Atomic Spectroscopy

Introduction

This publication is an overview of atomic absorption (AA) theory. This is based upon the Varian booklet 'Introducing Atomic Absorption Analysis' (Publication number 8510055700). For detailed graphite furnace and Zeeman theory, refer to 'Analytical Methods for Graphite Furnace Atomizers' (Publication number 8510084800).

An atomic absorption spectrometer is an instrument which is used to analyze the concentrations of metals in solution. Sixty eight elements can be determined directly over a wide range of concentrations from ppb to per cent levels, with good precision—typically better than 1 % RSD. Sample preparation is generally simple and frequently involves little more than dissolution in an appropriate acid. The instrument is easy to tune and operate.
Basic Principles of Atomic Absorption

The basic principles of atomic absorption spectroscopy can be expressed by three simple statements:

- All atoms can absorb light.
- The wavelength at which light is absorbed is specific for each element. If a sample containing nickel, for example, together with elements such as lead and copper is exposed to light at the characteristic wavelength for nickel, then only the nickel atoms will absorb this light.
- The amount of light absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases, and is proportional to the concentration of absorbing atoms.
- The relationship between the amount of light absorbed and the concentration of the analyte present in known standards can be used to determine unknown concentrations by measuring the amount of light they absorb. An atomic absorption spectrometer is simply an instrument in which these basic principles are applied to practical quantitative analysis.

A basic atomic absorption instrument consists of the following key components:

- A light source used to generate light at the wavelength which is characteristic of the analyte element. This is most often a hollow cathode lamp, which is an intense narrow line source (other sources being Electrodeless Discharge Lamps (EDLs) or boosted discharge hollow cathode lamps (UltrAA lamps)).
- An atomizer to create a population of free analyte atoms from the sample. The source of energy for free atom production is usually heat—most commonly in the form of an air/acetylene or nitrous-oxide/acetylene flame. The sample is introduced as an aerosol into the flame and the burner is aligned in the optical path so that the light beam passes through the flame, where the light is absorbed.
- An optical system to direct light from the source through the atom population and into the monochromator.
- A monochromator to isolate the specific analytical wavelength of light emitted by the hollow cathode lamp from the non-analytical lines including those of the fill gas.
- A light-sensitive detector (usually a photomultiplier tube) to measure the light accurately.
Suitable electronic devices which measure the response of the detector and translate this response into useful analytical measurements. The instrument readout may be one of several types. Older instruments used meter readout devices. These have been replaced by modern instrumentation using direct computer interfacing.

At its most basic level, the general analytical procedure is straight-forward:

1. Convert the sample into solution, if it is not already in solution form.
2. Make up a solution which contains no analyte element (the analytical blank).
3. Make up a series of calibration solutions containing known amounts of analyte element (the standards).
4. Atomize the blank and standards in turn and measure the response for each solution.
5. Plot a calibration graph showing the response obtained for each solution as shown below.
6. Atomize the sample solution and measure the response.
7. Determine the concentration of the sample from the calibration, based on the absorbance obtained for the unknown.

![Typical AA calibration graph](image)

Fundamentally, then, quantitative analysis by atomic absorption spectroscopy is a matter of converting samples and standards into solutions, comparing the instrumental responses of standards and samples, and using these comparative responses to establish accurate concentration values for the element of interest. This can be carried out using simple equipment and simple procedures. Inevitably, however, there are aspects of the technique which are not quite as simple and straight-forward as this brief introduction suggests.

**Nature of Atomic and Ionic Spectra**

In order to understand the atomic absorption process, one must first understand the Bohr model of the atom which describes the structure of the atom and its orbitals. The atom consists of the central core or nucleus, made up of positively charged protons and neutral neutrons. Surrounding the nucleus in defined energy orbitals are the electrons. All neutral atoms have an equal number of protons and electrons. Each of these electron orbitals has an energy associated with it—in general, the further away from the nucleus, the more readily can the electron be removed. Atomic spectroscopy involves energy changes in these outer electrons. When the atom and its associated electrons are in the lowest energy state, $E_0$, the atom is said to be in the ground state.
Atoms can absorb discrete amounts of heat or light at certain discrete wavelengths, corresponding to the energy requirements of the particular atom. When energy is added to the atom as a result of absorption of light, heat or collision with another particle (electron, atom, ion or molecule), one or more changes may occur. The energy absorbed may simply increase the kinetic energy of the atom or alternatively, the atom may absorb the energy and become excited. The permitted energy levels are finite and well defined, but an electron may be made to change to another level if the atom absorbs energy equal to the difference between the two levels. When this occurs, the electron moves to a higher energy level, such as $E_1$. This atom is now said to be excited.

Atomic absorption is the process that occurs when a ground state atom absorbs light of a specific wavelength and is elevated to a higher energy level (i.e. the process of moving electrons from the ground state to an excited state). Sodium atoms, for example, absorb light very strongly at 589.0 nm, because light at this wavelength has exactly the right energy to raise the sodium atom to another electronic state. This electronic transition is quite specific for sodium; atoms of any other element have different energy requirements and they cannot absorb light at this wavelength. If the sodium atom is in the 'ground state' when it absorbs light, it is transformed into an excited state–it is still a sodium atom, but it contains more energy.

The energy levels of each atom are quantized according to the number of protons and electrons present. Since each element has a unique set of electrons and protons, each element also has a unique set of energy levels. Usually these energies are measured in relation to the ground state, and a particular excited state for sodium, for example, may be 2.2 eV (electron volts) above the ground state. This means that an atom in the excited state contains 2.2 eV more energy than a ground state atom which, by convention, is ascribed an arbitrary energy of zero. An element may have several electronic energy states.

![Figure 3](image)

**Figure 3** Energy level diagram illustrating the excitation, ionization and emission processes for an atom. The energy levels within the atom are represented by the horizontal lines, and the vertical arrows signify energy transitions–a and b represent excitation.

The wavelength of the absorbed light is proportional to the spacing between the energy levels–this is characteristic of the element itself. The wider the spacing between the energy levels, the shorter the wavelength of light energy absorbed. Each transition between different electronic energy states is characterized by a different energy and hence by a different set of wavelengths at which the atom will also absorb. These characteristic wavelengths also correspond to those wavelengths at which an element will emit–the process of being at a higher energy level and relaxing to the ground state. These wavelengths are sharply defined and when a range of wavelengths is surveyed, each wavelength shows as a sharp energy maximum (a spectroscopic 'line'). Atomic spectra are distinguished by these characteristic lines. Lines which originate in the ground state atom are most often of interest in atomic absorption spectroscopy; these are called 'resonance lines'. Transitions from one excited state to another yield non-resonance lines.

The atomic spectrum characteristic of each element, comprises a number of discrete lines, some of which are resonance lines. Most of the other lines arise from excited states, rather than from the ground state. Since the resonance lines are much more sensitive and since most atoms in a practical atomizer are found in the ground state, these excited state lines are not generally as useful for atomic absorption analysis.
Ionization

Ionization may occur when the temperature of the flame is high enough to remove the outer electron from the atom. Atoms that undergo ionization reaction are not available to undergo atomic absorption, therefore the measured signal is decreased. Ionization occurs when an anion or cation in the sample reacts with the analyte to alter the rate of formation of the free ground state analyte atoms. They can be either enhancement reactions, giving higher absorbance or suppression reactions giving lower absorbance.

Ionization of the analyte reduces sensitivity and causes upward curvature at high concentrations. Thus, the characteristic upward curvature of the calibration curve when analyte ionization is significant, indicates that the effect of ionization is more severe at lower concentrations. At higher analyte concentrations—ion and electron recombinations are more probable, resulting in a greater proportion of ground state atoms being available for absorption. The hotter the flame, the greater the degree of ionization. The degree of ionization is different for each element, depending on the energy required to remove the electrons. Easily ionizable elements such as the group I elements are most susceptible to these effects.

Analyte ionization can be suppressed by adding a large concentration of a more easily ionized element such as sodium, potassium (e.g.: 0.2% KCl) or cesium at concentrations between 2000 and 5000 mg/L. This creates an excess of electrons in the flame and effectively suppresses ionization of the analyte.

Atomic Emission

As you will recall from earlier in this discussion, absorption lines used in atomic absorption analysis are due to transitions from the ground state to a higher energy level. Atoms in the excited state are generally unstable and will rapidly revert to the ground state, losing the acquired energy in the process. Emission lines are produced when these transitions from higher energy states to lower energy states occur. The wavelength at which these energy shifts take place are exactly the same for both emission and absorption.

Thus, atomic emission spectroscopy is a process in which the light emitted by excited atoms or ions is measured. The emission occurs when sufficient energy (which may be thermal, light or electrical) is provided to excite a free atom or ion to a higher unstable energy state (the atomic absorption process). At low temperatures, few atoms are excited. As the temperature increases to about 2000 K, some easily excited elements such as those of the alkali elements can be detected. As seen in absorption, the wavelength of emitted light is proportional to the spacing of the energy levels. Since each element has a unique set of energy levels, each element also has a unique set of wavelengths at which it will emit energy. Thus, the wavelengths of light emitted by the atoms or ions are specific to the elements which are present in the sample.

It is also possible to determine the concentration of analyte that is present in a sample by measuring the amount of light emitted and comparing this value with the amount of light emitted by known standards.

The basic instrument configuration for atomic emission is essentially the same as that for atomic absorption, except that a primary light source is not required. The most critical component in an atomic emission instrument is the atomization source—this must provide sufficient energy to atomize the sample and excite the free atoms. The earliest energy sources for excitation have been air/acetylene and nitrous-oxide/acetylene flames. Most atomic absorption instrumentation are provided with the capability for measurements by atomic emission. Selected elements such as Li, Na, K and the other alkali elements are easily measured by atomic emission because the excited states of these elements can be populated from the energy supplied by the flame.

