Atomic absorption spectrometry (AAS) is based on the absorption of element-specific primary source radiation by analyte atoms. If part of the radiation is absorbed by molecules or lost owing to scattering, a higher gross absorbance is measured. The difference between the net absorption of the analyte atoms and the measured gross absorbance is called background absorbance. Background absorption and scattering effects have much more serious effects on the results produced in electrothermal atomic absorption spectrometry (ETAAS) than flame atomic absorption spectrometry (FAAS).

The amount of incident light deflected or absorbed by nonatomic species must be measured to obtain the correct net absorbance of the analyte atoms only. Perfect background correction (BC) can be obtained only when the background absorbance measurement corresponds exactly in space, time, and wavelength with the atomic absorbance measurement. Since exact coincidence of all three parameters is obviously impossible, it is customary to give priority to the equality in space and to make the difference in time and/or wavelength as small as possible. Although molecular absorption and radiation scattering are both broadband phenomena, there is no spectral range where constant background attenuation can be guaranteed.

In all BC systems, two measurements are made. The total or gross absorbance is measured at the wavelength of the atomic absorption line, and the background attenuation is then subtracted to obtain the analyte absorbance. There are several ways in which the nonatomic absorption at the resonance wavelength can be estimated, including continuum-source (CS) or deuterium-lamp (D$_2$-lamp) BC, Zeeman-effect BC, and pulsed-lamp or Smith–Hieftje BC correction methods. The principle of each method, the instrumentation, and applications are discussed. D$_2$-lamp BC is widely used in FAAS and ETAAS. Pulsed-lamp BC is sometimes used in FAAS but more often in ETAAS. Zeeman-effect BC is only used in ETAAS.

1 INTRODUCTION

AAS is based on the absorption of element-specific primary source radiation by analyte atoms. If part of the radiation is absorbed by molecules or lost owing to scattering, a higher gross absorbance is measured. The difference between the net absorption of the analyte atoms and the measured gross absorbance is called background absorbance. In fact, we do not know which part of the background absorbance arises from scattering and which part is due to molecular absorption.

Scattering of primary source radiation from nonvolatile particles much smaller than the wavelength ($\lambda$)
follows Rayleigh’s law. The intensity of the scattering depends on the wavelength as $\lambda^{-4}$, so that short wavelengths are scattered more than long wavelengths. Scattering is directly proportional to the number of scattering particles per unit volume and to the square of the particle size. Consequently, radiation scattering occurs more strongly with increasing particle size. In FAAS, well-designed nebulizers and spray chambers are used and therefore, virtually, no unvolatilized particles pass into the optical beam. The flame is transparent for wavelengths $>230\,\text{nm}$ but scattering of radiation and absorption is observed below $230\,\text{nm}$ (Figure 1). The flame contains oxygen and hydrogen and therefore absorption by diatomic molecular species such as OH, NH, and NO is observed at specific wavelength positions.\(^{(1)}\) The reduced transparency of the flame contributes to increased noise, and adequate BC is needed when analyte absorption lines are located close to such molecular absorption bands.

In ETAAS, considerable numbers of particles can be observed. They may arise from organic sample materials during the pyrolysis step or from volatilized inorganic materials that condense in the cooler parts of the atomizer. Small solid particles can also appear owing to boiling, sputtering, and incomplete vaporization. Broadband molecular absorption of radiation is caused by molecular species formed or vaporized in the atomizer during the atomization step, particularly alkali and alkaline earth halides. Sharp fine structure of the vibrational bands in electronic spectra of the molecules can be superimposed on broadband background absorption.

The effects of molecular absorption in FAAS have long been recognized. The CaOH\(^+\) band has a maximum near the barium resonance line at 553.6 nm. Molecular absorption spectra of a number of halides, nitrates, and sulfates have also been reported. Molecular absorption by diatomic molecules with high dissociation energy, such as CS or PO, is quite common when atomization takes place in a graphite furnace. As an example, Figure 2 shows the molecular absorption spectrum resulting from vaporization of magnesium sulfate in a graphite furnace.\(^{(2)}\) Massmann and Gücer\(^{(3)}\) measured spectra resulting from the CN system with band heads at 386.2, 387.1, and 388.3 nm using nitrogen as the inert gas in ETAAS. Background absorption and scattering effects have much more serious effects on the results produced in ETAAS than in FAAS and therefore appropriate BC should always be applied in AAS when a graphite furnace is used for atomization.

The amount of incident light deflected or absorbed by nonatomic species must be measured to obtain the correct, net absorbance of the analyte atoms only. In electrothermal atomization, the spatial and temporal distribution of the atoms and the background-generating species may be entirely different.\(^{(4)}\) Perfect BC can be obtained only when the background absorbance measurement corresponds exactly in space, time, and wavelength with the atomic absorbance measurement.
Since exact coincidence of all three parameters is obviously impossible, it is customary to give priority to the equality in space and to make the difference in time and/or wavelength as small as possible. Although molecular absorption and radiation scattering are both broadband phenomena, there is no spectral range where constant background attenuation can be guaranteed.

In all BC systems, two measurements are made. The total or gross absorbance \( A_{\text{measured}} \) of the atoms and the nonatomic species is measured at the wavelength of the resonance line emitted by the hollow cathode lamp (HCL). The background attenuation \( A_{\text{bg}} \) is then subtracted from the measured absorbance to obtain the analyte absorbance \( A_{\text{analyte}} \) (Equation 1)

\[
A_{\text{analyte}} = A_{\text{measured}} - A_{\text{bg}} \tag{1}
\]

There are several ways in which the nonatomic absorption at the resonance wavelength can be estimated.

2 DEUTERIUM-LAMP BACKGROUND CORRECTION

2.1 Brief History of Background Correction

The first BC method was proposed by Willis\(^5\), in which a nonresonant analyte line emitted by the source that is not absorbed by the analyte is used to measure the nonspecific absorption in the vicinity of the analyte absorption wavelength. In the two-line BC method, argon or neon lines can also be used. Alternatively, another source emitting radiation of an element that is not found in the sample, can be inserted for the background measurement. The background spectral character must be known to be the same at the second line as it is at the primary line, and therefore, the closer the second line is to the primary line, the better will be the correction. These conditions cannot be met for all elements and all matrices. In some wavelength regions, the steep slope of molecular absorption bands makes it difficult to find a nonabsorbing line close enough to the analyte line to ensure accurate BC. Two-line BC went into practice earlier than the other methods but it has not widely been used.

