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Certain commercial instruments are identified in this paper

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Background Correction Errors Originating from Nonsimultaneous Sampling for Graphite Furnace Atomic Absorption Spectrometry

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Significant errors in computed background-corrected absorbances arise from nonsimultaneous measurement of the sample and reference signals. Processing the data in groups of three (two reference measurements bracketing the sample measurement) instead of in pairs (a reference and sample measurement) significantly reduces the absorbance errors. Error reduction in excess of 50-fold can be realized depending on the shape of the background profile. Integration of the corrected absorbance signal over the lifetime of the background signal results in a cancellation of all errors.

Accurate background correction is essential for analytical determinations by graphite furnace atomic absorption spectrometry. There are currently four methods (commercial and prototype) being used: (a) the two-source method (i.e., a hollow cathode lamp and an H₂ or D₂ continuum source, ref 1), (b) the Zeeman-effect method (2-4), (c) the wavelength-modulation continuum source method (5), and (d) the pulsed hollow cathode approach (6). All of these methods are similar in that two measurements are required to compute the background corrected absorbance; a sample measurement which reflects the combined analytical and the background-equivalent absorbance and a reference measurement which reflects only the background-equivalent absorbance (or the combined reduced sensitivity analytical and background-equivalent absorbance). In addition, each method employs only a single detector necessitating repetitive sequential measurements of the two signals. Since the two signals are not measured simultaneously, a rapidly changing background can lead to errors in the background corrected absorbances.

This paper will evaluate those errors arising from the finite time interval between the measurement of the sample and reference signals. Errors will not be considered which are caused by structured background (i.e., molecular absorption), nonuniform distribution of the analyte (7) or background within the furnace, or nonlinear electronics used in gathering and processing the data.

THEORY

Two approaches to the calculation of background corrected absorbances will be considered which are independent of the four background correction methods. As previously stated,

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all the background correction methods make repeated, sequential measurements of the sample and reference signals. The sample signal is measured at the analytical wavelength and reflects the analyte plus background absorbance, A_{l+b} . The background signal is measured either on or off the analytical wavelength and reflects the background alone, A_b . These absorbances can be used to compute the background corrected absorbance in two ways. The **asymmetric mode** uses a single pair of measurements

$$A_{l,ASYM} = A_{l+b} - A_b \quad (1)$$

where $A_{l,ASYM}$ represents the background-corrected atomic absorbance. The **bracketing mode** averages two A_b measurements made before and after A_{l+b} to give a background corrected absorbance

$$A_{l,BRAC} = A_{l+b} - \left[\frac{A_{b_1} + A_{b_2}}{2} \right] \quad (2)$$

As shown in eq 1 and 2, the asymmetric and bracketing modes can be different treatments of the same raw data, e.g., data from alternate sampling of A_{l+b} and A_b can be used in either eq 1 or 2. If the time interval between measurements is not uniform, then

$$A_{l,BRAC} = A_{l+b} - \left[\frac{\Delta t_2 A_{b_1} + \Delta t_1 A_{b_2}}{\Delta t_1 + \Delta t_2} \right] \quad (3)$$

where Δt_1 and Δt_2 are the time intervals in seconds between the sample (A_{l+b}) and background (A_{b_1} and A_{b_2}) measurements, respectively. It can be seen that eq 2 is a special case ($\Delta t_1 = \Delta t_2$) of the general expression, eq 3.

Currently, the bracketing mode of background correction is employed by two prototype instruments, the wavelength-modulated continuum source spectrometer (5) and a longitudinal Zeeman spectrometer (8), and one commercial instrument, the Perkin-Elmer Zeeman/30-30. All other commercial and prototype instruments, to the best of the authors' knowledge, use the asymmetric mode.

