sensitive than flame atomizers but was difficult to control. Other workers in the field, particularly West, Massman, and Robinson, refined carbon rod and furnace atomizers. Most commercial instruments use some version of a carbon tube atomizer for electrothermal atomization. The most common atomizer of this type uses a tube of graphite coated with pyrolytic graphite and heated by electrical resistance; therefore, this commercial ETA is called a **graphite furnace atomizer**. The acronym GFAAS, which stands for graphite furnace AAS, tells the reader that the atomizer used is a graphite furnace, as opposed to a flame.

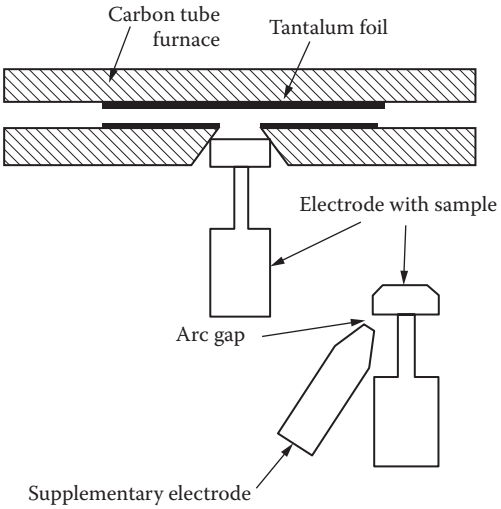


Figure 6.10 High-temperature furnace atomizer designed and used by L'vov.

A commercial graphite furnace atomizer is illustrated in Figure 6.11. This atomizer consists of a graphite tube, approximately 6 mm in diameter and 25–30 mm long, the electrical contacts required to heat the tube, a system for water-cooling the electrical contacts at each end of the tube, and inert purge gas controls to remove air from the furnace. An inert gas is used to prevent the graphite from being oxidized by air during the heating process. Quartz windows at each end of the furnace assembly permit the light from the HCL or EDL to pass through the furnace and out to the spectrometer. A small amount of sample solution, between 5 and 50 μL, is dispensed into the graphite

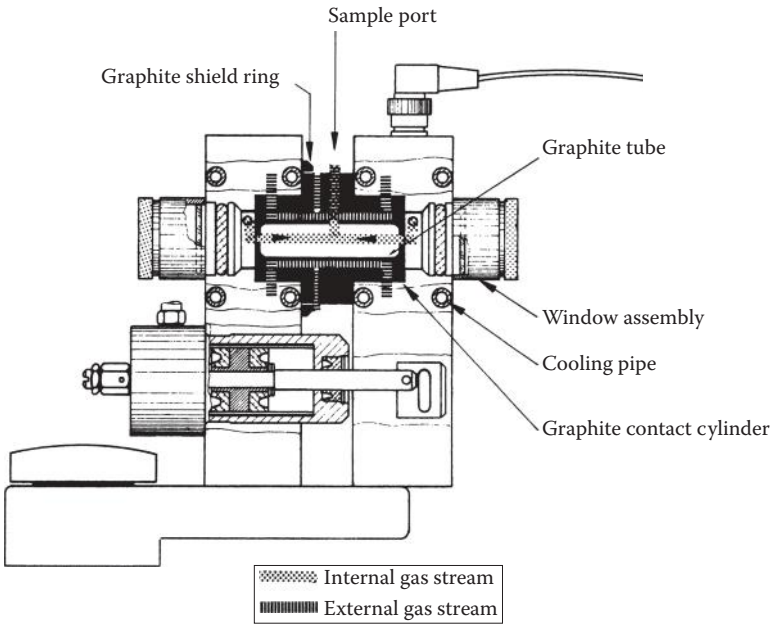


Figure 6.11 Graphite furnace atomizer. This is a longitudinally heated furnace design. The graphite tube is shown in greater detail in Figure 6.20. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

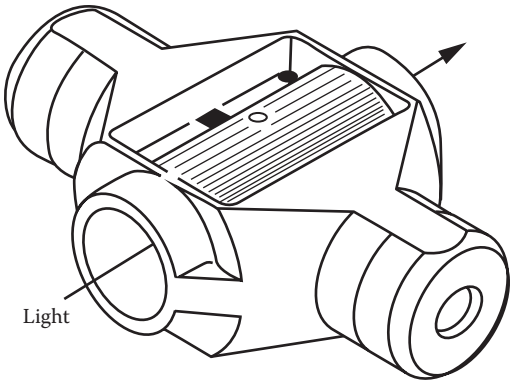


Figure 6.12 A graphite tube for a transversely heated furnace. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

tube through a small hole in the top of the tube. The furnace is heated in a series of programmed temperature steps to evaporate the solvent, decompose (ash, char) the sample residue, and finally to atomize the sample into the light path. Details of the graphite furnace atomization process and temperature program will be discussed later. The diagram in Figure 6.11 shows a longitudinally heated graphite furnace. The electrical contacts are at each end of the tube and they must be water-cooled. This longitudinal heating results in a temperature gradient in the heated furnace—the ends are cooler than the center. This may result in recondensation of vaporized species at the ends of the tube. This can be a problem for the next sample analysis if material from the previous sample is still in the furnace. The problem is called "carryover" or a "memory effect" and can result in poor accuracy and precision. To overcome this problem, new graphite furnaces that are heated transversely have been developed. A transverse graphite tube is shown in Figure 6.12. The electrical contacts are transverse to the light path, and the tube is heated across the circumference. This results in even heating over the length of the furnace and reduces the carryover problem significantly.

Modern graphite furnace atomizers have a separate power supply and programmer that control the electrical power, the temperature program, the gas flow, and some spectrometer functions. For example, the spectrometer can be programmed to "read," that is, collect absorbance data, only when the furnace reaches the atomization temperature. This saves data storage space and data processing time.

Researchers have developed other types of ETAs over the years, including filaments, rods, and ribbons of carbon, tantalum, tungsten, and other materials, but the only commercial ETA available is the graphite furnace atomizer.

6.2.2.3 Other Atomizers

Two additional commercially available atomizers (really analysis techniques with unique atomizers) must be discussed, because they are extensively used in environmental and clinical analysis. They are the **cold vapor AAS (CVAAS) technique** for determination of the element mercury, Hg, and the **hydride generation AAS (HGAAS) technique** for several elements that form volatile hydrides, including As, Se, and Sb. These elements are toxic; federal and state laws regulate their concentrations in drinking water, wastewater, and air, so their measurement at ppb concentrations is very important. Because the CVAAS and HGAAS "atomizers" are analysis techniques, they will be discussed under applications of AAS.

An atomizer based on glow discharge (GD) techniques is commercially available for the analysis of solid metal samples by AAS. It will be discussed in the applications sections under solid sample analysis.

6.2.3 Spectrometer Optics

6.2.3.1 Monochromator

A monochromator is required to separate the absorption line of interest from other spectral lines emitted from the HCL and from other elements in the atomizer that are also emitting their spectra. Because the radiation source produces such narrow lines, spectral interference is not common. Therefore the monochromator does not need high resolution.

A typical monochromator is shown in Figure 6.13. The most common dispersion element used in AAS is a diffraction grating. The grating disperses different wavelengths of light at different angles, as discussed in Chapter 2. The grating can be rotated to select the wavelength that will pass through the exit slit to the detector. All other wavelengths are blocked from reaching the detector. The *angle of dispersion* at the grating is a function of the density of lines ruled on the grating. The more lines/mm on the grating, the higher is the dispersion. Higher dispersion means greater separation between adjacent lines. A high-dispersion grating permits the use of wider entrance and exit slits on the monochromator to achieve the same resolution. Wider slits allow more light to pass through the system to the detector. Large high-quality gratings with high dispersion are expensive, but they offer better energy throughput than cheaper low-dispersion gratings. In addition to the number of lines ruled on the grating, the blaze angle affects the intensity of diffracted wavelengths. Gratings can be blazed for any wavelength; the farther away a given wavelength is from the wavelength for which the grating is blazed, the more light intensity will be lost in diffraction. The analytically useful wavelength range for commercial AAS is from 190 to 850 nm. If a grating is blazed for the middle of this range, there will be loss in intensity at both extremes. That is particularly bad for elements such as Se, As, P, Cd, and Zn, with resonance lines at the low-UV end, and for the alkali metals, with resonance lines at the high end of the visible region. To overcome this problem, the monochromator can be equipped with two gratings, one blazed for the UV and one for the visible. Modern spectrometers automatically control the movement and alignment of the grating or gratings, so that the correct one is used for the wavelength being measured.

Most commercial AAS systems have the monochromator, optics, and detector designed for the measurement of one wavelength at a time; they are single-element instruments. There are a few systems available that do perform multielement determinations simultaneously, using an echelle spectrometer (discussed in Chapter 2) and a bank of HCLs all focused on the atomizer. The limitation to this approach is not the sources or the spectrometer or the detector, but the atomizer. The atomizer can only be at one set of conditions, and those conditions will not necessarily be optimum for all of the elements being measured. There will be a trade-off in DLs for some of the elements.

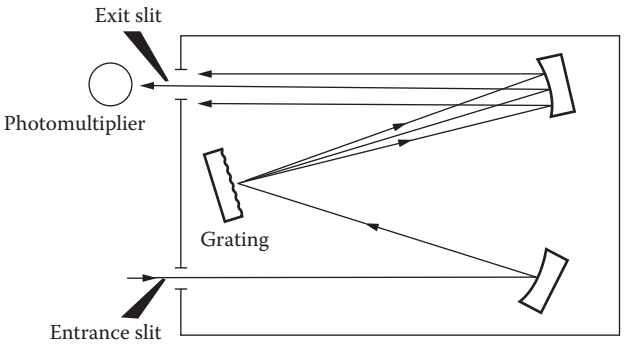
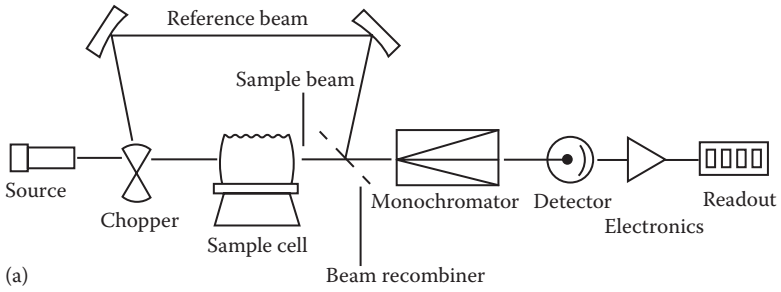


Figure 6.13 Typical grating monochromator layout. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

6.2.3.2 Optics and Spectrometer Configuration

The spectrometer system for AAS can be configured as a single-beam system, as shown in Figure 6.8; as a double-beam system, shown in Figure 6.14; or as a pseudo-double-beam system, which will not be discussed. (See the reference by Beaty and Kerber for a description of this system.) Note that in AAS, the sample cell is placed in front of the monochromator, unlike UV/VIS spectrometers for molecular absorption or spectrophotometry, where the sample is placed after the monochromator.

A single-beam system is cheaper and less expensive than a double-beam system, but cannot compensate for instrumental variations during analysis. In a double-beam system, part of the light from the radiation source is diverted around the sample cell (flame or furnace atomizer) to create a *reference beam*, as shown in Figure 6.14. The reference beam monitors the intensity of the radiation source and electronic variations (noise, drift) in the source. The signal monitored by the detector is the ratio of the sample and reference beams. This makes it possible to correct for any variations that affect both beams, such as short-term changes in lamp intensity due to voltage



(b)

Figure 6.14 (a) Schematic double-beam AAS configuration. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]** (b) The optical path of the Shimadzu Scientific Instruments AA-7000 superimposed over the actual instrument body. On the right, from front to back is the HCL, the beam splitter (slanted rectangle) and the deuterium lamp. In the center, from front to back, we have the burner head with the sample beam passing over it, the reference beam, and the monochromator at the center top. On the left is the mirrored chopper and in the back, the detector. (Courtesy of Shimadzu Scientific Instruments, Inc. www.shimadzu.com.)

fluctuations in the power lines feeding into the instrument. Compensation for these variations is performed automatically in modern double-beam spectrometers. Even though part of the source radiation is directed to the reference beam, modern double-beam instruments have the same signal-to-noise ratio as single-beam instruments with the advantage of more accurate and precise absorbance measurements.

Lenses or mirrors are used to gather and focus the radiation at different parts of the optical system. This avoids losing too much signal as a result of the light beams being nonparallel and focuses the light beam along the flame so that as much light as possible passes through the sample. Any light that does not pass through the sample cannot be absorbed and results in a loss in sensitivity. Quartz lenses have been used for this purpose, but most instruments today use front-surfaced concave mirrors, which reflect and focus light from their faces and do not lose much radiation in the process. The monochromator has two slits, an entrance slit and an exit slit. The entrance slit is used to prevent stray radiation from entering the monochromator. Light passes from the entrance slit to the grating. The entrance slit should be as wide as possible to permit as much light as possible to fall on the grating but must be narrow enough to isolate the wavelength of interest. After dispersion by the grating, the radiation is directed toward the exit slit. At this point, the desired absorption line is permitted to pass, but the other lines emitted from the source and atomizer are blocked from reaching the detector by the monochromator exit slit. The system of slits and grating enables the analyst to choose the wavelength of radiation that reaches the detector. There is rapid loss in sensitivity as the mechanical slit width, and hence, the spectral bandpass (spectral slit width) is increased.

Commercial AAS instrumentation may be purchased with fixed slits or with variable slits. Fixed mechanical slit widths are available so that the resolution and sensitivity are acceptable for most analytical purposes at lower cost than instruments with variable slit widths. Variable slit widths are desirable for maximum flexibility, especially if samples are varied and complex. Instruments that have both flame and graphite furnace atomizers often have separate sets of slits of different heights for each atomizer. The furnace slits are usually shorter to avoid having emission from the small diameter incandescent furnace reach the detector. In general, the analyst should use the widest slit widths that minimize the stray light that reaches the detector while spectrally isolating a single resonance line for the analyte from the HCL.

6.2.4 Detectors

The common detector for AAS is the photomultiplier tube (PMT). The construction and operation of a PMT has been described in Chapter 5. While PMTs are the most common detectors, solid-state single and multichannel detectors such as photodiode arrays (PDAs) (discussed in Chapter 5) and charge-coupled devices (CCDs) (discussed in Chapters 5 and 7) are increasingly being used in AAS spectrometers. Many small systems, particularly those dedicated to one element such as a dedicated CVAAS mercury analyzer, use solid-state detectors instead of PMTs. Multielement simultaneous AAS systems also use multichannel solid-state detectors to measure more than one wavelength at a time.

6.2.5 Modulation

Many metals, when atomized in a flame or furnace, emit strongly at the same wavelength at which they absorb. The emission signal can cause a serious error when the true absorption is to be measured. This problem is illustrated in Figure 6.15. Emission by the metal in the atomizer is at precisely the same wavelength as the absorption wavelength of the metal because the same electronic transition is involved. Better resolution cannot improve the situation. Furthermore,

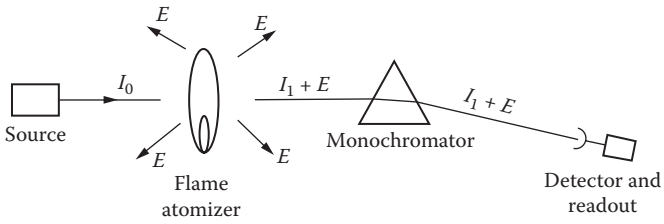


Figure 6.15 Emission by excited atoms in the atomizer can occur at the resonance wavelength, resulting in a direct error in the AAS measurement.

since we are trying to measure I_1, the interference by the emission from the flame will result in a direct error. Unless a correction is made, the signal recorded will be $(I_1 + E)$, where E is the emission intensity.

This problem is overcome most simply by the modulation of the radiation source. **Modulation** means that the source radiation is switched on and off very rapidly. This can be done by using a rotating mechanical *chopper* placed directly in front of the source. A chopper is shown in Figures 6.8 and 6.14. The mechanical chopper is a circle of metal sheet with opposite quadrants cut out. Every quarter turn of the chopper alternately blocks and passes the source radiation. Another way to modulate the source is by pulsing the power to the lamp at a given frequency. When modulated, the signal from the source is now an alternating current (AC) signal. Therefore, the signal for both I_0 and I_1 is AC but the sample emission E is not modulated. It is a direct current (DC) signal. The detector electronics can be "locked in" to the frequency of the AC signal. The modulated absorption signal will be measured and the DC emission signal will be ignored. This eliminates emission from the atomizer as a source of error. Modulation of the source is required for accurate results in AAS. All modern commercial instruments have some means of source modulation in the instrument.

6.2.6 Commercial AAS Systems

AAS is considered a mature analysis technique with decades-long production of instruments by a large number of companies around the world. The biggest change in most modern AA systems is in the size of the instruments and the capabilities of the software. Instruments today are much smaller than older designs. Some systems have automated switching between flame and furnace atomizers, eliminating what had been a labor intensive and potentially error-prone job; some have the ability to run both flame and furnace at the same time. Many have multiple lamp turrets, with lamps already warmed up to avoid waiting when switching from one element to the next. They incorporate features such as video cameras to observe what is happening in the furnace to enable better optimization and method development. Intelligent or smart software is found on most modern systems that will recognize the lamp installed, set the optimum instrument parameters or user-specified method parameters, and will even validate the performance of an instrument, all without any intervention by the analyst.

Complete systems are available from a large number of instrument companies. These include but are not limited to Agilent Technologies, Aurora Biomed, GBC, PerkinElmer, Shimadzu Scientific Instruments, which makes the only instrument with a vibration sensor to shut down the flame in case of earthquakes, and Thermo Fisher Scientific. There are numerous smaller companies, like Buck Scientific and companies in China, India, and elsewhere who only distribute locally. A completely new AAS concept is now available from Analytik Jena AG, as described in the next section.

CV- and hydride-AAS systems for mercury, As, Se, and other hydride-forming elements, discussed in Sections 6.5.3.4 and 6.5.3.5, are available from the major AAS manufacturers and also from companies making dedicated analyzers, including Teledyne Leeman Labs, Cetac Technologies, and Milestone, Inc.

6.2.6.1 High-Resolution Continuum Source AAS

AAS, as developed in the 1950s by Alan Walsh, required a narrow line source of light and modulation of that source. Recently, advances in source and detector technology, combined with a high-resolution double monochromator, have enabled the use of a continuum source for AAS (Welz and Heitmann; Welz et al.). The instruments, from Analytik Jena AG (www.analytik-jena.de), are the contrAA® high-resolution continuum source AAS (HR-CS AAS) systems. The source is a small xenon arc lamp, which provides a continuous source of radiation with high intensity, especially in the UV range. The systems use a high-resolution double monochromator consisting of a prism pre-monochromator followed by an echelle grating monochromator. The detector is a UV-sensitive CCD linear array detector. No modulation is required. Each pixel of the CCD functions as an independent detector, with all pixel information shifted simultaneously into a readout register. This configuration means that the analytical line does not need to be separated from the adjacent emission of the continuum source by an exit slit. There is no exit slit since the CCD array itself represents a large number of high-resolution detectors. Each individual detector accumulates a spectral range of about 2 pm; the entire array comprises a spectral range of about 0.4 nm.