To improve the sensitivity of FAAS, Koirtyohann and Pickett\(^6\) used a 40-cm long, 10-mm i.d. tube that was heated in a hydrogen–oxygen flame, providing a much longer effective absorption path than was previously used in the more conventional burners. They observed that, at higher sensitivities, absorption by matrix salts at the wavelength of an elemental resonance line can cause significant errors, and proposed to use a hydrogen lamp to correct for matrix absorption. In fact, this BC system is still widely used to correct for background absorption in FAAS and ETAAS.

2.2 Principle of Deuterium-lamp Background Correction

The gross absorbance \( A_{\text{measured}} \) is the sum of the atomic absorbance of the analyte atoms \( A_{\text{analyte}} \) and the background attenuation \( A_{\text{bg}} \). The gross absorbance is measured with the narrow HCL emission line of the element at the selected specific wavelength of the resonance line. An estimate of the background absorbance is obtained as an average over the spectral band-pass of the monochromator using a CS of radiation, e.g. a hydrogen lamp or D\(_2\)-lamp in the ultraviolet (UV) wavelength region or a tungsten-halogen lamp in the visible part of the spectrum. The width of the atomic absorption line is about 100 times smaller than the band-pass of the monochromator, so that the analyte absorption of the CS radiation can be neglected.

2.3 Instrumentation

For the correction of background attenuation, Koirtyohann and Pickett\(^6\) used a dual-channel system in which the radiation from an HCL was passed alternately with the radiation of a continuum hydrogen lamp through the flame. Nowadays, a D\(_2\)-lamp is most frequently used as the CS. Figure 3 shows the basic schematic configuration of a D\(_2\)-lamp BC system for FAAS. By using lamp pulsation or by means of a rotating chopper with a sector mirror, the radiation from the HCL with intensity \( I_{\text{HCL}}^0 \) and the radiation from the D\(_2\)-lamp with intensity \( I_{\text{D2}}^0 \) is passed alternately through the atomizer. After passing the monochromator, both radiation beams reach the same detector and the net atomic absorbance is derived.

The operation of the D\(_2\)-lamp BC system is explained in Figure 4(a–f). The monochromator separates the resonance line from the emission spectrum of the element-specific HCL. The width of this line is a few picometers. From the D\(_2\)-lamp emission spectrum, the monochromator isolates a band equivalent to the spectral band-pass, usually 0.2–1 nm. The primary

![Figure 3 Schematic configuration of a D\(_2\)-lamp BC system. Radiation from the HCL (\( I_{\text{HCL}}^0 \)) is passed alternately with radiation from the D\(_2\)-lamp (\( I_{\text{D2}}^0 \)).](image)
Figure 4 Mode of operation of a D₂-lamp BC system. (a) The line emission spectrum of the HCL and the continuum emitted by the D₂-lamp. (b) The monochromator isolates the resonance line from the spectrum of the HCL and passes a band of radiation from the D₂-lamp corresponding with the spectral band-pass. (c) The intensities \( I_{\text{HCL}}^0 \) and \( I_{\text{D₂}}^0 \) are equalized. (d) For atomic absorption by the analyte element, \( I_{\text{HCL}}^0 \) is attenuated by an amount corresponding to its concentration, whereas \( I_{\text{D₂}}^0 \) is not significantly attenuated. (e) Broadband background attenuates the intensity of both sources to the same degree. (f) Atomic absorption by the analyte in addition to the background attenuates the HCL intensity further as in (d), whereas the D₂-lamp intensity is not further attenuated. (Reproduced with permission from Wiley-VCH from Ref. 7.)

intensities of the two beams of radiation are equalized to obtain \( I_{\text{HCL}}^0 = I_{\text{D₂}}^0 \). When analyte atoms absorb HCL radiation, the intensity \( I_{\text{HCL}}^0 \) decreases with an amount corresponding to the atom concentration. Naturally, \( I_{\text{D₂}}^0 \) is also attenuated at the resonance wavelength, but since the half-width of the atomic absorption line is about 5 pm, whereas the continuum has a width equal to the spectral band-pass of 0.2–1 nm, the absorption of continuum radiation by the analyte atoms can be neglected. If nonspecific attenuation of the radiation occurs, whether through scattering or molecular absorption, both radiation beams will be attenuated to the same extent because background attenuation is usually a broadband phenomenon. In D₂-lamp BC, it is assumed that the background is constant over the observed spectral range, i.e. the attenuation of \( I_{\text{D₂}}^0 \) is measured as the average over the spectral band-pass and used for BC at the wavelength position of the analyte absorption line. If the background attenuation is not continuous within the observed spectral range, positive or negative BC errors will occur.

The two lamps are observed by the detector alternately in time. Instrument electronics separate the signals and compare the absorbances from both sources. A net absorbance will be displayed only when the absorbance of the two lamps differs. Since the continuous background attenuates both sources equally, it is ignored. Analyte atoms absorb the HCL radiation and negligibly absorb the broadband CS emission, and it is therefore still measured and displayed as usual without BC. Most modern AAS instruments permit almost simultaneous measurement of the uncorrected signal or background signal and the corrected signal. The speed of the BC system should be high enough to follow the fast transient signals in ETAAS (see Section 6.2).

BC with a CS has some disadvantages. The alignment and superposition of the HCL or electrodeless discharge lamp (EDL) and the CS are critical. The lamps are located at different positions in the instrument, the shape of the beams is different, and the intensity distribution in the beams is not the same. Even if it is possible to align the beams exactly, different absorption volumes may be irradiated. The application of two light beams requires a more complicated optical system. In many instruments, double-beam operation is available to compensate for intensity changes of the lamps. The D₂-lamp emits sufficient radiation in the short wavelength range from 190 to 330 nm, whereas a halogen lamp is used for BC above this range. In general, the signal-to-noise ratio (S/N) is worsened through the use of two radiation sources and a more complicated optical system is used to measure their intensities. If a D₂-lamp is used outside its optimum range, the radiant intensity of the line source must be reduced, leading to further deterioration of the S/N. Finally, it should be noted that the principle of operation of D₂-lamp BC limits...
its successful use to continuous background absorption only.

