Maintenance of the slope of linearized calibration curves in Zeeman graphite furnace atomic absorption spectrometry

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Abstract

L’vov and co-workers developed a theoretical model and computational procedure (B.V. L’vov, L.K. Polzik and N.V. Kocharova, Spectrochim. Acta Part B, 47 (1992) 889 and B.V. L’vov, L.K. Polzik, N.V. Kocharova, Yu.A. Nemets and A.V. Novichikhin, Spectrochim. Acta Part B, 47 (1992) 1187) that linearized calibration curves in Zeeman graphite furnace atomic absorption spectrometry by taking into account the presence of stray light. The calculations of L’vov and co-workers were based on three parameters: the rollover absorbance $A_r$, Zeeman sensitivity ratio $R$, and the original background corrected peak absorbance values $A_x$. In order to simplify the calculations, $R$ was assumed to be unity. In the studies reported here, this simplification is shown to be unsatisfactory because the slope obtained in the upper portion of the calibration curve, after linearization, is found to be different from the slope obtained in the normal linear region. Deviations between these slopes were found to be as high as 30%. The present work also shows that the theoretical model of L’vov and co-workers does not have a mathematical solution at high values of $A_r$. This failure of the model prevents its use at high $A_r$ values. The physical nature of this failure is still unclear, which points to the necessity for further work to understand the inadequacies of the present theory. In the present studies, calculations based on the Newton method of successive approximations (A.I. Yuzefovsky, E.G. Su, R.G. Michel, W. Slavin and J.T. McCaffrey, Spectrochim. Acta Part B, 49 (1994) 1643), allow incorporation of the experimental value of $R$ at the rollover point $R'$, which better linearizes the calibration curves. By use of this approach, a satisfactory result is obtained for lead ($R' = 0.67$) up to the point of failure of the model at high values of $A_r$.

Keywords: Calibration curves; Furnace atomic absorption spectrometry; Linearized calibration curves; Newton method of successive approximation; Stray light; Zeeman furnace atomic absorption spectrometry

1. Introduction

There have been considerable efforts to understand the processes that cause deviation from linearity of the calibration curve in graphite furnace atomic absorption spectrometry (GFAAS). These processes include the polychromaticity of the
absorbed radiation [1] and, in Zeeman GFAAS, incomplete separation of the $\pi$ and $\sigma$ components of the absorption line in the magnetic field [2]. A number of researchers have continued to explore a variety of possible reasons for the deviation from linearity in Zeeman AAS [3–5] of which the most recent detailed review is that of Su et al. [6].

De Loos-Vollebregt and de Galan [5] tried to correlate the shape and initial slope of the calibration curves with the background absorbance ($A_b$) for Zeeman GFAAS. They showed that the presence of non-absorbable radiation, or stray light, could cause errors in the determination of $A_b$ values, and they attempted to quantify stray light through consideration of the limiting absorbance values ($A_{lim}$). Although several authors have attempted to explain the variation of signal size with concentration, and other experimental parameters of atomic absorption, they have not necessarily tried to correct for calibration curvature [7,8].

One of the most recent discussions of the curvature of the analytical working curves was done by Gilmutdinov et al. [9]. They proposed a model that accounted for many spectral and other features of the analyte such as Doppler and pressure broadening of emission and absorption lines, hyperfine structure, nonisothermality of the atomizer, and analyte cloud density distribution. Voigtman et al. [10] employed a multiparametric polychromatic simulation and optical calculus to determine the contribution of various types of stray light. Simulated calibration curves, obtained for various monochromator spectral bandwidths, demonstrated calibration curve non-linearities of similar magnitude to those observed in practice. This indicated that the origin of a major fraction of stray light in Zeeman GFAAS could result mainly from polychromaticity in the light source.

Most of the models described above, either did not give a definite description of the quantity of stray light, or required significant preliminary experimental data. They were based on specific knowledge of spectral line shapes, which makes it difficult or impossible to apply them to the linearization of calibration curves on a routine basis. Indeed, they were not initially designed to correct non-linearities in calibration curves. From a practical point of view, it would be useful to have a simplified model that is specifically designed to evaluate and correct the deviations from linearity of the calibration curves in Zeeman GFAAS. Such a practical approach would ultimately allow the use of the characteristic mass $m_0$ as the only calibration parameter for the measurement of both small and large values of integrated absorbance signals throughout the calibration curve. There have been a number of attempts that have been directed toward these practical goals.

De Loos-Vollebregt et al. [11] proposed an instrumental approach for the extension of the working curves in Zeeman GFAAS. A spectrometer with a modified Zeeman background correction system obtained measurements at three different field strengths during each modulation cycle of the Zeeman a.c. magnet, compared to the conventional measurements at zero and at maximum field strengths only [12]. The instrument demonstrated the potential to extend the linear dynamic range by up to one order of magnitude. However, significant losses in sensitivity, due to a reduction in the slopes of the calibration curves, restricted the usefulness of the instrumentation. The method also required significant modification of the conventional instrumentation.

Bayunov and L'vov [13] proposed linearizing calibration curves by conversion of the measured values to true absorbance values ($A_o$) that satisfy the Bouguer–Lambert–Beer (BLB) law with an ideally monochromatic light source and no stray light. Their algorithm was based on the use of information gleaned from the shape of the atomic absorption pulses in the furnace, and included some fundamental parameters that were not included by others [14–16]. However, neither a working algorithm nor linearized data were presented in the publications [13,17].

Recently, L'vov and co-workers [18,19] proposed a computational peak correction procedure in order to correct the effect of stray light in conventional and Zeeman AAS. The model was designed to correct each datum point within the transient signal profile. Integration of this new signal profile gave a corrected integrated absorbance $A_o$. It was assumed that the source light that passes the spectral bandwidth of the monochromator includes only two components: monochromatic
radiation of intensity $I_0$ that is absorbed by the analyte in a fashion that obeys the BLB law, and non-absorbable radiation of intensity $\alpha I_0$. A theoretical expression for peak absorbance for conventional AAS was proposed

$$A = \log\left[\frac{(I_0 + \alpha I_0)}{(1 + \alpha I_0)}\right]$$

$$= \log\left[\frac{(1 + \alpha)}{(10^{-\alpha} + \alpha)}\right]$$

(1)

In order to develop a practical algorithm, L’vov et al. [19] simplified their theoretical model by use of three mostly empirical assumptions. Firstly, the calculation of $\alpha$ was done indirectly by measurement of the rollover absorbance $A_r$. Secondly, it was assumed that the background signal always changes with concentration in a fashion that obeys the BLB law ideally. Thirdly, the Zeeman sensitivity ratio $R$ was set equal to unity for all elements. And, for all experimental conditions of lamp current, slit width and concentration. The rollover absorbance was defined as the highest peak absorbance value that was measured for a given analyte and experimental conditions of lamp current, slit width, etc. The simplifications gave three advantages. Firstly, the computational procedure was based only on one starting parameter $A_r$. Secondly, it was shown that both the model and the computational procedure were independent of the nature of the stray light, and required information only about the ratio between the stray light and the absorbable radiation in the spectrometer. Thirdly, the relative error in the concentration axis for the extended dynamic range was calculated to be the same as for the conventional calibration curve [20]. This allowed Su et al. [6] to redefine the experimental parameter $\alpha$ as an “effective stray light” that was considered to be the sum of all effects that are either different types of stray light or that behave like stray light, without any attempt to distinguish between them.

