ELEMENTAL ANALYSIS

Product Specifications

Design Considerations for High Performance Background Correction Systems in Atomic Absorption Spectrometry

The Thermo Scientific iCE 3000 Series AA Spectrometers are fitted with highly efficient background correction systems for flame and furnace use. Their important design features are described in this article along with discussions on the advantages and disadvantages of other techniques.

What is Background Absorption?

The technique of atomic absorption spectrometry depends on the formation of an atomic vapor from a sample solution and on the measurement of element specific radiation absorbed by the vapor.

Any metallic element in atomic form will absorb light over a narrow range of wavelengths centred on the resonance wavelength whose value is specific to the element. The absorption line width is about 0.002 nm at normal atomization temperatures. In an atomic absorption spectrometer, the light source is usually a hollow cathode lamp, which produces resonance radiation of about 0.001 nm line width. The lamp also generates light at wavelengths other than the resonance wavelength, and this makes it necessary to pass the light through a monochromator.

The monochromator is tuned to the resonance wavelength, but will pass a range of wavelengths (typically 0.1 - 1.0 nm) - much greater than the atomic absorption line width.

When only the analyte atomic species are present, the amount of light absorbed will depend only on the concentration of the analyte element in the light path.

Materials other than the analyte, derived from the sample matrix and the atomization system itself, may also be present in the light path. In some circumstances, these can absorb or scatter the radiation, thus increasing the total absorbance and hence the apparent concentration of the analyte. This effect is known as non-specific, or background, absorption and, if present, can reduce the accuracy of the analysis unless steps are taken to correct for it.

Molecular Absorption

Many sample matrices contain halide salts at relatively high concentrations. In the atomizer, these will form molecular vapors, resulting in molecular absorption of the radiation. Molecular absorption spectra are broad band, with band widths of the order of tens of nanometres, and for alkali metal halide salts, absorption increases sharply in the deep ultra-violet region (below 220 nm) of the spectrum. Some typical vapor phase spectra of alkali metal halide salts are shown in Figure 1 below.

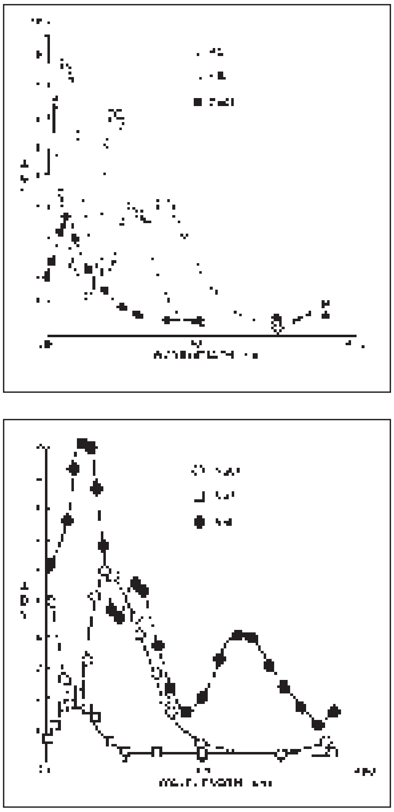

Figure 1: Molecular spectra of simple halide salts

Background absorption caused by molecules is thus particularly troublesome when measuring elements with their main resonance line below 220 nm and in sample matrices containing alkali metal halides. This includes many of the toxic heavy metals, such as lead, cadmium and arsenic in biological and environmental samples, such as natural waters, effluents and body fluids.

Scatter

Some types of sample matrix are not completely vaporized in the atomizer, but form small particles or clusters. These scatter the light from the hollow cathode lamp, preventing it from reaching the detector, and so cause an apparent absorption signal. The degree of scatter depends strongly on both the wavelength of the light and the size of the particles, and increases markedly at low wavelengths.

Background absorption caused by scatter is, therefore, also most significant for elements with their resonance lines below 220 nm, and depends both on the total dissolved solids content of the samples, and the nature of the dissolved solids - refractory metals and those forming very stable oxides, such as the alkaline earths, cause the greatest problems.

Structured Absorption

Other components of the sample matrix will be atomized, and their atomic absorption spectra may contain lines close to the analyte resonance line. Cases of direct line overlap are very rare, but it is possible that lines derived from the matrix components will fall within the monochromator band pass.

In most cases, the broadband background absorption is a relatively smooth function of wavelength, and may be regarded as virtually constant over the bandpass of the spectrometer monochromator.

Occasionally, examples are encountered of more complex background absorption spectra with line structure superimposed on this relatively constant background. An example of these so-called structured backgrounds is the determination of selenium in whole blood, where the iron content of the matrix exhibits such structure within the monochromator bandpass. Should such structure occur within the monochromator bandpass of a deuterium background correction system, systematic errors will be present in the corrected atomic absorption signal, and hence the analytical result. Such examples are relatively uncommon in AA analysis but, when present, may advantageously be dealt with using the Zeeman correction technique.

Methods of Compensating for Background Absorption

Introduction

Instrumental methods of correcting for background absorption depend upon making at least two separate measurements of the sample absorption. The first is the normal atomic absorption measurement made at the analyte resonance line, and gives the total (atomic plus background) absorption. A second measurement is then made, in such a way as to reduce the effect of the absorption from the analyte atoms to a negligible amount, while not affecting the background absorption. This second measurement gives only the background absorbance, so that subtraction of the two measurements will give the true atomic absorbance.