2.4 Analytical Performance and Applications

Many commercial AAS instruments are based on D\textsubscript{2}-lamp BC. In FAAS and hydride generation AAS, it is the most widely applied BC system. It is fully adequate for all applications of FAAS, except in some very unusual circumstances. During methods development, BC is considered. In many FAAS applications, there is no need to use BC at all. In general, in the lower UV wavelength region (<230 nm), BC is required for compensation of scattering and absorption by the flame.

BC systems employing CSs are incapable of correcting background attenuation caused by electronic excitation spectra because these comprise many narrow lines. The actual BC that is required depends on the degree of overlap between the elemental spectral line and individual molecular rotational lines. An example is the absorption line of Au at 267.6 nm, which lies exactly in the middle between two rotational lines of indium chloride so that the actual background attenuation is much lower than the mean background absorbance found over the spectral range. Several molecular absorption spectra have been studied in the vicinity of atomic absorption lines.\(^{1,8}\) Interferences have been reported for the determination of Bi at 306.8 nm and Mg at 285.2 nm through absorption bands of OH in an air–acetylene flame and also for Fe at 247.3 nm, Pd at 244.8 and 247.6 nm, and Yb at 246.4 nm owing to PO molecular absorption.\(^{8}\) Many of the possible interferences are very unlikely to be serious in FAAS. Although problems with D\textsubscript{2}-lamp BC in FAAS seldom occur, CS BC is not free from pitfalls. The limited energy of the D\textsubscript{2}-lamp lowers the S/N and the correction becomes inaccurate when the background is structured.

In the graphite furnace, the amount of matrix is typically much larger relative to the analyte and interferences can be more severe. Spectral interference in ETAAS with D\textsubscript{2}-lamp BC may result from atomic absorption of the ČS radiation by massive amounts of metals in the matrix, usually at secondary absorption lines of these elements. Probably, the first identified example of this type of BC error has been reported by Manning, for the determination of Se at the 196-nm line in the presence of iron.\(^{9}\) Potential interferences of this type can be predicted based on the wavelengths of atomic absorption lines. However, during method development, much time and effort are usually spent in obtaining an acceptable program for heating of the graphite furnace, and the application of chemical modifiers is also considered. Owing to the improved graphite furnace design, the optimization of the temperature program, and the application of chemical modifiers, potential interferences, and BC errors are not always found in real analysis.

BC errors are hard to identify when the background absorbance takes place simultaneously with the atomic absorption. If there is some time delay between the two processes, a positive or negative disruption of the baseline may be observed just before the atomic absorption starts or just after the atomic absorption is finished. It should be noted that the method of standard additions does not control BC errors.

Most ETAAS users distrust their results when the background level exceeds 0.5 absorbance unit. The limitations are probably related to the different geometry and possible misalignment of the optical beams of the HCL and the D\textsubscript{2}-lamp. The increasing interest in ETAAS as a selective and highly sensitive analytical method has stimulated the development of improved BC systems.

3 ZEEMAN-EFFECT BACKGROUND CORRECTION

3.1 Zeeman Effect

In 1897, the Dutch physicist Pieter Zeeman\(^{10}\) (Figure 5) reported the observation that if a source of light is placed between the poles of a magnet, the lines appear to broaden and, if the magnetic field is strong enough and the resolving power of the spectroscope is sufficiently high, they appear to be split into a number of components. The first splitting patterns studied by Zeeman follow from lines of singlet series. A single line was split into three polarized components.

Both splitting and polarization were explained by Lorentz with the classical electromagnetic theory. A few years later, it was demonstrated that the lines of other series do not split into the simple triplet but to a group of four or more components. The classical theory was unable to account for this. Therefore, the two types of splitting were labeled the normal and the anomalous Zeeman effects. An example of the normal Zeeman effect is presented in Figure 6. Figure 6(a) refers to the normal Zeeman effect, and Figure 6(b) shows an example of the anomalous Zeeman effect.\(^{11}\) The splitting pattern is always symmetrical around the position of the nondisplaced line. The components polarized parallel to the magnetic field are referred to as π-components, and the components polarized perpendicular to the magnetic field are referred to as σ-components (σ deriving from the German senkrecht). In the case of a normal Zeeman triplet, the π-component is located at the position of the original line at frequency ν, and two σ-components...
Dr Pieter Zeeman (1865–1943). Dutch physicist, who discovered the influence of a magnetic field on radiation in 1896.

are found at frequencies \( \nu \pm \Delta \nu \). Such a Zeeman splitting is observed from the direction perpendicular to the magnetic field (transverse Zeeman effect). In the direction of the magnetic field, the central component is not observed, whereas the two displaced components are circularly polarized and rotate in opposite directions (longitudinal Zeeman effect). Lines that do not belong to a singlet series split into more than three components. Their pattern is always symmetrical with respect to the position of the original line, with a central group of \( \pi \)-components and groups of \( \sigma \)-components on either side as illustrated in Figure 6(b) for a \( ^2S_{1/2} \rightarrow ^2P_{3/2} \) transition. All Zeeman splitting patterns are observed in absorption as well as in emission.

The sum of the intensities of the \( \pi \)-components is equal to the sum of the intensities of the \( \sigma \)-components, and if the various components are combined, the resulting beam is nonpolarized and the intensity is equal to the intensity observed without the magnetic field. The energy states generated around an original energy level \( E^0 \) are described by Equation (2)

\[
E = E^0 + \mu_B B M_J \tilde{g}
\]  

Figure 5 Dr Pieter Zeeman (1865–1943). Dutch physicist, who discovered the influence of a magnetic field on radiation in 1896.

Figure 6 Magnetic splitting of atomic energy levels and the corresponding Zeeman splitting patterns. (a) \( ^1S_0 \rightarrow ^1P_1 \) transition, normal Zeeman effect; (b) \( ^2S_{1/2} \rightarrow ^2P_{3/2} \) transition, anomalous Zeeman effect. (Reprinted from Ref. 11. Copyright with permission from Elsevier Science, 1985.)
BACKGROUND CORRECTION METHODS IN ATOMIC ABSORPTION SPECTROMETRY

3.2 Principle of Zeeman-effect Background Correction

In AAS, the nonshifted or slightly shifted π-components are used to measure the total absorbance of the analyte atoms and the background, whereas the shift of the (groups of) σ-components from the original line position is used to measure the background absorbance. Figure 8(a) shows the resonance line emitted by the HCL and the absorption line of the atoms in the graphite furnace at zero magnetic field strength. Note that the width of the absorption line is about twice the width of the lamp emission line owing to the higher temperature and higher pressure in the atomizer compared to those in the HCL.

