Evaluation of the use of Gaussian phi(roz) curves in quantitative electron probe microanalysis: a new optimization

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Evaluation of the Use of Gaussian φ(pz)
Curves in Quantitative Electron Probe
Microanalysis: a New Optimization

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A computer program based on the use of Gaussian expressions for the x-ray distribution with depth [φ(pz) curves] was tested on its usefulness for quantitative electron probe microanalysis. As the good results originally claimed for a similar program could not be reproduced initially, it was subjected to a detailed analysis. As a result, some modifications in the approach are proposed. Apart from increasing the speed of calculation considerably, the modified expressions provide a better insight into the delicate balance which has to exist between the relevant quantities involved. After a new optimization process the modified program was tested on about 450 published microanalyses. The results show that the φ(pz) approach is indeed very promising as a narrow histogram with an r.m.s. value of 5.4% could be produced. Finally, some suggestions are made for future improvements.

INTRODUCTION

In quantitative electron probe microanalysis a number of corrections have to be performed in order to convert the measured intensity data into concentration units. These corrections, which are usually calculated separately, deal with the effects of atomic number (Z), absorption (A) and fluorescence (F).

The atomic number correction requires a detailed knowledge of the processes of electron scattering and ionization within the target and is, in fact, a complicated procedure. The most commonly used method is that of Duncumb and Reed,1 which at present has been incorporated in most computer programs for matrix corrections in electron probe microanalysis. In 1978 a new atomic number correction was put forward by Love et al.,2 which was claimed to be an improvement over that of Duncumb and Reed, especially for high and low overvoltage ratios.

The absorption correction requires an intimate knowledge of x-ray distribution with depth in the target which is usually represented in terms of a so-called φ(pz) curve, in which φ represents the ionization and pz the mass depth in the sample. In spite of the fact that a number of φ(pz) curves were determined as early as 1955 by Castaing and Descamps,3 one has struggled for many years with expressions for φ(pz) which at best can be called approximations.

The most widely used absorption correction procedure today is still that of Philibert.4 It is based on a simplification of physical reality in that the surface ionization φ(0) is assumed to be zero and the φ(pz) curve is too strongly peaked too close to the specimen surface, which is partly compensated by a too long exponential tail deep in the specimen. It has been shown by many authors, not last by Philibert himself, that the resultant equation for correction has a limited range of applicability and that it is bound to give erroneous results for strongly absorbing systems as in the case of light element analysis. In these cases the full Philibert correction seems to yield a significant improvement.5,6

An even simpler model was devised by Bishop7 and extensively tested by Love et al.8 In this model φ(pz) is approximated by a rectangle with constant intensity up to a certain depth, after which it abruptly falls to zero. In spite of its astonishing simplicity the model seems to work very well although it has not yet been extensively tested for light element work.

The fluorescence correction in most correction procedures is based on the model of Reed.9 It seems that in recent years no new developments have taken place here. Most probably the uncertainty in the input parameters imposes a larger limitation than the model itself.

A completely new approach to matrix corrections was made by Brown and coworkers.10-13 Not only did they determine a large number of φ(pz) curves experimentally but they also provided equations which apparently are able to describe these curves fairly accurately. These equations served as the basis for a correction program to be used in quantitative electron probe microanalysis, a program which was claimed to be a genuine improvement over existing methods. This paper deals with our efforts to produce such a program for on-line use on our automated microprobe analyser and our experience with it so far.

THE GAUSSIAN φ(pz) EQUATION

As already shown by Castaing,14 the most direct way of relating the intensity I of element i-radiation emitted from a homogeneous specimen (sp) to the concent-
tron of i is to write

\[ I^0 = \text{constant} \times W_i \int_0 \phi_i(\rho z) \times \exp\left(-\mu^{\text{io}}\rho z \csc \Psi \right) d(\rho z) \]  

(1)

where \( W_i \) is the weight fraction of element i in the specimen, \( \rho z \) is the mass depth, \( \Psi \) is the x-ray take-off angle and \( \mu^{\text{io}} \) is the mass absorption coefficient for \( i \)-radiation in the specimen. The constant includes a number of parameters which cancel when the ratio with respect to a pure i-element standard is taken. A similar equation can be written for the intensity emitted from the pure i-standard (st).

