

A further improvement in the Gaussian $\Theta(\rho z)$ approach for matrix correction in quantitative electron probe microanalysis

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Original Paper

A Further Improvement in the Gaussian $\Phi(\rho z)$ Approach for Matrix Correction in Quantitative Electron Probe Microanalysis

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Abstract

An improved correction model for quantitative electron probe microanalysis, based on modifications of the Gaussian $\Phi(\rho z)$ approach, originally introduced by *Packwood* and *Brown*, is presented. The improvements consist of better equations for the input parameters of this model which have been obtained by fitting to experimental $\Phi(\rho z)$ data. The new program has been tested on 627 measurements for medium to heavy elements ($Z > 11$) and on 117 carbon measurements with excellent results: an r.m.s. value of 2.99% in the former case and 4.1% in the latter. Finally the new program has been compared to five other current correction programs which were found to perform less satisfactorily.

1. Introduction

For many years it has been common practice in quantitative electron probe microanalysis to treat the matrix correction procedure, necessary in order to convert the measured intensity ratios (k-ratios) into concentration units, in three separate steps:

– Firstly, a step in which backscattering of the electrons and x-ray generation in the target are separately considered in detail.

Both effects, called the R-factor (backscattering) and the S-factor (stopping power), respectively, are then combined to make up for the so-called atomic number correction, which is usually expressed by Z. This Z-factor is proportional to the total number of ionisations *generated* in the target.

– Secondly, it is necessary to adopt some kind of $\Phi(\rho z)$ curve (number of ionisations Φ , as a function of mass depth ρz) in order to calculate how much of the generated intensity is lost by absorption in the target on its way to the spectrometer.

The ratio between the *emitted* and the *generated* intensity is called the A-factor, which is more commonly known as the quantity F (χ), in which

$$\chi = \frac{\mu}{\rho} \operatorname{cosec} \psi \quad (1)$$

(μ/ρ is the mass absorption coefficient and ψ is the x-ray take-off angle).

– Finally, it is sometimes necessary to account for secondary fluorescence which can take place whenever one of the primary, electron beam generated, radiations is of sufficiently high energy to excite additional x-radiation of the element being measured. The correction for this effect is contained in the so-called F-factor.

The three factors Z, A and F are next calculated for standards and specimen and subsequently multiplied by the measured intensity ratio k of the element in question to yield the desired concentration c (in wt %) according to the relation

$$c = k Z A F. \quad (2)$$

Note that now terms like Z stand for the ratio between the intensity generated in the standard and that in the specimen. For details regarding the procedures followed in performing the corrections until a few years ago the reader is referred to the review article by *Beaman and Isasi (1972)*.

Of all the three correction factors involved the absorption correction has rightfully received the most attention because this usually constitutes the major correction required. The performance of any absorption correction procedure is completely dependent on the correctness of the $\Phi(\rho z)$ curve used. In this respect quite an evolution has taken place: from the original simplified *Philibert (1963)* model, which was later modified (*Ruste and Zeller 1977*) into the full *Philibert (1963)* model, through more or less rudimentary forms of $\Phi(\rho z)$ curves like rectangles (*Bishop 1974*, *Love and Scott 1978, 1980*) and quadrilateral shapes (*Sewell et al. 1985*) to the more sophisticated and realistic models introduced recently (*Packwood and Brown 1981*, *Pouchou and Pichoir 1984*).

In the latter two models, the artificial separation into atomic number and absorption effects is avoided altogether. Instead, the combined correction is carried out in one single procedure. All that is required is the integration of the *emitted* intensity vs. ρz curve (see Fig. 1). This curve is obtained by multiplying each point of the *generated* $\Phi(\rho z)$ curve by $\exp[-\chi\rho z]$ in order to correct for absorption.

Subsequent integration for ρz between zero and infinity immediately yields the quantity that is proportional to the *emitted* intensity. If it should be necessary to know the absorption factor $F(\chi)$, one simply integrates both the generated as well as the emitted intensity and the ratio will yield $F(\chi)$.

The latter models rely even more on the correctness of the $\Phi(\rho z)$ curves because now the complete [ZA] correction is based on the $\Phi(\rho z)$ curves generated by the models, contrary to the conventional ZAF approaches. Hence, it is of the utmost importance that the equations used in the calculations of $\Phi(\rho z)$ curves in both $\Phi(\rho z)$ models are sufficiently reliable. Both the Packwood and Brown, as well as the Pouchou and Pichoir models use four parameters to describe the $\Phi(\rho z)$ curves. In the latter model $\Phi(\rho z)$ is characterised by:

1. the surface ionisation $\Phi(0)$,
2. the ultimate depth of ionisation,
3. the depth of maximum ionisation (peak position),
4. the integral of $\Phi(\rho z)$, which is proportional to the number of ionisations *generated* by the incident electron.

Keeping the first three parameters fixed, a $\Phi(\rho z)$ curve is generated with a height sufficient to ensure that the integral of $\Phi(\rho z)$ is equal to parameter four. Although mathematical details of the Pouchou and Pichoir model have not been published so far, it is certain that a large amount of computational effort through complex equations is involved.

The Packwood and Brown model, which offers a substantial improvement in matrix correction procedures, is based on a completely different approach and is mathematically much simpler.

This model is based on the fact that $\Phi(\rho z)$ curves are basically Gaussian in shape with the peak of the Gaussian centered at the surface. The so-called "undisturbed" Gaussian (dotted curve in Fig. 1) is then described by

$$\gamma = \exp[-\alpha^2(\rho z)^2] \quad (3)$$

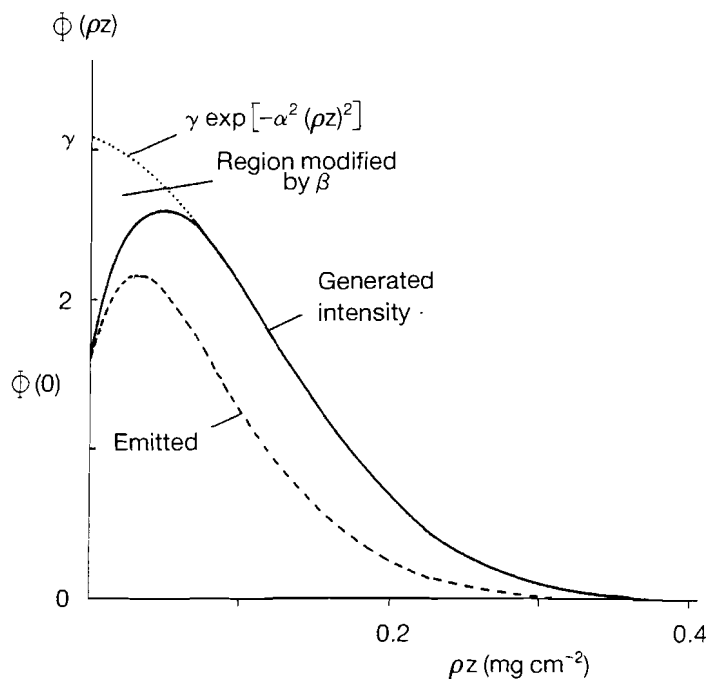


Fig. 1 Drawing showing the principles of the Gaussian $\Phi(\rho z)$ approach. Both the generated intensity (solid curve) as well as the emitted intensity (broken curve) as a function of mass depth (ρz) are shown. The dotted curve represents the hypothetical "undisturbed" Gaussian which is centered at the surface with amplitude γ . The decay rate in the Gaussian is given by α .

in which α is the decay rate in the Gaussian and γ the value of its maximum. The real $\Phi(qz)$ curve, however, is known to have its maximum somewhere deeper in the specimen and this is accounted for by the introduction of a transient function:

$$\left[1 - \frac{\gamma - \Phi(0)}{\gamma} \exp(-\beta qz)\right] \quad (4)$$

in which β is some kind of scattering factor which contributes to a spreading of the electron beam, making it finally a diffuse electron cloud. Summarizing, $\Phi(qz)$ can be described by:

$$\Phi(qz) = \gamma \left[1 - \frac{\gamma - \Phi(0)}{\gamma} \exp(-\beta qz)\right] \exp[-\alpha^2 (qz)^2] \quad (5)$$

It will be evident that the success of the $\Phi(qz)$ equation is strongly dependent on a correct parameterisation of the 4 input parameters α , β , γ and $\Phi(0)$.

The equations originally proposed by *Packwood* and *Brown* (1981), which were obtained through fits to measured $\Phi(qz)$ data, have been abandoned by the authors themselves (*Brown* and *Packwood* 1982) after testing them in a correction program on a large number of microanalyses. The reported value of 11.3% for the relative root-mean-square error (r.m.s.) would indeed suggest that it was one of the least accurate correction programs. In the same paper the authors produced new expressions for α and β , this time through an optimization process using the same data base. As a result they claimed an r.m.s. value of 4.8%, which would be very good indeed. However, we have shown that this claim was not correct and we carried out our own optimization (*Bastin* et al. 1984-1, 1984-2) with the result that our version of the *Packwood* and *Brown* model could match the results of the best programs then known. We have since tested (*Bastin* and *Heijligers* 1986) the same program on a set of 117 carbon measurements on 13 binary carbides between 4 and 30 kV, with excellent results: an r.m.s. value of 3.7% which must be called a remarkable achievement considering the wide range of accelerating voltages. Nevertheless, there were still some things which could be improved in the approach and these concerned, amongst other things, the $\Phi(qz)$ curves for high-energy radiations in heavy matrices, e.g. the case of Bi - L α in Au or Zn - K α in Cu.

