

Flame and Vapor Generation Atomic Absorption Spectrometry

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Atomic absorption spectrometry (AAS) is a means of specific analysis for most of the metallic and metalloid elements. It achieves its specificity from the highly selective absorption, by free atoms of the analyte, of atomic emission of the same element at characteristic wavelengths. In its simplest form of application the free atoms of the analyte are created by aspiration of a solution of the sample to be analysed into a suitable flame, flame atomic absorption spectrometry (FAAS). The other principal means employed for the production of atoms (atomization) are graphite furnace atomization (GFAAS) and vapor generation atomization (VGAAS). Sample volumes of a few milliliters are normally needed for FAAS and VGAAS, but smaller volumes are needed for GFAAS. For most of the approximately 65 elements amenable to measurement by AAS, detection limits are from parts per billion to parts per million by flame methods and from parts per trillion to parts per billion levels by GFAAS and VGAAS. FAAS is inherently simple and rapid to use, whereas GFAAS and VGAAS are less rapid. The instrumentation used for AAS is relatively inexpensive. Since all of these methods generally require the sample to be in solution form, the need for dissolution may be seen as a limitation in some cases. In the most common instrumentation employed, elements are only measured one at a time. It follows that for the determination of many elements in a large group of samples the method must be seen

to be slow by comparison with multielement techniques such as inductively coupled plasma mass spectrometry (ICPMS) and inductively coupled plasma atomic emission spectrometry (ICPAES). However, the equipment costs involved for these techniques are generally higher and they are more complex to employ.

1 INTRODUCTION

1.1 The Origins of Atomic Spectra

Although astronomical observations led to the discovery of the 'Fraunhofer (atomic absorption) lines' in the solar spectrum, it was not until about 1850 that the origin of these dark lines in an otherwise continuous bright spectrum started to be properly deduced. It appears that several workers, among them Foucault, Balfour Stewart and Stokes started to realize that these lines were the result of absorption of the continuous emission from the sun and other astronomical bodies by the atomic vapor of some elements occurring in their atmospheres. It was not until 1860 that Bunsen and Kirchhoff first comprehensively demonstrated experimentally, and then elucidated, the origin of such atomic emission and absorption spectra and drew attention to their interrelationship.

In what are now seen as classical experiments they demonstrated that atomic vapors of sodium and lithium, produced in a flame, would each not only emit radiation at specific wavelengths but would also absorb radiation at precisely the same wavelengths.^(1,2) Kirchhoff's original paper⁽¹⁾ is given only for completeness but the paper, and of course the title, are in German. However an English translation of this paper is also available.⁽²⁾ From these results Kirchhoff elucidated that atomic transitions between different energy levels might be observed either using absorption or emission.

He found that if, for example, a solution of a sodium salt was heated in a flame it would then spontaneously emit or absorb radiation at wavelengths characteristic *for sodium only*, the famous 'D lines'. Likewise a solution of a lithium salt would also, under the same circumstances, emit or absorb radiation at a wavelength different from those of sodium but equally characteristic *for lithium only*. By doing this he essentially drew attention to the potential usefulness of such observations to identify the presence or absence of sodium and lithium (qualitative analysis). This work was later extended, by Bunsen and Kirchhoff, to the qualitative determination of the presence of other elements (potassium, calcium, strontium and barium).⁽³⁾

As an interesting example of the powerful usefulness of atomic spectra, these workers also first discovered the existence of the elements rubidium and cesium by observing the presence of other characteristic (and

unexpected) lines when employing solutions of natural salt for their experiments.⁽⁴⁾ The salt they used was not produced from the evaporation of seawater but rather was natural salt from underground deposits.

(Note that the Kirchhoff articles^(3,4) are also translations of articles originally published in *Annalen der Physik und Chemie*.)

Bunsen and Kirchhoff only employed these observations in a qualitative mode and seem to have drawn no attention to the possible quantitative use of the phenomena of atomic emission and absorption.

This does not seem too surprising given that in 1860 means of quantitative measurement of emission or absorption signals were not readily available.

1.2 First Analytical Applications of Atomic Spectra

Later, starting with the further development of the photographic process, the means of recording intensities for at least semiquantitative purposes was to lead to the development of emission spectrography using (initially) electric arcs as the means of excitation.

Flames were also seen to be a potential means of excitation for observing emission and by 1928 Lundegardh developed suitable burners (using acetylene as the fuel gas and air as the support gas) and methods for sample introduction.⁽⁵⁾ From this time on, and for the period to the 1950s, developments continued in the above methods but the use of methods utilizing atomic absorption spectra were almost totally ignored. As will be described in section 2, this was in major part because the means of measuring atomic absorption with good sensitivity was not yet properly developed.

1.3 Suggestions for the Analytical Use of Atomic Absorption Spectra

After a significant period of research into atomic emission spectrometry (AES), Walsh became convinced that this neglect of the use of atomic absorption had gone on for too long. He recognized that there would be potential advantages in using the measurement of atomic absorption instead of atomic emission as a means of measuring the concentration of elements in samples.

The major advantages he postulated for the use of atomic absorption methods were as follows:

- Since ground-state atoms would be used for the measurement, the method should be independent of the excitation potential of the element to be measured.
- The method should be much less influenced by the temperature of the atomizing device used.

- There should be much less likelihood of spectral interferences impairing the accuracy of the method.

In 1955, Walsh published a landmark paper explaining, in major detail, these theories. Additionally, however, he also defined a practical approach to the necessary key elements required for instrumentation to measure atomic absorption.⁽⁶⁾

Completely independently, Alkemade and Milatz also published an article suggesting the use of atomic absorption spectra.⁽⁷⁾ They, however, did not develop the practical means of performing this measurement to the same extent as Walsh and this limited the importance of their paper in a practical sense.

In the following section, the theoretical basis of atomic absorption and its measurement will be dealt with in more detail.

2 THEORETICAL BASIS OF ATOMIC ABSORPTION SPECTROMETRY

2.1 General Comments

At this juncture, any comparisons made will be solely between flame emission and flame atomic absorption and no further reference will be made to emission measurements made following excitation by electric arc or spark or by inductively coupled plasma. These are all established methods in widespread use, although arc and spark spectrometry is currently in much less use than in previous years.

In order to measure atomic absorption, it is first necessary to produce free atoms of the element to be measured. However, it should be realized that it is also necessary to produce free atoms of any element to be measured by atomic emission. Atoms cannot be excited unless they are first converted to free atoms from any compound associations.

2.2 Atomization and Excitation

In most atomic absorption, or flame emission, methods atoms are produced from a sample in solution form by the application of heat. If a solution sample is introduced, for instance, into a flame then atomization will often occur. Depending on the excitation potential of the element in question, some of these atoms produced may also then be excited. It is this atomization, and subsequent excitation, which forms the basis of flame emission spectrometry. However, as Walsh pointed out, there are some important factors which should be considered. These are best expressed in some figures taken from a table in his first paper, shown here in Table 1.

Table 1 Values of N_j/N_0 for various resonance lines^a

Element	Wavelength of resonance line (nm)	N_j/N_0	
		2000 K	3000 K
Cs	852.1	4×10^{-4}	7×10^{-3}
Na	589.0	1×10^{-5}	6×10^{-4}
Ca	422.7	1×10^{-7}	4×10^{-5}
Zn	213.9	7×10^{-15}	6×10^{-10}

^a N_j is the number of atoms in the excited state at any given time and N_0 is the number of atoms in the ground (unexcited) state at any given time, and consequently the ratio N_j/N_0 is the fraction of atoms in the excited state at any given time. The figures quoted are taken from a table which appears in Walsh.⁽⁶⁾ They represent only some of the entries in that table and have been rounded off for convenience.

The figures in Table 1 show that

- the fraction of excited atoms at any time is always a very small fraction of the total atoms present;
- the fraction of excited atoms changes by a huge amount with any major temperature change;
- since the fraction of ground-state atoms is equal to one minus the fraction of excited atoms, this remains sensibly constant at very close to 1, regardless of temperature change.

Since atomic emission signals originate from excited atoms and atomic absorption signals from ground-state atoms, the consequences of the above are the following:

- Atomic emission signals will be dramatically affected by temperature changes but absorption signals will be affected to a much lesser extent.
- For many harder to excite elements (such as Zn in Table 1), atomic absorption will be much more sensitive than atomic emission at such temperatures.
- All excited states will, at any given time, have a very small population of atoms. As a result, sensibly only those transitions which originate in the ground state will be able to be measured by atomic absorption. It follows, then, that since there are only a very limited number of such transitions for each element, the atomic absorption spectrum of all elements will be very much simpler than the atomic emission spectrum of the same element. The major consequence of this is that the likelihood of spectral interference will be much lower for absorption measurements than for emission measurements.

Properly, the resonance line for any element is the line associated with the transition between the ground state and the first (lowest energy) excited state. There is therefore commonly only one true resonance line per element. In the years since atomic absorption analysis was

introduced, the convention has arisen that all lines which are associated with transitions involving the ground state are called resonance lines. This atomic absorption convention will generally be followed throughout this article.

2.3 Absorption and Emission Lines

A purely diagrammatic representation of the energy levels involved in the production of an emission and absorption line is shown in Figure 1.

The relationship between the difference of the two energy levels involved in the transition and the frequency of the radiation emitted or absorbed is given by Equation (1):

$$E_1 - E_0 = h\nu \quad (1)$$

where E_1 and E_0 are the two energy states, h is Planck's constant and ν is the frequency of the radiation emitted or absorbed. In spectroscopy in the ultraviolet and visible regions of the spectrum wavelengths are more commonly used rather than frequency, so Equation (1) may be rewritten as Equation (2):

$$E_1 - E_0 = \frac{hc}{\lambda} \quad (2)$$

where c is the velocity of light and λ is the wavelength of emission or absorption. Rearranging, we obtain Equation (3):

$$\lambda = \frac{hc}{E_1 - E_0} \quad (3)$$

Since h and c are both constants, it follows that the wavelength corresponding to the change of energy of the atom, from one energy level to another, is inversely proportional to the difference between the two energy levels. Since the same two energy levels are involved, it follows that the emission and the absorption wavelengths will be identical since the calculation is the same in both cases.

2.4 The Shape of Spectral Lines

The emission and absorption wavelengths are generally quoted in texts as being, for example, Cu 324.754 nm,

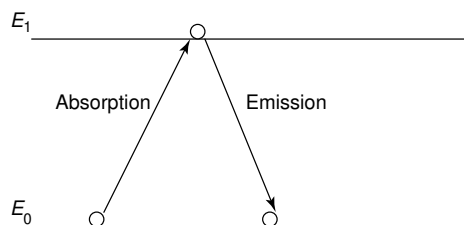


Figure 1 Relationship of emission and absorption lines.

and it might often be assumed that this means a line of virtually no shape, i.e. an infinitely narrow line. Such is not the case, however, and lines do have a finite width and shape, both of which will vary under certain conditions. The wavelength designated might be seen as the central wavelength, but there will be present under all conditions a distribution of wavelengths around that central wavelength (called the 'natural' line width). Various factors may increase the line width further ('broaden' the line).

