

AAS

APPLICATION NOTES

The effect of background correction speed on the accuracy of atomic absorption measurements

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Introduction

The most common method of background correction in atomic absorption spectrometry involves the use of a continuum source such as a deuterium lamp to measure the background¹.

However, the use of this method with some applications where the background changes sharply with wavelength can cause errors. This kind of background has been called “structured” background and attempts to correct for it have led to the commercialization of alternative methods of background correction such as Zeeman² and Smith-Hieftje³. These attempts have been successful in correcting some instances of structured background but, with other applications, the errors are not eliminated and may even be aggravated^{4,5}. Even with Zeeman AA, it is sometimes necessary to choose an alternative wavelength to avoid spectral interferences⁶.

It is clear that considerable attention has been focussed on the problem of structured background, even though structured background is very rarely encountered in atomic absorption measurements. In the light of this, it is somewhat surprising that relatively little attention has been paid to a much more common problem – that of a background signal which changes rapidly with time. A large proportion of graphite furnace applications involve fast background peaks and, in these cases, the speed of the background corrector has a critical effect on the accuracy of the measurements.

Effect of background correction timing

Although most modern AA spectrophotometers incorporate so-called “simultaneous” background correction, they rely on two measurements separated slightly in time. One measurement is of the total absorbance (atomic plus background) and the other is of the background only. The background is electronically subtracted from the total absorbance to give the background corrected atomic absorbance.

With the continuum source method of background correction, the total absorbance is measured during the hollow cathode lamp pulse and the background during the deuterium lamp pulse. With the Zeeman method, using a modulated magnetic field, the total absorbance is measured with the magnetic field off and the background with the field on. With the Smith-Hieftje method, the total absorbance is measured during a low-current lamp pulse and the background during a high-current lamp pulse.

The separation between the measurement of background and total absorbance can range from less than 1 millisecond up to about 10 milliseconds. Figure 1 shows the typical timing of the different methods of background correction.

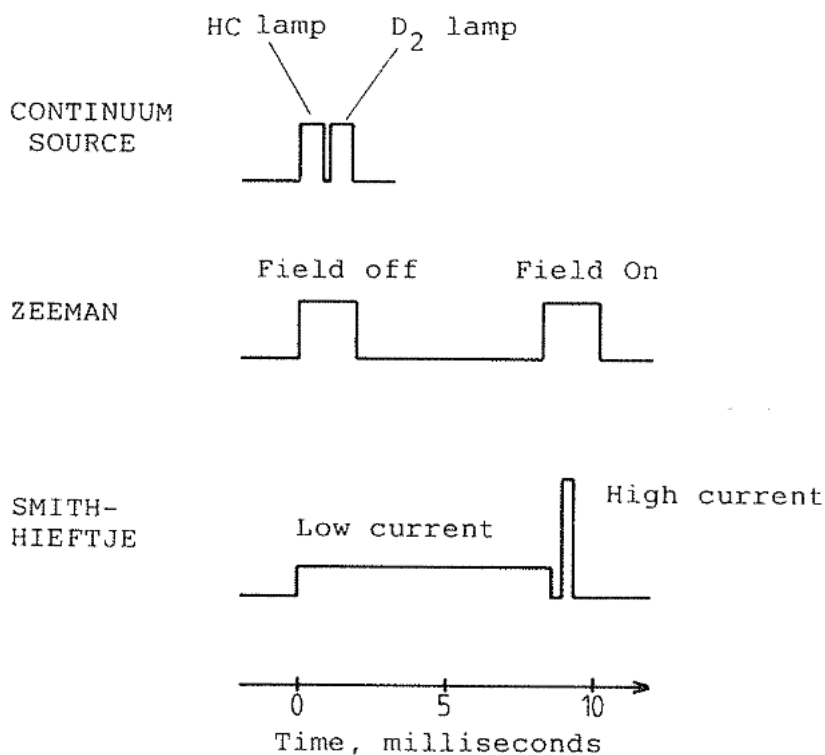


Figure 1: Signal timing used with different methods of background correction

Harnly and Holcombe⁷ have presented a thorough theoretical treatment of the errors that can result from this non-simultaneous sampling. However, their model assumed a maximum rate of change of the background of 2 absorbance/second. As they remarked, the rate of change with real samples can be much greater than this and, consequently, the errors can be much greater than those they calculated.