In those and similar cases it was observed that although the calculated $\Phi(qz)$ curves had a good shape and in general the peak at the right position, the absolute heights of the curves could not be brought

into agreement with measured $\Phi(qz)$ curves. We have previously concluded (*Bastin* et al. 1984-1) that our modified expression for α was probably reliable because it provided good fits to experimental data. However, we expressed our doubts about the equations for β and γ .

The object of the present work was to develop better equations for these parameters, not by optimization but by a renewed fitting procedure to experimental $\Phi(qz)$ curves in order to arrive at new empirical equations for β and γ .

Subsequently the new set of equations have been tested in a correction program applied to a large number of analyses and compared to other programs.

2. Mathematical Analysis of the Functional Behaviour of β and γ

In order to establish the influence of the parameters β and γ on the general shape of the $\Phi(qz)$ curve, and more specifically on the absolute height and the position of the maximum, two rather extreme cases were selected: one at an extremely high overvoltage ratio, e.g. C-K α radiation in Carbon at 40 kV (with an overvoltage ratio of 141; Fig. 2a), and one at a rather low overvoltage ratio, e.g. Bi-L α in Au (overvoltage ratio 2.16; Fig. 2b).

In Fig. 2a a number of calculations have been performed with varying values of γ and β . It is shown that when β is varied between zero and infinity for a fixed value of γ , then the position of the maximum follows a loop extending from $\Phi(0)$ ($\beta = 0$) up to γ ($\beta = \infty$).

It can be shown that the mathematical description of the loop, which is simply the locus of the maximum, is given by

$$\beta = \frac{2\alpha^2 x_m \Phi(m)}{[\gamma \exp(-\alpha^2 x_m^2) - \Phi(m)]} \quad (6)$$

in which x_m is the position of the maximum in units of qz and $\Phi(m)$ is the height of the maximum.

Three distinct regions in the loop can be distinguished:

- Firstly, a part close to γ , where a variation of β produces a variation in the peak position, and not so much in the peak height.
- Secondly, a part where the loop is almost vertical and where a variation in β produces a very strong variation in the peak height and hardly influences the position of the peak.

– Finally, a part close to $\Phi(0)$ where a variation in β produces mainly a variation in the peak position again.

This last part of the loop has no physical meaning because it is inconceivable that the peak should move closer to the surface again after having moved away from it first with increasing voltage.

It is interesting to note in Fig. 2a that even substantial changes in the values for γ (e.g. from 5 to 7) and β (e.g. from 800 to 1700) have hardly any influence on the peak position, because they both operate in the vertical part of the loop. They mainly affect the peak height.

Because we had the distinct impression that for high overvoltage ratios in light matrices the maximum of the $\Phi(\rho z)$ curves went increasingly too high, it is obvious that in such cases both the parameters β and γ could be responsible. However, the variation of γ with overvoltage is known to be very slow in this region; hence, it is most likely that the calculated values for β are increasingly too high.

The equation for β used previously was

$$\beta = 0.4 \alpha \frac{Z^{1.7}}{A} (U_0 - 1)^{0.3} \quad (7)$$

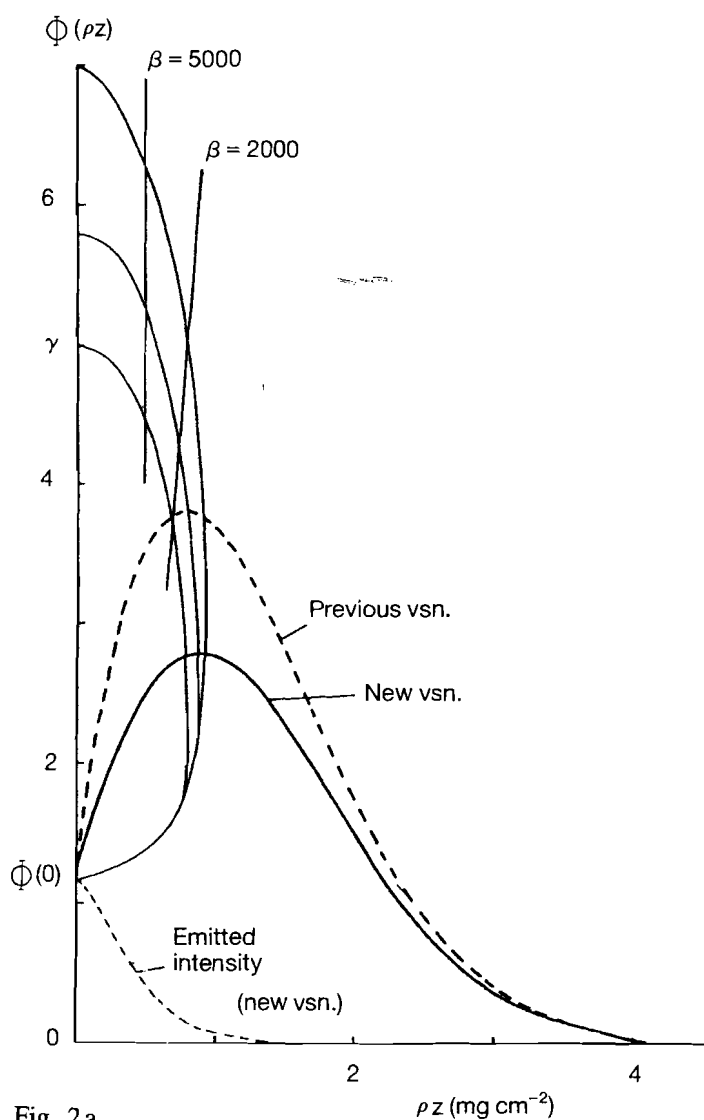


Fig. 2a

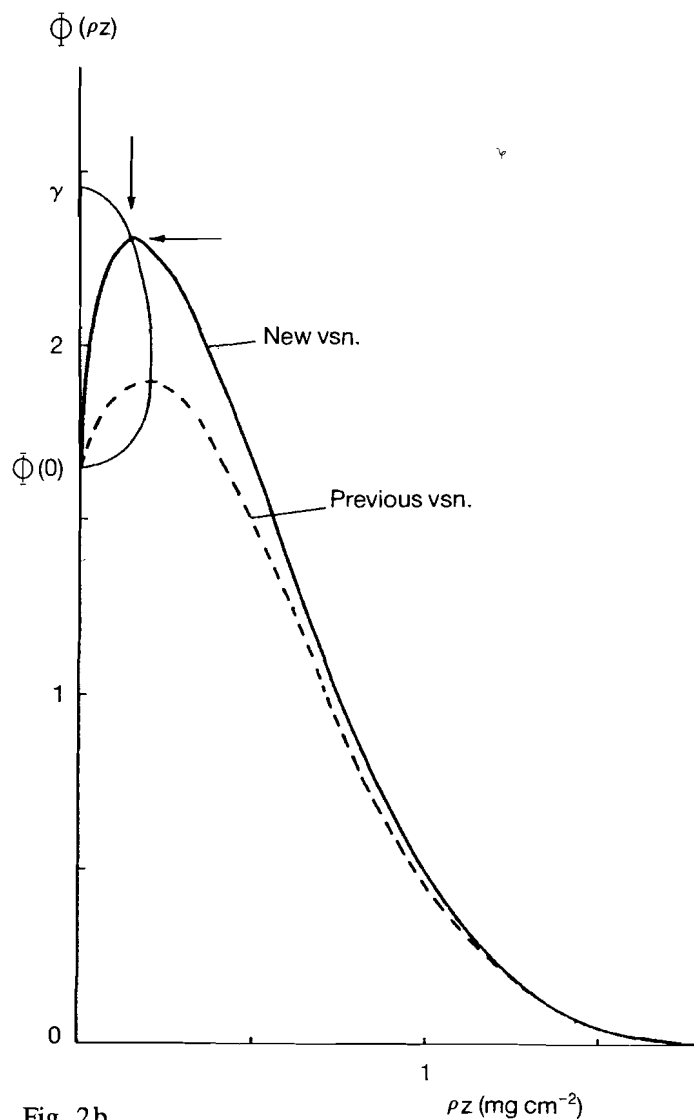


Fig. 2b

Fig. 2 Influence of the magnitude of β and γ on the shape of the calculated $\Phi(\rho z)$ curve for two extreme cases: (a) Very high overvoltage ratio (approx. 140) in very light matrix (C-K α in C at 40 keV). The loops are the locus of the maximum in the $\Phi(\rho z)$ curve when for a fixed value of γ (5, 5.8 and 7, respectively) β is varied between zero (lower end of loop) and infinity (upper end of loop). Dashed and solid curves are the $\Phi(\rho z)$ curves calculated by our previous program and present program, respectively. Lower dashed curve is the emitted intensity according to the present program (mass absorption coefficient 2373, take-off angle 40°). The straight lines show the variation in the position of the maximum for fixed values of β and varying values of γ . (b) Low overvoltage ratio (2.16) in heavy matrix (Bi-L α in Au at 29 keV). Arrows indicate the experimentally determined (Castaing and Descamps 1955) position of the maximum.

in which Z and A are atomic number and weight of the matrix element and U_o is the overvoltage ratio (E_o/E_c , E_o is acceleration voltage, E_c is critical excitation voltage).