All instrumental background correction systems are based on this principle. They differ in the means used to reduce the atomic signal to negligible levels for the background measurement, and in the frequency with which the two measurements are made.

Continuum Method

The second (background) measurement in this technique is made using radiation from a source with a broad spectral output, such as a deuterium arc lamp. The radiation intensity from such lamps is almost independent of wavelength over the monochromator band pass (i.e. over a wavelength range of about 1 nm), and so ‘fills’ the monochromator band pass. The analyte atomic absorption takes place over a wavelength range of about 0.002 nm; the amount of continuum source radiation absorbed by the analyte atoms is, therefore, negligible. Background absorption is largely a broad band phenomenon, and is also reasonably independent of wavelength over the monochromator band pass. Only the background absorption will, therefore, be measured by the continuum source. This situation is shown diagrammatically in figure 2.

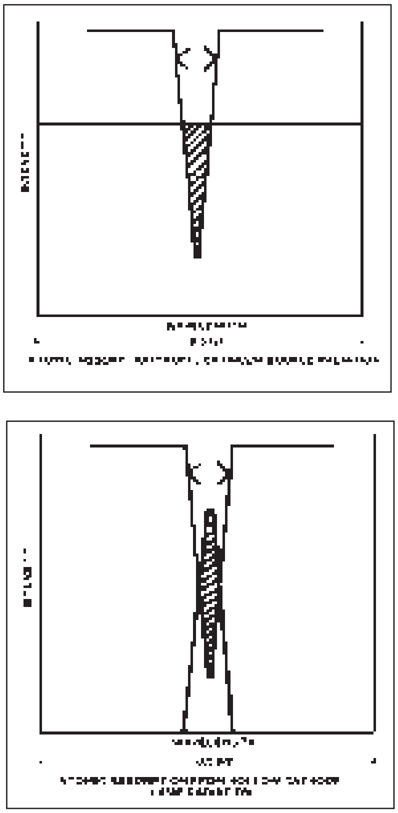

Figure 2: Atomic absorption from a hollow cathode lamp and a continuum source.

It is possible to use continuum source background correction with sequential measurements of total (line source) and background only (continuum source) absorbance, followed by manual subtraction to give the corrected atomic signal. It is also possible to design the spectrometer in such a way as to automatically make both measurements and subtract the results, and to do this sufficiently rapidly that many pairs of measurements can be made and subtracted over the normal sampling period, providing fully automatic background correction. This is the basis of almost all commonly used background correction systems, and most modern atomic absorption spectrometers are capable of making measurements that are automatically corrected for background absorption.

Well designed background correction systems based upon the continuum source technique are capable of correcting the majority of non-specific absorption problems encountered during both flame and graphite furnace atomic absorption measurements. Only in situations in which the background absorption is NOT independent of wavelength over the monochromator band pass, or where direct spectral overlap of the analyte atomic line and a narrow band absorption due to a matrix component occurs, will it give incorrect results.

Commonly used continuum sources, such as deuterium arc lamps, emit most of their radiation in the ultra-violet region of the spectrum, below 350 nm. Background correction in the visible region is, therefore, not possible, unless an additional source is used. However, almost all background absorption phenomena occur in the ultra-violet region - scatter and molecular absorption are usually negligible at wavelengths above 350 nm - so this is not a serious practical limitation.

Self Reversal Method

This technique (also known as the Smith-Hieftje technique) relies upon a broad band source to measure the background absorption. Rather than employ a separate source, the hollow cathode lamp itself is used.

Hollow cathode lamps are normally operated at lamp currents up to 25 mA, when they produce the narrow line emission spectra required for atomic absorption measurements. If the peak current is increased to several hundreds of milliamps, the emission lines broaden and self reverse (Figure 3). Under these conditions, the narrow atomic absorption line can only absorb a small part of the broadened emission line, while the broad band or continuous background absorption will occur as usual. Absorbance measurements made at very high lamp currents, will be mainly due to the non-specific absorption.

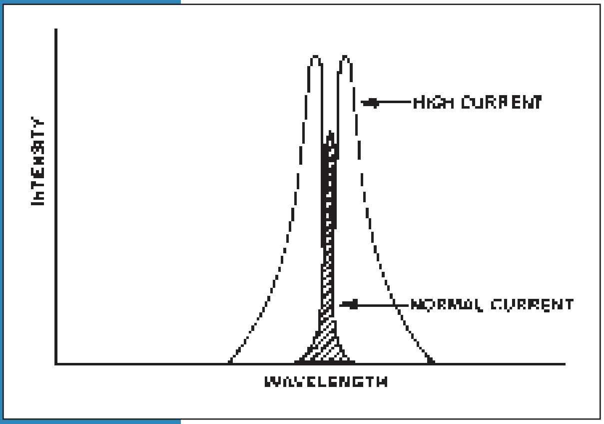

Figure 3: Hollow cathode lamp emission line broadening at high lamp currents.

The hollow cathode lamp is, run with alternating low and high current pulses. Total absorbance is measured during the low current pulse and the background absorbance is measured during the high current pulse. The two signals are automatically subtracted to give the corrected atomic signal.