We have graphed background peaks from some actual samples and calculated the effect of the timing of the measurements on the accuracy of background correction. A GBC atomic absorption spectrophotometer and a GBC automated graphite furnace system were used for all measurements.

Figure 2 shows a signal generated by a sodium chloride sample at the lead 283.3 nm wavelength. Since there was no lead in the sample, this peak is entirely background and should be completely removed by the background corrector. Any deviation from zero of the background corrected signal represents an error.

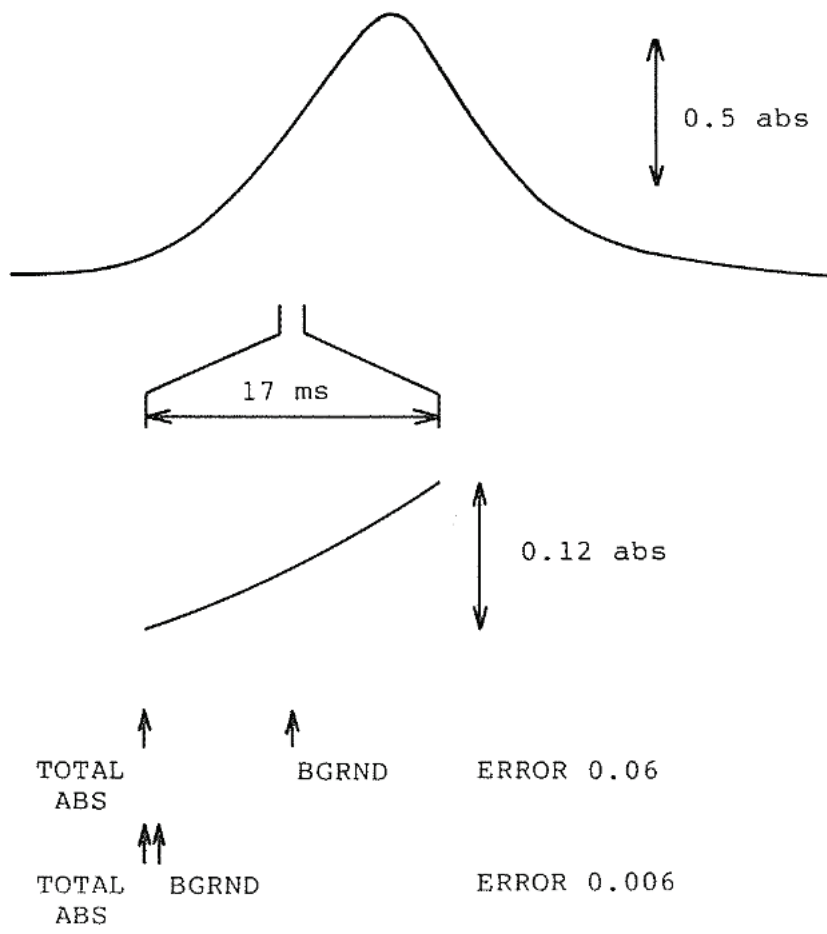


Figure 2: Furnace background peak due to NaCl, illustrating the origin of background correction errors. The background changes by 0.12 absorbance in 17 ms and, if the measurements of total and background absorbance are separated by 8 ms, the error is 0.06 absorbance. If they are separated by 0.8 ms, the error is 0.006 absorbance.

In Figure 2, one cycle of the mains power supply (16.7 milliseconds at 60 Hz) is expanded and it can be seen that the background changes by 0.12 absorbance over this time. Any change in the background between the measurement of total and background absorbance will result in an error. If the two measurements are separated by half a mains cycle (8.3 milliseconds) then this error will be approximately 0.06 absorbance. If the separation is 0.8 milliseconds then the error will be approximately 0.006 absorbance.