If, for the moment, the effects of characteristic and continuum fluorescence are ignored, the \( k \) ratio (intensity from specimen relative to the standard) is simply obtained by

\[ k_i = W_i \left[ \int_0 \phi_i(\rho z) \times \exp\left(-\mu^{\text{io}}\rho z \csc \Psi \right) d(\rho z) \right] / \left[ \int_0 \phi_i(\rho z) \times \exp\left(-\mu^{\text{io}}\rho z \csc \Psi \right) d(\rho z) \right] \]  

(2)

It must be emphasized that Eqn (2) formally represents a full and exact correction if fluorescence is ignored. A detailed knowledge of the \( \phi(\rho z) \) curves in both specimen and standard (and of course the other physical constants involved) is the only prerequisite for an exact correction procedure. In fact, eqn (2) incorporates both an atomic number correction \((Z)\) and an absorption correction \((A)\), which becomes obvious if one realizes that \( \int_0 \phi(\rho z) \times \exp\left(-\mu^{\text{io}}\rho z \csc \Psi \right) d(\rho z) \) for both specimen and standard represents the total x-ray intensity generated per electron in the target, i.e. the atomic number effect.

According to Packwood and Brown, the \( \phi(\rho z) \) curves can be accurately described by:

\[ \phi(\rho z) = \gamma_0 \left[ 1 - \frac{\phi(0)}{\gamma_0} \exp\left(-\beta \rho z \right) \right] \exp\left[\alpha^2(\rho z)^2\right] \]

(3)

What this equation essentially expresses is that \( \phi(\rho z) \) is, in principle, described by \( \gamma_0 \exp\left[-\alpha^2(\rho z)^2\right] \) in which \( \gamma_0 \) can be considered as some kind of amplitude or scaling factor and \( \alpha \) gives the decay rate with \( (\rho z)^2 \) (see Fig. 1). However, as the electron beam at and just below the specimen surface is still collimated to a large extent, the efficiency of the electrons to produce x-rays is not yet optimal. This is only achieved deeper in the specimen where the electron beam has been sufficiently scattered; hence the initial rise in ionization from \( \phi(0) \) at the surface to a maximum somewhere deeper. This region is described by a transient function, \( 1 - \left[ (\gamma_0 - \phi(0))/\gamma_0 \right] \exp\left(-\beta \rho z \right) \). On the basis of a random walk model, Packwood and Brown have produced expressions for \( \alpha \), \( \beta \) and \( \gamma_0 \) in terms of atomic number \( Z \), atomic weight \( A \) and ionization potential \( J \) for the matrix element and accelerating voltage \( E_0 \), critical excitation voltage \( E_c \) and overvoltage ratio \( U_0 \) (= \( E_0/E_c \)) for the x-ray line in question. The coefficients in the expressions for \( \alpha \) and \( \beta \) were obtained through best fits on measured \( \phi(\rho z) \) curves.

It must be mentioned here that although the results for \( \alpha \) can be considered reliable, as it is relatively easy to obtain the slope in a ln \( \phi(\rho z) \) vs \( (\rho z)^2 \) plot deeper in the specimen, the contrary is probably true for \( \beta \), as in this case the fitting procedure has to be applied to a relatively small area between specimen surface and the maximum in the \( \phi(\rho z) \) curve. Further, it is no longer a slope which has to be determined but the value of an exponent. These considerations probably cast some doubts on the published values of \( \beta \).

The expression for \( \gamma_0 \) was based purely on a theoretical derivation for which Webster et al. expression for the excitation efficiency in terms of the overvoltage ratio was used. Together with Reuter's expression for \( \phi(0) \), the equations were used originally in a correction program. For \( J \) the expression of Berger and Seltzer was used. For compounds, \( Z \), \( A \) and \( J \) were averaged on the basis of weight fractions and the combined \([ZA]\) correction was obtained by numerical integration (in 100 steps) of the \( \phi(\rho z) \) equations. For the fluorescence correction again a numerical integration was used (in fact a double integration), according to the geometry suggested by Castaing. Tests with this program performed on a data file representing about 450 measurements revealed that it was hardly satisfactory as the relative standard deviation was 11.3%.