Only 1–3 pixels are used for registering the analyte absorption, so all the remaining pixels are available for correction purposes. Both fluctuations in lamp emission and transmission of the atomizer are accounted for, making the system a simultaneous double-beam system of high precision with simultaneous background correction.

Since the intensity of the source does not affect sensitivity, but does influence the noise, the high-intensity source increases the DLs of this system by a factor of 2–5 over conventional AAS. The linear dynamic range of the system is 5–6 orders of magnitude, much broader than conventional AAS and similar to inductively coupled plasma-optical emission (ICP-OES) (discussed in Chapter 7).

The high-intensity continuum source offers a number of advantages over narrow line sources. Secondary lines (nonresonance lines) can be used in order to reduce sensitivity, thereby avoiding dilutions. All spectral lines are available, including lines for which no HCL or EDL sources are available, such as fluorine and chlorine. In addition, molecular absorptions, such as those of diatomic fragments like CS or PO, can be used to measure sulfur and phosphorus (Huang et al.)

The CCD detector permits not only simultaneous background correction but complete correction of spectral interferences such as structured background from molecular species such as OH and NO. The resolution permits collection of the spectra from these species and removal of them from the absorbance of the sample. Direct-line overlap can also be corrected, if the matrix has an additional absorption line within the registered spectral range of the detector. Direct-line overlap is rare and usually is due to line-rich matrices such as Fe, so the system can reliably correct for the direct overlap of Fe on Zn, for example.

We discussed earlier the desire to speed up AAS by having simultaneous multielement measurement and the compromises that current HCL/EDL systems make. The HR-CS AAS technique is not a simultaneous multielement system, but since it uses a single source, the “change” of elements, that is, the reading of a different line, is extremely fast, especially for FAAS. The system therefore functions as a fast sequential FAAS with the advantage that every element can be measured under automatically set optimum conditions, rather than the compromise conditions a bank of HCLs or a multielement HCL uses. The transient signals from a graphite furnace are still problematic due to the large amount of data collected with the concomitant increase in detector readout times.

6.3 ATOMIZATION PROCESS

6.3.1 Flame Atomization

Most samples we want to examine by AAS are solid or liquid materials. Examples of solid samples are soil, rock, biological tissues, food, metal alloys, ceramics, glasses, and polymers. Examples of liquid samples are water, wastewater, urine, blood, beverages, oil, petroleum products, and organic solvents. For FAAS and most GFAAS determinations, the sample must be in the form of a solution. This requires that most samples be prepared by acid digestion, fusion, ashing, or other forms of sample preparation (Chapter 1) to give us an aqueous, acidic solution or a solution in a combustible organic solvent. We will look at aqueous acidic solutions, since they are the most common form of sample for FAAS. Metals are present in aqueous acidic solutions as dissolved ions; examples include Cu^{2+}, Fe^{3+}, Na^{+}, and Hg^{2+}.

To measure an atomic absorption signal, the analyte must be converted from dissolved ions in aqueous solution to reduced gas-phase free atoms. The overall process is outlined in Figure 6.16. As described earlier, the sample solution, containing the analyte as dissolved ions, is aspirated through the nebulizer. The solution is converted into a fine mist or aerosol, with the analyte still dissolved as ions. When the aerosol droplets enter the flame, the solvent (water, in this case) is evaporated. We say that the sample is "desolvated." The sample is now in the form of tiny solid particles. The heat of the flame can melt (liquefy) the particles and then vaporize the particles. Finally, the heat from the flame (and the combustion chemistry in the flame) must break the bonds between the analyte metal and its anion, and produce free M^0 atoms. This entire process must occur very rapidly, before the analyte is carried out of the observation zone of the flame. After free atoms are formed, several things can happen. The free atoms can absorb the incident radiation; this is the process we want. The free atoms can be rapidly oxidized in the hostile chemical environment of the hot flame, making them unable to absorb the resonance lines from the lamp. They can be excited (thermally or by collision) or ionized, making them unable to absorb the resonance lines from the lamp. The analyst must control the flame conditions, flow rates, and chemistry to maximize production of free atoms and minimize oxide formation, ionization, and other unwanted reactions. While complete

	$M^+ + A^-$	(Solution)
1. Nebulization	↓	
	$M^+ + A^-$	(Aerosol)
2. Desolvation	↓	
	MA	(Solid)
3. Liquefaction	↓	
	MA	(Liquid)
4. Vaporization	↓	
	MA	(Gas)
5. Atomization	↓	
	$M^0 + A^0$	(Gas)
6. Excitation	↓	
	M^*	(Gas)
7. Ionization	↓	
	$M^+ + e^-$	(Gas)

Figure 6.16 The processes occurring in a flame atomizer. M^+ is a metal cation; A^- is the associated anion. M^0 and A^0 are the ground-state free atoms of the respective elements. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

Table 6.1 Temperatures Obtained in Various Premixed Flames (°C)

	Oxidant	
Fuel	**Air**	**N_2O**
H_2	2000–2100	
Acetylene	2100–2400	2600–3000
Propane (natural gas)	1700–1900	

atomization is optimum and will yield the highest signal, it is much more important that the atomization process be consistent. If the atomization is not complete, any variation in the fractional atomization will result in errors in analysis.

The flame is responsible for production of free atoms. Flame temperature and the fuel/oxidant ratio are very important in the production of free atoms from compounds. Many flame fuels and oxidants have been studied over the years, and temperature ranges for some flames are presented in Table 6.1. In modern commercial instruments, only air–acetylene and nitrous oxide–acetylene flames are used.

Lower temperature flames are subject to interferences from incomplete atomization of the analyte. The air–acetylene flame is useful for many elements, but the hotter and more chemically reducing nitrous oxide–acetylene flame is needed for refractory elements and elements that are easily oxidized, such as Al and Si. Appendix 6.A lists the usual flame chosen for each element. This appendix also gives the fuel/oxidant ratio conditions used for maximum sensitivity for each element. Flames are classified as oxidizing (excess oxidant) or reducing (excess fuel). Air–acetylene flames can be used in either an oxidizing mode or a reducing mode; nitrous oxide–acetylene flames are usually run in a reducing mode. In general, excess oxidant helps to destroy organic material in samples. However, excess oxidant can react with elements that exist as stable oxides to form oxide molecules. These oxide molecules cannot undergo atomic absorption. Elements that form stable oxides, such as aluminum, boron, molybdenum, and chromium, are therefore determined using reducing flame conditions, usually with the high-temperature nitrous oxide–acetylene flame, to prevent the formation of oxide molecules. The chemistry that occurs depends on what part of the flame is observed; the base of the flame differs from the inner core of the flame and both differ from the outer mantle of the flame.

If we measure the absorbance signal of an atom with respect to the height of the signal above the burner, we arrive at a relationship called a flame profile. The burner assembly can be moved up and down with respect to the light source, usually by turning a knob manually or through the software that controls the burner position. The beam of light from the source is fixed in position. The flame profile is determined by aspirating a solution of an element into a flame with the burner height set so that the light beam from the lamp is at the base of the flame, just above the burner head. Then the burner head is slowly lowered, so that the light beam passes through higher and higher regions of the flame. The absorbance is plotted versus the height above the burner. Flame profiles for Cr, Mg, and Ag in an oxidizing air–acetylene flame are shown in Figure 6.17. Let us look at each of these profiles. The signal for magnesium, Mg, starts off low at the base of the flame, because free atoms have not yet formed from the sample. The absorbance increases with increasing height in the flame (above the burner head), to a maximum. Moving farther up in the flame causes the absorbance to decrease. This curve is brought about by the complicated reactions that take place in a flame, including atomization, oxidation, and ionization. All of these processes compete in the flame. The maximum sensitivity for Mg will be obtained when the light beam is at the position of maximum absorbance, above the burner head, but not very high up in the flame. The decrease in absorbance as we go higher up in the flame is due to the formation of oxide molecules. Many elements have flame profiles similar to Mg, but not all, as can be seen in Figure 6.17. Chromium forms

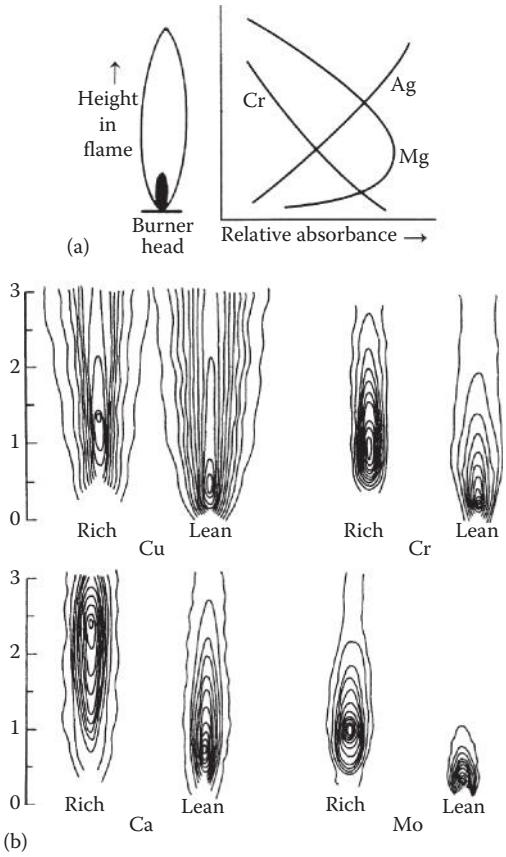


Figure 6.17 (a) Flame profiles for Cr, Mg, and Ag demonstrating differences in free atom formation as a function of height above the burner in an oxidizing air–acetylene flame. (b) 2D atom distributions in a 10 cm air–acetylene flame. Fuel-rich (reducing) and fuel-lean (oxidizing) results are shown. The scale on the left is the height above the burner head (in cm). Maximum absorbance is shown as the smallest circle in the plot with the contour lines separated by 0.1 in absorbance. For Cr, the fuel-lean plot shows maximum absorbance close to the burner, in accordance with the results shown in (a). The fuel-rich flame shows that the maximum absorbance for Cr moves up above the burner head by approximately 1 cm. Molybdenum is even more dramatically affected by the fuel/oxidant ratio. (The diagrams in (b) are adapted and reprinted with permission from Rann, C.S. and Hambly, A.N., *Anal. Chem*., 37, 879. Copyright 1965 American Chemical Society.)

very stable oxides that are hard to atomize. As can be seen from its profile, the absorbance by Cr atoms is actually highest at the base of the flame. Cr atoms combine with oxygen in air almost as soon as they are formed, and the absorbance decreases rapidly with height above the burner head (i.e., with increasing exposure to air). Chromium is an element that would be better determined in a fuel-rich (reducing) flame to minimize the formation of chromium oxide. Silver, on the other hand, starts with low absorbance at the base of the flame just like Mg. Then, the absorbance increases with increasing height in the flame, indicating that silver atoms are stable once formed; there is no decrease in absorbance due to oxide formation or ionization.

In practice, the optimum position for taking absorbance measurements is determined in exactly this way. A solution of the element to be determined is aspirated, the absorbance is monitored continually, and the burner head is moved up and down (and forward and back) with respect to the light beam until the position of maximum absorbance is located. Older instruments have

a ruler mounted along the burner compartment to indicate where the burner head is with respect to the light beam to assist in adjusting the height of the burner. Modern systems can control burner adjustment through the software. Figure 6.17b shows the 2D distribution of atoms in an air–acetylene flame for several elements. These are side views of the flames, as would be seen by the detector. The contour lines differ by 0.1 in absorbance, with the maximum absorbance at the center of the profile. Fuel-rich (reducing) and fuel-lean (oxidizing) conditions are displayed. As we discussed, Cr shows the highest absorbance in a fuel-lean flame just above the burner head; in a fuel-rich flame, the maximum absorption position is moved up in the flame. Molybdenum shows the same response, but even more strongly. Calcium can be determined in either a fuel-rich or fuel-lean flame, but the position of maximum absorbance is very different for each flame. In the fuel-rich flame, the optimum position is more than 2 cm above the burner, while in an oxidizing flame, the position is between 0.5 and 1 cm above the burner. The need to optimize the horizontal position of the burner with respect to the light source can be seen from the width of the intervals of the atom distributions.

The flame profile results from the complex physical and chemical processes occurring in the flame. The sample, introduced into the base of the flame, goes through the process of evaporation, forming solid particles, which are then decomposed by the hot flame to liberate free atoms. The latter can then oxidize, forming metal oxides in the upper and outer parts of the flame. The formation of free atoms depends on the flame temperature and on the chemical form of the sample. Chemical species with small dissociation energies at high temperatures will dissociate to form free atoms. For a given flame temperature, free atom formation depends on the chemical species and its dissociation constant. If the metal exists in the sample in a stable chemical form (small dissociation constant), it may be difficult to decompose, and **atomization efficiency** is low. On the other hand, if the metal is in a chemical form that is easily decomposed, the number of atoms formed is high and the atomization efficiency is high. The atomization efficiency is a measure of how many free atoms are formed from all the possible species containing the atom. It can be expressed as the fraction of the total element in the gaseous state that is present as free atoms at the observation height in the atomizer or as the fraction of the total element present as both free atoms and ions. By total element, we mean all atomic, molecular, and ionic species containing the atom of interest, M (e.g., M, MX, MO, M^+). The atomization efficiency can vary from 0 to 1, and the value will depend on where in the atomizer the observation of the fraction M/(total M-containing species) is made. The interested student should consult the more detailed discussions in the *Handbook of Spectroscopy*, Vol. 1, edited by Robinson, or the references by Dean and Rains (Vol. 1) or Ingle and Crouch listed in the bibliography.

The loss of free atoms in the atomizer is also a function of the chemistry of the sample. If the oxide of the analyte element is readily formed, the free atoms will form oxides in the flame and the population of free atoms will simultaneously decrease. This is the case with elements such as chromium, molybdenum, tungsten, and vanadium. On the other hand, some metal atoms are stable in the flame and the free atoms exist for a prolonged period. This is particularly so with the noble metals platinum, gold, and silver. Adjusting the fuel/oxidant ratio can change the flame chemistry and atom distribution in the flame as shown in Figure 6.17b. Atoms with small ionization energies will ionize readily at high temperatures (and even at moderate temperatures). In an air–acetylene flame, it can be shown that moderate concentrations of potassium are about 50% ionized, for example. Ions do not absorb atomic lines.

The maximum absorbance signal depends on the number of free atoms in the light path. These free atoms are in dynamic equilibrium with species in the flame; they are produced continuously by the flame and lost continuously in the flame. The number produced depends on the original concentration of the sample and the atomization efficiency (Table 6.2). The number lost depends on the formation of oxides, ions, or other nonatomic species. The variation of atomization efficiency with

Table 6.2 Efficiencies of Atomization[a] of Metals in Flames

	Flame	
Metal	**Air–C_2H_2**	**N_2O–C_2H_2**
Ag	1.0	0.6
Al	<0.00005	0.2
Au	1.0	0.5
B	<0.0005	0.004
Ba	0.001	0.2*
Be	0.00005	0.1
Bi	0.2	0.4
Ca	0.07	0.5*
Cd	0.5	0.6
Co	0.3	0.3
Cu	1.0	0.7
Cr	0.07	0.6
Cs*	0.7	—
Fe	0.4	0.8
Ga	0.2	0.7
In	0.6	0.9
K*	0.4	0.1
Li*	0.2	0.4
Mg	0.6	1.0
Mn	0.6	0.8
Na*	1.0	1.0
Pb	0.7	0.8
Rb*	1.0	—
Si	—	0.06
Sn	0.04	0.8
Sr	0.08	0.03
Ti	—	0.2
Tl	0.5	0.56
V	0.01	0.3
Zn	0.7	0.9

Source: Modified from Robinson, J.W. (ed.), *Handbook of Spectroscopy*, Vol. 1, CRC Press, Boca Raton, FL, 1975.

[a] The efficiency of atomization in the flames has been measured as the fraction of total element in the gaseous state present as free neutral atoms or ionized atoms at the observation height in the atomizer. That is, efficiency of atomization = (neutral atoms + ions)/total element. Entries marked * obtained using ionization suppression, discussed in Section 6.4.1. The data were obtained under a variety of conditions by multiple researchers and may not be directly comparable between elements. The reference should be consulted for details.

the chemical form of the sample is called *chemical interference*. It is the most serious interference encountered in AAS and must always be taken into account. Interferences are discussed in detail in Section 6.4. Table 6.2 can be used as a guide for choosing which flame to use for AAS determination of an element. For example, A1 will definitely give better sensitivity in a nitrous oxide–acetylene flame than in air–acetylene, where hardly any free atoms are formed; the same is true of Ba. But for potassium, clearly, an air–acetylene flame is a better choice in terms of sensitivity than the hotter

nitrous oxide–acetylene flame. This is because K is very easily ionized at high temperatures and ions do not give atomic absorption signals. Based on ionization energy trends, you should expect that Cs and Rb would also be more sensitive in the cooler air–acetylene flame. As you can see, there are no entries in the table for Cs or Rb in a nitrous oxide–acetylene flame; they ionize to such an extent that the nitrous oxide–acetylene flame cannot be used for determining Cs or Rb by FAAS, just as Si and Ti are too refractory to be determined in an air–acetylene flame.

6.3.2 Graphite Furnace Atomization

There are many differences in the atomization process in a flame and in a graphite furnace. One very important difference to keep in mind is that in FAAS, the sample solution is aspirated into the flame continuously for as long as it takes to make the absorbance measurement. This is usually not long—about 30 s once the flame has stabilized after introducing the sample solution, but it is a continuous process. GFAAS is not a continuous process; the atomization step produces a transient signal that must be measured in less than 1 s. We will again consider an aqueous acidic solution of our sample.

A small volume of solution, between 5 and 50 μL, is injected into the graphite tube via a micropipette or an autosampler. The analyte is once again in the form of dissolved ions in solution, and the same process outlined in Figure 6.16 must occur for atomic absorption to take place. The graphite furnace tube is subjected to a multistep temperature program. The program controls the temperature ramp rate, the final temperature at each step, the length of time the final temperature is held at each step, and the nature and flow rate of the purge gas through the furnace at each step. A typical graphite furnace program consists of six steps: (1) dry, (2) pyrolyze (ash, char), (3) cool, (4) atomize, (5) clean out, and (6) cool down.

A generic temperature program for GFAAS might look like that in Figure 6.18. The process of atomization is extremely fast and must be rigidly controlled. The temperature program is therefore very carefully controlled, both with respect to the times used for each section of the heating

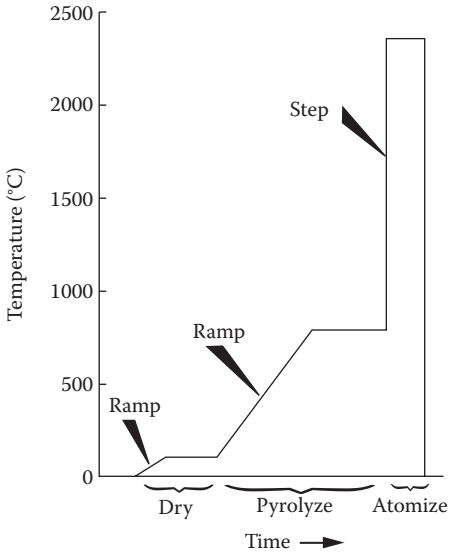


Figure 6.18 Typical temperature program for a graphite furnace atomizer. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

program and the temperature range involved in each step. It is vital to avoid loss of sample during the first two steps but it is also extremely important to eliminate as much organic and other volatile matrix material as possible.