ERROR FUNCTIONS

It can be shown that the errors arising from the asymmetric and bracketing modes of background correction calculation are proportional to the first and second derivatives, respectively, of the background absorbance function. By definition, the first derivative of an absorbance signal, A , which varies with time ($A = f(t)$) is given by

$$\frac{dA}{dt} = \lim_{\Delta t \rightarrow 0} \frac{f(t + \Delta t) - f(t)}{\Delta t}$$

or

$$\frac{dA}{dt} \cong \frac{f(t + \Delta t) - f(t)}{\Delta t} \quad (4)$$

where the approximation improves as Δt approaches zero. The second derivative, by the same argument (assuming equal spacing of the data with time), is defined as

$$\frac{d^2A}{dt^2} \cong \frac{[f(t + 2\Delta t) - f(t + \Delta t)] - [f(t + \Delta t) - f(t)]}{(\Delta t)^2} \quad (5)$$

The asymmetric mode acquires data at times t and $t + \Delta t$. The assumption required for accurate background correction is that the background absorbance remains constant over this time interval. However, with the background absorbance changing as a function of time, an absorbance error E_1 is generated which can be evaluated from eq 1 as

$$E_1 = f(t + \Delta t) - f(t) \quad (6)$$

Combining eq 4 and 6, it can be shown that

$$E_1 \cong \frac{dA}{dt} \Delta t \quad (7)$$

The bracketing mode of background correction assumes the background to be either constant or changing linearly with time if no error is to result. Assuming a uniform time interval between measurements, the three absorbance measurements of the bracketing mode are made at times t , $t + \Delta t$, and $t + 2\Delta t$, where A_{1+b} is measured at $t + \Delta t$ and the two values for A_b are measured at t and $t + 2\Delta t$. The bracketing mode error, E_2 , can be evaluated from eq 2 as

$$E_2 = f(t + \Delta t) - \left[\frac{f(t) + f(t + 2\Delta t)}{2} \right] \quad (8)$$

Rearrangement of this equation yields

$$-2E_2 = [f(t + 2\Delta t) - f(t + \Delta t)] - [f(t + \Delta t) - f(t)] \quad (9)$$

Comparing eq 5 and 9, it can be shown that the error in the corrected measurement is

$$E_2 \cong -\frac{1}{2} \frac{d^2A}{dt^2} (\Delta t)^2 \quad (10)$$

where the approximation improves as Δt approaches 0.

When A_{1+b} is not evenly spaced between A_{b1} and A_{b2} (eq 3), the bracketing mode error is

$$E_2 = f(t + \Delta t_1) - \left[\frac{\Delta t_2 f(t) + \Delta t_1 f(t + \Delta t_1 + \Delta t_2)}{\Delta t_1 + \Delta t_2} \right] \quad (11)$$

where Δt_1 and Δt_2 have been defined for eq 3. The uneven bracketing error is more easily defined if it is assumed that the time interval between A_{b1} and A_{b2} remains constant ($\Delta t_1 + \Delta t_2 = 2\Delta t$) and A_{1+b} is measured somewhere within the interval. Combining eq 5 and 11 shows that the error in the corrected measurement is

$$E_2 \cong -\frac{1}{2} \Delta t_1 \Delta t_2 \frac{d^2A}{dt^2} \quad (12)$$

When $\Delta t_1 = \Delta t_2$, eq 12 simplifies to eq 10. For all other values of Δt_1 and Δt_2 , the coefficient of the derivative for uneven spacing is less than the coefficient for even spacing since $\Delta t_1 \Delta t_2$ is always less than Δt^2 when $\Delta t_1 + \Delta t_2 = 2\Delta t$. Thus, shifting the sample measurement temporally closer to either of the bracketing background measurements reduces the background correction error.

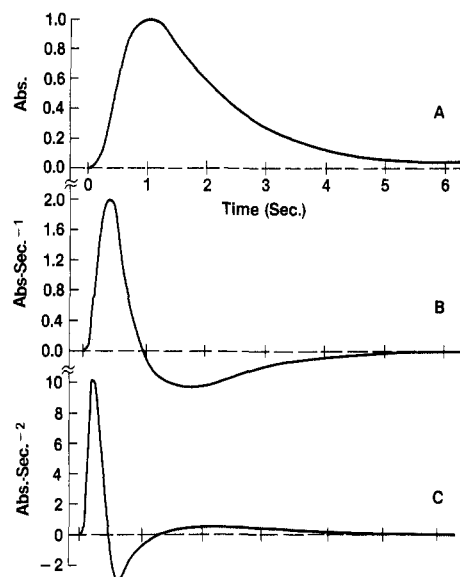


Figure 1. Plots of (A) the mathematical model of the background absorbance, (B) the first derivative (proportional to asymmetric errors), and (C) the second derivative (proportional to bracketing errors).