In a second effort, the approach was changed, the most important changes being that \( A \), \( Z \) and \( J \) were averaged on the basis of atom fractions, \( \beta \) was written in terms of \( \alpha \) and Love et al.'s expression for \( \phi(0) \) was introduced. After a process of optimization carried out on the test file, the following set of final equations were obtained:

\[ \alpha = 1134.5 \]
\[ \beta = 2801.3 \]
\[ \gamma_0 = 2.520 \]
\[ \beta(0) = 1.462 \]

(4)

Using these equations a relative standard deviation of 4.8% was claimed, which compares very favourably with the value of 6.8% reported for the so-called 'established' ZAF procedure.

At this stage, two remarks must be made: firstly, it would be interesting to see how the new values of \( \alpha \) compare with those formerly calculated with equations...
based on best fits to actual physical measurements, and secondly, by writing $\beta$ in terms of $\alpha$, one implicitly assumes $\beta$ and $\alpha$ to have the same $E_0$ dependence as the ratio $\beta/\alpha$ is now only a function of $Z$. It seems questionable if this is correct. We shall come back to this point later.

As a whole the $\phi(\rho z)$ approach has certain very attractive features, especially simplicity. This and the good results claimed for the correction program based on it encouraged us to produce our own program for use on-line and to test it on the same test file previously used by Brown and Packwood\textsuperscript{13} and Love and Scott.\textsuperscript{6}

**THE INITIAL CORRECTION PROGRAM**

While making a correction program (written in Flextran because it had to be used on-line in a Tracor Northern automation system on a JEOl Superprobe 733), it was soon realized that the numerical integrations involved were a major drawback for on-line use on a minicomputer (DEC LSI 11/02) as these were found to be very time consuming. It was therefore decided to replace the fluorescence correction by the standard Reed procedure as the accuracy of this correction is probably more limited by the inaccuracy in the input parameters than by the model itself.

An even more important change was brought about by avoiding the numerical integration of $\phi(\rho z)$ and solving it instead in closed form, a possibility which has already been indicated by Brown and Packwood.\textsuperscript{13} The solution we found is the following. It can be shown mathematically\textsuperscript{20} that

$$\int_0^\infty e^{-x^2} e^{-ax^3} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} e^{\sqrt{\frac{s}{2a}}} \text{erfc} \left( \frac{x}{\sqrt{2a}} \right)$$

The complementary error function itself can be approximated\textsuperscript{20} with high accuracy by

$$\text{erfc} y = (a_1 + a_2 t + a_3 t^2 + a_4 t^3 + a_5 t^4) e^{-y^2} + e(y)$$

with $t = 1/(1 + py)$ and $|e(y)| < 1.5 \times 10^{-7}$, in which $p = 0.3275911$ and:

- $a_1 = 0.254829592$
- $a_2 = -0.284496736$
- $a_3 = 1.421413741$
- $a_4 = -1.453152027$
- $a_5 = 1.061405429$

After rearranging and insertion of $\alpha$ and $\beta$, it follows that when $\phi(\rho z)$ is integrated for specimen and standard in the absence of absorption, the atomic number correction factor $Z$ is obtained:

$$Z = \left\{ \gamma_0 R \left( 2^{-\alpha} \right) \right\} \left[ \alpha_{\text{sp}} \right. \left. \right\} \left\{ \gamma_0 R \left( \beta \right) \right\} \left[ \frac{\beta + x}{2 \alpha} \right] \left[ \alpha_{\text{st}} \right] \right\}$$

where $\chi$ represents $(\mu/\rho) \cos \Psi_1$ for the radiation in question in the appropriate matrix. Apart from an enormous increase in speed with the calculations, this approach has the added advantage of providing equations which allow an easier insight into the physical functioning of the quantities involved and the rather delicate balance which has to exist between the parameters $\alpha$, $\beta$, $\gamma_0$, $\phi(0)$ and $x$.