However, the flame types available in atomic absorption instrumentation generally lack sufficient thermal energy to be truly effective at creating large numbers of excited atoms or ions. In addition, the monochromators used in most AA systems do not have the resolution required to isolate the selected emission wavelength from the many emission wavelengths which may be emitted by the sample. Because of these limitations of atomic emission, the technique does not enjoy the popularity of atomic absorption.
The development of Inductively Coupled Plasma (ICP) as a source for atomic emission has changed this dramatically. The temperature of the sample within the argon plasma of an ICP-AES system can reach between 5500 to 8000 K. These temperatures allow complete ionization of elements, minimizing chemical interferences, and providing ample thermal energy to excite most of the free atoms in the sample. The ICP-AES system provides a wide dynamic range and minimal chemical interferences. However, the optics design of an ICP-AES must have much greater resolution than that of an atomic absorption spectrometer so that the emission wavelength of interest can be isolated from the many wavelengths emitted by the sample within the plasma.

The ICP-AES system eliminates many of the problems associated with previous emission sources and has resulted in a dramatic increase in the use of emission spectroscopy as a technique for elemental analysis.

**The Absorbance - Concentration Relationship**

Once the absorbance is measured, this value can then be related to the concentration of an element in solution. The relation between light absorption and analyte concentration is called the Beer-Lambert law:

**Lambert’s Law** states that the portion of light absorbed by a transparent medium is independent of the intensity of the incident light, and each successive unit thickness of the medium absorbs an equal fraction of the light passing through it.

**Beer’s Law** states that the light absorption is proportional to the number of absorbing species in the sample.

Effectively for AA, this means that the amount of energy (light) absorbed is proportional to the concentration of atoms in the atomizer. Thus if a concentration of atoms ‘c’ produced an absorbance ‘a’, a concentration ‘2c’ would produce an absorbance ‘2a’.

The combined Beer-Lambert law can be expressed as:

$$\log_{10} \frac{I_0}{I_t} = \text{absorbance} = a \times b \times c$$

where:

- $I_0$ = incident light intensity
- $I_t$ = transmitted light intensity
- $a$ = absorption coefficient (absorptivity)
- $b$ = length of absorption path
- $c$ = concentration of absorbing atoms

For a given set of conditions, $a$ and $b$ are constants. The pathlength, $b$, will change if different burners are used, as an air/acetylene burner has a path length of 100 mm compared to 60 mm for the nitrous-oxide/acetylene burner. If this expression is plotted, and a curve of absorbance versus concentration is drawn, Beer’s Law predicts that a straight line will result. In practice, we find that several factors relating to spectral effects and instrumental design can combine to cause deviations from the linear calibration, especially at higher concentrations.

A further significant issue in atomic absorption is the residence time of atoms in the light path of the instrument. Typical flame residence times are only milliseconds. Longer residence times are usually associated with greater absorbances. This is used to good effect in the operation of the Atom Concentrator Tube (ACT-80).

**Atomization**

Atomization is the process by which atoms are made available for absorbance measurement. Atomic absorption analysis is dependent on creating a supply of free analyte atoms in the ground state and exposing this atom population to light of the characteristic wavelength for that element. As with other spectrochemical techniques, AAS is used to determine element concentrations, usually in liquid form. AAS is best suited to the analysis of elements in aqueous solutions of a dissolved or diluted sample, or samples diluted with other
solvents such as organic solvents. Since the development of AAS a number of different atomizer techniques have been developed. The three major classifications of atomizers are flames, graphite furnaces and vapor generation.

**Flame Atomization**

The flame atomization systems used in atomic absorption convert the analyte solution into free atoms in the optical path via successive stages, as illustrated below. The primary aim of the sample introduction system is to generate an aerosol of the sample in the fuel mixture. This requires the production of an aerosol with a sufficient number of small droplets and to introduce a portion of the sample in the flame without experiencing difficulties such as nebulizer or burner blockage. The usual means of sample introduction is to use a nebulizer to create the aerosol and a spray chamber to filter larger droplets from the aerosol.

The nebulizer draws the solution in through the capillary. The stream of solution passing through the venturi strikes the impact bead which breaks the stream of liquid into an aerosol of various droplet sizes. The spray chamber removes the large droplets and mixes the remainder with the flame gases. The spray chamber plays a crucial role in promoting intimate mixing of the nebulizer aerosol with the fuel. This mixture passes into the burner. In order to obtain maximum sensitivity, it is necessary to pass as much as possible of the light from the hollow cathode lamp through the flame. It is therefore necessary to adjust the burner position for each separate analysis so that the maximum population zone of free atoms coincides with the optical path. All atomic absorption instruments incorporate simple burner controls which allow the analyst to adjust the burner position in the vertical, horizontal and rotational planes until the maximum absorbance can be obtained. The heat of the flame evaporates the solvent, near the base of the flame, converting the aerosol droplets into very small solid particles. These particles are fused or melt, and are vaporized to form molecules. These dissociate to produce the mostly free ground state atoms in the optical path.

![Diagram of flame atomization process](image)

*Figure 4* Most samples used in flame atomic absorption are nebulized into an aerosol—a very fine mist of sample droplets. This diagram illustrates the processes that occur when the aerosol is introduced to the flame—the aerosol is quickly desolvated, any solids present are fused, molecules decomposed and elements atomized in a very short time.

A schematic diagram of the Varian Mark VI atomization system, which is fitted as standard to all SpectrAA series flame spectrometers is shown below. Every component, including the Mark VI spray chamber, burner and Hi-vac nebulizer, is designed for maximum flexibility for either best sensitivity or best resistance to burner blockage from high dissolved solids samples. All components are constructed from inert materials from the polypropylene or optional FHDPE Universal spray chamber to the platinum-iridium capillary of the Hi-vac nebulizer.
The externally adjustable impact bead breaks the large droplets in the aerosol into smaller ones and the removable twin head mixing paddles minimize burner blockage by filtering large droplets from the aerosol. The mixing paddles may also be removed, if maximum sensitivity is required. The Mark VI burner head has a triangular contoured cross section and large cooling fins to entrain air around the flame. As noted by Cresser, this design results in higher sensitivity and less burner blockage due to the cooler operating temperature of the burner slot. The unique flared slot design of the Mark VI burner also helps to reduce burner blockage and carbon build up. The Varian Mark VI flame atomization system can therefore be adjusted for maximum sensitivity or best long term stability with difficult samples by some simple adjustments to the impact bead position. Even with these capabilities for handling difficult samples the Mark VI flame atomization system can achieve a guaranteed 0.55 absorbance for 5 ppm copper solution (based on 4 sigma limits–average from factory tests is 0.73 abs).

It is difficult to predict theoretically the decomposition process for all elements under all analytical circumstances. However, as a result of extensive practical experience, we can specify which flame should be used for particular elements and indicate general reasons for the use of different flames, as the flame establishes the conditions under which ground state atoms are produced. For the purpose of this discussion it is convenient to classify determinations into three broad categories according to the relative difficulty of decomposition and the general nature and extent of the intermediate reactions which interfere with the production of analyte atoms. Generally solutions are prepared in 1% hydrochloric acid as the chlorides are the most volatile salts of the elements.

Elements by Air-Acetylene Flame

The air-acetylene flame is almost universally used for those elements classified as easily atomized (copper, lead, potassium and sodium for example).

With such elements, a high proportion of the available analyte compound is readily converted to atoms in an air-acetylene flame (the coolest flame in practical use with a temperature of about 2300 oC). Interferences are negligible, and the chemical environment within the flame (oxidizing, stoichiometric or reducing) is not a critical

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1 Cresser, M.S., J. Anal. At. Spectrom., 1993, 8, 270
factor. However, the air/acetylene flame is not hot enough to break down those elements which form refractory oxides.

Elements by Nitrous Oxide - Acetylene Flame

The second category includes those elements which form refractory compounds, which are not broken down in the air-acetylene flame and which require the use of the hotter nitrous oxide-acetylene flame, with a temperature of about 3000 °C. Some examples include Al, Si and W.

However, the temperature of the flame is not the only consideration—the stoichiometry is also important. A ‘lean’ flame containing a minimum amount of acetylene will be oxidizing. This flame will not produce atoms from elements forming strongly bound oxides. However if a flame rich in acetylene (reducing flame) is used, the effect of the excess carbon and hydrogen breaks down the strongly bound oxides. A good example is the determination of chromium using an air/acetylene flame. A lean flame produces no absorption—a rich flame does. Determinations of these elements requires an appropriate combination of flame temperature and chemical environment within the flame by careful adjustment of the flame stoichiometry.

The last consideration is the effect on atomization of other species in the flame. For example the presence of phosphate will suppress the atomization of several elements including calcium. In this case a ‘release agent’ such as a lanthanum salt is added. The lanthanum combines with the phosphate, thus releasing the calcium atoms for determination by atomic absorption.

Elements By Both Flame Types

Several elements such as As, Ca, Cr, Mg, Mo, Os, Se and Sr can be determined in either the air-acetylene or nitrous-oxide/acetylene flame. An air-acetylene flame is useful for these elements, but is not fully effective for all sample types, because inter-element interferences can occur.

While both flames can be used for determinations of these elements, interferences in the air/acetylene flame can be severe. It may be necessary to take appropriate counter measures to minimize the extent of the interferences by:

- Using the nitrous-oxide/acetylene flame, which is hotter and so may minimize or remove the interferences by decomposing the compounds involved, or
- Adding an excess concentration of a ‘buffer’ element or chemical modifier which will ‘compete’ with the analyte for attachment to the interfering group so that atomization is complete.

If such precautions are not taken, inaccurate results may be obtained.

Graphite Furnace Atomization

The major limitation of atomic absorption using flame atomization is that the atomization system is a relatively inefficient sampling device. Only a small fraction (about 10 %) of the sample aspirated through the atomization system reaches the flame. In addition, the sample is diluted with a large volume of gas, which carries the aerosol into the flame. The formation of atoms in the ground state is governed by many variables such as the flame temperature, interactions between flame gases, matrix components and analyte, chemical interferences and the extent to which the analyte molecular species are dissociated. The free atoms are only resident in the light path for a short period of time—typically 10^-4 seconds. The residence time depends on the velocity of the flame gases. This limits the minimum useful concentration at which measurements can be made by flame AA. This is generally around the low part per million level.