Figure 8(b) shows the situation where the graphite furnace is in a transverse magnetic field of 1 T. Absorption takes place within the π-components of the absorption line profile \( k^a \), whereas the σ-components of the absorption line profile \( k^b \) are shifted away to wavelengths \( \lambda_1 \) and \( \lambda_2 \). When a π-component-rejecting polarizer is positioned in the optical beam and when the magnetic field is switched on and off at high enough frequency, e.g. a 50 Hz alternating current (AC) magnetic field, the gross absorbance and the background absorbance can be measured alternately. The net analyte absorbance follows then from Equation (1). The background absorbance \( k^b \) is measured exactly at the wavelength of the analyte resonance line \( \lambda_a \) and within the width of the HCL emission line profile. Consequently, the background absorbance is measured correctly for any type of background, even if it is highly structured. The alternative approach is to use a constant magnetic field from a permanent magnet or a direct current (DC) magnet and to rotate the polarizer to permit alternate measurements with π-polarized radiation and σ-polarized radiation.

The π-polarized radiation is then absorbed by the σ-component of the analyte absorption line profile \( k^a \), and the background \( k^b \), providing the gross absorbance. The σ-polarized radiation is absorbed by the background only because the σ-components of the analyte absorption line profile are shifted to wavelengths \( \lambda_1 \) and \( \lambda_2 \), and they are too far away to absorb the lamp emission line. Combination of the two measurements again provides the net analyte absorbance.

Another possibility is to use a longitudinal magnetic field rather than a transverse magnetic field. Figure 8(c) shows that in the direction of the magnetic field, only the circularly polarized π-components of the analyte absorption line profile \( k^a \) and \( k^b \) are observed. In a longitudinal AC-modulated magnetic field, the gross absorbance is measured at zero field (see Figure 8(a)) and the absorbance of the background is measured at exactly the wavelength of the lamp emission line during the magnet on period. A longitudinal AC Zeeman-effect BC system does not require a polarizer and therefore the full intensity of the HCL resonance emission line can be used in both measurements.

In all AAS instruments using Zeeman-effect BC, two alternate intensity measurements are performed. One refers to the unshifted zero-field analyte absorption line (in an AC field) or the slightly shifted and broadened π-components (in a constant field). The intensity is given by Equation (3)

\[
I_1 = I_0^1 \exp(-k_1^a) \exp(-k_1^b)
\]

where \( I_0^1 \) is the incident intensity, \( k_1^a \) is the absorption coefficient of the background, and \( k_1^b \) is the analyte absorption coefficient. The other measurement refers to the situation when the σ-components are shifted away from the original line position (AC field) or when σ-polarized radiation is used (constant field). The intensity is given by Equation (4)

\[
I_2 = I_0^2 \exp(-k_2^a) \exp(-k_2^b)
\]

where \( I_0^2 \) is the incident intensity, \( k_2^a \) is the absorption coefficient of the background, and \( k_2^b \) is the...
remaining analyte absorption coefficient of the shifted \(\sigma\)-components, which should be close to zero. A simple subtraction of the absorbances measured in both situations corresponds to taking the log ratio of the intensities (Equation 5).

\[
\ln\left(\frac{I_2}{I_1}\right) = \ln\left(\frac{I_0^2}{I_0^1}\right) + (k_a^1 - k_a^2) + (k_b^1 - k_b^2) \quad (5)
\]

This expression forms the basis for all Zeeman-effect BC systems in AAS. When the incident intensities \(I_0^1\) and \(I_0^2\) are equal and when the same background attenuation is measured, the net analyte absorption follows from Equation (6)

\[
A = \log\left(\frac{I_2}{I_1}\right) = 0.43(k_a^1 - k_a^2)\gamma N_A \quad (6)
\]

It is clear that a linear analytical response proportional to the number of analyte atoms \(N_A\) is obtained. The assumption that \(I_0^1\) is equal to \(I_0^2\) is quite reasonable because it is the same beam of radiation in case of

---

Figure 7  Classification of Zeeman patterns for spectral lines of various elements. *indicates lines most frequently used in AAS. 10 Å = 1 nm. (Reprinted from Ref. 12. Copyright with permission from Elsevier Science, 1976.).

---

This article is © 2013 John Wiley & Sons, Ltd. This article was published in the Encyclopedia of Analytical Chemistry in 2013 by John Wiley & Sons, Ltd. DOI: 10.1002/9780470027318.a5104.pub2
the AC magnetic field or the π-polarized and the σ-polarized parts of the same beam in case of the constant magnetic field. The background absorbance is measured within the analyte emission line profile in all Zeeman-effect BC systems with the magnetic field applied to the atomizer. The only requirement is that the background is not influenced by the magnetic field when an AC magnet is used, which is usually the case (see Section 3.4). From Equation (6), it can be concluded that the σ-components in the Zeeman splitting pattern should be shifted as far away as possible from the original line position to reduce $k_a^2$ to a minimum, i.e. a strong magnetic field should be applied, especially when the analyte absorption line is broad by nature or when its Zeeman splitting pattern is relatively narrow. In contrast, maximum sensitivity also requires that $k_a^1$ is large, i.e. close to the conventional AAS absorption coefficient. Optimum sensitivity is obtained when a strong AC magnetic field is used. If a constant magnetic field is applied, the optimum magnetic field strength compromises a large shift for the σ-components simultaneous with minimum shift in the π-components. Even at optimum field strength, the sensitivity is significantly reduced by about a factor of two for many of the analyte absorption lines that show the anomalous Zeeman effect. This explains why the AC-modulated magnetic field is preferred in many of the commercially available AAS instruments with Zeeman-effect BC.

