Newton Method of Successive Approximations for the Linearization of the Calibration Curves of Chromium, Copper, Lead, Manganese, Silver, and Thallium in Zeeman Graphite Furnace Atomic Absorption Spectrometry

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A new approach for the linearization of calibration curves in graphite furnace atomic absorption spectrometry (GFAAS) with Zeeman background correction was tested experimentally in an intermediate concentration region before rollover. The computational procedure employed the Newton method of successive approximations and was based on the theoretical model of L’vov et al. The calculations were based on three measured parameters: the rollover absorbance, \( A_r \); the sensitivity ratio at the rollover point, \( R \); and the original back-ground-corrected peak absorbances \( A_z \). This computational procedure generated corrected normalized integrated absorbance values \( A_{0,n} \) with the slope identical to the slope of the original linear part of the calibration curve. The new computational procedure was employed for the linearization of calibration curves of chromium, copper, lead, manganese, silver, and thallium in Zeeman GFAAS under stabilized temperature platform furnace (STPF) conditions. Overall, the new computational procedure was able to extend the linear range of the calibration curves by a factor of 2–3 for the tested elements.

Index Headings: Linearization of calibration curves; Zeeman graphite furnace atomic absorption spectrometry; Stray light.

INTRODUCTION

One major obstacle for multielement graphite furnace atomic absorption spectrometry (GFAAS) with Zeeman background correction is the poor analytical working range. In the intermediate concentration region before rollover, the curvature of working calibration curves that restricts the linear dynamic range to 1–2 orders of magnitude is considered to be predominantly due to a combination of various stray light effects. At very high concentrations, other effects become important, such as significant contributions of the wings of the source line to the nonlinearity of the absorption measurement. In recent publications, a number of authors focused on the nature of stray light in Zeeman GFAAS. The goal of their research was to understand the variation of signal size with concentration, and with other experimental parameters of atomic absorption, while correction of the curvature of the analytical calibration curves was not necessarily highlighted. Most of the work on the effects and nature of stray light has been thoroughly discussed and summarized in a review by Su et al. The ultimate aim of the work on the investigation of stray light presented in this paper is to develop an experimental model to evaluate and correct the deviations from linearity of calibration curves in Zeeman GFAAS in the region of concentration before rollover. A number of such attempts have been reported in the literature. For example, recently Xiaoning et al. proposed a computational procedure for the correction of calibration curves in Zeeman AAS. The authors introduced a model that correlated the fraction of stray light in the system, \( \alpha \), and the corrected absorbance value, \( A' \), with the observed transmittance, \( T \):

\[
A' = \log \left( \frac{(1 - \alpha)}{(T - \alpha)} \right). \tag{1}
\]

Estimation of the amount of the stray light was done indirectly, by employment of Fibonacci and Uniplex optimization techniques. Thus, the model was based primarily on mathematical manipulation of the data rather than on fundamental parameters. The authors also applied the computational procedure directly to the integrated absorbance values which theoretically could lead to partial losses of information in the original transient peak signals. However, the main disadvantage of the model is the necessity to gather a large number of calibration data points for linearization of the calibration curves.

Independently, L’vov et al. proposed an alternative computational procedure for the correction of the effects of stray light in Zeeman AAS. However, unlike Xiaoning et al., who corrected the integrated absorbances, L’vov et al. attempted to correlate peak absorbances, \( A \), and the stray light fraction, \( \alpha \), with the corrected peak absorbances, \( A_0' \):

\[
A = \log \left( \frac{(1 + \alpha)}{(10^{-A_0} + \alpha)} \right). \tag{2}
\]

The model was designed to correct each data point within the transient signal profile. Integration of this new signal profile gave corrected integrated absorbance values.