Analytical sensitivity can be improved significantly if the entire sample is atomized at the one time and if the free atoms remain within the optical path for a longer period of time. This enhances the sensitivity of the AA technique. Graphite furnace atomization provides these benefits.
With graphite furnace atomization, the flame is replaced by an electrically heated graphite tube in an argon chamber. The argon gas prevents the graphite tubes from being rapidly oxidized at high operating temperatures and assists removal of the matrix components and other interfering species from the light path during the drying and ashing stages. A small volume of sample usually between 1 and 70 µL, but typically around 20 µL, is dispensed directly into a pyrolytically coated graphite tube. The pyrolytic coating on the graphite tube makes the tube resistant to oxidation, thereby extending the usable lifetime of the tubes. The coating is impervious to liquids, preventing the liquid from soaking into the graphite, thus improving the sensitivity and reproducibility of the measurement. The tube is heated by passing a controlled electric current through it in a programmed series of steps to remove the solvent and major matrix components and then atomize the sample to generate the ground state atoms. Molecular dissociation is governed by the atomization temperature, the heating rate and the reducing environment of the hot graphite tube surface.

All of the analyte introduced into the graphite tube is atomized, and the atoms are retained within the graphite tube, positioned in the optical path, for a slightly longer period (c.f. flame atomization). As a result, sensitivity and detection limits are lowered by at least an order of magnitude to around the part per billion level. This can be mainly attributed to the fact that solvent is not present at the time of measurement, and that dilution by the flame gases is avoided. Although the ground state atoms are still subject to interferences, they are of a different nature to those found in flame atomization and they are more amenable to control by proper choice of analytical conditions and chemical modification. A wide variety of matrices can be analyzed directly by graphite furnace AA, thus minimizing preparation and handling errors. The graphite furnace technique also lends itself very readily to unattended automation.

A typical graphite furnace program consists of three stages:

1. Drying
   Once the sample has been injected into the graphite tube, it is dried at a temperature at or just below the boiling point of the solvent (usually between 80 and 200°C). The solvent is evaporated, leaving a thin film of solid material deposited on the tube surface.

2. Ashing or Charring
   In the next step of the furnace program, the ashing step, the temperature is increased to remove as much of the matrix material as possible, without the loss of the analyte. Ashing temperatures used, typically range from 350–1600°C. During ashing, the solid material is decomposed to leave behind refractory compounds of the analyte such as oxides.

3. Atomization
   The third step is the atomization step, where the furnace is rapidly heated to a high temperature to vaporize the residues from the ashing stage. This creates a cloud of free atoms in the optical path. The absorbance is measured during this stage. The atomization temperature depends upon the volatility of the element and ranges from a minimum of 1800°C for cadmium to a maximum of 3000°C for boron.

The absorption signal produced in the atomization stage is a well defined transient peak, which is measured using peak height or peak area measurements. The height and area of the peak are proportional to the amount of analyte present in the sample. For some applications, the choice will be straight forward; for others, it will be necessary to obtain experimental measurements to decide which method is best suited to the particular analysis. Peak area measurements will often extend the calibration linearity. However, for many elements, the peak height sensitivity will be better than that of peak area measurement. This is especially the case with volatile elements such as Cd and Pb which produce narrow absorbance peaks. With elements requiring high atomization temperatures, the peaks are broader and the peak area sensitivity may be comparable to peak height sensitivity. Generally, it is preferable to use the method which gives the best compromise in respect of sensitivity, accuracy, linearity and precision.

The optimum analytical signal and maximum precision are largely determined by the drying temperatures used in the furnace program. Analysts may need to vary the drying times and temperatures depending upon the characteristics of the sample being analyzed. The sample must be deposited consistently in the graphite tube or pyrolytic platform, and should be dried evenly without loss or splattering inside the tube. Thus, as a part of
method development, the analyst should observe the drying of the sample droplet closely to ensure that the drying parameters have been correctly established.

Graphite furnace analysis times are significantly longer than those used for flame sampling, and fewer elements can be determined by graphite furnace AA. However, the enhanced sensitivity of graphite furnace AA significantly extends the capabilities of atomic absorption and therefore, finds widespread application.

**Platform Atomization**

The pyrolytic platform is a single piece of solid pyrolytic graphite which contains a central depression to enable it to contain liquid samples up to about 40 µL. The platform can be installed in the graphite tube. There is minimal physical contact between the tube and the platform as the platform is supported within the tube only at the edges.

![Platform Atomization Diagram](image)

*Figure 6 The forked pyrolytic platform shown installed inside the notched partitioned tube. Atomization of the sample is delayed until the graphite tube has reached a stable high temperature. This assists in minimizing interferences.*

The effect of the platform is to delay the atomization of the sample until the graphite tube has reached a stable (high) temperature. Atomization of the analyte from the platform therefore occurs into an environment which is significantly hotter than otherwise would have occurred, had atomization occurred from the tube wall. One of the benefits of the platform is that atomization into the high temperature environment provides greater freedom from interferences and background for volatile elements. This results from the delay in atomization of the element, due to the temperature lag between the temperature of the platform and that of the graphite tube itself.

Platforms do have some practical limitations. The volume of sample that can be dispensed onto the platform is limited to a maximum of 40 µL. Platforms also cause a slight reduction in light throughput—hence the alignment of the furnace workhead is critical to ensure that you achieve the maximum light throughput. Slightly higher programmed temperatures are required and the resultant peaks are often broad with severe tailing. Methods which eliminate the use of the platform and atomize the sample off the wall are preferred, where possible.

**Chemical Modifiers**

Obviously it is important to ensure that the analyte atoms are not 'lost' before the atomization stage. Whereas in flame we attempt to produce a salt of the element which is volatile, in furnace determinations a non volatile
salt is required. Generally the analyte solution is acidified with nitric or sulfuric acid. The nitrate or sulfate will break down into an oxide during ashing. Some elements are extremely volatile (for example As, Se) and other reagents (modifiers) are added to produce non-volatile compounds of these elements and thus prevent analyte loss during ashing.

Chemical modifiers are therefore used extensively in graphite furnace AAS to control the chemistry of the ashing and atomization processes. Modifiers have been developed for a variety of purposes including:

- To allow the use of higher ashing temperatures without analyte loss e.g.: palladium with 5% hydrogen in the inert gas
- To eliminate molecules which cause large background signals e.g.: ammonium nitrate eliminates sodium chloride and forms ammonium chloride and sodium nitrate

Refer to Analytical Methods for Graphite Tube Atomizers or the article by Tsalev for a complete review of chemical modifiers in graphite furnace AAS.

**Use of Alternate Gases**

Most modern graphite furnace systems provide complete flexibility for programming the gas type ('normal' or 'alternate') and gas flows through the graphite tube during any stage of the furnace program. This facility may be used in a number of ways. Atomization in an argon atmosphere will give better sensitivities than those obtained in a nitrogen atmosphere and tube lifetimes are improved when argon is used. A low purity gas may be used during the pre-atomization stages of the furnace program and a higher purity argon gas used during the atomization stage. This permits the economical use of argon only during the critical atomization steps.

Alternatively, a reactive gas such as oxygen or air may be used for ashing of biological samples or, for elements which form nitrides. The use of oxygen or air ashing for biological samples has been shown to give more efficient oxidation and removal of the matrix components, minimizing the background during atomization and permitting the use of lower ashing temperatures.

**Injection Modes**

In modern instrumentation a number of specialized injection modes for graphite furnace AAS are made available. These may include hot injection, multiple injection and injection of modifiers.

- **Hot Injection**
  
  The sample is injected into a pre-heated graphite tube so that drying occurs during dispensing. This Very Fast Furnace Analysis (VFFA) greatly reduces the analysis time. Hot Injection can also be used to aid dispensing of low viscosity organic solvents, which tend to spread along the tube because of their low surface tension. This can lead to poor precisions and inaccurate results. By injecting the sample into a preheated graphite tube, the solvent is rapidly evaporated, significantly reducing this effect.

- **Multiple Injection**
  
  For ultra-low level trace determinations, the multiple injection facility can be used to concentrate the sample inside the graphite tube and increase the absorption signal. The solution is injected repeatedly into the graphite furnace and after each injection, the drying and/or ash stage is performed. After the required number of injections, the furnace temperature cycle is allowed to run to completion and the absorbance is measured.

- **Pre- and Post-Injection of Modifiers**

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2 Rothery, E. (Editor), Analytical Methods for Graphite Tube Atomizers, Varian Publication No. 85 100848 00.
1988

This injection facility allows the operator to inject a chemical modifier before, or after the sample injection. These facilities are useful to reduce the formation of carbide bonds between the analyte and tube wall, or to avoid chemical reactions between different modifiers.

**Vapor Generation**

In recent years, it has become more important to be able to determine elements such as arsenic, selenium, antimony and mercury at low levels in the environment. These naturally occurring heavy elements are being redistributed in the environment by agricultural and industrial activities, and it is becoming increasingly important to understand their effects on biological systems. Vapor generation is an extremely sensitive method for determining mercury and certain hydride-forming elements which form stable metal hydrides such as arsenic, selenium, antimony, bismuth, tellurium, and tin. These elements may be determined by chemically reducing the element to the gaseous hydride and then dissociating the hydride in a heated quartz tube. This is the principle of operation of vapor generation.

Vapor generation is often preferred to graphite furnace analysis for arsenic, selenium and mercury because of the improved speed of analysis and the lack of background absorbance signals. Vapor generation AAS detection limits are usually in the sub parts per billion (µg/L) range. The cold vapor technique is the most sensitive method available for the detection of ultra-trace levels of mercury by AA. The improved sensitivity of the vapor generation technique is achieved by virtue of the 100 % sampling efficiency. All of the analyte in the sample solution used in the reaction is chemically reduced and transported to the sample cell for measurement. This process also effectively separates the analyte element from its chemical matrix, eliminating matrix interference effects in the atomization process and minimizing background absorption.

