

Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry

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and
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Second Edition

THE PERKIN-ELMER CORPORATION

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1 THEORETICAL CONCEPTS AND DEFINITIONS

THE ATOM AND ATOMIC SPECTROSCOPY

The science of atomic spectroscopy has yielded three techniques for analytical use: atomic emission, atomic absorption, and atomic fluorescence. In order to understand the relationship of these techniques to each other, it is necessary to have an understanding of the atom itself and of the atomic process involved in each technique.

The atom is made up of a nucleus surrounded by electrons. Every element has a specific number of electrons which are associated with the atomic nucleus in an orbital structure which is unique to each element. The electrons occupy orbital positions in an orderly and predictable way. The lowest energy, most stable electronic configuration of an atom, known as the “ground state”, is the normal orbital configuration for an atom. If energy of the right magnitude is applied to an atom, the energy will be absorbed by the atom, and an outer electron will be promoted to a less stable configuration or “excited state”. As this state is unstable, the atom will immediately and spontaneously return to its ground state configuration. The electron will return to its initial, stable orbital position, and radiant energy equivalent to the amount of energy initially absorbed in the excitation process will be emitted. The process is illustrated in Figure 1-1. Note that in Step 1 of the process, the excitation is forced by supplying energy. The decay process in Step 2, involving the emission of light, occurs spontaneously.

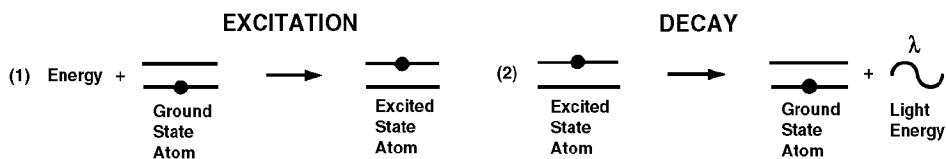


Figure 1-1. Excitation and decay processes.

The wavelength of the emitted radiant energy is directly related to the electronic transition which has occurred. Since every element has a unique electronic structure, the wavelength of light emitted is a unique property of each individual element. As the orbital configuration of a large atom may be complex, there are many electronic transitions which can occur, each transition resulting in the emission of a characteristic wavelength of light, as illustrated in Figure 1-2.



Figure 1-2. Energy transitions.

The process of excitation and decay to the ground state is involved in all three fields of atomic spectroscopy. Either the energy absorbed in the excitation process or the energy emitted in the decay process is measured and used for analytical purposes. In atomic emission, a sample is subjected to a high energy, thermal environment in order to produce excited state atoms, capable of emitting light. The energy source can be an electrical arc, a flame, or more recently, a plasma. The emission spectrum of an element exposed to such an energy source consists of a collection of the allowable emission wavelengths, commonly called emission lines, because of the discrete nature of the emitted wavelengths. This emission spectrum can be used as a unique characteristic for qualitative identification of the element. Atomic emission using electrical arcs has been widely used in qualitative analysis.

Emission techniques can also be used to determine how much of an element is present in a sample. For a “quantitative” analysis, the intensity of light emitted at the wavelength of the element to be determined is measured. The emission intensity at this wavelength will be greater as the number of atoms of the analyte element increases. The technique of flame photometry is an application of atomic emission for quantitative analysis.

If light of just the right wavelength impinges on a free, ground state atom, the atom may absorb the light as it enters an excited state in a process known as atomic ab-

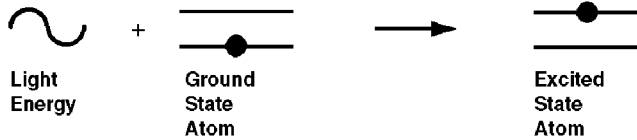


Figure 1-3. The atomic absorption process.

sorption. This process is illustrated in Figure 1-3. Note the similarity between this illustration and the one in Step 1 of Figure 1-1. The light which is the source of atom excitation in Figure 1-3 is simply a specific form of energy. The capability of an atom to absorb very specific wavelengths of light is utilized in atomic absorption spectrophotometry.

ATOMIC ABSORPTION PROCESS

The quantity of interest in atomic absorption measurements is the amount of light at the resonant wavelength which is absorbed as the light passes through a cloud of atoms. As the number of atoms in the light path increases, the amount of light absorbed increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of analyte element present can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual elements in the presence of others.

The atom cloud required for atomic absorption measurements is produced by supplying enough thermal energy to the sample to dissociate the chemical compounds into free atoms. Aspirating a solution of the sample into a flame aligned in the light beam serves this purpose. Under the proper flame conditions, most of the atoms will remain in the ground state form and are capable of absorbing light at the analytical wavelength from a source lamp. The ease and speed at which precise and accurate determinations can be made with this technique have made atomic absorption one of the most popular methods for the determination of metals.

A third field in atomic spectroscopy is atomic fluorescence. This technique incorporates aspects of both atomic absorption and atomic emission. Like atomic absorption, ground state atoms created in a flame are excited by focusing a beam of light into the atomic vapor. Instead of looking at the amount of light absorbed in the process, however, the emission resulting from the decay of the atoms excited by the source light is measured. The intensity of this "fluorescence" increases with increasing atom concentration, providing the basis for quantitative determination.

The source lamp for atomic fluorescence is mounted at an angle to the rest of the optical system, so that the light detector sees only the fluorescence in the flame and not the light from the lamp itself. It is advantageous to maximize lamp intensity with atomic fluorescence since sensitivity is directly related to the number of excited atoms which is a function of the intensity of the exciting radiation.

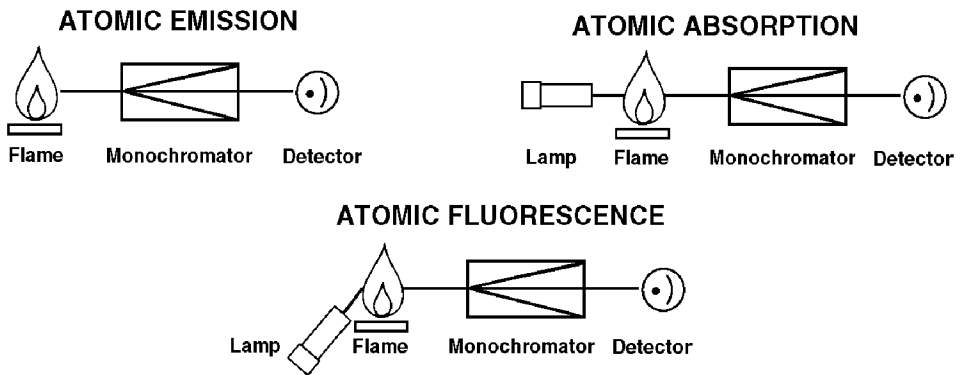


Figure 1-4. Atomic spectroscopy systems.

Figure 1-4 illustrates how the three techniques just described are implemented. While atomic absorption is the most widely applied of the three techniques and usually offers several advantages over the other two, particular benefits may be gained with either emission or fluorescence in special analytical situations. This is especially true of emission, which will be discussed in more detail in a later chapter.

QUANTITATIVE ANALYSIS BY ATOMIC ABSORPTION

The atomic absorption process is illustrated in Figure 1-5. Light at the resonance wavelength of initial intensity, I_0 , is focused on the flame cell containing ground state atoms. The initial light intensity is decreased by an amount determined by the atom concentration in the flame cell. The light is then directed onto the detector where the reduced intensity, I , is measured. The amount of light absorbed is determined by comparing I to I_0 .

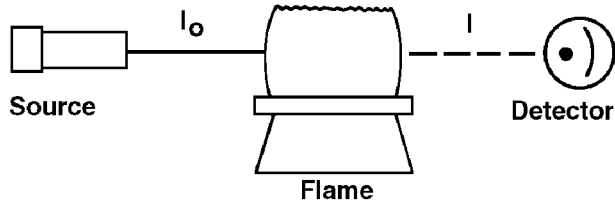


Figure 1-5. The atomic absorption process.

Several related terms are used to define the amount of light absorption which has taken place. The “transmittance” is defined as the ratio of the final intensity to the initial intensity.

$$T = I/I_0$$

Transmittance is an indication of the fraction of initial light which passes through the flame cell to fall on the detector. The “percent transmission” is simply the transmittance expressed in percentage terms.

$$\%T = 100 \times I/I_0$$

The “percent absorption” is the complement of percent transmission defining the percentage of the initial light intensity which is absorbed in the flame.

$$\%A = 100 - \%T$$

These terms are easy to visualize on a physical basis. The fourth term, “absorbance”, is purely a mathematical quantity.

$$A = \log (I_0/I)$$

Absorbance is the most convenient term for characterizing light absorption in absorption spectrophotometry, as this quantity follows a linear relationship with concentration. Beer’s Law defines this relationship:

$$A = abc$$

where “A” is the absorbance; “a” is the absorption coefficient, a constant which is characteristic of the absorbing species at a specific wavelength; “b” is the length of the light path intercepted by the absorption species in the absorption cell; and “c” is the concentration of the absorbing species. This equation simply states that the absorbance is directly proportional to the concentration of the absorbing species for a given set of instrumental conditions.

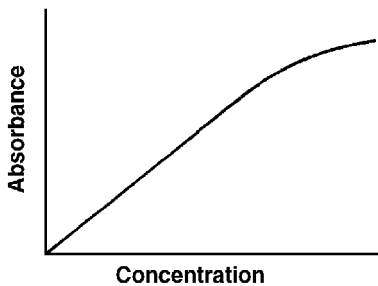


Figure 1-6. Concentration versus absorbance.

This directly proportional behavior between absorbance and concentration is observed in atomic absorption. When the absorbances of standard solutions containing known concentrations of analyte are measured and the absorbance data are plotted against concentration, a calibration relationship similar to that in Figure 1-6 is established. Over the region where the Beer's Law relationship is observed, the calibration yields a straight line. As the concentration and absorbance increase, nonideal behavior in the absorption process can cause a deviation from linearity, as shown.

After such a calibration is established, the absorbance of solutions of unknown concentrations may be measured and the concentration determined from the calibration curve. In modern instrumentation, the calibration can be made within the instrument to provide a direct readout of unknown concentrations. Since the advent of microcomputers, accurate calibration, even in the nonlinear region, is simple.

CHARACTERISTIC CONCENTRATION AND DETECTION LIMITS

Characteristic concentration and detection limit are terms which describe instrument performance characteristics for an analyte element. While both parameters depend on the absorbance observed for the element, each defines a different performance specification, and the information to be gained from each term is different.

Characteristic Concentration

The “characteristic concentration” (sometimes called “sensitivity”) is a convention for defining the magnitude of the absorbance signal which will be produced by a given concentration of analyte. For flame atomic absorption, this term is expressed as the concentration of an element in milligrams per liter (mg/L) required to produce a 1% absorption (0.0044 absorbance) signal.

$$\text{Char Conc. (mg/L)} = \frac{\text{Conc. of Std. (mg/L)} \times 0.0044}{\text{measured absorbance}}$$

As long as measurements are made in the linear working region, the characteristic concentration of an element can be determined by reading the absorbance produced by a known concentration of the element and using the above equation.

There are several practical reasons for wanting to know the value of the characteristic concentration for an element. Knowing the expected characteristic concentration allows an operator to determine if all instrumental conditions are optimized and if the instrument is performing up to specifications by simply measuring the absorbance of a known concentration and comparing the results to the expected value. A known characteristic concentration value also allows one to predict the absorbance range which will be observed from a known concentration range or to determine the concentration range which would produce optimum absorbance levels.

Detection Limits

It should be noted that, while the magnitude of the absorbance signal can be predicted from the value given for characteristic concentration, no information is given on how small of an absorbance signal can be measured. Therefore, it is not possible to predict the minimum measurable concentration from a known characteristic concentration value. To determine this quantity, more information on the nature of the measured absorbance signal must be considered.

The smallest measurable concentration of an element will be determined by the magnitude of absorbance observed for the element (characteristic concentration) and the stability of the absorbance signal. An unstable or “noisy” signal makes it more difficult to distinguish small changes in observed absorbance which are due to small concentration differences, from those random variations due to “baseline noise.” Figure 1-7 illustrates the concept of the effect of noise on the quantitation of small absorbance signals. Signal "A" and signal "B" have the same magnitude.

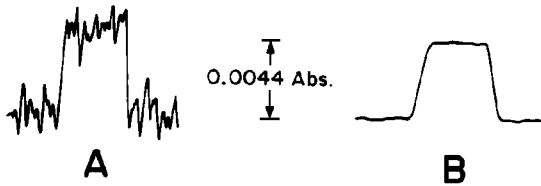


Figure 1-7. AA measurements near detection limits.

However, the much lower variability ("noise") of signal "B" permits even smaller signals to be detected. The sensitivity of the two signals is the same, but there is a real difference in detection limits.

The term "detection limit" incorporates a consideration of both signal size and baseline noise to give an indication of the lowest concentration of an element which can be measured. The detection limit is defined by the IUPAC as the concentration which will give an absorbance signal three times the magnitude of the baseline noise. The baseline noise may be statistically quantitated typically by making 10 or more replicate measurements of the baseline absorbance signal observed for an analytical blank, and determining the standard deviation of the measurements. The detection limit is then defined as the concentration which will produce an absorbance signal three times the standard deviation of the blank.

Routine analytical measurements at the detection limit are difficult, due to the fact that, by definition, noise makes up a significant percentage of the total measurable signal. By definition, the precision obtained at detection limit levels is $\pm 33\%$ RSD (relative standard deviation) when a three standard deviation criterion is used. Therefore, while it is possible to distinguish analyte concentrations at the detection limit from zero, for good precision it is necessary to limit routine analytical work to concentrations higher than the detection limit.

2 ATOMIC ABSORPTION INSTRUMENTATION

THE BASIC COMPONENTS

To understand the workings of the atomic absorption spectrometer, let us build one, piece by piece. Every absorption spectrometer must have components which fulfill the three basic requirements shown in Figure 2-1. There must be: (1) a light source; (2) a sample cell; and (3) a means of specific light measurement.

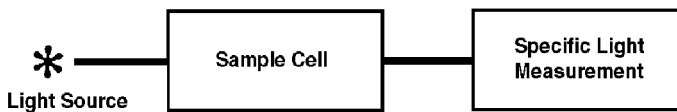


Figure 2-1. Requirements for a spectrometer.

In atomic absorption, these functional areas are implemented by the components illustrated in Figure 2-2. A light source which emits the sharp atomic lines of the element to be determined is required. The most widely used source is the hollow cathode lamp. These lamps are designed to emit the atomic spectrum of a particular element, and specific lamps are selected for use depending on the element to be determined.

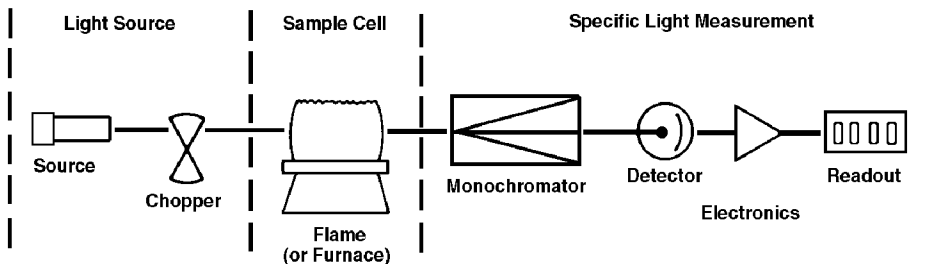


Figure 2-2. Basic AA spectrometer.

It is also required that the source radiation be modulated (switched on and off rapidly) to provide a means of selectively amplifying light emitted from the source lamp and ignoring emission from the sample cell. Source modulation can be accomplished with a rotating chopper located between the source and the sample cell, or by pulsing the power to the source.

Special considerations are also required for a sample cell for atomic absorption. An atomic vapor must be generated in the light beam from the source. This is generally accomplished by introducing the sample into a burner system or electrically heated furnace aligned in the optical path of the spectrophotometer.

Several components are required for specific light measurement. A monochromator is used to disperse the various wavelengths of light which are emitted from the source and to isolate the particular line of interest. The selection of a specific source and a particular wavelength in that source is what allows the determination of a selected element to be made in the presence of others.

The wavelength of light which is isolated by the monochromator is directed onto the detector, which serves as the “eye” of the instrument. This is normally a photomultiplier tube, which produces an electrical current dependent on the light intensity. The electrical current from the photomultiplier is then amplified and processed by the instrument electronics to produce a signal which is a measure of the light attenuation occurring in the sample cell. This signal can be further processed to produce an instrument readout directly in concentration units.

LIGHT SOURCES

An atom absorbs light at discrete wavelengths. In order to measure this narrow light absorption with maximum sensitivity, it is necessary to use a line source, which emits the specific wavelengths which can be absorbed by the atom. Narrow line sources not only provide high sensitivity, but also make atomic absorption a very specific analytical technique with few spectral interferences. The two most common line sources used in atomic absorption are the “hollow cathode lamp” and the “electrodeless discharge lamp.”

The Hollow Cathode Lamp

The hollow cathode lamp is an excellent, bright line source for most of the elements determinable by atomic absorption. Figure 2-3 shows how a hollow cathode lamp is constructed. The cathode of the lamp frequently is a hollowed-out cylinder

of the metal whose spectrum is to be produced. The anode and cathode are sealed in a glass cylinder normally filled with either neon or argon at low pressure. At the end of the glass cylinder is a window transparent to the emitted radiation.

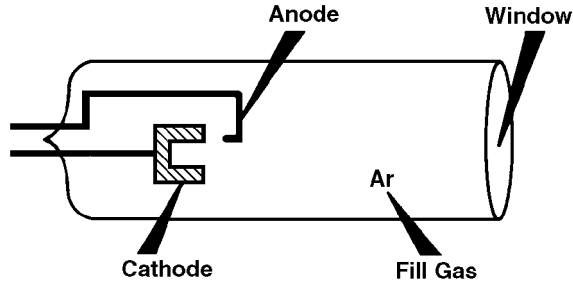


Figure 2-3. Hollow cathode lamp.

The emission process is illustrated in Figure 2-4. When an electrical potential is applied between the anode and cathode, some of the fill gas atoms are ionized. The positively charged fill gas ions accelerate through the electrical field to collide with the negatively charged cathode and dislodge individual metal atoms in a process called “sputtering”. Sputtered metal atoms are then excited to an emission state through a kinetic energy transfer by impact with fill gas ions.

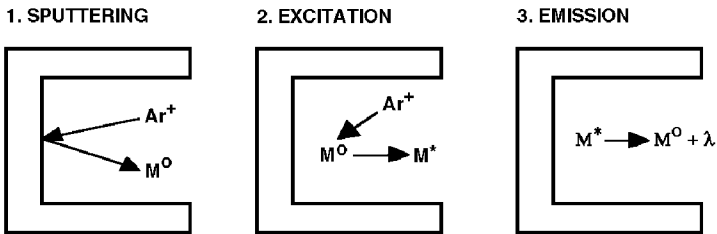


Figure 2-4. Hollow cathode lamp process, where Ar^+ is a positively-charged argon ion, M^0 is a sputtered, ground-state metal atom, M^* is an excited-state metal atom, and λ is emitted radiation at a wavelength characteristic for the sputtered metal.