The "dry" step is used to remove the solvent. The solvent must be removed without splattering the sample by rapid boiling, which would result in poor precision and accuracy. A slow temperature ramp from room temperature to about 110°C is used for aqueous solutions. The upper temperature is held for about a minute. The purge gas during this step is the normal inert gas (nitrogen or argon) at its maximum flow of about 300 mL/min to remove the solvent vapor from the furnace. The "pyrolyze" step is also called the ashing step or the "char" step. Its purpose is to remove as much of the matrix as possible without volatilizing the analyte. The "matrix" is everything except the analyte; it may consist of organic compounds, inorganic compounds, or a mixture of both. The sample is again subjected to a temperature ramp. The upper temperature is chosen to be as high as possible without losing the analyte and held for a short time. The gas flow is normally 300 mL/min and is usually the inert purge gas. With some organic sample matrices, switching to air is done in this step to help oxidize the organic materials.

A cool down step before the atomization step is used for longitudinally heated furnaces. This has been shown to improve sensitivity and reduce peak "tailing" for some refractory elements. This improves the accuracy of the measurement for these elements. The cool down step is not used in transversely heated furnaces.

The atomization step must produce gas-phase free analyte atoms. The temperature must be high enough to break molecular bonds. In general, the temperature is raised very rapidly for this step, as shown in Figure 6.18, and the purge gas flow is stopped to permit the atoms to remain in the light path. Stopping the purge gas flow increases the sensitivity of the analysis. The atomization occurs very rapidly and the signal generated is a transient signal; as the atoms form, the absorbance increases. As the atoms diffuse out of the furnace, the absorbance decreases, resulting in a nearly Gaussian peak-shaped signal. An idealized signal is presented in Figure 6.19a. Atomization signals for molybdenum from two different types of graphite furnace tubes are shown in Figure 6.19b. The spectrometer system is programmed to begin to acquire the absorbance data as soon as the atomization step begins. The integrated area under the absorbance peak is used for quantitative measurements.

Finally, the furnace is taken to a temperature higher than the atomization temperature to burn out as much remaining residue as possible; this is the "clean out" step. The furnace is allowed to cool before the next sample is injected. The entire program for one replicate of one sample is usually about 2 min long. Modern GFAAS systems may allow for temperature programs of up to 20 separate steps. GFAAS systems are now available with high-definition video cameras in the furnace, so that the analyst can watch the sample behavior as part of method development. The camera could show, for example, if the sample spatters during the dry step, permitting the analyst to lower the temperature to avoid loss of sample.

Early GFAAS instruments were operated by having the sample pipetted onto the bottom wall of the tube. The tube was heated in a programmed fashion as has been described and atomization occurred "off the wall" of the tube. Poor precision and a variety of interferences were serious problems with this approach. Modern graphite furnace atomizers make use of a pyrolytic graphite platform, first introduced by L'vov, inserted into the graphite tube or fabricated as an integral part of the tube. The sample is pipetted onto the platform and is atomized from the platform, not from the wall of the tube. The reasons for use of the L'vov platform will be discussed in Section 6.4. In addition, modern GFAAS methods add one or more chemicals to the sample in the furnace. These chemicals are called "modifiers" and are used to control interferences.

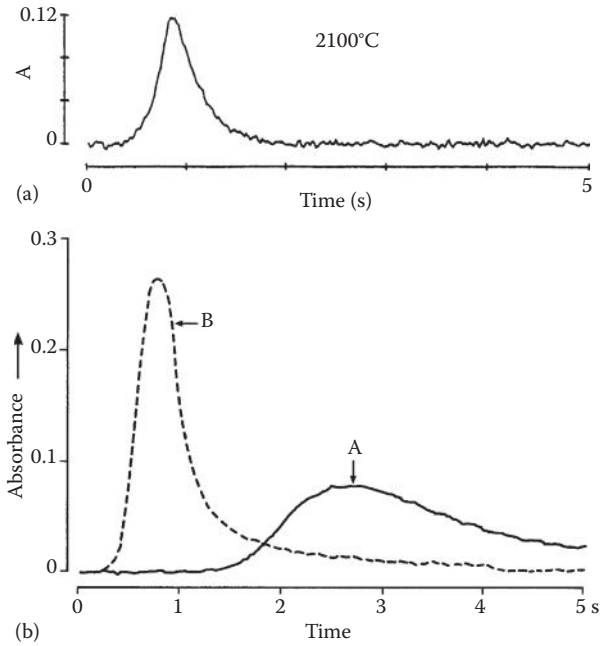


Figure 6.19 (a) An ideal Gaussian-shaped atomization signal from a graphite furnace. (b) Atomization signals for molybdenum in a graphite furnace atomizer. A is the signal resulting from an uncoated (normal) graphite tube atomizer. B is the signal from a graphite tube coated with pyrolytic graphite. The absorbance signal is transient in GFAAS. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

6.4 INTERFERENCES IN AAS

Interferences are physical or chemical processes that cause the signal from the analyte in the sample to be higher or lower than the signal from an equivalent standard. Interferences can therefore cause positive or negative errors in quantitative analysis. There are two major classes of interferences in AAS, spectral interferences and nonspectral interferences. Nonspectral interferences are those that affect the formation of analyte free atoms. Nonspectral interferences include chemical interference, ionization interference, and solvent effects (or matrix interference). Spectral interferences cause the amount of light absorbed to be erroneously high due to absorption by a species other than the analyte atom. While all techniques suffer from interferences to some extent, AAS is much less prone to spectral interferences and nonspectral interferences than atomic emission spectrometry and X-ray fluorescence (XRF), the other major optical atomic spectroscopic techniques.

6.4.1 Nonspectral Interferences

6.4.1.1 Chemical Interference

A serious source of interference is *chemical interference*. Chemical interference occurs when some chemical component in the sample affects the atomization efficiency of the sample compared with the standard solution. The result is either an enhancement or a depression in the analyte signal from the sample compared with that from the standard. This effect is associated most commonly with the predominant anions present in the sample. The anion affects the stability of the metal compound in which the analyte is bound, and this, in turn, affects the efficiency with which the

atomizer produces metal atoms. For example, a solution of calcium chloride, when atomized in an air–acetylene flame, decomposes to calcium atoms more readily than a solution of calcium phosphate. Calcium phosphate is more thermally stable than calcium chloride. A solution of calcium chloride containing 10 ppm Ca will give a higher absorbance than a solution of calcium phosphate containing 10 ppm Ca. If phosphate ion is added to a solution of calcium chloride, the absorbance due to Ca will decrease as the concentration of phosphate increases. This is a chemical interference. It occurs in the atomization process. Chemical interference is a result of having insufficient energy in the flame or furnace to break the chemical bonds in molecules and form free atoms.

There are three ways of compensating for chemical interference. The first approach is to match the matrix of the standards and samples; that is, to have the same anion(s) present in the same concentrations in the working standards as in the samples being analyzed. This supposes that the samples have been thoroughly characterized and that their composition is known and constant. This may be the case in industrial production of a material or chemical, but often, the sample matrix is not well characterized or constant.

A second approach is to add another metal ion that forms an even more stable compound with the interfering anion than does the analyte ion. Such an ion is called a "releasing agent" because it frees the analyte from forming a compound with the anion and permits it to atomize. For example, lanthanum forms a very thermally stable phosphate, more stable than calcium phosphate. To determine Ca in solutions that contain an unknown or variable amount of phosphate, such as those from biological samples, the analyst can add a large excess of lanthanum (as the chloride or nitrate salt) to all standards and samples. The lanthanum "ties up" the phosphate by forming lanthanum phosphate. If all of the phosphate is now present as lanthanum phosphate, this eliminates the dependence of the formation of Ca atoms on the phosphate concentration. The exact concentration of phosphate does not have to be measured; it is only necessary to add enough La to completely react with the phosphate in the solution to be analyzed. Usually 500–2000 ppm La is sufficient for most types of samples. The same amount of La must be added to all the solutions, including the blank. The releasing agent should be of the highest purity possible.

The third approach is to eliminate the chemical interference by switching to a higher-temperature flame, if possible. For example, when a nitrous oxide–acetylene flame is used, there is no chemical interference on Ca from phosphate, because the flame has sufficient energy to decompose the calcium phosphate molecules. Therefore, no lanthanum addition is required.

A fourth possible approach is the use of the method of standard additions (MSA), discussed in Chapter 2. This approach can correct for some chemical interferences but not all. For example, in the graphite furnace, if the analyte is present as a more volatile compound in the sample than the added analyte compound, MSA will not work. The analyte form in the sample is lost prior to atomization as a result of volatilization, while the added analyte compound remains in the furnace until atomization; therefore, the standard additions method will not give accurate analytical results.

6.4.1.2 Matrix Interference

Other potential sources of interference are the sample **matrix** and the solvent used for making the sample solution. The sample matrix is anything in the sample other than the analyte. In some samples, the matrix is quite complex. Milk, for example, has a matrix that consists of an aqueous phase with suspended fat droplets and suspended micelles of milk protein, minerals, and other components of milk. The determination of calcium in milk presents matrix effects that are not found when determining calcium in drinking water. Sample solutions with high concentrations of salts other than the analyte may physically trap the analyte in particles that are slow to decompose, interfering in the vaporization step and causing interference. Differences in viscosity or surface tension between the standard solutions and the samples, or between different samples, will result in interference. Interference due to viscosity or surface tension occurs in the nebulization process for FAAS

because different volumes of solution will be aspirated in a given period of time and nebulization efficiency will change as a result of the solvent characteristics. Metals in aqueous solutions invariably give lower absorbance readings than the same concentration of such metals in an organic solvent. This is due in part to enhanced nebulization efficiency of the organic solvent. In aqueous acidic solutions, higher acid concentrations often lead to higher solution viscosity and a decrease in absorbance due to decreased sample uptake. Matrix and solvent effects are often seen in GFAAS as well as FAAS and may be more severe in furnaces than in flames. The presence of matrix interference can be determined by comparing the slope of an external calibration curve with the slope of an MSA curve (discussed in Chapter 2). If the slopes of the two calibrations are the same (parallel to each other), there is no matrix interference; if the slopes are different (not parallel), interference exists and must be corrected for.

The solvent may interfere in the atomization process. If the solvent is an organic solvent, such as a ketone, alcohol, ether, or a hydrocarbon, the solvent not only evaporates rapidly but may also burn, thus increasing the flame temperature. The atomization process is more efficient in a hotter flame. More free atoms are produced and a higher absorbance signal is registered from solutions in organic solvents than from aqueous solutions, even though the metal concentration in the two solutions is equal.

Matching the solutions in the working standards to the sample solutions can compensate for matrix or solvent interferences. The type of solvent (water, toluene, methyl isobutyl ketone (MIBK), etc.), amount and type of acid (1% nitric, 5% HCl, 20% sodium chloride, etc.), and any added reagents such as releasing agents must be the same in calibration standards and samples for accurate results.

Alternatively, the MSA may be used to compensate for matrix interferences. This calibration method uses the sample to calibrate in the presence of the interference. Properly used, MSA will correct for the solvent interference but care must be taken. The assumption made in using MSA is that whatever affects the rate of formation of free atoms in the sample will affect the rate of formation of free atoms from the added analyte spike in the same way. MSA *will not* correct for spectral interference or for ionization interference. MSA can correct for interferences that affect the slope of the curve but not for interferences that affect the intercept of the curve.

6.4.1.3 Ionization Interference

In AAS, the desired process in the atomizer should stop with the production of ground-state atoms. For some elements, the process continues as shown in Figure 6.16 to produce excited-state atoms and ions. If the flame is hot enough for significant excitation and ionization to occur, the absorbance signal is decreased because the population of ground-state atoms has decreased as a result of ionization and excitation. This is called ionization interference. Ionization interferences are commonly found for the easily ionized alkali metal and alkaline-earth elements, even in cool flames. Ionization interferences for other elements may occur in the hotter nitrous oxide–acetylene flame, but not in air–acetylene flames.

Adding an excess of a more easily ionized element to all standards and samples eliminates ionization interference. This addition creates a large number of free electrons in the flame. The free electrons are "captured" by the analyte ions, converting them back to atoms. The result is to "suppress" the ionization of the analyte. Elements often added as ionization suppressants are potassium, rubidium, and cesium. For example, in the AAS determination of sodium, it is common to add a large excess of potassium to all samples and standards. Potassium is more easily ionized than sodium. The potassium ionizes preferentially and the free electrons from the ionization of potassium suppress the ionization of sodium. The DL of the sodium determination thereby decreases. The ionization suppression agent, also called an *ionization buffer*, must be added to all samples, standards, and blanks at the same concentration for accurate results. An example of the use of ionization suppression is shown in Figure 6.20. Absorbance at a barium resonance line (atomic absorption) and

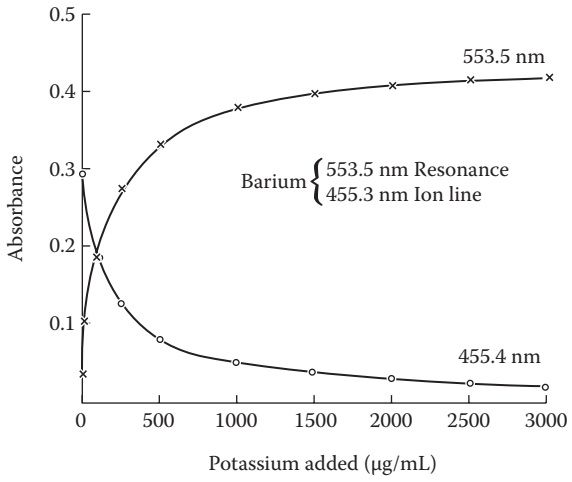


Figure 6.20 The suppression of barium ionization in a flame atomizer by addition of the more easily ionized element potassium. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

absorbance at a barium ion line (by barium ions in the flame) are plotted as a function of potassium added to the solution. As the potassium concentration increases, barium ionization is suppressed; the barium stays as barium atoms. This results in increased atomic absorption at the resonance line and a corresponding decrease in absorbance at the ion line. The trends in absorbance at the atom and ion lines very clearly show that barium ion formation is suppressed by the addition of 1000 ppm of the more easily ionized potassium.

6.4.1.4 Nonspectral Interferences in GFAAS

Graphite furnace atomizers experience significant nonspectral interference problems, some of which are unique to the furnace. Compensation or elimination of these interferences is different than what is done in flame atomizers.

Some analytes react with the graphite surface of the atomizer at elevated temperatures to form thermally stable carbides. These carbides do not atomize, thereby decreasing the sensitivity of the analysis. Carbide formation also results in poor precision and poor accuracy, because the amount of carbide formation depends on the condition of the graphite atomizer surface. Elements that tend to form carbides include W, Ta, B, Nb, and Mo, among others. The use of a dense pyrolytic graphite coating on the tube wall is highly recommended to minimize carbide formation. Normal graphite has a very porous structure that permits solution to soak into the graphite tube, thereby increasing the graphite/solution contact area and allowing more carbide formation at high temperatures. Pyrolytic graphic forms an impervious surface that prevents the solution from entering the graphite structure, decreasing carbide formation. Comparing the atomization profiles for Mo in Figure 6.19b, it is apparent that the atomization from an uncoated tube (peak A) appears at a much later time than that from a pyrolytic graphite-coated tube. This time delay is due to the need for Mo to diffuse out of the porous uncoated graphite. The result is not only a time delay but also a very broad absorbance signal that is difficult to integrate accurately. As you can see, the peak has not returned to the baseline, even after 5 min at the atomization temperature. The signal from the pyrolytic graphite-coated tube rises rapidly and returns to baseline rapidly, evidence that no significant diffusion of Mo into the graphite has occurred. This results in a higher absorbance signal and a peak that can be integrated accurately. It also permits a much shorter atomization step and increases tube life; both contribute to higher sample throughput.

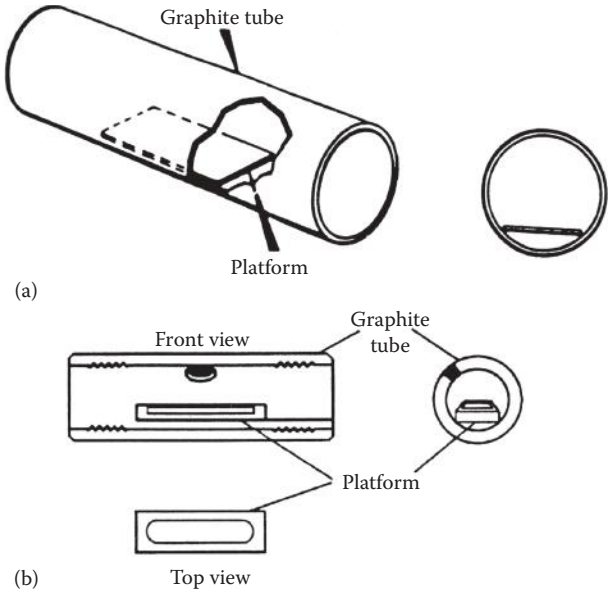


Figure 6.21 (a) Schematic of a L'vov platform inserted into a standard longitudinal graphite tube. The left diagram is a cutaway view of the platform inside the tube. The right diagram is an end-on view of the tube and platform looking along the light path. (b) Commercial platforms have a shallow depression into which the sample is pipetted through the opening in the top of the tube. The opening is shown as a dark area on the front and end-on views. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

When an analyte is atomized directly from the wall of the graphite tube, chemical and matrix interferences can be severe. The analyte, either as atoms or gas-phase molecules, is released from the hot wall at the atomization temperature into a cooler inert gas atmosphere inside the tube. The atmosphere is heated by conduction and convection from the tube walls, so the temperature of the atmosphere lags behind that of the walls. The atoms or molecules enter this cooler atmosphere where a number of processes may occur. For example, the atoms may recombine with matrix components into molecules or the temperature may be low enough that vaporized analyte-containing molecules fail to atomize. In either case, nonspectral interference occurs. A solution to this problem is the use of a platform insert in the tube, shown schematically in Figure 6.21. The platform surface is pyrolytic graphite and is deliberately designed to be in poor contact with the tube. The platform is heated by radiation from the tube walls. When an analyte is placed on the platform, it does not atomize when the wall reaches the right temperature, but later, when the platform and the atmosphere are both at the same, higher temperature. The difference in temperature of the gas phase inside the atomizer for wall and platform atomization is shown in Figure 6.22. This higher temperature improves the atomization of molecules and prevents recombination of free atoms. The result is a significant reduction in interferences and a significant improvement in precision.