Although one of their primary goals was to linearize the calibration curves [13,18], L’vov and co-workers [18,19,21,22] discussed neither independent tests that might confirm the linearity of the linearized data, nor the method that they employed to draw a straight line between the original data points and/or the linearized data points. The authors’ discussion implicitly assumed that the algorithm generated a linear extension of the dynamic range, and maintained the slope of the original curve. They used the relative standard deviation (RSD) between characteristic mass values, obtained from all linearized data points, in order to characterize “the error of linearization” [19]. The work described in the present paper confirms that the RSD approach is valid only when the slopes of the original and linearized parts of the calibration curve coincide exactly, as one would expect from a knowledge of linear regression. An RSD value is only an indicator of the total spread of the data points around a new computed calibration curve, and cannot evaluate the difference in slope between the original linear part of the calibration curve and the linearized parts of the calibration curve. Consequently, the resultant RSD values for $m_0$ were within the range 2.4-5.8% for all tested elements, but it is shown here that the absolute errors in the determination of $m_0$ values in the lower and upper parts of the linearized calibration curve can be as large as 30%. This was due to the difference in slope between the original linear part and the linearized part of the curve.

The computational procedure of L’vov et al. [19] was used in the present authors’ laboratory for the linearization of calibration curves for bismuth, manganese, copper, silver, thallium, and chromium under a variety of experimental conditions of slit widths, lamp currents, etc. [23,24]. The approach of L’vov and co-workers that used the RSD of the characteristic masses as a measure of the linearity of the linearized calibration curves, was employed to achieve linearization for a wide range of experimental conditions. The resultant extension in the linear range of the calibration curves was a factor of between three and five. As in the work of L’vov and co-workers, it was assumed that the slope of the original linear region of the calibration curve was maintained through the linearized parts of the curve.

Recently [24] the present authors attempted to introduce the Zeeman sensitivity ratio back into the simplified model of L’vov and co-workers. The resultant slopes were steeper than those obtained by the algorithm of L’vov et al. [19] for the same elements under the same experimental conditions. Meanwhile, the RSD between
characteristic masses obtained through the linearized part of the calibration curves remained almost the same for both models [24]. After these attempts to reproduce and improve upon the algorithm of L’vov and co-workers, the present authors began to question whether or not the linearization procedure was able to maintain the same slope in the linearized region as in the original linear part of the calibration curve. The present work reports detailed studies on this subject, together with an analysis of the theoretical model of L’vov et al. [18] in the context of all the prior experimental computational approaches [19,24].

2. Theory

2.1. Literature basis of the theory

The following symbols are used throughout this paper: \( A_0, A_{0,n} \), and \( A_z \) refer to integrated absorbance values; the subscripted versions \( A_0, A_{0,n}, A_b, A_r, A_{lim} \), and \( A_z \) refer to peak absorbance values. The definitions for the symbols are given in context as necessary throughout this paper.

Prior work on absolute analysis and linearization of calibration curves [6,19,25] has addressed the feasibility of computation of a stable linear calibration function \( A_0 = f(C) \) based on experimentally measured \( A_z, \alpha, \) and \( R \) values, with a slope inversely proportional to the theoretical characteristic mass value for a given element, \( m_0 \):

\[
dA_0 = 0.0044 \left( \frac{1}{m_0 / d(1/m_0)} \right)^{-1}
\]

(2)

The ideal \( A_0 \) must be independent of experimental parameters and the method of background correction, and must depend only on the geometry of the atomizer and the sensitivity of the instrument for a given analyte. This means that \( dA_0 \) is by definition an absolute slope for a given analyte.

The process of transformation of \( A_z \) into \( A_0 \), and subsequently \( A_z \) into \( A_0 \) values, was introduced as a “correction procedure” by Su et al. [6]. The studies were performed only on the original linear part of the Zeeman GFAAS calibration curves. These authors measured the changes in the slope of the original calibration curve as a function of different experimental conditions such as lamp current and slit width

\[
dA_z = 0.0044 \left( m_0 / d(m_0) \right)^{-1}
\]

(3)

For some elements the RSD between the original slopes obtained under the different experimental conditions was about 20% or higher. However, when the amount of stray light and the Zeeman sensitivity ratio for each experimental condition were measured and incorporated into the slope correction procedure, the RSD between the resultant slopes was only a few percent. Furthermore, for each tested element, a corrected characteristic mass \( m_0 \) was calculated from the corrected mean slope, and found to agree closely with the theoretical characteristic mass values for a given element

\[
dA_z \xrightarrow{R, \alpha} dA_0 = 0.0044 \left( m_0 / d(m_0) \right)^{-1}
\]

(4)

In other words, Su et al. [6] experimentally obtained a calibration function that coincided, within instrumental error, with the absolute calibration function, at least in the original linear part of the calibration curve of Zeeman GFAAS. Perhaps, more importantly, Su et al. [6] also showed that the resultant calibration function maintained a virtually constant slope regardless of experimental conditions. This last observation is an important indicator that an absolute calibration function is feasible.

The situation became more complicated for studies directed at the non-linear region of the calibration curve. L’vov et al. [19], instead of direct calculations of \( A_0 \) from \( A_z \) absorbances, proposed keeping the sensitivity and hence the magnitude of \( m_0 \) unchanged by the linearization, by use of normalization of the linearized values of \( A_z \) to a function \( A_{0,n} \). This new function was designed to have a slope that would be identical to the slope of the linear part of the original experimental calibration curve. The computational procedure was described as a “linearization”, and the linearized absorbance values were labeled as \( A_{0,n} \). The relationship [19] between \( A_0, A_{0,n}, \alpha, \) and \( R \) was given as

\[
A_0 = \frac{1 + \alpha}{R} A_{0,n}
\]

(5)
The linearized absorbance values $A_{o,n}$ rely on measurements of $\alpha$ and $R$ at each set of experimental conditions. Hence, the slope of the function $A_0,n = f(C)$ will be different for different experimental conditions. Ultimately, as the theory of linearization develops, the normalized and linearized absorbance values may be transformable into absolute absorbances after accounting for the amount of stray light $\alpha$, and the Zeeman sensitivity ratio $R$ (Eq. (5)) for a given set of experimental conditions. In the normalization approach one, and only one, function ($A_0,n = f(C)$) can correspond to a given set of experimental conditions described by the unique combination of $\alpha$, $R$ and $A_z$ values. The computation of the $A_0,n = f(C)$ function appears to be a very appropriate initial step for the computation of absolute absorbance values, because the construction of a linear calibration function based on the ideal absorbance $A_0$ up to the rollover point is still a challenge in GFAAS, as attested by the difficulties reported in the present paper.