Hollow cathode lamps have a finite lifetime. Adsorption of fill gas atoms onto the inner surfaces of the lamp is the primary cause for lamp failure. As fill gas pressure decreases, the efficiency of sputtering and the excitation of sputtered metal atoms also decreases, reducing the intensity of the lamp emission. To prolong hollow cathode lamp life, some manufacturers produce lamps with larger internal volumes so that a greater supply of fill gas at optimum pressure is available.

The sputtering process may remove some of the metal atoms from the vicinity of the cathode to be deposited elsewhere. Lamps for volatile metals such as arsenic, selenium, and cadmium are more prone to rapid vaporization of the cathode during use. While the loss of metal from the cathode at normal operating currents (typically 5-25 milliamperes) usually does not affect lamp performance, fill gas atoms can be entrapped during the metal deposition process which does affect lamp life. Lamps which are operated at highly elevated currents may suffer reduced lamp life due to depletion of the analyte element from the cathode.

Some cathode materials can slowly evolve hydrogen when heated. As the concentration of hydrogen in the fill gas increases, a background continuum emission contaminates the purity of the line spectrum of the element, resulting in a reduction of atomic absorption sensitivity and poor calibration linearity. To eliminate such problems, most modern hollow cathode lamps have a tantalum “getter” on the anode which irreversibly adsorbs evolved hydrogen as the lamp is operated.

The cathode of the hollow cathode lamp is usually constructed from a highly pure metal resulting in a very pure emission spectrum of the cathode material. It is sometimes possible, however, to construct a cathode or cathode insert from several metals. The resulting “multi-element” lamp may provide superior performance for a single element or, with some combinations, may be used as a source for all of the elements contained in the cathode alloy. However, not all metals may be used in combination with others because of metallurgical or spectral limitations.

Special consideration should be given before using a multi-element lamp as analytical complications may result. Often the intensity of emission for an element in a multi-element lamp is not as great as that which is observed for the element in a single-element lamp. This loss of intensity could be a disadvantage in applications where high precision or low detection limits are required. The increased spectral complexity of multi-element lamps may require that alternate wavelengths or narrower slits be used, which may also adversely affect sensitivity or baseline noise.

Each hollow cathode lamp will have a particular current for optimum performance. In general, higher currents will produce brighter emission and less baseline noise. As the current continues to increase, however, lamp life may shorten and spectral line broadening may occur, resulting in a reduction in sensitivity and linear working range. The recommended current specified for each lamp will usually provide the best combination of lamp life and performance. For demanding analy-

ses requiring the best possible signal-to-noise characteristics, higher currents can be used for the lamp, up to the maximum rated value. Lower lamp currents can be used with less demanding analyses to prolong lamp life.

Confusion over exactly what current is being used for a hollow cathode lamp may occur due to the method used for lamp modulation. As explained earlier, the source for atomic absorption must be modulated in order to accomplish selective amplification of the lamp emission signal. This can be accomplished mechanically by using a rotating chopper or electronically by pulsing the current supplied to the lamp, as illustrated in Figure 2-5. Both methods produce similar results; however, in some instruments the use of electronic modulation may create the impression that a lower lamp current is being applied than is actually the case.

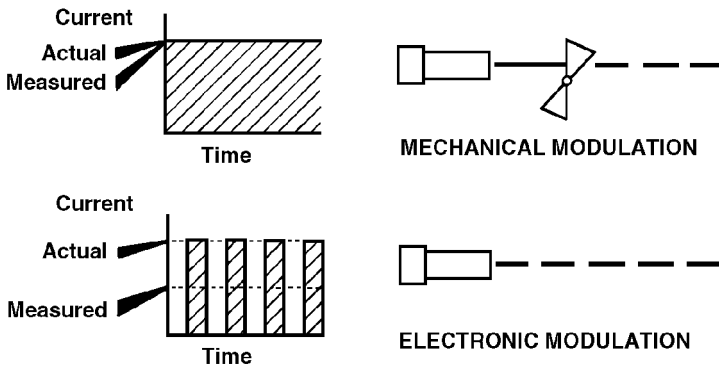


Figure 2-5. Mechanical vs. electrical modulation.

The cause for the apparent difference in measured currents with mechanically and electronically modulated systems is also shown in Figure 2-5. For mechanical modulation, the lamp is run at a constant current. Under these conditions, an ammeter reading of lamp current will indicate the actual current flow. For electronic modulation, the current is switched on and off at a rapid rate. An ammeter normally will indicate the time-averaged current rather than the actual peak current which is being applied.

While some instruments are designed to apply a correction factor automatically to electronically modulated lamp current readings to provide true peak current values, many do not. For electronically modulated systems without such correction, the actual peak current can be approximated from the measured current by divid-

ing it by the “duty cycle”, the fraction of time that current is applied to the lamp. For example, for a duty cycle of 40% and a measured lamp current of 10 milliamperes, the actual peak operating current for an electronically modulated system is:

$$10 \text{ milliamperes} / 0.4 = 25 \text{ milliamperes}$$

Specified lamp current settings may appear to be lower for atomic absorption instruments which modulate the source electronically and do not apply correction. The only valid basis of comparison between the current settings used by two different systems is one which includes compensation for the duty cycle, as shown above.

The Electrodeless Discharge Lamp

For most elements, the hollow cathode lamp is a completely satisfactory source for atomic absorption. In a few cases, however, the quality of the analysis is impaired by limitations of the hollow cathode lamp. The primary cases involve the more volatile elements where low intensity and short lamp life are a problem. The atomic absorption determination of these elements can often be dramatically improved with the use of brighter, more stable sources such as the “electrodeless discharge lamp”.

Figure 2-6 shows the design of the Perkin-Elmer System 2 electrodeless discharge lamp (EDL). A small amount of the metal or salt of the element for which the source is to be used is sealed inside a quartz bulb. This bulb is placed inside a small, self-contained RF generator or “driver”. When power is applied to the driver, an RF field is created. The coupled energy will vaporize and excite the atoms inside the bulb, causing them to emit their characteristic spectrum. An accessory power supply is required to operate an EDL.

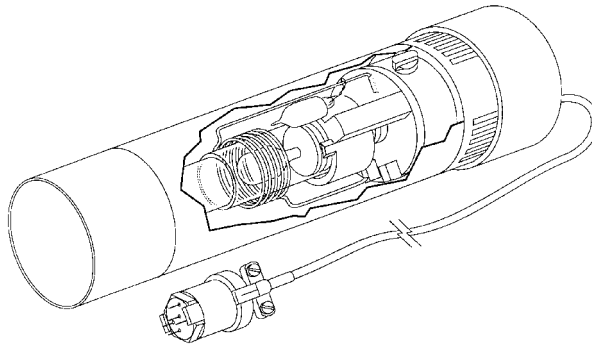


Figure 2-6. Electrodeless discharge lamp.

Electrodeless discharge lamps are typically much more intense and, in some cases, more sensitive than comparable hollow cathode lamps. They therefore offer the analytical advantages of better precision and lower detection limits where an analysis is intensity limited. In addition to providing superior performance, the useful lifetime of an EDL is typically much greater than that of a hollow cathode lamp for the same element. It should be noted, however, that the optical image for the EDL is considerably larger than that in a hollow cathode lamp. As a result, the performance benefits of the EDL can only be observed in instruments with optical systems designed to be compatible with the larger image.

Electrodeless discharge lamps are available for a wide variety of elements, including antimony, arsenic, bismuth, cadmium, cesium, germanium, lead, mercury, phosphorus, potassium, rubidium, selenium, tellurium, thallium, tin and zinc.

OPTICAL CONSIDERATIONS

Photometers

The portion of an atomic absorption spectrometer's optical system which conveys the light from the source to the monochromator is referred to as the *photometer*. Three types of photometers are typically used in atomic absorption instruments: single-beam, double-beam and what might be called compensated single-beam or pseudo double-beam.

Single-Beam Photometers

The instrument diagrammed in Figure 2-7 represents a fully functional "single-beam" atomic absorption spectrometer. It is called "single-beam" because all measurements are based on the varying intensity of a single beam of light in a single optical path.

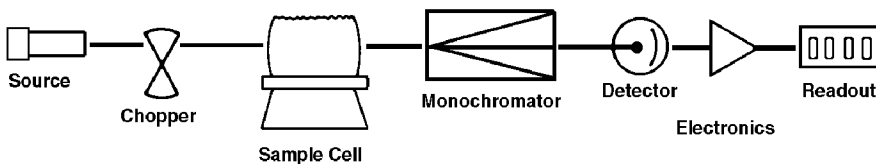


Figure 2-7. A single-beam AA spectrometer.

The primary advantage of a single-beam configuration is that it has fewer components and is less complicated than alternative designs. It is therefore easier to construct and less expensive than other types of photometers. With a single light path and a minimum number of optical components, single-beam systems typically provide very high light throughput. The primary limitation of the single-beam photometer is that it provides no means to compensate for instrumental variations during an analysis, such as changes in source intensity. The resulting signal variability can limit the performance capabilities of a single-beam system.

Double-Beam Photometers

An alternate photometer configuration, known as “double-beam” (Figure 2-8) uses additional optics to divide the light from the lamp into a “sample beam” (directed through the sample cell) and a “reference beam” (directed around the sample cell). In the double-beam system, the reference beam serves as a monitor of lamp intensity and the response characteristics of common electronic circuitry. Therefore, the observed absorbance, determined from a ratio of sample beam and reference beam readings, is more free of effects due to drifting lamp intensities and other electronic anomalies which similarly affect both sample and reference beams.

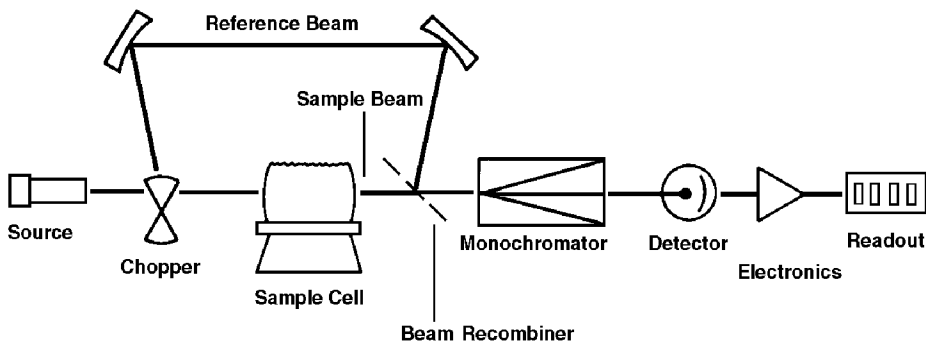


Figure 2-8. A double-beam AA spectrometer.

Modern atomic absorption spectrometers are frequently highly automated. They can automatically change lamps, reset instrument parameters, and introduce samples for high throughput multielement analysis. Double-beam technology, which automatically compensates for source and common electronics drift, allows these instruments to change lamps and begin an analysis immediately with little or no

lamp warm-up for most elements. This not only reduces analysis time but also prolongs lamp life, since lamp warm-up time is eliminated. Even with manual analyses, the ability to install a lamp or turn on the instrument and start an analysis almost immediately is a decided advantage for double-beam systems.

Double-beam photometers do divert some source energy from the sample beam to create the reference beam. Since it is the signal:noise ratio of the sample beam which determines analytical performance, modern double-beam instruments typically devote a much higher percentage of the source emission to the sample beam than to the reference beam. For example, a modern double-beam system which uses a beam splitter to generate sample and reference beams may use 75% of the source emission for the sample measurement and only 25% for the reference measurement. Using such techniques, modern double-beam instruments offer virtually the same signal-to-noise ratio as single-beam systems while enjoying the high-speed automation benefits and operational simplicity of double-beam operation.

Alternative Photometer Designs

There are several alternative system designs which provide advantages similar to those of double-beam optical systems and the light throughput characteristic of single-beam systems. Such systems can be described as compensated single-beam or pseudo double-beam systems. One such design uses two mechanically-adjusted mirrors to alternately direct the entire output of the source through either the sample path (during sample measurements) or through a reference path (Figures 2-9 and 2-10).

These alternative photometer designs provide light throughput comparable to that provided by single-beam photometer systems. They also compensate for system variations in a manner similar to that of double-beam photometers—similar, but not the same. This type of photometer performs compensation for drift much less frequently than do double-beam systems, typically only once per analytical reading. Double-beam systems typically provide drift compensation at rates in excess of 50 times per second. The lower compensation frequency limits the ability of alternative photometer systems to compensate for large, quickly changing variations in source intensity such as those that frequently occur when a source is first lighted.

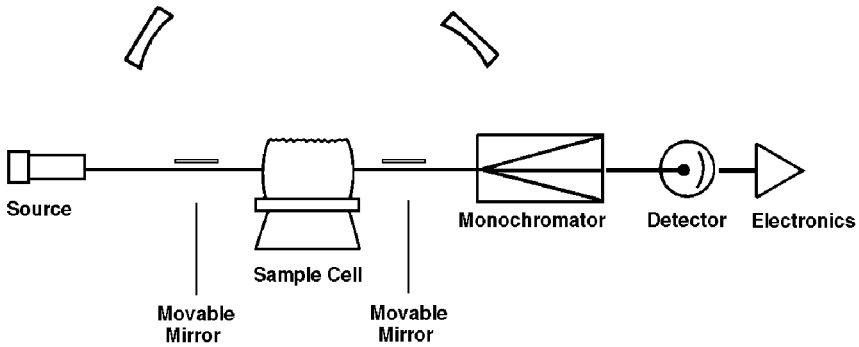


Figure 2-9. A compensated single-beam system with source light directed through the sample path.

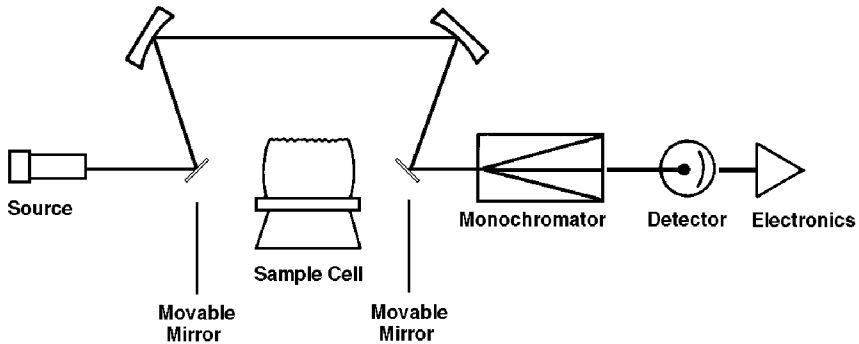


Figure 2-10. A compensated single-beam system with source light directed through the reference path.

Optics and the Monochromator System

As previously discussed, an important factor in determining the baseline noise in an atomic absorption instrument is the amount of light energy reaching the photomultiplier (PMT). Lamp intensity is optimized to be as bright as possible while avoiding line broadening problems. The impact of single-beam and double-beam photometer systems has been discussed above. But the impact of other components must also be considered to determine the capabilities of the complete optical system.

Light from the source must be focused on the sample cell and directed to the monochromator, where the wavelengths of light are dispersed and the analytical line of interest is focused onto the detector. Some energy is lost at each optical surface along the way. Front-surfaced, highly reflective, mirrors can be used to control the focus of the source lamp and the field of view of the light detector precisely and with minimal light loss. Alternately, focusing can be accomplished by refraction instead of reflection by using a lens system. Since the focal length of a lens varies with wavelength, additional optics (which may further reduce energy throughput) or complex optical adjustments must be used to obtain proper focus over the full spectral range for atomic absorption.

Particular care must be taken in the monochromator to avoid excessive light loss. A typical monochromator is diagrammed in Figure 2-11. Wavelength dispersion is accomplished with a grating, a reflective surface ruled with many fine parallel lines very close together. Reflection from this ruled surface generates an interference phenomenon known as diffraction, in which different wavelengths of light diverge from the grating at different angles. Light from the source enters the monochromator at the entrance slit and is directed to the grating where dispersion takes place. The diverging wavelengths of light are directed toward the exit slit. By adjusting the angle of the grating, a selected emission line from the source can be allowed to pass through the exit slit and fall onto the detector. All other lines are blocked from exiting.

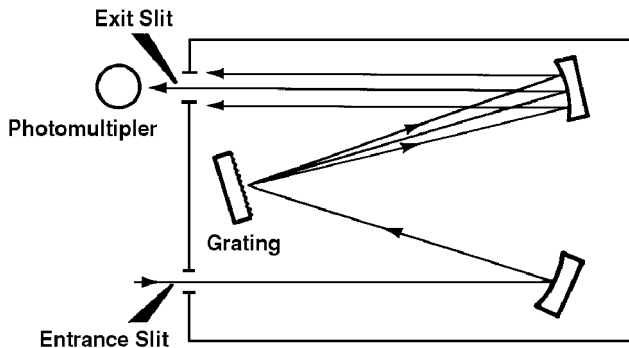


Figure 2-11. A monochromator.

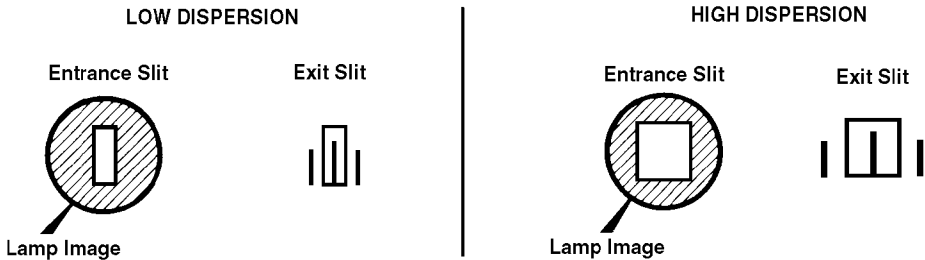


Figure 2-12. Advantages of high dispersion.

The angle of dispersion at the grating can be controlled by the density of lines on the grating. Higher dispersion will result from greater line density, i.e., more lines/mm. High dispersion is important to good energy efficiency of the monochromator, as illustrated in Figure 2-12.

The image of the source focused on the entrance slit and dispersed emission lines at the exit slit are shown for both a low-dispersion and a high-dispersion grating. In order to isolate a desired line from nearby lines, it is necessary to use a narrower exit slit in the low-dispersion example than is required in the high-dispersion case. Good optical design practices dictate that the entrance and exit slits be similarly sized. The use of a larger entrance slit will overfill the grating with the source image, while the use of a smaller entrance slit restricts the amount of light entering the monochromator. Both reduce the amount of energy available at the exit slit. For a low dispersion grating, this means that the size of the monochromator entrance slit is limited to the narrow size demanded of the exit slit to exclude nearby lines. Thus, much of the available light energy is prevented from ever entering the monochromator. In contrast, the greater wavelength separation provided by a high-dispersion grating allows the use of wider slits, which make use of more of the available light without any sacrifice in resolution.

To a first approximation, the energy throughput of a monochromator is proportional to the illuminated ruled grating area and inversely proportional to the *reciprocal linear dispersion*. To obtain the full energy benefit of high dispersion, it is necessary to use a grating with a ruled surface area large enough to capture all of the light from the magnified slit image. Large, quality gratings of high dispersion are difficult and expensive to make. Therefore, the incentive is great to accept smaller gratings with lesser line densities and poorer dispersion for atomic absorption instrumentation. However, better instruments take advantage of the superior energy throughput afforded by larger gratings.

