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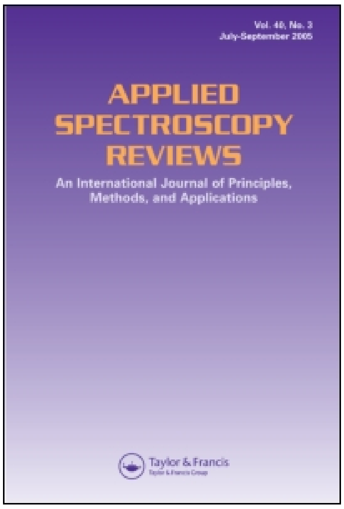

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Atomic Absorption Spectroscopy: A Tutorial Review

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Atomic Absorption Spectroscopy: A Tutorial Review*

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I. INTRODUCTION

Atomic absorption spectroscopy is one of the important instrumental techniques for both quantitative and qualitative analysis of metallic and nonmetallic elements in inorganic or organic materials. In this tutorial review, the principal components of atomic absorption instrumentation will be discussed. In order to understand the instrumental variables associated with these particular instruments, a brief discussion of the theory behind atomic absorption is presented, as well as some rudimentary aspects of the spectral information that is obtainable.

II. GENERAL DESCRIPTION

The phenomenon of atomic absorption was first observed in 1802 with Wollaston's observation of dark bands in the emission spectrum of the sun. In 1859, Kirchoff and Bunsen correctly explained Wollaston's observation by showing that the dark bands were due to the absorption of emission radiation by ground-state gas-phase atoms in the sun. However, the process of absorption of radiation by atomic vapors would not be used as a quantitative analytical tool until nearly a century later when Alan Walsh fabricated the first analytical atomic absorption spectrophotometer in 1953.

Since its invention, atomic absorption spectroscopy (AAS) has gained acceptance as a standard method for the analysis of both metallic and nonmetallic elements. AAS is widely accepted because the technique is element-selective and it provides analytical sensitivities at the parts-per-million level and less (where 1 part-per-million is 0.0001%). Example application areas that use AAS as a routine method of metal analysis include various forms of industrial manufacturing, geology, medicine, and agriculture. The technique of AAS is divided into two steps: the conversion of an analyte molecule into its constituent gas-phase atoms (atomization), and the subsequent absorption of radiation by these free atoms.

Quantitation in AAS is accomplished by measuring the amount of absorbing species produced at a given analytical wavelength. The principles of quantitation in AAS rely on the adherence to the Beer-Lambert law, namely that the increase in absorbance (measured as a decrease in transmittance) has a linear relationship to the concentration of gas-phase atoms. The instrumentation required for AAS (see Figure 1) is similar to that required by other high-resolution spectroscopic techniques. AAS differs from other spectroscopic techniques predominantly in the nature of the radiation source that is used and the use of heat to produce the absorbing species. The atomic lines produced by the radiation source must be of narrow enough width to overcome limitations due to the finite bandpass of the instrument. Usually, this requirement is met by using a line source, such as the hollow cathode lamp.

III. ATOMIZATION

The atomization step can be successfully executed by either flame or electrothermal methods. In either of the two methods, thermal energy is used to vaporize the analyte material and to break the chemical bonds within the component molecules. The percentage of the atoms of interest in the molecule that are converted to the gas-phase during the atomization process is called the atomization efficiency. The atomization efficiency is an important limiting factor in the analytical sensitivity of AAS.

A. Flame Atomization

Heating the sample in a flame is the most frequently used method for producing free atoms in AAS. In flame AAS, the sample to be analyzed must first be dissolved in a suitable solvent. The analyte-containing solution is typically converted to an aerosol and passed into the flame with a pneumatic nebulizer. Alternative techniques, such as ultrasonic nebulization have also been used. Pneumatic nebulizers utilize the flame oxidant gas as a nebulization gas. The differential pressure of the oxidant gas, between the solution to be analyzed and the burner head, draws solution through a sample capillary

FIG. 1. The essential components of an atomic absorption spectrophotometer.

into the oxidant gas stream (see Figure 2 for a typical burner head configuration). The stream is expanded through a small orifice to produce droplets with a broad size distribution. Viscosity, surface tension, and density of the analyte-containing solution are important factors influencing the droplet size obtained. Removal of large droplets (>20 μm) by a downstream impinger results in less than 10% of the actual sample being converted to an aerosol and reaching the burner head. The removal of the large droplets greatly reduces the flame noise, but fewer molecules of the analyte are available for atomization. Therefore, fewer free atoms are produced, and analytical sensi-