It will immediately be clear that the factor $(U_o-1)^{0.3}$, which was brought in through an optimization process using a data base of microanalyses, is responsible for the malfunctioning of β in cases like Fig. 2a because β may attain unrealistically high values for very high overvoltage ratios.

Hence, it follows that in developing a new expression for β special attention has to be paid to a proper behaviour of β at high overvoltage ratios in light matrices, which means generally lower β -values in those cases.

Next we shall consider the case depicted in Fig. 2b, where the situation is completely different. Because γ and $\Phi(0)$ are much closer together, a small change in γ may have a relatively larger influence on raising or lowering the maximum. The largest influence will be felt when U_o decreases towards unity, which means that γ should approach $\Phi(0)$ and both should approach unity. We have criticized (Bastin et al. 1984-1) Packwood and Brown's original equation for γ (Packwood and Brown 1981) in this respect because their expression had a limiting value of $\pi/2$ at $U_o = 1$. Our own expression, again obtained through optimizing, was

$$\gamma = \frac{4.9 \pi U_o}{(U_o - 1) \ln U_o} (\ln U_o - 5 + 5 U_o^{-0.2}) \exp(0.001Z) \quad (8)$$

This still suffers from the same shortcoming. After comparing our calculated $\Phi(qz)$ curves with experimental $\Phi(qz)$ data we concluded that as far as γ is concerned we need a new expression which

- (a) provides a limiting value of 1 for $U_o \rightarrow 1$, and
- (b) exhibits a faster increase between $U_o = 1$ and, say, $U_o = 3$.

At higher overvoltage ratios the absolute magnitude of γ slowly becomes less relevant. However, in order to ensure a smooth functioning it is necessary to develop a new expression for the whole range.

A close inspection of Fig. 2b reveals that a change in γ alone can never bring the peak position to the measured location (indicated by arrows). Apparently also a significant change in β is necessary.

A detailed comparison between available $\Phi(qz)$ data for cases like in Fig. 2b and calculated $\Phi(qz)$ curves showed that in general much too low values for β were calculated but that the peak position itself was quite satisfactory in the majority of cases.

We came to the conclusion that for light element radiation the expression for β used so far brought the peak somewhere at an optimum position in the upper half of the loop, where it should be. In the case of higher energy-radiations the optimum in the peak position was usually in the lower half of the loop, which has no physical meaning.

This is the quite logical result of developing equations through an optimization process: Optimization will lead to a setting for β which will be best in those areas where it matters most; i.e. in lighter element radiations ($Al - K\alpha$, $Si - K\alpha$) in medium to heavy matrices where serious absorption can occur. Thus one ends up with an expression which yields fairly realistic $\Phi(qz)$ curves for peak positions and, to a lesser extent, peak heights.

This conclusion is substantiated by the apparent success of our previous program (Bastin et al. 1984-2) on a data base containing medium to heavy element analyses and even more so by its success in Carbon analyses (Bastin and Heijligers 1986). On the other hand it is possible, and even likely, that an optimization process yields an expression for β that is less suited to a description of $\Phi(qz)$ curves of high-energy radiations in heavier matrices, i.e. cases where it matters less, because heavy absorption is rarely encountered here and usually atomic number effects prevail, which are generally much smaller than absorption effects.

Moreover, for use in a correction program it is the ratio between quantities in standard and specimen that matters and even a fairly bad program can turn out acceptable results by a process of error compensation.

Summarizing, we come to the conclusion that the previous equation for β produced too high values for very high overvoltages, fairly realistic values for e.g. $Al - K\alpha$ and $Si - K\alpha$ radiations, and too low values for high energy radiations in heavy matrices. Apparently the setting for β used so far is a kind of "weighted average" throughout the periodic system. Hence, it needs to be reexamined and we chose to do this by a critical reexamination of existing experimental $\Phi(qz)$ data.

3. Development of New Equations for β and γ

When trying to establish new empirical equations for β and γ , using measured $\Phi(qz)$ curves one is confronted with a number of practical problems. In spite of the rather extensive data available (see e.g.

Scott and Love 1983 for a review of existing $\Phi(qz)$ data) it is difficult to find consistent series of measurements over a wide range of accelerating voltages. In those few systems where this is the case one is frequently trapped in inconsistencies or deviations between measurements by different authors. Experimental difficulties in this tedious and cumbersome type of work are no doubt responsible for this.

In the fitting procedure for β and γ , one thus usually has only a very limited region for each system to fit values of β and γ – in the vast majority of cases only two to four points which are usually closely spaced. For another system two or three new data points are available, which give access to values of β and γ in a sometimes completely different region of U_0 , etc.

Besides, each $\Phi(qz)$ curve is valid only for one type of radiation in one single matrix element. It is obvious, therefore, that a lot of fragmentary evidence has to be joined together in order to arrive at consistent expressions for β and γ for a wide range of overvoltage ratios. Monte-Carlo simulations could be considered in a number of cases. The latest evidence in this field, however (Sewell et al. 1985), seems to suggest that simulated $\Phi(qz)$ curves are usually worse than measured ones.

The fitting procedure was carried out using, amongst other things, the extensive data gathered by Brown and Parobek (e.g. 1976) and Parobek and Brown (e.g. 1978), supplemented by measurements of Castaing and Descamps (1955), Castaing and Henoc (1966) and Shinoda (1966). Furthermore, in a number of cases $\Phi(qz)$ curves generated by the Pouchou and Pichoir (1984) program were used. These were obtained in a mutual comparison (Pouchou and Pichoir 1985) of $\Phi(qz)$ curves generated by their as well as our (previous) program and they obviously have the benefit of being supported by a separate expression for the total number of ionisations produced, which ensures that the variation of generated intensity with accelerating voltage is consistent. As far as can be judged from the impressive result (Pouchou and Pichoir 1984) this approach is successful.

3.1 New expression for γ

In section 2 we have discussed what the main requirements for γ should be:

1. Its value should approach unity for $U_0 \rightarrow 1$.
2. Its increase for $1 < U_0 < 3$ should be faster than in either Packwood and Brown's (1981) original equation or our modified version (Bastin et al. 1984-1, 1984-2).

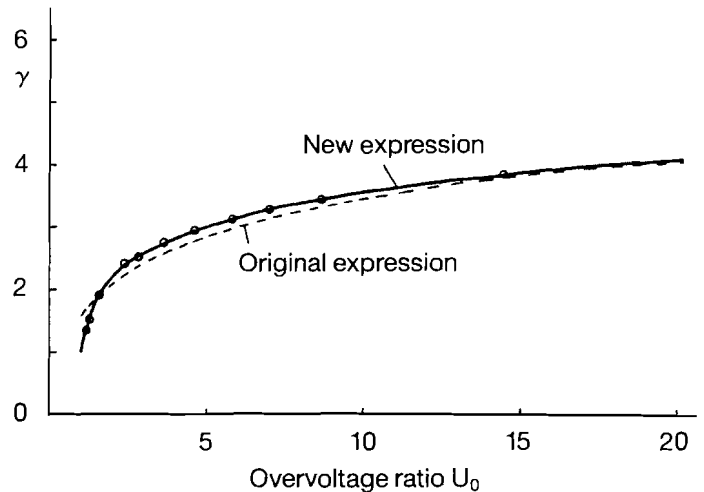


Fig. 3 Comparison between the original (Packwood and Brown 1981) and the new equation for γ , obtained by fitting to experimental $\Phi(qz)$ data. Open circles denote some of the fitted data.

Figure 3 shows the result of the fitting procedure for γ (solid line) as compared to the original equation of Packwood and Brown (1981) (dotted line). A number of data points obtained by fitting have been indicated. Considering the scatter in the measured $\Phi(qz)$ data it is surprising to see how smooth a variation of γ with U_0 is obtained.

It proved very difficult to find one simple mathematical function to represent the fitted graph. It is very interesting to note, though, that for $U_0 > 3$ the new γ -values for a certain value of U_0 are approximately equal to the original γ -value calculated at $(U_0 + 1)$

$$\gamma_{\text{new}}(U_0) = \gamma_{\text{old}}(U_0 + 1) \quad (9)$$

It was, therefore, decided to make a distinction between two discrete regions in U_0 : one for $1 \leq U_0 \leq 3$ and one for $U_0 > 3$.