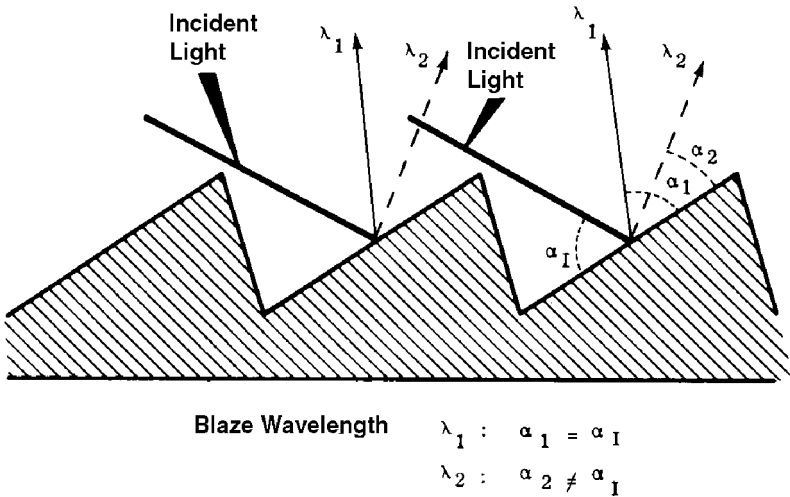


Figure 2-13. Grating blaze angle.

Another factor affecting the optical efficiency of the monochromator is the blaze angle of the grating, whether it is mechanically ruled or holographically generated. An illustration of a mechanically-ruled blaze angle appears in Figure 2-13.

Mechanical grating rulings are in the form of V-shaped grooves carved into the surface of the grating. As discussed earlier, an interference phenomenon causes light of different wavelengths to diverge from the grating at different angles. The particular wavelength which diverges from the blazed surface at an angle corresponding to specular reflectance (i.e., angle of reflection equals angle of incidence) will suffer the least loss in intensity as a result of the diffraction process. A grating can be constructed for a blaze at any desired wavelength by controlling the angle of cut during ruling. The farther removed a given wavelength of light is from the wavelength for which a grating is blazed, the greater will be the extent of monochromator light loss at that wavelength.

The useful atomic absorption wavelength range runs from 189 to 851 nanometers. With one grating blazed somewhere in the middle of this range, significant energy fall-off occurs at the wavelength extremities due to energy inefficiencies in the diffraction process. One technique used to overcome this problem and to provide enhanced energy throughput at the wavelength extremities is to equip the instrument with two gratings, one blazed in the ultraviolet and the other blazed in the visible region of the spectrum. Then by choosing the grating blazed nearest the working

wavelength, the optimum energy throughput can be achieved. Alternately, a single “dual-blazed” grating can be used, with two regions blazed for the two spectral regions. As the dual blazed grating rotates from one wavelength extreme to another, the region blazed for the current working wavelength is brought into alignment with the optical beam, thereby offering improved efficiency compared with a single grating blazed at one wavelength.

THE ATOMIC ABSORPTION ATOMIZER

Pre-Mix Burner System

The sample cell, or atomizer, of the spectrometer must produce the ground state atoms necessary for atomic absorption to occur. This involves the application of thermal energy to break the bonds that hold atoms together as molecules. While there are several alternatives, the most routine and widely applied sample atomizer is the flame.

Figure 2-14 shows an exploded view of an atomic absorption burner system. In this “premix” design, sample solution is aspirated through a nebulizer and sprayed as a fine aerosol into the mixing chamber. Here the sample aerosol is mixed with fuel and oxidant gases and carried to the burner head, where combustion and sample atomization occur.

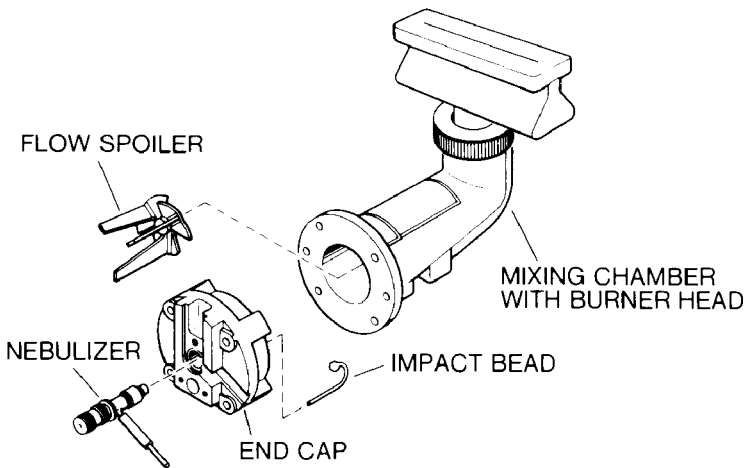


Figure 2-14. Premix burner system.

Fuel gas is introduced into the mixing chamber through the fuel inlet, and oxidant enters through the nebulizer sidearm. Mixing of the fuel and oxidant in the burner chamber eliminates the need to have combustible fuel/oxidant in the gas lines, a potential safety hazard. In addition to the separate fuel and oxidant lines, it is advantageous to have an auxiliary oxidant inlet directly into the mixing chamber. This allows the oxidant flow adjustments to be made through the auxiliary line while the flow through the nebulizer remains constant. Thus, for a burner system with an auxiliary oxidant line, the sample uptake rate is independent of flame condition, and the need to readjust the nebulizer after every oxidant flow adjustment is eliminated.

Only a portion of the sample solution introduced into the burner chamber by the nebulizer is used for analysis. The finest droplets of sample mist, or aerosol, are carried with the combustion gases to the burner head, where atomization takes place. The excess sample is removed from the premix chamber through a drain. The drain uses a liquid trap to prevent combustion gases from escaping through the drain line. The inside of the burner chamber is coated with a wettable inert plastic material to provide free drainage of excess sample and prevent burner chamber "memory." A free draining burner chamber rapidly reaches equilibrium, usually requiring less than two seconds for the absorbance to respond fully to sample changes.

Impact Devices

The sample aerosol is composed of variously sized droplets as it is sprayed into the mixing chamber. Upon entering the flame, the water in these droplets is vaporized. The remaining solid material must likewise be vaporized, and chemical bonds must be broken to create free ground state atoms. Where the initial droplet size is large, the sample vaporization and atomization process is more difficult to complete in the short time in which the sample is exposed to the flame. Incomplete sample vaporization and atomization will lead to increased susceptibility to analytical interferences.

Impact devices are used to reduce droplet size further and to cause remaining larger droplets to be deflected from the gas stream and removed from the burner through the drain. Two types of impact device are used typically, impact beads and flow spoilers.

Impact bead systems are normally used to improve nebulization efficiency, the percentage of sample solution converted to smaller droplets. The impact bead is normally a spherical bead made of glass, silica or ceramic. Glass or quartz impact beads may be less corrosion resistant and may cause more contamination problems than more chemically inert ceramic beads.

The impact bead is positioned directly in the nebulizer spray as it exits the nebulizer. The sample spray contacts the impact bead at high speed, causing some of the larger droplets to be broken up into smaller droplets. The design and positioning of the impact bead are critical in determining how well it will work. Properly designed impact bead systems will improve nebulization efficiency and remove many of the remaining large droplets from the spray. However, poorly designed or positioned impact beads may have little or no effect on nebulization efficiency and may be very inefficient at removing larger droplets from the spray. The increased population of large droplets in the aerosol may create undesirable effects, including poorer precision and increased interferences. Additionally, burner systems using an impact bead may exhibit memory problems with high concentration solutions or solutions with high dissolved solids content.

The quality of an impact bead system can frequently be determined by the increase in sensitivity it provides for selected elements. A poorly designed system will provide improved sensitivity for easily atomized elements simply because more sample is transported to the flame and less to the drain. However, there normally will be little or no improvement in sensitivity for the less easily atomized elements. A properly designed impact bead system will provide improved nebulization efficiency and improved sensitivity for all elements.

Flow spoilers normally do not improve nebulization efficiency. The primary use of a flow spoiler is to remove the remaining large droplets from the sample aerosol. The flow spoilers used in atomic absorption burner systems normally are placed between the nebulizer and the burner head. They typically have three or more large vanes constructed from or coated with a corrosion resistant material. Smaller droplets are transported through the open areas between the vanes while larger droplets contact the vanes and are removed from the aerosol.

For routine atomic absorption analyses where maximum sensitivity is not required, use of an efficient flow spoiler alone will provide the required analytical stability and freedom from interference. A burner system optimized for maximum sensitivity and performance should include both a high nebulization efficiency ceramic impact bead and an efficient flow spoiler.

Nebulizers, Burner Heads and Mounting Systems

Several important factors enter into the nebulizer portion of the burner system. In order to provide efficient nebulization for all types of sample solution, the nebulizer should be adjustable. Stainless steel has been the most common material used for construction of the nebulizer. Stainless steel has the advantage of durability and low cost but has the disadvantage of being susceptible to corrosion from samples with a high content of acid or other corrosive reagents. For such cases, nebulizers constructed of a corrosion resistant material, such as an inert plastic, platinum alloys or tantalum should be used.

Burner heads typically are constructed of stainless steel or titanium. All-titanium heads are preferred as they provide extreme resistance to heat and corrosion.

Different burner head geometries are required for various flame or sample conditions. A ten-centimeter single-slot burner head is recommended for air-acetylene flames. A special five-centimeter burner head with a narrower slot is required when a nitrous oxide-acetylene flame is to be used. Burner heads also are available for special purposes, such as use with solutions that have exceptionally high dissolved solids contents.

In addition to the flame, there are several options for atomic absorption atomizers. These options are discussed in detail in Chapter 4. Most of these options require removal of the premix burner system and replacement by an alternate atomizer in the spectrometer sample compartment. Since these alternate atomizers offer complementary and extended analytical capabilities, it is likely that the analyst will want to alternate between the use of flame AA and one or more of the other systems. A “quick change” atomizer mount is an important item to facilitate convenient changeover from one device to another without the use of tools. In addition to convenience, a “quick change” mount may reduce or eliminate entirely the need for realignment of the atomizer when it is replaced in the sample compartment.

ELECTRONICS

Precision in Atomic Absorption Measurements

We have already discussed the effects of light energy on the precision of an atomic absorption measurement. The analyst will have little control over these optical factors, as they are an inherent part of the instrument design. However, the analyst can exercise some degree of control over precision by proper selection of integration time with flame atomic absorption.

Observed precision will improve with the period of time over which each sample is read. Where analyte concentrations are not approaching detection limits, integration times of one to three seconds will usually provide acceptable precision. When approaching instrument detection limits where repeatability is poor, precision can be improved by using even longer integration times, up to 10 seconds. In most instances; however, there is little advantage to using integration times longer than 10 seconds. (To a first approximation, improvement in signal:noise ratio is proportional to the square root of the ratio of integration times.)

Since the detection limit is defined based on the observed precision, the detection limit also can be improved by increasing the integration time. The analyst, therefore, has control over the priorities for a particular analysis, maximum speed or optimum precision and detection limits.

Current instruments offer statistical functions for averaging and calculating standard deviation and relative standard deviation or coefficient of variation of replicate measurements. These functions can be used to determine the precision under various experimental conditions, allowing the analyst to optimize method parameters for each individual requirement.

Calibration of the Spectrometer

Most modern atomic absorption instruments include microcomputer-based electronics. The microcomputer provides atomic absorption instruments with advanced calculation capabilities, including the ability to calibrate and compute concentrations from absorbance data conveniently and accurately, even for nonlinear calibration curves. In the linear region, data on as little as one standard and a blank may be sufficient for defining the relationship between concentration and absorbance. However, additional standards are usually used to verify calibration accuracy. Where the relationship becomes nonlinear, however, more standards are required. The accuracy of a calibration computed for a nonlinear relationship depends on the number of standards and the equations used for calibration.

For the equation format which optimally fits atomic absorption data, it has been experimentally shown that accurate calibration can be achieved with a minimum of three standards plus a blank, even in cases of severe curvature. Figure 2-15 illustrates the accuracy of microcomputer-calculated results for cobalt with single standard "linear" and three-standard "nonlinear" calibrations. After the instrument was calibrated using the specified procedure, a series of standards were analyzed. Figure 2-15 shows plots of the actual concentrations for those standards versus the measured values for both calibration procedures. The results obtained

with “linear” calibration are accurate only where the absorbance:concentration relationship is linear, up to about 5 mg/mL. The results obtained with three-standard “nonlinear” calibration are still accurate at 30 mg/mL, significantly extending the useful working range. For versatility, current instruments allow fitting of more than three standards to these same basic equations.

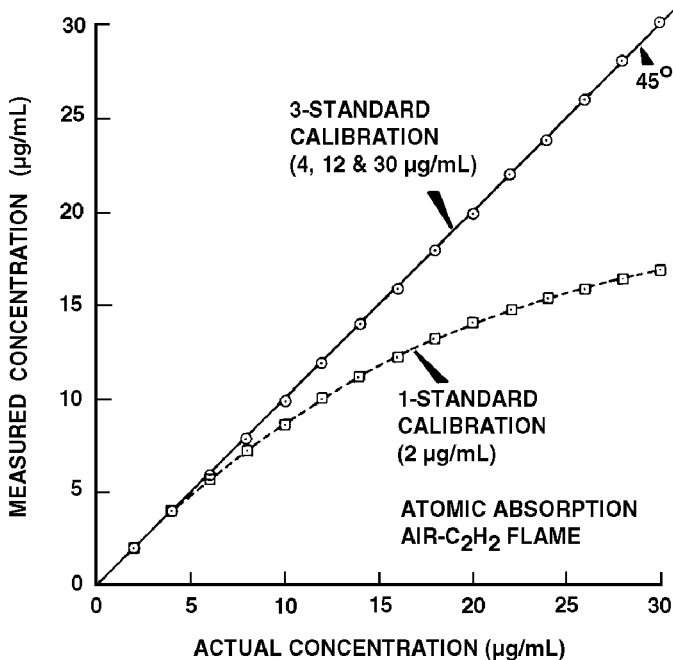


Figure 2-15. Cobalt Calibration Accuracy

AUTOMATION OF ATOMIC ABSORPTION

Automated Instruments and Sample Changers

One of the greatest contributions to the efficiency of the analytical laboratory is the automated atomic absorption spectrometer. Automatic samplers were the first step in freeing the analyst from the monotonous task of manually introducing each and every sample.

However, the real advancement in analysis automation came in the late 1970's, when automated multielement atomic absorption was introduced. In addition to automatic sample introduction, these instruments offer automatic setup of instrument parameters to preprogrammed values. These instrument "programs" can be accessed sequentially, making it possible to analyze a tray full of samples for multiple elements, without any operator intervention.

Automated Sample Preparation

While automated instrumentation has meant considerable time savings to the analyst, analytical throughput (i.e., the number of samples which can be analyzed in a given time) frequently is limited by the time required to prepare the sample. Even when the sample is available in a suitable solution form, there often are pretreatment steps which must be performed prior to analysis. The introduction of commercial systems based on techniques such as flow injection have directly addressed the need for automated sample preparation capabilities. Flow injection techniques can be used to automate relatively simple procedures such as dilution or reagent addition. They can also be used to automate complex chemical pretreatments, including analyte preconcentration and cold vapor mercury and hydride generation procedures.

The Stand-alone Computer and Atomic Absorption

Stand-alone and personal computers have extended the automation and data handling capabilities of atomic absorption even further. These computers can interface directly to instrument output ports to receive, manipulate, and store data and print reports in user selectable formats. Also, data files stored in personal computers can be read into supplemental software supplied with the system or third party software such as word processor, spreadsheet and database programs for open-ended customization of data treatment and reporting.

3 CONTROL OF ANALYTICAL INTERFERENCES

THE FLAME PROCESS

Atomic absorption is known as a very specific technique with few interferences. The ultimate analytical method which is absolutely free of any interferences from the nature of the sample will probably never exist. The next best thing to not having interferences is to know what the interferences are and how to eliminate them or compensate for them. The interferences in atomic absorption are well-defined, as are the means for dealing with them. In order to understand these interferences thoroughly, we will examine what goes on in the flame atomization process of atomic absorption.

In order to get the atomic absorption process to occur, we must produce individual atoms from our sample which starts out as a solution of ions. This process is diagrammed in Figure 3-1. First, by the process of nebulization, we aspirate the sample

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

Figure 3-1. The flame process. " M^+ " is a metal cation and " A^- " is the associated anion.

into the burner chamber, where it mixes as a fine aerosol with the fuel and oxidant gases. At this point, the metals are still in solution in the fine aerosol droplets. As these tiny droplets pass into the heat of the flame, the process of evaporation or desolvation removes the solvent and leaves tiny solid particles of sample material. As more heat is applied, liquefaction will take place, and additional heat will vaporize the sample. At this point the metal of interest, called the analyte, is still

bound up with some anion to form a molecule which does not exhibit the atomic absorption phenomenon we wish to measure. By applying still more heat energy, this molecule is dissociated into the individual atoms which make it up.

Since the thermal energy from the flame is responsible for producing the absorbing species, flame temperature is an important parameter governing the flame process. Temperatures for some flames that have been used in atomic absorption are listed in Table 3-1. Cooler flames are subject to more interference problems resulting from insufficient energy for complete atomization. The two premix flames now used almost exclusively for atomic absorption are air-acetylene and nitrous oxide-acetylene. While the air-acetylene flame is satisfactory for the majority of elements determined by atomic absorption, the hotter nitrous oxide-acetylene flame is required for many refractory-forming elements. The nitrous oxide-acetylene flame is also effective in the control of some types of interference.

Table 3-1
Temperatures of Premix Flames

<u>Oxidant-Fuel</u>	<u>Temp., °C</u>
Air-Methane	1850-1900
Air-Natural Gas	1700-1900
Air-Hydrogen	2000-2050
Air-Acetylene	2125-2400
N ₂ O-Acetylene	2600-2800

The number of ground state metal atoms formed in step 5 of the flame process (Figure 3-1) will determine the amount of light absorbed. Concentration is determined by comparing the absorbance of the sample to that of a known standard concentration. The relationship between the number of atoms in the flame and the concentration of analyte in solution is governed by the flame process. If any constituent of the sample alters one or more steps of this process from the performance observed for a standard, an interference will exist, and an erroneous concentration measurement will result if the interference is not recognized and corrected or compensated.

NONSPECTRAL INTERFERENCES

Interferences in atomic absorption can be divided into two general categories, spectral and nonspectral. Nonspectral interferences are those which affect the formation of analyte atoms.

Matrix Interference

The first place in the flame atomization process subject to interference is the very first step, the nebulization. If the sample is more viscous or has considerably different surface tension characteristics than the standard, the sample uptake rate or nebulization efficiency may be different between sample and standard. If samples and standards are not introduced into the process at the same rate, it is obvious that the number of atoms in the light beam and, therefore, the absorbance, will not correlate between the two. Thus, a matrix interference will exist.