In our basic version of the program we used the coefficients in the expressions for $\alpha$ and $\beta$ according to the optimized values given by Brown and Packwood.\textsuperscript{13} In agreement with one of Brown's own latest versions,\textsuperscript{21} however, we replaced the Berger and Seltzer expression for $J$ by that of Ruste,\textsuperscript{22} which is claimed by the latter author to be better for light ($Z < 11$) elements. Obviously this replacement has been made with a future application of the program to light elements in mind.

In order to test the performance of the program it was decided to apply it to the same test file\textsuperscript{23} (about 450 measurements) used before by Love and Scott\textsuperscript{6} and partially by Brown and Packwood.\textsuperscript{13} For the full details in this file, including mass absorption coefficients, the reader is referred to Ref. 23.

After a critical examination of this test file it was felt that the following remarks had to be made:

About 75% of the measurements are from before 1968, the rest from before 1972. As the instruments in those days are probably hardly comparable to modern instruments in terms of stability and exactness of probe voltage, etc., it is to be expected that the results show a larger scatter than would be necessary nowadays.

It should be realized that, in order to avoid a double correction procedure, the data in the file have necessarily been measured with respect to pure element standards. This implies that a large number of elements are missing from the file because they are not available as pure standards (gases, alkalis, etc.). This would especially apply to light ($Z < 22$) elements in which range only Al and Si are expected to be represented in the file. Further, it can be stated that measurements of, e.g., Ga, As and In, should be regarded with some suspicion as these elements are notoriously difficult to prepare as flat polished standards.

There are only five analyses between 5 and 10 kV in the file, which might have serious consequences for the performance of any optimized program on low-kV data.

Regarding the file as a whole, it can be concluded that the medium to heavy elements are very well represented whereas the reverse applies to the lighter elements. This could, of course, have serious consequences for the applicability to both light and heavier
element analysis of any correction program optimized with this file, as it is possible that optimizing for the majority of elements (\(Z > 22\)) automatically leads to a program which is not well suited to light elements.

The test was run in the usual way; that is, for each given value of the concentration of an element in the file the intensity ratio \(k' / k\) was calculated and compared with the measured \(k\) value (in fact, this means that the correction program is run backwards). The proximity of the ratio \(k' / k\) to 1 is then used as a measure of success of the program. The \(k' / k\) values are usually displayed in a histogram showing the number of analyses as a function of \(k' / k\) and the shape of the histogram, together with the root mean square (r.m.s.) value are used as an ultimate measure of success. In our case the calculated \(k' / k\) values are stored on-line in the channels of a Tracer Northern TN-2000 multichannel analyser and the resulting histogram was finally photographed from the CRT, stored on floppy disk and processed afterwards to obtain the relevant statistical data. The first result thus obtained with our initial program were very disappointing as Fig. 2 shows. The average value was 0.973, indicating a heavy bias and an r.m.s. value of 7.19%, which is very poor indeed. This left us the choice either of dropping this approach altogether as a basis for a useful correction program or of reoptimizing it. In view of its inherent attractiveness, it was decided in favour of the latter option.

For such an optimization procedure, clearly two ways are open. The first and fastest is to couple the program to a mathematical optimization program on a mainframe computer and merely judge the final results in terms of the quality of the histogram obtained. The inherent danger in such a procedure is that significant trends in certain series of data (e.g. kV dependence of the results) are overlooked as they may be averaged out by a sufficient number of other data in which deviations would perhaps hardly be noticed. The second and more tedious approach is to obtain a full output for the complete test file and carefully examine it after each run for trends such as the behaviour of the (relatively few) lighter element data, kV dependence of the results for a fixed composition and composition dependence for a fixed kV. If such trends are observed it is a matter of analysing where they stem from and trying to make adjustments in a suitable way.

We chose for the last approach and made the program such that it gives all relevant quantities \([\alpha, \beta, \gamma, \phi(0), \ldots]\) as well as \(Z, A\) and \(F\) factors if so desired.