Thus, the complete transformation process from $A_z$ into $A_0$ values for the original linear part of the calibration curve, which is the limiting case for a non-linear calibration curve, consists of several sequential steps as follows:

$$A_z \xrightarrow{\text{correction}} A_0 \rightarrow A_0$$

(6a)

The transformation from $A_z$ values into $A_0$ values for the non-linear part of the calibration curve includes one extra step

$$A_z \xrightarrow{\text{linearization}} A_{o,n} \xrightarrow{\text{correction}} A_0 \rightarrow A_0$$

or

$$A_z \xrightarrow{\text{linearization}} A_{o,n} \rightarrow A_0,n \xrightarrow{\text{correction}} A_0$$

(6b)

The complete transformation process, Eq. (6a,b) can work only when each step of the procedure generates a well-behaved function. This would be necessary to prevent error propagation through successive stages of the procedure. As a result of such errors, the number of final functions $A_0 = f(C)$ will be more than unity for a given element, which contradicts the definition of the absolute slope.

Yuzefovsky et al. [24] attempted to modify the L’vov et al. computational linearization procedure, in order to avoid several simplifications introduced into the original theoretical model [19]. It was found that the modified computational [24] and the simplified computational [19] procedures generated two different functions $A_0,n = f(C)$ from the same $A_z = f(C)$ under the same experimental conditions. Additionally, the slope of the calibration function [19] $A_0,n = f(C)$ turned out to be different from the slope of the original linear part of the same calibration curve.

The present paper addresses the impact of the empirical simplifications made in the algorithm of L’vov et al. [19]. There are two basic questions.

Firstly, which computational procedure is most appropriate for linearization? One is based on the theoretical model of L’vov et al. [19] (here called Model 1) and the other contains empirical simplifications of Model 1 (here called Model 2). Model 2 generates the linearized absorbance values $A_{o,n}$, that correlate with the true absorbance $A_0$ through Eq. (5). Based on the above discussion, the present authors propose that the ability for either model to generate an absolute slope from $A_z$ values (Eq. (6a,b)) should be the ultimate requirement for any proposed computational procedure.

Secondly, does either model have the potential to give a slope for the linearized data $A_{o,n}$ that is close to the slope of the linear part of the original data, at least up to the rollover point?

The present authors have attempted to address these questions sequentially. In the first step, both models were evaluated in the linear part of the calibration curve. In this case, because the linearized $A_{o,n}$ and the original absorbance values should coincide, the complete computational procedure (Eq. (6b)) can then be transformed into its limiting case (Eq. (6a)). This approach ultimately nullifies the second question above, because the requirement to maintain linearity is applicable only to the non-linear part of calibration curves. In the second step, the present authors addressed the model’s behavior in the non-linear part of calibration curves, up to the rollover point.
2.2. The theoretical model and its simplifications

2.2.1. The underlying theory — Model 1

In Zeeman AAS the signal is the difference between two signals, measured when the magnet is off (A) and when the magnet is on (A_b)

\[ A_z = A - A_b \]  

Eq. (7)

Some example experimental calibration curves from the present work are shown in Fig. 1(a) for the element lead. The Zeeman sensitivity ratio for lead decreases from 0.80 in the lower part of the calibration curve to 0.67 at the rollover absorbance value. Both conventional and background absorption curves disobey the BLB law at high analyte masses and deviate from linearity. The deviation from linearity of the A_b curve is only a few percent, which is comparable with the instrumental error, and can be neglected. These experimental results are in agreement with the assumption of L’vov et al. [19] that below the rollover point, A_b is small enough to change in a linear fashion.

In order to calculate A_o from the experimentally obtained A_z, the stray light must be taken into account for both “magnet on” and “magnet off” measurements, and for each datum point in the calibration curve. Because stray light most likely remains unaffected by switching the magnetic field “on” and “off”, the expression for A_z from Eqs. (1) and (7) can be written as

\[ A_z = A - A_b = \log \left( \frac{1 + \alpha}{10^{-A_o + \alpha}} \right) - \log \left( \frac{1 + \alpha}{10^{-A_o + \alpha}} \right) \]

Eq. (8)

where \(^bA_o\) is the true absorbance of the insufficiency split \(\sigma\) components of the analyte in the “magnet on” mode. The relationship between A_o and \(^bA_o\) should be the same as for conventionally measured A and A_b and is determined by \(^bA_o = (1-R)A_o\). For a detailed discussion of this relationship the reader should consult Ref. [6]. The substitution of \(^bA_o\) into Eq. (8) gives

\[ A_z = \log \left( \frac{1 + \alpha}{10^{-A_o + \alpha}} \right) - \log \left( \frac{1 + \alpha}{10^{-(1-R)A_o + \alpha}} \right) \]

Eq. (9)

The model can be simplified further, because it is possible to express A_b in terms of A_o in a linear fashion, instead of a logarithmic relationship

\[ A_b = \frac{1 - R}{1 + \alpha} A_o \]

Eq. (10)

Therefore Eq. (9) can be written as

\[ A_z = \log \left( \frac{1 + \alpha}{10^{-A_o + \alpha}} \right) - \frac{1 - R}{1 + \alpha} A_o \]

Eq. (11)

which is Model 1. A complete derivation of Eq. (11) was presented in Ref. [19].

Due to the occurrence of A_o simultaneously in a linear form and in an exponential form in the log
term, the model does not have an analytical solution with respect to $A_o$, therefore it must to be solved indirectly. Yuzefovsky et al. [24] recently demonstrated the use of the Newton method of successive approximations as an attempt to solve this problem.

2.2.2. Simplification — Model 2

For their computational procedure L’vov et al. [19] assigned $R = 1$ for all elements (Eq. (12a)). This simplification, according to the authors, had two goals; the first was to obtain an analytical solution for the algorithm, while the second was to achieve the simplest procedure because Eq. (12) requires only one initial parameter $\alpha$, instead of the two parameters required for Model 1 (Eq. (11)).

$$ A_z = \log \left( \frac{(1 + \alpha)}{(10^{-1(1+\alpha)A_o} + \alpha)} \right) \quad (12a) $$

The computational procedure can be re-written for the determination of absolute absorbances $A_o$, in the linear region, by substitution of Eq. (5) into Eq. (12a) giving

$$ A_z = \log \left( \frac{(1 + \alpha)}{(10^{-A_o} + \alpha)} \right) \quad (12b) $$

The drawback of the simplification of L’vov et al. [19] that assigned $R = 1$, can be seen from a comparison between Eqs. (1) and (12b). Mathematically, $A_z$ was essentially assigned to be equal to $A$, which meant that the curvatures of the calibration curves for Zeeman and conventional AAS were assumed to be the same. Fig. 1(b) illustrates graphically that the assumption causes much of the available information shown in Fig. 1(a) to be lost. The physical meaning and implications of this simplification can be seen in the following discussion, which is based on a comparison of the slopes of $A_o$, $A$, and $A_z$. In this discussion, the slopes are compared at low analyte masses where the calibration curves are linear.