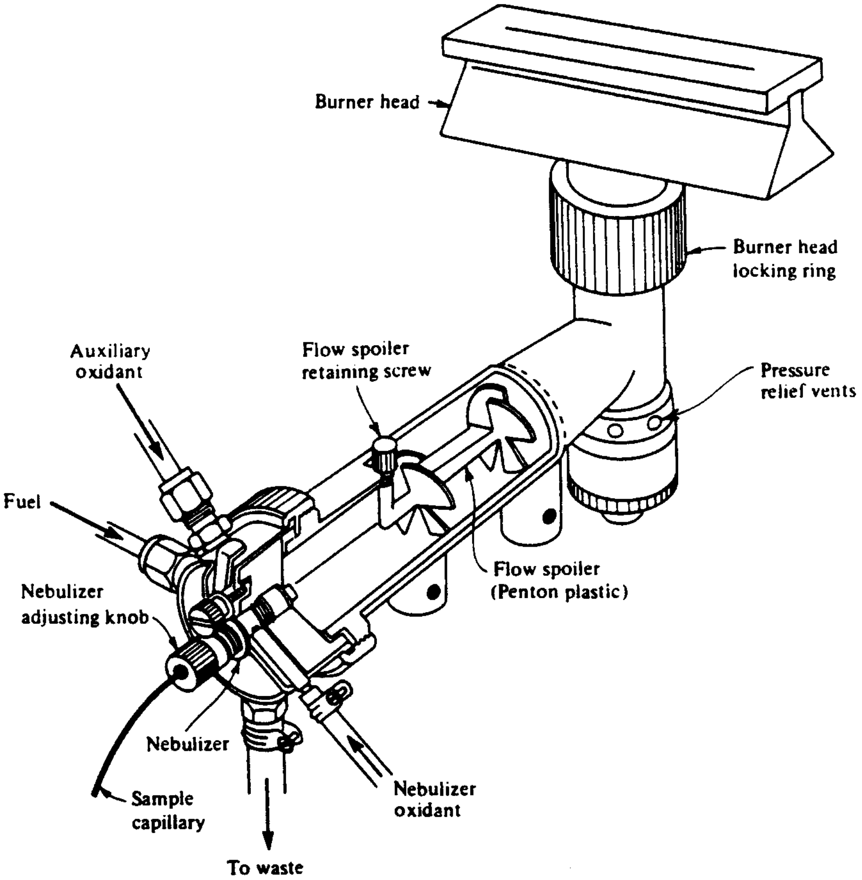

FIG. 2. The nebulizer and burner assembly for flame AAS. (Reproduction courtesy of Perkin-Elmer Corporation)

tivity is sacrificed. The aerosol portion of the sample is diluted in approximately 100 L min^{-1} of expanded flame gases. Although a high signal-to-noise ratio can be obtained by using flame atomization, the nebulization procedure and subsequent dilution by the flame gases greatly reduces the sensitivity of flame AAS.

Typical flame gases used in AAS include air-acetylene or nitrous oxide-acetylene, providing maximum operating temperatures of 2400°C and 2800°C, respectively. The air-acetylene flame typically uses a burner pathlength of 10 cm, whereas the nitrous-oxide acetylene flame requires a shorter pathlength (typically 5 cm). For safety reasons, care must be taken to avoid flashback occurring when using the nitrous oxide-acetylene flame, although the risk has been greatly reduced through computer control of the flame gases. The actual temperature of the flame, determined by the oxidant/fuel ratio, dictates the number of atoms in the excited state, N_{ex}, relative to the number of atoms in the ground state, N_{gr}. This ratio is defined by the Maxwell-Boltzmann equation:

$$\frac{N_{ex}}{N_{gr}} = \frac{g_{ex}}{g_{gr}} e^{-E/kT} \tag{1}$$

where E is the excited-state transition energy, k is the Boltzmann constant, T is the system temperature (expressed in Kelvin), and g_{gr} and g_{ex} are the statistical weights of the ground and excited states, respectively. According to the Maxwell-Boltzmann expression, the number of atoms in the excited state is negligible compared to the number of atoms in the ground state at typical flame temperatures. This distribution is fortuitous because the signal measured in AAS is due only to atoms that undergo electronic transitions from the ground-state to the excited-state. Any processes that remove atoms from their ground state are deemed interferences, and these are discussed later. Within the flame, the sample in aerosol form undergoes various processes: evaporation of the solvent, volatilization of the metal analyte, dissociation of the analyte to the gaseous metallic element, and excitation of the gaseous metallic element to the excited state. These are by no means trivial processes, and the flame chemistry must be tuned by adjusting the oxidant/fuel ratio to optimize the flame temperature for gaseous metal atom formation. Flames that operate in fuel-rich conditions are reducing flames, sometimes called “yellow” flames, whereas flames operating under fuel-lean conditions are oxidizing flames, sometimes called “blue” flames. The hotter flame temperature obtained by using the nitrous oxide-acetylene flame is necessary to atomize elements with higher heats of vaporization such as the rare earth elements. Of the 68 elements listed in Table 1, half are best analyzed using the nitrous oxide-acetylene flame.