The self-reversal technique is capable of correcting for most background absorption phenomena over the full wavelength range of the spectrometer. Although the emission line is broadened during the high current pulse, it does not 'fill' the monochromator band pass in the same way as a true continuum source. The system can, therefore, correct for some cases of structured background. It will not, however, correct for actual line overlap.

The disadvantages of the technique are the effect of the high current pulses on the hollow cathode lamp - unless specially designed lamps are used, the lamp lifetime will be significantly reduced - and the breakdown of the assumption that the atomic absorption is negligible during the high current measurement.

The degree to which the lines for the different elements broaden and self reverse, and hence the validity of this assumption, will depend on the element and on the detailed construction of the lamp, particularly the cathode material and the fill gas pressure. When the assumption breaks down, the background-only signal measured will actually contain a significant contribution from the atomic signal. When this is subtracted from the total signal, the apparent atomic signal that results will be over-corrected. The effect is to reduce analytical sensitivity (by as much as 70% in some cases) and increase the curvature of the calibration graph.

Zeeman Method

This technique does not rely on a continuum or pseudo-continuum source for the measurement of the background absorption. Instead, the absorption of the analyte atomic absorption line is cancelled, by applying an intense magnetic field to the atomizer. The effect of the magnetic field on the absorption spectra of free atoms is complex, but essentially causes the single sharp line to split into a family of lines spread around the wavelength of the original line (some examples are shown in Figure 4).

Furthermore, the split absorption lines are polarised in directions either parallel or perpendicular to the magnetic field. If the hollow cathode radiation is also polarized, by passing it through a suitable polarizer, measurements made with the magnetic field on will not contain any analyte atomic absorption, and so will be due solely to background absorption taking place at the analyte resonance wavelength.

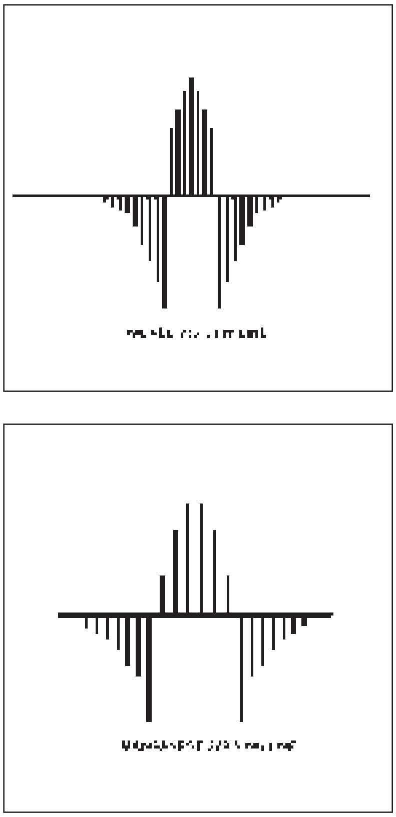

Figure 4: Zeeman splitting of atomic lines

The Zeeman technique is the only one in which measurement of the background absorption takes place at exactly the same wavelength, and over exactly the same band pass, as measurement of the total signal. It is, therefore capable of correcting for highly structured background spectra and even cases of spectral overlap. A disadvantage is the relatively complex magnet and its control electronics; magnetic field strengths up to almost 1 tesla (10 kilogauss) are required to obtain optimum line splitting for some elements.

Some elements, including many of those most commonly determined by atomic absorption spectrometry, exhibit a phenomenon known as 'anomalous' Zeeman splitting. Here a component of the split line remains at exactly the same wavelength as the unsplit line. The atomic absorption is not, therefore, reduced completely to zero when the magnetic field is on and the background-only measurement contains a contribution from the analyte atomic absorption. This, when subtracted from the total, magnet-off, measurement, results in over-correction of the atomic signal, reducing the apparent chemical sensitivity and increasing the calibration curvature, in a similar way to the self-reversal technique.

With Zeeman background correction, the magnet must be placed around the atomizer. It is impractical, therefore, to apply this technique to flame measurements, and commercially available systems are usually limited to graphite furnace analyses. It is also possible to apply the Zeeman effect to the radiation source, causing the emission lines, rather than the absorption lines, to split. Measurements made with the split lines (for elements exhibiting the 'normal' Zeeman effect, at least), will not include a contribution from the analyte atomic absorption. However, the background absorption is not then measured at exactly the same wavelength as the atomic absorption and, furthermore, is measured with a highly structured source. If the background absorption is also structured, large errors can be introduced. Normal hollow cathode lamps will not operate in intense magnetic fields and specially designed sources are required. Consequently, this arrangement has only been used in a limited way, and in special purpose instrumentation.

The magnetic field may be applied as either a DC (permanent) magnet system or as an AC (electromagnet) system. In the case of a DC system, the magnetic field is always present. Differentiation of total and background signals is obtained by switching the plane of polarization of the hollow cathode radiation. This is usually achieved by physically rotating the polarizer itself which requires a complex, high precision motor driver mechanism. The AC Zeeman method where differentiation is obtained by modulating the magnetic field, is preferable, as the field can be modulated by driving the magnet with a simple AC waveform. Furthermore, the higher the frequency of magnet modulation, the closer the two signals of total and background absorption are measured in time. With fast transient furnace absorption peaks, this reduces analytical errors.