The main requirement for a correction procedure is to maintain the slope of the corrected data to be the same as the slope of $A_o$ at the origin [6]. L’vov et al. [18] derived relationships that correlate the experimental data obtained from the linear part of the original calibration curve with the ideal absorbance values for conventional AAS (Eq. (13)) and for Zeeman AAS (Eq. (14)).

$$ \frac{dA}{dA_o} = \frac{1}{1 + \alpha} \quad (13) $$

$$ \frac{dA_z}{dA_o} = \frac{R}{1 + \alpha} \quad (14) $$

For the original (linear) part of the calibration curves, the validity of these expressions was tested and confirmed experimentally by Su et al. [6]. Fig. 2(a) shows the Model 1 relationship for Zeeman AAS in Eq. (14) and illustrates that the difference between the ideal and experimental slopes is due to the presence of stray light $\alpha$, and the loss in sensitivity $R$, in the Zeeman background correction mode.

For Model 2, it is assumed that there are no losses in sensitivity due to Zeeman background correction ($A_z \equiv A$), which means that the model corrects Zeeman absorbances as if they were
conventional absorbance values (Eq. (13)). Moreover, Eq. (12b) can be transformed into Eq. (13) when \( A_0 \to 0 \). This means that Model 2 only corrects the original data for the presence of stray light in the system, without taking into account the real difference between \( A \) and \( A_2 \) values. The resultant slope of the recalculated data will always be less than the true slope for the ideal absorbance, by \( A_0 \times (1 - R) \) (Fig. 2(b)). The deviation of the slope becomes significant, particularly at higher analyte masses when the absolute background signal sizes become significant.

### 2.3. Methods for the determination of \( \alpha \)

Because Eq. (11) is the only known expression that correlates \( \alpha \) with \( A_0 \), one of these variables has to be found independently. L'vov et al. [19] proposed expressing \( \alpha = f(A_r) \), which intuitively follows from the thought that rollover must be controlled by \( \alpha \) and therefore a measurement of \( A_r \) is a measure of \( \alpha \). From a practical point of view, the method is simple because it requires only one preliminary measurement of the \( A_r \) value at a high analyte concentration under any given experimental conditions. In studies conducted in the present authors' laboratories, the employment of the method demonstrated satisfactory results [6]. It was shown that the discrepancies between the theoretical characteristic mass and the experimental characteristic mass obtained from the linear region of the calibration curve, could be minimized to several percent.

Note that it is not possible at this stage to give a more critical evaluation of the above method, due to the absence of an independent algorithm with which to measure \( \alpha \). One possibility is to explore the calculation of \( \alpha \) at low analyte concentrations, where values of \( A_0 \) and \( A_2 \) have a linear relationship. If it can be assumed that the value of the theoretical characteristic mass is reliable enough for a given analyte, under a given set of experimental conditions, then a modified Eq. (14) could be employed for the determination of \( \alpha \):

\[
dA_2/dA_0 = R/(1 + \alpha) \Rightarrow \alpha = R/(dA_2/dA_0) - 1 = R/(m_0/m_0) - 1
\]

(15)

Theoretically, such a calculation requires only one measurement of a peak absorbance in the linear range of the original calibration curve, although it would be better to use the slope of the calibration curve, instead of a single datum point, in order to eliminate the error that is involved in solution preparation. In the work reported here this method was not used for the determination of \( \alpha \), but it might be worth testing in the future.

### 2.4. Solutions for the different models

A primary obstacle associated with the use of Eq. (11) is the lack of a mathematical solution. However, differences between the two models (Eqs. (11) and (12b)) can be viewed graphically. In order to obtain graphical solutions for the two models, their mathematical expressions can be represented as

\[
f(A_0) = 0
\]

(16)

Thus, the intercepts of Eq. (16) with the \( x \) axis \( (A_0) \) generate solutions for \( f(A_0) = 0 \). From Eq. (16), Eqs. (11) and (12b) can be written as Eqs. (17) and (18) and are shown graphically in several forms in Figs. 3(a) and (b) as

\[
f_1(A_0) = A_2 - \log \left( \frac{1 + \alpha}{10 - A_0 + \alpha} \right) + \frac{1 - R}{1 + \alpha} A_0 = 0
\]

(17)

and

\[
f_2(A_0) = A_2 - \log \left( \frac{1 + \alpha}{10 - A_0 + \alpha} \right) = 0
\]

(18)

respectively.

Fig. 3 represents general solutions for only one arbitrary point \( (A_2) \) in a single transient atomic absorption signal, with given values of \( R \) and \( \alpha \). By convention, the stray light parameter \( \alpha \) is maintained throughout the calibration curve. In order to obtain a solution for a new point, a new pair of \( A_2 \) and \( R \) values must be introduced into the equations. It can be seen from Fig. 3(a) that Model 1 has two solutions for \( A_0 \) that correspond to a given \( A_2 \), instead of the single solution obtained from Model 2 (Fig. 3(b)). Because only the first solution for the model produces values of \( A_0 \to 0 \) at \( A_2 \to 0 \), the appearance of the second
solution must be a mathematical artifact with no physical meaning, and can be neglected. In addition, the descending slope of $f_1(A_o)$ is less steep than the slope obtained from $f_2(A_o)$, which ultimately produces higher $A_o$ values for Model 1 compared to Model 2. This is the result of the presence of a positive background term $((1 - R)A_o/(1 + \alpha))$ in Eq. (17), and is consistent with Fig. 2, where Model 1 can be expected to give higher values of $A_o$ unless $R$ is close to unity.

Further, as the $A_z$ term increases, the function $f_1(A_o)$ will ascend the $y$ axis and, after a particular $A_z$ value, all of the function $f_1(A_o)$ will be positioned above the $x$ axis. This means that at $A_z$, and all higher values, the model has no mathematical solution and will fail with respect to $A_o$. Model 2, in contrast, has theoretical solutions for all possible $A_z$ values, because mathematical analysis of Eq. (18) indicates that $f_2(A_o)$ has no minima in the overall $[0, +\infty]$. A mathematical proof of the failure of Model 1 to give a solution for $A_o$ over a wide range of values of $A_z$, $R$, and $\alpha$ is developed in Appendix A. The physical meaning of the failure is not clear. It could be speculated that, in real situations, the stray light may be affected by varying amounts of analyte atoms, which would mean that the value of $\alpha$ might gradually change through the rising part of the calibration curve, instead of being constant, as assumed for both models [19].