In a short survey such as this article, only the two principle causes of line broadening will be considered. The first of these is Doppler broadening, caused by the fact that in a vapor cloud the atoms will be moving in all directions. Observations of emission from an atom coming towards the point of observation at the time of emission will record a wavelength shorter than that recorded from an atom going away from the point of observation at the time it emits. Obviously, as the temperature is increased the velocity of motion of the atoms is increased and this effect will therefore increase with increasing temperature, producing an increased line width.

The second cause is pressure broadening due to the concentration of atoms and molecules in the vapor in which the emission is occurring. The higher these concentrations are, the greater is the broadening which will occur.

The combined effects of these two (and some other minor) causes of broadening is to produce an emission line with an approximately Gaussian profile, as shown in Figure 2(a). The usual manner of describing the width of this line is the 'half-width', that is, the width at half the maximum peak intensity. The use of this manner of describing line width is necessary because the maximum width which exists, as zero intensity is approached, becomes progressively harder to measure and is dependent on the sensitivity of measurement available and the concentration of the atoms responsible for the absorption or emission.

Under the conditions prevailing in a flame, burning at atmospheric pressure at a temperature in the 2000–3000 K range, the half-width of the absorption lines will be of the order of 0.002–0.01 nm. An absorption line may be drawn, as shown in Figure 2(b), following the convention of drawing absorption lines downwards and emission lines upwards. For the understanding of this diagram, and for descriptions which will follow later, it is necessary to describe just what it illustrates, as far as atomic absorption measurement is concerned.

For any absorption spectrometric method, the absorption signal is always designated in terms of "absorbance" (A) and this is defined as $\log_{10}(I_0/I_t)$ where I_0 is the intensity of the original source radiation and

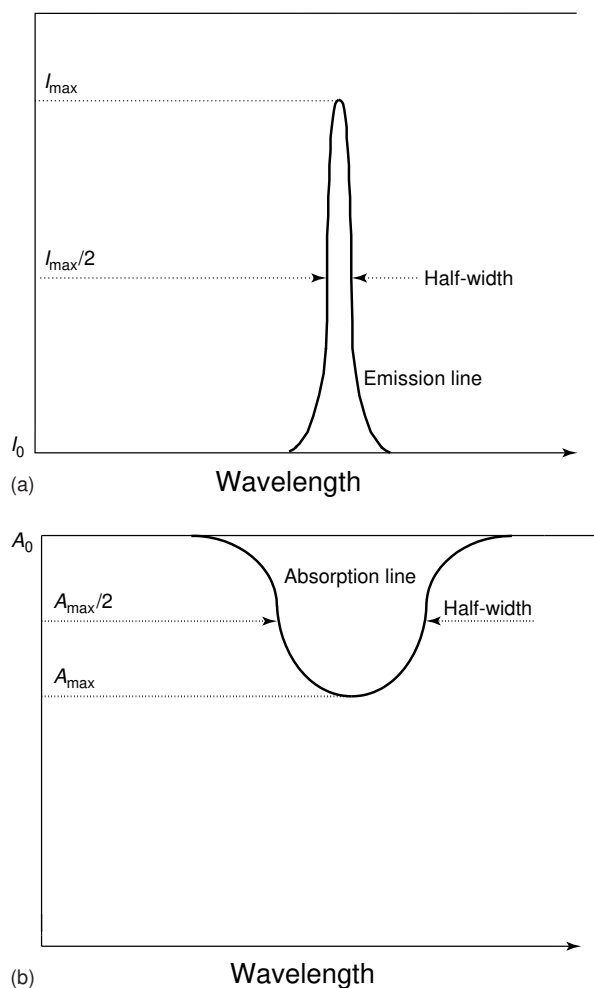


Figure 2 Representation of (a) an emission line and (b) an absorption line.

I_t the intensity of the same radiation after it has passed through the absorbing medium.

The absorbance (A) which will occur follows Beer's law, which may be expressed as Equation (4):

$$A = kcl \quad (4)$$

where k is the absorption coefficient, c the concentration of the absorbing species and l the absorption pathlength.

Returning to Figure 2(b), any point on the curve shown may be seen to represent the absorption coefficient at the particular wavelength. As a result, it may easily be understood that at the two wavelengths represented at the arrow points, where the half-width is defined, the absorption coefficient will be exactly half that at the peak of the absorption line, designated A_{\max} . From the same reasoning, the absorption coefficient at the extreme left and right of the absorption line will be approaching zero.

2.5 Measuring Atomic Absorption

2.5.1 Using Continuum Source Emission

Early concepts of measuring atomic absorption were based on the idea of measuring the absorption of light from a continuum source, but this approach has limited value for the following reason. The spectral band-pass of a monochromator of modest resolution, say 0.2 nm, can be represented as shown in Figure 3 with a representation of an absorption line with a half-width of approximately 0.01 nm superimposed on it. It can be seen that the sensitivity of this measurement will be limited, since even if the peak absorption at the center of the absorption line is, for example, 40%, perhaps less than 1% of the total energy reaching the detector will be absorbed. In addition, it is obvious that changes of absorption with concentration of the atoms of the analyte will give rise to a nonlinear function.

Naturally, the sensitivity may be improved by using a higher resolution monochromator as represented, for example, as 0.05 nm in Figure 3. However, the absorption will still probably be less than 2–3% of the total radiation. Also, and equally important, with such a narrow slit opening, the total intensity of radiation from a typical continuum source would be very low and the precision of the measurement function would therefore be limited by this low intensity.

2.5.2 Using a Sharp Line Emission Source

One of Walsh's major contributions to the subject was to suggest that peak absorption could be measured if use was made of a line source, providing emission at precisely

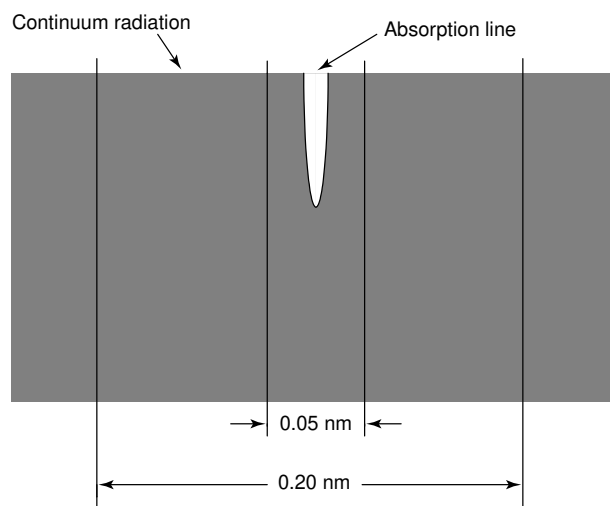


Figure 3 Measurement of atomic absorption using a continuum source.

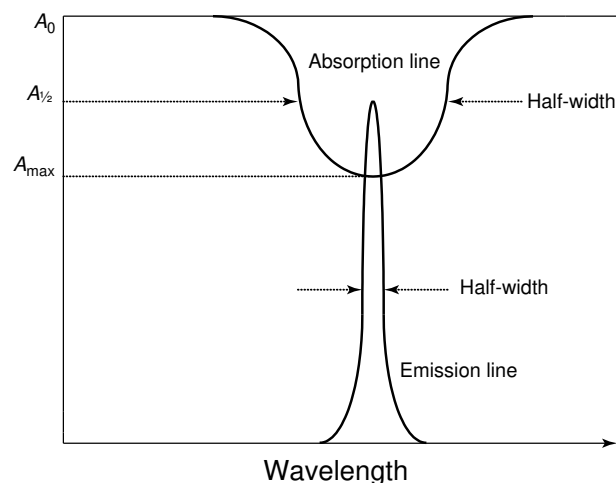


Figure 4 Measurement of atomic absorption using a sharp-line source.

the same wavelength as the absorption, and having a line width much less than that of the absorption line. This situation is represented in Figure 4.

The means of providing such a sharp line emission, at precisely the same wavelength as the absorption, was to use an individual hollow-cathode lamp (HCL) to provide the emission spectrum for each element to be determined. The construction and operation of such lamps will be discussed more in the next section, but at this stage it is useful to indicate why this sharp line emission occurs.

An HCL operates at reduced pressure, typically 1–2 kPa, so the concentration of atoms and molecules within the tube will be much less than in a flame at atmospheric pressure and this will reduce pressure broadening. Additionally, the temperature of the discharge will be only perhaps 500–600 K, compared with flame temperatures of 2000 K or more, and this will reduce Doppler broadening. Under these conditions, a HCL produces emission lines with half-widths of the order of 0.0004–0.002 nm.

As shown in Figure 4, it should be understood that the major part of the emission signal will be capable of absorption at or near the center of the absorption line, that is, at the wavelength where the absorption coefficient is at its maximum. This will result in maximum sensitivity of measurement. Quantitatively, the amount of energy at the maximum and minimum wavelengths of the emission line (the left- and right-hand flanks of the line as shown) will be very small. As a result, the fact that at these wavelengths the absorption coefficient will be slightly smaller will have only a small effect on the overall sensitivity achieved.

2.6 Spectral Interferences in Atomic Absorption Spectrometry

True spectral interferences may be defined as spectral interferences which, if undetected and uncontrolled, may lead to an error in the results obtained. There is another phenomenon, here termed “pseudo-spectral interference”, which can affect measurements and this will be described first. It is not really a spectral interference since it only contributes to the quality of the measurement function and does not cause incorrect results. This minor problem will be dealt with first.

2.6.1 Pseudo-spectral Interferences

As illustrated in Figure 4, it may be seen that the emitted line from the light source used to make the measurement may be absorbed by the atomic absorption process, the amount of absorption being dependent on the concentration of the analyte present. If for whatever reason there is an emission produced by the light source which results in a line within the spectral band-pass of the monochromator, but which is not overlapped by the absorption line, as shown in Figure 5, no interference will be produced.

However, since the extraneous line will not be absorbed, regardless of how great the concentration of the analyte is, some loss of sensitivity of the measurement will occur and the calibration function will be nonlinear. Two means are available which may successfully overcome this problem:

- employ a narrower spectral band-pass from the monochromator by altering the slit opening;
- remove the element which gives rise to the extraneous line.

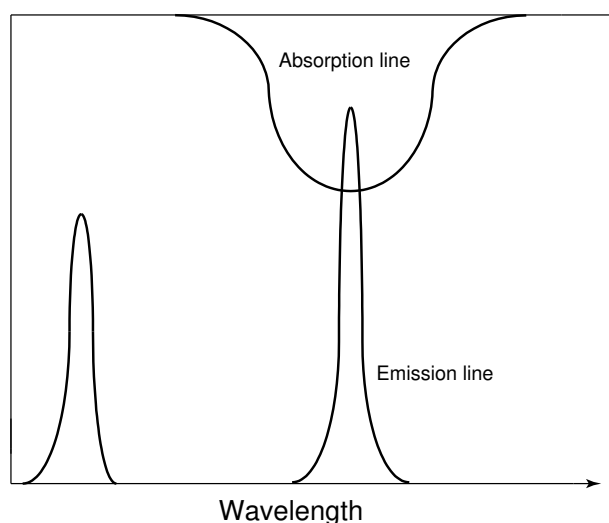


Figure 5 Atomic absorption measurement with a nearby emission line.