A number of different vapor generation systems are commercially available. Varian's Vapor Generation Accessory employs a peristaltic pump to provide continuous flow vapor generation. This is shown schematically in the figure below. In this technique the sample flow is combined with a flow of concentrated acid and sodium borohydride solution (the reductant), before being pumped into a reaction coil. Volatile hydrides are formed for a range of elements and these hydrides are separated from the flow of solutions using a gas liquid separator. The gaseous hydrides then pass to a heated quartz cell aligned in the optical path. The quartz cell is usually heated by an air/acetylene flame. The hydride is atomized in the cell and breaks down into the analyte and hydrogen. This allows the atomic absorption of the analyte to be measured.
The cold vapor technique for mercury is similar, except that atomic mercury vapor is produced instead of a hydride. Since pure atomic mercury vapor is generated, cell heating is not required unless it is required to remove water vapor from the absorption cell. The absorbance can therefore be measured in a cold cell (no flame heating is required). Mercury compounds in acidic solutions are reduced to the free element with stannous chloride reductant.

Where the need to determine Hg at even lower concentrations than those possible by the cold vapor technique are required, some systems offer an amalgamation option. The mercury vapor liberated from the cold vapor technique can be directed across the surface of a gold or gold alloy for a programmed time period. The mercury is concentrated on the gold surface by amalgamation. The gauze is then heated to drive off the trapped mercury, producing a transient signal. The mercury vapor produced is directed into a quartz cell positioned in the optical path for measurement by atomic absorption. This amalgamation technique allows the analytical working range for mercury to be lowered from ppb levels to ppt levels.

The Varian Vapor Generation Accessory produces a continuous signal, as long as the sampling capillary remains in the solution (similar to continuous aspiration into the flame) and hence normal signal processing techniques can be used including integration and PROMT. Elements can be determined at the µg/L concentration level with precisions or around 1–2 % RSD (comparable to the precision obtained for Cu at the mg/L concentration level). Typical sample throughput is around 60–70 samples per hour, determined in triplicate.

**Other Vapor Generation Designs**

Many AA manufacturers offer continuous flow vapor generators. Manual batch systems and Flow Injection (FIAS) designs are also available. Batch systems are usually manually operated and require the operator to add the sample directly to a reaction flask. The reductant is then added to the sample, initiating the chemical reaction. The volatile hydride is swept from the reaction cell by a flow of inert gas. This generates a transient signal, which is determined using peak height or peak area measurement modes. Sample throughput is low.
(about 10–15 samples per hour) as after each reading, the operator has to remove the reaction vessel, rinse it and then add the next sample to be determined. Operation is thus a slow procedure, particularly if multiple replicates are measured on each sample, and precisions are poor with about 5 to 10 % RSD between replicates.

A Flow Injection design is offered by Perkin Elmer. In this technique the sample is injected as a discrete slug into the flowing stream of reagents. FIAS vapor generation systems generate discrete signals, requiring multiple injections for precise determinations. Refer to the separate section on Flow Injection Systems for further information about the FIAS technique and competitive arguments.

Cell Heating

In most cases the quartz absorption cell is heated by the air-acetylene flame to dissociate the hydride into its component atoms. Alternatively, the absorption cell can be electrically heated. This approach makes unattended operation feasible and avoids the expense of flame gases. The cell is usually electrically heated to around 950 °C—a much lower temperature than the flame. The lower operating temperature results in a significant improvement in sensitivity of about 20 to 30 %.

Background correction

Non-specific absorption, or background absorption, occurs when radiation from the hollow cathode lamp is attenuated by molecular species or solid particles in the light path, that either absorb or scatter the energy from the hollow cathode lamp. Molecular absorption can occur when the atomizer is not hot enough to decompose all matrix components in the sample. The remaining molecules will then absorb light from the hollow cathode lamp. This molecular absorption and scatter is added to the atomic absorption giving a falsely high signal. In flame analysis, the background absorbance is generally less than 0.05 absorbance. Nonetheless, there are some practical analytical situations, particularly at low UV wavelengths, where background absorption can occur. However, in graphite furnace analysis, the background signals can exceed 2.0 absorbance and accurate correction is obviously important. In practice, analyte signals which are small should not be measured in the presence of large background signals. These high absorbances reduce the amount of light energy reaching the detector, reducing the signal-to-noise ratio and degrading the precision and accuracy of measurement. A number of background correction techniques have been developed to allow subtraction of the background signal from the total absorbance measurement.

The new generation SpectrAA instruments will allow measurement of analyte signals with background signals of up to 2.5 absorbance. In practice operating in the presence of these high levels of background can not be recommended. The reduction of the background and the generation of the highest atomic signal through the use of chemical modifiers, appropriate gas flows and suitable temperature programming of the graphite furnace during the drying and ashing stages are primary goals.

Background correction is a way of identifying the amount of non-specific absorption from the atomic absorption. All commercially available background correction systems employ the same basic principles: the total absorption (the sum of the atomic and non-specific absorption) and the non-specific absorption alone are measured at two separate time intervals, separated by a few milliseconds. The atomic absorption is obtained by subtracting the non-specific absorption from the total absorption. Signals in graphite furnace analysis are produced rapidly and decay rapidly (the maximum signal rise times can be up to 10 absorbance units per second). Ideally, the total and background signals should be measured simultaneously for accurate correction. This is not practical and therefore, the 2 signals should be measured as close as possible in time. The time difference in commercial instruments ranges from 2 ms to 10 ms—the larger the time difference, the greater the error in the background correction (Refer to the Technical Sales Arguments section in the Sales Manual for further detail on the extent of these errors in background correction).

There are a number of different background correction techniques available. The three most commonly used systems in order of priority are deuterium, Zeeman and Smith Heiflje background correction. In this section, a
brief review of the theory and operation of the various background correction techniques available is presented.

**Deuterium Technique**

The most common method of background correction involves the use of a continuum source such as a deuterium lamp to measure the background. This is a continuum source operating over the range from 180 to about 425 nm. Background signals become more significant the shorter the wavelength and the deuterium lamp covers the wavelength range in which background is most commonly experienced. As shown below, the optical configuration is such that radiation from both the hollow cathode lamp and the continuum lamp coincide along the optical path. It is important that both the deuterium source and the hollow cathode lamp are aligned to follow the same optical path through the atomizer. If they do not, then the two measurements may not be made on the same population and significant errors may occur. The narrow emission profile of the hollow cathode lamp is attenuated by both the atomic and background species and therefore represents a measure of the total absorbance. The attenuation of the broadband deuterium-lamp emission by the narrow band atomic absorption signal is relatively insignificant and so the attenuation of the deuterium profile is caused primarily by background alone. This is shown in the figure below.

![Figure 8](image)

*Figure 8 The attenuation of the narrow band hollow cathode lamp profile represents the total absorbance measurement (background and atomic), the attenuation of the broad band deuterium profile is caused primarily by background alone.*

The background signal is subsequently subtracted from the total absorbance measurement to obtain the corrected atomic absorption signal:

- Hollow cathode lamp = AA + BGD
- Deuterium lamp signal = BGD only
- Electronically processed signal = AA only

In the double beam system illustrated below, radiation from the continuum source traverses the same sample and reference paths as radiation from the hollow cathode lamp. The intensities of both sources can be concurrently monitored. Any drift in the intensity of either source can be automatically corrected for, so as to maintain the accuracy of background correction.
Smith Heiftje Technique

Another form of background correction offered is the Smith Heiftje technique. Smith Heiftje background correction was developed in 1983 by Stan Smith (of Instrumentation Laboratory–now Thermo Jarrell Ash) and Gary Heiftje (of Indiana University). Their paper describing their work[^4] describes the details and limitations of their design. Thermo Jarrell Ash (TJA) used to provide Smith Heiftje background correction. Shimadzu is currently the only AA manufacturer to offer Smith Heiftje background correction with their instrumentation.

When a hollow cathode lamp is run at a very high current, its emission line is broadened and there is significant loss of emission signal from the lamp at the wavelength of interest. The spectral profile is changed to show two emission peaks which appear on either side of the atomic absorption wavelength. It is this effect, called self reversal, on which the Smith Heiftje background correction technique is based.

The hollow cathode lamp is pulsed at normal operating currents for the measurements of the total absorbance. Interspersed with these are very brief pulses of high current which causes line broadening and self reversal of the lamp–basically eliminating the resonance line of the lamp itself. The self reversal effect of the hollow cathode lamp profile is used to cause the hollow cathode lamp to behave somewhat like a continuum source. The atomic absorption is reduced, allowing the background to be measured by the absorption of these other emission lines. Note that background correction does not occur at the exact analyte wavelength, but slightly displaced from it.

The advantage of this approach is that only one light source—the hollow cathode lamp—is required, but this advantage is outweighed by the practical disadvantages which include reduced lamp life, a reduction in sensitivity of up to factor of 6, with an average loss of a factor of 2 and the requirement for special lamps which can withstand the short intense lamp currents applied to the lamp. The sensitivity loss, associated with the Smith Heiftje technique is dependent upon the degree of line broadening and self reversal and ranges from a low of 16 % for Hg to a maximum of 87 % for Cd.

There are other problems associated with Smith Heiftje background correction including:

- Poor background correction accuracy (particularly for fast signals) because of the slow speed of data collection (10 Hz)
- Reduced dynamic range due to increased curvature of the calibration
- Inability to correct for all spectral or structured background since Smith Heiftje correction essentially produces a narrower version of a continuum source

Because of these problems with the Smith Heiftje technique, few practical application examples using Smith Heiftje correction have been published. Many of the reported examples of the benefits of the Smith Heiftje technique can be performed equally well with deuterium background correction.

**Zeeman Technique**

The use of continuum source or deuterium background correction has some practical limitations including:

- The intensity of the continuum source is sometimes inadequate
- Structured backgrounds, caused by narrow line molecular absorption spectra, cannot be accurately corrected, and
- Significant background correction errors can sometimes be introduced.
Zeeman background correction provides an alternative to the use of a continuum source as a means for background correction. Varian, Perkin Elmer, Hitachi, and TJA/Unicam all offer AA instruments with Zeeman background correction. The Varian, Perkin Elmer, and TJA/Unicam systems are dedicated furnace instruments only, whereas the Hitachi system is a combined flame/furnace system.