6.4.1.5 Chemical Modification

Chemical modification, also commonly called **matrix modification**, is the addition of one or more reagents to the graphite tube along with the sample. The use of these chemical modifiers is to control nonspectral interferences by altering the chemistry occurring inside the furnace. The reagents are chosen to enhance the volatility of the matrix or to decrease the volatility of the analyte or to modify the surface of the atomizer. The use of a large amount of chemical modifier may, for

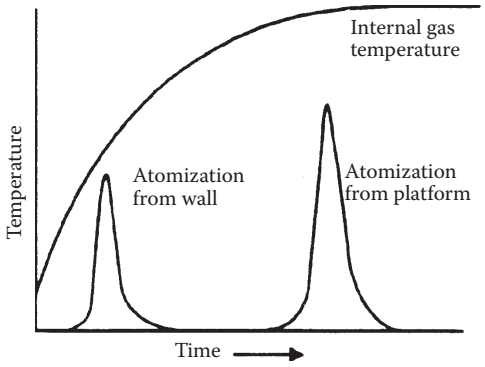


Figure 6.22 Tube wall and platform temperature profiles. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

example, convert all of the analyte into a single compound with well-defined properties. The end result of the use of chemical modifiers is to improve the accuracy and precision of the analysis by permitting the use of the highest possible pyrolysis temperature. This permits removal of the matrix with no loss of analyte.

Cadmium is one of the heavy metal elements whose concentrations in the environment are regulated by law due to the toxicity of Cd. Drinking water, blood, urine, and environmental samples are analyzed routinely for Cd at low ppb concentrations by GFAAS. Many common cadmium compounds, such as cadmium chloride, are relatively volatile. With no modifiers, Cd starts to volatilize out of the furnace at pyrolysis temperatures as low as 400°C, as seen in Figure 6.23. By adding either single compounds or mixtures of compounds, the pyrolysis temperature can be increased significantly, to over 1000°C. The addition of the modifier(s) converts cadmium in the sample to a much less volatile form. In general, this improves both the precision and accuracy of the analysis. If, for example, cadmium had been present in the sample in two different chemical forms, such as an organometallic Cd compound and an inorganic Cd compound, these two compounds might atomize at different rates and at different temperatures. The result would be multiple atomization signals, as shown in Figure 6.24. This can cause a serious error in the measurement of the signal.

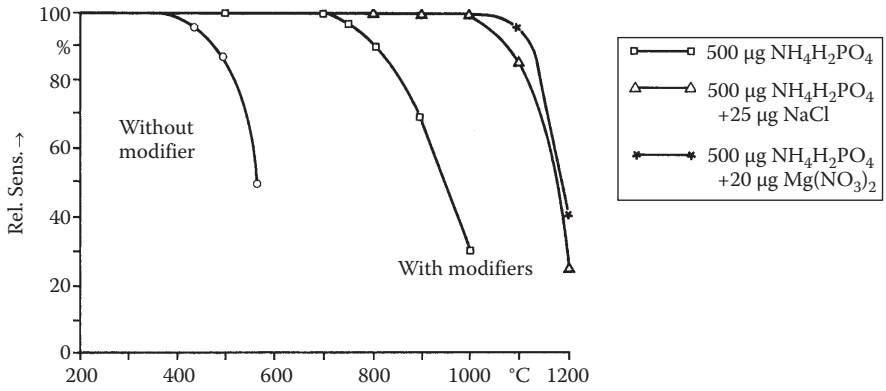


Figure 6.23 Effect of matrix modification on pyrolysis temperatures for cadmium. Without modification, Cd begins to volatilize out of the furnace at temperatures below 500°C. By adding modifiers or combinations of modifiers, Cd is retained in the furnace at much higher temperatures. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

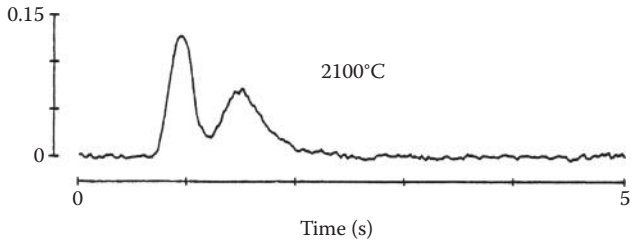


Figure 6.24 Multiple atomization signals caused by different chemical forms of analyte in the sample. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

Multiple analyte peaks can usually be eliminated through the use of an appropriate matrix modifier that converts the analyte to one common species.

Another example of a modifier used to stabilize the analyte is the use of nickel nitrate in the determination of selenium in biological tissues. Addition of nickel nitrate as a modifier retains Se in the furnace as nickel selenide while allowing the pyrolysis and removal of the organic matrix. Without the addition of nickel nitrate, the pyrolysis temperature must be 350°C or less to prevent loss of Se. With the use of nickel nitrate, temperatures up to 1100°C can be used.

In some cases, the matrix itself can be made more volatile through chemical modification. For example, in the determination of traces of elements in seawater the matrix in the graphite tube after drying would be primarily NaCl. NaCl is a high-melting ionic compound and requires relatively high temperatures to volatilize it. The NaCl molecule stays intact on volatilization, increasing the background absorbance (a spectral interference). If all the NaCl could be volatilized out of the furnace, very volatile analyte elements like Hg, As, Se, Pb, and many more would have been lost in the process. By adding an excess of ammonium nitrate as a *matrix modifier* to the sample in the graphite tube, the NaCl matrix can be converted to the much more volatile compounds ammonium chloride and sodium nitrate. Most of the matrix can be removed at a temperature below 500°C, which substantially reduces background absorption without loss of volatile analytes.

A generic "mixed modifier" of palladium and magnesium nitrate improves the GFAAS determination of many elements. The AAS cookbook of methods provided with commercial instruments should contain the recommendations for matrix modification for standard GFAAS determination of each element. Of course, it is imperative that very high-purity reagents be used for matrix modification and blank determinations that include the modifiers must be run.

6.4.2 Spectral Interferences

Spectral interferences occur when absorption of the hollow cathode resonance line occurs by species other than the element being determined. For example, the Pb 217.0 nm line may be absorbed by the components of a flame even though no lead is present in the sample or in the flame. This is a spectral interference.

6.4.2.1 Atomic Spectral Interference

The resonance absorption lines of the various elements are very narrow, on the order of 0.0002 nm, and at discrete wavelengths. Direct overlap between absorption lines of different elements is rare and can usually be ignored as a source of error. Absorption by the wings of the absorption lines of interfering elements present in high concentrations has been observed, but this is also a rare occurrence. A table of reported atomic spectral overlaps can be found in the handbook by Dean cited in the bibliography. The only cures for direct atomic spectral interference are

(1) to choose an alternate analytical wavelength or (2) to remove the interfering element from the sample. Extracting the interfering element away from the analyte or extracting the analyte away from the interfering element can accomplish the last option. There are many successful methods in the literature for the separation of interferences and analytes, but care must be taken not to lose analyte or contaminate the sample in the process. The extraction approach also permits the analyst to concentrate the analyte during the extraction, improving the accuracy and the sensitivity of the analysis when performed correctly.

6.4.2.2 Background Absorption and Its Correction

A common occurrence that results in spectral interference is absorption of the HCL radiation by molecules or polyatomic species in the atomizer. This is called "background absorption"; it occurs because not all of the molecules from the sample matrix and the flame gases are completely atomized. This type of interference is more commonplace at short wavelengths (<250 nm) where many compounds absorb, as discussed in Chapter 5. Incomplete combustion of organic molecules in the atomizer can cause serious background interference problems. If a flame atomizer is used, incomplete combustion of the solvent may take place, particularly if the flame is too reducing (fuel rich). The extent of the interference depends on flame conditions (reducing or oxidizing), the flame temperature used, the solvent used, and the sample aspiration rate. Background interference is much more severe when graphite furnace atomizers are used because the pyrolysis step is limited to a maximum temperature that does not volatilize the analyte. Consequently, many matrix molecules are not thermally decomposed. They then volatilize into the light path as the higher atomization temperature is reached and absorb significant amounts of the source radiation.

We have seen that atoms absorb over a very narrow wavelength range and that overlapping absorption by other atoms of the resonance lines of the analyte is extremely unlikely. However, molecular absorption occurs over broad bands of wavelengths and is observed in flame and graphite furnace atomizers. The molecular absorption may come from hydroxyl radicals generated from water in the flame, incomplete combustion of organic solvent, stable molecular residues, metal oxides, and so on. Solid particles in flame atomizers may scatter light over a wide band of wavelengths; this is not absorption but results in less light reaching the detector. Scattering of light therefore causes a direct error in the absorption measurement. If these broad absorption and scattering bands overlap the atomic absorption lines, they will absorb the resonance line from the hollow cathode and cause an increase in absorbance, a spectral interference. There are several ways of measuring this background absorption and correcting for it.

6.4.2.3 Two-Line Background Correction

An early manual method of measuring background and applying a correction for it used the absorption of a nearby nonresonance line. The emission spectrum from a hollow cathode is quite rich in emission lines and contains the resonance lines of the element of interest plus many other nonresonance emission lines from the element and the filler gas. The analyte atoms do not absorb these nonresonance lines; however, the broad molecular background absorbs them. Two measurements are made. The absorbance at a nonresonance line close to the analyte resonance line but far enough away that atomic absorption does not occur is measured. Then the absorbance at the resonance line of the analyte is measured. The absorbance at the nonresonance line is due *only* to background absorption. The absorbance at the resonance line is due to *both* atomic and background absorption. The difference in absorbance between the resonance and nonresonance lines is the net atomic absorption. The two-line method of background correction was convenient when all AAS instruments were manual instruments, since no change in light source or complicated instrumentation was necessary. However, this method is not always accurate. Unless the nonresonance line

is very close to the atomic absorption line, inaccurate correction of the background will result. Modern computerized instrumentation has made this technique obsolete.

6.4.2.4 Continuum Source Background Correction

Let us remind ourselves why we do not use a broadband, continuum lamp as a light source in AAS. The normal monochromator and slit system results in a spectral slit width about 0.2 nm wide. If we have a continuum source, the light from the source will fill the entire spectral window, as shown in the lower left-hand side drawing in Figure 6.25. When the continuum emission passes through the flame, the atoms can only absorb that portion of it exactly equal to the resonance wavelength. The atomic absorption line has a total width of about 0.002 nm. Consequently, if the atoms absorb all of the radiation over that linewidth, they will absorb only 1% of the radiation from the continuum lamp falling on the detector, as shown in the lower center drawing of Figure 6.25. All light within the 0.20 nm bandwidth, but not within the 0.002 nm absorption line, will reach the detector and not be absorbed by the sample. In other words, 99% or more of the emitted light reaches the detector. Consequently, the effect of atomic absorption on the continuum lamp is negligible and we can say that atoms do not measurably absorb the continuum lamp emission. It is this observation that permits the use of a continuum light source to measure and correct for broadband molecular background absorption.

In the continuum source background correction method, when an HCL source is used, the absorption measured is the total of the atomic and background absorptions. When a continuum lamp source is used, only the background absorption is measured. The continuum lamp, which emits light over a range or band of wavelengths, is placed into the spectrometer system as shown in Figure 6.26. This setup allows radiation from both the HCL and the continuum lamp to follow the same path to reach the detector. The detector observes each source alternately in time, either through the use of mirrored choppers or through pulsing of the lamp currents. When the HCL lamp is in position as the source, the emission line from the HCL is only about 0.002 nm wide; in other words, it fills only about 1% of the spectral window as shown in the upper left-hand-side drawing in Figure 6.25. When the HCL radiation passes through the flame, both the free atoms at the resonance

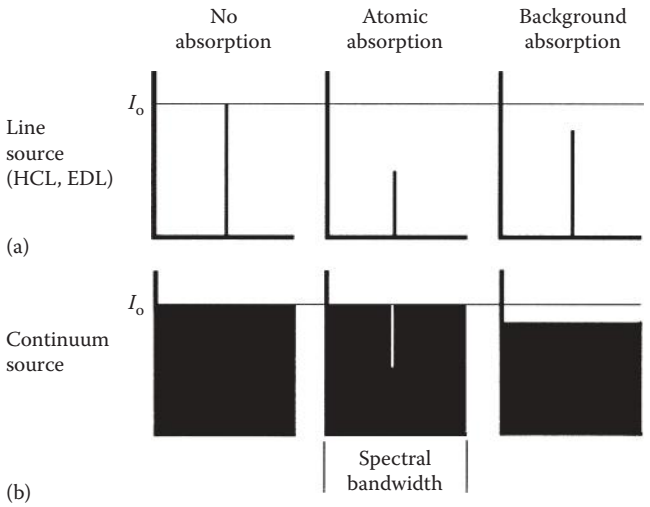


Figure 6.25 (a) Atomic and background absorption with a line source (HCL, EDL). (b) Atomic and background absorption with a continuum source (deuterium lamp, tungsten filament lamp). The width (*x*-axis) of each diagram is the spectral slit width. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

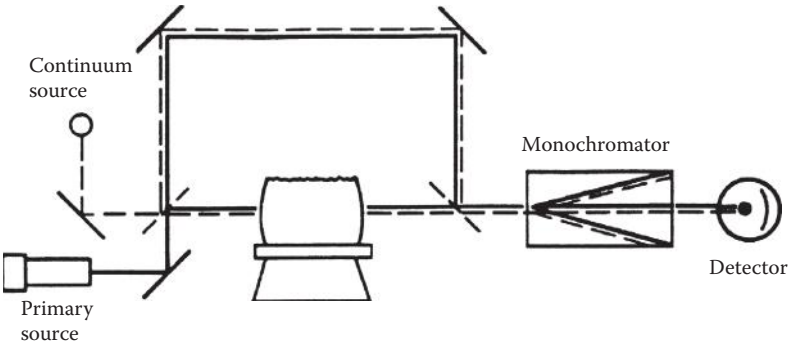


Figure 6.26 Continuum background corrector in a double-beam AAS system. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

line and the broadband absorbing molecules will absorb the line. This results in significant attenuation of the light reaching the detector, as shown in the upper center and right-hand-side drawing in Figure 6.25. When the continuum source is in place, the continuum lamp emission fills the entire spectral window as shown in the lower left-hand-side drawing in Figure 6.25. Any absorption of the radiation from the continuum lamp observed is broadband background absorption, since it will be absorbed over the entire 0.2 nm as seen in the lower right-hand-side drawing in Figure 6.25. We showed earlier that any *atomic* absorption of the continuum lamp is negligible. The absorbance of the continuum source is therefore an accurate measure of background absorption. An advantage of this method is that the background is measured at the same nominal wavelength as the resonance line, resulting in more accurate correction.

This correction method is totally automated in modern AAS systems. The HCL or EDL and the continuum lamp are monitored alternately in time; instrument electronics compare the signals and calculate the net atomic absorption.

The lamps used as continuum sources are a deuterium lamp (D_2) for the UV region and a tungsten filament lamp for the visible region. Commercial instruments using continuum background correction normally have both of these continuum sources installed to cover the complete wavelength range; the continuum lamp used is computer-selected based on the analyte wavelength.

Continuum background correction is used for FAAS and can be used for furnace AAS. There are limitations to the use of continuum background correction. If another element (not the analyte) in the sample has an absorption line within the spectral bandpass used, especially if this element is present is large excess, it can absorb radiation and result in inaccurate background correction. The background correction is made using two different sources. The correction can be inaccurate if the sources do not have similar intensities and if they are not aligned properly to pass through exactly the same region of the atomizer. This is especially true when the background levels are high. Continuum sources can generally correct for background absorbance up to $A = 0.8$. A problem can arise when the background absorption spectrum is not uniform over the spectral bandpass; such background absorption is said to have "fine structure." Absorption with fine structure may not be corrected properly using a continuum lamp corrector; the correction may be too large or too small. These limitations are particularly problematic in GFAAS, which is prone to high background levels.

6.4.2.5 Zeeman Background Correction

Atomic absorption lines occur at discrete wavelengths because the transition that gives rise to the absorption is between two discrete energy levels. However, when a vapor-phase atom is placed in a strong magnetic field, the electronic energy levels split. This gives rise to several absorption

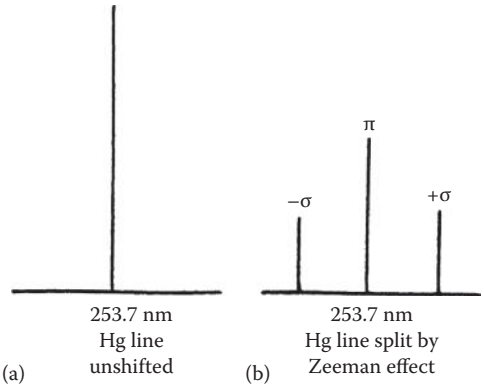


Figure 6.27 Zeeman effect causing shifts in electronic energy levels. (a) Hg resonance line in the absence of a magnetic field occurs as a single line at 253.7 nm. (b) Hg resonance line in the presence of a magnetic field. The π-component is at the original, unshifted wavelength (253.7 nm); the ±σ-components are shifted equally away from the original line to higher and lower wavelengths.

lines for a given transition in place of the single absorption line in the absence of a magnetic field. This occurs in all atomic spectra and is called **Zeeman splitting** or the Zeeman effect. In the simplest case, the Zeeman effect splits an absorption line into two components. The first component is the π-component, at the same wavelength as before (unshifted); the second is the σ-component, which undergoes both a positive and negative shift in wavelength, resulting in two equally spaced lines on either side of the original line. This splitting pattern is presented in Figure 6.27. The splitting results in lines that are separated by approximately 0.01 nm or less depending on the field strength. The strength of the magnetic field used is between 7 and 15 kG. Background absorption and scatter are usually not affected by a magnetic field.

The π- and σ-components respond differently to polarized light. The π-component absorbs light polarized in the direction parallel to the magnetic field. The σ-components absorb only radiation polarized 90° to the applied field. The combination of splitting and polarization differences can be used to measured total absorbance (atomic plus background) and background only, permitting the net atomic absorption to be determined.

A permanent magnet can be placed around the furnace to split the energy levels. A rotating polarizer is used in front of the HCL or EDL. During that portion of the cycle when the light is polarized parallel to the magnetic field, both atomic and background absorptions occur. No atomic absorption occurs when the light is polarized perpendicular to the field, but background absorption still occurs. The difference between the two is the net atomic absorption. Such a system is a DC Zeeman correction system.

Alternately, a fixed polarizer can be placed in front of the light source and an electromagnet can be placed around the furnace. By making absorption measurements with the magnetic field off (atomic plus background) and with the magnetic field on (background only), the net atomic absorption signal can be determined. This is a transverse AC Zeeman correction system. The AC electromagnet can also be oriented so that the field is along the light path (a longitudinal AC Zeeman system) rather than across the light path. No polarizer is required in a longitudinal AC Zeeman system.

The use of a polarizer in either DC or AC Zeeman systems cuts the light throughput significantly, adversely affecting sensitivity and precision. DC Zeeman systems require less power but have poorer linear working range and sensitivity than AC systems. AC Zeeman systems are more expensive to operate but have higher sensitivity and larger linear working ranges than DC systems.