With regard to the first of these solutions, it should be recognized that in Figure 5 the spectral band-pass is roughly 0.04 nm (if we assume that the half-width of the absorption line is about 0.01 nm). To eliminate the effect of the “interfering” line the slit opening would need to be closed to a spectral band-pass of about 0.02 nm and this would require a relatively high resolution monochromator.

The second solution will be possible, for example, if the foreign line is due to the fill gas of the HCL by replacing it with a different fill gas. If the foreign line is due to an element other than the analyte, and which is introduced in the construction of the cathode, then the construction of the cathode might be modified to remove this element.

Should the foreign line be a nonresonance line of the analyte itself, then the second solution is not possible and only the first solution can be used either to remove or at least to minimize this curvature of calibration. It must be emphasized again, however, that curvature of calibration is only a minor operational problem and does not in itself cause errors in the analysis.

2.6.2 True Spectral Interferences

By comparison, again with Figure 4, if another element has an absorption line within the spectral band-pass of the monochromator, as illustrated in Figure 6, then no interference will occur. This is because there is no overlap of the other absorption line with the emission from the sharp line source at the resonance wavelength.

Should there be, however, a much closer absorption line, such as shown in Figure 7, then interference is possible since the left-hand flank of the absorption line

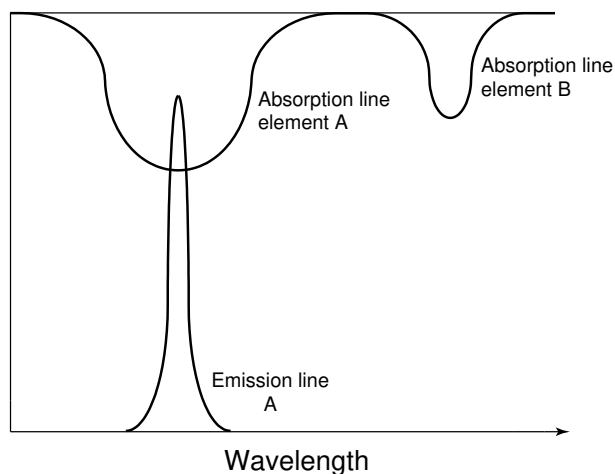


Figure 6 Atomic absorption measurement with a nearby absorption line.

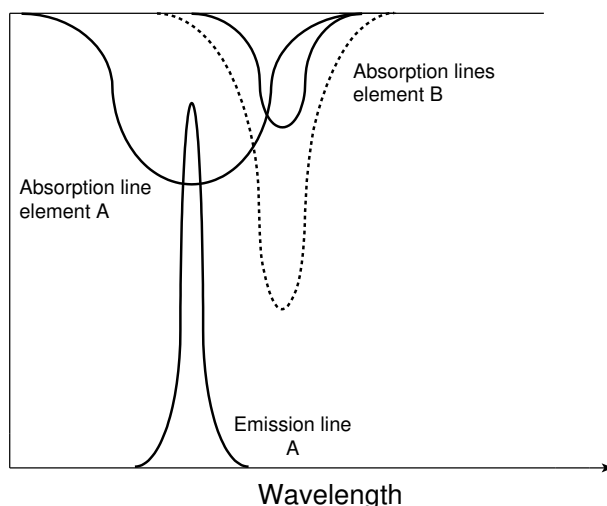


Figure 7 Interfering atomic absorption line.

of B does, as represented here, slightly overlap the right-hand flank of the emission line of the analyte (A).

It should be appreciated, however, that, in addition to the separation of absorption lines, the relative concentrations of the two elements A and B will affect this situation. In the absorption line for element B, at low concentration (shown as the full line) there is a small overlap but as represented it would cause only a slight absorption of a very small part of the total emission signal. However, the absorption due to a higher concentration (represented by the dotted line) is at a greater absorption coefficient, and the overlap is greater. This means that the potential interference will be more significant. Note that the absorption line, as represented, is actually effectively wider. This is because the concentration of atoms absorbing at these flank wavelengths is greater and so the effect will be more observable. Remembering that $A = kcl$, this may be seen as the effect that even though k may be very low as zero absorption coefficient is approached, the effect of multiplying a low k by a high c will result in a larger signal.

Nothing can be done about this type of interference except to use a different resonance line of A for the measurement, since clearly limiting the spectral band-pass of the monochromator will not remove the problem.

When the method was first proposed, it was suggested that since the total atomic absorption spectra of all elements were relatively simple, such interferences might be expected to be rare. This has proven to be the case and no more than 10–12 such interferences have been reported, often rather exotic and unlikely to be encountered in practice. For example, such an interference does occur between copper and europium, as illustrated in Figure 8. The most sensitive line of copper at

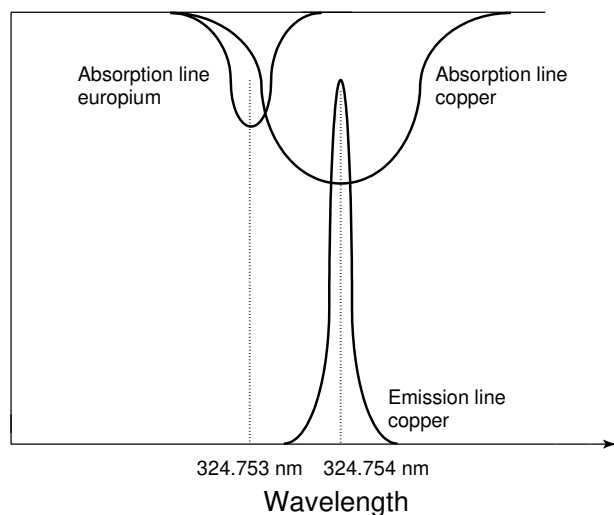


Figure 8 Atomic absorption measurement of copper in the presence of europium.

324.754 nm is very close to an absorption line of europium at 324.753 nm. Referring to Figure 8, if we assume that the half-width of the emission line is 0.0002 nm, then the separation of the central wavelengths of the two absorption lines shown is about 0.001 nm. As may be seen, the copper emission line from the HCL is slightly overlapped by the tail of the europium absorption line. This line is not the most sensitive line for europium so its absorption coefficient would be very low, and additionally the overlap is very small.

In fact, significant interference will only be observed if the Eu–Cu ratio is greater than about 500:1. However, if copper needed to be determined, in a sample which contained a very high concentration of europium an error would occur. In what is, after all, a rare analytical

situation, the solution to the problem would be to measure copper at the alternative resonance wavelength of 327.4 nm where no such interference occurs and where the sensitivity for copper measurement is reduced by a factor of only about two.

Another case of true spectral interference is the possible absorption of the resonance line of the analyte by molecular absorption. Some molecular species, which might be produced in the atomizer from certain sample types, might have absorption bands which overly the resonance wavelength. Such nonspecific absorption can occur in the presence of high salt concentrations, particularly at wavelengths in the low-ultraviolet region of the spectrum (below 300 nm).

This type of interference is seldom very major in flame atomization but may be needed for the most precise analyses, particularly for measurements at very short wavelengths. It is, however, very important in furnace atomization methods and for this reason background correctors have been developed and will be discussed briefly in the next section.

3 INSTRUMENTATION FOR ATOMIC ABSORPTION SPECTROMETRY

Following the publication of his first paper,⁽⁶⁾ Walsh, with some colleagues, described a suitable instrument for the practical measurement of atomic absorption spectra.⁽⁸⁾

The essential component sections of an atomic absorption spectrometer are shown in Figure 9. As illustrated these are as follows:

- a light source (usually an HCL) which provides a sharp line emission at the resonance wavelength for the element to be measured (analyte);

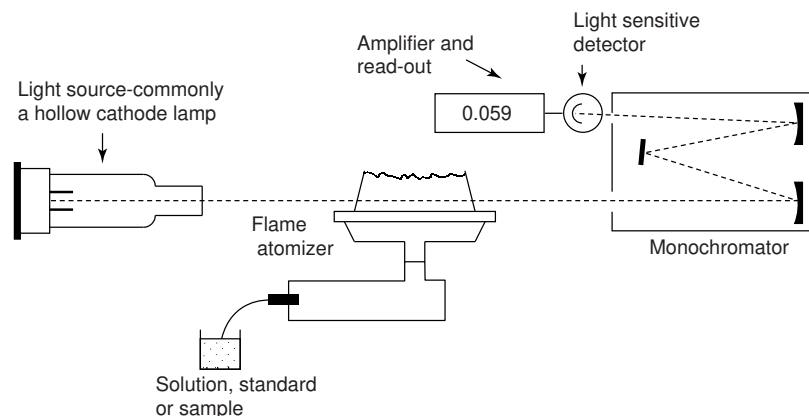


Figure 9 Diagrammatic representation of an atomic absorption spectrometer. (Reproduced by permission of Varian Australia Pty Ltd. from *Introducing Atomic Absorption*, 1983.)

- an atomizer (shown here as a flame) which produces free atoms of the analyte;
- a wavelength selection device (usually a monochromator) which allows the isolation of this resonance line from other lines produced in the spectrum of the lamp;
- a detector (usually a photomultiplier tube) which measures the intensity of the signal which is passed by the wavelength selection device;
- an amplifier–read-out device which processes the signal from the photomultiplier and converts it into a suitable form from which the result is obtained.

Each of these component sections will now be examined in some detail.

3.1 Light Sources

3.1.1 Hollow-cathode Lamp

The principal light sources which were first used in the development of a practical atomic absorption instrument, in the early 1950s, were HCLs. Such lamps were, at the time, relatively uncommon and an initial task of Walsh and his colleagues was to perfect the means of making such lamps which were both stable and exhibited adequately long lives.⁽⁹⁾ Possibly surprisingly, nearly 50 years later, such lamps still remain the basis of most atomic absorption instruments. A sketch of such a lamp and an illustration of its operation appear in Figure 10(a) and (b), respectively.

The lamp consists of a glass envelope into which are sealed the contacts leading to the anode and cathode. The cathode is either made from the element whose spectrum is sought, an alloy containing this element, or an insertion

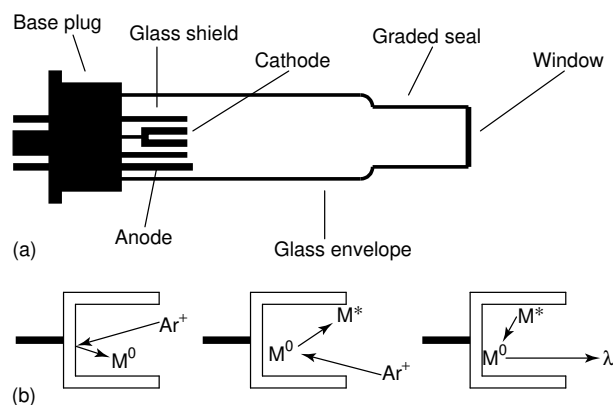


Figure 10 (a) An HCL and (b) its operation. (Reproduced by permission of Varian Australia Pty Ltd. from *Introducing Atomic Absorption*, 1983.)

of the element or a compacted powder mixture containing the element.