The Zeeman Effect

The Zeeman effect is the splitting of atomic spectral lines in the presence of a magnetic field. In the normal or simple Zeeman effect, the line is split into a pi and 2 sigma components. The pi component remains at the original wavelength and the sigma components are symmetrically displaced by a few picometers around the original wavelength. The amount of the wavelength shift is dependent upon the strength of the applied magnetic field. The pi and sigma components are also polarized—the pi component parallel and the sigma components perpendicular to the applied magnetic field.

![Figure 11](image.png) The principle of operation of Zeeman background correction.

The total absorbance is measured with the magnet off. With the magnet on, Zeeman splitting of the atomic spectral profile occurs and the central pi component is excluded by the polarizer allowing the background absorbance only to be measured. Note that background correction measurement occurs at the exact analyte wavelength of the hollow cathode lamp. Molecular species remain relatively unaffected by the magnetic field and since these and other species are responsible for causing background absorption, an accurate background correction technique can be realized. The atomic absorbance is determined by subtracting the background (magnet on measurement) from the total absorbance (magnet off measurement). By this means, the limitations of deuterium background correction can be minimized or eliminated. There is no wavelength limitation to the Zeeman background correction technique.

Different Zeeman Configurations

There are several possible configurations of the Zeeman technique—the magnetic field may be applied to either the light source or the atomization system (flame or furnace). In practice, the field is typically applied to
the atomization system, as light sources may be unstable in a strong magnetic field. The magnetic field may also be fixed (DC permanent magnet) or modulated (AC magnet).

In addition, there are two types of application of the magnetic field in Zeeman systems—longitudinal and transverse. In transverse Zeeman systems, the magnetic field is applied at right angles to the optical path, while in Longitudinal Zeeman, the field is applied parallel to the light path. Most AA instruments with Zeeman effect background correction rely on splitting of the absorption line by placing the magnet in the transverse position (at right angles to the optical path).

**DC Zeeman Design**

With the DC Zeeman design, a rotating polarizer is required to distinguish between the parallel and perpendicularly polarized atomic lines. With this design, the atomic splitting is always present and severe sensitivity losses are observed⁵ for many elements.

**AC Zeeman Design**

In this configuration, an electromagnet is rapidly switched on and off, to permit alternate measurements of the total and the background absorbance. Varian patented all possible Zeeman configurations in 1971⁶, and chose to adopt the more sensitive AC modulated Zeeman technique. This system has proven to give the best detection limits of any Zeeman spectrometer available today.

**Longitudinal Zeeman Design**

In Longitudinal Zeeman systems, the magnetic field is applied parallel to the optical path. The atomic spectral line is split into rotationally polarized sigma components which are symmetrically displaced away from the original wavelength. There is no central pi component. Therefore, a polarizer is not required. Because there is no polarizer fitted in the optical path of a longitudinal Zeeman furnace system, an improvement in light throughput may be expected, resulting in better detection limits, but in practice, other aspects such as graphite furnace design and optics performance dominate.

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⁶ For example: US Patent No. Re. 32, 022
polarized sigma components are observed, hence a polarizer is not required

Transverse Zeeman Design

In Transverse Zeeman systems, such as the SpectrAA-800 Zeeman furnace systems, the magnetic field is applied at right angles to the optical path. The magnet is also modulated (AC Zeeman design). The atomic spectral line is split into a central pi component and two or more sigma components. A polarizer is inserted into the optical path to remove the pi component of the transmitted radiation.

Figure 13: In Transverse Zeeman systems, the magnetic field is applied perpendicularly to the optical path. The atomic absorption line is split into parallel polarized pi components at the central wavelength, and perpendicularly polarized sigma components symmetrically displaced from the analyte wavelength. The pi components are removed by a polarizer in the optical path.

Advantages of Zeeman Background Correction:

One of the key advantages of the Zeeman technique is that background correction takes place at the exact analyte wavelength. In addition, only one light source is required—the hollow cathode lamp. Therefore, the light throughput is maximized. The rapid sequential measurement of the hollow cathode lamp intensity with the magnetic field on and then off, provides the performance of a true double beam instrument i.e. this design allows automatic compensation for any lamp drift which may have occurred. The other advantages of the Zeeman technique include:

- Correction over the complete wavelength range
- Correction for structured background
- Correction for some spectral interferences
- Faster correction speed for improved background correction accuracy
- Correction of high background absorbances.

However, there are also two disadvantages of the Zeeman technique:

✗ Calibration Roll-over

Calibration curves in atomic absorption generally asymptote towards a limiting absorbance at high concentrations. In Zeeman systems, depending upon the element and measurement wavelength, the calibration curve may roll over. In such cases with the peak height mode, the calibration curve levels off horizontally whereas in the peak area mode, the curve bends over towards the concentration axis. This
phenomenon of reflex curvature means that two different analyte concentrations can give the same absorbance and corrective action must be taken.

Figure 14  Comparison between the calibration curves for normal and Zeeman atomic absorption. The Zeeman calibration curve shows the effect of roll-over at high concentrations. Most instruments recommend a maximum absorbance for each element and flag an error if this maximum absorbance has been exceeded to warn the operator of the potential error.

To prevent such problems with roll-over occurring in practice, the maximum permissible absorbances in the peak height mode have been determined for each element and wavelength. These values are listed in the Varian cookbook conditions. This defines the maximum peak height Zeeman absorbance which can be used for the analyte at the wavelength selected. All measurements must be below this maximum peak absorbance. An error message will be automatically reported if the peak analytical signal exceeds the maximum absorbance for a particular analyte.

✗ Sensitivity Loss for Some Elements

A number of atomic spectral lines exhibit more complex splitting patterns called the anomalous Zeeman effect. The atomic spectral lines are split into several pi and sigma components, which may overlap. At practical field strengths, the sigma components may not be completely separated from the hollow cathode lamp emission profile. This attenuation of the hollow cathode lamp intensity reduces the sensitivity of Zeeman AA determinations for a number of elements including Al, As, Sb, Cu, Se and Te. The extent of the sensitivity loss is usually expressed as the magnetic Sensitivity Ratio (MSR)—the ratio of the Zeeman absorbance divided by the normal absorbance expressed as a percentage. Typical MSR values range from 49 to 100 %, depending upon the element and the wavelength. Although there is no comparable loss in sensitivity when deuterium background correction is used, the majority of elements show a sensitivity loss of 10 % or less.

Zeeman background correction is recognized as an impressive and effective addition to graphite furnace technology. The major reason customers purchase a Zeeman furnace spectrometer is for 'better background correction accuracy' when they are required to complete difficult and demanding applications where the sample has a complex matrix and high background is present. For example, the determination of Se in blood suffers from a spectral interference from Fe and structured background from phosphates originating in the blood, when deuterium background correction is used. Selenium is also very volatile, which restricts the ashing temperature that can be used, without chemical modification. There are about 40 iron lines between 195.0 nm and 197.0 nm—the lines at 196.014 and 196.32 nm being the closest. Obviously, even the narrowest slit will not isolate the Se line, and with deuterium background correction, an overcorrection is observed. These problems of over correction and spectral interferences can be overcome with Zeeman background correction7.

7 Knowles, M. and Frary, B.D., International Lab., April 1988
Comparison of Background Correction Techniques

<table>
<thead>
<tr>
<th>Feature</th>
<th>Deuterium</th>
<th>Smith Heiftje</th>
<th>SpectrAA Zeeman</th>
<th>Perkin Elmer Zeeman</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity Loss</td>
<td>None</td>
<td>From 2–6 times</td>
<td>From 0–2 times</td>
<td>From 0–3 times</td>
</tr>
<tr>
<td>Useful in all Atomizer Modes (flame, furnace and vapor)</td>
<td>All</td>
<td>All</td>
<td>Furnace only</td>
<td>Furnace only</td>
</tr>
<tr>
<td>Covers complete wavelength</td>
<td>No</td>
<td>No(^{a})</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Covers complete wavelength</td>
<td>From 180-425 nm</td>
<td>No(^{a})</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Lamp Life</td>
<td>Normal</td>
<td>Reduced</td>
<td>Normal</td>
<td>Normal</td>
</tr>
<tr>
<td>Calibration Linearity</td>
<td>Normal</td>
<td>Rollover occurs at higher concentrations</td>
<td>Rollover occurs at higher concentrations</td>
<td>Rollover occurs at higher concentrations</td>
</tr>
<tr>
<td>Dynamic Range</td>
<td>Full range</td>
<td>Reduced</td>
<td>Reduced</td>
<td>Reduced</td>
</tr>
<tr>
<td>Measurement Frequency(^{b})</td>
<td>50/60 Hz</td>
<td>10 Hz</td>
<td>100/120 Hz</td>
<td>54 Hz (ZL Series)</td>
</tr>
<tr>
<td>Delay Time between measurement of Total Abs. and Background Abs.(^{c})</td>
<td>2 ms</td>
<td>4.5 ms</td>
<td>4.5 ms</td>
<td>~ 9 ms (ZL series)</td>
</tr>
</tbody>
</table>

1. Smith Heiftje background correction can in theory cover the complete wavelength range—however, Visimax lamps are not available for all elements and some elements do not work.

2. The measurement frequency determines the ability of the instrument to accurately define the shape of the atomic and background signals for fast atomic peaks. The slow measurement frequency of the Smith Heiftje background correction technique (10 Hz) prevents accurate definition of the peak shape and may affect result accuracy.

3. Most AA spectrometers subtract a single background measurement from the total absorbance measurement to calculate the true atomic absorption signal. In this correction mode, the correction accuracy is directly proportional to the elapsed time between the total and background absorbance measurements and the slope of the background signal\(^{d}\). During this time interval, the background can change significantly, resulting in correction errors. Inadequate correction of the background will cause inaccuracies in the sample results. By reducing the time interval between the total and background absorbance measurements, the background correction accuracy can be improved.