An example of this type of interference is the effect of acid concentration on absorbance. From Figure 3-2, it can be seen that as phosphoric acid concentration increases (and the sample viscosity increases), the sample introduction rate and the sample absorbance decrease. Increased acid or dissolved solids concentration normally will lead to a negative error if not recognized and corrected. Matrix interferences can also cause positive error. The presence of an organic solvent in a sample will produce an enhanced nebulization efficiency, resulting in an increased

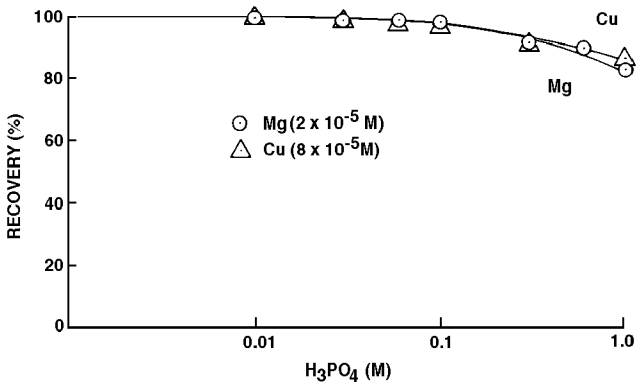


Figure 3-2. Matrix interference from viscosity effects.

absorption. One way of compensating for this type of interference is to match as closely as possible the major matrix components of the standard to those of the sample. Any acid or other reagent added to the sample during preparation should also be added to the standards and blank in similar concentrations.

Method of Standard Additions

There is a useful technique which may make it possible to work in the presence of a matrix interference without eliminating the interference itself, and still make an accurate determination of analyte concentration. The technique is called the method of standard additions. Accurate determinations are made without eliminating interferences by making the concentration calibration in the presence of the

matrix interference. Aliquots of a standard are added to portions of the sample, thereby allowing any interferent present in the sample to also affect the standard similarly.

The standard additions technique is illustrated in Figure 3-3. The solid line passing through the origin represents a typical calibration line for a set of aqueous standards. Zero absorbance is defined with a water blank, and, as the concentration of analyte increases, a linear increase in absorbance is observed.

Let us now take equal aliquots of the sample. Nothing is added to the first aliquot; a measured amount of standard is added to the second; and a larger measured amount is added to the third. The first volume of added standard is usually selected to approximate the analyte concentration in the sample, and the second volume is normally twice the first volume. However, for the method of standard additions to be used accurately, the absorbances for all of the solutions must fall within the linear portion of the working curve.

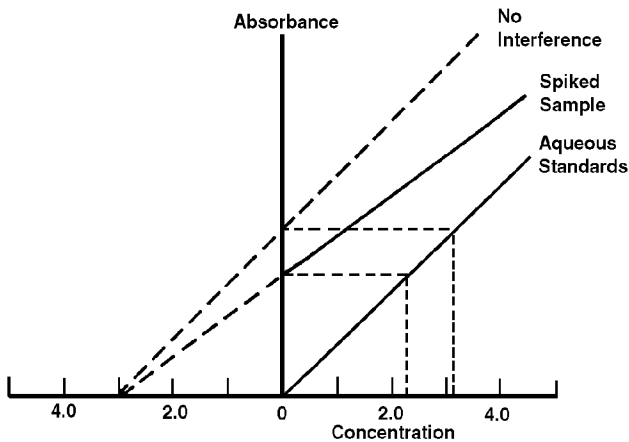


Figure 3-3. The method of standard additions.

Finally, all portions are diluted to the same volume so that the final concentrations of the original sample constituents are the same in each case. Only the amount of added analyte differs, and then by a known amount.

If no interference were present in this sample, a plot of measured absorbance versus the concentration of added standard would be parallel to the aqueous standard calibration, and offset by an absorbance value resulting from the analyte present in the unspiked sample. If some material is present in the sample which causes a matrix interference, the number of ground state atoms producing atomic absorption will be affected, as will be the absorbance from the analyte in the unspiked sample. However, the absorbance increase from added standard will also be

changed by the same proportional amount since the concentration of interferent is the same in each solution. Therefore, a straight line will still result, but because of the interference, its slope will be different from that observed for the aqueous standards.

In this situation, if the absorbance of the unspiked sample were to be compared directly to the aqueous calibration, an error would result. If, however, the slope determined by the standard additions to our sample is used as the calibration slope, an accurate determination of the sample concentration can still be made. By continuing the concentration calibration on the abscissa backward from zero and extrapolating the calibration line backward until it intercepts the concentration axis, the concentration responsible for the absorbance of the unspiked sample is indicated. An accurate determination has been made by calibrating in the presence of the interference.

Properly used, the method of standard additions is a valuable tool in atomic absorption. The presence of an interference can be confirmed by observing the slope of the spiked sample calibration and determining whether or not it is parallel to the aqueous standard line. If it is not, an interference is present. If an interference is present, the method of standard additions *may* allow an accurate determination of the unknown concentration by using the standard additions slope for the calibration. Caution should be used with the technique, however, as it can fail to give correct answers with other types of interference. *The method of standard additions will not compensate for background absorption or other types of spectral interference, and normally will not compensate for chemical or ionization types of interference.*

Chemical Interference

A second place where interference can enter into the flame process is in step number 5 of Figure 3-1, the atomization process. In this step, sufficient energy must be available to dissociate the molecular form of the analyte to create free atoms. If the sample contains a component which forms a thermally stable compound with the analyte that is not completely decomposed by the energy available in the flame, a chemical interference will exist.

The effect of phosphate on calcium, illustrated in Figure 3-4, is an example of a chemical interference. Calcium phosphate does not totally dissociate in an air-acetylene flame. Therefore, as phosphate concentration is increased, the absorbance due to calcium atoms decreases.

There are two means of dealing with this problem. One is to eliminate the interference by adding an excess of another element or compound which will also form a thermally stable compound with the interferent. In the case of calcium, lanthanum is added to tie up the phosphate and allow the calcium to be atomized, making the calcium absorbance independent of the amount of phosphate.

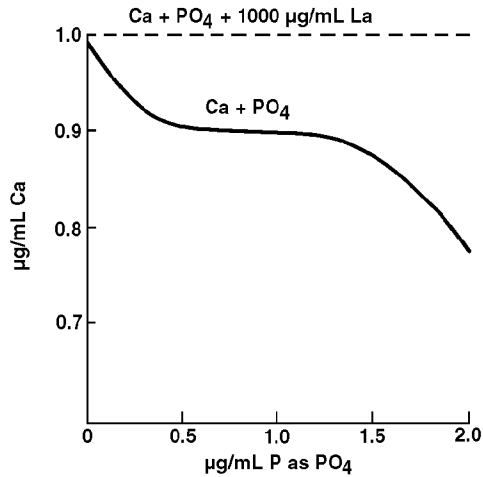


Figure 3-4. Interference of phosphate on calcium.

There is a second approach to solving the chemical interference problem. Since the problem arises because of insufficient energy to decompose a thermally stable analyte compound, the problem can be eliminated by increasing the amount of energy; that is, by using a hotter flame. The nitrous oxide-acetylene flame is considerably hotter than air-acetylene and can often be used to minimize chemical interferences for elements generally determined with air-acetylene. The phosphate interference on calcium, for instance, is not observed with a nitrous oxide-acetylene flame, eliminating the need for the addition of lanthanum.

Ionization Interference

There is a third major interference, however, which is often encountered in hot flames. As illustrated in Figure 3-1, the dissociation process does not necessarily stop at the ground state atom. If additional energy is applied, the ground state atom can be thermally raised to the excited state or an electron may be totally removed from the atom, creating an ion. As these electronic rearrangements deplete the number of ground state atoms available for light absorption, atomic absorption at the resonance wavelength is reduced. When an excess of energy reduces the population of ground state atoms, an ionization interference exists.

Ionization interferences are most common with the hotter nitrous oxide-acetylene flame. In an air-acetylene flame, ionization interferences are normally encoun-

tered only with the more easily ionized elements, notably the alkali metals and alkaline earths.

Ionization interference can be eliminated by adding an excess of an element which is very easily ionized, creating a large number of free electrons in the flame and suppressing the ionization of the analyte. Potassium, rubidium, and cesium salts are commonly used as ionization suppressants. Figure 3-5 shows ionization suppression for the determination of barium in a nitrous oxide-acetylene flame. The increase in absorption at the barium resonance line, and the corresponding decrease in absorption at the barium ion line as a function of added potassium, illustrate the enhancement of the ground state species as the ion form is suppressed. By adding 1000 mg/L to 5000 mg/L potassium to all blanks, standards and samples, the effects of ionization can usually be eliminated.

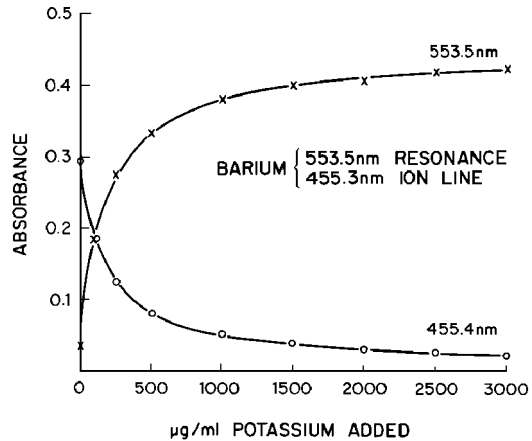


Figure 3-5. Effect of added potassium on ionization.

SPECTRAL INTERFERENCES

Spectral interferences are those in which the measured light absorption is erroneously high due to absorption by a species other than the analyte element. The most common type of spectral interference in atomic absorption is “background absorption.”

Background Absorption

Background absorption arises from the fact that not all of the matrix materials in a sample are necessarily 100% atomized. Since atoms have extremely narrow absorption lines, there are few problems involving interferences where one element absorbs at the wavelength of another. Even when an absorbing wavelength of another element falls within the spectral bandwidth used, no absorption can occur unless the light source produces light at that wavelength, i.e., that element is also present in the light source. However, undissociated molecular forms of matrix ma-

terials may have broadband absorption spectra, and tiny solid particles in the flame may scatter light over a wide wavelength region. When this type of nonspecific absorption overlaps the atomic absorption wavelength of the analyte, background absorption occurs. To compensate for this problem, the background absorption must be measured and subtracted from the total measured absorption to determine the true atomic absorption component.

While now virtually obsolete, an early method of manual background correction illustrates clearly the nature of the problem. With the “two line method”, background absorption, which usually varies gradually with wavelength, was independently measured by using a nonabsorbing emission line very close to the atomic line for the analyte element, but far enough away so that atomic absorption was not observed, as illustrated in Figure 3-6. By subtracting the absorbance measured at the nonabsorbing line from the absorbance at the atomic line, the net atomic absorption was calculated. Nearby, nonabsorbing lines are not always readily available, however, and inaccuracies in background correction will result if the wavelength for background measurement is not extremely close to the resonance line. Therefore, for accuracy, as well as convenience, a different method was needed.

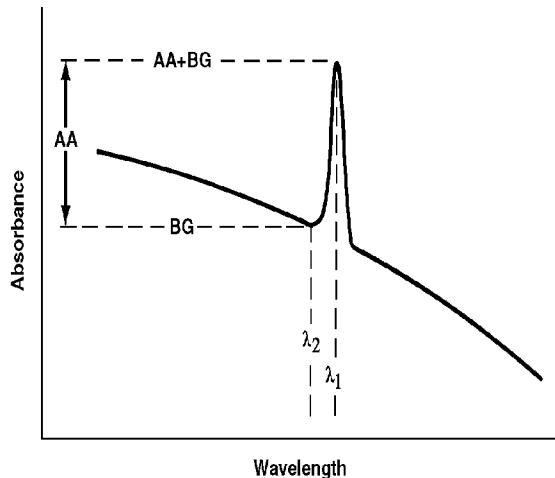


Figure 3-6. Two-line background correction.

Continuum Source Background Correction

Continuum source background correction is a technique for automatically measuring and compensating for any background component which might be present in an atomic absorption measurement. This method incorporates a continuum light source in a modified optical system, illustrated in Figure 3-7.

The broad band continuum (“white” light) source differs from the primary (atomic line) source in that it emits light over a broad spectrum of wavelengths

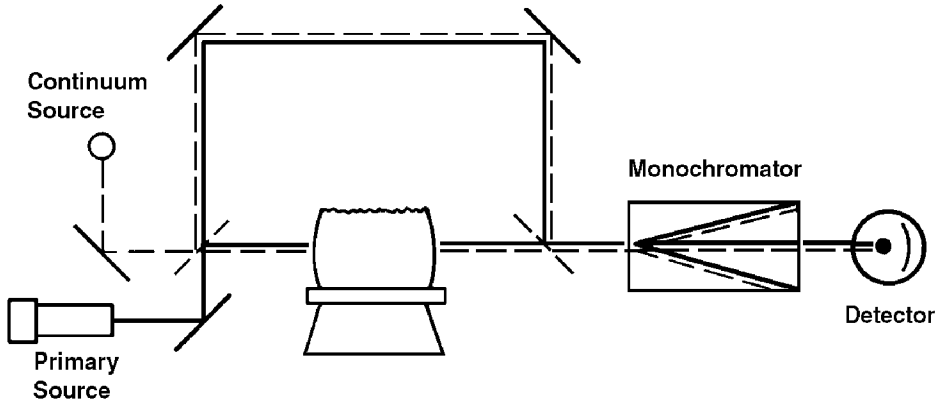


Figure 3-7. Continuum Source Background Corrector.

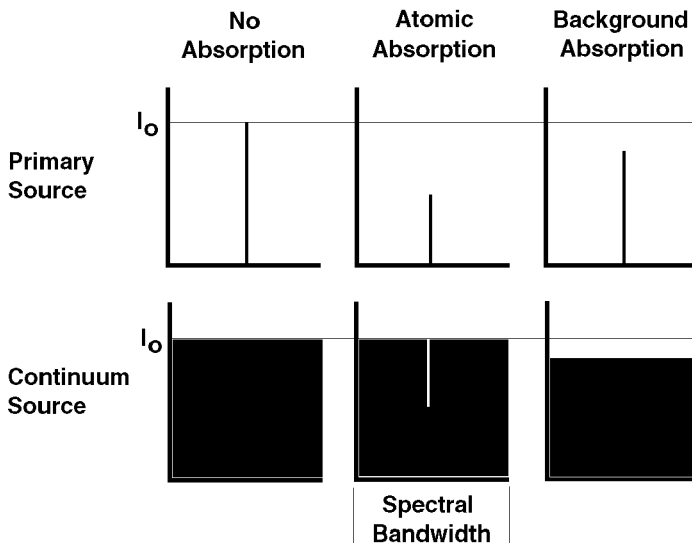


Figure 3-8. Atomic and background absorption with a primary (line) source and a continuum (broadband) source.

instead of at specific lines. From Figure 3-8, it can be seen that atomic absorption, which occurs only at very discrete wavelengths, will not measurably attenuate the emission from the continuum source. However, background absorption which has very broad absorption spectra will absorb the continuum emission as well as the line emission.

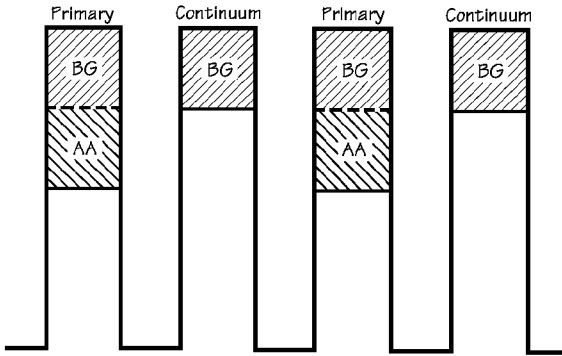


Figure 3-9. Simplified timing diagram.

As shown in Figure 3-7, light from both the primary and continuum lamps is combined and follows a coincident path through the sample, through the monochromator, and to the detector. The two lamps are observed by the detector alternately in time, and as illustrated in Figure 3-9, instrument electronics separate the signals and compare the absorbance from both sources. An absorbance will be displayed only where the absorbance of the two lamps differs. Since background absorption absorbs both sources equally, it is ignored. True atomic absorption, which absorbs the primary source emission and negligibly absorbs the broad band continuum source emission, is still measured and displayed as usual.

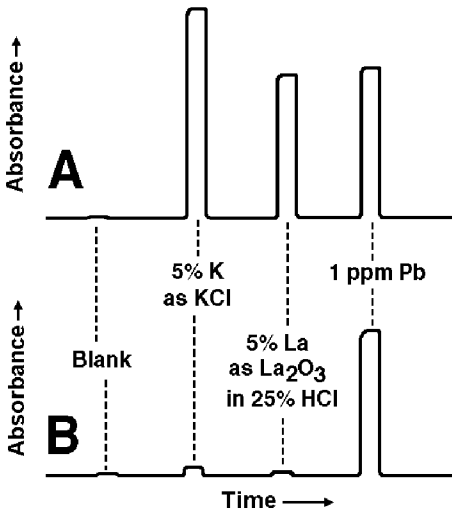


Figure 3-10. Automatic background correction.

Figure 3-10 shows how background absorption can be automatically eliminated from the measured signal using continuum source background correction. In the ex-

ample, a lead determination is shown without background correction (A) and with background correction (B). Both determinations were performed at the Pb 283.3 nm wavelength with 15x scale expansion and a 10-second integration time.

Continuum source background correction is widely applied, and except in some very unusual circumstances, is fully adequate for all flame AA applications. There are some limitations to continuum source background correction, however, which especially impact graphite furnace atomic absorption, to be discussed in later chapters. These limitations are summarized in Table 3-2.

Table 3-2
Limitations of Continuum Source Background Correction

1. Requires additional continuum light source(s) and electronics.
2. Requires the intensities of the primary and continuum sources to be similar.
3. Two continuum sources are required to cover the full wavelength range.
4. Requires critical alignment of the continuum and primary sources for accurate correction.
5. May be inaccurate for structured background absorption.

The fact that continuum source background correction requires two sources (primary and continuum) imposes convenience, economic, and performance considerations on the use of the technique. The convenience and economic factors come from the fact that the continuum source has a finite lifetime and must be replaced on a periodic basis. The performance factor originates from the fact that the background component of the absorption signal is measured from one source, while the total uncorrected signal is measured with another. This leads to the possibility of inaccurate compensation if the two sources do not view exactly the same portion of the atom cloud, especially at higher background absorption levels. Finally, since the two sources are spectrally different, background absorption exhibiting fine spectral structure may attenuate the two source lamps to different degrees, leading to inaccuracies in background correction for such cases.

Introduction to Zeeman Background Correction

For those applications where the limitations of the continuum source approach are significant to the analysis, the Zeeman background correction system may be preferable. Zeeman background correction uses the principle that the electronic energy levels of an atom placed in a strong magnetic field are changed, thereby changing

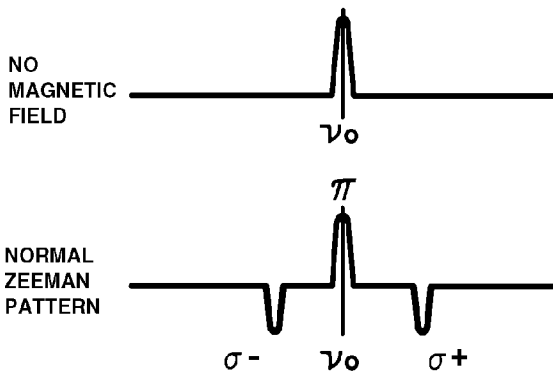


Figure 3-11. The Zeeman effect.