As the background signal passes through a peak, the error follows the shape of the derivative of the peak, as shown in Figure 3. The shape of the error graph is independent of the delay between the measurement of total and background absorbance but the magnitude of the error is critically dependent on this delay.

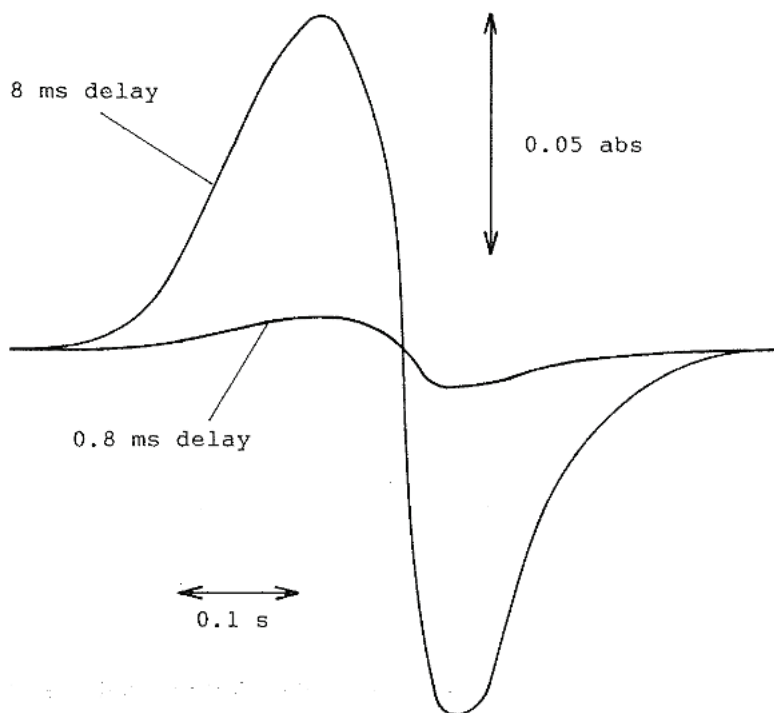


Figure 3: Absorbance versus time graphs of the background correction errors produced by the NaCl peak in Figure 2. Errors are graphed for 8 and 0.8 ms separation between the measurement of total and background absorbance.

The error with the 8 millisecond delay is ten times that with the 0.8 millisecond delay. The 0.8 millisecond delay was chosen for this illustration because it is used in the HYPER-PULSE background correction system of the GBC atomic absorption spectrophotometer, whereas delays of 8 milliseconds are common in other AA spectrophotometers.

Effect of interpolation

One possible means of reducing the error is to use the background measurement either side of the total absorbance measurement to calculate the magnitude of the background at the time the total absorbance is measured⁷. If the background is changing linearly with time, this interpolation (or bracketing) method is very effective in reducing the error. However, when the background passes through a peak or a trough there may still be a significant error.

It is not uncommon for the background signal to comprise several sharp peaks and this type of signal provide a particularly stringent test for the background corrector. Figure 4 shows the background signal produced by a seawater sample with ammonium nitrate added as a modifier, again at the lead 283.3 nm wavelength. The magnitude of this signal could probably have been reduced by careful optimization of the temperature program but, since the aim was simply to generate examples of background signals, no attempt was made to do this.

Figure 4 also shows the background correction errors produced with a 8 millisecond delay, an 8 millisecond delay with interpolation and a 0.8 millisecond delay. Compared to the 8 millisecond delay, the errors are reduced by factors of about 2 and 10.