Table 1.

Elemental Atomic Lines and Recommended Flame Gases for Analysis

Element	λ (Å)	Flame Gases	Element	λ (Å)	Flame Gases
Ag	3281	A-Ac	Nb	3344	N-Ac
Al	3093	N-Ac	Nd	4634	N-Ac
As	1937	A-Ac	Ni	2320	A-Ac
Au	2428	A-Ac	Os	2909	N-Ac
B	2497	N-Ac	p	2136	N-Ac
Ba	5536	N-Ac	Pb	2833	A-Ac
Be	2349	N-Ac	Pd	2476	A-Ac
Bi	2231	A-Ac	Pr	4951	N-Ac
Ca	4227	A-Ac	Pt	2659	A-Ac
Cd	2288	A-Ac	Rb	7800	A-Ac
Co	2407	A-Ac	Re	3460	N-Ac
Cr	3579	A-Ac	Rh	3435	A-Ac
Cs	8521	A-Ac	Ru	3499	A-Ac
Cu	3247	A-Ac	Sb	2176	A-Ac
Dy	4212	N-Ac	Sc	3912	N-Ac
Er	4008	N-Ac	Se	1960	A-Ac
Eu	4594	N-Ac	Si	2516	N-Ac
Fe	2483	A-Ac	Sm	4297	N-Ac
Ga	2874	N-Ac	Sn	2863	A-Ac
Gd	4079	N-Ac	Sr	4607	A-Ac
Ge	2651	N-Ac	Ta	2715	N-Ac
Hf	2866	N-Ac	Tb	4326	N-Ac
Hg	2536	A-Ac	Tc	2615	A-Ac
Ho	4104	N-Ac	Te	2143	A-Ac
In	3039	A-Ac	Ti	3653	N-Ac
Ir	2640	A-Ac	Tl	2768	A-Ac
K	7665	A-Ac	Tm	3718	N-Ac
La	5501	N-Ac	U	3585	N-Ac
Li	6708	A-Ac	V	3184	N-Ac
Lu	3360	N-Ac	W	2551	N-Ac
Mg	2852	A-Ac	Y	4102	N-Ac
Mn	2795	A-Ac	Yb	3988	N-Ac
Mo	3133	A-Ac	Zn	2139	A-Ac
Na	5890	A-Ac	Zr	3601	N-Ac

A-Ac = Air-Acetylene
N-Ac = Nitrous Oxide-Acetylene

The atomization of an analyte is not homogeneous throughout the flame. The maximum production of free atoms in the flame is dictated by the variation in temperature in the different zones of the flame and by the rate of diffusion of the flame gases that serve to dilute the free-atom population. To achieve maximum sensitivity, the radiation from the line source must pass through the area of the flame that contains the greatest number of free atoms. This condition is met by optimizing the height and alignment of the burner head relative to the radiation beam as it passes through the flame parallel to the major axis of the burner.

B. Electrothermal Atomization

To overcome the sensitivity problems associated with flame AAS, the nebulizer and burner assembly of a flame AAS instrument can be replaced with an electrothermal atomizer. Electrothermal atomizers include the graphite furnace (Figure 3), carbon rod, and tungsten ribbon atomizers. In these atomizers, a 5 to 50 μL aliquot of the sample is placed in the resistively heated element and then heated stepwise to the temperatures conducive to gaseous atom formation. The heating element design commonly used in the graphite furnace atomizer is a modified L'vov platform. A typical heating program involves a solvent evaporation step (110°C), an ashing step for the removal of any volatile organic materials (450–900°C) and a 5 to 10 second atomization step (2000–3000°C). The entire heating cycle can be accomplished in less than one minute. In contrast to flame AAS, electrothermal