Instrumental Design

Range

Irrespective of the physical technique employed to derive the background absorbance signal, all systems have to subtract this signal from the total signal to obtain the corrected atomic absorption. To obtain an accurate result, both the total and the background absorbance signal must be within the measuring range of the spectrometer.

Accuracy

As the analytical signal (from which the final result is derived) is the difference between the total and the background-only signal, it will contain errors originating in both of these signals, in addition to any errors introduced by the signal subtraction itself. The accuracy with which the primary signals are measured, therefore, needs to be significantly greater than the accuracy required for the analytical signal.

It can be shown from statistical considerations that the error in the corrected absorbance signal will be minimized when the errors in the total absorbance and background-only absorbance signals are of similar magnitude. This implies that the intensities of the radiation sources used to measure the absorbance signals should also be similar.

Emssion

Flame, and particularly graphite furnace atomizers, can produce intense emissions of radiation as a result of the high temperatures used.

The spectrometer must be capable of accurately measuring the source lamp intensities in the presence of the atomizer emission, in order to derive the two absorbance signals. Bright source lamps, and an optimized optical system are, therefore, essential.

The internal dimensions of the Thermo Scientific cuvette have been considered in the design of the spectrometer optical systems, to ensure that thermal emission from the cuvette walls is, as far as possible, screened from the detector without compromising the high optical transmission efficiency and low noise characteristics of the spectrometer.

This is particularly useful when determining refractory elements requiring high atomization temperatures and with main resonance lines above 320 nm.

Transient Response

Atomic and background signals generated by flame atomization systems are normally stable, steady state measurements. Graphite furnace atomization, however, can generate rapidly changing signals. A modern, fast heating design, such as the Thermo Scientific GFS35, can generate total and background signals that are varying independently at rates of up to 50 absorbance units per second. Pairs of measurements must, therefore, be taken at a sufficiently fast rate to enable the background correction system to accurately track these two signals and subtract them to give an accurate, undistorted corrected signal.

Background Correction Systems

Quadline

The continuum source technique used in the Thermo Scientific AA Series of spectrometers offers the performance required by the vast majority of analysts in a cost effective, and theoretically sound, package. Detailed improvements in the source design, the optical configuration of the spectrometer and the signal processing functions overcome many of the limitations traditionally associated with the technique. This results in a high performance system capable of handling the most demanding applications.

Source Lamp

A high intensity deuterium arc lamp is used as the continuum source, with a novel 4 electrode design that allows the lamp to be electronically modulated at four times the mains frequency, without the use of mechanical choppers. This modulation frequency, together with the digital signal processing described below, permits accurate correction of signals changing at rates of up to about 70 absorbance units per second.

The novel lamp design, coupled with an innovative power supply, allow the arc current, and hence the intensity of the emitted radiation, to be varied over a wide range while maintaining excellent stability at any particular setting. The continuum source intensity can, therefore, be accurately matched with the hollow cathode lamp intensity over a wide range of elements and wavelengths, ensuring that the corrected signal is measured as accurately as possible.

Optical System

Source Location and Alignment

Although the deuterium arc lamp has a long useful lifetime, it will eventually require replacement.

For accurate operation a continuum source background correction system, it is essential that the two sources are precisely aligned relative to each other and to the atomizer. In the Thermo Scientific iCE 3000 Series AA Spectrometers, the deuterium arc lamp, once initially aligned, does not require further adjustment. The hollow cathode lamps are automatically aligned to the deuterium beam using the spectrometer's automatic lamp alignment facilities.

iCE 3500 Optical System Layout

The novel echelle optical system layout of the Thermo Scientific iCE 3500 AA is shown in Figure 5. Front and rear beam selector mirrors act together to direct the light beam through either the flame or the furnace atomizer. The optics have been optimized for furnace use so that the “pencil-beam” optics eliminate potential emission problems and half height slits (traditionally used but with an attendant loss of energy) are not required.

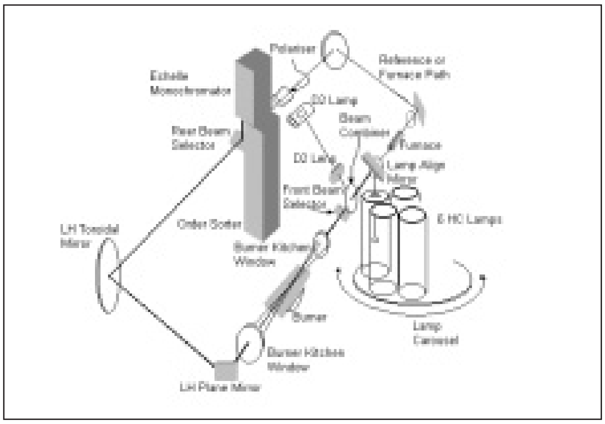

Figure 5: iCE 3500 optical system showing the echelle design.

Echelle technology is the only solution to providing high energy throughput and pencil beam optics, without going to a very large traditional Czerny-Turner design (which would need a 500 mm focal length and an 1800 lines/mm grating). The echelle reciprocal linear dispersion of 0.5 nm/mm is the best in this class of instrument.