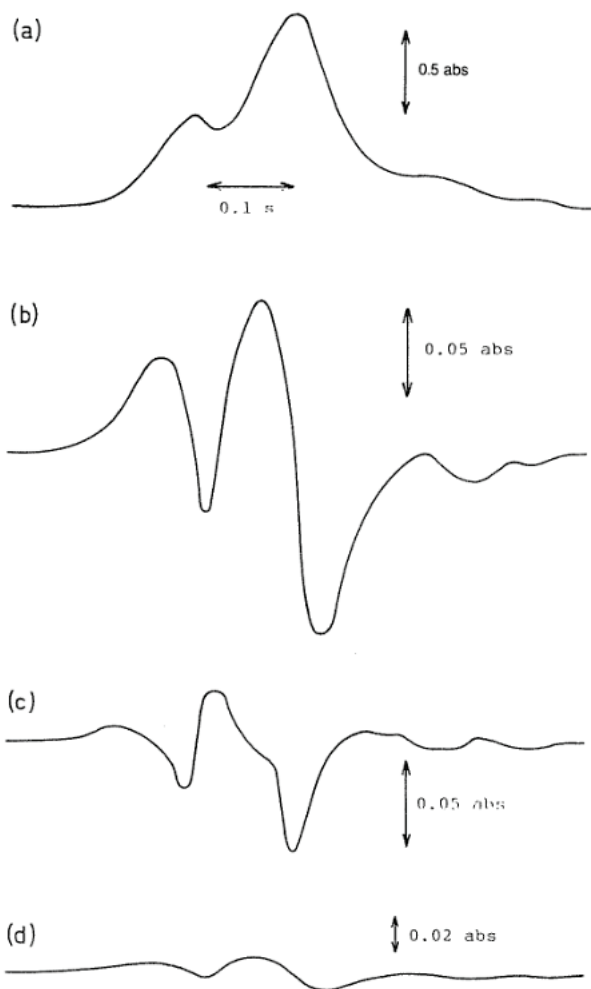


Figure 4: Background peak and errors for seawater with NH_4NO_3 . (a) Background scan. (b) Error graph for 8 ms separation between the measurement of total and background absorbance. (c) Error graph for 8 ms separation with interpolation. (d) Error graph for 0.8 ms separation.

It should be noted that the background signals shown in Figures 2 and 4 were obtained with atomization off the wall of the furnace. It is possible that the signals might be slower and the errors smaller with atomization from a platform. However, a rate of change in the background of 10 absorbance/second has been reported with atomization from a platform⁸. This compares with a maximum rate of change of 14 absorbance/second in Figure 4, so the errors would not be expected to be significantly lower with platform atomization.

Harnly and Holcombe⁷ have suggested that, if the area of the peak is measured and the measurement covers the entire duration of the background signal, the positive and negative errors will cancel. This would be a viable solution with some applications but not with others. It is uncommon for the analyte peak to appear at the end of a long background signal extending from the ashing or charring stage or to appear at the start of a high background peak.

In these cases it is highly desirable that for the measurement not to span the full duration of the background peak.

Performance of GBC atomic absorption spectrometer

The foregoing calculations have shown that an instrument with a very small delay between the measurement of background and total absorbance should give the most accurate correction for fast background peaks. Figure 5 is a scan illustrating the performance of the HYPER-PULSE background correction system of the GBC atomic absorption spectrophotometer.

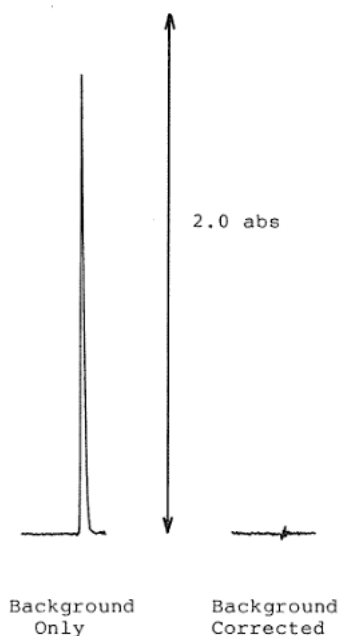


Figure 5: Scans showing background and corrected absorbance with a NaCl sample.

The background signal of about 1.8 absorbance was generated by a sodium chloride sample. The maximum rate of change was approximately 15 absorbance/second. It is important to note that no damping has been applied to these scans.