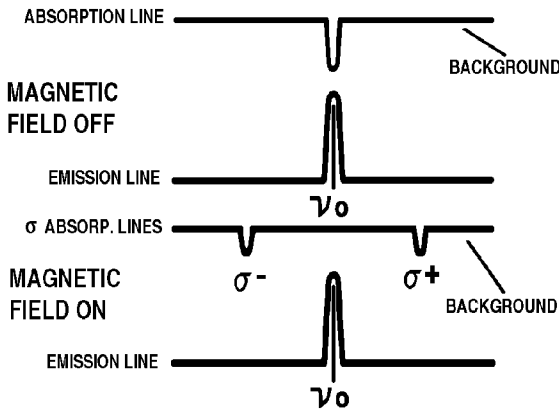


Figure 3-12. Zeeman effect background correction.

the atomic spectra which are a measure of these energy levels. When an atom is placed in a magnetic field and its atomic absorption profile observed with polarized light, the normal single-line atomic absorption profile is split into two or more components symmetrically displaced about the normal position, as illustrated in Figure 3-11. The spectral nature of background absorption, on the other hand, is usually unaffected by a magnetic field.

By placing the poles of an electromagnet around the atomizer and making alternating absorption measurements with the magnet off and then on, the uncorrected total absorbance (magnet off) and “background only” absorbance (magnet on) can be made, as in Figure 3-12.

The automatic comparison made by the instrument to compensate for background correction is similar to that for

the continuum source technique, except that only the one atomic line source is used. As a result, there are no potential problems with matching source intensities or coincident alignment of optical paths. Also, background correction is made at the analyte wavelength rather than across the entire spectral bandwidth, as occurs with continuum source background correction.

With Zeeman background correction, the emission profile of the line source is identical for both AA and background measurements. As a result, most complex

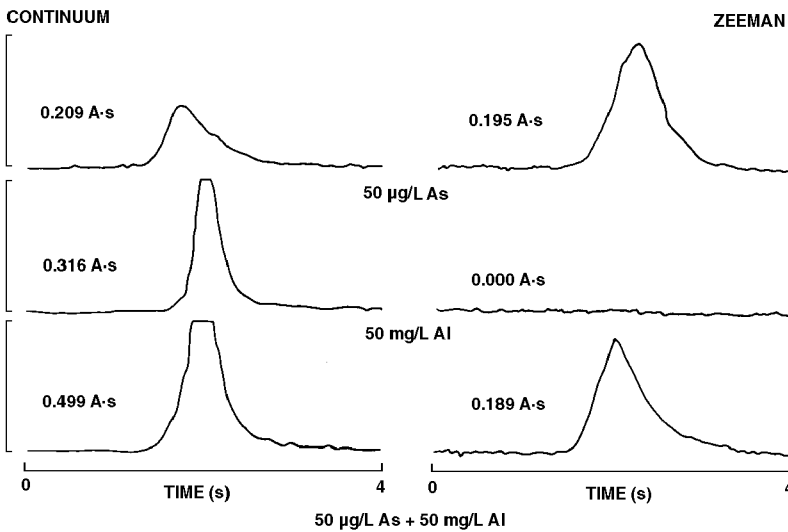


Figure 3-13. Zeeman vs. Continuum Background Correction. From Letourneau, Joshi and Butler, *At. Spectrosc.* **8**, 146 (1987).

structured background situations can be accurately corrected with Zeeman background correction. This can be seen in Figure 3-13, where background absorption due to the presence of aluminum in a graphite furnace determination of arsenic is completely compensated using Zeeman correction but produces erroneously high results with continuum source background correction. Table 3-3 summarizes the advantages of Zeeman effect background correction.

Table 3-3
Advantages of Zeeman Effect Background Correction

1. Corrects for high levels of background absorption.
2. Provides accurate correction in the presence of structured background.
3. Provides true double-beam operation.
4. Requires only a single, standard light source.
5. Does not require intensity matching or coincident alignment of multiple sources.

The examples used above to illustrate Zeeman effect background correction are based on the use of a transverse AC Zeeman system, the type most commonly used

with commercial AA instrumentation. However, there are three types of Zeeman effect background correction systems available on commercial atomic absorption instruments: DC Zeeman, transverse AC Zeeman and longitudinal AC Zeeman. These systems differ in the way the magnetic field is applied and by the means used to measure the combined (atomic absorption plus background absorption) and background absorption only signals. DC Zeeman systems use a permanent magnet and a rotating or vibrating polarizer to separate the combined and background only signals. AC systems use an electromagnet, and measure the combined and background only signals by turning the magnetic field on and off. The difference between transverse (magnetic field applied across the light path) and longitudinal (magnetic field applied along the light path) AC Zeeman systems is that transverse systems uses a fixed polarizer, while the longitudinal system does not require a polarizer. The advantages and limitations of each type of Zeeman system are summarized in Tables 3-4 and 3-5 on the following page.

Other Spectral Interferences

If the atomic absorption profile for an element overlaps the emission line of another, a spectral interference is said to exist. As has already been mentioned, this is an infrequent occurrence, because of the very wavelength-specific nature of atomic absorption. Even if an absorption line for an element other than the analyte but also present in the sample falls within the spectral bandpass, an interference will occur only if an emission line of precisely the same wavelength is present in the source. As the typical emission line width may be only 0.002 nanometers, actual overlap is extremely rare. The chances for spectral interference increase when multi-element lamps are used, where the source may contain close emission lines for several elements. Particular care should be exercised when secondary analytical wavelengths are being used in a multi-element lamp. Procedures for circumventing spectral interference include narrowing the monochromator slit width or using an alternate wavelength.

INTERFERENCE SUMMARY

The major interferences in atomic absorption include: (1) matrix interference, (2) chemical interference, (3) ionization interference, and (4) background absorption. For the first type, special considerations in sample preparation or the use of the method of standard additions may compensate for the problems generated. For the second and third, addition of an appropriate releasing agent or ionization buffer or changing the flame type used will normally remove the interference. For the fourth, background absorption, an instrumental correction technique will automat-

ically compensate for the biasing effects. Application of the techniques described here will make possible accurate atomic absorption determinations in very complex samples.

Table 3-4
DC Zeeman Systems

Advantages:

Less expensive to operate (lower power consumption)

Disadvantages:

Has poorer sensitivity and analytical working range relative to AC Zeeman systems.

The polarizer reduces light throughput by as much as 50%, affecting analytical performance.

A mechanical assembly is required to rotate or vibrate the polarizer.

Table 3-5
AC Zeeman Systems

Advantages:

Offers better sensitivity and expanded analytical working ranges relative to DC Zeeman systems.

No polarizer is required, so it provides higher light throughput and improved analytical performance. (*Longitudinal AC Zeeman systems only*)

Requires no additional mechanical devices.

Disadvantages:

Requires more electrical power than DC Zeeman systems, so has higher operating expenses.

The polarizer causes reduced light throughput by as much as 50%, affecting analytical performance. (*Transverse AC Zeeman systems only.*)

4 HIGH SENSITIVITY SAMPLING SYSTEMS

LIMITATIONS TO FLAME AA SENSITIVITY

Flame atomic absorption is a rapid and precise method of analysis. Determinations of analyte concentrations in the mg/L concentration region are routine for most elements. However, the need for trace metal analyses at $\mu\text{g/L}$ and even sub $\mu\text{g/L}$ levels calls for a more sensitive technique.

For atomic absorption to occur, free ground state atoms must be placed in a beam of light of a wavelength corresponding to an appropriate electron transition of the analyte. Any sampling process conceived must therefore address the process of creating ground state atoms and directing them to the spectrometer light path.

In examining the flame AA process, we can find a number of areas limiting the sensitivity of the technique. The absorbance depends on the number of atoms in the optical path of the spectrometer at a given instant. The nebulization process, which draws sample solution into the burner chamber at approximately 3-8 milliliters per minute, limits the sample introduction rate, and, therefore, the amount of sample available for transport to the flame. Further, the premix burner design, which has been universally adopted due to its many desirable characteristics, has the undesirable characteristic of being very wasteful of sample. Only a small fraction of the sample nebulized ever reaches the flame, with the remainder being directed to the drain. Finally, that sample which is introduced into the flame is resident in the light path for only a fleeting moment as it is propelled upwards through the flame.

The sensitivity of atomic absorption can be improved by addressing the limitations of flame sampling. By improving the sampling efficiency and/or constraining analyte atoms to the light path for a longer period of time, a greater absorption for the same analyte concentration can be achieved.

THE COLD VAPOR MERCURY TECHNIQUE

Principle

Since atoms for most AA elements cannot exist in the free, ground state at room temperature, heat must be applied to the sample to break the bonds combining atoms into molecules. The only notable exception to this is mercury. Free mercury atoms can exist at room temperature and, therefore, mercury can be measured by atomic absorption without a heated sample cell.

In the cold vapor mercury technique, mercury is chemically reduced to the free atomic state by reacting the sample with a strong reducing agent like stannous chloride or sodium borohydride in a closed reaction system. The volatile free mercury is then driven from the reaction flask by bubbling air or argon through the solution. Mercury atoms are carried in the gas stream through tubing connected to an absorption cell, which is placed in the light path of the AA spectrometer. Sometimes the cell is heated slightly to avoid water condensation but otherwise the cell is completely unheated.

As the mercury atoms pass into the sampling cell, measured absorbance rises indicating the increasing concentration of mercury atoms in the light path. Some systems allow the mercury vapor to pass from the absorption tube to waste, in which case the absorbance peaks and then falls as the mercury is depleted. The highest absorbance observed during the measurement will be taken as the analytical signal. In other systems, the mercury vapor is rerouted back through the solution and the sample cell in a closed loop. The absorbance will rise until an equilibrium concentration of mercury is attained in the system. The absorbance will then level off, and the equilibrium absorbance is used for quantitation.

The entire cold vapor mercury process can be automated using flow injection techniques. Samples can be analyzed in duplicate at the rate of about 1 sample per minute with no operator intervention. Detection limits are comparable to those obtained using manual batch processes. The use of flow injection systems also minimizes the quantity of reagents required for the determination, further reducing analysis costs.

Advantages of the Cold Vapor Technique

The sensitivity of the cold vapor technique is far greater than can be achieved by conventional flame AA. This improved sensitivity is achieved, first of all, through a 100% sampling efficiency. All of the mercury in the sample solution placed in the reaction flask is chemically atomized and transported to the sample cell for measurement.

The sensitivity can be further increased by using very large sample volumes. Since all of the mercury contained in the sample is released for measurement, increasing the sample volume means that more mercury atoms are available to be transported to the sample cell and measured. The detection limit for mercury by this cold vapor technique is approximately 0.02 µg/L. Although flow injection techniques use much smaller sample sizes, they provide similar performance capabilities, as the entire mercury signal generated is condensed into a much smaller time period relative to manual batch-type procedures.

Where the need exists to measure even lower mercury concentrations, some systems offer an amalgamation option. Mercury vapor liberated from one or more sample aliquots in the reduction step is trapped on a gold or gold alloy gauze. The gauze is then heated to drive off the trapped mercury, and the vapor is directed into the sample cell. The only theoretical limit to this technique would be that imposed by background or contamination levels of mercury in the reagents or system hardware.

Limitations to the Cold Vapor Technique

Of all of the options available, the cold vapor system is still the most sensitive and reliable technique for determining very low concentrations of mercury by atomic absorption. The concept is limited to mercury, however, since no other element offers the possibility of chemical reduction to a volatile free atomic state at room temperature.

HYDRIDE GENERATION TECHNIQUE**Principle**

Hydride generation sampling systems for atomic absorption bear some resemblances to cold vapor mercury systems. Samples are reacted in an external system with a reducing agent, usually sodium borohydride. Gaseous reaction products are then carried to a sampling cell in the light path of the AA spectrometer. Unlike the mercury technique, the gaseous reaction products are not free analyte atoms

but the volatile hydrides. These molecular species are not capable of causing atomic absorption. To dissociate the hydride gas into free atoms, the sample cell must be heated.

In some hydride systems, the absorption cell is mounted over the burner head of the AA spectrometer, and the cell is heated by an air-acetylene flame. In other systems, the cell is heated electrically. In either case, the hydride gas is dissociated in the heated cell into free atoms, and the atomic absorption rises and falls as the atoms are created and then escape from the absorption cell. The maximum absorption reading, or peak height, or the integrated peak area is taken as the analytical signal.

Advantages of the Hydride Technique

The elements determinable by hydride generation are listed in Table 4-1. For these elements, detection limits well below the $\mu\text{g/L}$ range are achievable. Like cold vapor mercury, the extremely low detection limits result from a much higher sampling efficiency. In addition, separation of the analyte element from the sample matrix by hydride generation is commonly used to eliminate matrix-related interferences.

Table 4-1
Hydride Generation Elements

As	Bi	Ge
Pb	Sb	Se
Sn	Te	

The equipment for hydride generation can vary from simple to sophisticated. Less expensive systems use manual operation and a flame-heated cell. The most advanced systems combine automation of the sample chemistries and hydride separation using flow injection techniques with decomposition of the hydride in an electrically-heated, temperature-controlled quartz cell.

Disadvantages to the Hydride Technique

The major limitation to the hydride generation technique is that it is restricted primarily to the elements listed in Table 4-1. Results depend heavily on a variety of parameters, including the valence state of the analyte, reaction time, gas pressures, acid concentration, and cell temperature. Therefore, the success of the hydride generation technique will vary with the care taken by the operator in attending to

the required detail. The formation of the analyte hydrides is also suppressed by a number of common matrix components, leaving the technique subject to chemical interference.

GRAPHITE FURNACE ATOMIC ABSORPTION

Principle

By far the most advanced and widely used high sensitivity sampling technique for atomic absorption is the graphite furnace. In this technique, a tube of graphite is located in the sample compartment of the AA spectrometer, with the light path passing through it. A small volume of sample solution is quantitatively placed into the tube, normally through a sample injection hole located in the center of the tube wall. The tube is heated through a programmed temperature sequence until finally the analyte present in the sample is dissociated into atoms and atomic absorption occurs.

As atoms are created and diffuse out of the tube, the absorbance rises and falls in a peak-shaped signal. The peak height or integrated peak area is used as the analytical signal for quantitation.

Advantages of the Graphite Furnace Technique

Detection limits for the graphite furnace fall in the ng/L range for most elements. The sample is atomized in a very short period of time, concentrating the available atoms in the heated cell and resulting in the observed increased sensitivity. Even though this technique uses only microliter sample volumes, the small sample size is compensated by long atom residence times in the light path. This provides detection limits similar to the techniques discussed above which use much larger samples.

The graphite furnace is much more automated than the other techniques. Even though heating programs can be very sophisticated, the entire process is automated once the sample has been introduced and the furnace program initiated. Automatic samplers make completely unattended operation for graphite furnace AA possible.

Early experiences with the graphite furnace were plagued with interference problems, requiring detailed optimization procedures for every sample to obtain accurate results. However, extensive studies into the theory of the furnace technique combined with the development of improved instrumentation have changed furnace AA into a highly reliable, routine technique for trace metal analysis.

The final and most obvious advantage of the graphite furnace is its wide applicability. The graphite furnace can determine most elements measurable by AA in a wide variety of matrices. The importance of this technique requires a more detailed discussion in the following chapters.

5 INTRODUCTION TO GRAPHITE FURNACE ATOMIC ABSORPTION

CONSIDERATIONS IN ULTRA TRACE ANALYSIS

Performance Criteria

Differences in graphite furnace performance characteristics require redefinition of some basic AA performance criteria. Since the magnitude of the graphite furnace signal observed depends on analyte mass rather than concentration, the term “characteristic mass” is used as a measure of the sensitivity of the furnace. Characteristic mass is analogous to characteristic concentration for flame AA except that mass, rather than concentration, is related to absorbance. The characteristic mass of an analyte is defined as the mass of analyte in picograms required to produce a peak height signal of 0.0044 absorbance or an integrated peak area signal of 0.0044 absorbance-seconds (A·s).

Similar to characteristic concentration for flame AA, characteristic mass may be used as an indicator of instrument optimization. Typical characteristic mass values for a properly adjusted instrument are usually given in the instrument documentation. Experimental values for characteristic mass (m_0) can be determined for comparison by measuring the peak area absorbance of a known mass of analyte and calculating m_0 according to the following equation.

$$m_0 \text{ (pg)} = \frac{\text{Sample vol. } (\mu\text{L}) \times \text{Analyte Conc. } (\mu\text{g/L}) \times 0.0044 \text{ A}\cdot\text{s}}{\text{Observed Peak Area (A}\cdot\text{s)}}$$

Note that for this equation to be valid, the analyte mass used to measure m_0 must produce a signal in the linear range of the calibration curve. By comparing the experimental value obtained from this equation to the reference value given in the instrument documentation, the state of instrument optimization can be evaluated. If the calculated m_0 is significantly greater than the reference value, adjustments should be made to improve the sensitivity of the measurement. Calculated values

for m_0 which are significantly less than the reference value, suggesting better than specified sensitivity, may in fact be a warning sign of analyte contamination in the standard.

Another term characterizing graphite furnace instrument performance is “detection limit”. Similar to flame AA, the detection limit is an indicator of the lower limits of analyte detectability and is limited by the instrument signal-to-noise ratio. Graphite furnace detection limits are usually stated in mass units (pg) rather than concentration units, again reflecting the furnace signal’s dependency on analyte mass, rather than concentration. However, in real analytical situations the detection limit will depend both on the system sensitivity (characteristic mass) and the maximum sample size which can be accommodated.

Graphite Furnace Applications

The sensitivity of graphite furnace atomic absorption makes it the obvious choice for trace metal analysis applications. Routine determinations at the $\mu\text{g/L}$ level for most elements make it ideal for environmental applications. Advances in instrumentation and techniques have made it possible to analyze very complex sample matrices, such as those frequently found in biological and geological samples. The microliter sample sizes used offer additional benefits where the amount of sample available for analysis is limited, as in many clinical analyses.

COMPONENTS OF THE GRAPHITE FURNACE SYSTEM

The graphite furnace is made up of three major components, the atomizer, the power supply, and the programmer. The atomizer is located in the sampling compartment of the atomic absorption spectrometer, where sample atomization and light absorption occur. The power supply controls power and gas flows to the atomizer under the direction of the programmer, which is usually built into the power supply or spectrometer. A description of each of these major components follows.

The Graphite Furnace Atomizer

A basic graphite furnace atomizer is comprised of the following components:

- graphite tube
- electrical contacts
- enclosed water cooled housing
- inert purge gas controls

A graphite tube is normally the heating element of the graphite furnace. The cylindrical tube is aligned horizontally in the optical path of the spectrometer and serves as the spectrometer sampling cell. A few microliters (usually 5-50) of sample are measured and dispensed through a hole in the center of the tube wall onto the inner tube wall or a graphite platform. The tube is held in place between two graphite contact cylinders, which provide electrical connection. An electrical potential applied to the contacts causes current to flow through the tube, the effect of which is heating of the tube and the sample.