Su et al. continued development of the theoretical model of L’vov et al. by redefinition of the \( \alpha \) parameter as an “effective stray light” that was considered to be the sum of all effects that are different types of stray light or that behave like stray light, without any attempt to...
distinguish among them. This approach allowed the differences between corrected and calculated characteristic mass values to be reduced to the 4–8% range for four elements under a variety of experimental conditions of lamp currents and slit widths. Building on this approach, L’vov et al.\textsuperscript{13} introduced a procedure that required some additional measurements but attempted to account separately for the effects of self-absorption and nonabsorbable radiation. This approach was different from the “effective” stray light method developed earlier by Su et al. The result was that the average variation between corrected and calculated characteristic mass values for nine elements, calculated under different experimental conditions of lamp current and slit width, was below 10%. Basically, L’vov et al.\textsuperscript{3,10} proposed the use of fundamental parameters for the calculation of $\alpha$, rather than the use of curve fitting optimization routines.\textsuperscript{8} For the computation of corrected peak absorbance values in Zeeman GFAAS, the model of L’vov et al. was transformed into the following set of equations:\textsuperscript{10}

$$A_z = \log \frac{(1 + \alpha)}{(10^{-b} + \alpha)} - \frac{1 - R}{1 + \alpha}$$

and

$$\alpha = (10^{b} - 1)^{-1}$$

where $R$ is the Zeeman sensitivity ratio, and $A_z$ is the peak absorbance at rollover. Theoretically the construction of the calibration function based on Eqs. 3 and 4 requires only one additional measurement for the determination of $\alpha$ for a given set of experimental conditions and should not depend on the number of data points in the calibration curve.

The computational procedure that was based on this theoretical model used three semi-empirical simplifications.\textsuperscript{10} First, the Zeeman sensitivity ratio was set equal to unity for all elements at all experimental conditions. Second, the nature of the failure of the computational procedure was unclear, and third, the data generated by the use of the Newton method of successive approximations. The new procedure was named the Newton linearization method for the sake of convenience. (Note that Ref. 16 used a modified version of the Newton method of approximations that was described in Ref. 12 as the pseudo-Newton method. Reference 11, which reported results only for lead, used the same unmodified Newton method used in the present paper.) The authors\textsuperscript{11} made several observations based on preliminary studies of the Newton linearization method. First, it was shown theoretically that Eq. 3 does not have a mathematical solution at high absorbances for wide ranges of $R$ and $\alpha$ values. Second, the nature of the failure of the computational procedure was unclear, and third, the data generated by this method maintained the slope of the original linear part of the calibration curve up to the point of failure. The ability to generate a linearized calibration curve that has the same slope as the linear part of the original calibration curve is a unique feature of the Newton linearization algorithm in comparison to other computational algorithms. The preliminary study of the Newton linearization was applied to lead calibration curves.\textsuperscript{11} The present paper reports a direct continuation of the prior studies on the linearization of calibration curves by the use of the Newton linearization method. In the previous work, the authors\textsuperscript{11} focused on the theoretical aspects of the problem, but there were two reasons to further investigate the behavior of the Newton linearization method, even though it was already clear that the model failed to provide a mathematical solution at high absorbance values and, thus, could not be used for linearization of calibration curves even up to the rollover point. First, the authors wanted to investigate whether Newton linearization could maintain the slope of the calibration curves up to the point of failure for different analytes.
Second, studies of the different models should provide a better understanding of the fundamental reasons that cause deviation from linearity below the rollover point in Zeeman GFAAS. It is emphasized that the limiting factors that determine nonlinearity of calibration curves throughout the concentration range of atomic absorption are well understood in principle, but that an exact model, which can give valid correction over the full range of the working curves, would be quite cumbersome and of little practical use. This paper uses the above-cited simple models developed by L’vov’s group, and concentrates on a region of the calibration curve, just below rollover, where the “effective stray light” approximation seems to allow for useful extension of the linear range. A previous paper looked at the extension of the linear range for lead, by use of the unmodified Newton approximation, while the present paper extends the range of elements to six more.