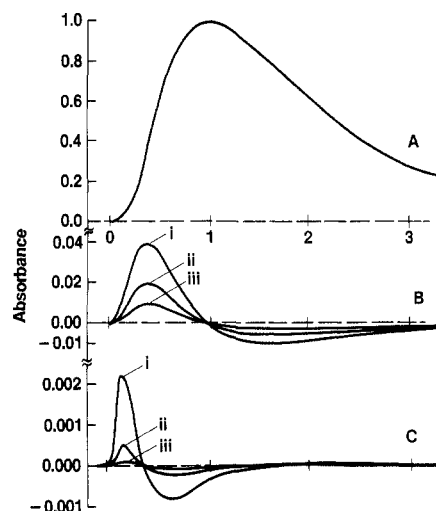


Figure 2. Effect of Δt on the background-corrected absorbance errors: (A) background absorbance, (B) asymmetric errors, and (C) bracketing errors where (i) $\Delta t = 0.020$ s, (ii) $\Delta t = 0.010$ s, and (iii) $\Delta t = 0.005$ s.

BACKGROUND ABSORBANCE MODEL

A mathematical model was selected to illustrate the error functions described in the previous section. The log-normal distribution equation, $A = \exp[-(\ln t)^2]$, was used to approximate the time-dependent background signal. Figure 1A shows this absorbance-time profile. In this figure and all subsequent models, it will be assumed that there is no analytical absorbance signal. Although background absorbance often displays a more complex profile, this model will be useful in illustrating the magnitude of the errors and their dependency on the general shape of the background signal. In Figure 1, curves B and C show the first and second derivatives of this function. It must be remembered that the asymmetric and bracketing errors are proportional to these derivatives with proportionality constants of Δt and $-(\Delta t)^2/2$, respectively.

Figure 2 shows the errors E_1 and E_2 (eq 7 and 10) for the asymmetric and bracketing modes for Δt values ($\Delta t_1 = \Delta t_2$) of 0.02, 0.01, and 0.005 s. The absorbance-time profile has been repeated in this figure for reference. A comparison of E_1 and E_2 in Figure 2 shows that the bracketing mode produces a significantly lower error (note change in the Y-axis scale) at nearly all time intervals. Plots of E_2 using uneven

spacing ($\Delta t_1 \neq \Delta t_2$ and $(1/2)(\Delta t_1 + \Delta t_2) = 0.02, 0.01$, and 0.005 s) will have amplitudes less than the plots shown in Figure 2. For example, if $\Delta t_1 = 3\Delta t_2$, then $\Delta t_1\Delta t_2/\Delta t^2 = 3/4$. In this case, the absolute errors for curves i, ii, and iii (Figure 2) are reduced by 25%.

It is obvious from this figure and eq 7 and 10 that both errors are independent of the absolute magnitude of the background signal. The asymmetric mode error is a linear function of Δt and the slope of the background absorbance. The maximum slope of the leading edge of the background absorbance peak in Figure 1A is 2.0 A s^{-1} . Grobowski et al. (9) have reported slopes of 3 to 5 A s^{-1} for seawater with platform atomization and maximum heating rate at the Cu resonance line. Slopes as high as 10 A s^{-1} were reported under the worst conditions. As a result, the errors shown for asymmetric correction in Figure 2 can be several times larger in real samples depending on the matrix.

The time-dependent behavior of the bracketing mode error is less intuitive. The largest errors are found at the points of inflection, i.e., where the slope changes and the plot of three successive data points deviate from a straight line. Both the asymmetric and bracketing mode are sensitive to the "sharpness" of the background absorbance peak, but the maximum errors occur at different locations. In general, the faster the background absorbance changes the larger the background corrected absorbance errors.

Consequently, increasing the sample size or increasing the furnace heating rate, with all other conditions held constant, will increase the absorbance errors caused by nonsimultaneous correction of the background signal.

FILTERING

Digital or analog filters are commonly employed in processing the absorbance signal. Lundberg and Frech (10) have clearly shown that excessive filtering in early instruments produced misleading results when absorbance-time information was to be used. In addition, only filtering of the absorbance data is discussed here, as filtering of the raw intensity data can lead to inaccuracies (11). Only the impact of filtering on the accuracy of the background corrected absorbances will be evaluated in this study. The effect of filtering on the signal-to-noise ratios has been considered elsewhere (12).