The entire assembly is mounted within an enclosed, water-cooled housing. Quartz windows at each end of the housing allow light to pass through the tube. The heated graphite is protected from air oxidation by the end windows and two streams of argon. An external gas flow surrounds the outside of the tube, and a separately controllable internal gas flow purges the inside of the tube. The system should regulate the internal gas flow so that the internal flow is reduced or, preferably, completely interrupted during atomization. This helps to maximize sample residence time in the tube and increase the measurement signal. Figure 5-1 illustrates one type of atomizer assembly, a longitudinally-heated furnace.

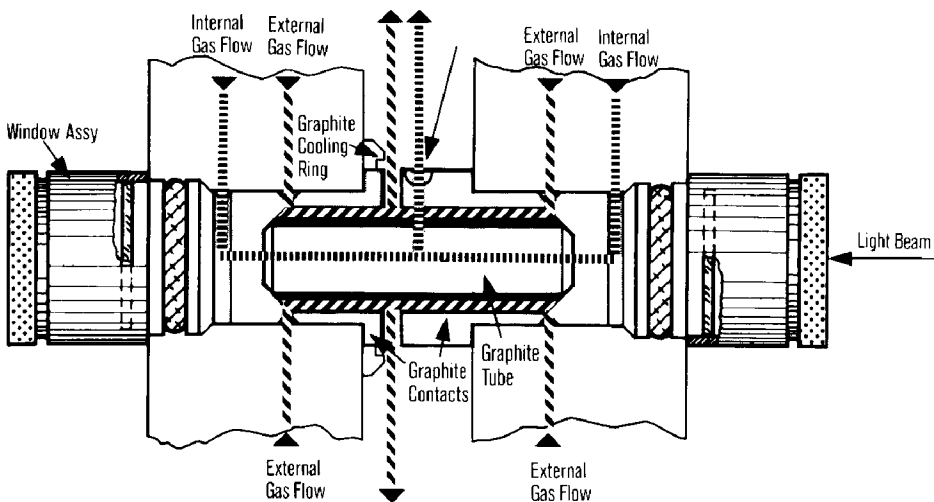


Figure 5-1. Longitudinally-heated graphite furnace atomizer.

The tube in Figure 5-1 is heated by passing electrical current from the graphite contacts at the ends of the tube through the length of the tube. This type of furnace is similar to the original design of Massmann, which is the basis for most currently available commercial graphite furnace systems.

The longitudinally-heated furnace has a major liability. The electrical contacts at each end of the tube must be cooled. As a result, there must always be a temperature gradient along the length of the tube, the tube ends adjacent to the electrical contacts being cooler than the central portion. This temperature gradient can cause vaporized atoms and molecules to condense as they diffuse to the cooler tube ends. This may produce interferences, the most common type being the incomplete removal of analyte or matrix from the tube. Incomplete removal of matrix during pyrolysis can increase the magnitude of background absorption during atomization. Incomplete removal of analyte during atomization is more serious. It creates "carryover" or "memory", wherein a portion of the analyte in the current sample remains in the tube and contributes to the analytical signal for the following sample. This produces erroneously high analytical results and poor precision.

To minimize carryover, most longitudinally-heated furnace heating programs use one or more cleanout steps after the atomization step. A cleanout step involves the application for several seconds of full internal gas flow and a temperature equal to or greater than that used for atomization to remove residual sample components. While this technique works well for the more easily atomized analytes, it is not always successful with those analytes that require higher atomization temperatures. The use of a high temperature cleanout step may also reduce tube lifetime.

The transversely-heated graphite furnace eliminates many of the problems associated with the longitudinally-heated furnace. The graphite tube of the transversely-heated furnace, shown in Figure 5-2, includes integral tabs which protrude from each side. These tabs are inserted into the electrical contacts. When power is applied, the tube is heated across its circumference (transversely). By applying power in this manner, the tube is heated evenly over its entire length, eliminating or significantly reducing the sample condensation problems seen with longitudinally-heated furnace systems.

An additional advantage of the transversely-heated furnace is that it allows the use of longitudinal Zeeman-effect background correction. As described in Chapter 3, longitudinal Zeeman offers all of the advantages of transverse Zeeman correction without the need to include a polarizer in the optical system. This provides a significant improvement in light throughput.

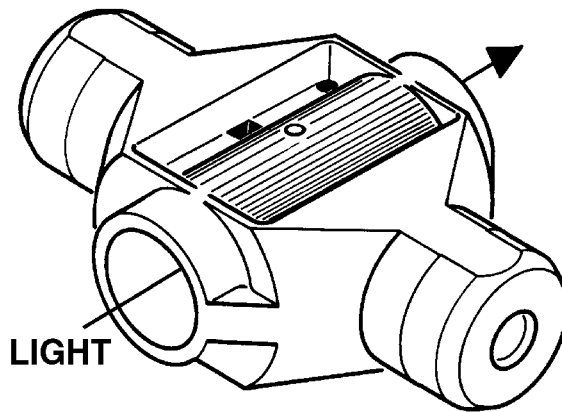


Figure 5-2. A graphite tube for a transversely-heated furnace.

The Graphite Furnace Power Supply and Programmer

The power supply and programmer perform the following functions:

- electrical power control
- temperature program control
- gas flow control
- spectrometer function control

The power supply controls the electrical current supplied to the graphite tube, which causes heating. The temperature of the tube is controlled by a user-specified temperature program. Through the programmer the operator will enter a sequence of selected temperatures vs. time to carefully dry, pyrolyze, and finally atomize the sample. The program may also include settings for the internal inert gas flow rate and, in some cases, the selection of an alternate gas. Certain spectrometer functions, such as triggering of the spectrometer read function, also may be programmed and synchronized with the atomization of the sample in the furnace.

SUMMARY OF A GRAPHITE FURNACE ANALYSIS

A graphite furnace analysis consists of measuring and dispensing a known volume of sample into the furnace. The sample is then subjected to a multi-step temperature program. When the temperature is increased to the point where sample atomi-

zation occurs, the atomic absorption measurement is made. Variables under operator control include the volume of sample placed into the furnace and heating parameters for each step. These parameters include:

- | | |
|-----------------|--|
| 1) temperature | final temperature during step |
| 2) ramp time | time for temperature increase |
| 3) hold time | time for maintaining final temperature |
| 4) internal gas | gas type and flow rate |

In addition to the above, spectrometer control functions can be programmed to occur at specified times within the graphite furnace program. While the number of steps within each program is variable, 6 steps make up the typical graphite furnace program. These steps include:

- 1) Drying
- 2) Pyrolysis
- 3) Cool down (optional)
- 4) Atomization
- 5) Clean out
- 6) Cool down

Figure 5-3 illustrates a typical graphite furnace program. The following paragraphs will discuss each operator controlled variable, and how they may affect the analysis.

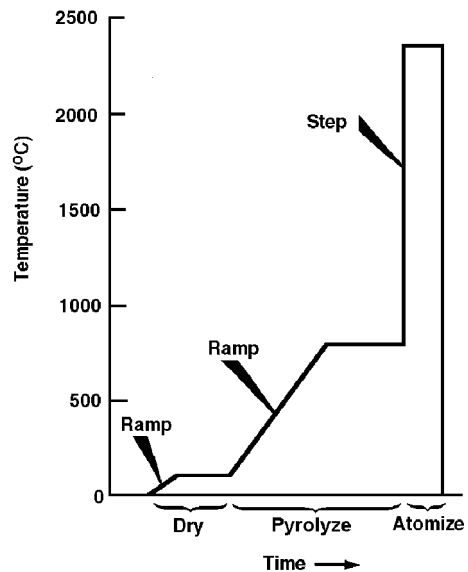


Figure 5-3. A graphite furnace temperature program.

Sample Size

Since the graphite furnace signal depends on analyte mass, the operator has an effective degree of control on measured absorbance by controlling the sample volume. Larger volumes of sample solution contain more analyte and result in greater signals. The analytical range of furnace analysis can therefore be controlled, to some extent, by varying sample volume. For very low concentrations, the maxi-

mum volume of analyte can be used, while for higher concentrations, the sample volume can be reduced. Smaller sample volumes can also be used where sample availability is limited or where background absorption is excessively large.

The maximum volume of sample usable will depend on the tube configuration. Where the graphite platform is not used, sample volumes up to 100 μL can be used, depending on the type of tube and sample. With the platform in place, a sample volume of less than 50 μL is recommended. A convenient sample volume for most analyses is 20 μL . Where larger volumes are required, i.e., for improved detection limits, multiple injections can be used with appropriate drying and pyrolysis steps between each injection to increase the effective sample size.

The use of an autosampler is strongly recommended for dispensing samples into a graphite furnace. While skilled operators may obtain reasonable reproducibility by manual injection on a short term basis, autosamplers have been proven to provide superior results. With many graphite furnace systems, autosamplers can also generate working standards from stock standard solutions; add appropriate reagents; and provide method of additions analyses or recovery measurements, all automatically.

The Drying Step

After the sample is placed in the furnace, it must be dried at a sufficiently low temperature to avoid sample spattering, which would result in poor analytical precision. Temperatures around 100-120 $^{\circ}\text{C}$ are common for aqueous solutions.

Use of a temperature “ramp” provides a variable time over which the temperature is increased. A longer ramp time provides a slower, more “gentle” increase in heating. When a platform is used, the temperature lag of the platform versus the tube walls provides a natural “ramping” effect. Therefore shorter ramp times are usually used with the platform. Longer ramp times are used when the sample is to be atomized from the tube wall.

After the temperature ramp, the furnace is held at the selected drying temperature until drying is complete. Since only a few microliters of sample are used, the drying “hold” time is usually less than a minute.

During the drying process, the internal gas flow normally is left at its default maximum value (250-300 mL per minute) to purge the vaporized solvent from the tube.

The Pyrolysis Step

The purpose of the pyrolysis step (sometimes referred to as the ashing, char or pre-treatment step) is to volatilize inorganic and organic matrix components selectively from the sample, leaving the analyte element in a less complex matrix for analysis. During this step, the temperature is increased as high as possible to volatilize matrix components but below the temperature at which analyte loss would occur.

The temperature selected for the pyrolysis step will depend on the analyte and the matrix. Suggested temperatures normally are provided in the documentation supplied with the graphite furnace. The internal gas flow is again left at 250-300 mL per minute in the pyrolysis step, to drive off volatilized matrix materials. For some sample types, it may be advantageous to change the internal gas, e.g., to air or oxygen, during the pyrolysis step to aid in the sample decomposition.

The Pre-atomization Cool Down Step

With longitudinally-heated furnaces, it is frequently advantageous to cool the furnace prior to atomization since the heating rate is a function of the temperature range to be covered. As the temperature range is increased, the rate of heating also increases. The use of a cool down step prior to atomization maximizes the heating rate and extends the isothermal zone within the tube immediately after heating. The extended isothermal zone has been shown to improve sensitivity and reduce peak tailing for a number of elements, including those which characteristically are difficult to atomize in the graphite furnace.

A pre-atomization cool down step normally is not required for transversely-heated furnaces as the isothermal zone extends the length of the tube with that type of system.

The Atomization Step

The purpose of the atomization step is to produce an atomic vapor of the analyte elements, thereby allowing atomic absorption to be measured. The temperature in this step is increased to the point where dissociation of volatilized molecular species occurs.

The atomization temperature is a property of the analyte element. By following recommended procedures of analysis, it is usually possible to use the temperatures provided in the graphite furnace documentation without further optimization. Care should be taken to avoid the use of an excessively high atomization tempera-

ture, as the analyte residence time in the tube will be decreased and a loss of sensitivity will occur. Also, the use of excessively high atomization temperatures can shorten the useful lifetime of the graphite tube.

For atomization, it is desirable to increase the temperature as quickly as possible. Therefore, ramp times normally will be set to minimum values to provide the highest heating rate. It also is desirable to reduce or, preferably, to totally interrupt the internal gas flow during atomization. This increases the residence time of the atomic vapor in the furnace, maximizing sensitivity and reducing some interference effects. At the beginning of this step, the spectrometer “read” function is triggered to begin the measurement of light absorption.

The Clean Out and Cool Down Steps

After atomization, the graphite furnace may be heated to still higher temperatures to burn off any sample residue which may remain in the furnace. An optional cool down step then allows the furnace to return to near ambient temperature prior to the introduction of the next sample. With some systems, a preset cool down step is automatically included in each furnace cycle, and need not be programmed separately.

FAST FURNACE ANALYSIS

The most time consuming portions of a graphite furnace AA analysis are the drying and pyrolysis steps. Analysts have long sought some means to reduce or eliminate the time required for these pretreatment stages. For years, an inability to compensate for the high background signals generated with incomplete pretreatment and matrix-related interferences precluded reducing the time required for these steps.

The situation changed dramatically with the introduction of two developments: Zeeman effect background correction and Stabilized Platform Graphite Furnace (STPF) technology, which is described in detail in Chapter 6. Zeeman effect background correction is far superior to continuum source background correction in its ability to correct accurately for high levels of background absorption. The use of STPF technology provides almost constant characteristic mass values independent of sample matrix. The combination of these two techniques was the key to providing faster graphite furnace analyses.

In fast furnace analysis, the pyrolysis step and matrix modification are usually eliminated. The drying step is minimized by injection of the sample onto a preheated platform. Drying time is also minimized by using as small a sample size as possible consistent with the required analytical precision and detection limits.

To further reduce the furnace program time, the cool down step at the end of the program is frequently reduced or eliminated. This is possible since most furnace systems typically require 20 seconds or more between the end of a temperature program and the point at which the next sample is ready to be introduced into the furnace. That 20 second period is usually sufficient to allow the furnace to cool reproducibly to the preheated drying temperature required for the next sample.

Using these procedures, typical furnace program times frequently can be reduced from 2-4 minutes to 30 seconds or less per determination, a considerable time savings, without sacrificing analytical precision or accuracy.

Fast furnace analysis techniques are not compatible with all AA instrumentation. To fully realize the benefits of fast furnace analysis, the instrumentation used must provide Zeeman background correction, be capable of handling very high absorbance measurements and be compatible with the requirements of STPF technology. Also, the fast furnace technique may not be compatible with all sample types. Very complex matrices may still require at least a short pyrolysis step and use of a matrix modifier for optimum results.

MEASURING THE GRAPHITE FURNACE AA SIGNAL

Nature of the Graphite Furnace Signal

In flame atomic absorption, the absorption signal is steady state. That is, as long as solution is aspirated into the flame, a constant absorbance is observed. For graphite furnace analyses, however, the signal is transient. As atomization begins, analyte atoms are formed and the signal increases, reflecting the increasing atom population in the furnace. The signal will continue to increase until the rate of atom generation becomes less than the rate of atom diffusion out of the furnace. At that point, the falling atom population results in a signal which decreases until all atoms are lost and the signal has fallen to zero. To determine the analyte content of the sample, the resulting peak-shaped signal must be quantitated.

Peak Height Measurement

For many years, measuring the height of the transient signal was the only practical means for quantitating furnace results. The constantly changing signal was monitored on a strip chart recorder, and peak height was measured manually in chart divisions. Later instrumentation allowed peak height to be measured directly by electronic means.

While peak height does depend on the analyte concentration in the sample, it is also affected by other factors. Peak height is only a measure of the maximum atom population which occurred in the furnace during atomization. If matrix components in the sample affect the rate of atom formation, the maximum atom population and the peak height are also affected, as shown in Figure 5-4 for the determination of lead in blood. While the two solutions contain identical amounts of lead (0.2 ng), the peak shapes and appearance times are dramatically different.

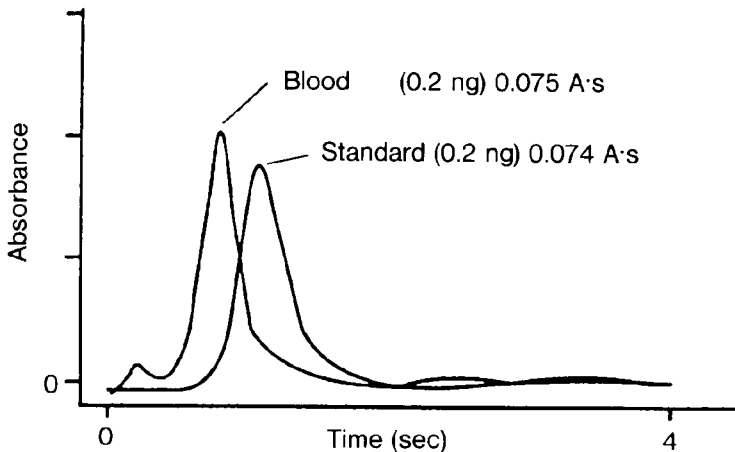


Figure 5-4. Effect of matrix on peak height and area.

This susceptibility to matrix effects makes graphite furnace AA vulnerable to interferences when peak height measurement is used for quantitation. Therefore, peak height measurements are seldom used with modern graphite furnace AA systems.

Peak Area Measurement

Modern instrumentation provides the capability to integrate absorbance during the entire atomization period, yielding a signal equal to the integrated peak area, that is, the area under the peak signal. If the temperature in the furnace is constant during the measurement process, the peak area will represent a count of all atoms present in the sample aliquot, regardless of whether the atoms were generated early or late in the atomization process. Integrated peak area measurements ($A \cdot s$) are independent of the atomization rate, and are therefore much less subject to matrix effects as shown in Figure 5-4. As a result, peak area is preferred for graphite furnace analysis.

SOLID SAMPLING WITH THE GRAPHITE FURNACE

The ability to analyze solid samples directly with little or no sample preparation offers a number of potential benefits. It reduces total analysis time, minimizes the potential for contamination or analyte loss, and reduces the cost of sample pretreatment reagents and their disposal.

The first published information on the use of graphite furnace AA for the direct analysis of solid samples appeared in 1971. However, the technique was fraught with problems. The small sample sizes required (1-2 mg) frequently were not representative of the original sample due to inhomogeneous distribution of the analyte. Samples were difficult to handle as insertion of the sample into the furnace was a cumbersome, manual procedure. Analytical results frequently were not reproducible as each replicate had to be sampled, weighed and transferred separately. Finding a suitable means of calibrating the determination varied from difficult to impossible. Aqueous standards or the method of additions frequently could not be used. Matrix-matched standards (if available) were required for many determinations.

Today, many of the problems associated with solid sampling with the graphite furnace have been overcome. The key to removing the previous limitations was the development of slurry sampling. With slurry sampling, the sample is reduced to a fine powder, usually by freeze-drying or grinding depending on the sample type. The powder is weighed directly into an autosampler vial, and a measured amount of liquid is added. The vial is then placed into the tray of the furnace autosampler. Just prior to the analysis, the mixture is agitated to form a slurry. Most commonly, the agitation is performed using an ultrasonic probe. The slurry is then sampled by the autosampler capillary.

Slurries can be analyzed exactly as though they were true solutions. Replicates can be measured from the same sample vial. Matrix modifiers and spikes can be added. Sample size can be varied conveniently. True Stabilized Temperature Platform Furnace (STPF) conditions are maintained, allowing calibration against simple aqueous standards.