The data from the calibration curve in Fig. 1(a) were linearized by the use of Eqs. (17) and (18), in order to see the trend in the $A_o$ values produced by the two models. The results are presented in two sets of graphical solutions in Fig. 4. Because each datum in Fig. 1 represents peak absorbance, the linearization procedure covers a wide range of $A_z$ values up to the rollover point. The data points in Fig. 4, where the curves intercept the ordinate axis ($A_o = 0$) represent the set of original $A_z$ values from Fig. 3. Individual corrected absorbance data points for each $A_z$ are located at the corresponding intercepts on the $x$ axis. As discussed above, each model provides a different set of corrected absorbances, that are not due to the difference in descending slopes. Moreover, for each pair of linearized data points calculated from the same original $A_z$ value, Model 1 generally gave higher values with a gradually increased difference between corrected absorbance values relative to Model 2. However, at very low values, the absolute difference between corrected peak absorbances generated by both models was not as great as at higher values. It follows that the difference between integrated absorbance values at low concentrations would also be relatively small. This explains the initial impressions that Model 2 was able to linearize data, and maintain the slope of the calibration curve, regardless of the Zeeman sensitivity ratio of the analyte [19,23]. Further, Model 1 failed to provide values for $A_o$ at $A_z$ values higher than 0.8 absorbance. This means that the results that were obtained by Model 2 for $A_z > 0.8$ were physically meaningless, because the model did not take into account the Zeeman sensitivity ratio.

In this paper, a comparison between computed $A_o$ ideal absorbance values, rather than between $A_{0,n}$ normalized absorbance values for Models 1
Fig. 4. Graphical solution for linearization of peak absorbance values of the lead calibration curve shown in Fig. 1(a). Sets of solid and dotted lines represent functions \( f(A_o) = 0 \) for Models 1 and 2, respectively. Both functions coincided at the intercepts with the ordinate axis \((A_o = 0)\) and at these points represent a set of original peak absorbance values that corresponds to 0, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0, 3.0, 4.0, 5.0, 7.0 ng of lead. The multiple intercepts of each function \( f(A_o) = 0 \) with the abscissa form two sets of linearized absorbance values \((A_z)\) for each model respectively. Other starting parameters: \( \alpha = 0.037 \); experimentally measured \( R \) values were 0.00, 0.80, 0.78, 0.79, 0.77, 0.79, 0.77, 0.75, 0.73, 0.69, 0.67, respectively, with respect to the latter masses of the analyte.

and 2 as done in order to analyze the behavior of both models independently of any given set of experimental conditions. If \( A_{o,n} \) values were to be substituted instead of \( A_o \) values in the models, for the same set of experimental conditions represented by use of the same \( \alpha \) and \( R \) values, the shape of the curves in the graphical solutions for both models would remain the same, because \( A_o \) correlates to \( A_{o,n} \) through a simple linear relationship (Eq. (5)). The \( A_{o,n} \) values would merely be smaller than the corresponding \( A_o \) values. All the \( A_z \) and the corresponding \( A_o \) values are located at the intersection of the set of equations with the \( y \) and \( x \) axes, respectively. Hence, the relationship between \( A_o \) and \( A_{o,n} \) is well defined, as \( A_z \leq A_{o,n} < A_o \) for all possible values of \( \alpha \) and \( R \). If model 1 is rewritten for calculations of \( A_{o,n} \)

\[
f_1(A_{o,n}) = A_z - \log \left( \frac{1 + \alpha}{(10^{-(1+\alpha)A_{o,n}/R} + \alpha)} \right)
+ \frac{1 - R}{R} A_{o,n}
\]

(19)

analysis of the linear relationship between \( A_{o,n} \) and \( A_o \) (Eq. (5)) indicates that Model 1 (Eq. (19)) has to fail for the same \( A_z \) values as it failed for the calculations of \( A_o \). This was confirmed experimentally and is discussed further in Section 4.

3. Experimental

Experiments and data correction procedures were performed only for lead, while the rest of the data were retrieved from earlier publications by the present authors and co-workers [23,24] and by L’vov et al. [26].

3.1. Instrumentation, calibration solutions, and measurements

Experiments with lead were performed on a Perkin-Elmer spectrometer, model Zeeman 4100ZL, equipped with a transversely heated graphite atomizer (THGA), an AS-70 autosampler,
and a Perkin-Elmer data acquisition system DEC-Station 425c (Digital Equipment Corporation, Maynard, MA), equipped with software GEM BASED PEELAB, version 7.3 (Perkin-Elmer Corporation, Norwalk, CT). Appropriate communication and calculation programs were used, and were written in the BASIC language. They are described in more detail below.

Lead aqueous calibration solutions were made by serial dilution of 1 mg ml\(^{-1}\) stock solution. The stock solution was a “Baker Analyzed”\(^{\text{R}}\) Reagent atomic spectral standard (J.T. Baker Chemical Co., Phillipsburg, NJ 08865). Calibration studies were made with sub-boiled deionized water and were 0.2% in nitric acid (Ultrex\(^{\text{R}}\) II Ultrapure Reagent from J.T. Baker Chemical Co., Phillipsburg, NJ 08865). Sample preparation was performed in a class 100 (US Federal 209b) clean air hood and a class 100 clean air bench. All glassware was soaked firstly in soap solution, then in 20% nitric acid solution, for 24 h in each, and rinsed with sub-boiled deionized water prior to use.

A lead hollow cathode lamp (HCL) manufactured by Perkin-Elmer was employed as a light source. In the experiments standard transversely heated graphite furnaces were employed. Argon with no more than 10\(^{-3}\)% O\(_2\) and N\(_2\) (Aero All-Gas Co., Hartford, CT) served as the sheath gas.

The wavelength, slit width, and lamp current were typical of those usually adopted for THGA conditions [27]. The lead atomization temperature was chosen to be 100 K lower than the recommended one [27] as this gave slightly higher sensitivity. A 20 \(\mu\)l aliquot of sample solution was employed with no matrix modification. Atomization was performed in the gas stop mode. The pyrolysis stage was not used, because all studies were performed on aqueous standards. In all experiments the blank signals were taken into account in the calculations.

The \(R\) value, was measured as the ratio of the slopes between the “Zeeman” and “single-beam” modes. The concentrations and volume of the injected solutions were chosen so that the peak amplitude, for the largest amount of analyte, did not exceed 0.2 absorbance, because the dependence of \(R\) on \(\alpha\) becomes more significant above 0.2 absorbance [6]. The \(R'\) value was determined by measurements of the peak absorbance at the rollover point, for the same amount of analyte, in the “Zeeman” and the “single-beam” \(A_{SB}\) modes, where \(R' = A_t/A_{SB}\) [24].