### The Optimization Process

After a few efforts to optimize the program within the framework given by Brown and Packwood\(^\text{13}\) it was soon realized that this approach was not likely to give acceptable (r.m.s. <6%) results and that more drastic changes were necessary. It was therefore decided to turn back to the base and start with Brown’s original equations,\(^\text{12}\) which are at least based on close fits to physical measurements. An exception was hereby made for \(\beta\), for which it was felt that the existing data are not reliable enough. This is substantiated by the fact that the values calculated by Brown’s most recent program\(^\text{13}\) differ widely from the fits obtained from measured \(\phi(\rho z)\) curves.\(^\text{12}\) A first consequence of this new approach is that all physical quantities are again related to the weight fraction of an element as is done by all correction programs.

#### Optimization of \(\alpha\)

While considering the problem of which constants and exponents were to be used in Eqn (4), it was realized that the factor 2.14Z\(^{1.66}\)/A, which is contained in the original equation for \(\alpha\) in Ref. 12, was essentially a constant throughout the Periodic System. For atomic numbers between 20 and 80 a slight scatter between 1.69 and 1.72 with an average of 1.705 was found, which can be taken as evidence that within experimental error \(\alpha\) is independent of \(Z\) and \(A\) of the matrix element. In fact, a best fit to the published \(\alpha\) values in Ref. 12 was obtained by adopting a value of 1.86. As the r.m.s. value of the results produced by the program was indeed found to be extremely sensitive to small changes in the \(E_o\) dependence of \(\alpha\), as already reported by Brown and Packwood,\(^\text{13}\) it was decided to start the optimization procedure with

\[
\alpha = \frac{1.86 \times 10^5}{E_0^{1.25}} \left[ \ln \left(1.166 E_o J J\right) \right]^{0.5} \tag{9}
\]

The equations used for \(\beta\) and \(\gamma\) were Eqns (5) and (6), respectively, while for \(\phi(0)\) Love \textit{et al.}'s\(^\text{19}\) expression was used.

Further, it was felt that it is probably an oversimplification to describe \(\alpha\) for the interaction of element \(i\)-radiation with a compound target merely by inserting the weighted average of \(Z, A\) and \(J\) for the matrix into the equation for \(\alpha\). It seems more appropriate to calculate separate values of \(\alpha_i\), describing the interaction of element \(i\)-radiation with each of the elements 1 to \(J\) in the matrix, and to find some way of composing \(\alpha_i\) afterwards from the available \(\alpha_i\) values for element \(i\)-radiation. Such a process would be very similar to the way in which the stopping power

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*Figure 2. Histogram obtained with the initial correction program mainly based on the recommendations of Ref. 13. Each channel represents an increase of 0.01 in \(k' / k\).*
in the atomic number correction of Duncumb and Reed\(^1\) is evaluated. A suitable means of doing this is through the use of the Bethe\(^2\) equation, which is evidently incorporated in Eqn (4) and which describes the energy loss of an electron in the target:

$$\frac{dE}{d\rho s} = -78500 \frac{Z}{AE_0} \ln \left( \frac{1.166E_0}{J} \right)$$

where \(\rho s\) is a small increment of path length along the electron trajectory in the target. Now, according to Duncumb and Reed,\(^1\) the energy loss in a multielement target can be regarded as an additive process, hence

$$\left[ \frac{dE}{d\rho s} \right]_{\text{spec}} = \Sigma W_j \left[ \frac{dE}{d\rho s} \right]_j$$

where \(E\) is the energy and \(W_j\) is the weight fraction of element \(j\). When our new equation for \(\alpha\) is squared, it becomes obvious that it contains the essential features of the Bethe equation. Hence it is possible to write the Bethe equation in terms of \(\alpha_i^2\) for each element \(j\) in the matrix. Using the ‘additive energy loss’ principle, it follows that

$$\alpha_i^2 = \frac{A}{Z} \Sigma W_j \frac{Z_j}{A_j} \alpha_j^2$$

where \(\bar{A}\) and \(\bar{Z}\) are the weight fraction averaged atomic weight and number of the specimen, \(A_j\) and \(Z_j\)

those of the matrix element \(j\) and \(W_j\) its weight fraction.