A fused-silica window is sealed to the end of the lamp with a ‘graded seal’ joining the window to the envelope. This is necessary as the coefficient of expansion of the glass in the envelope is much greater than that of the silica and cracking would result following the heating and cooling which take place during lamp operation.

The lamp is filled with a monatomic inert gas such as argon, helium or neon, at a low pressure (1–2 kPa). Early lamps generally used argon as the fill gas but for some time neon has been used as the ‘standard’ fill gas. Argon is used for a few lamps, principally for lamps of elements where the presence of neon causes the emission of lines which are closely adjacent to the resonance lines commonly used for the measurement of that element. In operation, a potential difference of 400–500 V is applied between the anode and the cathode. Initially this ionizes some of the neon (or argon) and once current flow commences the potential difference across the electrodes will fall to about 250 V. The positively charged ions of the inert gas are attracted to the (negatively charged) cathode by electrostatic forces, causing the ions to be rapidly accelerated towards the cathode.

The rapidly moving ions of the inert gas, on striking the interior of the cathode, dislodge atoms from the cathode material (“cathodic sputtering”), creating a cloud of atoms at the mouth of the cathode. Many of these atoms are excited by collision with more of the rapidly moving ions of the inert gas and then, on spontaneously returning to the ground state, emit the emission spectrum of the element.

The total spectrum produced by this process will consist of atomic and ionic emission lines of the inert gas and atomic and ionic emission lines of the element(s) contained in the cathode. Of course, for any element the strongest atomic emission lines will be the resonance lines, since the resonance transitions will be the most likely to occur.

Such HCLs can be made for all of the elements which may be determined by atomic absorption, and are the standard light sources used for most analytical atomic absorption measurements. They do, however, have finite lifetimes due to a process which is called “clean-up”.

As described earlier, HCLs operate by some of the material of the cathode being removed, as atoms, by a sputtering process. After these atoms have been excited and given off their emission signals, they eventually condense on a cooler part of the lamp as a thin film of the metal. In general, most of this thin film of metal appears on the portion of the inner wall of the lamp which is immediately adjacent to the cathode itself as a mirror like layer. Since this film is literally deposited atom by atom, it has a very large surface area and adsorbs

some small amount of the fill gas used in the lamp. Eventually this adsorption process reduces the fill gas pressure sufficiently that the lamp will no longer sustain a hollow-cathode discharge and the signal of the resonance line is no longer strongly produced. At this stage the lamp must be replaced.

Operating lifetimes of lamps were initially a problem, particularly for some volatile elements, but, with progressive development, today are typically from 1000 to as much as 10 000 h or longer.

Light sources other than HCLs have been used through the period of development of the technique but only two of these are commercially available and in serious use today. These are the boosted discharge HCL (initially called the “high-intensity lamp”) and the so-called electrodeless discharge lamp.

3.1.2 Boosted-discharge Hollow-cathode Lamp

This has the essential construction of an HCL, but with additional auxiliary electrode(s) sealed into the lamp beside the open end of the hollow cathode, as shown in Figure 11.⁽¹⁰⁾ Similar designs have been used by various manufacturers, variously called “high-intensity lamps” and “super lamps”, but the principle remains essentially the same.

For probability reasons, such as described earlier for flame excitation, most of the atoms in a hollow-cathode discharge are in the ground state at any given time. Many

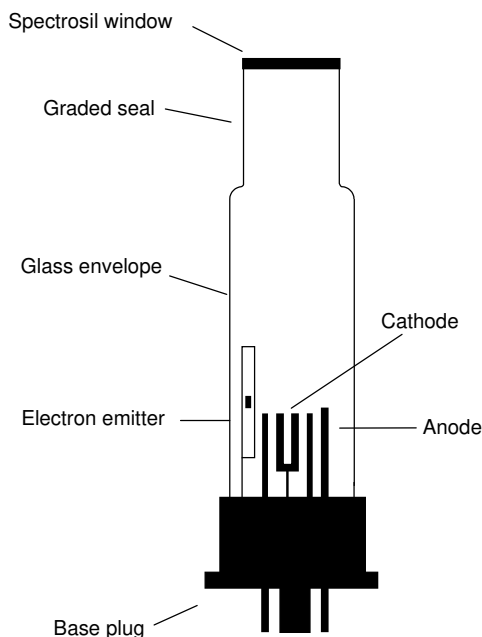


Figure 11 A boosted discharge HCL. (Reproduced by permission of Photron Pty Ltd. from *Photron Lamps*.)

of these atoms may be excited by the passage of a low-voltage discharge from the auxiliary electrode(s) through the atom cloud which exists in front of the cathode. The result is a more intense emission signal and, because the auxiliary discharge is of low energy (voltage), a greater proportion of the extra emission signal occurs at the resonance lines.

3.1.3 Electrodeless Discharge Lamps

A typical commercially available electrodeless discharge lamp is illustrated in Figure 12.

An electrodeless discharge lamp consists of a small, sealed-off silica bulb containing a very small mass of the element whose emission spectrum is required and a low pressure of inert fill gas. Excitation is by a radiofrequency signal coupled into the contents of the bulb via an induction coil surrounding the bulb. Such lamps are only readily produced for relatively volatile elements such as As, Se, Na and K, but for these elements more intense signals are produced compared with HCLs. Additionally, since HCLs for these volatile elements have shorter lifetimes, as described above, the electrodeless discharge lamps often also have the advantage of longer operating lifetimes.

3.1.4 Operation of Light Sources

Since the most sensitive wavelengths for atomic absorption are generally also the most sensitive wavelengths for atomic emission, some interferences may occur for elements which are significantly excited in the flame atomizer. This is because the flame atomic emission signal would add to the total signal incident on the detector. To overcome this, the signal from the light source is modulated, and an alternating current (AC) amplifier is then able to discriminate this signal from the (essentially) direct current (DC) signal produced by flame atomic emission. Such a modulated signal may be produced by applying a modulated current to the light source or by

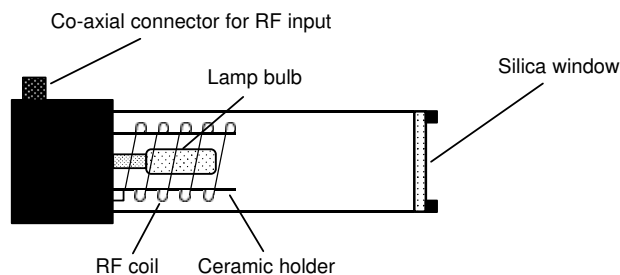


Figure 12 An electrodeless discharge lamp. (Reproduced by permission of Perkin-Elmer Corporation from *Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry*, 1978.)

mechanical chopping. Both techniques are in use in commercial instruments, as will be shown later in this section. A stable power supply is necessary, regardless of which of these modulation procedures are used, in order to produce a stable output from the light source.

3.2 Atomizers for Atomic Absorption Spectrometry

Without the production of free atoms, atomic absorption cannot be measured. It is in this section of the instrumentation that the operator of an atomic absorption spectrometer has the most control over the actual analysis and its veracity. Since the choice of the means of atomization employed and its detailed operation are of such fundamental importance to the technique, more detailed discussion will be postponed until later.

3.3 Wavelength Selection

As has already been discussed, the real resolution of atomic absorption measurement is provided by the absorption process itself. The function of the monochromator in the technique is therefore only to 'tidy up' the emission spectra from the light source. This is illustrated diagrammatically in Figure 13.

Here it may be seen that the light source is producing a spectrum, in the vicinity of the desired resonance wavelength R, containing a number of other lines. These lines may consist of other lines of the analyte, lines produced by other elements in the cathode material and lines of the fill gas of the lamp. Separating the resonance line (R) from all other lines in the vicinity is desirable in order to maximize sensitivity and limit calibration curvature.

Generally a modest monochromator will achieve this fairly readily, with a spectral band-pass of 0.7–1 nm usually being adequate. In a few cases where the analyte itself has another line near the resonance line (and this occurs with Fe, Co and Ni), a spectral band-pass of 0.2 nm will be advantageous in the interests of achieving a calibration graph which is as linear as possible.

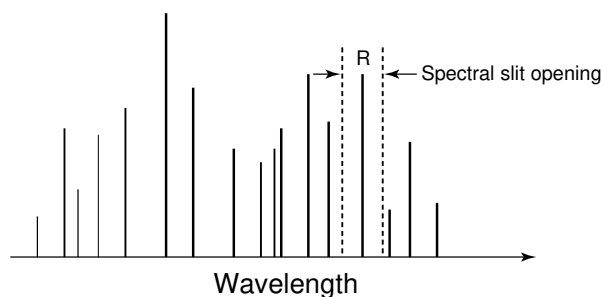


Figure 13 Isolation of a resonance line.

Initially monochromators which employed prisms for dispersion were commonly employed. However, for several years now most atomic absorption spectrometers have employed a monochromator with a diffraction grating as the means of wavelength dispersion. Such monochromators are more desirable than those employing prisms for dispersion as the wavelength settings are less prone to drift with temperature change. Obviously this is an important property when hot flames are being used as the means of atomization.

3.4 Detectors

The universal detectors of atomic absorption spectrometers for many years have been photomultiplier tubes. In the formative years of the technique it was often considered necessary, for the best results, to employ two different types. The range of AAS, as normally used, is from 193.7 nm for arsenic to 852 nm for cesium. In the 1950s there were no photomultipliers that covered this entire range with good sensitivity. Users who wished to measure arsenic and selenium as well as potassium needed two different types (rubidium and cesium, if needed, made this situation even more acute, but very few analysts measured these elements).

Two factors have altered this situation since that time. First, more intense light sources, including electrodeless discharge lamps, made the problem less acute. Second, the technology of photomultiplier tubes has improved and much better tubes with a wider wavelength range have been developed. Both of these improvements, of course, had a compound effect and today a single photomultiplier tube is all that is needed.

3.5 Amplifier and Read-out

As indicated before, the amplifier should respond only to a modulated AC signal and ignore any essentially DC signal resulting from flame emission. For the best performance this is accomplished by employing an amplifier tuned as closely as possible to the frequency at which the light source signal is modulated. Preferably it should be a synchronously demodulated amplifier which is "locked in" to the frequency of the lamp modulation.

The relationship between the concentration of the analyte and its absorption is logarithmic so that the amplifier will incorporate a logarithmic function to achieve a linear, or close to linear, read-out. Modern amplifier systems also incorporate mathematical processing of curved calibration functions to achieve direct concentration read-out of the result, regardless of whether the calibration function is linear or otherwise.