In principle, Zeeman-effect BC systems can have the magnetic field either around the atomizer or around the primary source of radiation. When the primary source of radiation is in the magnetic field, σ-components of the lamp emission line are located at the wavelength positions $\lambda_1$ and $\lambda_2$. These lines are then used to measure the background absorbance at both sides of the analyte atomic absorption line. Equations (3–6) apply also to this situation.

### 3.3 Instrumentation

The application of the Zeeman effect for BC in AAS was proposed by Prügger and Torge\(^{(13)}\) in 1969. The authors claimed that a shift of the primary source resonance line of about 10 pm is required to allow successive measurements of the gross AAS signal and the background absorbance and to propose a system based on magnetic splitting of the source line in a DC or AC magnetic field. However, AAS instruments based on this type of Zeeman-effect BC have not been developed. The main reason is that the HCLs and EDLs traditionally used in AAS do not fit into the gap of a magnet that has to provide a magnetic field strength
close to 1 T at reasonable size, power requirements, and price. Specially designed lamps are required for stable operation in a magnetic field.

The more useful alternative is to apply the magnetic field to the atomizer, as discussed in the previous section. This approach has been followed by Koizumi and coworkers incorporating a 1.1-T permanent magnet around a metal atomizer or a graphite furnace atomizer respectively.\(^\text{[12,14]}\) The plane of polarization is rotated at 100 Hz to provide for BC, whereas the intensity of the HCL radiation is modulated at 1.5 kHz to eliminate the signal caused by emission of radiation from the atomizer. Several laboratories have built and tested ETAAS instruments with Zeeman-effect BC\(^\text{[15–18]}\) and since that time, instrument companies have marketed ETAAS instruments with Zeeman-effect BC. Only one FAAS instrument has become available, with a 0.95-T field of a permanent magnet applied to a conventional 10-cm burner.\(^\text{[19]}\) The Zeeman-effect BC system for FAAS is complicated and, in general, there is no need for it.

The transverse Zeeman-effect BC system presented in Figure 9(a) is marketed by various manufacturers and most of them use an AC-modulated magnetic field of 0.8–1.0 T in combination with a fixed polarizer to reject \(\pi\)-polarized radiation and transmit only \(\sigma\)-polarized radiation. The longitudinal Zeeman-effect BC system presented in Figure 9(b) has been described by Liddell and Brodie,\(^\text{[17]}\) De Loos-Vollebregt et al.,\(^\text{[20]}\) and Shuttler\(^\text{[21]}\) and is also commercially available. A transverse heated atomizer is placed in the longitudinal magnetic field and there is no polarizer in the optical system (see Section 3.2). This gives a considerable improvement in light throughput and simplifies the optical system so that detection limits are lower although the length of the graphite furnace is somewhat compromised. The tube has to fit in the gap of the magnet and the optical beam has to pass through holes drilled in the core of the magnet.

3.4 Analytical Performance and Applications

Zeeman-effect BC is nowadays widely used in ETAAS. The BC is performed exactly at the wavelength of the analyte atomic absorption line. High non-specific absorbance (up to about two) can be corrected and in the AC Zeeman system, sensitivities are similar to those obtained in conventional AAS. Nevertheless, there are a few elements that show somewhat reduced sensitivity because their lines are relatively broad and/or the Zeeman splitting pattern is relatively narrow. An overview of the early applications of Zeeman-effect BC shows that a wide variety of elements have been measured in different samples and certified reference materials,\(^\text{[11]}\) and in recent years, many applications followed. The relatively volatile elements, e.g. Pb and Cd, have been measured by many analytical chemists using ETAAS with Zeeman-effect BC. This is not surprising because in the determination of volatile elements, the pyrolysis temperature is not high enough to remove most of the matrix compounds that are responsible for the background absorption during atomization. Pb and Cd are often determined in a rather difficult matrix, such as blood and urine, and the low concentrations of the analyte elements do not permit dilution of the samples. The results obtained with Zeeman-effect BC have been compared with those obtained with \(\text{D}_2\)-lamp BC, looking at the baseline of the net AAS signals. Zeeman-effect BC is often superior, although a fair comparison would require that the same atomizer and atomization conditions are used. There are an increasing number of solid sampling applications where the Zeeman-effect BC system is the key to success.

In general, the dynamic range is slightly limited when Zeeman-effect BC is used. In a strong magnetic field, the \(\sigma\)-components are shifted almost completely away from the absorption line profile so that, according to Equation (6), the shape of the AC Zeeman AAS analytical curve is completely determined by the zero-field absorbance. The analytical curve will therefore be very similar to the corresponding conventional AAS analytical curve measured without BC. The relatively small contribution of the \(\sigma\)-components to the measurement of the background has only a minor influence on the slope and the curvature of the AC

**Figure 9** Schematic diagrams of different Zeeman-effect BC systems for AAS. (a) Transverse magnetic field, i.e. the magnetic field is perpendicular to the optical axis of the spectrometer. The polarizer provides alternately \(\pi\)- and \(\sigma\)-polarized radiation if the magnetic field is constant, or transmits only \(\sigma\)-polarized radiation if an AC-modulated magnetic field is applied. (b) Longitudinal magnetic field oriented parallel to the optical axis of the spectrometer. No polarizer is required in this configuration.
Zeeman AAS analytical curve. This is equally valid for the normal Zeeman effect and the anomalous Zeeman effect. The same is essentially true when a constant magnetic field is used as long as the spectral line displays a normal Zeeman effect. For the majority of the transitions that show an anomalous Zeeman effect, the splitting in the $\pi$-components broadens the absorption line profile and therefore the linearity of the Zeeman AAS analytical curve is somewhat improved, although the slope is lower.