In the former case satisfactory γ -values could be calculated by the fitted expression

$$\gamma = 1 + (U_0 - 1)/[0.3384 + 0.4742(U_0 - 1)] \quad (1 \leq U_0 \leq 3) \quad (10)$$

whereas in the latter case simply the value of $(U_0 + 1)$ was inserted in Packwood and Brown's original equation, to yield:

$$\gamma = \frac{5\pi(U_0 + 1)}{U_0 \ln(U_0 + 1)} [\ln(U_0 + 1) - 5 + 5(U_0 + 1)^{-0.2}] \quad (U_0 > 3) \quad (11)$$

A final remark on γ must be made as far as high overvoltages ($U_0 > 25$) are concerned. Due to an obvious lack of $\Phi(qz)$ data in this range the values for γ are necessarily somewhat speculative.

3.2 New expression for β

According to *Packwood and Brown* (1981) the parameter β is related to the rate at which the focussed electron beam becomes randomized through electron scattering in the target. Hence, it would appear that β could be calculated using electron scattering equations. However, their original equation has been abandoned (*Packwood and Brown* 1982) in favour of an equation in which β was related to α . This was justified by the assumption that both α and β are to a certain extent subject to the same scattering laws and hence, there should be a close relationship between the two quantities.

We also followed the latter approach, apparently with success (*Bastin et al.* 1984). However, there are some areas in which the behaviour of our expression for β was unsatisfactory. In the present work we will try to find a new expression for β , which relates β to α according to an equation of the type

$$\beta = \alpha \frac{Z^n}{A} \quad (12)$$

in which the value of n has to be determined from experimental $\Phi(\rho z)$ data. Note that now no effort is made to include a term containing U_o , as this was found to cause errors at high overvoltages.

When trying to establish the value of the exponent n it was soon realized that this could never have a constant value throughout the periodic system. Figure 4 shows the variation of n with atomic number Z .

A number of representative data points, obtained by backcalculation and fitting, have been included. The error bars indicate the most likely range for n , corresponding to the possible variation in β , arising from measuring uncertainties etc. Due to the proportionality to Z^n , the value of n becomes all the more important for very high atomic numbers. For low atomic numbers, on the other hand, the value of n is less critical.

A satisfactory fit to the data points was obtained by the following equation:

$$n = Z / (0.4765 + 0.5473 \times Z) \quad (13)$$

It is tempting, to try to explain the observed variation of n with Z in terms of the growth of the electron cloud with increasing atomic number. However, the final equation for β becomes rather complicated through its relationship with α . We satisfy ourselves with the empirical relationship. The final equations for α (*Bastin et al.* 1984), β and γ are thus

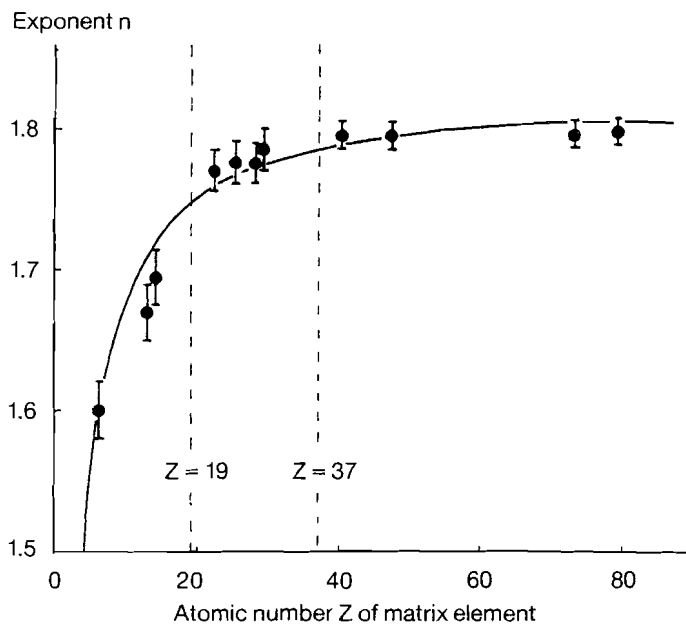


Fig. 4 Variation of the exponent n in the equation $\beta = \alpha Z^n/A$ with atomic number Z of the matrix element. Solid points are fitted data points; error bars indicate estimated uncertainty. Solid curve represents the equation for β fitted through these data points. Broken vertical lines indicate the regions with different growth rates of n .

$$\alpha = \frac{1.75 \times 10^5}{E_o^{1.25} (U_o - 1)^{0.55}} \left[\frac{\ln(1.166E_o/J)}{E_c} \right]^{0.5} \quad (14)$$

in which J is the ionisation potential.

$$\beta = \alpha \frac{Z^n}{A}, \text{ with } n = Z / (0.4765 + 0.5473 \times Z)$$

$$\gamma = 1 + (U_o - 1) / [0.3384 + 0.4742 \times (U_o - 1)] \quad \text{for } 1 \leq U_o \leq 3$$

$$\gamma = \frac{5\pi(U_o + 1)}{U_o \ln(U_o + 1)} [\ln(U_o + 1) - 5 + 5(U_o + 1)^{-0.2}] \quad \text{for } U_o > 3$$

The expression for J we use is that of *Ruste* (1979) while the expression for $\Phi(0)$ is that of *Love et al.* (1978).

4. Comparison Between Experimental and Calculated $\Phi(\rho z)$ Curves

We shall now compare the calculated $\Phi(\rho z)$ curves, using the new equations for β and γ , to experimental $\Phi(\rho z)$ data. Figures 5a–5g show a number of calculated $\Phi(\rho z)$ curves which have been selected to give a