4 ATOMIZATION SYSTEMS AND THEIR USE

4.1 Historical

Historically the first actual use of atomic absorption measurements for quantitative analysis occurred in the late 1930s, long before Walsh's first suggestions. The British company Adam Hilger (later Hilger and Watts) developed an instrument to measure the concentration of mercury in air samples.⁽¹¹⁾ This was a specialized approach to serve a particular need and was, of necessity confined to mercury. Of all the elements which may be measured by AAS, mercury is the only one which can exist at room temperature and pressure in the stable form of free atoms. Later discussions will concentrate on mercury individually but, for the moment, more general approaches need to be considered.

4.2 Flame Atomization

4.2.1 Early History of Flame Atomic Emission

Flame atomization methods had been in use for many years when atomic absorption methods started to be developed in the 1950s. They had been used in flame emission analysis since the beginning of the century although probably seriously only after the important work of Lundegardh in 1928.⁽⁵⁾

The fact that these were indeed means of flame atomization was obscured by the fact that they were also means of excitation and were viewed more in this vein. However, as stated earlier, in flame emission methods the process is first of all the production of atoms and only then the excitation of those atoms produced.

From what has been said before, it should be clear that since the wavelength of radiation resulting from atomic emission is inversely proportional to the energy level of the excited state, then low-energy excitation sources can only produce emission for elements which emit radiation at long wavelengths.

Although Lundegardh's development of the use of the air-acetylene flame did extend the range of elements which could be determined by atomic flame emission, the temperature of this flame (ca. 2500 K) was not high enough to excite very many elements significantly. Since inadequate temperature was obviously the major limitation, investigators in the 1940s and later were drawn to the use of gas mixtures which would give rise to hotter flames, notably the readily available oxygen-acetylene mixture, which produced a temperature of about 3300 K. However it was found that the use of this gas mixture in a premix system could easily lead to serious explosion hazards and so alternative systems were developed. Particularly this led to the development of the so-called "total consumption

burner", in which the gases were only mixed with each other near the burner mouth. As will be mentioned later, such a burner system, although providing higher temperatures, introduced many problems to the technique.

4.2.2 Initial Developments of Flame Atomizers of Atomic Absorption

When investigations into the use of atomic absorption spectra for chemical analysis first commenced, the emphasis was initially on those elements which, although easy to atomize, were difficult to excite.⁽⁸⁾ These include Zn (213.8 nm), Cd (228.8 nm), Ni (232.0 nm) and Pb (283.3 nm). Because of the short wavelengths associated with these resonance lines, the energy required to excite the atoms is relatively high.

Initial use was made of burner systems from existing (emission) flame photometers which employed premix systems and employed relatively cold flames such as air-coal gas (ca. 2100 K). It was immediately found that it was possible to measure elements such as Zn and Cd with excellent sensitivity, comparable, for example, to the sensitivity obtainable for Na and K. This immediately proved one of the major benefits, initially claimed for atomic absorption, that it would be independent of the excitation energy required to populate the first excited state. It was also realized that since the method did measure absorption, a longer absorption pathlength increased the sensitivity, and suitable elongated slot burners were soon developed. Such burners had to employ slot dimensions which were matched, as closely as possible, to the geometry of the beam of light from the HCL.

4.2.3 The Use of the Air-Acetylene Flame

It was soon realized that although high energy was not needed for excitation purposes, it was, for some elements, needed to achieve atomization. The development of elongated slot burners suitable for use with the air-acetylene flame (in the early 1960s) extended the technique to a number of additional elements so that by this period about 35 elements could be determined by AAS using this flame. (The scientist most instrumental in the first development of air-acetylene burners, suitable for atomic absorption, was Allan⁽¹²⁾).

Relatively soon this flame became virtually the standard flame in use,⁽¹³⁾ and this remains the situation today. Several of the additional elements, however, either had modest sensitivities or suffered from a number of matrix interferences, or both.

4.2.4 Development of Hotter Flames

It had become clear that a number of additional elements, although potentially amenable to measurement by atomic

absorption, were not readily available because they were very difficult to atomize. These included important elements such as aluminum, titanium and silicon. These, and many other, elements readily formed very stable monoxides in the flame and at the temperature of the air–acetylene flame produced virtually no free atoms. Attempts were made to use total consumption burners, with various modifications, in order to use the oxygen–acetylene flame, but these proved to be of limited success.

The design problem lay in the very high burning velocity of the oxygen–acetylene flame compared with the air–acetylene flame.

In a premixed system, where the fuel and the oxidant gases are mixed in a chamber before passing through the burner slot, it is of vital importance that the velocity of the mixed gases through the burner slot is never exceeded by the burning velocity of the mixture of gases. Should it do so then a “flashback” of the flame into the chamber will result in a severe explosion.

In designing a suitable burner for safe operation with an air–acetylene flame, the slot opening had to be reduced compared with the opening in use with air–coal gas. However, examination of the burning velocities for the acetylene flames, supported by air and oxygen, respectively, made it clear that a huge (and impractical) reduction in slot dimensions would be required to burn oxygen–acetylene safely in a premixed system.

Some developments were first made using physical mixtures of air and nitrogen, as the support gas, and successful determinations of aluminum, titanium, silicon and many other elements were achieved with this approach. Mixtures containing as much as 85% oxygen were investigated, albeit with some hazards.⁽¹⁴⁾

The use of nitrous oxide as a support gas, however, was a major breakthrough as it permitted the safe burning of nitrous oxide–acetylene using a burner with a sensibly reduced slot opening.⁽¹⁵⁾ As may be seen in Table 2, this flame provided a high temperature with a moderate flame velocity.

Compared with the potentially variable composition of a physical mixture of nitrogen and oxygen, nitrous oxide, on thermal decomposition in the flame, provides

a mixture containing 67% (v/v) nitrogen and 33% (v/v) oxygen. However, it produces a flame more equivalent in temperature to that achieved with 50% N₂–50% O₂ owing to the exothermic decomposition of nitrous oxide.

With the additional use of this flame, a total of about 65 elements could, from 1965, be determined by AAS using flame atomization. More detailed examination of the flame atomization process will be presented later in this article.

4.2.5 Nebulizer–Burner Systems

Many different types of flame nebulizer–burner systems have been employed for atomic absorption. Some of these have been very useful for certain applications but for the purposes of this article the description will be confined to those commonly employed in available commercial instrumentation. A typical system is illustrated in Figure 14.

This system operates as follows. A flow of support gas (air or nitrous oxide), under pressure, passes into the nebulizer. The gas is expanded through a venturi throat and develops a pressure difference which draws a flow of sample solution through the inlet capillary. This solution, on emerging from the mouth of the venturi throat at a very high velocity, is shattered into droplets ranging in size from as small as 1–2 μm up to 100 μm or more, and this spray of droplets passes into the spray chamber. In this chamber, the oxidant gas and the droplets of sample solution are mixed with the fuel gas (acetylene). The flow spoiler, in this case a set of baffles, encourages the precipitation of the larger and heavier droplets of solution and these are drained from the chamber to waste. Most droplets larger than 10 μm in diameter will precipitate in the chamber. The mixture of oxidant, fuel and fine

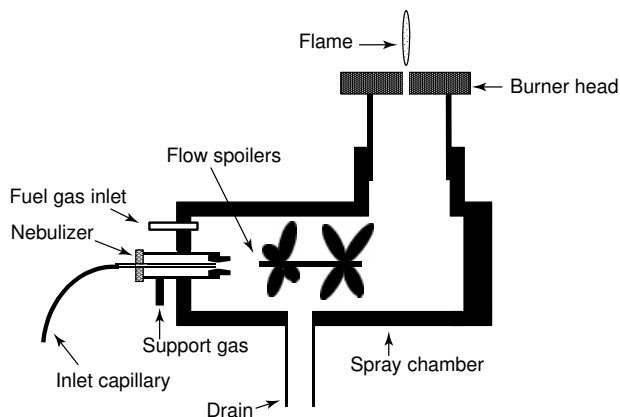


Figure 14 A nebulizer–burner system with flow spoilers. (Reproduced by permission of Perkin-Elmer Corporation from *Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry*, 1978.)

Table 2 Characteristics of various types of flames

Gas mixture	Burning velocity (cm s ⁻¹)	Maximum temperature (K)	Burner slot (mm)
Air–coal gas	55	2100	100 × 1.5
Air–propane	85	2200	100 × 1.5
Air–acetylene	160	2500	100 × 0.5
Nitrous oxide–acetylene	280	3100	50 × 0.5
Oxygen–acetylene	1130	3300	–

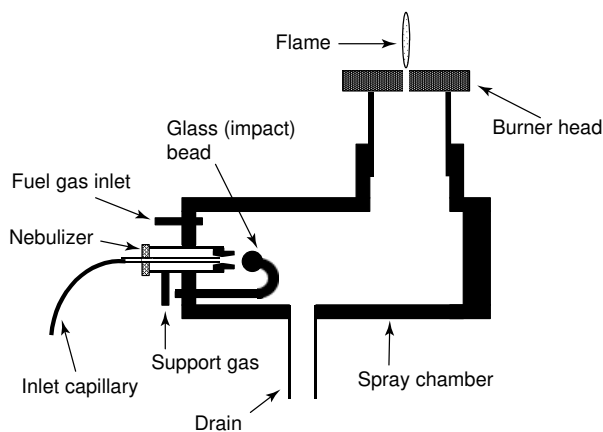


Figure 15 A nebulizer–burner system with a glass impact bead. (Reproduced by permission of Varian Australia Pty Ltd. from *Introducing Atomic Absorption*, 1983.)

spray (aerosol) then passes into the burner head and through the burner slot to the flame, burning above the slot.

A minor variation of the system illustrated in Figure 14 is shown in Figure 15. In this system, an impact bead, adjustable in position, is set in front of the nebulizer throat. When this is adjusted to its optimum position (which is critical), larger signals are produced, indicating that a greater amount of fine aerosol is being produced, presumably owing to the bead causing a more efficient shattering of the larger droplets into smaller ones. Both of these systems are in use in commercial instruments currently available.

Overall, the total nebulizer–burner system has changed little in principle since the 1950s when Walsh and his colleagues first used such a system to demonstrate the method.

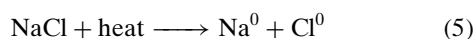
Nebulizers were developed which were more corrosion resistant when it was realized that the solutions required to keep some elements in stable solution were very corrosive.

Early burner heads were of relatively light construction, but the development of the nitrous oxide–acetylene flame made additional demands. In particular, since the flame was much hotter, more robust construction was needed to avoid distortion after protracted use. Also, a more massive construction was needed to provide a better “heat sink” to avoid overheating, which could detonate the combustible mixture of gases in the spray chamber. In general practice today the above system is used with two different types of burner head. First, for use with an air–acetylene flame, a burner with a slot of dimensions 100×0.5 mm is used. For burning a nitrous oxide–acetylene flame, a burner with slot dimensions of 50×0.5 mm is suitable.