It is possible to get an apparent improvement in the accuracy of background correction by applying damping to the signal. However, this distorts the analyte peak, reduces sensitivity and may increase interferences, so the performance of the background corrector must be assessed with no damping applied.

In Figure 5, there is a slight disturbance of the background corrected signal but it is not more than the unavoidable increase in noise produced by the high background. (At 2 absorbance, the light level is reduced by a factor of 100 causing the noise to increase by a factor of 10).

Figure 5 also demonstrates that it is possible for a deuterium lamp background corrector to correct for high background absorbance. It has often been asserted that deuterium lamp systems cannot be used with high background but there is no fundamental reason why a well-designed deuterium lamp system should not correct up to the same absorbance as the alternative Zeeman and Smith-Hieftje techniques.

The GBC HYPER-PULSE system corrects to 2 absorbance and the reason for not going higher is the increase in noise rather than any fundamental failure above this level.

Background correction GBC atomic absorption spectrometer

Although the need for fast background correction is most obvious with graphite furnace work, it is also a consideration with flame AA.

At low wavelengths, flame noise provides the main limitation to improved detection limits and precision at low absorbance⁹. If the background corrector is able to eliminate this noise there will be significant improvement in performance for elements such as arsenic, selenium, zinc and lead. Figure 6 shows scans of the baseline noise for arsenic. These scans were taken with the flame on but no sample aspirating. It is clear that the GBC HYPER-PULSE background corrector reduces the baseline noise by at least a factor of 5.

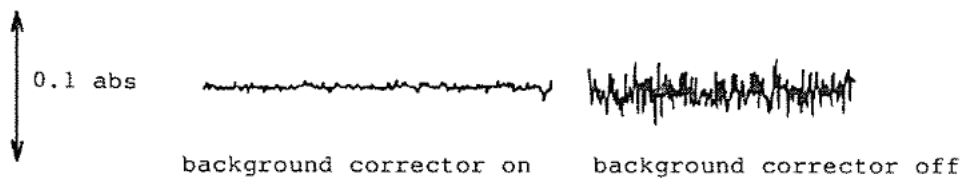


Figure 6: Scans showing the effect of background correction on flame noise with arsenic.

Signal timing in the GBC atomic absorption spectrophotometer

As mentioned, the 0.8 millisecond delay between the measurement of total and background absorbance was chosen for some of the previous calculations because it is used in the GBC atomic absorption spectrophotometer. Figure 7 shows the timing diagram for the atomic absorption spectrophotometer. This is a double beam instrument. During each cycle of the mains power supply there are four measurements of the hollow cathode lamp and deuterium lamp signals in the sample beam and two in the reference beam.

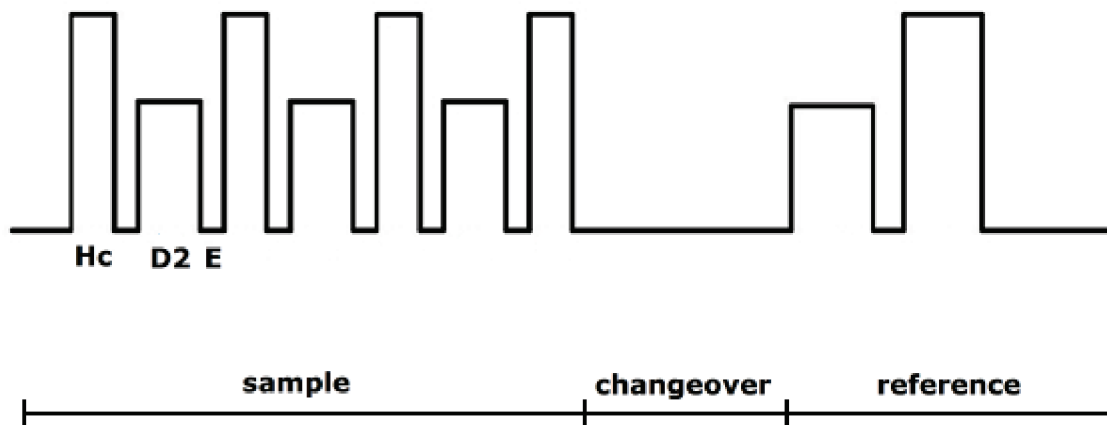


Figure 7: Signal timing for the GBC atomic absorption spectrophotometer. D2 is the deuterium lamp pulse, HC is the hollow cathode lamp pulse and E is the emission correction.