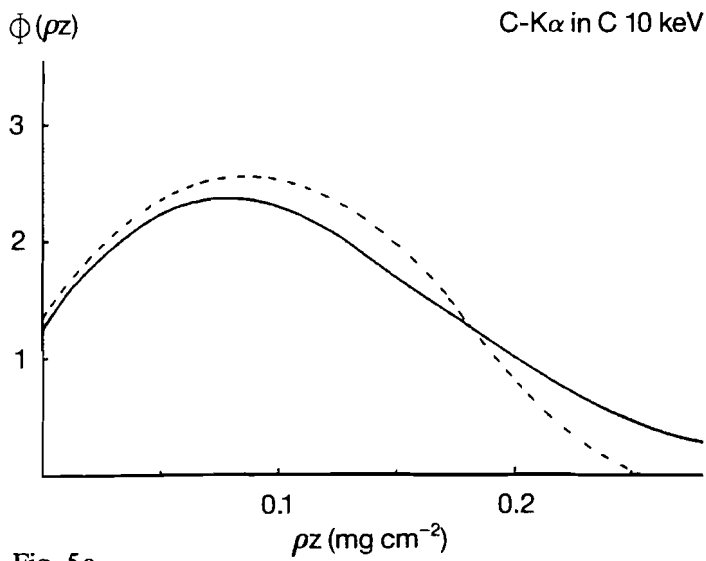


Fig. 5a

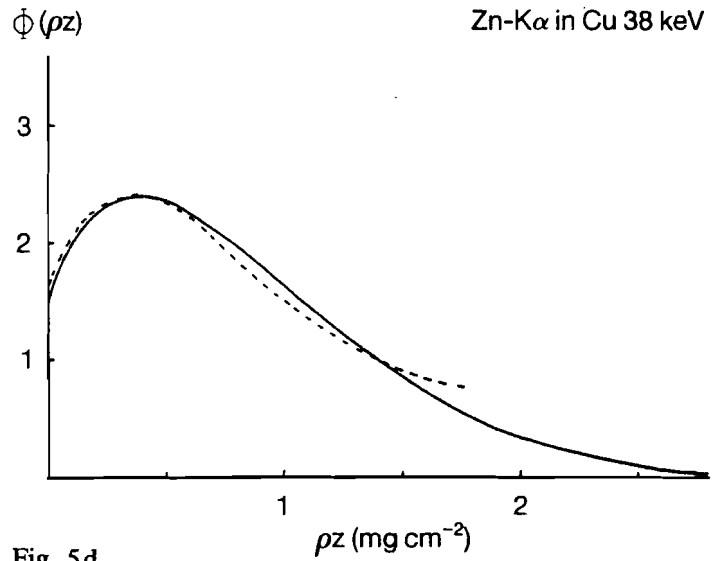


Fig. 5d

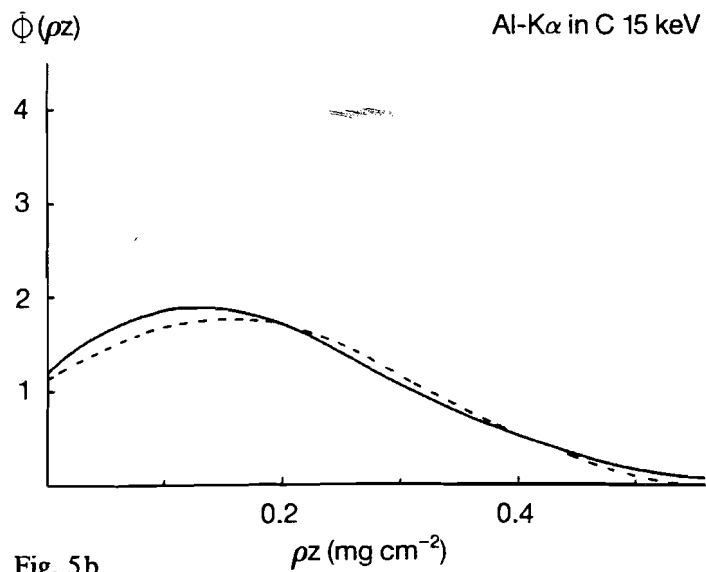


Fig. 5b

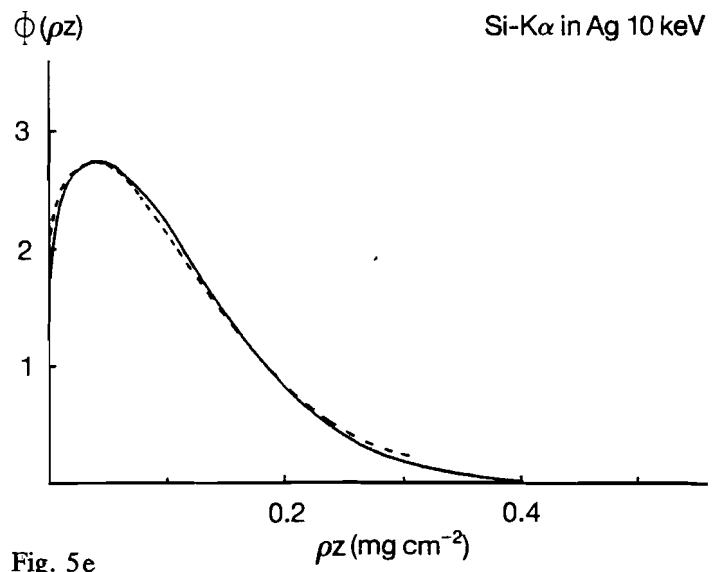


Fig. 5e

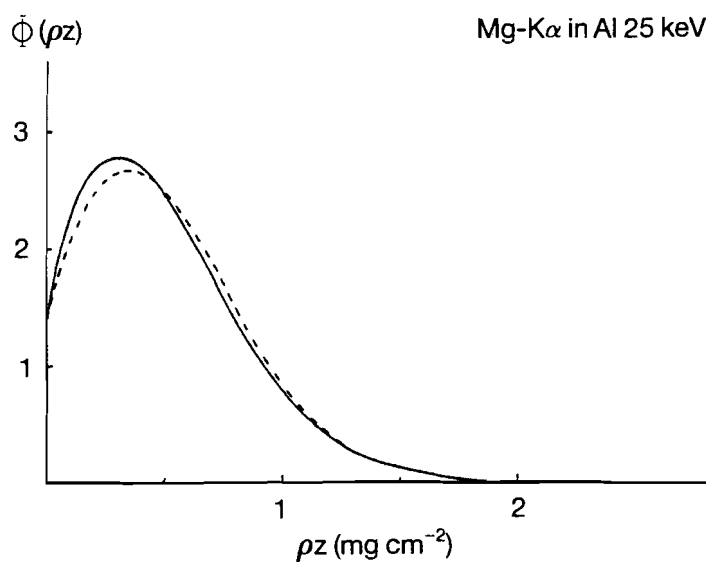


Fig. 5c

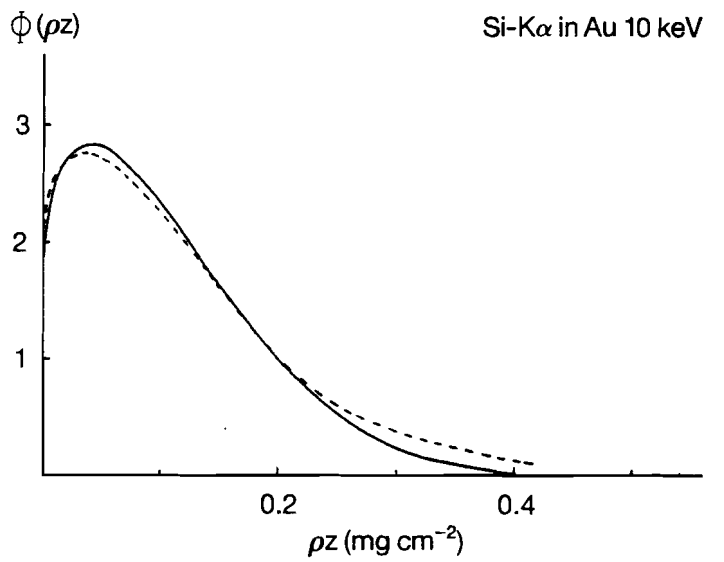


Fig. 5f

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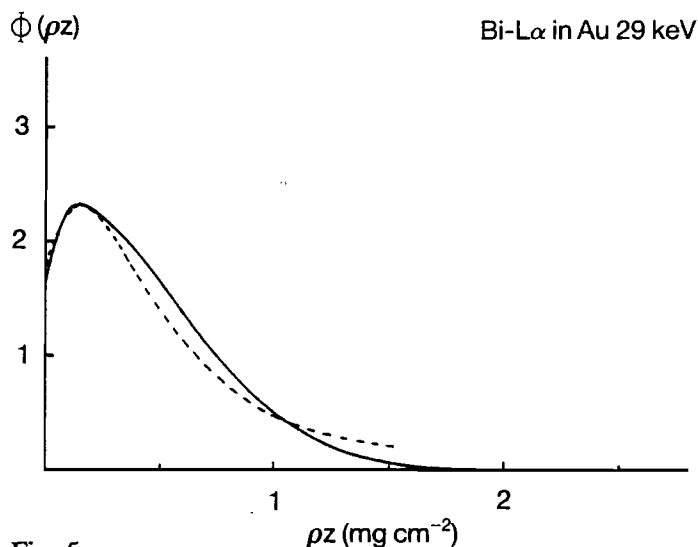


Fig. 5g

Fig. 5 Comparison between a number of calculated $\Phi(\rho z)$ curves according to the present version (solid lines) and experimental $\Phi(\rho z)$ data (broken curves). All experimental curves have been obtained by tracer measurements, except Fig. 5a, which was obtained by Monte-Carlo simulations. References: (a) Love and Scott 1980, (b) Sewell et al. 1985, (c) Castaing and Hénoc 1966, (d) Shinoda 1966, (e) Brown and Parobek 1976, (f) Brown and Parobek 1976, (g) Castaing and Deschamps.

representative cross-section through the periodic system. With one exception (Fig. 5a) the experimental $\Phi(\rho z)$ data have also been represented (broken lines). The only exception concerned the case of C-K α radiation in C, for which system no experimental data are available for obvious reasons. Instead, the results of Monte Carlo simulations (Love and Scott 1980) have been used here. The general impression from Fig. 5 is that the new expression for β and γ are apparently highly successful in modeling the $\Phi(\rho z)$ curves correctly, the more so when the wide range of systems and experimental conditions is considered.

Our conclusion seems, therefore, justified that the new set of equations is capable of predicting $\Phi(\rho z)$ curves for a wide variety of conditions within the experimental error. A comparison with calculations based on the previous equations showed that the main improvement was achieved for higher-energy radiations in heavy matrices (cf. Figs. 2b and 5g). For lighter element radiations like Al-K α the new results are virtually the same as the previous ones, whereas for very light element radiation like C-K α the improvement probably concerns mainly a reduction of the (excessive) peak heights at extreme overvoltages (see Fig. 2a). These are exactly the objectives mentioned in the introduction.

5. Test of the New Equations in a Matrix Correction Program

5.1 Some general remarks

The usual way of testing a correction program is to subject it to a large number of microanalyses, calculate the k-ratio (k') for the known composition in each case and compare it to the measured k-ratio (k). The proximity of k'/k to 1 is used as a measure of success.

A convenient way of displaying the results is in a histogram representing the number of analyses as a function of k'/k . The narrowness of the histogram (usually expressed in terms of the relative root-mean-square error (r.m.s) with respect to the average k'/k value) and its shape are used as the final measures of success. Several demands have to be made upon such a test:

1. The data base used should be of a very high quality and should contain analyses of a widely varying nature, performed over a wide range of accelerating voltages.

We have previously criticized (Bastin et al. 1984) the data base used so far (Love et al. 1975) in these respects. Our main objection was that a large proportion of the data were really too old (from before 1968).

2. A test should be meaningful. If it is desired to show that one absorption correction is better than another, one should select a large number of heavy absorption cases. In their latest paper Sewell, Love and Scott (1985) have done the opposite. From their original set of 430 analyses they eliminated virtually all cases of heavy absorption. These mainly concerned large series of Al-K α and Si-K α measurements (Thoma 1970), specially performed at three different take-off angles with the specific purpose of comparing the performances of correction programs.

Nevertheless, the remaining 313 analyses were supplemented by 168 analyses on Au-Cu and Au-Ag alloys, published by Heinrich et al. (1971) and a number of analyses (frequently on non-conducting systems) produced by the authors themselves. A total number of 554 analyses were thus accumulated and used as a "heavy element" data base on which a number of correction programs were compared.