4.2.6 The Atomization Process in the Flame

As the aerosol produced from the sample solution passes into the flame, the first process will be “desolvation”, that is, the boiling off of the solvent (which is generally water). This will result in the production of extremely minute solid particles of the constituents of the dissolved material in the solution.

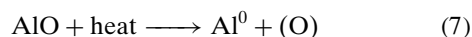
The effect of the higher temperature, as these particles move into the hotter part of the flame, will then be, in many cases, to dissociate the salts present and produce atoms of the constituent elements. However this is not always as simple as this might sound. Simple compounds such as NaCl and ZnCl₂ will very readily dissociate in the simplest manner possible, e.g. as shown in Equation (5):



where Na⁰ and Cl⁰ represent free atoms of sodium and chlorine. For many elements this simple process will apply in the air–acetylene flame. However, for some elements the process will be more complex and this may be represented for aluminum as Equation (6):

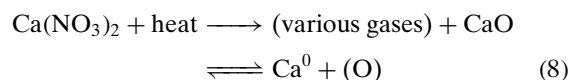


This is due to the great affinity for aluminum with oxygen and will occur regardless of which compound of aluminum is present. At the temperature of the air–acetylene flame, AlO is so stable it is virtually completely undissociated, so that no Al atoms are formed, and no atomic absorption signal can therefore be measured. However, at the temperature of the nitrous oxide–acetylene flame the next stage (Equation 7):



will occur. Most of those elements which demand the nitrous oxide–acetylene flame for atomization will react in this manner as most of them form very stable monoxide compounds.

Some elements occupy an intermediate position between these two extremes, and this may be typified with calcium. In this case it is appropriate to represent the reactions as Equation (8):



When air–acetylene is employed as the flame, the equilibrium represented is very much an incomplete reaction and only a portion of the calcium is converted to atoms. At the higher temperature of the nitrous oxide–acetylene flame, however, the equilibrium will be very much pushed

in the direction of almost complete production of atoms and greater sensitivity of measurement will result.

It is worth adding some comments here about the above description as it relates to the so-called “total consumption” burner. Such burners were developed to provide safe oxygen–acetylene flames for flame atomic emission measurement. In such burners, constructed as shown in Figure 16, all of the solution droplets pass into the flame, since there is no intermediate spray chamber.

Referring to the description above it follows that, since very many large droplets will pass to the flame, relatively large solid particles are formed following desolvation. These very large solid particles are poorly dissociated in the obviously very limited residence time available. Additionally, such burners provide a much lower temperature than the theoretical oxygen–acetylene flame temperature owing both to the lack of adequate mixing of the two gases and to the cooling effect of the larger solvent volume. All of these factors make such burners very limited as atomizers, whether used for atomic emission or atomic absorption, compared with premix systems such as those described previously.

It is worth pointing out that in the discussions above the accent has almost solely on the temperature of the flame atomizer. This is almost certainly the major factor, but it is not the only factor. The chemical environment of the flame is extraordinarily complex, and of course the chemistry of every single element which may be measured by atomic absorption is different from that of almost every other element. Flames used for atomization

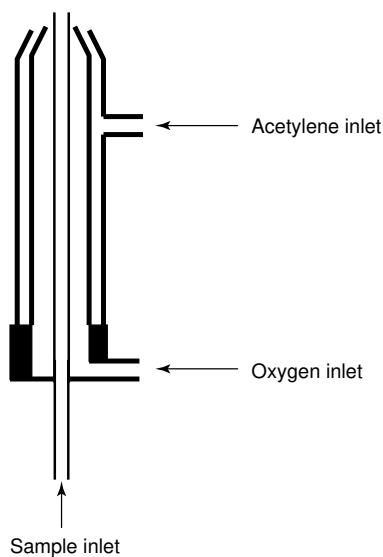


Figure 16 A total consumption burner. (Reproduced by permission of Wiley-VCH from B. Welz, *Atomic Absorption Spectrometry*, VCH, Weinheim, 1985.)

may, for simplicity, be classified as stoichiometric, fuel lean or fuel rich. A stoichiometric flame may be defined as a flame where the amount of oxygen present is exactly the amount required to totally burn the hydrocarbon of the fuel in conformity to the equation of the combustion process. For example (Equation 9):



For any given fuel and oxidant combination the highest temperature will be provided by such a stoichiometric flame.

A flame which has an excess of the fuel gas present, compared with the amount of oxidant present, is classified as fuel rich, is sometimes also called a reducing flame and will be somewhat cooler than the stoichiometric flame.

However, for many elements, better atomization, as indicated by larger atomic absorption signals, will occur for mildly or even strongly reducing flames. Chromium in the air–acetylene flame is a good example of this, as is silicon in the nitrous oxide–acetylene flame. The full understanding of all of the processes involved probably still evades the scientific investigators of flame chemistry, but as will be discussed later, a practical means of achieving optimum adjustments is still attainable.

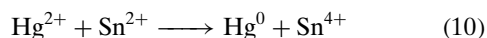
4.3 Vapor Generation Techniques

4.3.1 Mercury Cold Vapor

It has been pointed out earlier that mercury was measured by atomic absorption in the 1930s. Using flame atomic absorption, the sensitivity obtained for this element is very poor, particularly when viewed against the background that since mercury is a very toxic element it often needs to be determined at very low concentrations. However, it was found that mercury can be released from any compound associations in solution, and converted to elemental mercury, by adding a reducing agent (such as stannous chloride) to the solution.⁽¹⁶⁾ By bubbling a stream of a gas, such as nitrogen, through the solution the mercury atomic vapor is carried from the solution in this stream. The flow of gas is then passed through a flow cell placed in the light path of the atomic absorption apparatus, which then records the absorption signal. Because the reaction is fairly rapid, a very high transient concentration of atomic vapor of mercury is achieved, giving rise to a large absorption signal peak. Whereas flame methods only allow the detection of about 1 mg L^{-1} of mercury, the “cold vapor” method permits the detection of small fractions of $1 \text{ } \mu\text{g L}^{-1}$.

In general, the equipment commonly used for this type of measurement is the same as that used for hydride methods employed for some other elements, and which will be described below.

In the case of stannous chloride the reduction reaction, in solution, is as shown in Equation (10):



It is also possible to use sodium borohydride (NaBH_4), as a means of generating hydrogen, as a reductant as described below for hydride methods.

4.3.2 Hydride Methods

Another group of metals, which exhibit poor sensitivities by flame atomization methods, may also be determined by a different vapor generation method. First suggestions of such an approach were made in 1969.⁽¹⁷⁾ As now employed, the addition of a sodium borohydride solution to an acid solution of the analyte causes the production of hydrogen, and this in turn induces volatilization of hydrides of these elements. Such hydrides may be typified by arsine (AsH_3), which has a very low boiling point and so is readily evolved from solution once formed. These hydrides are readily decomposed, in a quartz flow cell, at modest temperatures (800–1000 °C) to produce free atoms of the analyte. A diagrammatic representation of the principle is shown in Figure 17.

The quartz cell may be heated either by mounting it above a flame produced using a normal burner system or by electrically heating the cell. (Initially the method used was to add metallic zinc powder to the acidic solution, but sodium borohydride gives a faster and more reproducible reduction of the metal to the hydride. In both cases the reduction depends upon the production of nascent hydrogen.) This method is only applicable to those elements which readily produce hydrides of very low boiling point, viz. arsenic, antimony, bismuth, selenium, tellurium and tin.

Using this method, most of these elements have detection limits of $<0.1 \mu\text{g L}^{-1}$, whereas in the flame their detection limits are at best around 1000 times poorer at ca. 0.1 mg L^{-1} .

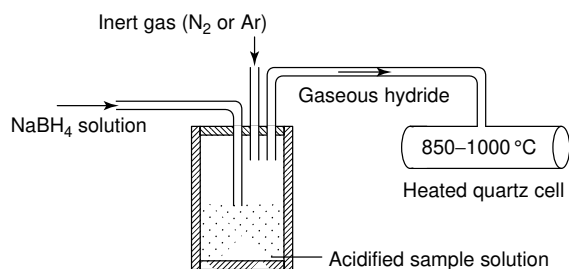


Figure 17 Diagrammatic representation of a vapor generation system. (Reproduced by permission of Wiley-VCH from B. Welz, *Atomic Absorption Spectrometry*, VCH, Weinheim, 1985.)

Lead has been determined by this technique but with some operational difficulty, which limits the appeal of the method for this element.

4.4 Graphite Furnace Atomization

This method was first described in 1961⁽¹⁸⁾ and has been in use with commercial equipment since about 1970. It produces detection limits for many elements which are several hundred times better than flame detection limits of the same elements. It also has the advantage that only very small sizes of sample are needed (a few microliters compared with a few milliliters typically required for flame methods). It has the disadvantages of requiring a moderately expensive accessory apparatus and of being a very slow method. However, it is readily automated, which overcomes at least some of the disadvantages of the slowness. This method is outside the scope of this article and will be dealt with in detail elsewhere.

5 OPTICAL DESIGN OF INSTRUMENTS FOR ATOMIC ABSORPTION SPECTROMETRY

5.1 Atomic Absorption Spectrometer Design

Two basic types of optical system have been employed since the first atomic absorption instruments were produced commercially. These are the single-beam system and the double-beam system and simplified diagrams of such types are illustrated here.

In Figure 18 is shown a very simple single-beam system. This contains an absolute minimum of optical components and is therefore optically very efficient, and also relatively inexpensive. The major disadvantage of such a system is that any instability in light source output will result in a variable base line reading.

In Figure 19 is shown a simple double-beam system where the beam is split and two paths of light, one through the atomizer (sample beam) and the other around it (reference beam), are produced. These are subsequently recombined and both signals measured and compared with one another.

The obvious advantage is that since comparison of the two signals is continually and frequently being made, variations in source intensity are cancelled out. Two means of achieving this are in use in commercial instruments. That illustrated in Figure 19 employs a beam splitter and recombiner. The same result can be achieved by employing a system of chopping with a rotating mirror, as shown in Figure 20. In both cases the systems are not as simple as the single-beam system and consequently the cost is greater.

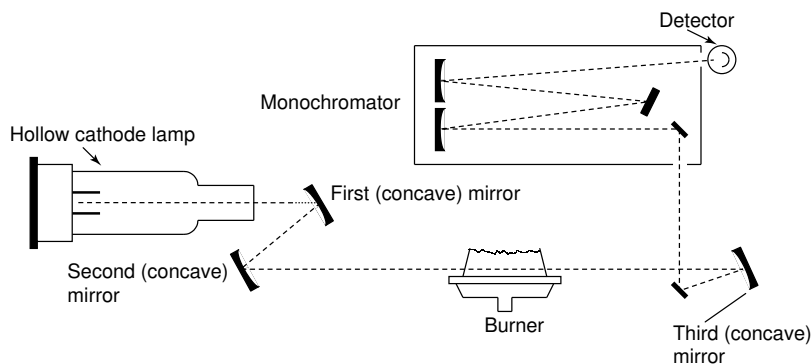


Figure 18 An optical system for a single-beam atomic absorption spectrometer. (Reproduced by permission of Varian Australia Pty Ltd. from *Introducing Atomic Absorption*, 1983.)