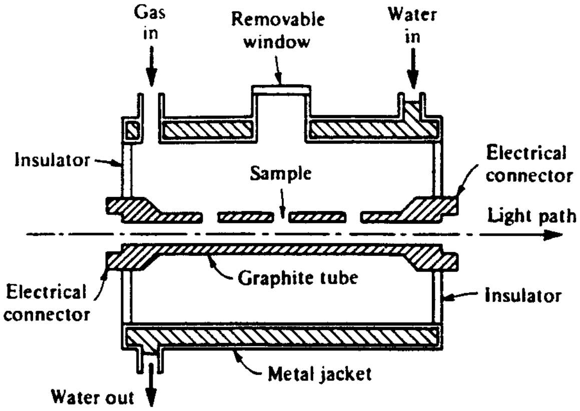

FIG. 3. A graphite furnace electrothermal atomizer. (Reproduction courtesy of Perkin-Elmer Corporation)

AAS samples are not diluted by flame gases, nor do they depend on nebulization efficiencies. The entire sample to be analyzed is vaporized within a small internal volume (∼2 mL) by using electrothermal atomizers, and this results in an increase in sensitivity of three orders of magnitude over flame AAS. Typically, analytes present in picogram quantities can be determined by electrothermal AAS. Furthermore, electrothermal atomizers can be used to directly analyze solid materials without any form of modification. A major limitation of electrothermal atomizers, however, is the reduced precision of the results obtained, compared to flame AAS. The difference is that the atomization occurs as a single event in time compared to the continuous process of flame atomization. In electrothermal atomizers, the lifetime of a free atom in the optical path is typically on the order of 0.01 seconds, in comparison to flame AAS, in which a sample can be continuously nebulized in a flame and where the signal can be averaged over long periods. Replicate results are difficult to obtain with electrothermal atomizers because of the reproducibility associated with the furnace operation, although computer control of the furnace has reduced the impact of many of these difficulties.

IV. EXCITATION SOURCES

The full width at half-height of the absorption line produced by either flame or electrothermal atomization as measured by emission spectroscopy is approximately 0.002 nm. Factors that modify (broaden) this line width include natural, pressure, resonance, and Doppler broadening. To provide both sensitivity and selectivity, the line sources used for excitation must be stable and narrower than the full width at half-height of the absorption of the analyte. The narrow full-width-at-half-height criterion ensures that all of the radiation produced by such a line source is available for absorption by the gas-phase atoms. Line sources typically used include the hollow cathode lamp and the electrodeless discharge lamp. With proper instrumental design, even continuum sources can be used.

A. Hollow-Cathode Lamps

The line source of radiation most frequently employed in AAS is the hollow-cathode lamp (HCL)—see Figure 4 for a schematic rendering. Commercially, hollow cathode lamps are available as both a single element and multi-element sources. A potential of 350V to 500V (producing a current of 1 to 50 mA) is placed across the cathode and anode terminals. The element selectivity of the HCL is achieved by fabricating the cathode from, or coating the interior of the cathode with, the element of interest. The anode and cath-

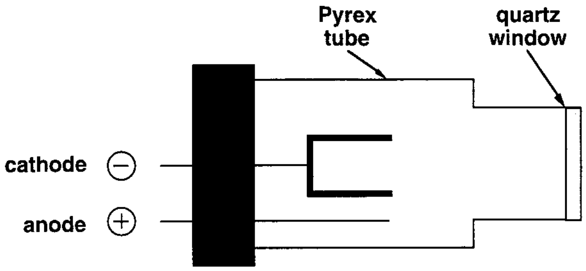

FIG. 4. Schematic of a hollow-cathode lamp.

ode are sealed in a Pyrex tube containing a quartz window at the opposite end for transmission capability throughout the ultraviolet spectral region. The interior of the tube is evacuated and filled with an inert gas, such as neon. Under the applied potential, the neon atoms become ionized at the anode and are accelerated toward the cathode. The kinetic energy of the accelerated neon ions is imparted to the material of the cathode upon impact, causing metal atoms to be sputtered off the cathode surface into the gas phase. The sputtered metal atoms undergo collisions with other neon ions, producing excited state metal atoms. Upon relaxation to the ground state, the metal atoms emit radiation at their characteristic wavelengths. The full width at half-height of the atomic line produced is approximately 0.0002 nm, and therefore all of the radiation produced is available for absorption by the atomized sample. The intensity of the atomic line radiation produced depends on the number of sputtered metal atoms, which depends on the kinetic energy of the neon ions, which, in turn, is dictated by the lamp current. Consequently, a higher lamp current produces a greater spectral line intensity from the source, which in turn provides a greater analytical sensitivity. However, at high lamp currents, an excess of metal atoms is sputtered from the cathode surface. The resulting dense cloud of metal atoms absorbs radiation emitted from nearby excited-state metal atoms. When self-absorption of this type occurs within the HCL, the level of radiation available for absorption by the free atoms from the sample, produced via atomization, is reduced and sensitivity is lost. This process of self-absorption is called “self-reversal” and dictates the maximum operating current of the HCL. Following emission of radiation, the gaseous metal atom will ideally redeposit on the cathode surface, making it available for removal by other accelerated neon ions. Alternatively, the metal atoms may migrate and be deposited on the Pyrex wall of the HCL, a process that reduces the lifetime of the lamp. Restrictive shields placed around the cathode, and optimization of the wall geometry of the HCL can minimize migration of the gas-phase atoms to the HCL walls.