At very high analyte concentrations, all the ETAAS signals show a dip (see Figure 10) when Zeeman-effect BC is applied, which can be explained from the phenomenon that is known as roll-over. From the very early days when Zeeman-effect BC was used, rumors were around that the analytical curve first increases, then reaches the maximum absorption level at relatively high analyte concentration, and beyond the maximum, decreases again toward the concentration axis. Such a double-valued behavior has indeed been reported for FAAS systems with Zeeman-effect BC.\(^\text{(19)}\) From a theoretical analysis of the roll-over phenomenon,\(^\text{(11)}\) it became clear that the nonabsorbed radiation that is emitted by the primary source and reaches the detector is responsible for this. With increasing analyte concentration, the zero-field absorbance or $\pi$-component absorbance, $k'^1$, in Equation (6), increases much more rapidly than the $\sigma$-component absorbance, $k'^2$. With increasing analyte concentration, the $k'^1$ curve levels off. The $\sigma$-component absorbance is subject to the same curvature, but at much higher concentration. At a certain concentration, a situation is reached where the $k'^1$ and $k'^2$ curves show the same rate of increase, or equal derivative with respect to concentration. At that concentration, the difference signal according to Equation (6) shows a zero slope, i.e. the analytical curve reaches a maximum. Thereafter, a FAAS analytical curve would bend back to the concentration axis. The absorbance and concentration of roll-over are indicated in Figure 10, where the dotted line illustrates the decreasing absorbance values.

Figure 10 Analytical curve for Cu 324.8 nm measured in ETAAS with Zeeman-effect BC at magnetic field strength 0.8 T. The peak absorbance reaches a maximum at high analyte concentration, whereas the integrated absorbance increases slowly beyond the roll-over absorbance.

Zeeman-effect BC systems allow the extension of the analytical curve by taking measurements at three different field strengths, i.e. zero, intermediate, and maximum field strength.\(^\text{(23,24)}\) The analytical curves derived from three-field measurements allow the sensitivity to be decreased so that high analyte concentrations otherwise measured by FAAS can be determined by ETAAS. The three-field operation provides up to about 10-fold extension of the dynamic range, which is advantageous for direct solid sampling ETAAS.

A few problems with Zeeman-effect BC have been reported. Molecules such as OH, NO, NO\(_2\), and SO\(_2\) indeed show a Zeeman effect. Therefore, the background measured in two different polarization planes (with constant magnetic field) or measured with and without a magnetic field present (with AC-modulated magnetic field) may differ.\(^\text{(22,25–27)}\) If matrix absorption lines or molecular bands very close to the analyte wavelength exhibit a Zeeman splitting, correction errors may occur. A matrix absorption line that does not overlap with the lamp emission line at zero-field strength may do so at maximum field strength or the other way around.\(^\text{(22)}\) Massmann\(^\text{(25)}\) reported a BC error for Zeeman-effect BC in FAAS from OH rotational lines at Bi 306.8 nm, using a DC magnetic field applied to the acetylene–air flame. However, in ETAAS, such OH interferences do not generally occur.
Wibetoe and Langmyhr\textsuperscript{(26)} systematically investigated spectral interferences and BC errors. They have surveyed atomic line tables to find pairs of elements that have contiguous lines, and found several cases of possible spectral interferences at recommended analyte wavelengths, e.g. the 459.4 nm Eu line (interference from V and Cs), the 247.6 nm Pb line (interference from Pb), and the 265.9 nm Pt line (interference from Eu).

Overcorrection problems for Pb caused by Zeeman splitting of the PO molecular absorption band has been discussed by Zong et al.\textsuperscript{(27)} Phosphate causes an overcorrection for Cd at the alternate 326.1 nm line. BC errors have also been reported for determination of Fe at the alternate 271.9 nm line in the presence of Pt and for determination of Hg at 253.6 nm in the presence of Co.\textsuperscript{(22,26)} The observed BC errors depend on the strength of the magnetic field and they can be diminished or avoided by optimization of the temperature program and modifier selection. Moreover, it should be noted that many listed interferences do not take place at the recommended analyte absorption line or only when the analyte is determined in a very unusual matrix.

4 PULSED-LAMP BACKGROUND CORRECTION

4.1 Principle

Ling\textsuperscript{(28)} first advanced the idea of BC based on the subtraction of the absorbances measured alternately with a normal lamp emission line and a broadened lamp emission profile showing a dip in the center. The author described a simple method to correct for nonatomic absorption in a portable mercury photometer that included two mercury vapor lamps emitting the mercury resonance line broadened to different extents. Smith and Hieftje\textsuperscript{(29)} proposed a method for BC in AAS based on the broadening, which occurs in an HCL emission line when the lamp is operated at very high currents. Under such conditions, the absorbance measured for a narrow atomic line is low, whereas the apparent absorbance caused by a broadband background contributor remains the same as when the lamp is operated at conventional current level. BC can therefore be effected by taking the difference in absorbances measured with the lamp operated at high and low currents. The so-called Smith–Hieftje BC system applies its correction very near the atomic line of interest.

4.2 Instrumentation

The HCL power supply and drive circuitry\textsuperscript{(29)} generate a 9-ms low-current pulse of 5–10 mA, followed by a 0.3-ms high current pulse of 200–300 mA, as presented in Figure 11(a). A total pulse cycle repetition time of 50 ms allows the atomic cloud generated in an HCL during the high-current mode to clear before measurement is made again in the low-current mode for a broad range of elements. Figure 11(b) presents the conventional lamp emission line profile observed at low lamp current and the broadened and self-reversed lamp emission line during the high-current operation of the lamp. It is clear that the narrow line profile emitted under low-current operation is affected equally by atomic absorption or a broadband spectral feature. In contrast, the broadened and self-reversed profile obtained at high current is affected by a broadband absorber or scatterer but there is not so much overlap with the atomic absorption line profile. Absorbances calculated under low- and high-current operation are subtracted to yield a difference value that is free of any broadband background contribution.

4.3 Analytical Performance and Applications

The pulsed-lamp BC method is equally applicable to FAAS, hydride generation AAS, and ETAAS. For effective operation, it is necessary to broaden appreciably the emission line of the element under investigation. However, the degree of broadening is different for each element and also depends on the peak current at which the HCL is driven. To achieve the desired degree of line broadening and line reversal while maintaining HCL
reliability and acceptable lifetime, a special design of the lamp modulation circuitry and optimum high lamp current adjustment for each element are required. The slope of the analytical curves is decreased to some extent when pulsed-HCL BC is applied. The measurement at high lamp current is intended to measure the background. Unfortunately, the broadening of the lamp emission line profile is limited and self-reversal is not complete. The remaining radiation in the central part of the lamp emission line profile is therefore absorbed by analyte atoms and the corresponding absorbance is subtracted from the gross absorbance together with the background. The loss of sensitivity ranges from about 13% for Cd to 84% for Hg.\(^{29}\) Similarly to the Zeeman-effect BC system, the analytical curves show roll-over at high analyte concentrations and ETAAS signals show a dip at very high analyte concentrations.\(^{30,31}\) The ability of the pulsed-HCL BC system to overcome background interferences in real samples has been demonstrated. Similarly to the Zeeman approach, the pulsed-lamp BC method requires only a single primary source of radiation and single beam optics so that optical alignment is simplified.