Sewell et al. also used a data base of 94 oxygen and fluorine analyses to test the correction programs for light element radiation. It was found that their latest program with the "quadrilateral" absorption correction model was the best, and the authors concluded that their absorption correction was the best.

We have some serious objections against both the procedure followed as well as the conclusions drawn. As far the "heavy element" file is concerned we can be brief: In this data base there is not much left to correct for, as a quick glance at the k-ratios and the concentrations in the file shows. This is the result of eliminating all heavy absorption cases. This conclusion is substantiated by the fact that 330 out of 554 analyses were suited to a test on the atomic number correction (absorption factor $< 10\%$; atomic number correction greater than absorption correction). Considering the use of the "light element" file our objections are more serious. It is suggested that the analysis of oxygen and fluorine present difficult cases of absorption which would be true in some cases if these elements could be measured relative to pure element standards. The use of complex standards, like Al_2O_3 and LiF , reduces the problem to a medium case of absorption which most modern correction programs should be able to deal with.

For example, at 30 kV the absorption factor for O-K α in Al_2O_3 , relative to a pure oxygen standard, is approximately 3.6; that for O-K α in MoO_3 (one of the most difficult cases) is approximately 11.3; hence, it follows that the absorption factor shows an increase of only 3.14.

In many of the heavy absorption cases, which have been removed from the data file, the absorption factor ranges from 3 up to more than 12. Thus the real test cases for absorption are precisely those analyses that have been removed. A further objection concerns the use of non-conducting specimens such as oxides and fluorides for a comparative test. The influence of non-conductivity on the shape of the $\Phi(\rho z)$ curves is not even mentioned. The mere application of a conductive surface coating, with noticeable deleterious effects on the measurements themselves, does not change the intrinsic conductivity of a specimen; it only prevents surface charging.

In our opinion, however, it is inconceivable that an electron can start anything like a random walk in a "hostile" environment. There simply must be an additional driving force pushing it back, leading to a distortion of the $\Phi(\rho z)$ curve. Needless to say that none of the existing correction programs take these phenomena into account.

However, as long as these problems have not been solved we will not use measurements on non-conducting specimens like the oxides and fluorides used by *Sewell et al.* The fact that all programs tested show a significant positive bias on these data may be taken as further evidence against their use. The fluorides may exhibit the additional problem of chemical instability under electron bombardment. A

total lack of documentation on these measurements prevents any further comments on this issue.

Considering all the objections raised here we have decided to compose a new data base, partly based on more recent measurements.

5.2 The new data base

In composing the new data base a total number of 681 measurements were selected mainly on criteria of documentation, consistency and wide range of conditions applied.

Full details on the data base, including the mass absorption coefficients used, are given in Appendix 1.

The following analyses were selected:

Number	Reference
1- 16	Pouchou and Pichoir (1984)
17- 76	Willich (1983)
77-244	Heinrich et al. (1971)
245-292	Christ et al. (1982)
293-328	Colby (1968)
329-437	Thoma (1970)
438-472	Peisker (1967)
473-480	Springer (1966)
481-625	Bastin and Heijligers (1984)
626-681	Pouchou and Pichoir (1984)

Note (1) that many recent measurements performed on modern instruments have been included, and (2) that a relatively large number of heavy absorption cases have been (re)introduced, including the measurements by *Thoma (1970)* and *Pouchou and Pichoir (1984)*.

In addition a compilation of 117 carbon analyses (*Bastin and Heijligers 1984-3*) have been used in the present test.

Finally, a number of oxygen analyses (*Willich et al. 1985*), performed on non-coated electrically conducting oxides were used to test the performance of our new program in these cases.

5.3 Results

A total number of 6 current correction programs were used. Apart from our own new version, henceforth designated by BAS851, these were three different versions of Love and Scott's programs, called LOS, LOSI and LOSII. The LOS and LOSI versions employ Bishop's rectangular model for absorption in which either the original (*Love and Scott 1978*) equation for the main input parameter $\bar{\rho z}$ is used (LOS) or the new equation (*Sewell et al. 1985*),

obtained by optimization (LOSI). In the LOSII version the latest so-called "quadrilateral" model is used. In all LOS versions the same atomic number correction is used (*Love and Scott 1980*). For details concerning the other two programs, ZAF (commercially obtained from Tracor Northern) and that by RUSTE, the reader is referred to our previous papers.

We have previously noted that our $\Phi(\rho z)$ program performed less satisfactory for low overvoltage ratios and this suspicion was confirmed in the present test. The equation for α is no longer reliable for low overvoltages. The largest deviations were always found for high-energy radiations in heavy matrices, e.g. Cu-K α in Au. For $U_0 > 1.5$ the performance was quite satisfactory. We, therefore, decided, to make a restriction and only admit analyses at $U_0 > 1.5$; which was found beneficial for all programs tested. The total number of analyses actually used in the test was thereby reduced to 627.

In Figs. 6a–6f the results obtained with the 6 programs for the large database have been represented in the form of histograms. In Table 1 the averages and r.m.s. values are given.

Table 1 Relative root-mean-square values* (%) and averages* for various programs; 627 analyses, $U_0 > 1.5$

Program	r.m.s.(%)	Average
BAS 851	2.99	1.0012
LOS	5.05	1.0016
LOSI	5.45	1.0016
LOSII	4.33	0.9904
ZAF	6.13	1.0196
RUSTE	8.15	1.0313

* These apply to the ratio between the calculated and the measured k-ratios.

The figures speak for themselves. One should not jump to premature conclusions, however, because too much depends on the choice of the mass absorption coefficients. As long as these are not known with an accuracy of, say 1%, definite statements on the performance of a particular absorption correction model cannot be made.

Simple and rudimentary models like Bishop's square model can never deal with heavy cases of absorption. This is evident in Figs. 6b and 6c where a long tail is developed, mainly caused by the Al-K α and Si-K α measurements by *Thoma (1970)*. Such a tail

becomes even more pronounced in the ZAF and RUSTE models and confirms the expectations based on earlier experiences with these models.

The LOSI version is not necessarily an improvement over the original LOS version (cf Figs. 6c and 6b) and the LOSII version, based on the quadrilateral model, does not give a dramatic improvement over the original LOS version. The parameters for the LOSII version have been optimized with different mass absorption coefficients for the cases of heaviest absorption (Al-K α , Si-K α). The results would improve with their choice of mass absorption coefficients, but at the expense of the performance of the other two versions which would rapidly deteriorate.

The detailed results for two cases of heavy absorption are represented in Figs. 7a and 7b, together with the mass absorption coefficients used in this test. It must be mentioned that, if *Henke et al.'s (1982)* mass absorption coefficients had been used, as was done by *Sewell et al. (1985)*, then all calculated k-ratios would have been higher: in some cases (e.g. Al-K α in Ni) up to 10% higher. This shows again the importance of the mass absorption coefficients.

The results for the 117 carbon analyses, relative to Fe₃C as a standard, have been represented in Fig. 8 and Table 2. The mass absorption coefficients used in this test are the values proposed by *Bastin et al. (1984–3, 1986)*. It must be emphasised that these values produced improvements for all the programs tested. This was further corroborated by the findings of *Willich (1985)* who tested the *Pouchou and Pichoir (1984)* model on some of our carbon measurements. Considering the results of the present comparison in Fig. 8 and Table 2 we can again say that the histograms show the value of the present method.

Moreover, it would appear again that the LOSI version is not necessarily an improvement over the original LOS version and that the performance of the LOSII version is somewhat disappointing, regarding the claim that has been made (*Sewell et al. 1985*) for light element analysis. The worst performance of the three LOS programs was observed in heavy matrices, like TaC, WC and W₂C (Figs. 9a and 9b), where very large deviations were found. In those and similar cases it is not only a matter of the absorption correction model, for which the parameterization is apparently unsatisfactory; but also the atomic number correction behaves in a most peculiar way – an effect which has been noticed earlier already (*Bastin et al. 1984–2*). After an initial very slow increase of the Z-factor for carbon up to 12 keV, an ever increasing acceleration takes place which is partially compensated by the absorption factor which goes through a maximum at 25 keV and then decreases again.