The multi-element HCL operates under the same principles governing the singleelement HCL, except that the cathode is fabricated from pressed alloys or powders of several elements, instead from just a single element. For a cost comparable to that of the single-element HCL, the multi-element HCL provides simultaneous detection of several metals. Despite the economic advantages, the multi-element HCL typically has a shorter lifetime than the single-element HCL, primarily because the metal atoms of the cathode have different degrees of volatility. In time, the element with the highest volatility will redeposit preferentially over the surface of the cathode, causing the other metals of the cathode to be rendered inaccessible to the impacting neon ions. The sensitivities of the inaccessible metal atoms will decrease over time and ultimately shorten the effective lifetime of the HCL.

B. Electrodeless Discharge Lamps

The electrodeless discharge lamp (EDL) is another atomic line source used in AAS. The EDL is also available in a multi-element format. The EDL is fabricated by sealing a small amount of the metal or metal iodide of interest in a quartz tube filled with an inert gas, usually argon, at reduced pressures. The EDL is placed in a microwave, radio-frequency field to ionize the inert gas. The metal or metal iodide species collides with the free electrons from the ionized inert gas, producing excited-state metal atoms. In a process analogous to that described for the HCL, these excited-state metal atoms emit the characteristic atomic lines of the metal as they relax to the ground state. In comparison to the HCL, the EDL produces an atomic line source of greater intensity, resulting in enhanced analytical sensitivities. However, the EDL requires a separate power supply that increases the instrumental cost of the AAS.

C. Continuum Sources

For purely economic reasons, the use of a continuum source in AAS is attractive because it eliminates the need to purchase multiple HCL sources. However, in practice the bandpass of a typical monochromator (0.1 to 0.2 nm) is much greater than the atomic line-width of the absorbing atoms (0.002 nm). Consequently, a large fraction of the radiation produced by the source falling on the detector is unabsorbed. The small amount of radiation that is actually absorbed results in a low analytical sensitivity. Continuum sources utilizing scanning Echelle grating monochromators have largely overcome the bandpass difficulty, but overall they still provide lower sensitivity in comparison to the narrow lines produced by the HCL. When using a continuum source, the high-intensity xenon arc lamp is preferred over the deuterium continuum source because of the higher analytical sensitivity obtainable.

V. BACKGROUND CORRECTION

In AAS, a background correction is necessary to compensate for non-atomic absorption of the radiation produced by the source and for emission from interfering species in the flame. When non-atomic absorption occurs, a falsely high analyte concentration is detected because the signal measured according to the Beer-Lambert law is due to the concentration of atomic and non-atomic species at a given wavelength. In the case of non-analyte emission, a falsely low analyte concentration is detected because, at a given wavelength, both the non-absorbed radiation from the source and the background emission are detected. Background emission is an excess of radiation that is detected which is caused by emitting species in the flame. This excess radiation includes (1) the band spectra produced by various molecular fragments and radical species, such as OH, O_2, CH, CO, CN, CH, and NH, and (2) the continuum spectra produced by hot solids and chemiluminescent reactions.

The three primary methods for background correction are (1) the addition of a broadband or continuum source, (2) pulsing the HCL source, and (3) application of the Zeeman effect to the source or sample.

A. Continuum Source

The continuum radiation sources previously described find more applicability in AAS as an additional source used for background correction. Incorporation of a continuum source (hydrogen or deuterium lamp) in combination with a line source permits correction for non-atomic absorption. Non-atomic absorption is broad in comparison to the narrow absorption line of atoms produced by atomization. At the wavelength produced by the HCL, the absorption is due to both atomic and non-atomic species distributed in the flame. Over the bandpass of the monochromator, the absorption of the continuum source radiation is attributable to primarily non-atomic species. The difference between the absorption due to the HCL and the absorption due to the continuum source represents the absorption due to atomic species in the flame. By modulating the signal received at the detector between the line source and the continuum source (i.e., chopping), a background-corrected absorbance signal is obtained. For background correction at longer wavelengths, where the hydrogen or deuterium sources are less intense, a tungsten or quartz halogen lamp can be used. When using continuum sources for background correction, care must be taken to align the line source and the continuum source so that the irradiation passes through the same spatial volume of the flame (i.e., the sources must be co-axially aligned). This alignment will ensure measurement of the same species in the flame, this allows