HYPER-PULSE – GBC's improved modulation system for AA's.

Since GBC's first atomic absorption spectrophotometer we have used an asymmetric modulation system on double beam AA's. This system is designed so that the hollow cathode lamp and deuterium lamp signals are pulsed in the sample beam measurement for twice the time as the reference beam measurement. This gives an improvement in the signal to noise ratio in the sample beam of the square root of the time ratio difference.

The diagram below illustrates this modulation system, where the HC is the hollow cathode lamp pulse and the D2 is the deuterium lamp pulse.

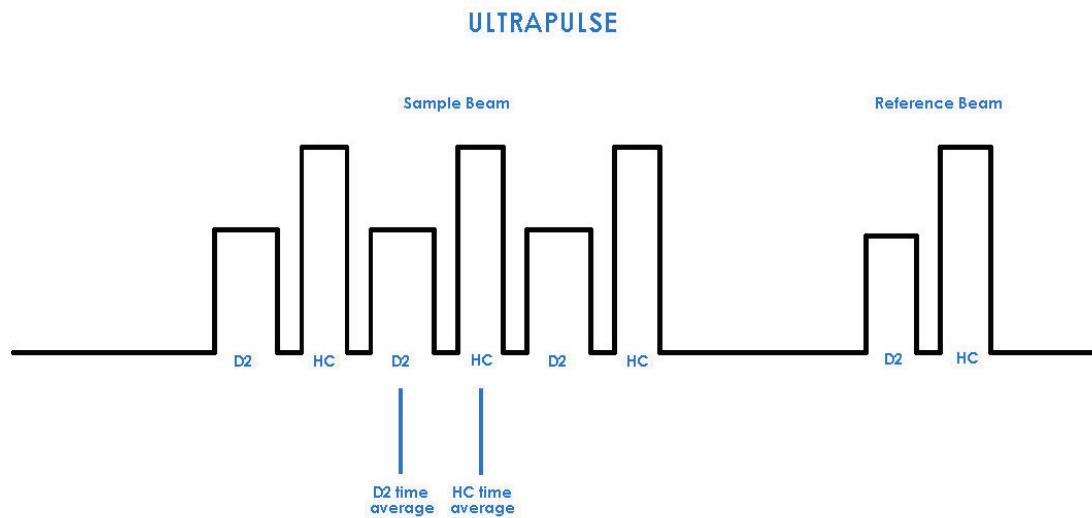


Figure 8: ULTRA-PULSE modulation scheme

It can be seen that with the ULTRA-PULSE system, that the symmetry of the accumulated lamp signals occurs in slightly different times. This will create a small error on fast moving signals such as furnace peaks. Note that this is still superior to systems which have a single pulse of each lamp in the sample beam period of the optical chopper.

To remove this error, GBC uses the HYPER-PULSE system, as shown below.