The computer collected the signal \(A_t = \int f(t)\) (54.5 points s\(^{-1}\)) from the spectrometer, for each atomization cycle, in the form of the integral function \(AZ = \int A_t dt\), where \(A_t\) is the transient integrated absorbance value. Lead data were collected and stored in ASCII format which was easily accessible for later data processing. The lead ASCII data file consisted of eleven integrated transient peaks (\(AZ_1, AZ_2, \ldots, AZ_{11}\)) that represented the calibration curve up to rollover point. Before the peak correction procedure was applied, a five-point, third order Savitzky–Golay technique [28] was applied to the original sets of data in order to smooth the temporal profiles of the absorbance signals. The peak correction procedure for all the lead data was done later, “off-line” as described in detail elsewhere [23,24].

### 3.2. Data correction procedure

The data correction procedure for the linearization of calibration curves were based on both Models 1 and 2. In order to compare both models, the linearization procedure was applied to each peak height datum point in the transient signal profile to obtain a linearized calibration curve within the region before the Model 1 algorithm fails. For both models the normalized absorbance values \(A_o, n\) were used in the computational procedure in order to compare the slopes for the linearized curves with the linear part of the original curve, where \(A_{o,n} = A_o R/(1 + \alpha)\) [19]. In more detail, the following steps were done in order: an “off-line” correction program recalled the original data set \(AZ_1, AZ_2, \ldots, AZ_{11}\); values of \(A_t\) and \(A_{SB}\) that corresponded to the particular experimental conditions were entered manually into the program; the program calculated values of \(R'\) and \(\alpha\); Eq. (11) was solved by the Newton method of successive approximations [24]. Only the first iterative step was employed in the procedure. \(A_{o,n}\) values obtained from Eq. (20) were used as the initial estimate of corrected absorbance.
values [19,24]

\[ A_{0,n}^{\text{int}} = (1 - 10^{-A_{r}}) \times \log \frac{10^{A_{r}} - 1}{10^{A_{r}} - A_{r} - 1} \] (20)

Thus for the first iteration, the linearization algorithm can be written as

\[
A_{0,n} = A_{0,n}^{\text{int}} - \frac{f(A_{0,n}^{\text{int}})}{f'(A_{0,n}^{\text{int}})} = A_{0,n}^{\text{int}}
\]

\[
A_{0,n}^{\text{int}} \times \frac{1 - R'}{R'} + A_{r} - \log(1 + \alpha) + \log[10^{-((1 + \alpha)A_{r}^{\text{int}})} + \alpha]
\]

\[
\frac{1 - R'}{R'} - \frac{1 + \alpha}{R'} \times 10^{-((1 + \alpha)A_{r}^{\text{int}})} \times [10^{-((1 + \alpha)A_{r}^{\text{int}})} + \alpha]^{-1}
\] (21)

The computational procedure generated a set of linearized integrated data points \((A_{0}, n_{1}, A_{0}, n_{2}, \ldots, A_{0}, n_{7})\), where each normalized transient absorbance value was computed as \(A_{0}, n = \int A_{0,n} \, dt\), and where \(A_{0}, n\) is the integrated corrected absorbance value. \(A_{0}, n_{i}\) represented the linearized data point that corresponded to the highest analyte concentration before the failure of the linearization algorithm. Here, this linearization is called the Newton linearization for the sake of convenience. The set of integrated data points obtained directly from Eq. (20) without the first iterative step, represented the calibration curve for the algorithm of L’vov et al. [19]. All the values obtained included one original and two linearized data sets (Models 1 and 2) which were plotted as integrated absorbance versus mass of analyte.

### 4. Results and discussion

Previous data, from the papers of L’vov and co-workers [19,28] and from the work of the present authors and co-workers [23,24], were inspected to determine whether or not the slopes of the linearized part of the calibration curves were the same as in the linear part of the original calibration curve. The first data that were inspected were those of L’vov et al. from the original article [19]. However, it was not possible to draw any conclusions, because the authors reported very few points on the calibration curve. Usually, only a single datum was presented in the linear part of the original calibration curve, which prevented calculation of the slope of the original calibration curve.

For several elements, an analysis was performed on our data [23, 24] that clearly demonstrated the presence of differences between the slopes of the linearized data and the original linear part of the calibration curves (Fig. 5(a, b, d)). Fig. 5 shows the original calibration points; a linear regression through all the linearized data up to the rollover point, and a linear regression through the first three integrated absorbance data points located in the linear part of the original calibration curves. For the data in Fig. 5, the slope of the linear part of the original calibration curves and the linearized curves obtained by the use of L’vov et al. algorithm [19] can be represented by characteristic mass values \(m_{0}\) and \(m'_{0}\), respectively. A method for the computation of these values has been described in detail elsewhere [6,24]. The \(m_{0}\) and \(m'_{0}\) values that were obtained were 7.0 pg and 9.1 pg for copper (a 30% difference), and 1.6 pg and 2.0 pg for silver (a 25% difference), respectively. A set of digitized and re-plotted data for silver from Ref. [28] also demonstrated a 25% difference between \(m_{0} = 1.2\) pg and \(m'_{0} = 1.5\) pg (Fig. 5(c)). The results for chromium calibration curves from Ref. [23] \((R > 0.95)\) had a smaller difference (12%) between \(m_{0} = 2.5\) pg and \(m'_{0} = 2.8\) pg (Fig. 5(d)). Chromium has an \(R\) value much closer to unity than copper or silver, as discussed later. These experimental results indicated that the algorithm of L’vov et al. [19] does not produce linearized calibration curves in Zeeman GFAAS, because the slopes of the linear part of the calibration curves were not maintained after linearization.

The results in Fig. 5 indicated that the algorithm of L’vov et al. keeps the slope of the linearized data close to the slope of the original data when the \(R\) value of the element of interest is very close, or equal to unity, which was assumed by the authors to be the case for all elements [19]. The assignment \(R = 1\) means that their model does not take into account the presence of any background signals for any analyte, because \(R\) is the ratio of the Zeeman corrected signal \((A_{x})\) to the conventional atomic absorption signal in the absence of true background: \(R = A_{x}/A = (A - A_{b})/A\). The assumption that \(R = 1\) might be a safe for chromium in an
aqueous standard, but the logical conclusion from the above observations is that the computational procedures of L'vov et al. may have potential for the linearization of calibration curves only if it becomes possible to take into account the change in $R$ value as a function of the mass of analyte.

For the present studies lead was chosen as a model element because its $R$ and $R'$ experimental values were significantly different from unity. Hence, if Model 1 were to be used for linearization, the low $R$ and $R'$ values should not cause any significant deviation of the slope of the linearized data from the slope of the linear part of the original slope.