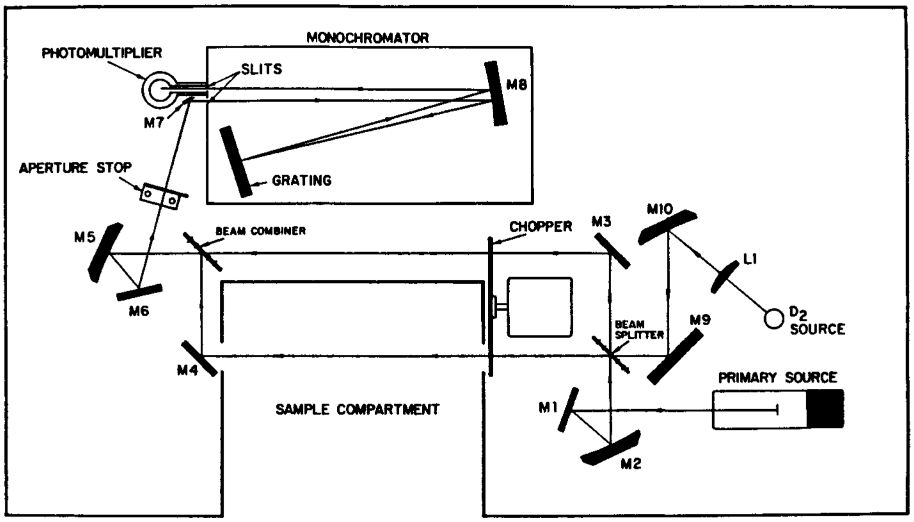

FIG. 5. A schematic of a dual-beam AAS instrument operating in the background mode. (Reproduction courtesy of Perkin-Elmer Corporation)

for the fact that the flame chemistry will differ between the various temperature zones within the flame.

B. Pulsed Hollow-Cathode Lamp

A pulsed HCL can also be used as a method of background correction. Often called “the poor man’s continuum source,” it relies on the previously mentioned process of self-reversal in the HCL. By pulsing the HCL between low (5 to 20 mA) and high (100 to 500 mA) currents, a background-corrected spectrum can be obtained. At low currents, absorption by species in the flame again accounts for both atomic and non-atomic absorption. At high currents, the lamp emission spectra are broadened owing to Doppler effects and, over the bandpass of the instrument, it mimics a continuum source. Therefore, the absorbance in the high-current mode is due to non-atomic absorbance, and the two signals can be subtracted to give a corrected absorbance signal. Although the pulsed design requires no special lamp alignment, as a continuum source does, the HCL must be stable at the high currents used. In contrast to the continuum-background correction method, the high current of the HCL does not produce a constant value over all wavelengths passing to the detector. Therefore, the atomic absorption can constitute a small but significant amount of the high current signal. The non-negligible amount of atomic absorption during the high current part of the cycle reduces the sensitivity of the calibration curve.

C. Zeeman Effect

Zeeman background correction is yet another method of providing a background-corrected signal for non-atomic absorption during atomization. Two configurations of Zeeman splitting are often used, the analyte-shifted Zeeman correction and the source-shifted Zeeman correction. Zeeman correction is based on the principle that the atomic lines of the analyte or the source can be split into degenerate spectral lines of differing polarization in an applied magnetic field. For example, in analyte-shifted Zeeman splitting, an atomic line is split into σ (perpendicularly polarized) and π (parallel polarized) components. The π component remains at the same wavelength as the original atomic line, but the wavelength of the σ component is shifted away from the original wavelength. Absorption measured from the source radiation at the π wavelength can be attributed to both the atomic and background absorbance, whereas absorption measured at the σ wavelength can be attributed solely to the background absorbance. By placing a polarizer either before (dc technique) or after (ac technique) the atomizer, the σ and π components can be measured independently and subtracted to give the background-corrected absorbance.

The analyte shifted Zeeman correction is easier to implement in electrothermal AAS than in flame AAS because the atomization chamber in an electrothermal atomizer is smaller, requiring a less powerful magnet. In source-shifted Zeeman corrections, an EDL is often used because the HCL is not a magnetically stable lamp. In this case, the source atomic line is split into its π and σ components and is measured independently. Zeeman background correction is attractive because it is essentially a double-beam technique contained in a single-beam instrument. However, the technique sacrifices sensitivity because the full intensity of the analytical atomic line is compromised when it is separated into its lower-intensity degenerate spectral lines.