Linear filtering of the corrected absorbances can be represented by an integration procedure operating on the error functions given in eq 6 and 9. For the asymmetric mode, the time constant of the filter δt can be applied to the error function given in eq 6 to approximate the filtered error $E_{1,f}$ as

$$E_{1,f} \cong \frac{1}{\delta t} \int_{(t-\delta t/2)}^{(t+\delta t/2)} E_1 dt \quad (13)$$

where $1/\delta t$ is the normalization constant to provide errors in absorbance units. By use of the approximation given in eq 6, integration of this error function yields the original background absorbance function evaluated between the appropriate intervals

$$E_{1,f} \cong \frac{\Delta t}{\delta t} \left[f(t) \right]_{(t-\delta t/2)}^{(t+\delta t/2)} \quad (14)$$

Figure 3 shows the first derivative evaluated for filters of 0.0, 0.2, and 0.5 s. Smoothing does not diminish the magnitude of the error to any significant extent, i.e., the maximum error is reduced by only 25% using a 0.5-s filter.

Maximum filtering (e.g., $\delta t \rightarrow \infty$) represents the "integration mode" or "peak area" option available on most instruments. It is obvious from eq 11 that if $f(t) = 0$ at the start and end of integration, then $E_{1,f} = 0$ also. Thus, integration over the

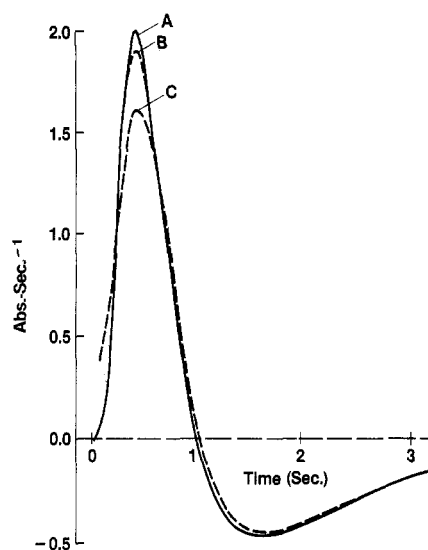


Figure 3. Effect of filtering on asymmetric errors for (A) no filter, (B) 0.2 s filter, and (C) 0.5 s filter.

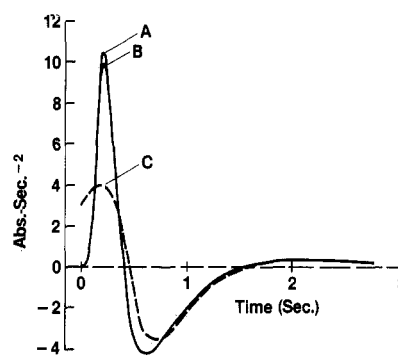


Figure 4. Effect of filtering on bracketing errors for (A) no filter (B) 0.2 s filter, and (C) 0.5 s filter.

entirety of the background absorbance signal cancels the absorbance computation errors.

An analogous treatment can be presented for filtering in the bracketing mode to generate the filtered error $E_{2,f}$

$$E_{2,f} \cong - \frac{(\Delta t)^2}{2\delta t} \left[\frac{dA}{dt} \right]_{(t-\delta t/2)}^{(t+\delta t/2)} \quad (15)$$

Figure 4 shows the second derivative evaluated for filters of 0.0, 0.2, and 0.5 s. The reduction in error is greater than that observed for the asymmetric mode but is still not significant. Filtering over the entirety of the background absorbance peak again results in $E_{2,f} = 0$. In addition, since the first derivative has a zero crossing at the peak maximum (Figure 1), integration from the start of atomization to the background absorbance maximum or from the maximum to the end of the background absorbance signal also results in cancellation of the bracketing mode errors.

CONCLUSION

Errors resulting from nonsimultaneous measurement of the sample and reference absorbance signals can be significant. In all cases, employment of the bracketing mode (as compared to the asymmetric mode) leads to a substantial reduction in the background corrected absorbance error. This reduction could be realized simply through a different data handling routine for existing commercial instruments and does not require any alteration in the mode of data acquisition, i.e., alternate collection of A_{1+b} and A_b can still be employed.