Signal Processing

Analogue versus Digital Processing

Automatic background correction systems require significant amounts of signal processing to derive the analytical signal. The basic measurements taken at the detector give the intensities of radiation from the hollow cathode lamp and the continuum source lamp, each with, and without, the presence of sample in the atomizer. From these signals, the total and background absorbance values are derived by taking the logarithm of the measured radiation intensities from each source with, and without, sample. Finally, the two absorbance values are subtracted to give the corrected atomic absorbance.

Traditional instruments performed this processing using analogue electronics. They inevitably have a number of variable elements which have to be set up individually to compensate for small differences in the electronic components. This adds to the initial cost of the instrument, and means that regular maintenance and adjustment is needed to maintain the original performance.

With the development of digital microprocessor based electronics, an alternative has become available. In a digital system, the values of the different quantities are represented by numbers, not voltages, and are manipulated by a microprocessor. The major advantage of this approach is that there are no variable components in the system that need to be set up, and that can later go out of adjustment. The long term performance is more stable and little, or no, maintenance is required.

Digital systems are also more versatile. Operations such as averaging successive signal values, which are difficult to perform with analogue circuits, can be simply achieved by programming the microprocessor. For these reasons, the signal processing functions in the iCE 3000 Series are carried out by a digital system. Radiation intensities are measured by a photomultiplier, and converted immediately to digital form using a device known as an Analogue-to-Digital convertor. All subsequent processing, including logarithmic conversion to give the absorbance values and subsequent subtraction of the background-only signal, are performed by the microprocessor.

The microprocessor also optimizes both the gain of the photomultiplier and the intensity of the deuterium arc lamp, ensuring that the raw intensity measurements are made under optimum conditions.

Signal Bracketing

It is not possible in a practical background correction system to measure the total and background absorbance signals at exactly the same time. If the signals are changing rapidly, the actual value of the total signal when the background signal is measured could be slightly different, resulting in an error in the corrected signal. Consider the sequence of measurements shown in Figure 6a for simple correction, where T1, B1 are the first pair of total and background absorbance measurements, taken at times t_{T1} and t_{B1}, and T2, B2 are the second pair, taken at times t_{T2} and t_{B2}. Simple subtraction of B1 from T1 gives the result C for the corrected atomic absorbance, underestimating the true value C1 by the amount that the total signal has changed in the time from t_{T1} to t_{B1}.

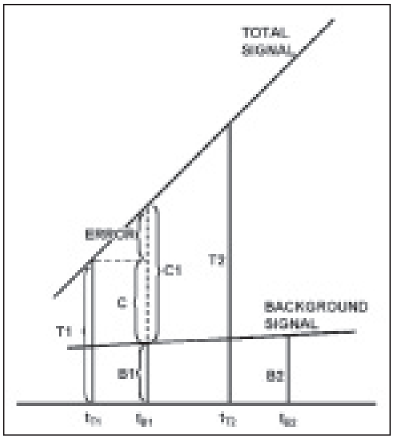

Figure 6a: Measurement sequence for simple correction.

Errors from this source can be reduced by using fast modulation of the sources and detector system, so that many pairs of measurements are made rapidly and the amount that the signals change between individual measurements is reduced. The versatility offered by microprocessor based digital signal processing allows a further refinement to be made, further improving the accuracy of the background correction (as shown in Figure 6b for bracketing correction).

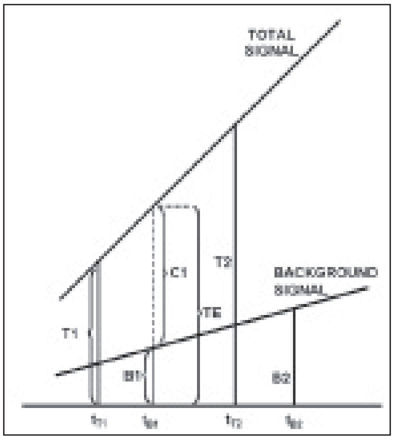

Figure 6b: Measurement sequence for bracketing correction.

If we wait to perform the calculation until t_{T2}, when the next measurement of the total signal T2 is taken, we can use the values of T1 and T2, together with the known times t_{T2}, t_{B1} and t_{T2}, to estimate the actual value, TE, of the total absorbance at time t_{B1}.

$$TE = T1 + (T2 - T1) x (t_{B1} - t_{T1})/(t_{T2} - t_{T1})$$

Subtracting B1 from TE will then give a very much better estimate of the true atomic absorbance C1.

This technique is known as signal bracketing, and only becomes practicable when digital signal processing is used. In combination with the fast modulation system used in the iCE 3000 Series, it will reduce errors in the corrected signals caused by timing effects, to less than 1% for signals changing at up to 70 absorbance units/second.

Quadline Conclusions

The key aspects of the QuadLine method of background correction may be summarized as follows:

- highest possible measurement sensitivity compared with alternative techniques
- novel wideband source allowing continuous intensity variation and fast modulation frequency
- optical matching of the beam profiles from both the background correction source and HCLs
- fast modulation frequencies of 200/240 Hz
- beam combining techniques ensuring homogeneity within the beam profile
- bracketing correction of both background and dark level signals to overcome time dependence of measurement periods
- dark level correction to zero every 10 mS to improve dynamic range of ADC conversion
- intensity matching of background source and HCL to improve dynamic measurement range

Zeeman Correction

Employing the alternative major background compensation technique of Zeeman correction can be shown to be of analytical benefit in a number of specific situations as outlined earlier, in particular those of structured backgrounds and spectral overlaps. Furthermore, some analysts may find the technique fundamentally less prone to operator variability, since no source alignment is required, beyond maximising the HCL energy throughput.