Our first effort with the thus modified program, although producing an r.m.s. value of 7.50% (Fig. 3), gave us hope insofar as now, contrary to Fig. 2, a sharp maximum and a better shaped histogram were obtained. A successive series of efforts in which the r.m.s. value could slowly be reduced to 6.49% (see Table 1), mainly by reducing the proportionality constant in \(\alpha\) from 1.86 to 1.705 [i.e. the constant value calculated originally in Eqn (4) for 2.142\(^{1.16}/\)Al], showed that the value of 1.705 was probably an optimum in \(\alpha\) for the time being.

A further improvement was obtained through the observation that up to then most of the Al and Si measurements, which happen to be present for an extended range of probe voltages in the file, showed a persistent tendency for increasing undercorrection (too high \(kV/k\) values) with increasing voltage. An analysis of these data, considering the magnitude of all quantities involved, showed that for the \(\alpha\) values calculated at that time the combined correction factor \([ZA]\) could never be made large enough, irrespective of whether \(\beta\) was varied between zero and infinity.

Inspection of Eqns (7) and (8) shows that, as far as the \(Z\) correction is concerned, this is not determined by the absolute magnitude of \(\alpha\) and \(\beta\) but rather by their ratio. It is also evident that factors such as proportionality constants and powers (such as the \(kV\) dependence) in the equation for \(\alpha\) play no role at all for the \(Z\) correction as they are all divided out in Eqn (7). Hence, as long as \(\beta\) is written in terms of \(\alpha\) as in Eqn (5), the ratio \(\beta/\alpha\) is only a function of \(Z\) and the magnitude of the \(Z\) correction remains essentially constant no matter what \(kV\) dependence or constants are introduced in \(\alpha\). The only hope, therefore, of getting matters right is through the absorption correction incorporated in \([ZA]\). In contrast to the \(Z\) correction, the total ZA correction is, of course, very sensitive to the absolute magnitudes of \(\beta\) and \(\alpha\) because now the terms \(\gamma/\alpha\) and \((\beta + \gamma)/\alpha\) play a dominant role.

It was soon realized that the \([ZA]\) correction for Al and Si could be considerably improved by reducing \(\alpha\) further. The problem here was to find a way of doing this while conserving the good results for the heavier

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**Table 1. A selection of a number of versions run in the optimization process and their results**

<table>
<thead>
<tr>
<th>Version</th>
<th>(\alpha)</th>
<th>(\beta)</th>
<th>(\gamma)</th>
<th>(\text{Av. kV/k}^\ast)</th>
<th>(\text{R.m.s.} (%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Eqn (9)</td>
<td>Eqn (5)</td>
<td>(\gamma_0) [Eqn (6)]</td>
<td>1.0255</td>
<td>7.50</td>
</tr>
<tr>
<td>2</td>
<td>1.73 (rest ident.)</td>
<td>0.3 (rest ident.)</td>
<td>(\gamma_0)</td>
<td>1.0137</td>
<td>6.67</td>
</tr>
<tr>
<td>3</td>
<td>1.705 (rest ident.)</td>
<td>0.3 (rest ident.)</td>
<td>(\gamma_0)</td>
<td>1.0112</td>
<td>6.49</td>
</tr>
<tr>
<td>4</td>
<td>Eqn (11)</td>
<td>0.3 (rest ident.)</td>
<td>(\gamma_0)</td>
<td>0.9873</td>
<td>5.97</td>
</tr>
<tr>
<td>5</td>
<td>Eqn (11)</td>
<td>According to Ref. 12</td>
<td>(\gamma_0)</td>
<td>1.0058</td>
<td>6.13</td>
</tr>
<tr>
<td>6</td>
<td>Eqn (11)</td>
<td>As version 4</td>
<td>0.911(\gamma_0) exp (0.0022)</td>
<td>0.9955</td>
<td>6.05</td>
</tr>
<tr>
<td>7</td>
<td>Eqn (11)</td>
<td>1.0Z(^{1.16}/)A</td>
<td>0.954(\gamma_0) exp (0.0012)</td>
<td>0.9941</td>
<td>5.91</td>
</tr>
<tr>
<td>8</td>
<td>Eqn (11)</td>
<td>0.8Z(^{1.16}/)A</td>
<td>0.954(\gamma_0) exp (0.0012)</td>
<td>0.9931</td>
<td>5.88</td>
</tr>
<tr>
<td>9</td>
<td>Eqn (11)</td>
<td>Eqn (12)</td>
<td>0.954(\gamma_0) exp (0.0012)</td>
<td>0.9920</td>
<td>5.73</td>
</tr>
<tr>
<td>10</td>
<td>Eqn (11)</td>
<td>Eqn (12)</td>
<td>(\gamma_0) exp (0.0012)</td>
<td>0.9924</td>
<td>5.68</td>
</tr>
<tr>
<td>11</td>
<td>Eqn (11)</td>
<td>Eqn (12)</td>
<td>(\gamma_0)</td>
<td>0.9924</td>
<td>5.68</td>
</tr>
<tr>
<td>12</td>
<td>Eqn (11)</td>
<td>Eqn (12)</td>
<td>0.990(\gamma_0) exp (0.0012)</td>
<td>0.9902</td>
<td>5.46</td>
</tr>
</tbody>
</table>