Zeeman correction can also be achieved by having an alternating magnetic field surround the hollow cathode, causing the emission line to be split and then not split as the field is turned on and off. By tuning the amplifier to this frequency, it is possible to discriminate between the split and unsplit radiation. A major difficulty with the technique is that the magnetic field used to generate Zeeman splitting also interacts with the ions in the hollow cathode. This causes the emission from the hollow cathode to be erratic, which in turn introduces imprecision into the measurement. Most commercial instruments with Zeeman background correctors put the magnet around the atomizer. Zeeman correction systems can be used with flame atomizers and are commercially available; one disadvantage to using this approach is that the magnet blocks the analyst's view of the flame. This makes it impossible to visually check that the flame conditions are correct, since the analyst cannot see the color of the flame. The analyst cannot see if the burner slot is partially blocked or if charred material is building up on the burner when organic solvents are run. These unobserved problems might result in errors in the analysis. The significant advantage of Zeeman background correction is to compensate for the high background absorption in graphite furnace atomizers.

The advantages of Zeeman background correction are numerous. Only one light source is required. Since only one light source is used, there is no need to match intensity or align multiple sources. The physical paths of the split and unsplit light are identical, as opposed to the use of a continuum lamp, where the radiation may not pass along the identical path as the HCL radiation. The background correction is made very close to the resonance line and at the same absorption bandwidth as the atomic absorption signal. Therefore, the correction is generally very accurate, even for background with fine structure and for high background levels, up to absorbance = 2.0. The Zeeman correction system can be used for all elements at all wavelengths. One limitation to the use of Zeeman background correction is that it shortens the analytical working range. The relationship between absorbance and concentration becomes nonlinear at lower absorbances than in a non-Zeeman corrected system, and then the absorbance–concentration relationship "rolls over." That is, as concentration increases, absorbance first increases linearly, then nonlinearly until a maximum absorbance is reached. After the maximum, absorbance actually *decreases* with increasing concentration. It is possible for two completely different concentrations, one on either side of the absorbance maximum, to exhibit the same absorbance value. The rollover point must be established by carefully calibrating the instrument and unknown samples may need to be run at more than one dilution factor to ensure that an unknown is not on the "wrong side" of the absorbance maximum. If this well-understood potential problem is kept in mind, the use of Zeeman background correction with modern GFAAS instrumentation and methodology provides accurate and precise GFAAS results. The use of Zeeman correction causes significant loss in sensitivity compared to continuum background correction for some elements, notably Li, Cs, Tl, Be, Hg, B, and V. Systems with Zeeman background correction are more expensive than those with only continuum background correction.

6.4.2.6 Smith–Hieftje Background Corrector

It will be remembered that the HCL functions by the creation of excited atoms that radiate at the desired resonance wavelengths. After radiating, the atoms form a cloud of neutral atoms that, unless removed, will absorb resonance radiation from other emitting atoms.

If the HCL is run at a high current, an abundance of free atoms form. These free atoms absorb at precisely the resonance lines the hollow cathode is intended to emit; an example is shown in Figure 6.28, with the free atoms absorbing exactly at λ over an extremely narrow bandwidth (Figure 6.28b). The result is that the line emitted from the HCL is as depicted in Figure 6.28c instead of the desired emission line depicted in Figure 6.28a. The emitted lines are broadened by the mechanisms discussed in Section 6.1.1. The phenomenon of absorption of the central portion of the emission line by free atoms in the lamp is called "self-reversal." Such absorption is not easily

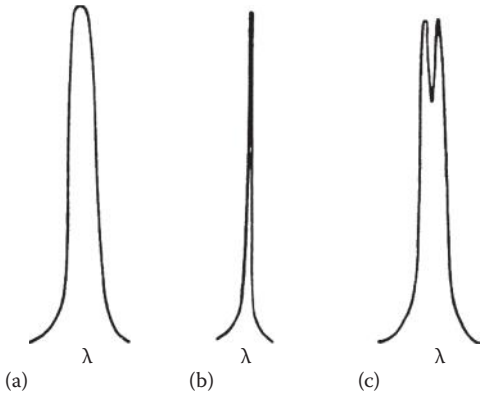


Figure 6.28 Distortion of spectral line shape in an HCL due to self-reversal. (a) Shape of the spectral line emitted by the HCL. (b) Shape of the spectral energy band absorbed by cool atoms inside the HCL. (c) Shape of the net signal emerging from an HCL, showing self-absorption of the center of the emission band.

detectable, because it is at the very center of the emitted resonance line and very difficult to resolve. It is, of course, exactly the radiation that is most easily absorbed by the atoms of the sample. In practice, if the HCL is operated at too high a current, the self-reversal decreases the sensitivity of the analysis by removing absorbable light. It also shortens the life of the lamp significantly.

The Smith–Hieftje background corrector has taken advantage of this self-reversal phenomenon by pulsing the lamp, alternating between high current and low current. At low current, a normal resonance line is emitted and the sample undergoes normal atomic absorption. When the HCL is pulsed to a high current, the center of the emission line is self-absorbed, leaving only the wings of the emitted resonance line; the emitted line would look similar to Figure 6.28c. The atoms of the sample do not significantly absorb such a line. The broad background, however, absorbs the wings of the line. Consequently, the absorption of the wings is a direct measurement of the background absorption at the wavelength of the atomic resonance absorption. The Smith–Hieftje technique can be used to automatically correct for background. In practice, the low current is run for a fairly short period of time and the absorbance measured. The high current is run for a very short, sharp burst, liberating intense emission and free atoms inside the hollow cathode and the absorbance is again measured. The difference between the measurements is the net atomic absorption. There is then a delay time to disperse the free atoms within the lamp before the cycle is started again.

The advantages of the Smith–Hieftje technique are that it can be used in single-beam optics and it is not necessary to align the beam measuring background absorption and atomic absorption since it is the same beam. In addition, the electronics are much simpler than that used in a Zeeman background correction system and no expensive magnet is needed. There are some disadvantages to the technique. It requires a special type of HCL that can operate both at low and high currents and the life of the special HCLs is significantly less than that of standard HCLs (150–500 h depending on the element vs. 5000 h for standard HCLs). The loss in sensitivity for this technique is about 50% of that obtained using a continuum correction system, the dynamic range is shorter, and the technique cannot correct for structured background. The Smith–Hieftje background correction system is commercially available in Shimadzu Scientific AAS instruments, where it is known as rapid self-reversal background correction. All lamps for the Shimadzu instruments are self-reversing lamps that can be run at low current for D_2 background correction work. A more detailed comparison of the methods used for background correction is given in the reference by Carnrick and Slavin listed in the bibliography.

6.4.2.7 Spectral Interferences in GFAAS

Graphite furnace atomizers have their own particular spectral interference problems. Any emission from the light source or atomizer that cannot be absorbed by the analyte should be prevented from reaching the detector. Usually, the emission from flames is low. At atomization temperatures in excess of 2200°C, the graphite furnace is a white-hot emission source. If this intense visible radiation reaches the PMT, noise increases, which decreases precision. The emission from the hot graphite is essentially blackbody radiation, extending from 350 to 800 nm and varying in intensity with wavelength. The extent of emission interference caused by this radiation falling on the detector varies with analyte wavelength. Elements with resonance lines in the 400–600 nm region like Ca and Ba can be seriously affected. The control of emission interference lies in spectrometer design, which is not controlled by the analyst and in the correct installation, alignment, and maintenance of the furnace and optical windows, which are very definitely controlled by the analyst.

Background absorption can be severe in GFAAS. Decreasing the sample volume and choosing alternate wavelengths can be used to reduce background levels in some cases. Control of the chemistry in the furnace is key to reducing background. The pyrolysis step must be designed to volatilize as much of the matrix as possible without loss of analyte. Ideally, the matrix would be much more volatile than the analyte, so that 100% matrix removal could occur in the pyrolysis step with 100% retention of analyte in the furnace. This situation rarely occurs. It is possible to control the volatility of the matrix and analyte to some extent through matrix modification as discussed earlier. The use of matrix modifiers seems to control background (a spectral interference) by controlling nonspectral interferences.

A potential problem with any automatic background corrector is that the analyst may be unaware of the extent to which the background is present. It should be remembered that when absorbance $A = 2$, the transmittance $T = 1/100$, and the absorbed radiation is 99% of the available radiation. Therefore, the total signal falling on the detector is only 1% of I_0. If quantitative analysis is carried out using this very small signal, major errors may result. A 1% error in measuring the background may result in a 100% error in measuring the atomic absorption by the sample. Instrument manufacturers claim quantitative atomic absorption measurements while correcting background absorption in excess of 99% using Zeeman background correction. Analysts should be aware of the magnitude of the background signal, because a small error in measuring the background becomes a major error in the net atomic absorption measurement. Steps such as the use of L'vov platforms, matrix modification, alternate wavelengths, reduction in sample volume, and other techniques to minimize background should be taken to keep background absorbance as low as possible to obtain accurate results.

6.5 ANALYTICAL APPLICATIONS OF AAS

AAS is a mature analytical technique. There are thousands of published methods for determining practically any element in almost any type of sample. There are books and journals devoted to analytical methods by AAS and other atomic spectrometry techniques. The bibliography provides a list of some texts on AAS. Journals such as *Analytical Chemistry*, *Applied Spectroscopy*, *Journal of Analytical Atomic Spectroscopy*, *The Analyst*, *Spectroscopy Letters*, *Spectrochim. Acta Part B*, and others are sources of peer-reviewed articles, but many applications articles can be found in specialized journals on environmental chemistry, food analysis, geology, and so on. The applications discussion here is necessarily limited, but the available literature is vast.

AAS is used for the determination of all metal and metalloid elements. Nonmetals cannot be determined directly because their most sensitive resonance lines are located in the vacuum UV region of the spectrum. Neither flame nor furnace commercial atomizers can be operated in a vacuum. It is

possible to determine some nonmetals indirectly by taking advantage of the insolubility of some compounds. For example, chloride ion can be precipitated as insoluble silver chloride by adding a known excess of silver ion in solution (as silver nitrate). The silver ion remaining in solution can be determined by AAS and the chloride ion concentration calculated from the change in the silver ion concentration. Similar indirect approaches for other nonmetals or even polyatomic ions like sulfate can be devised.

6.5.1 Qualitative Analysis

The radiation source used in AAS is an HCL or an EDL, and a different lamp is needed for each element to be determined (except for the new continuum source system discussed earlier). Because it is essentially a single-element technique, AAS is not well suited for qualitative analysis of unknowns. To look for more than one element requires a significant amount of sample and is a time-consuming process. For a sample of unknown composition, multielement techniques such as XRF, ICP-mass spectrometry (ICP-MS), ICP-OES, and other atomic emission techniques are much more useful and efficient.

6.5.2 Quantitative Analysis

Quantitative measurement is one of the ultimate objectives of analytical chemistry. AAS is an excellent quantitative method. It is deceptively easy to use, particularly when flame atomizers are utilized.

6.5.2.1 Quantitative Analytical Range

The relationship between absorbance and concentration of the analyte being determined in AAS follows Beer's law (discussed in Chapter 2) over some concentration range. There is an optimum linear analytical range for each element at each of its absorption lines. The *minimum* of the range is a function of the DL of the element under the operating conditions used. The ultimate limiting factor controlling the DL is the noise level of the instrument being used. The LOD in AAS is defined by the International Union of Pure and Applied Chemistry (IUPAC) and by many regulatory agencies as the concentration giving a signal equal to three times the standard deviation of a blank solution measured under the same operating conditions being used for the analysis. However, the LOD is never used as the minimum for reporting quantitative data. The limit of quantitation (LOQ) is defined as that concentration giving a signal equal to 10 times the standard deviation of a blank solution measured under the operating conditions for the analysis. This is the lowest quantitative concentration that should be reported. Concentrations between the LOD and the LOQ should be reported as "detected but not quantifiable" and concentrations below the LOD should be reported as "not detected." The *maximum* of the analytical range is determined by the sample. The linear working range for AAS is small for most systems, generally only one to two orders of magnitude at a given wavelength. The calibration curve deviates from linearity, exhibiting a flattening of the slope at high absorbance values. With a flat slope, changes in concentration of the sample produce virtually no changes in absorption. Hence, it is impossible to measure concentrations accurately at extremely high absorbance values. Many calibration curves deviate from linearity below $A = 0.8$, and Zeeman background correction shortens the analytical working range even more. With modern computerized instruments, nonlinear curve fitting can be used to some advantage to measure concentrations beyond the linear range. However, it is advisable to keep the absorbance values of samples and standards below 0.8, as was discussed in Chapter 2, unless your system can handle a higher linear working range. When a concentration range is quoted for an analytical method, it is important to know how the lower and upper limits were determined. Approximate upper limits for the linear range of elements determined by FAAS are listed in Appendix 6.A. DLs for elements by FAAS, GFAAS, CV Hg and HGAAS, and other atomic spectroscopic techniques discussed in later

chapters are given in Appendix 6.B. For AAS, it had been customary to report *method sensitivity*, where sensitivity was defined as the concentration of analyte that gives an absorbance of 0.0044 (equal to 1% absorption), so this term may be encountered in the literature. Sample sensitivities for FAAS and GFAAS are tabulated in Appendix 6.B. Both the LOD and the sensitivity are highly dependent on the sample matrix, operating conditions, the particular instrument used, and the way in which the data is processed.

Modern AAS instruments have computerized data collection and data processing systems. These computer-based systems have the ability to fit different types of calibration curves to the data using a variety of equations, including linear, quadratic, and higher-order polynomial functions. Such systems are capable of calculating concentration results from nonlinear calibration curves. The accuracy of such calculated results depends on the equations used for calibration and on the number and concentrations of the standards used to provide the calibration data. It is not advisable to use a nonlinear calibration curve without verification that the results are accurate. When in doubt, dilute the samples into the linear region, especially if using Zeeman background correction.

6.5.2.2 Calibration

Calibration of AAS methods can be performed by the use of an external calibration curve or by MSA; both calibration methods were presented in Chapter 2. Internal standards are not used in AAS because it is usually a single-element technique; we cannot measure an internal standard element at the same time we measure the analyte.

External calibration curves are prepared from solutions of known concentrations of the sample element. High-purity metals dissolved in high-purity acids are used to make the stock standard solution. For AAS, stock standard concentrations are either 1,000 or 10,000 ppm as the element. Working standards are diluted from the stock standard. For example, if we wanted to make a calibration curve for copper determination in the range of 2–20 ppm, we would make a stock standard solution of 1000 ppm Cu by dissolving Cu metal in nitric acid. Then we would dilute this solution to make a series of working standards. The concentrations of the working standards must cover the complete range of 0–20 ppm. A calibration blank (the 0.0 ppm standard) is of course required to correct for any analyte present in the water or reagents used to prepare the standard solutions. In this example, the calibration blank would be prepared from deionized water and the same high-purity nitric acid used to make the standard solutions. Three to five working standards are typical, so we might make Cu solutions of 0, 2, 5, 10, 15, and 20 ppm. These standard solutions would then be aspirated into the flame and the absorbance of each standard would be measured. The absorbance would be plotted versus concentration. A calibration curve like that in Figure 6.29 results. It

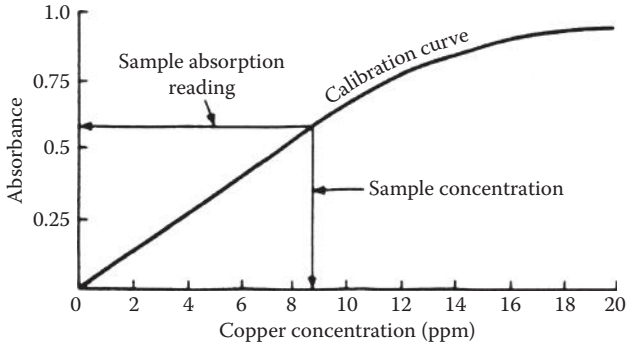


Figure 6.29 AAS calibration curve for the copper 324.8 nm line showing linear and nonlinear regions of the curve.

should be noted that the relationship between absorbance and concentration is linear over the range of 0–10 ppm Cu, but at higher concentrations, the relationship deviates from linearity. Provided that the slope of the curve is fairly steep, it may possible to distinguish between concentrations outside the linear range, such as between 12 and 14 ppm. Above 16 ppm, the curve becomes so flat that accurate concentration results are difficult or impossible to obtain.

When a quantitative analysis is to be performed, the sample is atomized and the absorbance measured under exactly the same conditions as those used when the calibration standards were measured. The calibration standards are usually measured first, and the sample solutions should be measured immediately following calibration. If the sample has been prepared using reagents such as acids, it is necessary to prepare a method blank that is carried through the same sample preparation steps as the sample. The method blank is used to correct for any contamination that may have occurred during sample preparation. The absorbance of the method blank is subtracted from the sample absorbance to give the corrected or net sample absorbance. The concentration of the unknown copper solution is determined from the calibration curve. For example, suppose that the corrected absorbance reading of the sample solution was 0.58. Using the calibration curve shown in Figure 6.29, it can be deduced that the concentration of the solution is about 8.7 ppm.

Stock standard solutions of single elements at 1,000 and 10,000 ppm can be purchased from a number of companies making these solutions. Purchasing the stock solutions saves a great deal of time and effort and is often more accurate and less expensive than making these solutions "in-house." The US National Institute for Standards and Technology (NIST) also sells standard reference material (SRM) solutions of many elements, certified for their concentration. NIST SRM solutions are expensive but are often used as verification standards to confirm that the analyst has made the working standard solutions correctly as part of a method quality control process. Stock standards of most elements have a shelf life of at least 1 year; commercial solutions will have the expiration date marked on the bottle. Working standards should be prepared fresh daily or as often as needed as determined by a stability test. Low concentrations of metal ions in solution are not stable for long periods of time; they tend to adsorb onto the walls of the container. In addition, evaporation of the solvent over time will change the concentration of the solution, making it no longer a "standard."

It is most important in preparing external calibration curves that the solution matrix for samples and standards be as similar as possible. To obtain reliable quantitative data, the following should be the same for the samples and standards:

1. The same solvent (e.g., water, 5% nitric acid, alcohol, methyl ethyl ketone [MEK]); same matrix modifier if used
2. The same predominant anion (e.g., sulfate, chloride) at the same concentration
3. The same type of flame (air–acetylene or nitrous oxide–acetylene) or the same graphite tube/platform
4. Stable pressure in the flame gases during the analysis
5. Absorbance measured at the same position in the flame/furnace
6. Background correction carried out on each sample, blank, and standard using the same correction technique

Sample solutions should be measured immediately following calibration. If the instrument is shut down for any reason (the gas tank runs out, the power fails in a thunderstorm, the lamp burns out, the nebulizer clogs up and needs to be cleaned, the graphite tube cracks, the analyst goes to lunch, etc.), the calibration must be repeated when the instrument is turned back on to be sure that items 3–6 are exactly the same for samples and standards. For GFAAS, the platform and tube must be the same for the calibration curve and the samples. If a tube cracks during a run, a new tube and platform are inserted, conditioned per the manufacturer's directions and the calibration standards rerun before samples are analyzed. For extremely complex sample matrices, it may not be possible to make external standards with a similar matrix. In this case, the MSA should be used for quantitative analysis.