VI. INTERFERENCES

A. Chemical Interferences

Of all the interferences, chemical interferences are predominantly responsible for removing metal atoms from their ground state. Chemical interferences arise during the vaporization processes in atomization. Radical species are produced that can react with the metal compound undergoing vaporization to produce metal hydroxides, metal hydrides, or metal oxide species. In flame AAS, these species cannot be dissociated at cooler flame temperatures. This fact effectively reduces the number of free metal atoms produced in the flame, resulting in a loss in sensitivity. One method to reduce the effects of chemical interferences is to adjust the flame-gas stoichiometry. A fuel-rich flame produces a reducing environment, with correspondingly fewer of the reactive oxide species. An alternate approach is to use a hotter flame, such as the nitrous oxide-acetylene flame, to vaporize and dissociate any refractory metal oxides. A third commonly employed technique is to use a releasing agent that can compete with the metal-oxide formation equilibrium. An example often cited is the addition of lanthanum when analyzing for calcium in the presence of high concentrations of phosphate ions. In this example, the lanthanum competes with the calcium for complex formation with the phosphate ions in the flame. The lanthanum phosphate complex is more stable than the calcium phosphate complex and predominates, resulting in a greater number of free calcium atoms in the flame providing a higher sensitivity for the calcium. Another useful scavenging agent is ethylenediaminetetraacetic acid (EDTA). EDTA forms stable complexes with most metals that can be vaporized in a flame. Furthermore, the carbon atoms of EDTA surrounding the metal effectively produce a reducing environment during the dissociation step.

B. Ionization Interferences

To some extent, all metallic atoms produced at the temperatures of the flame undergo ionization. This can certainly be minimized by using cooler flames such as the acetylene-air flame and by adjusting the flame-gas stoichiometry. Another method is to chemically alter the ionization equilibrium within the flame. The ionization of a metal written as an equilibrium expression is:

$$M^0 \rightarrow M^{n+} + ne^- \qquad (2)$$

Therefore, elements that provide electrons to the flame will shift this equilibrium to the left. Such a species is called a “radiation buffer” or an “ionization buffer”. Radiation buffers are species that are easily ionized, such as cesium. To ensure similar atomization efficiencies for quantitation, the buffer is typically added in excess to both standards and unknowns.

C. Matrix Interferences

A matrix interference involves the bulk physical properties of the sample to be analyzed. In practice, first a blank solvent is atomized and the instrument zeroed so that the measured voltage at the photo-multiplier tube (PMT) corresponds to 100% transmittance. Solutions containing the analyte of interest are subsequently atomized, and their atomic absorbances are measured. The Beer-Lambert law is used to relate the unknown analyte concentration to the concentration of standard solutions. To ensure that the Beer-Lambert law is followed, atomization efficiencies must be matched between the calibration curve and the unknown sample. In flame AAS, matrix interferences will affect nebulization efficiencies during the atomization stage, primarily because nebulization efficiencies are affected by the physical properties of viscosity, surface tension, and density. For quantitative results using the Beer-Lambert law, these properties must be matched in both standard and unknown solutions. Instead of taking the time to matrix-match standards and unknown solutions, if the unknown is sufficiently concentrated, it can be diluted to approximately match the physical properties of the standard solutions, which are typically dilute.

The most common way to overcome a matrix interference is to use the method of standard additions (Figure 6). This method effectively creates a calibration curve by using incremental additions of a standard solution to an unknown. The incremental additions are of a minuscule volume so as not to alter the bulk physical properties of the unknown, effectively providing a matched matrix. The plot obtained is extrapolated to the x-axis intercept. The absolute value of the x-axis intercept gives the analyte concentration in the

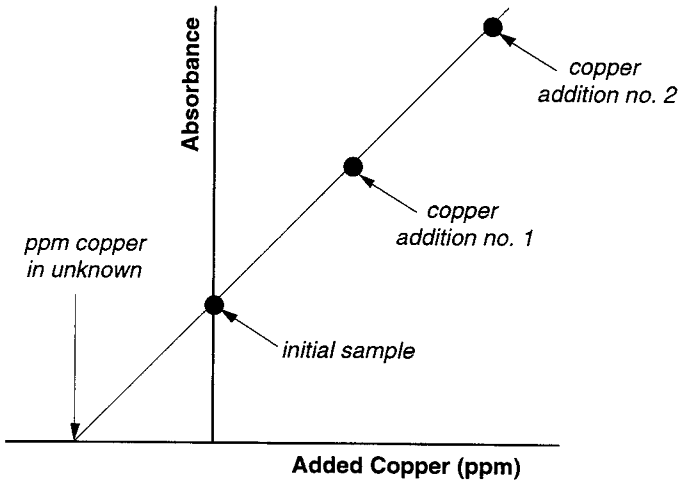

FIG. 6. An example of the method of standard additions for the analysis of copper concentration in an unknown.

unknown sample. When using the method of standard additions, care must be taken to ensure that one is operating in the linear region of the calibration curve. In AAS, the Beer-Lambert typically holds at low concentrations, and the calibration plot often exhibits nonlinearity at higher analyte concentrations. This is caused by stray source radiation that reaches the detector and to flame-diffusion effects, both of which can severely reduce the accuracy of the measurement and the results.