For these reasons, Thermo Fisher Scientific provide the iCE 3500 (dual atomiser), and iCE 3400 Zeeman-only furnace systems. The system employ the electromagnetic, or AC, Zeeman technique applied at the atomizer. Uniquely, all these systems also provide the QuadLine background correction technique as standard within the same spectrometer. Thus, the technique of preference may be chosen for a particular analysis by a simple option within the operating software.

QuadLine correction may be employed for the highest measurement sensitivity, whereas Zeeman correction may be selected when encountering a structured background. An additional benefit is the ability to employ both techniques in combination within a furnace analysis. Since any modulated Zeeman system is limited to correction during the atomize phase only, due to potential overheating of the magnet system, vitally important method development information may be lost in the earlier pre-treatment furnace phases due to the inability to monitor the corrected absorption signal. By selecting the combined mode, QuadLine correction may be employed in all but the atomize phase, during which the Zeeman technique is used. By this unique means, much valuable method development information may be obtained.

Zeeman Technique

The magnet, placed around the furnace head, is modulated at a high 100/120Hz frequency in order to achieve minimal time separation of total and corrected signals. The magnet drive circuit achieves a maximum field strength of almost 0.9 Tesla (9 kilogauss) - optimum for all AA analytes. A trapezoidal wavefom is used for the drive current, ensuring that the measurement period is performed totally during maximum and constant magnetic field conditions, unlike sinusoidal field modulation techniques.

The magnet pole pieces are so designed to provide a magnetic field constant to within 5% in the key central working volume of the graphite cuvette in the furnace head. Due to the inhomogeneity of atomic and molecular species within the graphite cuvette volume, such a constant magnetic field is vital in providing reliable data.

The design of the Zeeman magnet system must also achieve other vitally important objectives. The system must be readily demountable for routine service and user maintenance operations. It must be extremely durable in the presence of the potentially aggressive chemicals employed in the AA technique and, of course, must minimize extraneous stray fields due to their detrimental effects on nearby, sensitive electronics and displays. Finally, the entire system must be comprehensively equipped with safety interlocks which, together with similar furnace devices, ensure operator and equipment safety.

Operation

On selection of the Zeeman-based correction system, measurements are alternately taken in both the magnet on and magnet off conditions. With the magnet off, the instrument provides a measure of the total (atomic + background signal). With the magnet on, the instrument provides a measure of the background-only signal at the analyte wavelength. This is achieved by effectively "removing" the analyte absorption profile from the measurement wavelength, as shown in Figure 7. Subtraction of these signals then provides the displayed, corrected absorption profile.

A further benefit of the Zeeman correction system is that effectively the two measurements (magnet on and magnet off) provide a referenced measurement and source drift correct ion without the necessity of conventional double beam optics. Since only a single optical beam is employed, alignment of the measurement source and atomization unit is also relatively straightforward.

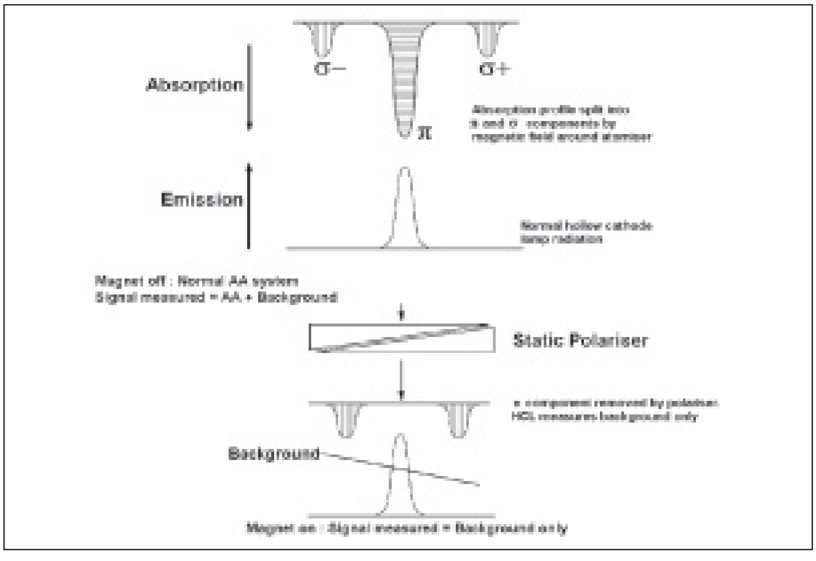

Figure 7: Inverse AC Zeeman method of correction.