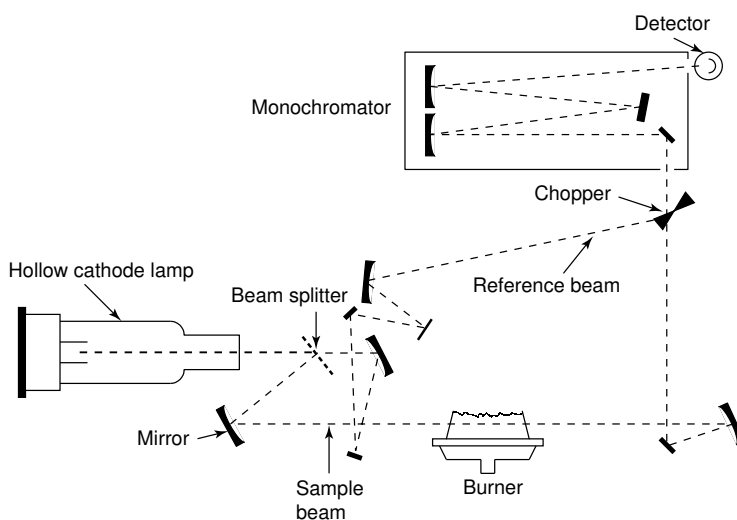


Figure 19 An optical system for a double-beam atomic absorption spectrometer with beam splitters. (Reproduced by permission of Varian Australia Pty Ltd. from *Introducing Atomic Absorption*, 1983.)

5.2 Optical Design for Background Correction

As mentioned previously, attenuation of the signal at the resonance wavelength by molecular absorption can cause errors in some cases, particularly when GFAAS is used. However, even in flame atomic absorption if the concentration of the analyte is low (giving rise to a very small atomic absorption signal), and the concentration of species producing molecular absorption at the analyte wavelength is high, errors will be introduced if correction is not made.

Figure 21 shows how a simple means of correction using a continuum light source may overcome this problem, a method first described in 1965.⁽¹⁹⁾ This is illustrated by comparison with the double-beam instrument shown in Figure 19, but such an approach can be similarly used with the systems illustrated in Figures 18 and 20.

Alternative measurements with the sharp line source and the continuum source will measure as indicated in Equations (11) and (12):

$$\text{sharp line source} = AA + MA \quad (11)$$

$$\text{continuum source} = MA \quad (12)$$

where AA = atomic absorption and MA = molecular absorption. Subtracting the second reading from the first then gives (Equation 13):

$$(AA + MA) - MA = AA \quad (13)$$

Some of the radiation from the continuum source will be absorbed by atomic absorption. However, the instrument will be looking at the radiation from the continuum across a spectral band-pass of, say, 0.7 nm.

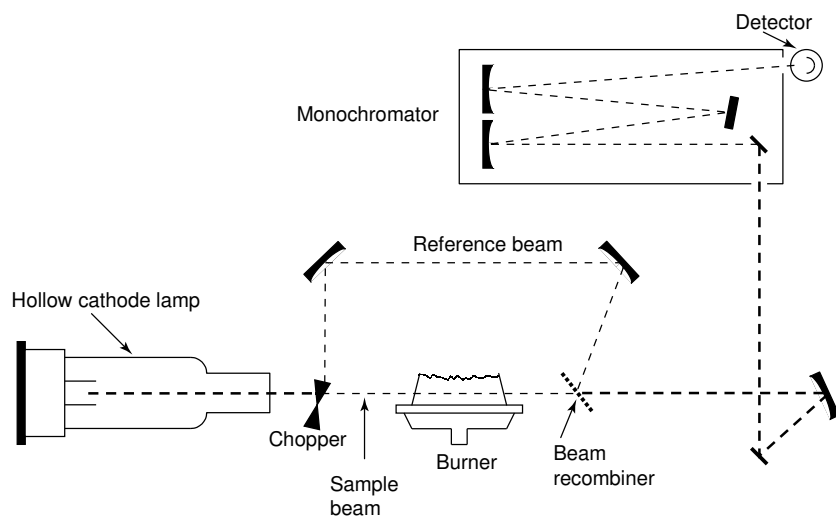


Figure 20 An optical system for a double-beam atomic absorption spectrometer with a reflecting chopper. (Reproduced by permission of Perkin-Elmer Corporation from *Concepts, Instrumentation and Techniques in Atomic Absorption Spectrophotometry*, 1978.)

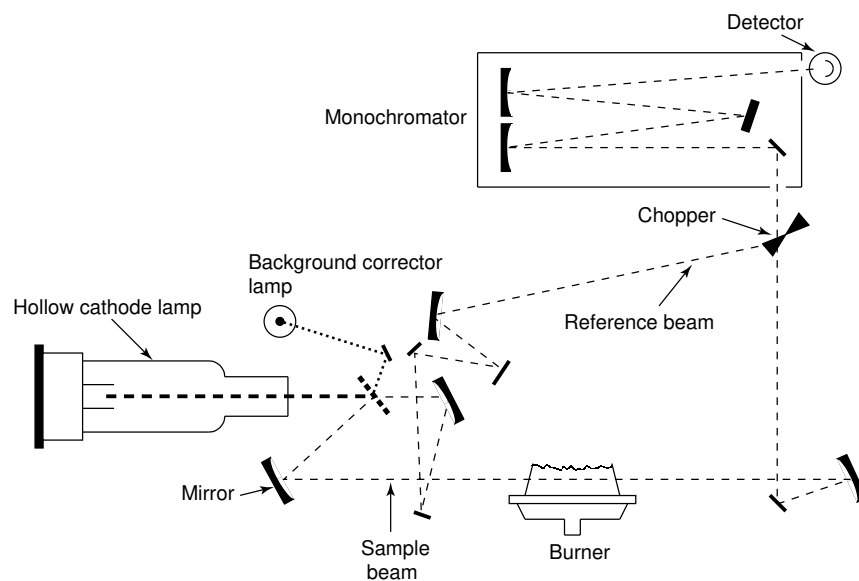


Figure 21 An optical system for a double-beam atomic absorption spectrometer with background correction. (Reproduced by permission of Varian Australia Pty Ltd. from *Introducing Atomic Absorption*, 1983.)

Since the atomic absorption will only be over an absorption profile maybe 0.01 nm wide, less than 1% of this radiation will be absorbed and as a first approximation this may be ignored with very little resultant error.

The situation is completely different for GFAAS methods. Here it may be commonplace for the background absorption to be of a magnitude which is

greater than that of the atomic absorption signal. Very careful design of the background corrector and its very careful adjustment are then most important. For this reason, a much better means of background correction is the use of the Zeeman effect background correction system. This is outside the scope of this article since it is applied only to the graphite furnace method.

6 PRACTICES OF ATOMIC ABSORPTION SPECTROMETRY

6.1 General

Like most spectroscopic methods, AAS is a comparative method, that is, it requires the calibration of the instrument with standards of known concentration before the analytical measurement of the samples may be made. However, as will be discussed later, it is generally not necessary to match the composition of the calibration standards to the samples with regard to elements other than the analyte. The calibration standards may generally be simple aqueous solutions containing nothing but accurately controlled concentrations of the analyte. Like almost all instrumental methods, the performance is limited by the signal-to-noise ratio, with regard to both the detection limit and the precision achieved. In the following sections these factors will be discussed more and attention given to means of optimization in order to obtain the best possible detection limits and precision.

6.2 Optimization of Instrumental Parameters

Because the optimization process involves two factors, signal (size) and noise, it often involves some sensible compromise. This will be briefly discussed in relation to the various parameters which may be set by the operator of an atomic absorption spectrometer.

6.2.1 Hollow-cathode Lamp Currents

Referring to earlier discussion on line shapes, the selection of lamp currents is very much a compromise. As the HCL current is increased, two things occur. A stronger signal is produced but inevitably the line width of the emission signal of the resonance line is also increased. The first of these changes will allow the use of a lower gain in the photomultiplier and amplifier system and this will decrease the “noise” produced from the photomultiplier and amplifier system. However, the broader emission line will decrease the sensitivity and this will reduce the absorbance for a given concentration and may also increase the curvature of calibration. In method development, the best compromise should be experimentally determined with reference to obtaining the best detection limit and/or the best precision.

6.2.2 Wavelength Selection

In general, for a majority of elements, the most sensitive line will be used for the measurement. However, this is not always the case and some brief examples will be mentioned.

In the measurement of lead, the most sensitive line is at 217.0 nm and this will produce a signal, for a given concentration, which is about twice as large as that obtained if the 283.3-nm line is used. However, the signal at 217.0 nm has a much greater noise component because of two factors:

1. The photomultiplier response at 217.0 nm is much poorer than at 283.3 nm so the photomultiplier will have to be operated at higher dynode volts, giving rise to more noise.
2. At 217.0 nm the flame gases absorb more radiation than they do at 283.3 nm and so minor fluctuations in the flame will generate some noise.

As a result, the best signal-to-noise ratio and hence the best detection limits and precision will be achieved using the 283.3-nm line even though it has the lesser sensitivity.

For the measurement of low concentrations of nickel, the 232.0-nm line (which is the most sensitive line for nickel) is preferable. However, owing to a very closely adjacent (and virtually non-absorbing) line of nickel, curved calibration graphs are produced for this element, this effect becoming very pronounced at high concentrations. Obviously, at the extreme of curvature when the calibration graph becomes almost flat, measurement is no longer possible. If samples containing high concentrations of nickel are to be measured, the less sensitive line at 341.5 nm will provide almost linear calibration graphs over a wide range of concentration.

Many similar cases may be cited – the rule should be that for optimum results each element and each application need to be investigated.

6.2.3 Monochromator Settings

The slit opening selected is generally a matter of recommendation by the equipment manufacturer as a function of the element to be measured and the wavelength to be employed. For example, considering the case of nickel discussed above, if this is to be measured at the 232.0-nm line a slit opening of, say, 0.2 nm should be chosen, rather than a wider slit to maximize the exclusion of the adjacent nonabsorbing line of nickel. However, if the 341.5-nm line is used, a larger slit opening should be chosen to increase the light throughput as this will improve the signal strength. Since there are no lines closely adjacent to this line, this may be done with impunity.

6.2.4 Flame Selection

For those elements which are easy to atomize, the air–acetylene flame should be used. It is less expensive to operate and will give rise to better sensitivity than if the

nitrous oxide–acetylene flame is used (unnecessarily). In general, nitrous oxide will be used for those elements which are either atomized poorly, or not at all, with the air–acetylene flame.

There are some elements which occupy a central ground in this case. Elements such as calcium and strontium are only modestly atomized in air–acetylene and are subject to some interferences. By employing the nitrous oxide–acetylene flame, not only is the sensitivity improved but also the interferences are overcome. There are a number of such cases and again for each element the recommendations of the instrument manufacturers need to be accepted or the actual element and sample type need to be studied for each analysis by the analytical chemist.