The signal in FAAS is a continuous, steady-state signal; as long as sample is aspirated into the flame, the absorbance stays at a constant value. Measurement of the absorbance in FAAS is fairly simple. In GFAAS, the signal is transient and the shape and height of the peak depend on the rate of atom formation. That rate can be affected by interferences from the sample matrix. The *integrated peak area* is independent of the rate of atom formation. For quantitative analysis by GFAAS, the concentration should be plotted against the peak area, not the peak height, for the most accurate results. Modern instruments are equipped with integrators to measure absorbance over the atomization period.

The accuracy can be excellent for both FAAS and GFAAS. The precision of FAAS is usually less than 1% relative standard deviation (RSD). The precision of GFAAS can be in the 1%–2% RSD range but is often 5%–10% for complex matrices.

6.5.3 Analysis of Samples

6.5.3.1 Liquid Samples

Liquid solutions are the preferred form for sample introduction into flame and furnace atomizers. Frequently, liquid samples can be analyzed directly or with minimal sample preparation, such as filtration to remove solid particles. Typical samples that have been analyzed directly include urine, electroplating solutions, petroleum products, wine, fruit juice, and, of course, water and wastewater. If the samples are too concentrated, they may be diluted prior to analysis. If they are too dilute, the solvent may be evaporated or the analyte concentrated by solvent extraction or other methods.

Milk may be analyzed for trace metals by FAAS by adding trichloroacetic acid to precipitate the milk proteins. The precipitate is removed by filtration or centrifugation. The standards should also contain trichloroacetic acid to match the samples. Trace metals can be determined in seawater, urine, and other high-salt liquid matrices by complexing the metals with a chelating agent and extracting the metal complexes into organic solvent. For example, ammonium pyrrolidine dithiocarbamate (APDC) will complex Cu, Fe, Pb, and other metals. Complexation allows the metals to be extracted into MIBK. The standards are made in MIBK and aspirated directly into the flame. This permits not just extraction but preconcentration; for example, 1 L of seawater can be extracted into 50 mL of MIBK, resulting in a 20-fold concentration factor. Seawater can be analyzed for the major cations by preparing an artificial seawater solution for making calibration standards in a matrix similar to the samples. Artificial seawater contains calcium carbonate, magnesium oxide, potassium carbonate, and sodium chloride at levels that reflect the cation and anion levels found in real seawater. Oils may be diluted with a suitable organic solvent such as xylene and the soluble metals determined directly. Organometallic standards soluble in organic solvent are commercially available for preparing calibration curves for these types of analyses.

There are liquid sample matrices, such as blood, serum, very viscous oils, and the like, that require sample preparation by acid digestion or ashing prior to FAAS determination. In many cases, these matrices can be analyzed without digestion or prior ashing by GFAAS.

6.5.3.2 Solid Samples

Solid samples are usually analyzed by dissolving the sample to form a liquid solution that can be introduced into the flame or furnace. Dissolution can be accomplished by mineral acid digestion (“wet ashing”), fusion of solids with molten salts and dissolution of the fusion bead, dry ashing of organic solids with acid dissolution of the residue, combustion in oxygen bombs, and other procedures too numerous to mention. Dissolution is time consuming, even with fast microwave digestion and ashing systems, automated fusion fluxers, and other automated sample preparation devices

now available. In many cases, solid samples have to be ground into smaller particles before digestion, sometimes in a multistep process requiring the use of a variety of grinding tools or mixers to ensure a homogeneous sample. Care must be taken that these tools do not contain analytes of interest, such as heavy metals. Grinding generates heat and volatile elements may be lost; cooling the grinder with liquid nitrogen or dry ice is often used to prevent loss of volatiles. Dissolution entails the possibility of introducing impurities or losing analyte, causing error. This is particularly problematic at ppb and lower levels of analyte. However, hundreds of types of solid samples are dissolved for AAS analysis on a daily basis; it is still the most common approach to AAS analysis of solids. Types of samples that have been analyzed after dissolution include metals, alloys, soils, animal tissue, plant material, foods of all types, fertilizer, ores, cements, polymers, cosmetics, pharmaceuticals, coal, ash, paint chips, and many solid industrial chemicals. Solid particulates in air, gas, and fluid streams can be collected by filtration and analyzed by digesting the filter and the collected particulates.

For example, grains, plant tissues, and many other organic materials can be digested on a hot plate in a mixture of nitric and other mineral acids to destroy the organic matrix. The cooled, clear solution is diluted to volume and analyzed against aqueous acidic calibration standards. Dry ashing of food, plant, and biological tissue is performed by placing 10–50 g of the sample in a suitable crucible and heating in a muffle furnace for several hours to burn off the organic material. The ash is dissolved in mineral acid (nitric, HCl, or acid mixtures) and diluted to volume with deionized water. An aqueous acidic calibration curve would be used. Inorganic materials, ceramics, and geological materials often require fusion in molten salts at high temperatures to convert them to soluble forms. For example, bauxite, an aluminum ore, can be fused in a Pt crucible with a mixture of sodium carbonate and sodium borate. The mixture is heated over a Bunsen burner to form a clear melt. The fusion salts convert the aluminum, silicon, and titanium compounds in bauxite to salts that will dissolve in aqueous HCl. The calibration standards must contain HCl, sodium chloride, and sodium borate at levels that match those in the diluted fused samples. It is critical that a blank be prepared in the same manner as samples are prepared, to correct for any traces of analytes that might be present in the acids, salts, and other reagents used and for contamination from "the environment." Dust in the air is often a major source of contamination of samples by "the environment," especially for analytes such as Al and Si.

The analysis of solids is time consuming and is prone to many sources of error. Analytical chemists have been trying for many years to analyze solid samples directly, without having to dissolve them. For some types of samples, this can be done by AAS. Solids can be analyzed using *a glow discharge (GD) atomizer*, by inserting small pieces or particles of sample directly into the flame or furnace or by the use of *laser ablation*.

A unique direct solid analysis approach for graphite furnace AAS, solid AA®, is the combination of the SSA 600 autosampler from Analytik Jena AG with their contrAA systems (Figure 6.30). The SSA 600 is a fully automated solid sampler that will analyze up to 84 samples. All that is required is to place the solid samples onto the sample carriers. The autosampler weighs the sample using an integrated microbalance with a precision of 1 μg, transports it to the graphite furnace, and returns the reusable carrier back to the sample tray. Sample sizes are on the order of 100 μg–10 mg. Samples can be in the form of powders, granulates, fibers, and paste-like materials such as creams, sludge, and viscous oils.

Some of these approaches are also used in atomic emission spectrometry and in ICP-MS and are discussed in greater detail in Chapters 7, 9, and 10, and in the references by Sneddon, Robinson, and Skelly Frame and Keliher listed in the bibliography.

One approach to the direct analysis of solids is to form a *slurry* of the sample in a suitable solvent and introduce the slurry directly into a graphite furnace atomizer. A slurry is a suspension of fine solid particles in a liquid. Slurry preparation requires that the sample either is in the form of a

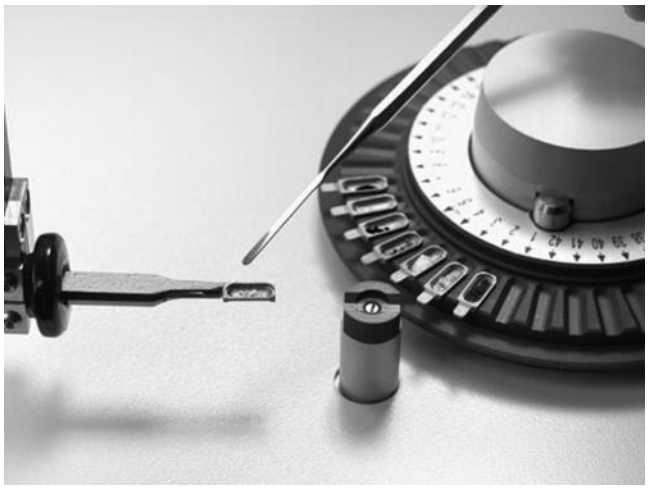


Figure 6.30 The SS600® solids autosampler for direct solids analysis by graphite furnace AAS. (© 2013 Analytik Jena, www.analytik-jena.de. Used with permission.)

fine powder or can be ground to a fine powder without contamination from the grinding process. This can be done successfully for many types of samples, such as foods, grains, pharmaceuticals, and sediments. A key development in achieving reproducible results from slurry samples introduced into graphite furnace atomizers was to keep the slurry "stirred" with an ultrasonic agitator during sampling, as discussed in the reference by Miller-Ihli listed in the bibliography.

A commercial GD source, the AtomSource® (Teledyne Leeman Labs, Inc., Hudson, NH, www.teledyneleemanlabs.com), is available for the analysis of solid metals and metal alloys. A GD is more commonly used as an atomic *emission* source, but this source acts as a unique atomizer for conductive samples. The source is shown in Figure 6.31a. The atomizer cell is a vacuum chamber with the light path along the axis. The conductive sample is positioned as shown and is bombarded with six streams of ionized argon gas. This process sputters the sample, releasing free atoms into the light path, as shown in Figure 6.31b. The method does not rely on a high temperature for atomization, so refractory metals such as boron, tungsten, zirconium, niobium, and uranium can be atomized easily. In addition to ground-state atoms, the source also produces excited atoms. The emission from the excited atoms can be used to measure elements not able to be measured by AAS. Carbon in steels can be determined by emission, for example, while the other steel components are determined by absorption. The AtomSource atomizer is shown incorporated into the entire spectrometer system in Figure 6.32.

6.5.3.3 Gas Samples

There are some metal-containing compounds that are gaseous at room temperature and in principle the gas sample can be introduced directly into a flame atomizer. More commonly, the gas is bubbled through an appropriate absorbing solution and the solution is analyzed in the usual manner.

The introduction of a gas-phase sample into an atomizer has significant advantages over the introduction of solids or solutions. The transport efficiency may be close to 100%, compared to the 5%–15% efficiency of a solution nebulizer. In addition, the gas-phase sample is homogeneous, unlike many solids. There are two commercial analysis systems with unique atomizers that introduce a gas-phase sample into the atomizer. They are the CV technique for mercury and the HGAAS technique. Both are used extensively in environmental and clinical chemistry laboratories.

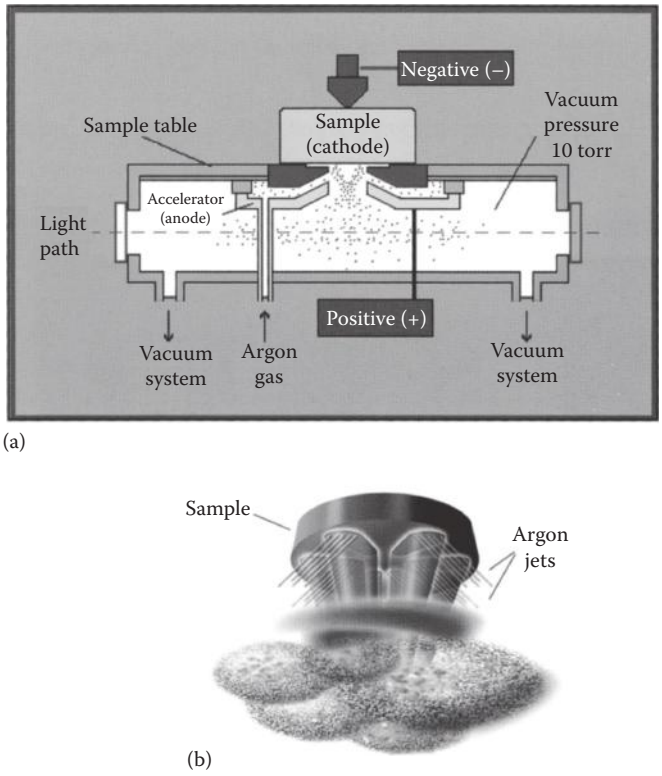


Figure 6.31 (a) The AtomSource GD atomizer for conductive solid samples. (b) Schematic of the sputtered atom cloud produced by the bombardment of the sample surface by ionized argon. (Courtesy of Teledyne Leeman Labs, Inc., Hudson, NH, www.teledyneleemanlabs.com.)

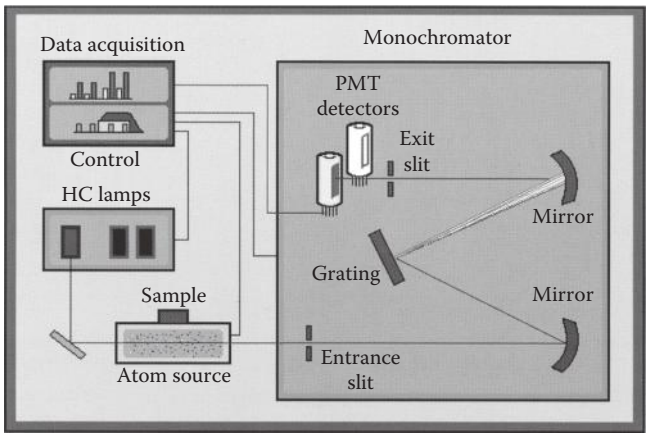


Figure 6.32 The AtomSource GD atomizer incorporated into an analyzer for solid metals and metal alloys (the pulsar system). (Courtesy of Teledyne Leeman Labs, Inc., Hudson, NH, www.teledyneleemanlabs.com.)

6.5.3.4 Cold Vapor Mercury Technique

Mercury is unusual in that it exists as gas-phase free atoms at room temperature. Elemental mercury is a liquid at room temperature, but a liquid with a very high vapor pressure. So it is not necessary to apply heat from a flame or furnace to measure mercury vapor by AAS.

The CV or CVAAS technique requires the *chemical reduction* of mercury in a sample solution to elemental Hg. This is usually done with a strong reducing agent such as sodium borohydride or stannous chloride in a closed reaction system external to the AA spectrometer. The Hg atoms are then purged out of solution (sparged) by bubbling an inert gas through the solution or pumping the postreduction solution through a gas/liquid separator. The gas stream containing the free Hg atoms is passed into an unheated quartz tube cell sitting in the AAS light path. The cell is usually clamped into the position normally occupied by the burner head. Mercury atoms will absorb the HCL or EDL Hg wavelength and the measurement is made. The cell is sometimes heated to prevent water condensation in the cell, but no heat is required to atomize the Hg. The mercury atomization process is a chemical reduction reaction. CVAAS can be performed manually or can be automated using a technique called flow injection, described below. Because Hg determinations are required in many environmental samples including drinking water, instrument companies have built small AAS CV systems just for Hg measurements. Figure 6.33 shows a schematic of an automated dedicated mercury analyzer that uses a gas–liquid separator, a mercury lamp, a long optical path quartz cell, and a solid-state detector. Samples are pumped from the autosampler tray and mixed automatically with the stannous chloride reductant. Stannous chloride will reduce mercuric ion, Hg^{2+}, to Hg^0, but will not reduce organomercury compounds or mercurous ion. Samples are normally predigested with a strong oxidizing agent to ensure that all Hg in the sample is in the form of mercuric ion before adding the stannous chloride (Figure 6.33).

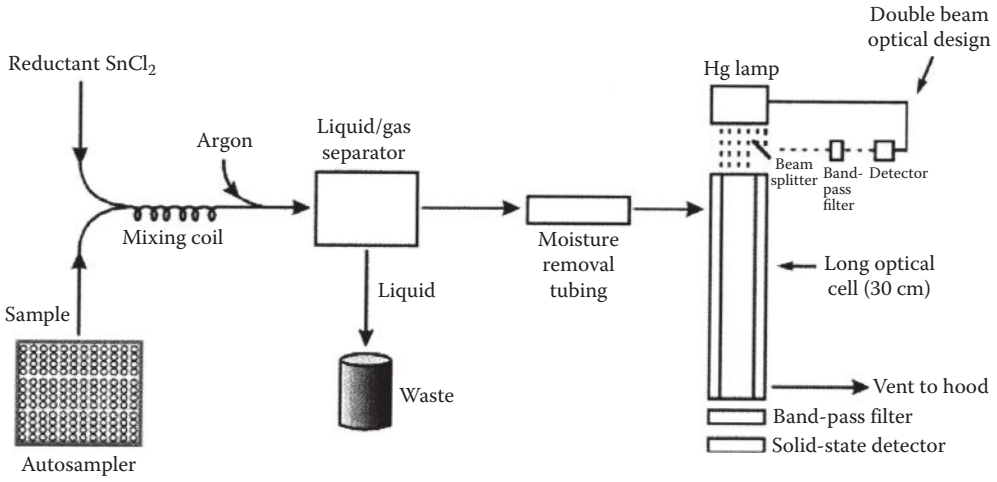


Figure 6.33 Automated CV mercury analyzer. Mercury in the sample is reduced to Hg. The Hg vapor is separated from the solution by a gas–liquid separator and carried to the optical cell. The Hg vapor absorbs the 253.7 nm emission line from the Hg lamp and the amount of atomic absorption is measured using a solid-state detector. (Courtesy of Teledyne Leeman Labs, Inc., Hudson, NH, www.teledyneleemanlabs.com.)

The sensitivity of the CVAAS technique for Hg is about 0.02 ppb, much better than that obtained from FAAS or GFAAS. The reasons are simple; the sampling is 100% efficient and a large sample volume is used. All of the reduced Hg atoms are sent into the light path of the spectrometer, unlike the 5% or so efficiency of a flame nebulizer system. Unlike GFAAS, the CV technique uses large sample volumes (10–100 mL of sample) compared with the microliter sample volume put into a graphite furnace. Incorporating a gold amalgamation accessory can increase the sensitivity of the CVAAS technique even further. The mercury vapor can be trapped and concentrated in the gold as an amalgam at room temperature and then released into the optical path as a concentrated "plug" of vapor by rapidly heating the gold.

For example, the PerkinElmer CVAAS systems are available as flow injection accessories for their AAS systems or dedicated flow injection mercury systems (FIMS), with or with amalgamation capability. Flow injection is described in Section 6.5.3.6. The DL for mercury varies with the system. Using a flow injection atomic spectroscopy (FIAS)-100 or 400 system with amalgamation, the DL for Hg is 0.009 ppb; without an amalgamation system, the DL is 0.2 ppb with a HCL and 0.05 ppb with an EDL. The DL using dedicated FIMS-100 or FIMS-400 systems is <0.005 ppb without an amalgamation and <0.0002 ppb with amalgamation. Dedicated Hg analyzers for the analysis of solid samples are also available, for measuring total Hg in hair, biological tissues, coal, whole blood, food, soil, and the like, using sample pyrolysis. Samples are usually weighed into quartz sample boats and placed into a solid sample autosampler. The DMA-80 from Milestone, Inc. (www. milestonesci.com) has a 40-position autosampler, the ability to store specific sample methods and unattended operation. Mercury results can be obtained in about 6 min with no sample preparation. This can result in faster, cheaper analyses with less hazardous waste to dispose of.

6.5.3.5 Hydride Generation Technique

The HGAAS technique is similar in many ways to CVAAS. The atomizer is a quartz tube cell sitting in the light path of the AA spectrometer. In the HGAAS technique, the cell must be heated. Having the cell clamped above the burner head and lighting an air–acetylene flame accomplishes this. The flame surrounds the cell and heats it. Alternatively, some systems have electrically heated cells.