For comparison, two sets of linearized data, constructed by the use of Models 1 and 2 in the lower part of the calibration curve, are presented in Fig. 6. The linearizations were performed for

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Fig. 5. Calibrations curves for (a) copper (0.7 nm slit width/15 mA lamp current; original data from Fig. 2(b), Ref. [24]), (b) silver (0.7 nm/15 mA, original data from Fig. 7(vi), Ref. [23]), (c) silver (2.0 nm/22 mA, re-plotted data digitized from Fig. 10, Ref. [28]), (d) chromium (0.7 nm/10 mA original data from Fig. 11(a), ii, Ref. [23]). O, Original values of integrated absorbances; •, corrected values of integrated absorbances, constructed by use of the algorithm of L'vov et al. [19], Eq. (20). Solid line, linear regression through all the linearized data up to the rollover point; dashed line, extrapolated linear regression through first three integrated absorbance data points that are located in the linear part of the original calibration curves. The analyte mass where rollover absorbance was first experienced is indicated with ↓ (for (c) the corresponding analyte mass was not specified in the original paper).
Fig. 6. Expanded calibration graph for the region of 0–2 ng of lead (12 mA lamp current 0.7 nm slit width 283.3 nm wavelength, \(A_{i} = 1.45, \ R = 0.79, \ R' = 0.67\)). ○. original values of integrated absorbances; ●. corrected values of integrated absorbances, constructed by use of L’vov et al. algorithm [19], Eq. (20); △. corrected values of integrated absorbances, constructed by use of the Newton approximation iterative solution for Model 1, Eq. (21). Dashed line, extrapolated linear regression through first three integrated absorbance data points that were located in the linear part of the original calibration curves.

up to 2 ng of lead by the use of the Newton approximation approach (Model 1), and by the approach of L’vov et al. [19] (Model 2). The results showed that for Model 1, the linearized data points turned out to be positioned fairly close to the slope extrapolated from the linear part of the original calibration curve (1% deviation), while the data points that correspond to Model 2 began to deviate from the slope of the original data at an analyte mass of 1 ng (7% deviation). The failure of Model 1 in this example occurred when \(A_{2}\) values were around 0.8–1 absorbances (\(Az \approx 0.36A_s\)), which was consistent with the failure of Model 1 for the calculation of \(A_{o}\) values for the same element, under the same experimental conditions (Fig. 4). This result experimentally demonstrated the linear correlation between \(A_{o}\) and \(A_{o,n}\), and allowed the authors to believe that all of the above theoretical calculations with regard to Model 1 with respect to \(A_{o}\) (Eq. (17)) were also valid for \(A_{o,n}\) (Eq. (19)).

Consistent with the previous examples (Fig. 5(a–d)), the use of Model 2 resulted in the generation of linearized data that were positioned below the extrapolated original linear slope. The overall deviation of Model 2 from the origin would be progressively worse toward the rollover mass, which was at 7 ng for lead under the experimental conditions used here. Fig. 6 tends to confirm that an approach to the extension of the linear range of calibration curves is more likely to be successful when based on Model 1 up to the points of its failure, rather than Model 2.

5. Conclusions

Analysis of the computational procedure of L’vov et al. [19] indicated that the slopes of the linearized curves were not the same as the slopes obtained from the already linear portion of the calibration curves. This deficiency was most likely due to the simplification of \(R = 1\) [19]. Overall, for the four elements discussed in this paper, the differences in slopes between the linearized and linear parts of the original calibration curves were between 12% and 30%, depending on the element. Despite the success of Model 1 used in conjunction with the Newton linearization approach, it is unclear why Model 1 did not have a mathematical
solution at high values of the background corrected peak absorbance values.

The data obtained for lead, with its relatively low \( R \) value \((R < 0.8)\) showed that when the Zeeman sensitivity ratio was incorporated into the linearization algorithm, the model was able to provide the same slope of the linearized data points as the slope of the linear part of the original curve. One important observation of this work was that the algorithm for Model 2, where \( R \) was assumed to be unity, failed at concentrations of analytes significantly below the rollover concentration. Meanwhile, the more theoretically substantiated Model 1 provided satisfactory linearizations up to the point where the model had no mathematical solution. Hence, these preliminary results for lead demonstrated that it is necessary to use the Zeeman sensitivity ratio for the extension of calibration curves in the region below the rollover absorbance point.

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Appendix A: Mathematical proof of the failure of Model 1 to give a solution for \( A_o \) over a wide range of values of \( A_z, R, \) and \( \alpha \)

It is important to demonstrate that the absence of a mathematical solution for Eq. (17) (Model 1) at high \( A_z \) values is not limited to the case of one set of lead data, measured under particular experimental conditions. In order to do this it is enough to prove that starting from a certain \( A_z \) value, a plot of \( f_1(A_o) \) (Eq. (17)) under a variety of experimental conditions does not intercept the \( x \) axis, and locates above it (Fig. 4).

In the present calculations all the variables in Eq. (17) were assigned to take any value in the following ranges: \( 0 < A_z \leq 3, 0.5 \leq R \leq 0.9, \) and \( 0.001 \leq \alpha \leq 0.3. \) These starting conditions attempt to show that in any possible combination of \( R \) and \( \alpha \) values from the chosen ranges, \( f_1(A_o) = 0 \) fails with increase in the \( A_z \) value toward the upper limit of the assigned interval. These selections of variation in \( R \) and \( \alpha \) cover most of the experimental values that were obtained in recent studies of the linearization of calibration curves in Zeeman AAS [6,19,23,24]. Indeed, because the \( R \) value can be measured directly at any point on a calibration curve, it was not difficult to assign a range for this variable in order to cover the majority of the \( R \) values for most of the elements. There was a different situation with the selection of the range for \( \alpha \). In one of the earliest papers on the subject L'vov et al. [19] derived \( \alpha \) as a function of \( A_{\text{lim}} \)

\[
\alpha = (10^{4\text{lim}} - 1)^{-1}
\]

(A1) rather than \( A_z \)

\[
\alpha = (10^{4z} - 1)^{-1}
\]

(A2)

However, L'vov et al. [19] accepted Eq. (A2) for the calculation of \( \alpha \) for the sake of simplicity and practicality, with the note that “... the curvature of the rising part of a real calibration curve in Zeeman AAS is assumed to be the same as that of a calibration curve in conventional AAS if one sets \( A_{\text{lim}} = A_z \)” (Ref. [19], p. 1189).