**EXPERIMENTAL**

**Instrumentation, Calibration Solutions, and Measurements.** Experiments with chromium, manganese, lead, thallium, silver, and copper 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 DECStation 425c (Digital Equipment Corporation, Maynard, MA), equipped with GEM BASED PEALAB software, version 7.3 (Perkin–Elmer Corporation, Norwalk, CT). Additional experiments with chromium and manganese were performed on a Perkin–Elmer spectrometer, Model Zeeman 5000, equipped with an HGA power supply, an AS-40 autosampler, and a personal computer, WYSIEpc 286, Model 2108. The computer was directly connected to the RC232C/TTY port on the Perkin–Elmer spectrometer. The communication and calculation programs have been described in detail elsewhere.

Aqueous calibration and matrix modification solutions were made by serial dilution of 1 mg mL\(^{-1}\) stock solutions. The stock solutions were Baker Analyzed® reagent atomic spectral standards (J.T. Baker Chemical Co., Phillipsburg, NJ). The preparation procedures for calibration solutions and samples have been described in detail elsewhere.

The light sources were hollow cathode lamps (HCLs) for chromium, manganese, lead, silver, and copper and an electrodless discharge lamp (EDL) for thallium, manufactured by Perkin–Elmer. In the experiments on 4100ZL and 5000 Zeeman spectrometers, respectively, standard transversely heated graphite furnaces and standard pyrocoated graphite tubes with platforms of anisotropic pyrolytic graphite were employed. Argon with no more than 10\(^{-3}\)% of O\(_2\) and N\(_2\) (The 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 and HGA conditions (Table I), except for lead. The lead atomization temperature was chosen to be one hundred degrees lower than the recommended one in order to decrease the diffusion rate of the analyte atoms from the THGA furnace and to collect more data points for each transient atomization signal profile. A 20-μL aliquot of sample solution was employed with appropriate matrix modification where it was recommended. Atomization was performed in the gas stop mode. In all experiments the blank signals were taken into account in the calculations.

The \( R' \) value was determined as the ratio 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 \( R' = A_r/A_{SB} \).

Before the peak correction procedure was applied, a five-point, third-order, Savitzky–Golay technique was applied to the original set of data in order to smooth the temporal profiles of the absorbance signals.

**Data Correction Procedure.** The data correction procedure for the linearization of calibration curves was based on Eqs. 3 and 4. It was applied to all points including those in the original linear region of the calibration curves. The normalized absorbance values, \( A_{0a} \), were employed in the computational procedure in order to compare the slopes for the linearized curves with the linear part of the original curve. In more detail, the following steps were done in order: an “off-line” cor-

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**TABLE I. Instrumental and experimental parameters in Zeeman GFAAS for the tested elements.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Instrumental parameters</th>
<th>Measured parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavelength (nm)</td>
<td>Slit width (nm)</td>
</tr>
<tr>
<td>Ag</td>
<td>328.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Cr</td>
<td>357.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Cu</td>
<td>324.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Mn</td>
<td>279.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Pb</td>
<td>283.3</td>
<td>0.7</td>
</tr>
<tr>
<td>TI</td>
<td>276.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Zeeman 5000 spectrometer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>357.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Mn</td>
<td>279.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(a\) Charring/atomization temperatures.

\(b\) Obtained from the slope of the linearized curves, which were generated by the use of the Newton method of successive approximations.

\(c\) Power source: EDL System 2, the Perkin–Elmer Corporation.
Correction program recalled the original data set \( A_z \), \( A_{z_2} \), \( \ldots \), \( A_{z_k} \), \( \ldots \), \( A_{z_r} \), values of \( A_0 \) and \( A_{SB} \) that corresponded to the particular experimental conditions were entered manually into the program; the program calculated values of \( R^\prime \) and \( \alpha \); finally, Eq. 3 was solved by the Newton method of successive approximations. Here \( A_{z_k} \) is the integrated absorbance value that corresponds to the mass of analyte at which rollover is detected for the first time. Only one iterative step was employed in the procedure. \( A_{0,n} \) values obtained from Eq. 5 were used as the initial estimates of corrected absorbance values.  