Zeeman Conclusions

The key aspects of this Zeeman method of background correction may be summarized as follows:

- accurate correction of structured backgrounds and spectral overlaps
- correction at the exact analyte wavelength
- not limited to a wavelength range, as with a deuterium source
- self-referenced to reduce drift
- less alignment necessary, due to single source
- efficient, optimized magnetic field modulation ensures that the complete measurement is at full magnetic field strength
- field strength of almost 0.9 Tesla to ensure complete line separation
- rapid field modulation of 100/120Hz to ensure faithful tracking of fast furnace signals
- relatively constant magnetic field strength along the length of the furnace cuvette to achieve efficient spatial correction
- alternative QuadLine method for the highest sensitivity requirements and combined QuadLine/Zeeman mode for method development work

Correction Performance

Steady State

It is difficult to generate large background signals using conventional flame atomization. Metal gauzes held in the light path are, therefore, used to generate large background-only signals. Since there can be no atomic absorption in this experiment, any deviation of the background corrected result from zero reflects the residual errors in the system.

The results from a typical experiment performed on an iCE 3000 Series AA spectrometer set up for nickel analysis using the default parameters and making 10 replicate measurements, each of 2 seconds duration, are shown in Table 1.

They show that, even with a background signal approaching 2 absorbance units, residual background correction errors are of a similar order to the optical noise in the system. In a real sample measurement, these errors would be lost completely in flame and atomization noise.

Emission Breakthrough

The background corrected determination of chromium in a nitrous oxide/acetylene flame is a severe test of the background correction systems ability to reject flame emission signals. Not only is the chromium resonance line at 357.9 nm extremely bright, but the deuterium arc lamp intensity is also beginning to fall in this region of the spectrum. The optimum flame conditions for the determination are such that an intense cyanide molecular emission, centred around 355 nm, is produced from the flame. The effects of these phenomena on the background correction signal can be illustrated by comparing the chromium flame detection limits with and without, background correction. The results obtained from an earlier, analogue instrument are compared with the digital spectrometer in Table 2 .

The chromium detection limits of the earlier analogue instruments are clearly degraded when the background correction system is used, while the Thermo Scientific AA maintains its performance with no significant change.

GAUZE	ABSORBANCE	CORRECTED ABSORBANCE	STANDARD DEVIATION
1	0.353	0.0019	0.0006
2	0.506	0.0017	0.0009
3	0.860	0.0027	0.0007
4	1.285	0.0031	0.0028
5	1.803	0.0059	0.0044

Table 1: Background correction tests with gauzes

INSTRUMENT	BC OFF DETECTION LIMIT (μg/mL)	BC ON DETECTION LIMIT (μg/mL)
Analogue 1	0.033	0.115
Analogue 2	0.028	0.211
Digital Thermo Scientific AA	0.033	0.029

Table 2: Rejection of Emission effects

Transient Accuracy and Transient Response

Large transient background signals are relatively easy to generate by vaporizing relatively large amounts of a typical matrix material such as sodium chloride from a graphite furnace cuvette. Furthermore, if the spectrometer is set up on a non-atomic emission line, the 'atomic' signal must be zero, so that any errors produced by the background correction system will become immediately apparent.

Figure 8 shows the result of atomising 100 µg of sodium chloride at 1500 °C, with the spectrometer set up on the non-absorbing lead line at 220.4 nm. A background signal approximately 1.4 absorbance units high has been produced, but the corrected signal (shown in Figure 9) shows no significant deviation from the baseline. Increasing the amount of sodium chloride to 200 µg increases the background peak height to around 2.6 absorbance units (Figure 10). Expanding the corrected signal (Figure 11) reveals a significant increase in noise at the background peak maximum (a 2.6 absorbance signal will reduce the intensity of light reaching the detector to approximately 0.25 % of the value at zero absorbance), but, as before, there is no indication of a systematic error present.

By expanding the time axis of these signals, it is possible to measure the actual rate at which the background signal is changing. At the point at which it is changing most rapidly, on the leading edge of the peak between 0.7 and 0.9 absorbance units, the measured rate of rise is slightly over 25 absorbance units per second.

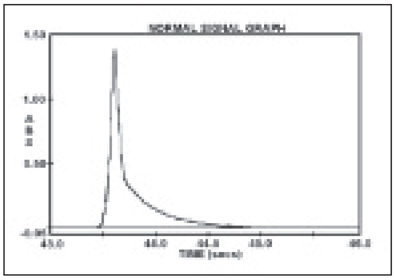

Figure 8: Background signal from 100 µg of NaCl

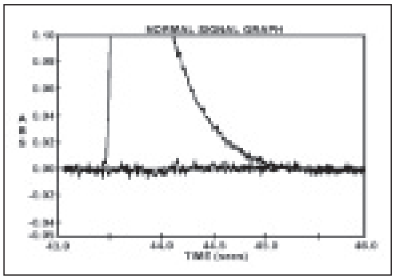

Figure 9: Corrected signal under 1.4A background peak

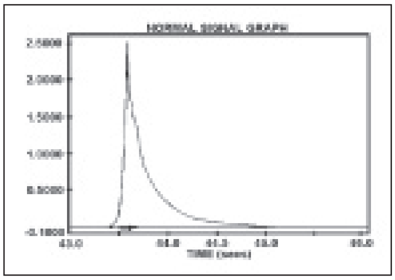

Figure 10: Background signal from 200 µg of NaCl

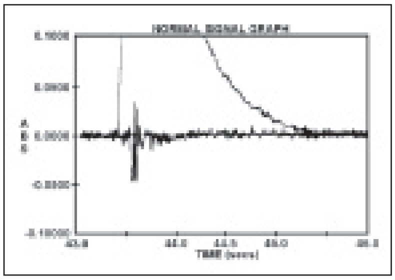

Figure 11: Corrected signal under 2.6A background peak

Figure 12 shows the corrected signal generated by atomising 10 µL of a reference sea water containing less than 0.2 µg L^{-1} of chromium, while the same sample when spiked with 4 µg L^{-1} gives the signal shown in Figure 13. The chromium signal is clean and undistorted, and can be readily quantified.