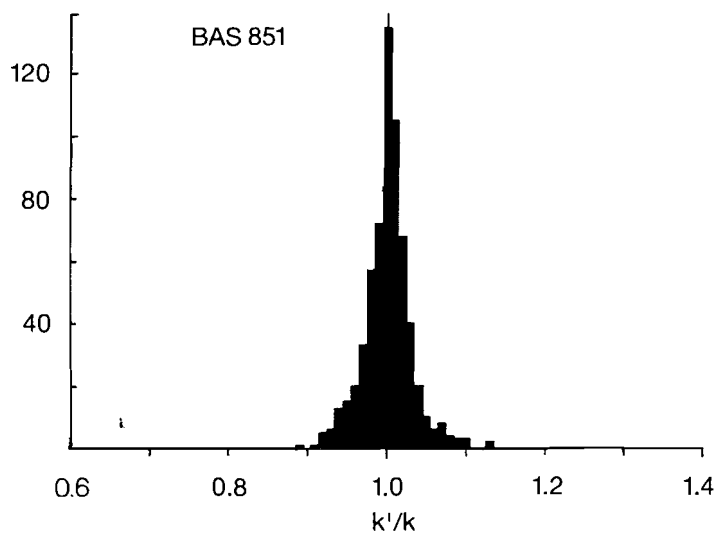


Fig. 6a

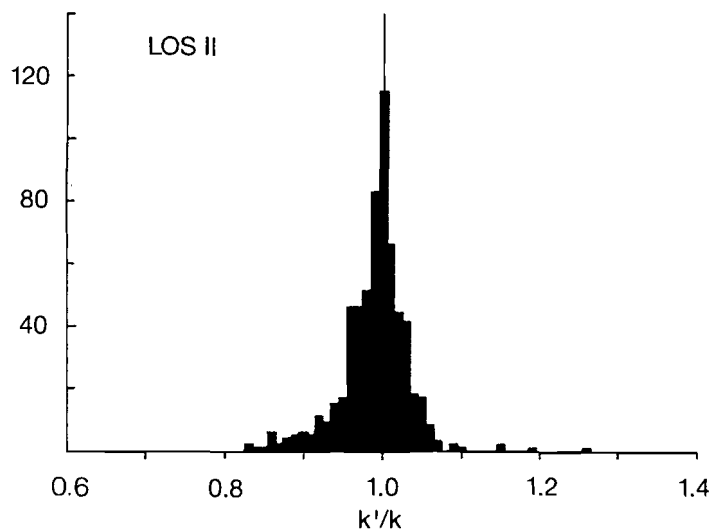


Fig. 6d

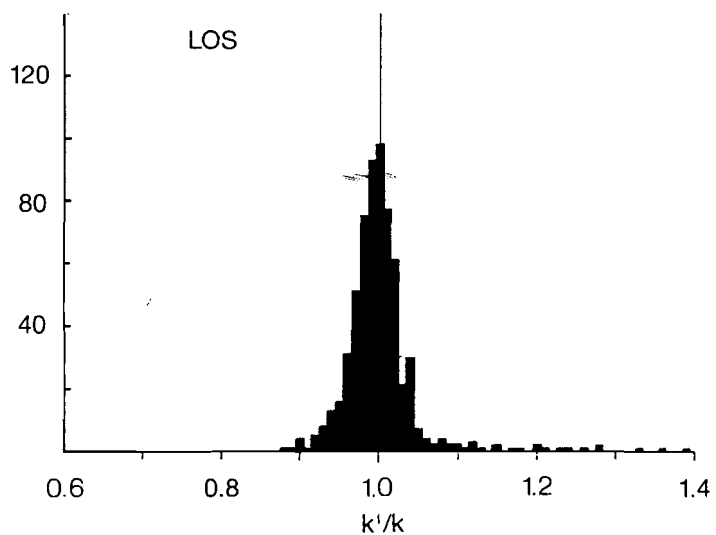


Fig. 6b

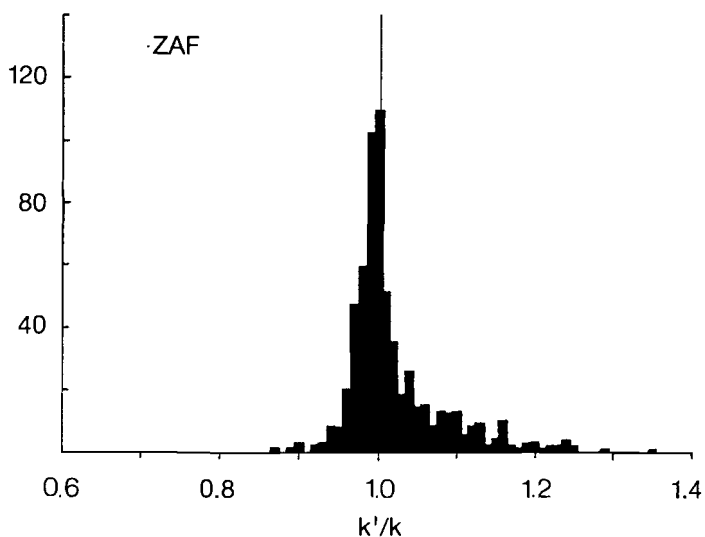


Fig. 6e

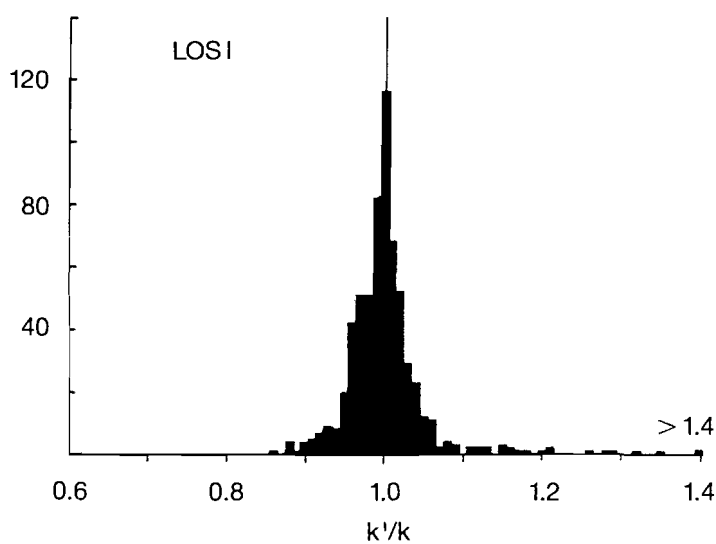


Fig. 6c

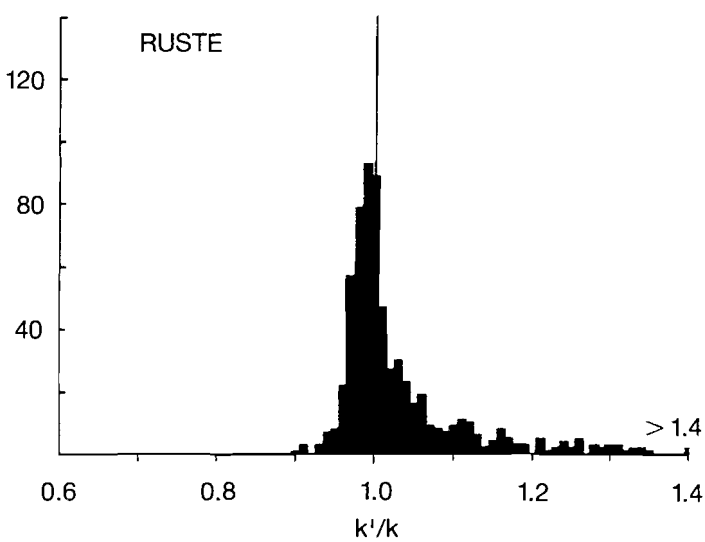


Fig. 6f

Fig. 6 Histograms representing the results for 6 correction programs tested on 627 analyses (overvoltage ratio > 1.5). k' is the calculated and k the measured intensity ratio.

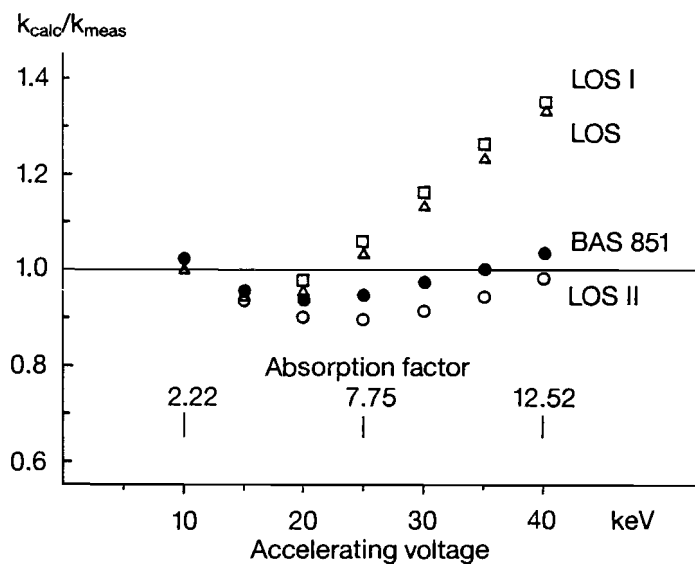


Fig. 7a

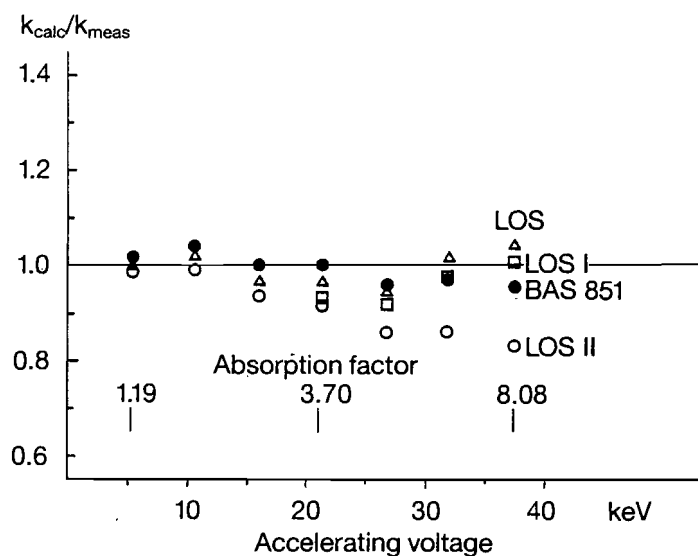


Fig. 7b

Fig. 7 Comparison of the performance of some programs for two cases of heavy absorption: (a) Al-K α in Mg (9.1 wt% Al), take-off angle 20°. Experimental data by Thoma (1970). Mass absorption coefficient: Al-K α in Al 386; Al-K α in Mg 4377. (b) Al-K α in Ni (12.50 wt% Al), take-off angle 40°. Experimental data by Pouchou and Pichoir (1984). Mass absorption coefficient: Al-K α in Al 386; Al-K α in Ni 4600.