5 BACKGROUND CORRECTION IN HIGH-RESOLUTION CONTINUUM SOURCE ATOMIC ABSORPTION SPECTROMETRY

High-resolution continuum source atomic absorption spectrometry (HR-CS AAS) has been discussed in detail in High-resolution Continuum Source Atomic Absorption Spectrometry – Theory and Applications. The broadband spectral distribution of a CS conveniently permits observation of the background spectrum in the vicinity of the analyte absorption line. Correction for background with a flat spectral distribution is based on simultaneous intensity measurements outside the analysis line. The analyte atomic absorption is typically measured in 3–5 pixels of a linear charge-coupled device detector, at the position of the analysis line. Intensities measured at other selected pixels are used for BC but also for compensation of lamp fluctuations and emission of radiation from the atomizer. After correction for continuous background absorption, the spectrum may still be disturbed by nearby atomic absorption of concomitant elements or molecular absorption with rotational line structure. Such background may arise from the atomizer, e.g. the background absorption by OH, NH, and NO in FAAS (Figure 1). The interfering molecular spectrum can be measured with a blank flame and subtracted from the sample spectrum using a least-squares-based BC approach. Molecular absorption caused by the sample matrix or modifier is more common in ETAAS, e.g. molecular absorption by PO as discussed in Section 3.4 or SO\(_2\) (Figure 2). Only few diatomic molecules with relatively high dissociation energy have been observed during the atomization step. The CS, NO, and PO absorption spectrum can be created from H\(_2\)SO\(_4\), HNO\(_3\), and NH\(_4\)H\(_2\)PO\(_4\), respectively. The software should select the appropriate reference spectrum or combination of spectra. An example of correction for structured molecular background in HR-CS AAS is shown in Figure 12 for the determination of Sb in sediment reference material at the less-sensitive resonance line at 231.147 nm, using direct solid sampling and electrothermal atomization.\(^{32}\)

HR-CS AAS shares with the Zeeman-effect and pulsed-lamp BC correction systems the advantage of using only a single light source, so that lamp alignment is not so much of a problem as in the D\(_2\)-lamp BC method. The structured background is measured at the wavelength of the analysis line, although in a separate run using the spectrum of the appropriate interferent(s).

6 COMPARISON OF METHODS

6.1 Sensitivity and Dynamic Range

From the principle of D\(_2\)-lamp BC (Section 2.1), it is clear that the conventional AAS sensitivity is not influenced by the BC system. The additional measurement with the D\(_2\)-lamp provides the background absorbance and absorption in the vicinity of the analyte absorption line. The absorbance for each pixel is calculated as the difference between the measured intensity and the background intensity. The absorbance for each analyte line is calculated as the sum of the absorbances for all pixels. The absorbance is then converted to the concentration of the analyte using a calibration curve. The concentration of the analyte is then calculated as the sum of the absorbances for all analyte lines.

Figure 12 Time- and wavelength-resolved absorbance spectrum for NIST SRM 8704 Buffalo River Sediment in the vicinity of the Sb line at 231.147 nm after automatic correction of continuous background absorption. (Reproduced with permission from Ref. 32. Copyright 2009, Elsevier.)
the analyte atoms do not contribute significantly to the background signal because of their narrow absorption line profile.

In all Zeeman-effect BC systems, the measurement that is intended to provide the background absorbance is slightly influenced by the absorption of the analyte atoms owing to incomplete shift of the Zeeman $\sigma$-components away from the lamp emission line profile. The contribution of the remaining $\sigma$-components decreases the net analyte absorbance by about 10% for most elements and by up to 45% for a few elements (Cu, Be, Bi). A further decrease in sensitivity is observed in Zeeman-effect BC systems on the basis of a constant magnetic field from a permanent magnet or a DC magnetic field for all analyte absorption lines that show anomalous Zeeman splitting patterns. The sensitivity reduction is more severe when a central $\pi$-component is missing. The best Zeeman AAS sensitivity for all elements is obtained in a strong AC magnetic field, as nowadays used in most commercially available ETAAS instruments with Zeeman-effect BC.

Pulsed-lamp BC provides sensitivity close to conventional AAS for a few elements only. It is hard to achieve sufficient broadening and self-reversal in the lamp emission line profile during the high-current pulse. Similarly to Zeeman-effect BC, the contribution of the remaining part of the lamp line profile that is insufficiently shifted is subtracted from the gross absorbance together with the estimated background. The loss of sensitivity varies from 13% for Cd to 84% for Hg.\(^{(29)}\)

In HR-CS AAS, there is no influence of BC on the sensitivity. Correction for continuous background is derived from simultaneous measurements at correction pixels on both sides of the absorption line, whereas correction for structured background is based on subtraction of the reference spectrum of the interfering compound(s). Further explanation is found in High-resolution Continuum Source Atomic Absorption Spectrometry – Theory and Applications.

Additional analytical curves of reduced sensitivity can be obtained in AC Zeeman-effect BC by the three-field approach discussed in Section 3.4, whereas in HR-CS AAS, the sensitivity can also be selected between the sensitivity of conventional AAS and lower sensitivities by using selected pixels at the wings of the line profile. The various calibration graphs become available simultaneously.

The dynamic range of AAS is limited owing to the presence of a small amount of radiation from the HCL within the spectral band-pass, which cannot be absorbed by the analyte atoms. Starting from the detection limit, absorbance can be measured over about three orders of magnitude, i.e. from about 0.001 up to 1 absorbance unit. This range is not influenced by the D\(_2\)-lamp BC system. In Zeeman-effect and pulsed-lamp BC systems, the dynamic range is further limited owing to the roll-over phenomenon discussed in Section 3.4. The analytical curves in peak absorbance level off at somewhat lower absorbances than in conventional AAS, whereas the analytical curves in integrated absorbance continue to increase, slowly, up to very high analyte concentrations.