Even with slurry sampling, however, some limitations remain. Although a larger portion of the original sample is weighed relative to direct solid sampling, sample homogeneity problems can still occur. Particle size may affect reproducibility and accuracy if it is inconsistent or too large. The degree to which the solvent used may extract the analyte can also affect analytical results. However, the major hurdles to solid sampling with the graphite furnace have been overcome.

6 CONTROL OF GRAPHITE FURNACE INTERFERENCES

INTERFERENCES AND THE GRAPHITE FURNACE

In the earlier days of the technique, graphite furnace atomic absorption was widely recognized as a highly interference-prone technique. In spite of this, much good analytical work was done on the furnace by careful method development and attention to the potential interferences. The role of the graphite furnace as a routine analytical tool, however, was severely impaired by its susceptibility to interference.

At first, the interferences were accepted as being an unavoidable part of the technique, and procedures were developed for observing and compensating for the biasing effects. Later research into the mechanisms of the graphite furnace technique resulted in a better understanding of the causes of the interferences. New instrumentation and analytical procedures were developed which avoided the conditions found to be the source of the interference problems. With today's procedures and instrumentation, the graphite furnace has, in fact, become a relatively interference-free technique.

It is important to note that the successful solution to the interference problem does not involve just a change in instrument design. Many of yesterday's graphite furnace procedures involved recommendations which are actively discouraged today. It is the authors' observation that a significant population of graphite furnace users is applying yesterday's procedures to today's instrumentation, thereby failing to realize the full benefit of the newer developments. The following discussion is offered to provide insight into the factors affecting furnace measurements, in the hope that this understanding will result in a more widespread realization of the potential inherent in current graphite furnace technology.

The discussion of interferences is divided into two broad categories, spectral and nonspectral interferences. Spectral interferences are those resulting from light absorption by molecules or by atoms other than those of the analyte element. Non-

spectral interferences are those which affect the production or the availability of analyte atoms which create the measured atomic absorption.

SPECTRAL INTERFERENCES

Emission Interference

Emission interference arises when “black body” radiation (the intense light emitted by the hot graphite tube or platform) reaches the instrument’s light detector, the photomultiplier tube (PMT). This problem is manifested by increased signal variability (noise) which degrades analytical performance. In severe circumstances, emission interference may temporarily blind the PMT, resulting in erratic, meaningless readings at atomization.

The potential for observing emission interference varies with analyte wavelength, increasing at longer wavelengths. As seen in Figure 6-1, the emission from the furnace is a continuum, with maximum intensity in the near infrared wavelength region.

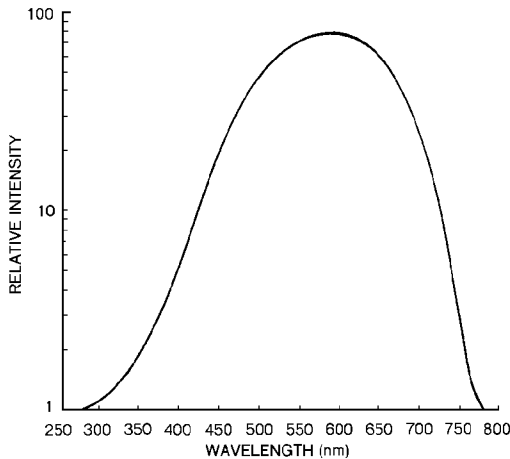


Figure 6-1. Black body radiation spectrum.

Elements determined at UV wavelengths, such as zinc at 213.9 nm, are not particularly susceptible to emission interference. However, chromium, at 357.9 nm, and calcium, at 422.7 nm, are more greatly affected. Barium, at 553.6 nm, is especially vulnerable.

Emission interference is controlled primarily by spectrometer optical design. Monochromator slit heights for graphite furnace instruments have been reduced, narrowing the angle of view of the PMT. With this narrowed field of view, a properly aligned spectrometer can “see” through the graphite tube, but it does not see the tube wall or

platform, which are the sources of black body emission. Many instruments designed for both flame and furnace analyses will have two sets of monochromator slits. The “low” (sometimes designated “alternate”) slits are used with the graphite furnace to eliminate the emission interference problem.

While instruments are designed to deal effectively with the emission interference problem, analyst attention to furnace alignment and maintenance is still required. If the graphite furnace is misaligned in the spectrometer optical path, the graphite tube wall or platform may be brought back into the field of view of the PMT, thereby negating the instrument's optical design and causing a reoccurrence of the emission problem. Cleanliness of the graphite furnace and spectrometer sample compartment windows also must be maintained to prevent light scattering, which might deflect black body radiation into the line of sight of the PMT. Finally, and possibly most important, the atomization temperature used should be no higher than required for efficient analyte atomization. This will minimize the black body emission from the tube wall and platform and also prolong the lifetime of the tube and platform.

Background Absorption

The most severe spectral interference problem encountered with graphite furnace analyses is "background absorption". Background absorption is a nonspecific attenuation of light at the analyte wavelength caused by matrix components in the sample. Unlike atomic absorption, background absorption is broad band, sometimes covering tens or even hundreds of nanometers. This broad band absorption normally is due to molecular absorption or light scattering caused by undissociated sample matrix components in the light path at atomization.

Since background absorption is broad band, the chance of overlap with a desired analyte wavelength is significant. Techniques for controlling background absorption must, therefore, be applied for almost all graphite furnace work. These techniques include reduction of background absorption through sample treatment (i.e., matrix modification) and furnace control procedures, and spectral compensation for background absorption through optical background correction techniques.

Background Reduction Techniques

The purpose of the pyrolysis step in the graphite furnace program is to volatilize matrix components from the sample. If this process were 100% efficient, that is, if all of the matrix could be driven off during pyrolysis, there would be no background absorption since the sample components which cause background would be removed prior to atomization. Analyte atoms, however, must not be lost during pyrolysis. Therefore, the pyrolysis temperature and the effectiveness of the pyrolysis step in matrix removal are limited by the temperature at which analyte atoms are lost.

The degree of completeness of matrix removal during pyrolysis will depend on the relative volatilities of the matrix components and the analyte. It is desirable that the matrix be more volatile than the analyte, so that the bulk of the sample material can be driven off at a pyrolysis temperature where no analyte is lost.

The relative volatilities of the matrix and analyte can frequently be controlled through a procedure known as “matrix modification”. Through matrix modification, a reagent or “matrix modifier” is added to the sample. The matrix modifier is selected to generate either an increased matrix volatility or decreased analyte volatility.

One of the first published matrix modification procedures is illustrated in Table 6-1. While superior matrix modifiers have since been identified for the removal of NaCl (e.g., ammonium phosphate), this early example provides a clear illustration of how matrix modifiers function. The procedure involves the addition of ammonium nitrate to samples with a high sodium chloride matrix. Sodium chloride is a relatively nonvolatile compound, requiring pyrolysis temperatures which would result in the loss of many analytes. By adding ammonium nitrate, however, the sample matrix is converted to more volatile components which can be driven off with high efficiency at lower pyrolysis temperatures.

Table 6-1
Matrix Modification Using NH₄NO₃



Decomposition Temperatures (°C):

NaCl	1400
NH ₄ NO ₃	210
NaNO ₃	380
NH ₄ Cl	330

Other classical procedures for matrix modification involve addition of a matrix modifier which renders the analyte less volatile, allowing the use of higher pyrolysis temperatures for more thorough matrix removal. One such example, illustrated in Figure 6-2, is the addition of nickel nitrate for selenium determinations. Selenium as an analyte is highly volatile in most media. In the presence of nickel, however, selenium can be heated to temperatures of 900 °C or more without loss. This can allow removal of the sample matrix, which could otherwise not be driven off without loss of selenium.

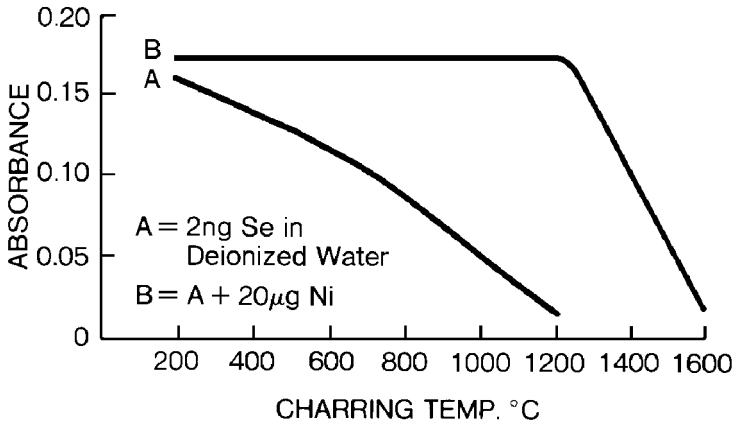


Figure 6-2. Ni matrix modification for Se determination.

The use of mixed modifiers, such as palladium plus magnesium nitrate, is now recommended for many graphite furnace determinations. Mixed modifiers may provide superior results and, while not universally applicable, frequently can be used effectively with a variety of different elements.

Varying the sample volume is also an effective means of background control when sensitivity is not limited. Larger sample volumes contain a greater number of analyte atoms, and therefore, improve the ability to detect low analyte concentrations. However, larger sample volumes contain more of the other sample components, as well. Where high background absorption is limiting the quality of the analysis, it is frequently desirable to reduce the sample size, thereby reducing the mass of the background-producing matrix components with a corresponding reduction in background absorption.

Another procedure that can minimize the effects of background absorption involves modification of the atomization step of the furnace temperature program. For example, one might use a different atomization temperature to remove the sample components that contribute to background absorption prior to the analyte atomization.

As the degree of background absorption is wavelength dependent, an alternative technique to minimize background absorption is to use a different absorption wavelength where one exists and sensitivity requirements will allow. As a general rule-of-thumb, background absorption is usually greater at lower wavelengths.

Automatic Instrumental Background Correction

Seldom will the analyst be successful in completely eliminating background absorption through the techniques described above. Therefore, it is usually necessary to compensate for residual background to obtain unbiased analytical results, as discussed in Chapter 3.

Continuum source background correction was the first automatic means of compensating for residual background. Continuum source background correction employs the use of a continuum source to measure the contribution of background to the total measured signal. Instrument electronics then automatically remove the unwanted background contribution, providing a background corrected AA result.

Most good continuum source background correction systems can be used with combined atomic absorption plus background absorption signals up to 2 absorbance units. However, for best analytical results it normally is desirable to maintain background absorption below 0.5-1 absorbance. At higher background absorption levels instrument noise increases and poorer analytical precision and accuracy may result. For complex matrices, therefore, it is advisable to optimize the furnace program, sample volume, and other procedures carefully to reduce the observed background to reasonable levels.

Zeeman-effect background correction offers a number of advantages compared with continuum source background correction. Properly designed Zeeman-effect background correction systems measure the background absorption signal at exactly the same wavelength and absorption bandwidth as the atomic absorption signal. Zeeman correction systems can therefore correct for higher and more spectrally complicated background absorption and provide more precise and accurate analytical results. They are also usable for all elements at all wavelengths.

Interpolated Background Correction

Regardless of the background correction system being used, the spectrometer alternates between measuring the background signal and the uncorrected background plus AA signal. The corrected AA signal is then calculated as:

$$[AA] = [AA+BG] - [BG]$$

It is important to note that the uncorrected [AA+BG] and background [BG] measurements are not made at precisely the same point in time, as illustrated in Figure 6-3. For flame AA this has little impact, since flame signals are steady state. However, with the graphite furnace, background and atomic absorption signals are

changing rapidly as the atomization process proceeds. This means that the background measured in the uncorrected total signal [AA+BG] and the background during the background only measurement [BG] are not necessarily the same. Therefore, the corrected signal [AA] calculated according to the previous equation may not be accurate if a correction for the timing offset is not made.

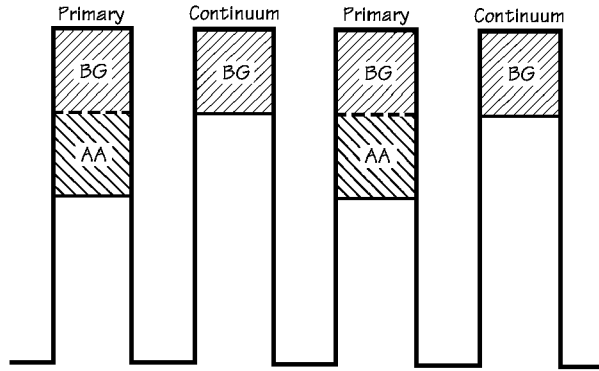


Figure 6-3. Background corrector timing diagram.

To compensate for this timing problem, an interpolation technique, similar to that illustrated in Figure 6-4, can be used to determine the background present at the time that the total uncorrected signal was measured. With an interpolation technique, [BG] readings taken before and after the [AA+BG] reading are used to mathematically estimate the [BG] reading at the same time as the [AA+BG] reading. This technique improves the accuracy of correction when the background absorption varies significantly with time.

With an interpolation technique, the corrected atomic absorption signal is represented by:

$$[AA] = [AA+BG] - [BG_{int}]$$

where [AA+BG] is the total uncorrected AA reading between two background absorption readings, BG1 and BG2; [BG_{int}] is the interpolated background

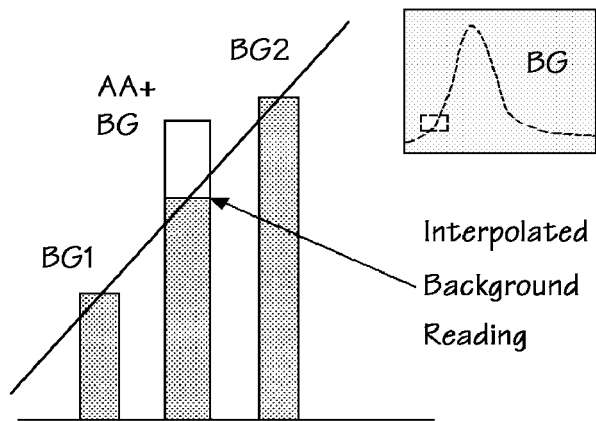


Figure 6-4. Interpolated background correction.

correction reading at the time of the [AA+BG] signal; and [AA] is the net corrected AA reading.

Interpolated background correction must be employed if accurate background correction is to be expected for rapidly changing signals such as those observed with the graphite furnace.

NONSPECTRAL INTERFERENCES

Definition

In order for atomic absorption to occur, free atoms of the analyte element must be present in the spectrometer light path. Nonspectral interferences result when diverse components in the sample matrix inhibit the formation of free analyte atoms. Nonspectral interference is generically represented by the following equation:



where M° = free analyte atoms and X° = diverse matrix component atoms.

Historically, nonspectral interference was as common to graphite furnace analyses as background absorption. Unfortunately, accurate compensation for nonspectral interferences is not as easy as compensation for background absorption.

Method of Standard Additions

An often used approach to compensate for nonspectral interference is known as the “Method of Standard Additions”. In the method of standard additions, described in Chapter 2, a known amount of analyte (spike) is added to an aliquot of the sample. The absorbance values of the unspiked and spiked samples are measured and compared to the added analyte. By calculation or plotting the results and extrapolating to zero absorbance, the analyte content in the original, unspiked sample is determined.

The major problem with the method of standard additions is that it assumes that the matrix components affecting the formation of free analyte atoms originally present in the sample will similarly affect free atom formation for analyte which is added to the sample. If this does occur, then the method of standard additions is valid. However, this assumption is frequently untrue.

Sometimes, by adding additional analyte, the equilibrium illustrated in the previous equation is changed. Other times, the interfering reaction is a slow process and does not immediately compete with free atom formation for added analyte. In either case, the calibration established by the method of standard additions is inaccurate, and, therefore, the results determined by this technique are correspondingly inaccurate. The method of additions also fails to compensate for spectral interferences such as background absorption.

A major weakness of the technique is that no indication of inaccuracy will be obtained. Perfectly straight lines for the method of standard additions plot may be observed, even though the results may be totally incorrect. It is for this reason that compensating for nonspectral interference through the method of standard additions is a far less desirable option than eliminating the presence of the interference. Current graphite furnace technology makes this latter option realistic.

The remainder of this chapter will address instrumental factors and analytical procedures designed to lead to the elimination of nonspectral interference.

The Graphite Tube Surface

The nature of the graphite tube surface makes graphite furnace analyses susceptible to certain types of nonspectral interferences, especially carbide formation. A number of elements tend to form nonvolatile carbides by interaction with the graphite surface.

A reduced tendency toward carbide formation is observed where a more dense graphite surface is used. A pyrolytically coated graphite tube offers a more dense, impervious surface than an uncoated tube. Uncoated tubes are porous, allowing sample solution to soak into the structure of the graphite during drying. In addition, atomic vapor which comes in contact with the hot graphite tube wall at atomization interacts with a porous surface much more readily than a dense surface to produce analyte carbides, thereby decreasing free atom population. Therefore, the use of a good quality, pyrolytically coated graphite tube is an important first step to avoiding nonspectral interferences. Pyrolytic coating can also increase the useful lifetime of the graphite tube.

The L'vov Platform

A goal of any technique to control nonspectral interference should be to delay the appearance of the analyte in the furnace atmosphere until the furnace has reached the actual temperature set for the atomization step of the furnace program. This favors free atom formation, maximizing sensitivity and producing a constant sen-

sitivity regardless of sample matrix. The role of the L'vov platform in accomplishing this goal is described below.

B. V. L'vov, one of the pioneers in graphite furnace atomic absorption, developed the use of a small platform made from a flat piece of solid pyrolytic graphite or pyrolytically-coated graphite which is placed in the bottom of the graphite tube (Figure 6-5). Sample is pipetted into a shallow depression in the platform. The presence of the L'vov platform helps to eliminate nonspectral interferences in several ways.

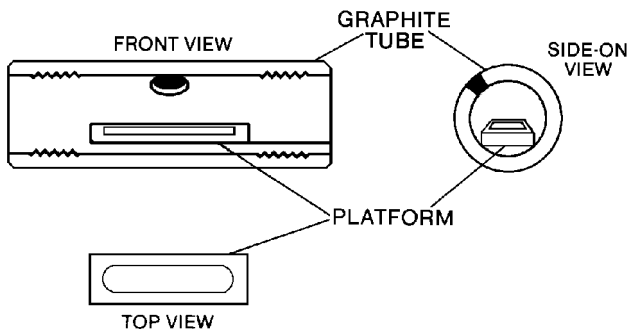


Figure 6-5. The L'vov platform.

The platform surface is solid pyrolytic graphite, and therefore resists any tendency for sample solution to soak into the surface prior to or during drying. The platform also tolerates high acid concentrations. But the benefits of the L'vov platform far exceed that of just providing a dense surface to receive the sample solution.

To understand the contribution of the L'vov platform, let us first consider what happens when analyte is atomized directly from the graphite tube wall when no platform is used. At the beginning of the atomization step, the temperature of the tube wall rises rapidly. The sample, which is in direct contact with the tube wall, will immediately experience the increase in wall temperature. When the tube wall reaches the temperature at which analyte atoms are produced, atoms are released from the hot tube surface into an inert gas atmosphere, the temperature of which lags behind that of the tube walls and which is cool relative to the surface. This sudden cooling inhibits atomization of the vaporized molecular species, and nonspectral interference results.