\(\ast\) \(\gamma\) is introduced here to distinguish it from the original equation (6) for \(\gamma_0\).
elements and to keep the measured $\alpha$ values as close as possible.

The solution was eventually found in the observation that it was probably not the fact that we were dealing with relatively light elements but rather with the inherent high overvoltage ratios involved: between 6 and 25 for Al between 10 and 40 kV, compared with 1.5 up to 4 for most of the heavier elements. Apparently $\alpha$ is not well described for higher overvoltage ratios by the expression used so far. This might have a very serious impact on the results which goes far beyond the importance of the present Al and Si measurements if one realizes that in possible future applications of the program to light element ($Z<11$) analyses overvoltage ratios up to 50 or higher are common.

The best compromise for $\alpha$ was found by replacing the implicit $(U_0-1)^{0.5}$ dependence in Eqn (4) by a $(U_0-1)^{0.55}$ dependence and replacing the proportionality constant by 1.75, which was found to restore both the close connection with experimental $\alpha$ values and the good results for the heavier elements. The use of this expression for $\alpha$ led to the histogram shown in Fig. 4, which for the first time gave an r.m.s. value below 6%. It was then decided to keep the expression for $\alpha$ fixed in further runs. The final expression is thus

$$\alpha = \frac{1.75 \times 10^5}{E_0^{1.25}(U_0-1)^{0.55}} \left[ \ln \left( \frac{1.166E_d}{J} \right) \right]^{0.5}$$ (11)

**Optimization of $\beta$**

Next our attention was directed towards optimizing the expression for $\beta$. In the foregoing we already expressed our doubts on the accuracy of the fitted $\beta$ values,$^{12}$ and this is partly supported by the fact that the introduction of the original equation$^{12}$ for $\beta$ gave an increased r.m.s. value (see Table 1).

Reintroduction of a factor $Z^n/A$, with $n$ between 1.6 and 1.7, to restore the original relationship between $\beta$ and $\alpha$ proposed by Brown and Packwood$^{13}$ offered a negligible improvement (Table 1). A small but significant improvement was achieved by introducing a $(U_0-1)^{0.5}$ dependence into $\beta$. Our final expression is thus

$$\beta = 0.4\alpha \frac{Z^{1.7}}{A} (U_0-1)^{0.3}$$ (12)

**Optimization of $\gamma_0$**

As far as $\gamma_0$ is concerned, it has been stated before$^{13}$ that there is perhaps a small $Z$ dependence in $\gamma_0$ which may have been overlooked so far. Some runs with various equations for $\gamma_0$ with such a slight $Z$ dependence eventually led to the following expression:

$$\gamma = 0.98\gamma_0 \exp (0.0012Z)$$ (13)