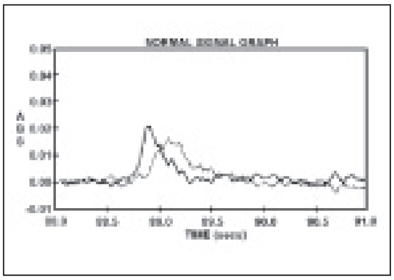

Figure 12: Corrected chromium signal and background for unspiked seawater

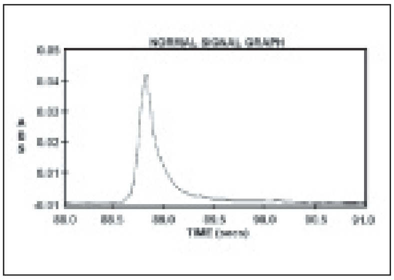

Figure 13: Corrected chromium signal and background for spiked seawater

Correction Method Continuum Source

It will normally be the case that advantageous measurement sensitivity improvements can be obtained by employing the QuadLine correction method in preference to Zeeman. Figure 14 illustrates a typical improvement achieved in the case of the analysis of copper. This may often prove to be the difference between being able to actually perform a given analysis, or not, when working at the extreme trace levels.

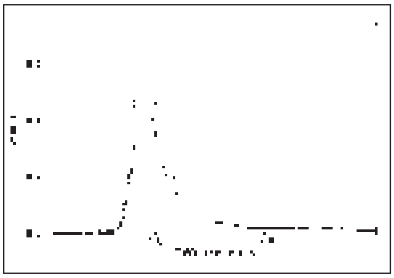

Figure 14: Improved sensitivity for QuadLine (- - -) compared with Zeeman (----) for 200pg Cu

Zeeman

When structured backgrounds, spectral overlaps or correction in the visible part of the spectrum are encountered, Zeeman correction will often solve the problem. Figure 15 illustrates the example of a cobalt interferent at the gold wavelength, an analysis that would prove impossible if only the continuum source method were available.

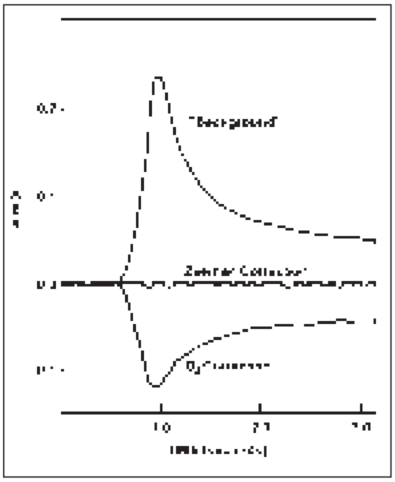

Figure 15:The improved accuracy of Zeeman analysis for Au in the presence of 150µg Co

Combination Mode

Since the Zeeman technique can only be applied during the relatively short atomization phase of the furnace, due to magnet overheating restrictions, adequate knowledge of the efficiency of other pretreatment phases, or clean-out phases, of the furnace cycle will not normally be available.

Using the unique Thermo Scientific iCE 3500 and iCE 3400 Combination mode, it is now possible to view the progress of the analysis in all phases by employing Zeeman for the main measurement phase and using the Quadline technique in all other phases.

Summary

The QuadLine and Zeeman background correction systems designed for the Thermo Scientific iCE 3000 Series range of atomic absorption spectrometers are capable of correcting for background signals up to at least two absorbance units, which can be changing at rates exceeding 25 absorbance units per second. They provide a level of performance likely to meet the needs of all analysts performing flame or furnace atomic absorption measurements.

iCE 3300

iCE 3400

iCE 3500

ISO 9001
QMI-SAI Global

Thermo Electron Manufacturing Ltd (Cambridge) is ISO Certified.

PS40690_E 01/10C

Africa-Other	+27 11 570 1840
Australia	+61 2 8844 9500
Austria	+43 1 333 50 34 0
Belgium	+32 53 73 42 41
Canada	+1 800 530 8447
China	+86 10 8419 3588
Denmark	+45 70 23 62 60
Europe-Other	+43 1 333 50 34 0
Finland/Norway/Sweden	+46 8 556 468 00
France	+33 1 60 92 48 00
Germany	+49 6103 408 1014
India	+91 22 6742 9434
Italy	+39 02 950 591
Japan	+81 45 453 9100
Latin America	+1 608 276 5659
Middle East	+43 1 333 50 34 0
Netherlands	+31 76 579 55 55
South Africa	+27 11 570 1840
Spain	+34 914 845 965
Switzerland	+41 61 716 77 00
UK	+44 1442 233555
USA	+1 800 532 4752

www.thermo.com

Thermo
SCIENTIFIC