\[
A_{0,n}^{int} = (1 - 10^{-A}) \times \log \frac{10^{A} - 1}{10^{A} + 1} - \frac{1}{10^{A} + 1}.
\]

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

\[
A_{0,n} = A_{0,n}^{int} - \frac{f(A_{0,n}^{int} - f(A_{0,n}^{int}))}{f(A_{0,n}^{int})} = \frac{A_{0,n}^{int}}{A_{0,n}^{int}} \left\{ \frac{1 - R^\prime}{R^\prime} + A_z - \log(1 + \alpha) \right. \\
\left. + \log[10^{-(1+\alpha)r}d\zeta / R^\prime + \alpha] \right\} \\
= \frac{1 - R^\prime}{R^\prime} - 1 + \frac{1 - 10^{-A}}{R^\prime} \times 10^{-(1+\alpha)r}d\zeta / R^\prime \\
\times [10^{-(1+\alpha)r}d\zeta / R^\prime + \alpha]^{-1}.
\]

The computational procedure generated a set of linearized data points \( A_{0,n_1}, A_{0,n_2}, \ldots, A_{0,n_k}, \) where each normalized transient absorbance value was computed as \( A_{0,n} = \int A_{0,n} \, df \), and where \( A_{0,n} \) is the integrated corrected absorbance value. \( A_{0,n} \) represents the linearized data point that corresponds to the highest analyte concentration before the failure of the linearization algorithm, where \( k < r \). The set of integrated data points obtained directly from Eq. 5 without the first iterative step, represented the calibration curve for the algorithm of L’vov et al. All the values obtained included one original and two linearized data sets, which were plotted as integrated absorbance vs. mass of analyte up to the point of failure of the Newton linearization model.

RESULTS AND DISCUSSION

Elements were tested with different \( A \) values, \( R^\prime \) values significantly different from unity (\( R^\prime < 0.90 \)), and \( R^\prime \) values close to unity (Table I). This approach was designed to test whether or not the Newton linearization is able to produce slopes of the linearized data that coincide with the slope of the original linear parts of the calibration curves under a variety of conditions.

For comparison, two sets of linearized data, constructed by the use of the Newton linearization (Eq. 6) and the L’vov et al. simplified model of Eq. 5, are presented in Figs. 1 and 2. For each element the curves were linearized and plotted up to the point of failure of the Newton linearization procedure. For all tested elements, the linearized data from the Newton approximation method resulted in slopes that were positioned fairly close to the slope extrapolated from the linear part of the original calibration curve. The linearization was satisfactory regardless of the type of spectrometer used or the \( R^\prime \) value of the element. Overall, the deviation between the slopes of the linearized data and the slopes of the original calibration curves did not exceed 2%.

Consistent with previous experience, the use of the simplified computational model of L’vov et al. resulted in the generation of linearized data that were positioned below the extrapolated original linear slope. The overall deviation of the model of L’vov et al. from the origin was
observed to be progressively worse toward the rollover mass. Moreover, the data points that correspond to the method of L’vov et al. began to deviate from the slope of the original data at analyte masses just slightly above the original linear part of the calibration curve.

As hinted at before, the largest deviation of the model of L’vov et al. from the original slope was observed for elements with $R^9$ values significantly different from unity. Thus for silver ($R^9 = 0.93$) the deviation was 5%, while for thallium ($R^9 = 0.64$) the deviation was already 12%, far below the rollover point (Fig. 1). However, despite the fact that the deviation pattern is quite obvious, as presented Figs. 1 and 2, it would be difficult to derive an exact relationship between the deviation from the linearity and $R^9$ values for the simplified model of L’vov et al. for the following reasons: First, the deviation of the linearized absorbance values from the original slope can be affected to some extent by sample preparation errors which are usually different for individual calibration standards. An absolute sample preparation error can shift the original data points on the calibration curve along the y-axis. Such a shift affects the accuracy of the plotted data, particularly in the lower part of the calibration curve. Second, the authors believe that at the present time there are still some unknown factors that may cause deviation from the linearity for calibration curves in Zeeman AAS, and even the known factors that affect the linearity of the calibration function are still not fully understood.