The final run gave an r.m.s. value of 5.46% and a very symmetrical histogram (Fig. 5), thus showing that the $\phi(pz)$ approach indeed shows excellent promise for use in quantitative electron probe analysis. The results obtained are at least as good as those with the most recent correction procedure$^6$ and certainly much better than the so-called established ZAF procedure,$^{25}$ with a reported r.m.s. value of 6.8%. A detailed inspection of all output obtained so far revealed two remarkable facts. First, it seems that the $Z$ correction obtained through the $\phi(pz)$ approach described so far is much less dependent on kV than that of Duncumb and Reed$^1$ and possibly also that of Love et al.$^2$ This will be part of the subject of a separate paper in which a detailed comparison will be made between those programs. Work to this effect is at the moment in progress. Second, it is apparent that overvoltage ratios smaller than 1.5 are best avoided as in those cases a persistent undercorrection ($k'/k$ too high) was observed, which increased with decreasing overvoltage. This is undoubtedly the result of the $1/(U_0-1)^{0.55}$ dependence in $\alpha$ which for $1<U_0<2$ shows a very sharp increase towards infinity whereas for $U_0$ values larger than 2 it has a rather monotonous appearance.

**DISCUSSION AND FUTURE PROSPECTS**

It has been shown that our newly optimized version of the $\phi(pz)$ approach gives good results in quantitative
electron probe microanalysis, although it is not clear to us what might be the reason for the large discrepancies between our results and those reported by Brown and Packwood. Nevertheless, some matters of concern still remain. In our opinion, for the quantities $\alpha$, $\beta$, $\gamma$ and $\phi(0)$ involved, the expressions for $\alpha$ and $\phi(0)$ can be considered reliable. This would be expected for $\alpha$ because the values were obtained from reliable fits to actual physical measurements and in our fitting procedure we have taken care to keep it as close as possible to physical reality.

The expression for $\phi(0)$ stems from Love et al., and was based on Monte Carlo simulations, the results of which are in general considered reliable; hence their expression is probably the most reliable to date.

The expressions for $\beta$ and $\gamma_0$ probably deserve much less confidence and the fact that Eqn (12) and (13) yield, at the moment, optimal results in terms of a best r.m.s. value does not imply that these are physically the most significant expressions. We feel that the expression for $\beta$ is probably much more complex than described so far. This can easily be seen when Eqn (3) for $\phi(pz)$ is differentiated with respect to $(pz)$ in order to find the position of the maximum in the $\phi(pz)$ curve. When $(pz)$ for this maximum is replaced by $x_m$ we obtain

$$2\alpha^2x_m\gamma_0 = [\gamma_0 - \phi(0)] \exp(-\beta x_m(\beta + 2\alpha^2x_m))$$

which shows that there must be a complicated relationship between $\beta$, $\alpha$, $\gamma_0$, $\phi(0)$ and $x_m$.

As it seems much easier to determine exactly the position of the maximum in the existing $\phi(pz)$ data than to try and extract a reliable $\beta$ value from an often limited area between surface and maximum, it is worthwhile to re-examine the existing data in the light of these considerations.

A last point of concern is the relationship between $\gamma_0$ and $\phi(0)$. The main questions here are if $\gamma_0$ is properly scaled with respect to $\phi(0)$ and if the expression for $\gamma_0$ is correct for a wide enough range of overvoltages, with special interest for very high or very low overvoltages. In this connection it is interesting that for the limiting case that $U_o \to 1$, $\phi(0)$ also takes the value 1, as indeed it should. This is, however, not the case for $\gamma_0$, which, in Eqn (6), takes the value $0.5\pi$. Nevertheless, one would expect that, as $U_o$ approaches 1 (see also Fig. 1) the maximum in the $\phi(pz)$ curve would shift closer and closer to the surface while its magnitude would decrease. As a result, one would expect that the value of $\gamma_0$ would approach that of $\phi(0)$ and become unity at $U_o = 1$. This is evidently not the case and this may well contribute to the unsatisfactory behaviour of the program for $U_o < 1.5$.

A solution to these problems can only be expected when more data are available. Regarding future applications of the program to light element analyses, this is mainly hampered by the lack of reliable measurements on which the results are to be tested. In order to satisfy at least partially this need, an extended series of carbon measurements are being performed in our laboratory, the results of which will be reported later.

**REFERENCES**