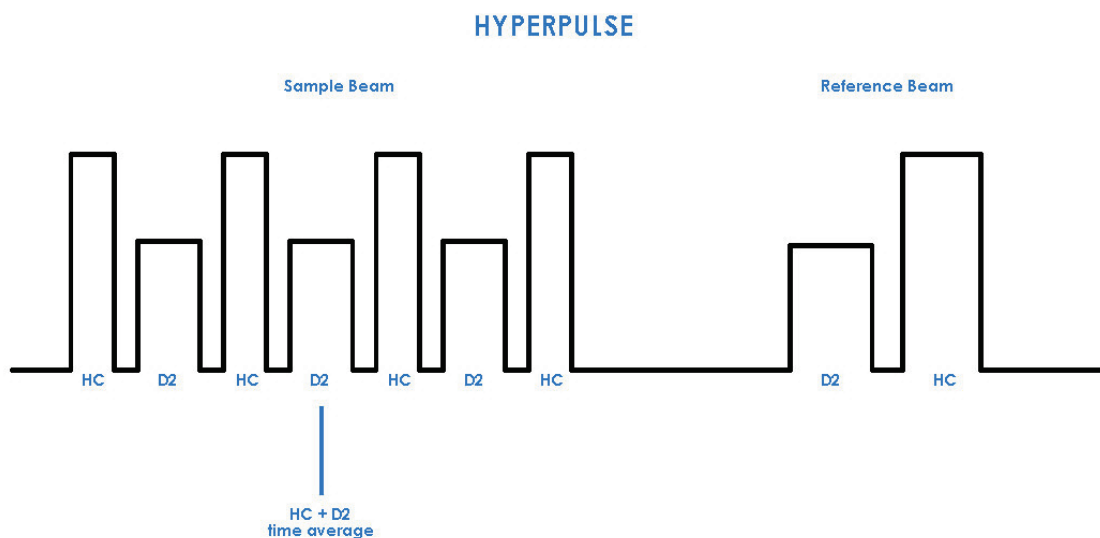


Figure 9: HYPER-PULSE modulation scheme

With the HYPER-PULSE system, it can easily be seen that the time averaged position of each lamp pulse is exactly coincident. This allows superior accuracy for transient signals such as graphite furnace peaks. Further, the lamp pulses are widened to allow full use of the optical chopper window. This allows maximum signal time for a lower signal to noise ratio. Naturally this

improves detection limit by the same amount. A further advantage of a high on time ratio of the lamps is that the effective duty cycle is higher. This allows lamp currents to run with lower peak currents, for a given average current. This enables longer lamp life than systems with short duty cycle.

Thus with a mains frequency of 60 Hz, there are 240 sample beam measurements of background and total absorbance each second (plus 120 reference beam measurements). By comparison, most other AA spectrophotometers take 60 sample measurements per second (one each mains cycle).

Each lamp pulse in the GBC atomic absorption spectrophotometer is of 0.8 millisecond duration and, since there is a negligible gap between the hollow cathode and deuterium lamp pulses, the average delay can be considered to be 0.8 milliseconds. Between each pair of lamp pulses there is a period where both lamps are off. During this period, any emission from the graphite furnace or the flame is measured and corrected for. Since the emission is measured four times in the sample beam each mains cycle, the GBC atomic absorption spectrophotometer is also very effective at correcting for rapidly changing or fluctuating emissions.

Figure 7 also illustrates another feature of the GBC atomic absorption spectrophotometer – the “asymmetric modulation”. Most double beam AA spectrophotometers spend equal time measuring the sample and reference beams. However, the purpose of the reference beam is merely to compensate for lamp flicker noise and long-term drift.

The effect of these changes in lamp intensity can be almost completely eliminated by measuring the reference beam for a short time each mains cycle and applying heavy electronic filtering (damping).

There is therefore no need to spend half of the available measurement time on the reference beam. With the sample beam, on the other hand, it is not possible to apply damping since a fast response is needed to follow the rapidly changing signals. The only ways of reducing the noise in the sample beam are to use a more intense light source or to measure for a longer time. By reducing the time spent in the reference beam, the GBC atomic absorption spectrophotometer is able to spend a longer time in the sample beam – twice as long as most other double beam AA spectrophotometers. This leads to a significant reduction in noise and improved detection limits.

Conclusion

It has been demonstrated that the signal timing in an AA spectrophotometer has a significant effect on performance. Rapid pulsing of the lamps leads to more accurate background correction and more accurate emission correction. Asymmetric modulation of a double beam system leads to lower noise. The most significant of these benefits is the ability to correct for rapid changes in background absorbance, the most common source of background correction errors in graphite furnace AA.

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