The linearized calibration curves for chromium and manganese obtained on the 4100 ZL and Zeeman 5000 spectrometers are compared in Fig. 2. The fraction of the stray light for the tested elements was greater in the 4100 ZL instrumentation rather than in the Zeeman 5000 instrumentation for the experimental conditions that were used. Throughout the calibration curves, in the case of the Newton linearization, the linearized absorbance values did not deviate from the slope of the original linear part of the calibration curve, regardless of the instrumentation upon which the original data were gathered. The results were different in the case of the simplified model of L’vov et al. The slopes obtained from the linearized absorbances for Zeeman 5000 were not very different from the slopes of the original absorbance values in the lower part of calibration curves. However, at higher masses, since the method of L’vov et al. was not sensitive to changes in the $R^9$ value, the differences between the slopes of the linearized absorbance values and the slopes at the origin were much larger in the case of the 4100 ZL spectrometer, compared to the Z5000. This result was due to the presence of a larger fraction of stray light, as well as lower $R^9$ values. The differences were 8% for manganese and silver in the case of the 4100 ZL instrument, vs. 5 and 3% deviation for manganese and silver, respectively, for the Zeeman 5000. These experiments with different spectrometers emphasized the importance of the presence of the $R^9$ value in the computational model. More importantly, the small deviation of the linearized absorbances from the original slope, when the calibration curves were constructed by the use of the computational model of L’vov et al., may be safe only for particular elements or for a limited range of experimental conditions in which the $R^9$ value is close to unity.

All the data in Figs. 1 and 2 tend to confirm that the approach to the extension of the linear range of calibration curves is more likely to be successful when it is based on the Newton computational procedure up to the point of its failure. The original and extended linear ranges of the calibration curve for the discussed elements are presented in Fig. 3. Overall, the Newton computational model was able to extend the linear range of calibration curves by a factor of 2–3.

The following conclusion from the above observations can be drawn: The basic theoretical model (Eqs. 3 and 4) has potential for the linearization of calibration curves only if the change in Zeeman sensitivity ratio is introduced into the computational procedure as a function of the type of analyte atoms, along with the experimental conditions of lamp current and slit width. The present authors found that it also was very critical to report more than a few points for the lower part of the calibration curves that define the slope at the origin. In more detail, this subject was recently analyzed by Yuzefovsky et al. and goes beyond the scope of the present article.

CONCLUSION

An important outcome of the use of the Newton linearization method was that, for the first time, a computational procedure, based on fundamental parameters rather than on optimization routines, provided satisfactory extension of the linear range of calibration curves. Both the ability of the Newton linearization to extend the linear range of calibration curves and the model’s failure at high peak absorbance values were predicted theoretically in the earlier publication on this subject.

Analysis of the Newton linearization method indicated that the slopes of the linearized curves were the same as the slopes obtained from the original linear portion of the calibration curves. Overall, the Newton method of successive approximations provided satisfactory linearization, with <2% deviation between the original and lin-
linearized slopes, up to the point of failure for all six elements discussed in the paper. Thus the experimental data proved the necessity of the incorporation of $R'$ back into the simplified computational procedure of L'vov et al.\textsuperscript{10,11}

The analyte concentration at which the Newton linearization method failed primarily depended on the $R'$ value of the analyte. Thus, for the elements with the relatively low $R'$ values (copper, lead, manganese, and thallium; $R' < 0.90$) the algorithm failed closer to the origin of the calibration curve, and for the elements with $R'$ values closer to the unity (chromium and silver; $R' > 0.90$) the algorithm failed further toward the rollover concentration. Overall, extension of the linear range of calibration curves was a factor of 2–3 for the tested elements.

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