6.2.5 Flame Optimization

It should be understood that each element has its own optimum atomization conditions, although for some elements the differences between them may be relatively small. This applies specifically to the composition of the flame used and the position of the burner in the light path.

Some elements give a more efficient atomization, resulting in a larger signal, if the flame is very “lean”, that is, oxidizing or deficient in fuel. On the other hand, certain elements, such as chromium, require very ‘fuel-rich’ flames, that is, reducing and having an excess of fuel. Additionally for each element, and for each flame composition, the portion of the flame in which the maximum population of atoms occurs will be different. Since the maximum absorption signal will result when the beam from the HCL passes through this region of maximum atom population, efforts must be made to adjust the burner position to achieve this situation.

The best means of achieving both of the above two optimizations is, while aspirating a solution of the analyte, first to adjust the gas mixture to achieve maximum absorption and then to adjust the burner position. Sometimes, with elements for which the atomization conditions are critical, more than one iteration of these two adjustments might be necessary.

7 INTERFERENCES IN ATOMIC ABSORPTION SPECTROMETRY

7.1 Spectral Interferences

This subject has been already covered in some detail. True spectral interferences will only occur when an absorbing line of another element overlaps the emission line of the analyte from the light source and the interfering element is also present in the sample. This

is, as previously stated, a rare occurrence and probably all such cases have, by now, been documented in the literature.

7.2 “Chemical” Interferences

Such interferences are sometimes also called “matrix interferences”, and arise when an element, or compound, present in the sample (but not in the calibration standards) interferes with the production of atoms. A classical case has already been mentioned in passing.

If a simple solution of calcium of a given concentration is sprayed into the flame a certain reading will result. If, instead of the simple calcium solution, one containing the same calcium concentration, but also a significant concentration of phosphorus, is sprayed into the flame a much lower reading will be obtained. This is caused by the formation in the flame of some calcium phosphate type of compound which is harder to convert to atoms than the CaO usually formed. Obviously one could match the standards with the same P concentration but this would require the prior determination of P in each sample. Similar interferences will occur for all of the alkaline earth group – Ca, Mg, Sr, Ba and Mg – in the presence of P, Al and Si.

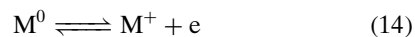
Such interference may be overcome in two ways:

1. By adding a large concentration of strontium or lanthanum a competing mechanism is set-up. Because the Sr or La is present in much greater concentration than Ca, and because Sr and La are chemically similar to Ca, the P will preferentially associate with the Sr or La rather than the Ca. In practice, the Sr or La is added both to the samples and to the calibration standards.
2. If the nitrous oxide–acetylene flame is used, the interference disappears because the flame is hot enough to dissociate readily the compounds formed.

These are probably the most severe cases but minor interferences of a similar nature occur with some other element combinations and the literature should always be consulted before embarking on any totally new application.

7.3 Ionization Interferences

At the elevated temperatures occurring in flame atomizers, the atoms of some elements will be ionized, that is, the equilibrium shown in Equation (14) will occur:



where M^0 is the ground-state atom of element M, M^+ is the ion of the same element and e is an electron. Since

this particular atom is now an ion and not an atom it will not absorb radiation at the same wavelength.

This effect will occur with elements that have ionization potentials which are low relative to the energy of the flame used for atomization. With air–acetylene flames significant ionization will occur only for the alkali metals, Cs, Rb, K and Na, all of which have very low ionization potentials.

In the much hotter nitrous oxide–acetylene flame, however, many elements will be significantly ionized. The most extreme are the alkaline earths, Ca, Sr and Ba, but ionization will also occur significantly for many elements such as Al and the rare earth elements.

The ionization reaction shown above, being an equilibrium, is subject to the law of mass action (Equation 15):

$$K = \frac{[M^+][e]}{[M^0]} \quad (15)$$

where K is an equilibrium constant, $[M^+]$ is the concentration of the ion of the atom in the flame, $[M^0]$ is the concentration of the atom of the element in the flame and $[e]$ is the concentration of electrons in the flame. If there is present in a sample, apart from the analyte, any element which readily ionizes (such as Na), then the additional electrons contributed to the flame by the ionization process will cause the equilibrium to shift back to the left in the equation and favor the production of more ground-state atoms. This will increase the atomic absorption reading. If the calibration standards have no sodium present then the readings obtained for the standards will be relatively lower. The net result will be a high result for the sample. In the case of the measurement of a number of samples with varying Na content, this will produce errors which will also vary.

To overcome this problem all solutions, calibration standards and samples should have added to them a large excess of a salt of an easily ionized element as an ionization suppressor. The most common such suppressor used is cesium, generally added as the chloride, which has the lowest ionization potential of all elements. This suppressor will ionize very substantially and in doing so will generate a high concentration of electrons. As described before, this high concentration of electrons will push the equilibrium back very strongly in the direction of simple (nonionized) atoms.

7.4 “Physical” Interferences

Some errors may also occur due to the physical composition of the sample solutions, by comparison with the calibration standard solutions. For example, if solutions of a solid sample are prepared by using high concentrations of sulfuric and/or phosphoric acid, the viscosity of the solutions will be high compared with simple aqueous

solutions. This will diminish the uptake rate of the solution by the nebulizer and also will diminish the yield of fine spray to the burner. The error caused by this effect can only be prevented either by avoiding the use of such viscous acids or, if this is not possible, preparing the standards with the same concentrations of these acids. Similar viscosity effects may occur with very high concentrations of dissolved solids and again such problems can only be avoided in the same way.

The presence of a miscible organic compound may have the effect of reducing the viscosity of a solution and thus enhance the efficiency of nebulization. Ethanol, for example, will cause this effect. If an element in a sample of wine is measured by comparison with aqueous standards of the same element, high results will be obtained. Again, the solution to the problem will be to match, or at least approximate, the alcohol concentration of the calibration standards to that of the wine.

8 VALIDATION OF RESULTS OBTAINED BY ATOMIC ABSORPTION SPECTROMETRY

As may be seen from much of the preceding discussion, many factors may influence the veracity of results obtained using atomic absorption. In order to avoid errors due to an unexpected influence, it is wise to accompany any batches of samples analyzed with one or more standard reference materials, as close as possible in type to the samples. Control charts should be kept of the results obtained and remedial action taken if any deterioration in the quality of results is observed.

9 AUTOMATION IN ANALYSIS USING ATOMIC ABSORPTION SPECTROMETRY

Many automatic or semi-automatic atomic absorption spectrometers are now available. It is possible with such instruments, generally computer controlled, to store various parameters such as lamp currents, wavelengths, monochromator slit openings and flame gas flows. Although clearly such instruments are more costly, they do permit analyses to be performed by semiskilled operators once the parameters have been determined and stored by an expert analyst.

Automatic sample presentation to the instrument permits unattended operation, once a suitable type of automatic sampler has been loaded with samples and the analysis programmed. With instruments such as those described above, it is possible to measure sequentially a large batch of samples for more than one element as part of an automatic process.

Caution is suggested, however, with the totally unattended use of flame atomic absorption instruments for obvious safety reasons.

One of the most important developments for automated analysis by AAS is the use of flow injection analysis (FIA). This method represents a means of faster automated analysis and also permits minimization of the sample volume. Suitable FIA methods and equipment have been developed for use with flame and vapor generation methods of atomization. Details of such methodology properly belongs in an article on FIA and so are not considered further here.

10 COMPARISON WITH OTHER ANALYTICAL TECHNIQUES

10.1 Flame Emission

At the time when atomic absorption methods were first introduced, the obvious comparison was with flame atomic emission. Today it can safely be said that the atomic absorption method has all but replaced flame atomic emission in practical analytical chemistry.

FAAS provides a method which is rapid and easy to use, combined with simplicity of operation, and is not very prone to unexpected errors. It has a good sensitivity for most elements, adequate for many purposes. However, it measures only one element at a time and so is not particularly rapid for multielement analysis.

10.2 Inductively Coupled Plasma Atomic Emission Spectrometry

By comparison with FAAS, ICPAES is more sensitive for the more difficult to atomize elements such as B, W and Si, but is not as sensitive as some of the easy to atomize elements such as Zn and Cd. ICPAES methods, however, are ideally suited for simultaneous, or rapid sequential, multielement analysis and are thus faster than FAAS for this purpose.

In general FAAS instruments will cost less than ICPAES equipment and are easier to use. For the determination of low concentrations of elements such as As, Se and Hg, vapor generation AAS is more sensitive than ICPAES methods.

10.3 Inductively Coupled Plasma Mass Spectrometry

In more recent times, ICPMS has offered a much faster means of determining extremely small traces of most elements, and provides real competition for GFAAS. However ICPMS requires very expensive equipment and very skilled operation.

10.4 Choice of Methods

As discussed immediately above, there is major competition for AAS as a means of analysis. Certainly, for the determination of very low concentrations of several elements in large numbers of samples, ICPMS is probably the method of choice by comparison with graphite furnace AAS. The very high cost of the equipment and the high operating costs, plus the skills requirement, however, will keep the former technique out of the reach of most small laboratories.

In a similar manner, but to a lesser extent, ICPAES instruments offer some advantages for some users but remain less attractive to the smaller laboratory. It seems unlikely that major developments will occur in AAS to alter this scene. Rather, the inevitable lowering of costs for ICPAES and ICPMS will make it increasingly hard for expensive types of AAS to survive. A versatile and major analytical service laboratory may certainly justify the installation of ICPMS, ICPAES and AAS with flame, vapor generation and furnace modes.

In such a situation, the desirability of having individual AAS instruments for flame and furnace operation should be considered for the sake of convenience and the avoidance of contamination of the clean environment needed for graphite furnace methods. With such a versatile combination, the advisability of having a Zeeman background-corrected furnace instrument might also be considered.

11 FUTURE DIRECTIONS

Because of the lower costs of equipment and the simplicity of operation, AAS appears to be likely to continue to be attractive to most analytical laboratories, particularly the smaller ones. It also seems, to the author, that low-cost atomic absorption modules, serving as specialized detectors, in association with sample preparation and handling techniques, such as those associated with flow injection methods, are one of the important directions in which development might occur. Such an approach would continue to use the highly specific capabilities of the atomic absorption method, which have made it so popular since its inception.

ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrometry
AC	Alternating Current

AES	Atomic Emission Spectrometry
DC	Direct Current
FAAS	Flame Atomic Absorption Spectrometry
FIA	Flow Injection Analysis
GFAAS	Graphite Furnace Atomization
HCL	Hollow-cathode Lamp
ICPAES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICPMS	Inductively Coupled Plasma Mass Spectrometry
VGAAS	Vapor Generation Atomization

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NOTE

The number of references available in AAS is, by now, huge and the following represent only a judicious selection. There are many detailed text books available and those readers requiring a more detailed treatment of particular aspects are advised to consult any of these. One particular text book is, however, recommended as

being very detailed in its blend of theoretical and practical details.⁽²⁰⁾

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