Optics

In this section, theoretical aspects of optical design for atomic absorption are explained. The spectrometer collimates light from the hollow cathode lamp and then isolates the analyte wavelength from other line and broadband emissions. The absorption of the light by the analyte of interest is measured, relative to the initial intensity of the lamp, using a detector. This is then converted into a measurable electronic signal for comparison with a previously established calibration. The optics of an ideal spectrometer would:

- Pass 100 % of the source energy to the detector (without an absorbing species in the optical path)
- Have a very high signal-to-noise ratio
- Zero stray light
- Introduce no aberrations
- Have absolute selectivity of the required wavelength, and
- Have constant dispersion with wavelength.

Unfortunately, such a perfect optical system cannot exist, but the design used in any AA spectrometer should be the best possible.

Two types of optical components may be used for focusing the light beam inside the optical design of an AA spectrometer—lenses and mirrors:

**Lenses**

The focal length of a lens varies with wavelength because the refractive index is wavelength dependent and changes sharply below 300 nm. In optical systems employing lenses, it is not convenient to relocate the lenses, atomizer or hollow cathode lamp whenever the wavelength is changed, and it is the usual practice to design the lens so that it is in focus at a selected wavelength and accept any losses occurring at other regions of the spectrum. Lenses for atomic absorption are normally focused in the ultra-violet because most wavelengths of analytical interest fall within this range and because the median refractive index occurs at approximately 250 nm.

The issue of the focal point of the light from the hollow cathode lamp is not critical for an air/acetylene flame because of the longer pathlength, but this should be considered when using a nitrous-oxide/acetylene flame. However, the focus is critical in graphite furnace AA. In the graphite furnace technique, the sample is dispensed into the centre of the graphite tube. If lenses have been used in the optical path, then the focus of the beam may move away from the centre of the graphite tube as the wavelength is increased. For these reasons, high quality spectrometers should only use mirrors as optical components.

Lenses are usually made from high quality silica glass that provides good optical transmission over the wavelength range from 190 nm to 900 nm. The only significant losses are those caused by reflection at each air-glass surface. This is commonly about 5-7% at each surface or about 10-15% for each lens in the optical path.

**Mirrors**

The focal length of a mirror does not vary with wavelength and mirrors usually have far lower light losses than lenses, as the energy is reflected from the surface of the mirror. In all-reflective systems, plane mirrors can be used to fold the optical beam where necessary, and curved mirrors can be used as focusing elements to focus the image as required. Although the focus does not vary with wavelength, the design of the mirror for focusing elements can present other challenges for optics designers.

The geometry of reflective systems requires that the focusing mirrors be used to gather light from off-axis angles. In this circumstance the spherical concave mirror suffers severely from astigmatism and the images
may be grossly distorted. This distortion can only be avoided by using toroidal mirrors—that is, mirrors which have different horizontal and vertical radii.

When a plane mirror is used to deflect a beam of light, coma occurs. Coma is the flaring or spreading of the beam of light in one orientation. When this occurs, the optical image tends to spread across the detector resulting in light loss. To prevent coma, SpectrAA systems use two mirrors in a ‘Coma Eliminating Pair’ (CEP) to perform the deflection. The CEP consists of a plane mirror and a toroidal focusing mirror.

Mirrors invariably have their front surface coated with aluminium by vacuum deposition. A properly controlled aluminium coating has a reflectivity of better than 90% over the entire wavelength range from 190 nm to 900 nm. The aluminium coating is extremely thin (e.g.: 1.5 microns) and can be easily damaged by even a soft tissue. Chemical fumes may also attack the coating and even a fingerprint may cause irreparable damage. The delicate aluminium can be protected by overcoating with evaporated films of materials such as silica or magnesium fluoride but physical contact with optical surfaces should still be avoided. The overcoating may also give a slight improvement in reflectivity.

All the mirrors used in Varian instrumentation are manufactured to high quality standards and are quartz over coated for longer life.

**Slit width**

The slit width affects the spectral isolation of the analytical line and thus contributes to the ability of the AA spectrometer to resolve adjacent wavelengths from the analyte wavelength. The slit width required is normally dictated by the nearest adjacent line in the spectrum. In practice the selection of operating slit width involves a compromise since the slit also controls the amount of light that is transmitted into the monochromator. If the slit is too wide, the light throughput will be high and the signal-to-noise ratio may be excellent, but the resonance line may not be isolated from other lines and the calibration may be badly curved.

![Figure 15](image.png)

*Figure 15* The slit width required is normally dictated by the nearest adjacent line in the spectrum. In practice the selection of operating slit width involves a compromise between the selected slit width calibration linearity and the signal-to-noise ratio, since the slit also controls the amount of light that is transmitted into the monochromator.

Calibration curvature occurs because the detector observes the neighboring non-analyte emission lines (such as fill gas lines from the hollow cathode lamp) which are not subject to absorption. Conversely, if the slit is too narrow, the resolution may be excellent but the signal-to-noise ratio may be unacceptable because of the reduced light throughput. By studying the effect of altering the slit width on the absorbance of an analyte solution, the optimum slit width can be determined. Most AA manufacturers provide a set of recommended cookbook or operating parameters for each element, which includes the optimum slit width.
Monochromator

In practice, all but the most elementary monochromators consist of an entrance slit to confine the source radiation to a usable area, mirrors to pass the light through the system, a dispersing element to spread the source radiation into its component wavelengths and an exit slit to select the wavelength for analytical measurement. Since the hollow cathode lamp emits many narrow emission lines, the sole function of the monochromator is to isolate a single atomic resonance line from the total spectrum of lines emitted by the hollow cathode lamp. In effect, it is an adjustable filter which selects a specific, narrow region of the spectrum for transmission to the detector and rejects all wavelengths outside this region. Essentially the monochromator is tuned to select a particular wavelength of light much as you would tune a radio to a particular radio station.

![Cu Spectrum](image1)

**Figure 16** The atomic spectrum for copper near 324.7 nm

Ideally, the monochromator should be capable of isolating the resonance line only and excluding all other wavelengths. For some elements this is relatively easy; for others it is more difficult. Copper for example has a comparatively simple spectrum as shown above with the nearest line being 2.7 nm from the 324.7 nm resonance line. Iron, on the other hand, has a complex spectrum, as shown below, with quite strong lines at 248 nm and 249 nm—one at each side of the 248.3 nm resonance line.

![Fe Spectrum](image2)

**Figure 17** Atomic spectrum of iron near the 248.3 nm resonance line illustrating a complex spectrum where a narrow slit width would be required to isolate the resonance line.
The ability to discriminate between different wavelengths (usually referred to as resolution) is thus a very important characteristic of the monochromator. Monochromators designed for emission techniques need very high resolution due to the complexity of the emission spectra generated by a high temperature source such as the Inductively Coupled Plasma (ICP). An ICP monochromator can isolate wavelength regions less than 0.01 nm; however, for atomic absorption spectrometers, a typical requirement is about 0.2 nm ‘bandpass’. The SpectrAA Czerny-Turner monochromator design is illustrated below. Other designs use different arrangements of the optical components but the operating principle is the same for all of them.

The light emitted by the spectral source is focused on a narrow entrance slit. The light passing through the slit then diverges until it reaches the first mirror where it is collimated into a parallel beam and directed towards the grating.

The grating is the heart of the monochromator. Light focused on the grating is diffracted as a spectrum of all the component wavelengths of the incident light, and is dispersed at different angles according to its wavelength. The resulting spectrum is spread over a wide angle on leaving the grating surface. By rotating the grating relative to the incident light, the spectrum is scanned across the second mirror. By rotating the grating to a specific angle, a specific wavelength can be focused onto the exit slit via the second mirror, and so may be directed at the detector. The remainder of the spectrum either does not fall onto the second mirror, or is focused away from the exit slit.

Several different monochromator designs are available. A brief description of each of the major designs follows:

**Czerny-Turner:**

![Figure 18 Optical design of the Czerny-Turner monochromator design used in Varian AA instrumentation.](image)

The Czerny-Turner design, such as that used in Varian instrumentation, uses 2 separate mirrors; one to focus the incoming light onto the grating and the other to focus the outgoing beam on the photomultiplier. The two mirrors have different optical properties. This permits a reduction in aberrations to be achieved, improving the resolution and light throughput, as these mirrors can be prepared with greater accuracy.
Ebert-Fastie:

The Ebert-Fastie design monochromator uses one large focussing mirror (in place of the two used in the Czerny-Turner design) to focus the incoming light beam on the grating and then also to collect the returned light from the grating and direct it to the detector. A large mirror is required and a large area of the mirror is unused. The primary disadvantage of this approach is that it uses a single large mirror to focus the light on the grating. Due to the size of this component, control over surface inaccuracies becomes critical. This cheap design is therefore more susceptible to aberrations than the two mirror Czerny-Turner approach. In addition, the overall light transmission is a compromise as the mirror cannot be manufactured for aberration correction, without going to excessive expense.

Littrow:

Figure 19 Optical design of the Ebert-Fastie monochromator design. Note the large single mirror surface used to focus the light on the grating. Due to the size of this component, control over surface inaccuracies is critical and makes this design more susceptible to aberrations.

Figure 20 Optical design of the Littrow monochromator design. Like the Ebert-Fastie monochromator design, a single mirror is used to focus the light on the grating, but this is much smaller however. The same area of the mirror is illuminated, which introduces aberrations.
This design is similar to the Ebert-fastie design and uses one mirror for collection and focussing of the light. Approximately the same area of the mirror surface is illuminated by the incident and the reflected light beams—this gives even poorer aberration control than the Ebert-Fastie design.

**Gratings**

Before the use of diffraction gratings, all atomic spectroscopy instrumentation used a glass or quartz refracting prism as the means of dispersion (separation of the wavelengths). The next development was the introduction of the diffraction grating. The grating monochromator is now universally used in atomic absorption instruments. The diffraction grating consists of a series of parallel grooves ruled in a reflecting surface. Originally master gratings were ruled by a ruling engine installed in a temperature and humidity controlled room and isolated from vibration so as to achieve the desired groove accuracies. A very flat piece of glass was coated with a thin film of aluminium using vacuum deposition. A carefully shaped diamond tool was then drawn across the surface to rule a groove of the desired shape. The grating was then accurately advanced, and another groove ruled at a precise distance from and exactly parallel to the last. This process could take as long as a week.