While filtering reduces the error, it does not have a major impact unless integration over the entire duration of the background absorbance signal is employed. This results

in the cancellation of all errors. Integration times just covering the duration of the analytical absorbance signal can result in background errors which are larger than would be present were integration omitted. For the bracketing mode, shorter intervals from the start to the maximum of the background signal or from this maximum to the end of the background signal also produce a cancellation of all errors. However, variability in the time location of the background peak may not make this approach possible for samples with variable matrix concentrations.

This study suggests that simple modifications in instrument data reduction procedures to employ the bracketing mode and careful use of the peak integration feature can significantly reduce errors in computed background-corrected absorbances caused by nonsimultaneous collection of the sample and reference signals.

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Mass Spectral Analysis of Monodeuterio-Labeled Compounds Exhibiting Significant $(M - H)^+$ Peaks

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A method is presented for computing the relative amounts of unlabeled and monodeuterio-labeled materials in isotopic mixtures for compounds whose mass spectra contain significant $(M - H)^+$ peaks. The method is applied to the isotopic dilution experiment where it produces a linear relationship between the measured and actual isotope ratios. The slope of the resulting line is directly related to the relative concentration of labeled compound in the initial sample.

Techniques using stable isotopes have become increasingly important in many areas of chemistry, biology, and geology. The isotope dilution technique is the analytical method of choice for the quantitation of a variety of materials (1). Stable isotopes are widely used as tracers in studying metabolic processes (2). Kinetic isotope effects are used as probes into the mechanisms of organic reactions (3-5).

Mass spectrometry is the most commonly used method for the analysis of compounds labeled with stable isotopes. Several mathematical analyses of the general relationship between a mass spectrometrically determined ratio of ion currents and the ratio of the labeled to unlabeled compounds in the sample have been published (6, 7). The analysis, however, becomes much more difficult if the compound gives rise to an abundant $(M - H)^+$ peak. The usual ways of handling this difficulty have been either to derivatize the compound to one which does not give an $(M - H)^+$ peak or to lower the ionizing electron energy until the $(M - H)^+$ fragment ion becomes insignificant (8). Both of these methods have potential drawbacks. Derivatization may change the ratio of labeled to unlabeled species and decreasing the ionizing electron energy lowers the overall sensitivity which may lessen

the precision of the determination.

Recently, Benz described a computer program which makes approximate corrections for the presence of $(M - H)^+$ peaks (9). While this numerical method is fairly general, it is quite complex and is, in some cases, subject to serious limitations. The purpose of this paper is to present a simple method of calculating the ratio of isotopic abundances for the special case of mixtures of unlabeled and monodeuterio-labeled compounds which produce significant $(M - H)^+$ peaks.

EXPERIMENTAL SECTION

The mass spectral data were acquired with an HP5982A GC/MS. The ionizing voltage was 70 V and the source temperature was $70 \pm 10^\circ\text{C}$. The benzhydrol samples were introduced with the direct insertion probe. The sample pressure could be held constant for several minutes by controlling the probe temperature. The ion currents at each of the relevant masses were cyclically sampled 1000 times over a period of approximately 3 min, simulating simultaneous detection. The ion current ratios represent 12 determinations (of 1000 measurements) for each isotopic mixture and have standard deviations of approximately 0.2%.

Under these experimental conditions the ratio, $(M_D - H)^+ / MD^+$, for benzhydrol was about 0.3. This ratio was sensitive to the ionizing voltage and source temperature. Isotopic analysis under experimental conditions which gave $(M_D - H)^+ / MD^+$ ratios ranging between 0.2 and 0.6 gave essentially identical results. Somewhat surprisingly, perhaps, the loss of H from the benzhydrol- α -d ion is favored over D loss; $(M_D - H)^+ / (M_D - D)^+$ was approximately 7 in these experiments.

The benzhydrol- α -d was prepared by reduction of benzophenone with lithium aluminum deuteride and recrystallized from petroleum ether to give colorless needles with a melting range of $64-65^\circ\text{C}$. The proton NMR of the product showed no detectable signal at δ 5.2, indicating that the benzhydrol- α -d was $0 \pm 3\%$ undeuterated.