Sample solutions are reacted with sodium borohydride in a closed reaction system external to the AA spectrometer, as in CVAAS. Some elements will react with the sodium borohydride to form volatile hydride compounds. Arsenic, for example, forms arsine gas, $AsH_3(g)$. The volatile hydrides are sparged from solution by an inert gas and sent to the heated quartz cell. Arsine is a molecule, not an atom, so to measure atomic absorption by arsenic, the hydride species must be decomposed (by breaking bonds) and reduced to free atoms. That is done in the heated quartz cell, and the absorption signal measured as usual. The elements that form volatile hydrides include As, Bi, Ge, Pb, Sb, Se, Sn, and Te. The HGAAS technique can also be operated in manual mode or automated through the use of flow injection techniques. The sensitivity for As, Se, and other elements is excellent because of the efficient transport of the hydride to the atomizer and the larger sample volumes used. DLs for CVAAS and HGAAS are given in Appendix 6.B. Similar analyzers based on atomic fluorescence will be discussed in Chapter 7.

6.5.3.6 Flow Injection Analysis

The term **flow injection analysis** (FIA) describes an automated continuous analytical method in which an aliquot of sample is injected into a continuously flowing carrier stream. The carrier stream usually contains one or more reagents that react with the sample. A transient signal is monitored as the analyte or its reaction product flows past a detector. We have just described CVAAS, where a reduction reaction occurs and the analyte must be swept in a carrier stream into the optical path. This results in a transient signal. All of the components for a FIA are present—sample, reagent,

carrier stream, and transient signal measurement. The same is true of HGAAS. The implementation of FIA for CVAAS and HGAAS permits these determinations to be carried out completely automatically, from sample uptake to printout of concentrations measured.

An FIA system consists of four basic parts: a pump or pumps for regulation of flow, an injection valve to insert sample volumes accurately and reproducibly into the carrier stream, a manifold, and a flow-through detector. A manifold is the term used for the tubing, fittings, mixing coils, and other apparatus used to carry out the desired reactions. The flow-through detector in AAS is the atomizer/detector combination in the spectrometer.

FIA techniques for AAS are described in detail in the reference by Tyson. In addition to automated CVAAS and HGAAS, FIA has been used to automate online dilution for the preparation of calibration curves, online matrix matching of solutions, online preconcentration and extraction for GFAAS, automated digestion of samples, and much more. Commercial FIA systems are available for most AAS instruments.

6.5.3.7 Flame Microsampling

Most FAAS determinations are performed using a continuous flow of solution taken up by the types of nebulizers described in Section 6.2.2.1. Uptake rates in these types of nebulizers can be as high as 5 mL/min, so a significant amount of sample solution is needed for a measurement.

The Shimadzu Scientific Instruments AA-7000 has a flame microsampling option that uses a sampling port, which allows 50–100 μL of sample solution to be injected into the flame for a measurement. This microsampling option can be used when sample is in limited supply. In addition, it minimizes salt buildup on the burner and minimizes waste. The use of such small volumes allows autocalibration using one standard and also permits "autodilution" of the sample, simply by injecting less volume into the flame. More details are available at www.shimadzu.com.

SUGGESTED EXPERIMENTS

For the following experiments, prepare at least 25–100 mL of each solution in acid-cleaned volumetric flasks. If the solutions must be stored before analysis, be certain that the solutions are acidified and that an acid blank is prepared, stored, and analyzed with the samples.

6.1 Prepare solutions of zinc chloride in deionized water containing 1% (v/v) HNO_3. The solutions should contain known concentrations of zinc over the range of 0.5–50.0 ppm and an acid blank of 1% (v/v) nitric acid containing no added zinc should be prepared. Aspirate each solution in turn into the burner. Measure the absorbance of the solutions at 213.9 nm, the zinc resonance line. Plot the relationship between the absorbance and the zinc concentrations. Note the deviation from Beer's law. Indicate the useful analytical range of the calibration curve. If your instrument permits it, try different curve-fitting algorithms and evaluate how they affect the working range of the analysis.

6.2 (a) Look up the wavelength, preferred flame conditions, and linear range for calcium in Appendix 6.A or your instrument "cookbook" and set up the AAS to measure Ca. Prepare 1 L of a stock standard solution of 1000 ppm calcium using calcium phosphate. Prepare 1 L of a 10,000 ppm La standard using lanthanum chloride. Make two sets of calcium working standards. The two sets should have the same concentrations of Ca, but to one set of standards (including the blank), add enough of the La stock solution to make each of these solutions 2000 ppm in La. The La must be added before the Ca standards are made

to volume. For example, to make a 10 ppm Ca standard, take 1 mL of the 1000 ppm Ca stock and dilute it to 100 mL in a volumetric flask. To make the 10 ppm Ca standard with added La, take 1 mL of the Ca stock solution and add it to an empty 100 mL volumetric flask. Add 20 mL of the stock La solution to the same flask and then add deionized water to bring the solution to volume. Optimize the burner position for maximum absorbance. Run both sets of solutions and plot absorbance vs. concentration of Ca. Explain your observations.

(b) Using one of the Ca working standards with La and the same concentration solution without La, aspirate each solution in turn while moving the burner position. Start with the HCL beam just above the burner head (at the base of the flame) and then lower the burner in increments, making note of the absorbance. Construct a flame profile for Ca with and without La by plotting absorbance versus height above the burner. Are the two profiles different? Give a reasonable explanation for the observed flame profiles, based on your reading of the chapter.

(c) You can use the 1–10 ppm Ca working standards with La to determine the amount of Ca in commercial multivitamin tablets. Grind 1–2 coated multivitamin tablets into a fine powder using a mortar and pestle. For tablets containing about 200 mg Ca, accurately weigh out approximately 200 mg of the powder into a beaker and add 20 mL of concentrated HCl (analytical or trace metal grade). Stir well. Quantitatively transfer to a 100 mL volumetric flask that should already contain some deionized water and dilute to the mark with deionized water (Solution A). Pour this solution through coarse filter paper into a beaker. Dilute 10.0 mL of the filtrate to 100 mL with deionized water (Solution B). Test solution: Put 10.0 mL of Solution B and 20.0 mL of La solution into a 100 mL volumetric flask and dilute to the mark with deionized water. Using your instrument cookbook parameters (usually 422.7 nm, air–acetylene flame), run the calibration standards and the test solution. Using the instrument software, determine the amount of Ca in the test solution. The % calcium in the multivitamin is calculated taking into account the two dilutions:

$$\%\text{Ca in tablet} = \left[\frac{(10)(10)(X\ \text{mg Ca/L})(0.1000\ \text{L})}{\text{mg of tablet powder}}\right] \times 10^2$$

For tablets containing more than 200 mg Ca per tablet, use a higher dilution factor.

Why should there be some deionized water in the volumetric flask before you transfer the HCl solution?

Is there undissolved material in the first volumetric flask? If so, the analysis would be described as determining "leachable" calcium.

How does your measured %Ca compare to the amount of Ca listed on the label of the vitamin? If your measured amount is less than expected, explain why. If your measured amount matches what is on the label, why?

6.3 Prepare a series of standard solutions containing sodium at concentrations of 1, 3, 5, 7, 9, and 10 ppm. Measure the absorbance of each solution and plot the absorbance against the sodium concentration. Take water samples from various sources, such as tap water, bottled drinking water, distilled water, river water, distilled water stored in a polyethylene bottle, and distilled water stored in a glass bottle. Determine the sodium concentration in each sample. (If you choose any carbonated bottled waters as samples, allow the sample to "go flat" or loosen the cap and shake it slightly to release the dissolved gases to avoid poor precision in your measurements. If you want to make the comparison, analyze a carbonated water sample that is not flat. The reproducibility of the absorbance measurements should be better in the "flat" sample.) All samples should be at room temperature when measured.

6.4 Prepare a solution containing 20 ppm of Pb as Pb $(NO_3)_2$. Prepare similar solutions containing 20 ppm of Pb as (a) $PbCl_2$, (b) lead oxalate, and (c) lead acetate. Measure the absorbance by the solutions of the Pb resonance line at 283.3 nm. Note the change in absorbance as the compound changes. This is chemical interference. Find a literature method for the elimination of chemical interference using excess ethylenediaminetetraacetic acid (EDTA). Following the literature method, see if the use of EDTA does eliminate the chemical interference you observed.

6.5 Prepare an aqueous 1% HNO_3 solution containing 5 ppm of NaCl; also prepare five separate aqueous 1% HNO_3 solutions (100 mL each) containing 500 ppm of (a) Ca, (b) Mg, (c) Fe, (d) Mn, and (e) K. Take an aliquot of each of these solutions (10–25 mL, but use the same volume for all of the solutions). Spike each aliquot with 5 ppm Na. Be sure to prepare an acid blank and use the same acid for all solution preparation. Measure the absorbance at the Na resonance line at 589.0 nm by all solutions. Compare the absorbance of the Na-spiked solutions (a) through (e) with the aqueous acidic Na solution (i.e., compare all the 5 ppm Na solutions in all matrices). Are any of the signals enhanced compared to the aqueous acidic solution? Which ones? Explain. Are any suppressed? Again, explain. For the solutions (a), (b), (c), (d), and (e) with and without Na, plot two-point standard addition calibration curves and calculate the amount of Na present in the unspiked solutions. Any sodium present was caused by a Na impurity in the original (500 ppm) solutions. Look at the slopes of all five plots. Are they the same? If not, why not?

6.6 For laboratories with a graphite furnace atomizer, the following experiments can be run. The instrument should be set up for the element according to the instrument "cookbook." (a) Dilute the lead solutions from Experiment 6.4 to give 10 ppb lead solutions (or some other concentration within the linear range of your furnace). Using the "cookbook" furnace program and background correction but *no matrix modifiers*, run triplicate injections of each solution (20 μL is a usual injection volume) and observe the peak shape, appearance time of the peak maximum, the peak height, and area. Do the peak maxima appear at the same time? Do all peaks have the same shape? If not, why not? Repeat using a lower pyrolysis temperature. If the background absorbance is printed out, compare the background absorbance values at both sets of conditions. How is the background affected by pyrolysis temperature? Does it depend on the compound? (b) Using background correction *and the matrix modifiers* and furnace program recommended by the "cookbook" for Pb, rerun the 10 ppb solutions of lead compounds. Compare the peak appearance time, shape, and so on with and without matrix modification. Comment on the approach you would use to obtain accurate results, based on your observations. (c) If your system has the ability to run atomization from the tube wall and from a L'vov platform, run the lead nitrate solution both ways (wall and platform). Perform 20 replicate injections at each condition and compare the precision of wall vs. platform measurements. Explain your results.

PROBLEMS

6.1 Why are atomic absorption lines very narrow?

6.2 Why must HCLs or EDLs be used as the radiation source for most AAS instruments? Illustrate schematically an HCL for lead (Pb). How would you make the cathode?

6.3 Why is "modulation" of the line source necessary for accurate results? How is modulation achieved?

6.4 If the radiation source is not modulated, will emission from the analyte in the atomizer result in a positive or negative error? Show your calculation to support your answer.

6.5 Why is atomic absorption not generally used for qualitative analysis?

6.6 What causes chemical interference in AAS? Give three examples.

6.7 How are solid samples analyzed by AAS?

6.8 Several standard solutions of copper were prepared. These were aspirated into a flame and the absorption measured with the following results. Prepare a calibration curve from the data.

Sample Concentration (ppm)	Absorbance
Blank (0.0)	0.002
0.5	0.045
1.0	0.090
1.5	0.135
2.0	0.180
2.5	0.225
3.0	0.270

6.9 Samples of polymer were brought to the lab for a determination of their copper content. They were ashed, the residue was dissolved in mineral acid, and diluted to a known volume. The absorbance of each solution and a digestion blank was measured. Using the calibration curve from Problem 6.8, calculate the copper concentration in each solution and the blank and fill in the following table.

Sample	Absorbance	Concentration (ppm)
Blank	0.006	
A	0.080	
B	0.105	
C	0.220	
D	0.250	

Exactly 2.00 g of each sample were digested and the final solution volume for each sample and the blank was 100.0 mL. Calculate the concentration of copper in the original polymer for each sample.

6.10 What is shown in a Grotrian diagram?

6.11 Why can nonmetal elements not be determined directly by AAS?

6.12 What is the relationship between the amount of light absorbed and the oscillator strength of the transition involved?

6.13 How can the population distribution of atoms in various energy levels be calculated?

6.14 What is the basis for concluding that at temperatures up to 3000 K the great majority of an atom population is in the ground state?

6.15 Describe the two major light sources used in AAS—the HCL and the EDL.

6.16 Why are EDLs used? List the elements that benefit from use of an EDL instead of an HCL.

6.17 What is meant by a flame profile?

6.18 Describe the atomization process that takes place in a flame.

6.19 How does the rapid formation of a stable oxide of the analyte affect its flame profile?

6.20 Define chemical interference. Give an example of how this interference is corrected.

6.21 What is the source of background absorption?

6.22 How is the background corrected?

6.23 Describe the operation of a Zeeman background corrector. Discuss its advantages and disadvantages compared with the use of a deuterium lamp for background correction.

6.24 Describe the operation of a deuterium (D_2) lamp background corrector.

6.25 Draw a schematic of a typical graphite furnace atomization tube.

6.26 Describe the L'vov platform.

6.27 What is the advantage of the L'vov platform?

6.28 What are the advantages of graphite furnace atomizers over flames?

6.29 What are the disadvantages of graphite furnace atomizers versus flames?

6.30 Define ionization interference and give an example. How is this interference corrected?

6.31 You need to determine potassium in serum samples by FAAS. What will you add to correct for ionization interference in the determination?

6.32 Distinguish between spectral and nonspectral interference in AAS.

6.33 The indirect determination of chloride ion by precipitation as silver chloride was described. What metal element could you use to determine sulfate ion in water indirectly by AAS? Describe how you would do this experiment and give an example calculation for a sulfate solution containing 200 mg SO_4^{2-}/L. (You may need to consult some external references on this question.)

6.34 Briefly explain the advantages of the newly developed HR-CS AAS compared to line source instruments.

6.A APPENDIX

Absorption Wavelengths, Preferred Flames, and Characteristic Concentrations for Elements by FAAS

Abbreviations Used

A.A.	Air–acetylene flame
Char. conc.	Characteristic concentration in ppm (mg/L) in aqueous solution equivalent to an absorbance = 0.2.
EDL	Electrodeless discharge lamp
Linear range	The upper concentration limit in ppm of the linear region of the concentration–absorbance plot.
N.A.	Nitrous oxide–acetylene flame
ox.	Oxidizing flame (excess oxidant, either air or nitrous oxide). An oxidizing A.A. flame is clear and blue in color. Oxidizing conditions are rarely used for N.A. flames.
red.	Reducing flame (excess fuel, acetylene.) A reducing A.A. flame is yellow in color; a reducing N.A. flame is red in color.

Absorption Wavelength (nm)	Preferred Flame	Char. Conc. (ppm)	Linear Range (ppm)
Aluminum			
309.3	N.A. (red.)	1.1	100.0
396.2	N.A. (red.)	1.1	150.0
308.2	N.A. (red.)	1.5	150.0
394.4	N.A. (red.)	2.2	—
237.3	N.A. (red.)	3.3	—
236.7	N.A. (red.)	4.8	—
257.5	N.A. (red.)	6.7	—
Antimony			
217.6	A.A. (ox.)	0.55	30.0
206.8	A.A. (ox.)	0.85	50.0
231.2	A.A. (ox.)	1.3	50.0
Arsenic[a]			
189.0	A.A. (ox.)	0.78	180.0
193.7	A.A. (ox.)	1.0	100.0
197.2	A.A. (ox.)	2.0	250.0
Barium			
553.5	N.A. (red.)	0.46	20.0
350.1	N.A. (red.)	5.6	—
Beryllium			
234.8	N.A. (red.)	0.025	1.0

(*continued*)

(continued)

Absorption Wavelength (nm)	Preferred Flame	Char. Conc. (ppm)	Linear Range (ppm)
Bismuth			
223.1	A.A. (ox.)	0.45	20.0
306.8	A.A. (ox.)	1.3	100.0
206.2	A.A. (ox.)	3.7	—
227.7	A.A. (ox.)	6.1	—
Boron			
249.7	N.A. (red.)	13.0	400.0
208.9	N.A. (red.)	27.0	—
Cadmium			
228.8	A.A. (ox.)	0.028	2.0
326.1	A.A. (ox.)	11.0	—
Calcium			
422.7	A.A. (ox.)	0.092	5.0
239.9	A.A. (ox.)	13.0	800.0
Cerium			
520.0	N.A. (red.)	30	—
Cesium			
852.1	A.A. (ox.)	0.21	15.0
894.4	A.A. (ox.)	0.40	15.0
455.5	A.A. (ox.)	25.0	—
459.3	A.A. (ox.)	94.0	—
Chromium			
357.9	A.A. (red.)	0.078	5.0
359.3	A.A. (red.)	0.10	7.0
360.5	A.A. (red.)	0.14	7.0
425.4	A.A. (red.)	0.20	7.0
Cobalt			
240.7	A.A. (ox.)	0.12	3.5
242.5	A.A. (ox.)	0.15	2.0
241.2	A.A. (ox.)	0.22	3.0
252.1	A.A. (ox.)	0.28	7.0
352.7	A.A. (ox.)	3.2	—
Copper			
324.8	A.A. (ox.)	0.077	5.0
327.4	A.A. (ox.)	0.17	5.0
216.5	A.A. (ox.)	0.17	20.0
222.6	A.A. (ox.)	1.1	50.0
249.2	A.A. (ox.)	5.8	100.0
224.4	A.A. (ox.)	14.0	—
244.2	A.A. (ox.)	24.0	—
Dysprosium			
421.2	N.A. (red.)	0.70	20.0
404.6	N.A. (red.)	0.97	50.0
418.7	N.A. (red.)	1.0	—
419.5	N.A. (red.)	1.3	—

(continued)

Absorption Wavelength (nm)	Preferred Flame	Char. Conc. (ppm)	Linear Range (ppm)
Erbium			
400.8	N.A. (red.)	0.068	40.0
415.1	N.A. (red.)	1.2	150.0
389.3	N.A. (red.)	2.3	150.0
Europium			
459.4	N.A. (red.)	0.67	200.0
462.7	N.A. (red.)	0.79	300.0
466.2	N.A. (red.)	0.98	—
Gadolinium			
407.9	N.A. (red.)	19.0	1,000
368.4	N.A. (red.)	19.0	1,000
405.8	N.A. (red.)	22.0	—
Gallium			
287.4	N.A. (red.)	1.3	100.0
294.4	N.A. (red.)	1.1	50.0
417.2	N.A. (red.)	1.5	100.0
403.3	N.A. (red.)	2.8	400.0
Germanium			
265.1	N.A. (red.)	2.2	200.0
259.3	N.A. (red.)	5.2	300.0
271.0	N.A. (red.)	5.0	400.0
275.5	N.A. (red.)	6.1	—
Gold			
242.8	A.A. (ox.)	0.33	50.0
267.6	A.A. (ox.)	0.57	60.0
274.8	A.A. (ox.)	210.0	—
312.8	A.A. (ox.)	210.0	—
Hafnium			
286.6	N.A. (red.)	11.0	500.0
294.1	N.A. (red.)	14.0	—
307.3	N.A. (red.)	16.0	—
Holmium			
410.4	N.A. (red.)	0.87	50.0
405.4	N.A. (red.)	1.0	50.0
416.3	N.A. (red.)	1.4	70.0
Indium			
304.9	A.A. (ox.)	0.76	80.0
325.6	A.A. (ox.)	0.80	60.0
410.5	A.A. (ox.)	2.5	200.0
Iridium			
264.0	A.A. (red.)	12.0	1,000.0
266.5	A.A. (red.)	13.0	—
285.0	A.A. (red.)	15.0	—