Today, holographic techniques are employed to produce blazed interference grating masters. These are manufactured by spinning a layer of photoresist onto a glass blank, and then exposing this resist to an interference pattern produced by two coherent, collimated beams of light. The beams of light interfere with each other and produce a standing wave pattern in the photosensitive material deposited on the glass substrate. When the photoresist is developed, a surface contour results, which can be coated with aluminium to produce a reflection grating. The main advantage of holographic gratings is their lower stray light performance. Because the grating is produced by recording a perfect optical phenomenon, the grooves are free from periodic error which can be a major source of stray light. The surface is scored with a number of fine grooves usually between 500 and 3000 grooves/mm. The grooves must be equally spaced, parallel and of identical shape.

Production gratings are replicated from the masters. The master is first coated in a vacuum evaporator with a monolayer of oil, followed by a thin layer of aluminium. Epoxy resin is then poured onto this substrate and backed up by a piece of plate glass. The entire sandwich is separated at the oil layer after the resin has cured, producing an accurate copy of the master grating.

![Figure 21. Schematic representation of the grating surface (magnified) showing the surface scored with fine equally spaced grooves](image)

When light strikes such a grating, the light is diffracted at an angle that is dependent on the wavelength of the light and the line density of the grating, or number of grooves per millimetre. In general, the longer the wavelength and the higher the line density, the larger the angle of dispersion. The line density is one of a number of parameters which are used in the calculation of Reciprocal Linear Dispersion (RLD) which is a measure of the resolution of the system. The longer the focal length of a monochromator, the greater is the...
possible linear dispersion. However, increasing the focal length reduces the light throughput and degrades overall optical performance.

Most of the analytical wavelengths used in atomic absorption are in the UV region of the spectrum. Elements with resonance wavelengths above 400 nm have simple spectra and resolution and selectivity is not therefore a problem at the higher wavelengths. For these reasons, most AA manufacturers blaze their gratings in the UV region of the spectrum so that the grating will give its maximum reflected light intensity at that wavelength. Two gratings, each blazed at a different wavelength, can be used in an AA spectrometer. It is important in such an optical layout that the light beam is incident on only one grating and does not spill over to the other. If light is incident on both gratings at the same time, the optical performance is degraded.

**Detectors**

Once the proper atomic resonance line has been isolated by the spectrometer, the detector and its associated electronics are used to measure the intensity of the atomic absorption or emission. The detector universally used is the photomultiplier tube. This has high sensitivity, a wide dynamic range and can be used across the complete wavelength range required for atomic absorption analysis.

The photomultiplier tube is a vacuum tube that produces an electrical signal which is proportional to the intensity of the light which reaches the device. Light admitted through a window in the photomultiplier tube falls directly onto a photosensitive material—the photocathode. The cathode is coated with a material which emits electrons whenever it is illuminated. The higher the intensity of the incident light—the greater the number of electrons emitted. The electrons emitted are accelerated towards an adjacent electrode, maintained at a positive electrical potential with respect to the cathode. This is called a dynode. When each electron reaches the dynode, it liberates a number of secondary electrons which are in turn attracted to another dynode, emitting even more electrons. This is the multiplier process that gives the photomultiplier its name. A dynode chain of between 9 to 16 stages is usually fitted inside the PMT, causing an increase in the electron current generated at the cathode. As many as $10^8$ secondary electrons may be collected as the result of a single photon striking the photocathode.

The electrical current measured at the anode is then used as a relative measure of the intensity of the radiation reaching the PMT. Thus the light intensities which are obtained in atomic spectroscopy lead to an electric current of useful magnitude which can be further amplified to provide the required quantitative measurement.

The major advantage of the PMT over other detection devices are that it can be used to measure light over the complete wavelength range of analytical interest, it can amplify very weak incident light levels and it has a wide dynamic range.

**Single vs Double Beam Configurations**

In AAS, the basic purpose of the optical system is to gather light from the source, direct it through the analyte atom population, and then direct it into the monochromator. Optical configurations may be either single beam, single beam Zeeman or double beam. Mirrors and/or lenses can be used as the light transfer elements. The simple, single beam mirror system illustrated below is used in many instruments. The second mirror focuses the image of the lamp cathode at the centre of the atomizer. The third mirror focuses this image in turn on to a plane mirror where the beam is folded and passed to the entrance slit of the monochromator. Lenses can be used to achieve the same effect, but are less effective as their focal length changes with wavelength. There are also energy losses as the light passes through the lens.
Figure 22. The optical layout of a typical single beam instrument. Any change in the intensity of the source lamp will cause some baseline drift to occur, so before operation the lamp should be allowed to warm up for a short period.

**Single Beam Optics**

In the single beam configuration shown, the light from the source traverses only one path—through the atomizer. In this system it is necessary to measure the initial intensity $I_0$ of the resonance line before inserting the sample and measuring the transmitted intensity $I_t$. The single beam system therefore relies on the light source remaining stable during the period of analysis—that is, intensity $I_0$ should not drift or fluctuate while it is being measured. With modern hollow cathode lamps, $I_0$ will generally remain sufficiently stable after a suitable warm up period. Any change in the intensity of the lamp will be reflected in a change in the baseline of the instrument—i.e. drift occurs. Therefore, it is important that the lamp be allowed sufficient time to warm up before analytical measurements are made. The warm up time required is totally dependent upon the element and the absorbances being measured, but for the majority of the elements, 10 minutes is a suitable warm up period—this will usually produce a stable signal. Exceptions to this are As, P, TI and the Cu/Zn multi-element lamps which require longer warm up times.

However, as lamps age, they are more susceptible to drift and become noisier—this limits the analytical stability of single beam instruments. This instability can be compensated for by more frequent calibration and resloping—this is particularly necessary for graphite furnace work. For customers performing a large number of analyses and for graphite furnace AAS the stability of a double beam or Zeeman optical system is recommended.

In single beam instruments, all of the source energy passes through the sample cell—thus a good signal-to-noise ratio is obtained. Under such conditions, the increased light throughput and improved signal-to-noise ratio should provide slightly improved precision and detection limits when compared with a double beam instrument. Note however that if the single beam instrument is fitted with deuterium background correction, then it is usually fitted with a beam splitter (half silvered plane mirror). This immediately reduces the energy available, thus degrading the signal-to-noise ratio by about half and removing any potential advantage of the single beam design. Note however, that the detection limit reflects the signal-to-noise performance of an instrument, and this can be affected by many other parameters—not just the optics design. The two major parameters influencing the detection limit are the precision of measurement or standard deviation of the blank signal (signal stability) and the analytical sensitivity. It is thus unlikely that there will be any significant difference in the detection limit between a single beam instrument and a single beam instrument fitted with deuterium background correction.
Double Beam Optics

A typical double beam optical system, shown below, is designed to correct for drift in $I_o$. Light from the source is directed at a beam splitter. This is an optical component designed to reflect a proportion (usually half) of the incident light from the surface and allow the remainder to pass through the surface. This usually consists of a partially aluminized quartz plate. The beam splitter is normally designed so that the energy is equally divided–50% of the incident beam forms the sample beam and 50% is used to form the reference beam.

![Image of double beam optical system]

The sample beam is focused by mirror M1 on the atomizer and is directed at the entrance slit of the monochromator by mirrors M2 and M3. The reference beam is directed around the atomizer and reflected into the monochromator. In many AA designs another beam splitter is used to direct the sample and reference beams into the monochromator. A rotating ‘chopper’ consisting of a perforated disk alternately allows the sample and reference beams to fall on the beam splitter. This optical design throws away 50% of the incident light, so that only 25% of the light from the hollow cathode lamp enters the monochromator.

The signal-to-noise ratio of the double beam system may be improved by replacing the second beam splitter (beam combiner) with a rotating mirror which collects all the energy from the sample and reference beams and passes it into the monochromator. In SpectrAA double beam designs, a Rotating Beam Combiner (RBC) is used to alternately pass all of the sample beam or all of the reference beams into the monochromator. The RBC is a rotating sectored mirror. This optical design would give the best signal-to-noise ratio possible for a double beam instrument and is equivalent to a single beam instrument fitted with a deuterium background corrector in this respect.

The optical design of a double beam instrument allows the source intensities $I_o$ and $I_1$ of both reference and sample beams to be measured in succession at high frequency. This high frequency of measurement provides near-continuous monitoring so that corrections for variations in source intensity, including the intensity of the deuterium lamp for the background corrector, can be instantaneously applied. The analytical result is thus unaffected by any drift which may occur in the source lamps. Although a double beam instrument is able to correct for changes in the source intensity and so eliminate drift, it is still desirable to allow a short warm up before attempting precise analytical measurements. This is because the profile of the emission line from the lamp can change during this period, and small changes in the analytical signal may result. Note however that the zero absorbance levels will always be maintained.
Glossary of Technical Terms in AA

The following is a glossary of common terms used in atomic absorption spectroscopy.

**Accuracy**
A measure of how close the measured result is to the ‘true’ value. Note that any analytical measurement that is made by comparing unknowns to standard solutions can be no more accurate than the least accurate of the standards. The accuracy of a measurement is therefore dependent on the care with which the chemist prepares known standards and sample solutions for the analysis. Interference effects can also affect the accuracy of a measurement.

**Aerosol**
A fine mist of droplets created by a nebulizer.

**Analyte**
The element to be determined.

**Atomic Absorption**
An elemental analysis technique that relies on the absorption of light by atoms. When this happens, an electron is promoted to a higher energy level within the atom. The atom is then said to be in an excited state.

**Atomic Emission**
An elemental analysis technique that relies on the emission of light by excited atoms as they revert to the ground state.

**Atomization**
The process that converts the analyte, or its compounds, to an atomic vapor.

**Blaze**
The shape of the groove in the grating which determines the distribution of energy with respect to wavelength.

**Blaze Angle**
The blaze angle of the grating will determine at which wavelength the maximum intensity of the diffracted light occurs.