### 6.2 Frequency of Background Correction

BC systems involving sequential measurements of the gross absorbance and the background according to Equation (1) should operate fast enough to follow fluctuations in the background absorbance. In the D\(_2\)-lamp BC, this requires switching, at a certain frequency, between the HCL and the D\(_2\)-lamp. The frequency should be high enough to obtain a good estimate of the background at the time of the measurement of the gross absorbance. The nearest (temporally) measured background absorbance is subtracted from the gross absorbance. The background can also be estimated from two measurements, before and after the gross absorbance measurement, which are combined using bracketing techniques.\(^{(31)}\) In ETAAS, the atomic and background absorption signals may rise to a maximum in times ranging from 0.1 s or less to several seconds, depending on the furnace design, the heating rate, and the composition of the sample. The beam switching frequency should be high enough to enable the fastest rates of change of the atomic and background absorption signals to be followed. The upper limit to the chopping frequency follows from practical considerations, whereas HCLs can be pulsed up to very high frequencies. A high enough BC frequency of 200–400 Hz can easily be achieved.

In Zeeman-effect BC systems, the frequency is related to the modulation frequency of the AC magnetic field or the frequency of rotating the polarizer in the case of a constant magnetic field. In most of the instruments, the BC frequency is 50–100 Hz. It is complicated to rotate a polarizer at high speed and it is expensive to modulate an AC magnetic field at a frequency higher than the mains frequency. In the pulsed-lamp BC system, the HCL is pulsed repetitively with a cycle of 50 ms, but the actual time between low-current and high-current measurements is only 4.5 ms, indicating the temporal proximity of BC.\(^{(29)}\) Oppermann et al.\(^{(34)}\) described a high-speed self-reversal BC method using pulsed HCLs with a frequency of 100 Hz and lamp currents up to 600 mA. In all BC approaches, an increase in the operating frequency decreases the time available to measure the signals and consequently decreases the S/N.
6.3 Accuracy of Background Correction

The accuracy of the correction for background absorbance must be perfect up to high levels of background absorption. In the absence of analyte, the base line should be a straight line even at high background absorbance levels. Three conditions should be fulfilled to accomplish this. The background must be measured at the wavelength of the analyte absorption line or very close to the line. In the previous section, we have also seen that the transient ETAAS signal requires a good approximation of the background at the time of measurement of the gross absorbance signal. In addition, the background must be measured at the same position in the atomizer. This is easily achieved if only one source of radiation is used as in the Zeeman-effect BC system and the pulsed-lamp BC system. In D2-lamp BC, lamp alignment is always difficult because of the different positions of the lamps in the instrument, the different optical paths, the different geometries of the beams, and the different intensity distributions. Since the atomic vapor in both the flame and the graphite furnace is not truly homogeneous, nor is the radiant cross-section of either source, perfect matching is difficult.

Background absorbance in FAAS is usually low and it can be corrected easily with the D2-lamp BC system. In ETAAS, the D2-lamp BC system is often also successful. BC problems have been observed when the background is higher than about 0.5–1 absorbance unit, often owing to misalignment of the radiation beams. Many instruments are fitted with both a D2-lamp for the UV and a visible lamp for the visible wavelength region. The intensity of the D2-lamp is quite low when a low spectral band-pass is selected, which may be a limiting factor for the HCL intensity also because most instruments require more or less equal intensities of the two radiation beams. D2-lamp BC systems are not able to correct for structured background. The background is measured as an average background absorbance level over the spectral band-pass of the monochromator, i.e. within 0.2–2 nm. Numerous over- and undercorrections have been reported. Several of them are well known and can be found in textbooks on AAS; others are only observed under very special experimental conditions. Zeeman-effect BC systems, pulsed-lamp BC systems, and CS AAS instruments measure the background at exactly the wavelength position of the analyte absorption line or very close to the line, i.e. within an interval of 10 pm. Although perfect BC correction is not guaranteed, there is a better chance that the right background absorbance is measured at a wavelength position close to the absorption line in comparison to the average value over the full spectral band-pass. The Zeeman-effect BC system that applies the magnetic field to the atomizer is the only system that provides correction for the background exactly at the wavelength of the analyte absorption line. Even here, perfect BC is not guaranteed because, in a very few cases, the background may change with the strength of the magnetic field in AC Zeeman-effect BC systems (Section 3.4). Most of the errors reported for the D2-lamp BC system are not found when Zeeman-effect or pulsed-lamp BC is applied or when CS AAS is used. Finally, it should be noted that high background absorbance should be avoided when possible so as to minimize light losses and maintain the best S/N available.

ABBREVIATIONS AND ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>BC</td>
<td>Background Correction</td>
</tr>
<tr>
<td>CS</td>
<td>Continuum Source</td>
</tr>
<tr>
<td>CS AAS</td>
<td>Continuum Source Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>D2-Lamp</td>
<td>Deuterium Lamp</td>
</tr>
<tr>
<td>EDL</td>
<td>Electrodeless Discharge Lamp</td>
</tr>
<tr>
<td>ETAAS</td>
<td>Electrothermal Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>FAAS</td>
<td>Flame Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>HCL</td>
<td>Hollow Cathode Lamp</td>
</tr>
<tr>
<td>HR-CS AAS</td>
<td>High-resolution Continuum Source Atomic Absorption Spectrometry</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal-to-Noise Ratio</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
</tbody>
</table>

RELATED ARTICLES

Atomic Spectroscopy (Volume 11)
Atomic Spectroscopy: Introduction • Flame and Vapor Generation Atomic Absorption Spectrometry • Graphite Furnace Atomic Absorption Spectrometry

Clinical Chemistry (Volume 2)
Atomic Spectroscopy in Clinical Chemistry

Environment: Water and Waste (Volume 3)
Flame and Graphite Furnace Atomic Absorption Spectrometry in Environmental Analysis

Food (Volume 5)
Atomic Spectroscopy in Food Analysis

Steel and Related Materials (Volume 10)
Atomic Absorption and Emission Spectrometry, Solution-based in Iron and Steel Analysis
Modifiers in Graphite Furnace Atomic Absorption Spectrometry – Mechanisms and Applications

High-resolution Continuum Source Atomic Absorption Spectrometry – Theory and Applications

REFERENCES