It is still reasonable to investigate the potential difference between the theoretically defined \( \alpha \) (Eq. (A1)) and the practically measured \( \alpha \) values (Eq. (A2)), especially as Eq. (A2) is widely employed by the present authors for both models in the present paper and in earlier work [23,24], and by L'vov and co-workers [19,21,22]. The significance of the difference between values of \( \alpha \) defined by Eqs. (A1) and (A2) can be seen by inspection of one of the largest observed differences between \( A_{\text{lim}} \) and \( A_z \) values for copper, a factor of two [24].
The typical range of $A_r$ values for different experimental conditions of lamp currents and slit widths, was found to be between 0.4 and 1.4 peak absorbances [6,25]. Hence, it is possible to assume that for typical mean experimental conditions $A_{r, Cu} = 0.9$ and $A_{lim, Cu} = 1.8$, which gives $\alpha_{Cu} = f(A_{lim}) = 0.016$ and $\alpha_{Cu} = f(A_{r}) = 0.144$ from Eqs. (A1) and (A2), respectively. It follows that the chosen interval for the $\alpha$ variable covers the values obtained by either method. Similar analysis of the discrepancy in $\alpha$ values due to the use of different equations can be done for any other element, but for the majority of elements, the experimental difference between $A_r$ and $A_{lim}$, i.e. between $\alpha = f(A_{lim})$ and $\alpha = f(A_r)$, can be expected to be smaller rather than larger [6,24]. The authors believe that at this point it is reasonable to conclude that the failure of Model 1 is most unlikely to be associated with the error that was introduced due to the calculation of $\alpha$ from Eq. (A2) rather than from Eq. (A1). Note that the solution for Model 1 ($f_1(A_o) = 0$), searched through an interval of $0 < A_o \leq 100$, is also much broader than the expected real values for $A_o$.

Because the shape of $f_1(A_o) = 0$ is already known (Figs. 3(a), 4), and in order to show that this function does not have a mathematical solution in the assigned interval, it is necessary to show that, (a) the values at both boundary conditions ($f_1(0)$, $f_1(100)$) are positive; (b) the function has only one and only one minimum ($A_0^{min}$); and (c) at a certain $A_0$ value, $f_1(A_0^{min})$ becomes positive.

The signs of $f_1(A_o)$ at the boundaries can be determined at $A_o = 0$ as
\begin{equation}
f_1(0) = A_z > 0
\end{equation}
and at $A_o = 100$ as
\begin{equation}
f_1(100) \approx A_z - \log\left(1 + \frac{1}{\alpha}\right) + \frac{1 - R}{1 + \alpha} \times 100
\end{equation}

In order to find the smallest theoretically possible value for $f_1(100)$ it is necessary to subtract the largest possible negative term ($-\log(1 + 1/\alpha)$) from $A_z$, and to add the smallest possible positive term ($(1 - R)/100/(1 + \alpha)$) to the resultant difference. The largest negative term can be created if $\alpha = 0.001$, and the smallest positive term can be created at $R = 0.9$, $\alpha = 0.1$. Hence
\begin{equation}
f_1(100) \approx A_z - \log\left(1 + \frac{1}{0.001}\right) + \frac{1 - 0.9}{1 + 0.3} \times 100
\approx A_z - 3 + 7.69 > 0
\end{equation}
for any $0 < A_z < 3$.

Also, this means that all other possible combinations of $R$ and $\alpha$ values can generate only positive, and higher values for $f_1(100)$. Therefore, at the extreme of the interval the function $f_1(A_o)$ is always positive, i.e. the solution always locates above the $x$ axis.

When the first derivative of $f_1(A_o)$ is zero, this indicates the presence of a minimum between the boundaries. The minimum ($A_0^{min}$) determines the smallest positive, largest negative, value for $f_1(A_o)$. Therefore, if the $f_1(A_0^{min}) > 0$, then $f_1(A_o) > 0$ for all $A_o$ (Figs. 3(a), 4)
\begin{equation}
f_1'(A_o) = -\frac{1}{1 + \alpha} 10^{\alpha} + \frac{1 - R}{1 + \alpha} = 0 \Rightarrow A_0^{min}
\end{equation}
\begin{equation}
= \log\left(\frac{\alpha + R}{\alpha(1 - R)}\right)
\end{equation}

By substitution of $A_0^{min}$ into $f_1(A_o)$, the value of $f_1(A_0^{min})$ can be found
\begin{equation}
f_1(A_0^{min}) = A_z + \log\left(\frac{\alpha(1 - R)}{\alpha + R} + \alpha\right) - \log(1 + \alpha)
\begin{equation}
\begin{aligned}
&+ \frac{1 - R}{1 + \alpha} \log\frac{\alpha + R}{\alpha(1 - R)} \\
&= A_z + \log\left(\frac{\alpha(1 + \alpha)}{\alpha + R}\right) - \log(1 + \alpha)
\begin{equation}
\begin{aligned}
&+ \frac{1 - R}{1 + \alpha} \log\frac{\alpha + R}{\alpha(1 - R)} \\
&= A_z - \log\left(\frac{\alpha + R}{\alpha}\right) + \frac{1 - R}{1 + \alpha} \log\left(\frac{\alpha + R}{\alpha}\right)
\begin{equation}
\begin{aligned}
&- \frac{1 - R}{1 + \alpha} \log(1 - R) \\
&= A_z - \frac{1 - R}{1 + \alpha} \log(1 - R)
\begin{equation}
\begin{aligned}
&- \frac{\alpha + R}{1 + \alpha} \log\left(1 + \frac{1 - R}{\alpha}\right) \leq 0
\end{equation}

It can be seen that the second term in the resultant equation is always positive, and that the third term
is always negative. Once again, in order to obtain
the theoretically smallest positive, largest nega-
tive, value for \( f_1(\mathcal{A}_0\,\text{min}) \) it is enough to subtract
the largest possible negative term, which is
\( ((-0.901) \times \log(1 + 0.9/0.001)) = 2.66 \) from \( \mathcal{A}_2 \),
and to add the smallest possible positive term
which is \( -(1 - 0.9)/1.001 \times \log(1 - 0.9)) = 0.10 \). Thus

\[
\begin{align*}
f_1(\mathcal{A}_0\,\text{min}) &= \mathcal{A}_2 + 0.10 - 2.66 = \mathcal{A}_2 - 2.56 \leq 0 \\
(A8)
\end{align*}
\]

This means that for all \( \mathcal{A}_2 > 2.56, f_1(\mathcal{A}_0) = 0 \), the
equation fails regardless of the type of analyte
atom, for any combination of the predetermined
experimental conditions. For a given set of experi-
mental conditions, the failure certainly may occur
at \( \mathcal{A}_2 \) values lower than 2.56 because, in practice,
values of \( \alpha \) and \( R \) cannot vary between the different
terms of \( f_1(\mathcal{A}_o) = 0 \).

References

[1] B.V. L'vov, Atomic Absorption Spectrochemical Analysis,
1171.
1075.
[10] E. Voigman, A.I. Yuzefovsky and R.G. Michel, Spectro-
621.
B, 30 (1975) 361.
1 (1986) 85.
[18] B.V. L'vov, L.K. Polzik and N.V. Kocharova, Spectro-
1187.
[21] B.V. L'vov, L.K. Polzik, P.N. Fedorov and W. Slavin,
[22] B.V. L'vov, L.K. Polzik, A.V. Novichikhin, P.N. Fedorov
1625.
367.
1643.
[26] B.V. L'vov, L.K. Polzik, A.V. Borodin, P.N. Fedorov and
1609.
[27] The THGA Graphite Furnace: Techniques and Recom-
mended Conditions, Bodenseewerk, Perkin-Elmer GmbH,
Ueberlingen, Germany, 1991.
1627.