**Blaze Wavelength**
The wavelength at which the maximum intensity of light diffracted from a grating occurs.

**Calibration**
The establishment of an analytical calibration graph that describes the relationship between the concentration of an analyte and the absorbance. In atomic emission, a plot of emission intensity versus concentration is normally used.
Calibration Blank

A solution that does not contain any added analyte. This solution is usually prepared in the same matrix as the standards and so represents the contamination from the reagents used. This is used for calibration.

Characteristic Concentration

The concentration of an analyte that would typically give an absorbance of 0.0044 (1 % absorption). Different instruments have different characteristic concentrations. It can be calculated from the linear portion of the calibration curve (usually based on absorbances < 0.2) using the equation:

Char. Conc. = (Standard Concentration * 0.0044) / Mean Abs.

This provides a convenient way for the analyst to check the instrument performance.

Characteristic Mass

The mass of an analyte, in picograms, that would typically give an absorbance of 0.0044 in graphite furnace AA in the peak height mode. It can be calculated from the linear portion of the calibration curve (usually based on absorbances < 0.2) using the equation:

Char. Mass = (Standard Concentration * 0.0044 * volume injected) / Standard Absorbance

Chemical Modifier

A chemical modifier is a reagent which when added to the sample, chemically alters the sample matrix in order to change the volatility of the analyte element and/or the bulk matrix constituents to either reduce interferences, or isolate the analyte in a specific form that allows separation between background and analyte atomic absorption signals. In complex matrices, modifiers can improve results by enhancing atomic signals and/or reducing background signals produced during atomization. An ideal chemical modifier is a reagent that performs both of these functions.

Coefficient of Variation

The reproducibility or precision of a series of measurements. This is also known as the % RSD (Relative Standard Deviation). It is simply the standard deviation divided by the mean expressed as a percentage.

Desolvation

The process by which droplets of an aerosol are dried to form minute solid particles.

Detection Limit

Concentration of an analyte that results in an absorbance that is three times the standard deviation of the blank at the measurement wavelength. This is the lowest concentration that can be determined above the background noise level. Some definitions may use twice the standard deviation of the blank, but the latest IUPAC recommendation is three times the standard deviation of the blank (the criteria used should always be stated).

The detection limit is a measure of the signal-to-noise ratio and is influenced by the overall optical design and the optical parameters used for a measurement (slit width, wavelength, lamp current etc). It may be calculated using the equation:

\[ DL \ (pg) = \frac{(3 \ \cdot \ SD \ \cdot \ C \ \cdot \ Vol)}{\text{Mean Abs.}} \]
where:

SD is the standard deviation of the blank signal
C is the concentration of the analyte in the standard solution
Vol is the volume of the standard solution injected into the graphite tube

Detection limits are a statistically derived number and can vary by a factor of about 8 for the same element. For this reason, differences between competitor's quoted detection limits should not be considered significant unless they differ by a factor of 5–10 times. At the detection limit, the precision of measurement is 33 % RSD, which makes it impossible to make accurate measurements. Routine analyses should be carried out at levels 5–10 times greater than the detection limit. At these levels, a precision of about 3–5 % RSD can be expected.

Digestion

The process of dissolving a solid sample in an acid matrix to convert it to a solution form.

Dynode

One of the intermediate stages in a photomultiplier tube that amplifies the signal by emitting more secondary electrons when struck by an electron.

Emission

The radiant energy resulting from electronic transitions between energy levels in excited atom species

Emission Intensity

The measure of the amount of light at a given wavelength emitted from a spectral source.

Excitation

A process in which an atom which is in the ground state, absorbs energy from a collision with another particle or from heat or light. When this happens, an electron is promoted to a higher energy level within the atom. The atom is then said to be in an excited state.

Filter

A material which attenuates incident radiation energy in a selective manner with respect to spectral distribution.

Grating Density

The number of lines or grooves per unit length on a grating, usually expressed as lines/mm or as grooves/mm. The higher the grating density, the greater the dispersion of the light diffracted from the grating surface.

Grating Diffraction

An optical device, consisting of a mirror scored or etched with a series of close, equally spaced grooves capable of dispersing light its spectrum.

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**Ground State**

The lowest or most stable energy state of an atom. When an atom is in the ground state, all electrons are in their lowest energy levels.

**Holographic Grating**

A grating produced by a photographic process in which interference fringes of laser light are etched onto the surface to create grooves. It has lower stray light characteristics than ruled gratings.

**Hydride Generation**

A technique in which the analyte is reacted with a reductant, usually sodium borohydride, to form a volatile hydride of the analyte. This is reduced to free atoms in a quartz cell mounted in the optical path using heat from a flame or an electrical heater.

**Interference**

An interference is any effect whether chemical or physical which changes the measured absorbance obtained for a given concentration of the analyte. The most common form of interference is caused by interferents which form compounds which do not completely dissociate during atomization, and so prevent the formation of neutral ground atoms. This reduces the sensitivity.

**Ionization**

The process where a neutral atom is converted to a charged ion through the gain or loss of an electron.

**Linear Dispersion**

The separation of different wavelengths caused by the grating, expressed as the derivative $\frac{dx}{dg}$, where:

- $x =$ distance along the spectrum
- $g =$ wavelength

Linear dispersion is usually expressed as mm/nm.

**Linear Dynamic Range**

The concentration range over which the calibration graph is linear. In AA, this range can extend to $10^2$–$10^3$.

**Magnetic Sensitivity Ratio (MSR)**

The ratio of the Zeeman absorbance to the normal absorbance expressed as a percentage. This term defines the sensitivity loss when determining an analyte by Zeeman furnace AA (c.f. normal furnace AA). An MSR of 100 % indicates no sensitivity loss, whereas an MSR < 100 % indicates that there is some sensitivity loss. The MSR may be calculated for any element using this equation:

$$\text{MSR} = \frac{\text{Absorbance (Zeeman Background On) \times 100}}{\text{Absorbance (Zeeman Background Off)}}$$

**Matrix**

The major chemical components of a sample.
Matrix Matching
An analytical approach to counter matrix interferences in which the standards are prepared in the same matrix as the samples. By close physical matching of standards and samples, physical interferences can often be eliminated or minimized.

Matrix Interference
Interferences of a non-spectral nature which are caused by differences between the sample matrix and that of the standards. These interferences can occur if the samples are very viscous or if they have a significantly different surface tension characteristics to the standards.

Maximum Absorbance
The maximum absorbance is the maximum peak height Zeeman absorbance which can be used for that analyte at that wavelength. All measurements must be below this maximum peak absorbance to avoid calibration roll over. An error message is reported if the peak analytical signal exceeds the maximum absorbance for a particular analyte. Note that when peak area measurements are made, it is the peak height absorbance which is governed by the MAX ABS limit.

Monochromator
An optical device for isolating a narrow wavelength region of radiation from a spectrum.

Nebulizer
A device for nebulization of a liquid—i.e. the process that converts a liquid into an aerosol.

Precision
The reproducibility of a series of measurements often expressed as the % RSD (Relative Standard Deviation) or the Standard Deviation (SD). Alternatively, it can also be expressed as the percent Coefficient of Variation (CV). The precision is affected by the manner in which the absorbance measurements are taken and is dependent on the care with which standards and sample solutions are prepared and the stability of the optical system. In graphite furnace AA, the precision can also be influenced by the care taken in injecting the solutions, and by the selection of the correct program parameters.

Reagent Blank
A solution that does not contain any added analyte. This solution is usually prepared in the same matrix as the samples and so represents the contamination from the reagents used.

Reciprocal Linear Dispersion
This is a measure of the resolution of the complete optical efficiency of the monochromator. A smaller number for the RLD indicates better light throughput. But RLD is really more relevant for techniques which deal with complex emission spectra, like ICP-AES. The RLD is wavelength dependent and is usually expressed as nm/mm.
Resolution
A measure of the ability of a spectrometer to separate or isolate two adjacent wavelengths. This term usually indicates the smallest difference between two adjacent wavelengths which can be distinguished from one another.

% RSD
The % Relative Standard Deviation is a measure of the precision of measurement (or how reproducible the result is) when multiple replicate readings are made on a given sample. The % RSD is directly related to the Standard Deviation (SD) by the following formula:

\[ \% \text{ RSD} = \left( \frac{\text{Standard Deviation} \times 100}{\text{Mean Absorbance}} \right) \]

Spectrometer
An optical instrument used to separate, isolate and measure light according to wavelength.

Spectral Interference
An interference caused by incomplete resolution of the analytical line from other lines overlapping the measurement wavelength. This may change the measured absorbance and give an error in the measurement.

Spray Chamber
A device positioned between a nebulizer and the atomizer which filters the large droplets from the aerosol and promotes intimate mixing of the aerosol with the gas.

Standard Additions
In this calibration method, physical and chemical mismatch between samples and standards are minimized because the standards are matrix matched and prepared from the actual sample. This helps to correct for interference effects, where these can not be removed by other means such as chemical modification.

Standard Deviation
The standard deviation is a statistical calculation which determines the maximum variation over a series of measurements. The standard deviation may be calculated from the following formula:

\[ SD = \sqrt{\sum \frac{(Abs - \overline{Abs})^2}{n-1}} \]

where \( n \) = number of replicates

Standard Solution
A solution with an accurately known concentration of analyte used for calibrating an instrument.
Stray Light
Radiant energy that reaches the detector from wavelengths other than that indicated by the monochromator setting.

Structured Background
Molecules which have complex spectra containing many sharp peaks are said to be 'structured'. The peaks are usually produced by rotational and vibrational excitations within the molecule. If the structured background is not co-incident with the analytical wavelength, deuterium lamp background correctors measure the absorption as an average value across the slit width, causing over correction. Under correction may also occur if the sharp background peaks are coincident with the analyte wavelength.

Working Range
This is the concentration range for the particular analyte over which an accurate determination can be made. It ranges typically from about 10 times the detection limit to a maximum of about 1.0 absorbance. Useful measurements can be made outside this range. However, precisions may be degraded at very low absorbances unless longer integration times are used.

Bibliography and Further Reading
These references are provided as a guide to source general information about the AA technique for further reading, or to advise customers where to source further information:
Mavrodineanu, R and Boiteux, H., Flame Spectroscopy, John Wiley and Sons.

References
For example: US Patent No. Re. 32, 022