By contrast, when sample is placed on a L'vov platform, the sample experiences the temperature of the platform, not the temperature of the tube wall. Since the

platform is, by design, in poor physical contact with the round tube surface, the platform is heated primarily by radiant rather than conductive energy. This means that the platform will heat more slowly than the graphite tube. During the rapid heating in the atomization step, when the platform does finally reach the atomization temperature for the analyte, atoms are released into a furnace environment the temperature of which is similar to that of the platform, as shown in Figure 6-6. Under these conditions, dissociation is favored and recombination is minimized.

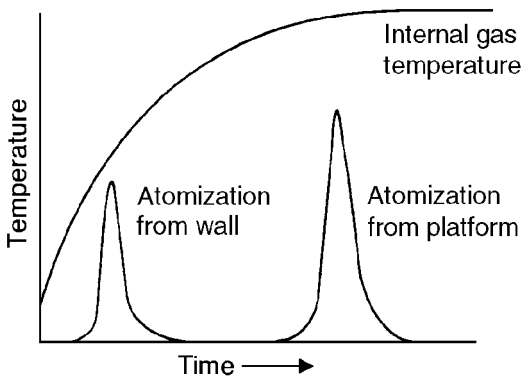


Figure 6-6. Tube wall and platform temperature profiles.

Figure 6-6 compares the atomization signals of a sample volatilized from the tube wall and from a L'vov platform versus tube temperature. When the wall of the furnace tube reaches a temperature at which the analyte will vaporize, the metal is driven from the surface into the gas phase. Both the temperature at which the analyte first starts to volatilize and the rate at which it volatilizes will depend on the quantity and the specific nature of the matrix constituents.

Since the platform is heated by radiation from the walls of the tube, the temperature of the sample on the platform is delayed relative to the wall of the tube and, therefore, to the vapor within the tube. Instead of volatilizing the analyte as the temperature is changing, appropriate conditions can be found to volatilize the analyte after the tube wall and the gas phase have reached a more stable or steady state condition.

Matrix Modification

Matrix modification was introduced earlier in this chapter as a technique for enhancing the ability to remove matrix materials from the sample, during the pre-treatment step. It also has another use. By adding a matrix modifier which stabilizes the analyte, the appearance temperature, i.e., the temperature at which the analyte absorption signal first appears, will be increased. This delays the release of the analyte into the furnace, allowing additional time to establish a constant furnace temperature before atomization occurs. The recommendations for

almost every element will suggest a matrix modifier. When recommended, a matrix modifier should always be used to improve resistance to nonspectral interferences.

Maximum Power Atomization

Whereas a matrix modifier can be added to delay atomization until higher temperatures are reached, an alternative technique is to heat the furnace more rapidly. In our discussion of the graphite furnace program in the previous chapter, we pointed out the desirability of rapid heating (zero ramp time) for the atomization step. The reason for this can now be addressed.

Before the introduction of the L'vov platform, it was observed that rapid heating at atomization produced better peak height sensitivities for most elements. In light of the above discussion, the reasons for this can be understood. Rapid heating, or maximum power atomization, increases the temperature of the tube atmosphere more rapidly, and analyte is volatilized into a hotter environment. As a result, more energy is available to atomize the sample resulting in an increase in free atoms and enhanced sensitivity. However, even with the use of maximum power atomization, the temperature of the tube atmosphere is not in equilibrium with the tube wall temperature when the sample is volatilized directly from the tube surface.

It is in combination with the L'vov platform that maximum power atomization offers its greatest benefits. By increasing the temperature of the furnace at the maximum possible rate during atomization, the tube wall and atmosphere are heated much faster than the platform, thus insuring a stabilized tube atmosphere temperature at the time of analyte volatilization, as shown in Figure 6-7. This helps to assure that this desirable stable condition will be established before the release of even the most volatile analyte forms. The release of analyte atoms into the same furnace environment for all analyte forms is the prerequisite for elimination of nonspectral interference.

A few words should be said about the way maximum power heating is achieved. To produce the fastest possible heating rate, the full, or maximum power capabilities of the furnace power supply are applied to the graphite tube at the beginning of the atomization step. If this power level were to be applied continually, the final temperature would reach levels which would virtually destroy the graphite tube. Therefore, the application of maximum power is reduced to the level required to hold the selected atomization temperature whenever that temperature is reached.

The point at which maximum power is reduced to the holding level is controlled by one of two means. Some furnace systems employ an optical temperature sensor, which sends a signal to the furnace power supply whenever a preset tube temperature is reached. In other cases, the time for maximum power heating is programmed into the furnace power supply based on the final atomization temperature desired. In either case, the more rapid attainment of the final atomization temperature is the desired result.

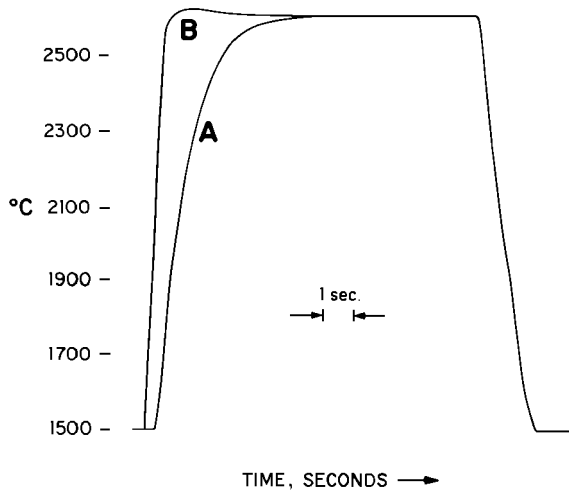


Figure 6-7. Normal (A) vs. "Max Power" (B) temperature profiles.

Peak Area Measurement

The combination of maximum power heating and the L'vov platform go a long way toward eliminating nonspectral interferences. However, one potential problem still exists. The rate at which atoms are released from the platform surface into the furnace environment will still be controlled by the sample matrix in which the analyte resides. Any measurement technique which depends on atomization rate would therefore show matrix effects.

As discussed previously, the use of peak height to quantitate furnace absorption signals may be affected by the atomization rate, which in turn is influenced by the sample matrix. Peak height actually measures the maximum concentration of analyte atoms occurring in the furnace during the atomization process. If atoms are formed rapidly, that peak concentration will be greater than if atoms are released more slowly, allowing the first atoms produced to diffuse out of the furnace before the later atoms appear.

Peak area, on the other hand, depends not on the maximum concentration of atoms, but rather is a measure of the total number of atoms passing through the light path

during the atomization process. As long as the residence time of each individual atom in the light path is the same, it is “counted” with the same weight as any other atom, regardless of when it was volatilized. By using the techniques described above to establish stable furnace conditions prior to the release of any atoms, the residence time, or “counting sensitivity” of each atom will be the same. The measured signal is, therefore, independent of sample matrix, and nonspectral interference is eliminated.

Fast Electronics and Baseline Offset Correction

In order to provide accurate analytical results, a graphite furnace AA system must be capable of accurately quantitating the peak absorbance signal. One of the potential limitations is the speed of the instrument’s electronics. The instrument must provide a sufficient number of readings to provide accurate quantitation of the peak absorbance signal. The rate at which readings are taken must therefore be based on the duration of the shortest peak signal.

In general, peak height measurements require a greater number of readings during the peak lifetime than peak area. The more stringent requirements for peak height are necessary because the accuracy and reproducibility of the determination depends entirely on making the measurement at exactly that point in time where the peak reaches a maximum. Even slight deviations from the peak maximum can cause significant reductions in the measured absorbance and degradation of analytical performance. In contrast, peak area integration is dependent only on obtaining a sufficient number of integrated readings to accurately define the peak area.

One complication with peak area measurement has been the exaggerated effect of baseline drift. Peak area is measured by summing all observed signals over the measurement period. While current instrument electronics are very stable, the effect of even a slight baseline change becomes noticeable when summed over several seconds. Automatic zero adjustments immediately prior to atomization could be used to compensate for such offsets. However, baseline zero adjustments normally are used to compensate for sample or reagent blank readings. As the drift compensation must be performed just prior to atomization, it is impossible to perform both the baseline compensation and the blank compensation with the same adjustment.

To eliminate this potential problem, “baseline offset correction” (BOC) was developed. BOC is a totally separate function which complements an automatic zero function. The automatic zero function is used to provide initial signal balance and

compensate for any blank reading. When BOC is in use, it measures the instrument baseline reading immediately prior to atomization. Each reading during the peak area integration is then automatically corrected for this baseline offset. This eliminates all drift effects and improves the accuracy of peak area measurement while also maintaining the correction for sample blanks implemented with the automatic zero adjustment.

Mathematically, the relationship between the uncorrected peak area readings, the BOC reading, and the corrected peak area readings is as shown below:

$$A \cdot s = [\sum(A_N - \text{BOC})]/f$$

where $A \cdot s$ is the corrected peak area reading in absorbance seconds, A_N are the individual area integrations, BOC is the baseline offset correction measurement, and f is the sampling frequency, i.e., the number of integrated readings per second.

STABILIZED TEMPERATURE PLATFORM FURNACE (STPF)

The Goals

Having examined the details of a number of factors which can affect the outcome of a graphite furnace analysis, it is now time to bring these factors together and evaluate the current status of the graphite furnace as an analytical technique.

To be at all usable, an analytical technique must deliver accurate measurements. To be practical, it must be easy to use. The goals for an analytical technique should be to have all interferences under control and to be able to use straightforward, standardized procedures when applying the technique. Let us see how graphite furnace atomic absorption lives up to these goals.

The STPF System

Earlier in this chapter, we discussed the benefits of eliminating interferences as opposed to compensating for them. We have examined a number of techniques, which contribute to desirable analytical conditions. Each of these techniques does its part to avoid complications which lead to interference problems.

When all of the techniques are applied together, with each contributing its share in maintaining the conditions required for an interference-free analysis, an analytical system results. This system has come to be known as, "Stabilized Temperature Platform Furnace" (STPF). The system is made up of a collection of instrumental factors and analytical procedures. Every part of the system is crucial

to the effectiveness of the system in providing accurate results. The function of each element comprising the STPF system is listed in Table 6-2.

From the background we have developed, we can see how strict adherence to STPF conditions will favor an interference-free analysis. It does this by establishing stable and repeatable conditions for an analytical measurement. This stable, repeatable environment offers another benefit. Under STPF conditions, graphite furnace performance is remarkably consistent. The observed characteristic mass, for each analyte, in almost any sample, normally will compare closely to that obtained from reference solutions where STPF is in use.

Matrix-independent performance means that all samples can be treated similarly, for graphite furnace analysis. Therefore, under STPF conditions, graphite furnace analysis has become very routine. A typical analysis involves setting up the graphite furnace program recommended in the reference manual, and establishing all analysis parameters according to STPF recommendations. While the wary analyst would never claim absolute interference-freedom for any analytical technique, STPF has been demonstrated to approach that status.

Table 6-2
The “Stabilized Temperature Platform Furnace” Concept

High quality pyrolytically-coated graphite tubes:

- provide an impervious, non-reactive surface

L’vov platform:

- delays atomization until stable temperature conditions are achieved

Maximum power atomization:

- hastens establishment of stable atomization temperature and enhances the temperature lag between heating of the tube wall (and atmosphere) and the platform

Internal gas stop:

- maximizes residence time of atoms in the furnace

Fast spectrometer electronics:

- provide accurate measurement of rapidly changing signal

Peak area measurement:

- quantitates all analyte atoms passing through the furnace
- independent of matrix-dependent analyte volatilization rates

Baseline offset correction:

- improves accuracy of peak area measurement by compensating for small changes in the baseline

Matrix modification:

- improves matrix removal during pretreatment
- delays analyte volatilization allowing additional time for stabilization of the gas phase temperature

Zeeman effect background correction:

- corrects for high sample background, structured background absorption and spectral interferences for all elements at all wavelengths

7 ALTERNATE ANALYTICAL TECHNIQUES

Atomic absorption is a mature analytical technique. Its interferences are well documented and, for the most part, easy to control. The various atomizer alternatives make atomic absorption one of the most versatile analytical techniques, capable of determining a great number of elements over wide concentration ranges. Even so, there are competing techniques which should be considered as alternatives or complements to AA for certain applications. In this chapter, we will examine the advantages and disadvantages of these techniques compared to atomic absorption. A summary comparison is given in Table 7-1.

DIRECT CURRENT PLASMA (DCP) EMISSION

DCP is an atomic emission technique. Sample is aspirated into a premix spray chamber through a nebulizer using a system very similar to that for atomic absorption. However, instead of combustible gases, argon is used as a transport gas for the sample. The sample aerosol in a stream of argon is directed at a set of electrodes, across which a high voltage electrical potential is applied.

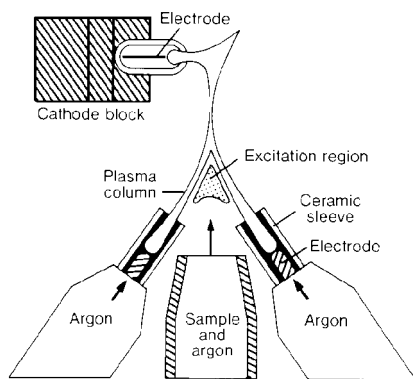


Figure 7-1. The DCP Torch

The resulting electrical discharge between the electrodes supplies enough energy to ionize the argon into a “plasma” of positively charged argon ions and free electrons. The thermal energy of the plasma, in turn, atomizes sample constituents and creates excited state atoms, which emit their characteristic atomic emission spectra.

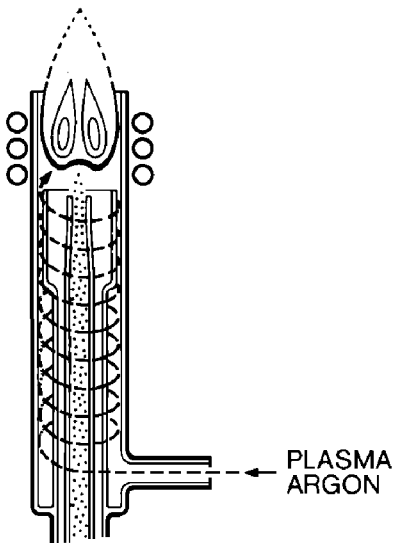
DCP was the first plasma technique applied to routine atomic emission analyses. In its early days, it was an especially valuable complement to atomic absorption in that DCP provided good detection limits

for the refractory elements, for which atomic absorption was not particularly sensitive. DCP is also capable of simultaneous multielement analysis and qualitative, as well as quantitative, analysis.

DCP carries with it some significant disadvantages, however. The electrodes which form the DC arc are continually eroded and burned away during operation. This imposes a maintenance problem of continual adjustment and replacement of the electrodes. In addition, the very high temperatures for which plasmas are known are not fully realized in the DCP design. Due to a highly resistant “skin effect”, the sample does not penetrate into the hottest part of the plasma, but is instead deflected around it. The analytical measurement normally is made just underneath the hottest part of the plasma, where temperatures are hot enough to provide good sensitivity for refractory elements but not hot enough to eliminate chemical and ionization effects. Procedures for reagent addition usually are prescribed to deal with these interferences. Because these limitations are not normally encountered with inductively coupled plasma (ICP) systems, ICP emission is normally a preferred emission technique.

INDUCTIVELY COUPLED PLASMA (ICP) EMISSION

Similar to DCP, ICP is an atomic emission technique using an argon plasma as an excitation source. However, the design of the source is completely different. Sample



is again introduced into a premix spray chamber, where it is directed up the central tube of the ICP “torch”. The torch consists of concentric tubes with independent argon streams flowing through each. The top of the torch is centered within a radio frequency (RF) induction coil, which is the source of energy for the system.

After ignition, the plasma is propagated through inductive coupling with the RF field generated from the coil. Unlike DCP, there are no electrodes to maintain and replace. Further the ICP torch is designed specifically to promote penetra-

Figure 7-2. The ICP torch.

tion of the plasma skin by the sample, allowing sample atoms to experience the full energy of the plasma source.

The high temperatures provided by the ICP provide excellent sensitivities for refractory elements and also essentially eliminate chemical interferences. Like all emission techniques, there are no source lamps. By monitoring several wavelengths, either all at once or in a programmed sequence, many elements can be determined in one automated analysis. ICP emission, therefore, offers significant speed advantages over atomic absorption for multielement analyses. Except for the refractory elements, which may be substantially better than even graphite furnace AA, ICP detection limits are comparable to flame atomic absorption.

The high temperatures of the ICP carry one disadvantage. The plasma is so effective in generating excited state species that the rich emission spectra produced increase the probability of spectral interferences. High resolution monochromators and sophisticated software for background and interelement correction are used to deal with this potential problem. Another limitation of ICP emission is the initial cost of the instrumentation. The price for basic ICP systems starts at about the same level as the prices for top-of-the-line automated AA systems. More sophisticated instrumentation can cost two to four times the price of basic systems.

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICP-MS)

ICP-MS is one of a growing number of “hyphenated techniques”, where the output of one technique becomes the input of another. For ICP-MS, the ICP is used as the ion source for a mass spectrometer. The ions are then spatially separated according to their mass and charge, and measured individually.

The major attractiveness of ICP-MS is its exceptional sensitivity combined with high analysis speed. For most elements, ICP-MS offers detection limits which are comparable to or better than those of graphite furnace AA. But ICP-MS can determine many elements in the time required for the determination of one element by graphite furnace AA. ICP-MS also offers the ability for isotopic analysis.

As with the other techniques, ICP-MS also has its limitations. The relative newness of ICP-MS means, while the required instrumentation is well developed, many developments in analytical methodology are yet to be made. This translates into additional effort for the analyst in adapting the technique to his or her particular analytical needs. Since ICP-MS is not a spectroscopic technique, spectral interferences do not occur. Interferences from mass overlaps due to other isotopes and polyatomic species do occur, however, and may provide erroneous results un-

less properly corrected. The major limitation of ICP-MS at this time, however, may be its cost. ICP-MS systems typically are two to four times as expensive as basic ICP emission systems. However, the unique abilities of ICP-MS to provide graphite furnace detection limits with the analytical speed of ICP emission and to perform isotopic analysis capabilities frequently provide the justification needed to overcome cost limitations.

SUMMARY

While other analytical techniques may offer specific advantages over atomic absorption, it can be seen from the above comparison that no single technique offers all of the advantages. The versatility, moderate cost, and established methodology of atomic absorption will continue to make it a valuable tool for the laboratory.

**Table 7-1
Comparison of Analytical Techniques**

Maturity:

Flame AA	well established
Furnace AA	well established
DCP	superseded by ICP
ICP	established and growing
ICP-MS	new and growing

Speed:

Flame AA	fast (single-element)
Furnace AA	slow (single-element)
DCP	fast (multi-element)
ICP	fast (multi-element)
ICP-MS	fast (multi-element)

Sensitivity:

Flame AA	moderate; poor for refractories
Furnace AA	excellent; limited for refractories
DCP	moderate; very good for refractories
ICP	moderate; excellent for refractories
ICP-MS	excellent

Interferences:

Flame AA	few; well understood
Furnace AA	many; controlled with STPF
DCP	many
ICP	spectral
ICP-MS	moderate, mass overlap

Relative Cost:

Flame AA	low to moderate
Furnace AA	moderate to high
DCP	moderate to high
ICP	moderate to very high
ICP-MS	very high