(*continued*)

(continued)

Absorption Wavelength (nm)	Preferred Flame	Char. Conc. (ppm)	Linear Range (ppm)
Iron			
248.3	A.A. (ox.)	0.11	6.0
252.3	A.A. (ox.)	0.18	10.0
248.8	A.A. (ox.)	0.19	10.0
302.1	A.A. (ox.)	0.40	10.0
296.7	A.A. (ox.)	0.81	20.0
Lanthanum			
550.1	N.A. (red.)	48.0	1,000.0
418.7	N.A. (red.)	63.0	2,000.0
495.0	N.A. (red.)	72.0	3,000.0
Lead			
217.0	A.A. (ox.)	0.19	20.0
283.3	A.A. (ox.)	0.45	20.0
205.3	A.A. (ox.)	5.4	—
202.2	A.A. (ox.)	7.1	—
Lithium			
670.8	A.A. (ox.)	0.035	3.0
323.3	A.A. (ox.)	10.0	—
610.4	A.A. (ox.)	150.0	—
Lutetium			
336.0	N.A. (red.)	6.0	500.0
331.2	N.A. (red.)	11.0	—
337.7	N.A. (red.)	12.0	—
451.9	N.A. (red.)	66.0	—
Magnesium			
285.2	A.A. (ox.)	0.0078	0.50
202.6	A.A. (ox.)	0.19	10.0
Manganese			
279.5	A.A. (ox.)	0.052	2.0
279.8	A.A. (ox.)	0.067	5.0
280.1	A.A. (ox.)	0.11	5.0
Mercury[a]			
253.7	A.A. (ox.)	4.2	300.0
Molybdenum			
313.3	N.A. (red.)	0.67	40.0
317.0	N.A. (red.)	1.1	30.0
319.4	N.A. (red.)	1.4	60.0
390.3	N.A. (red.)	2.9	—
Neodymium			
492.4	N.A. (red.)	7.3	200.0
463.4	N.A. (red.)	11.0	200.0
471.9	N.A. (red.)	19.0	—
Nickel			
232.0	A.A. (ox.)	0.14	2.0
231.1	A.A. (ox.)	0.20	5.0
352.5	A.A. (ox.)	0.39	20.0
341.5	A.A. (ox.)	0.40	—

(continued)

Absorption Wavelength (nm)	Preferred Flame	Char. Conc. (ppm)	Linear Range (ppm)
Niobium			
334.4	N.A. (red.)	15.0	600.0
334.9	N.A. (red.)	15.0	600.0
408.0	N.A. (red.)	20.0	—
412.4	N.A. (red.)	26.0	—
353.5	N.A. (red.)	42.0	—
374.0	N.A. (red.)	47.0	—
Osmium			
290.9	N.A. (red.)	1.0	10–200
305.9	N.A. (red.)	1.6	—
263.7	N.A. (red.)	1.8	—
301.8	N.A. (red.)	3.0	—
Palladium			
244.8	A.A. (ox.)	0.22	10.0
247.6	A.A. (ox.)	0.25	15.0
276.3	A.A. (ox.)	0.74	—
340.5	A.A. (ox.)	0.72	—
Phosphorus[a]			
178.3	N.A. (red.)	5.0	2,000.0
213.6	N.A. (red.)	290.0	10,000.0
214.9	N.A. (red.)	460.0	20,000.0
Platinum			
265.9	A.A. (ox.)	2.2	60.0
306.5	A.A. (ox.)	3.2	—
262.8	A.A. (ox.)	4.2	—
283.0	A.A. (ox.)	5.4	—
293.0	A.A. (ox.)	6.1	—
Potassium			
766.5	A.A. (ox.)	0.043	2.0
769.9	A.A. (ox.)	0.083	20.0
404.4	A.A. (ox.)	7.8	600.0
Praseodymium			
495.1	N.A. (red.)	39.0	5,000.0
513.3	N.A. (red.)	61.0	—
492.5	N.A. (red.)	79.0	—
Rhenium			
346.0	N.A. (red.)	14.0	500.0
346.5	N.A. (red.)	24.0	500.0
345.2	N.A. (red.)	36.0	1,000.0
Rhodium			
343.5	A.A. (ox.)	0.20	15.0
369.2	A.A. (ox.)	0.35	20.0
339.7	A.A. (ox.)	0.45	15.0
350.3	A.A. (ox.)	0.65	20.0

(*continued*)

(continued)

Absorption Wavelength (nm)	Preferred Flame	Char. Conc. (ppm)	Linear Range (ppm)
Rubidium			
780.0	A.A. (ox.)	0.11	5.0
794.8	A.A. (ox.)	0.19	5.0
420.2	A.A. (ox.)	8.7	—
421.6	A.A. (ox.)	19.0	—
Ruthenium			
349.9	A.A. (ox.)	0.66	20.0
372.8	A.A. (ox.)	0.86	20.0
379.9	A.A. (ox.)	1.6	—
392.6	A.A. (ox.)	7.5	—
Samarium			
429.7	N.A. (red.)	6.7	400.0
476.0	N.A. (red.)	12.0	—
511.7	N.A. (red.)	14.0	—
Scandium			
391.2	N.A. (red.)	0.30	25.0
390.8	N.A. (red.)	0.40	25.0
402.4	N.A. (red.)	0.41	25.0
408.2	N.A. (red.)	2.1	25.0
Selenium[a]			
196.0	A.A. (ox.)	0.5	50.0
204.0	A.A. (ox.)	1.5	—
206.3	A.A. (ox.)	6.0	—
207.5	A.A. (ox.)	20.0	—
Silicon			
251.6	N.A. (red.)	2.1	150.0
251.9	N.A. (red.)	3.0	200.0
250.7	N.A. (red.)	5.9	—
252.9	N.A. (red.)	6.1	—
252.4	N.A. (red.)	7.0	—
Silver			
328.1	A.A. (ox.)	0.054	4.0
338.3	A.A. (ox.)	0.11	10.0
Sodium			
589.0	A.A. (ox.)	0.012	1.0
330.2	A.A. (ox.)	1.7	—
Strontium			
460.7	N.A. (red.)	0.11	5.0
407.8	N.A. (red.)	2.0	20.0
Sulfur			
180.7	A.A. (ox.)	9.0	—
Tantalum			
271.5	N.A. (red.)	11.0	1,200.0
260.9	N.A. (red.)	23.0	—
277.6	N.A. (red.)	24.0	—

(continued)

Absorption Wavelength (nm)	Preferred Flame	Char. Conc. (ppm)	Linear Range (ppm)
Technetium			
261.4	A.A. (red.)	3.0	70.0
260.9	A.A. (red.)	12.0	1,000.0
429.7	A.A. (red.)	20.0	1,000.0
Tellurium			
214.3	A.A. (ox.)	0.43	20.0
225.9	A.A. (ox.)	4.4	—
238.6	A.A. (ox.)	18.0	—
Terbium			
432.6	N.A. (red.)	5.9	200.0
431.9	N.A. (red.)	6.8	200.0
390.1	N.A. (red.)	9.5	400.0
406.2	N.A. (red.)	11.0	200.0
Thallium			
276.8	A.A. (ox.)	0.67	40.0
377.6	A.A. (ox.)	1.6	100.0
238.0	A.A. (ox.)	3.7	200.0
258.0	A.A. (ox.)	13.0	—
Thorium			
324.6	N.A. (red.)	500	—
Thulium			
371.8	N.A. (red.)	0.45	60.0
410.6	N.A. (red.)	0.66	50.0
374.4	N.A. (red.)	0.74	60.0
409.4	N.A. (red.)	0.80	100.0
Tin[a]			
224.6	N.A. (red.)	1.7	300.0
235.5	N.A. (red.)	2.2	—
286.3	N.A. (red.)	3.2	400.0
Titanium			
364.3	N.A. (red.)	1.8	100.0
365.4	N.A. (red.)	1.9	100.0
320.0	N.A. (red.)	2.0	200.0
363.5	N.A. (red.)	2.4	200.0
Tungsten			
255.1	N.A. (red.)	9.6	500.0
294.4	N.A. (red.)	13.0	1,500.0
268.1	N.A. (red.)	12.0	1,000.0
272.4	N.A. (red.)	13.0	500.0
Uranium			
351.5	N.A. (red.)	110.0	5,000.0
358.5	N.A. (red.)	47.0	—
356.7	N.A. (red.)	76.0	—

(*continued*)

(continued)

Absorption Wavelength (nm)	Preferred Flame	Char. Conc. (ppm)	Linear Range (ppm)
Vanadium			
318.4	N.A. (red.)	1.9	200.0
306.6	N.A. (red.)	4.6	200.0
306.0	N.A. (red.)	4.7	400.0
305.6	N.A. (red.)	6.2	500.0
320.2	N.A. (red.)	13.0	—
390.2	N.A. (red.)	13.0	—
Ytterbium			
398.8	N.A. (red.)	0.12	15.0
346.4	N.A. (red.)	0.45	15.0
246.4	N.A. (red.)	1.0	—
267.2	N.A. (red.)	5.0	—
Yttrium			
410.2	N.A. (red.)	1.6	50.0
407.7	N.A. (red.)	1.9	50.0
412.8	N.A. (red.)	1.9	50.0
362.1	N.A. (red.)	2.9	100.0
Zinc			
213.9	A.A. (ox.)	0.018	1.0
307.6	A.A. (ox.)	79.0	—
Zirconium			
360.1	N.A. (red.)	7.0	600.0
303.0	N.A. (red.)	11.0	600.0
301.2	N.A. (red.)	11.0	600.0
298.5	N.A. (red.)	13.0	—
362.4	N.A. (red.)	17.0	—

Source: The data are from *Analytical Methods for Atomic Absorption Spectrometry*, PerkinElmer, Inc., Shelton, CT, 1994. **[© 1993–2014 PerkinElmer, Inc. All rights reserved. Printed with permission.** (www.perkinelmer.com).**]**

Note: At least the three most intense lines (where available) are listed for each element. Some elements (e.g., Hg, S, P) have their most intense lines in the vacuum UV region (<190 nm); these lines are not accessible on most commercial AAS systems. Data not from the aforementioned reference are courtesy of the late Dr. Fred Brech.

[a] The Char. conc. obtained by using EDL.

6.B APPENDIX

Table B.1 Representative Atomic Spectroscopy DLs (μg/L)

Element	Flame AA	Hg/Hydride	Graphite Furnace	ICP Emission	ICP-MS
Ag	1.5		0.005	0.6	0.002
Al	45		0.1	1	0.005[a]
As	150	0.03	0.05	1	0.0006[b]
Au	9		0.15	1	0.0009
B	1,000		20	1	0.003[c]
Ba	15		0.35	0.03	0.00002[d]
Be	1.5		0.008	0.09	0.003
Bi	30	0.03	0.05	1	0.0006
Br					0.2
C					0.8[e]
Ca	1.5		0.01	0.05	0.0002[d]
Cd	0.8		0.002	0.1	0.00009[d]
Ce				1.5	0.0002
Cl					12
Co	9		0.15	0.2	0.0009
Cr	3		0.004	0.2	0.0002[d]
Cs	15				0.0003
Cu	1.5		0.014	0.4	0.0002[c]
Dy	50			0.5	0.0001[f]
Er	60			0.5	0.0001
Eu	30			0.2	0.00009
F					372
Fe	5		0.06	0.1	0.0003[d]
Ga	75			1.5	0.0002
Gd	1,800			0.9	0.0008[g]
Ge	300			1	0.001[h]
Hf	300			0.5	0.0008
Hg	300	0.009	0.6	1	0.016[i]
Ho	60			0.4	0.0006
I					0.002
In	30			1	0.0007
Ir	900		3.0	1	0.001
K	3		0.005	1	0.0002[d]
La	3,000			0.4	0.0009
Li	0.8		0.06	0.3	0.001[c]
Lu	1,000			0.1	0.00005
Mg	0.15		0.004	0.04	0.0003[c]
Mn	1.5		0.005	0.1	0.00007[d]
Mo	45		0.03	0.5	0.001
Na	0.3		0.005	0.5	0.0003[c]
Nb	1,500			1	0.0006
Nd	1,500			2	0.0004
Ni	6		0.07	0.5	0.0004[c]
Os	(120)			6	
P	75,000		130	4	0.1[a]
Pb	15		0.05	1	0.00004[d]

(*continued*)

Table B.1 (continued) Representative Atomic Spectroscopy DLs (μg/L)

Element	Flame AA	Hg/Hydride	Graphite Furnace	ICP Emission	ICP-MS
Pd	30		0.09	2	0.0005
Pr	7,500			2	0.00009
Pt	60		2.0	1	0.002
Rb	3		0.03	5	0.0004
Re	750			0.5	0.0003
Rh	6			5	0.0002
Ru	100		1.0	1	0.0002
S				10	28[j]
Sb	45	0.15	0.05	2	0.0009
Sc	30			0.1	0.004
Se	100	0.03	0.05	2	0.0007[b]
Si	90		1.0	10	0.03[a]
Sm	3,000			2	0.0002
Sn	150		0.1	2	0.0005[a]
Sr	3		0.025	0.05	0.00002[d]
Ta	1,500			1	0.0005
Tb	900			2	0.00004
Te	30	0.03	0.1	2	0.0008[k]
Th				2	0.0004
Ti	75		0.35	0.4	0.003[l]
Tl	15		0.1	2	0.0002
Tm	15			0.6	0.00006
U	15,000			10	0.0001
V	60		0.1	0.5	0.0005
W	1,500			1	0.005
Y	75			0.2	0.0002
Yb	8			0.1	0.0002[m]
Zn	1.5		0.02	0.2	0.0003[d]
Zr	450			0.5	0.0003

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Notes:

All DLs are given in micrograms per liter and were determined using elemental standards in dilute aqueous solution. All DLs are based on a 98% confidence level (3 standard deviations or 3 SD). All atomic absorption DLs were determined using instrumental parameters optimized for the individual element, including the use of System 2 EDLs where available. All Optima ICP-OES DLs were obtained under simultaneous multielement conditions with the axial view of a dual-view plasma using a cyclonic spray chamber and a concentric nebulizer. CV mercury DLs were determined with a FIAS-100 or FIAS-400 flow injection system with amalgamation accessory. Hydride DLs shown were determined using an MHS-15 Hg/hydride system. GFAA DLs were determined on a PerkinElmer AA using 50 μL sample volumes, an integrated platform, and full stabilized temperature platform furnace (STPF) conditions. Unless otherwise noted, ICP-MS DLs were determined using a PerkinElmer ICP-MS equipped with Ryton™ spray chamber, Type II cross-flow nebulizer, and nickel cones. All DLs were determined using 3 s integration time and a minimum of eight measurements.

Letters following ICP-MS DLs refer to the use of specialized conditions or a different model instrument: [a]Run on a PerkinElmer ICP-MS in standard mode using Pt cones and quartz sample introduction system. [b]Run on a PerkinElmer ICP-MS in dynamic reaction cell (DRC) mode using Pt cones and a quartz sample introduction system. [c]Run on a PerkinElmer ICP-MS in standard mode in a Class-100 clean room using Pt cones and quartz sample introduction. [d]Run on a PerkinElmer ICP-MS in DRC mode in a Class-100 clean room using Pt cones and quartz sample introduction. [e]Using C-13. [f]Using Dy-163. [g]Using Gd-157. [h]Using Ge-74. [i]Using Hg-202. [j]Using S-34. [k]Using Te-125. [l]Using Ti-49. [m]Using Yb-173.

Osmium FAAS data is provided by the authors, not by PerkinElmer.

Table B.2 Sensitivity (1% Absorption) in FAAS

Element	λ (nm)	Sensitivity (ppm)	Element	λ (nm)	Sensitivity (ppm)
Al	309.2	1.0	Nd	463.4	10.0
Sb	217.6	0.1	Ni	232.0	0.1
As	193.7	1.0	Nb	334.9	20.0
Ba	553.5	0.2	Pd	247.6	0.5
Be	234.9	0.1	Pt	265.9	1.0
Bi	223.1	0.1	K	766.5	0.1
B	249.7	30.0	Pr	495.1	10.0
Ca	442.7	0.05	Re	346.0	15.0
Cs	852.1	0.1	Rh	343.5	0.1
Cr	357.9	0.1	Rb	780.0	0.1
Co	240.7	0.1	Ru	349.9	0.8
Cu	324.7	0.1	Sm	429.7	10.0
Dy	421.2	1.0	Sc	391.2	1.0
Er	400.8	1.0	Se	196.1	1.0
Eu	459.4	2.0	Si	251.6	0.8
Gd	368.4	20.0	Ag	328.1	2.5
Ga	287.4	1.0	Na	589.0	2.5
Ge	265.2	2.0	Sr	460.7	0.1
Au	242.8	1.0	Ta	471.4	10.0
Hf	307.2	10.0	Te	214.3	0.5
Ho	410.4	2.0	Th	377.6	0.4
In	304.0	0.1	Sn	235.4	0.5
Fe	248.3	0.1	Ti	364.3	1.0
La	392.8	75.0	W	400.9	1.0
Pb	217.0	0.05	U	351.5	100.0
Li	670.7	0.03	V	318.4	1.0
Mg	285.2	0.001	Y	398.8	2.0
Mn	279.5	0.05	Zn	218.9	0.01
Hg	253.7	1.0	Zr	360.1	50.0
Mo	313.3	0.1			

Note: Data includes air–acetylene and nitrous oxide–acetylene flames as appropriate for the element (see Appendix 6.A for standard flame).

Table B.3 Sensitivity (1% Absorption) in the Graphite Tube Furnace (HGA-70)

Element	Absolute Sensitivity (g × 10^{-12})	20 µL Solution (mg/µL)
Al	150	0.007
As	160	0.008
Be	3.4	0.0002
Bi	280	0.014
Ca	3.1	0.05
Cd	0.8	0.00004
Co	120	0.006
Cr	18	0.01
Cs	71	0.004
Cu	45	0.02
Ga	1,200	0.06
Hg	15,000	1.5
Mn	7	0.01
Ni	330	0.10
Pb	23	0.001
Pd	250	0.013
Pt	740	0.02
Rb	41	0.002
Sb	510	0.15
Si	24	0.10
Sn	5,500	0.2
Sr	31	0.0015
Ti	280	0.5
Tl	90	0.1
V	320	0.2
Zn	2.1	0.0001

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