D. Spectral Interferences

Spectral interferences in AAS, although rare, do occasionally occur and can be corrected by manipulation of instrumental variables. Spectral interferences arise when radiation of a wavelength different from that of the wavelength of the element of interest falls on the detector. An example of direct overlap of spectra produced by atomic species in the unknown occurs when sodium and magnesium are both present. When analyzing for dilute amounts of magnesium in a sample with a high concentration of sodium, the 285.28 nm sodium line will overlap the 285.21 nm magnesium line. Therefore, in the flame, sodium atoms will absorb radiation from the magnesium HCL, resulting in a falsely high magnesium concentration detected at the PMT. As most monochromators do not have a resolution sufficient to separate the two closely spaced lines, an alternative wavelength for magnesium quantitation must be selected in such cases. Another similar spectral interference occurs when using a multi-element HCL. In this instance, lines from other elements in the HCL occur near, or overlap, the line of the analytical element of interest. This is the case when using the nickel 232.0 nm line in a multi-element HCL containing iron, chromium, and manganese. To overcome the problem, either the slit can be narrowed to permit transmission of only the nickel wavelength, or a single-element HCL can be used. Other spectral interferences include emission interferences and non-atomic absorption. These have been addressed in the section on background correction.

VII. CONTINUING RESEARCH

Although the major innovations in AAS appear to have been accomplished, research still continues in many laboratories to improve atomization efficiencies. Despite the fact that flame AAS instruments are the most commonly used type of instrument, new electrothermal atomizers are being developed to increase sensitivity levels of AAS. Modern computer control has reduced much of the operator error in use of both flame and electrothermal atomizers, and if the precision of electrothermal AAS can be increased to rival flame AAS, the technique could become more widely accepted. AAS is finding increasing use as an element-selective detector in liquid chromatography, gas chromatography, and even supercritical fluid chromatography. The element selectivity of AAS has secured the place of AAS in diverse analytical laboratories, just as the inefficiency of the atomization process will surely stimulate novel sensitivity breakthroughs in the future.

BIBLIOGRAPHY

Brown, S. D. *"Zeeman Effect-Based Background Correction in Atomic Absorption Spectrometry,"* Anal. Chem. 1977, 49, 1269A.

Christian, G. D., Feldman, F. J. *Atomic Absorption Spectroscopy*, John Wiley and Sons, New York, 1970.

Harnley, J. M. *"Multielement Atomic Absorption with a Continuum Source,"* Anal. Chem. 1986, 58, 933A.

Ingle, J. D., Crouch, S. R. *Spectrochemical Analysis*, Prentice Hall, New Jersey, 1988.

Robinson, J. W. *Atomic Spectroscopy*, Marcel Dekker, New York, 1996.

Slavin, W. *"Atomic Absorption Spectroscopy,"* Anal. Chem. 1982, 54, 685A.

Slavin, W. *"Flames, Furnaces, Plasmas,"* Anal. Chem. 1986, 58, 589A.

Zander, A. T., *"Atomic Emission Sources for Solution Spectrochemistry,"* Anal. Chem. 1986, 58, 1139A.

Sneddon, J., *"Atomic Absorption Spectrometry," Handbook of Instrumental Techniques for Analytical Chemistry*, ed. Frank Settle, pp. 373–393, Prentice Hall PTR, NJ, 1997.

Dean, J. A., "Atomic Spectroscopy," Analytical Chemistry Handbook, McGraw Hill, NY, 1995.

Kellner, R. A., Mermet, J.-M., Otto, M., and Widmer, H. M. Eds., *"Elemental Analysis: Atomic Absorption Spectrometry," Analytical Chemistry*, pp. 453–463, Wiley-VCH Verlag GmbH, Weinheim, 1998.

Parsons, M. L., *"Atomic Absorption and Flame Emission Spectrometry," Analytical Instrumentation Handbook*, 2nd Edition, Galen Wood Ewing Ed., pp. 257–325, Marcel Dekker, NY, 1997.

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