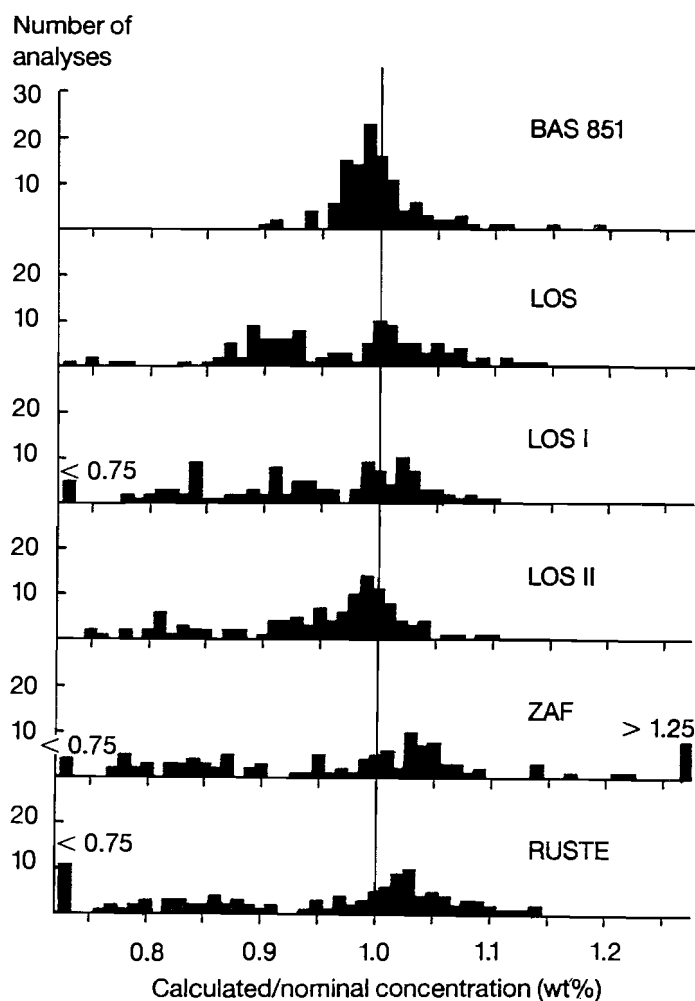


Fig. 8 Performance of various programs for the analysis of carbon in 13 binary carbides. 117 analyses, relative to Fe₃C, between 4 and 30 keV. Integral intensity measurements.

Table 2 Relative root-mean-square values* (%) and averages* for various programs; 117 Carbon Analyses, rel. to Fe₃C, 4–30 keV; Integral intensity measurements

Program	r.m.s.(%)	Average
BAS 851	4.11	0.999
LOS	8.33	0.964
LOSI	9.60	0.936
LOSII	7.78	0.948
ZAF	17.86	0.989
RUSTE	11.94	0.946

* Note that this time these apply to the ratio between the calculated and the nominal concentration in wt%.

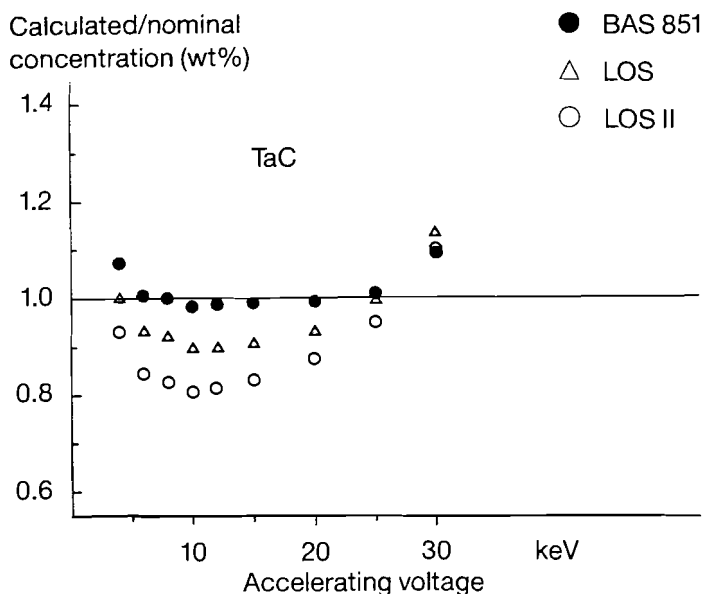


Fig. 9a

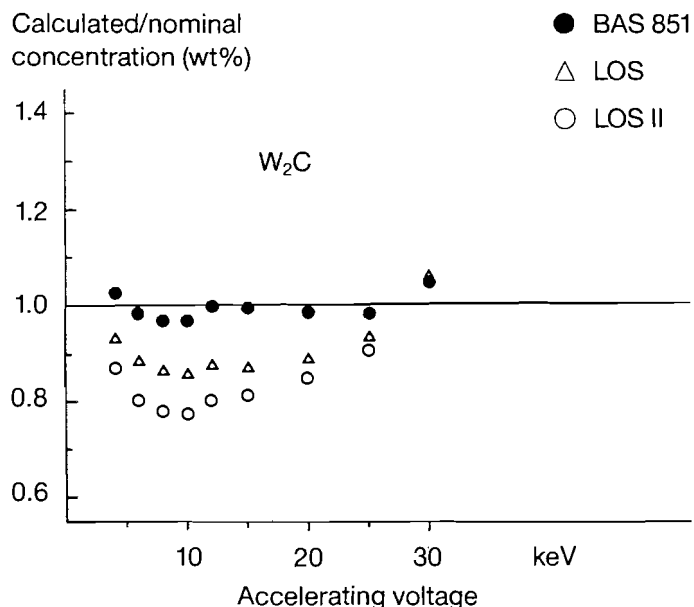


Fig. 9b

Fig. 9 Results for the analysis of carbon in two heavy-metal carbides as a function of accelerating voltage: (a) C-K α in TaC, take-off angle 40°. Standard Fe₃C. Integral intensity measurements. Mass absorption coefficient: C-K α in C 2373, C-K α in Fe 13500, C-K α in Ta 16000. (b) C-K α in W₂C. Mass absorption coefficient: C-K α in W 17000.

Finally, our new version was tested on a number of oxygen analyses (Willich et al. 1985). It is very important to note that these analyses were performed on non-coated electrically conductive oxides.

Table 3 Results of the BAS851 program for oxygen analyses. Non-coated, electrically conductive specimens. Standard Y₃Fe₅O₁₂ *

Sample	Comp. (wt%)	Acc.Volt. (keV)	k _{meas}	k _{calc}	deviation (%)
BaFe ₁₂ O ₁₉	Ba 12.7	5	1.257	1.247	- 0.8
	Fe 59.8	7.5	1.433	1.443	+ 0.7
	Ga 0.2	10	1.647	1.661	+ 0.9
	O 27.3	12.5	1.841	1.879	+ 2.1
PbFe ₁₂ O ₁₉		5	1.117	1.085	- 2.9
	Pb 21.0	7.5	1.197	1.175	- 1.8
	Fe 54.0	10	1.278	1.267	- 0.8
	O 25.0	12.5	1.361	1.350	- 0.8
RuO ₂		5	0.694	0.714	+ 2.9
	Ru 76.0	7.5	0.576	0.590	+ 2.4
	O 24.0	10	0.498	0.513	+ 3.0
		12.5	0.459	0.467	+ 1.8

* Composition (wt%): Y 35.8, Fe 37.5, Si 0.2, Pb 0.7, O 25.8.

Given the success of both our previous as well as the new correction program for the analysis of carbon, considering the wide range of accelerating voltages applied, they should be expected to work equally well or even better for oxygen. Table 3 clearly demonstrates that this is the case. The results shown are those of the new version, which are virtually identical to those of the previous version (mass absorption coefficients of Henke et al. 1982).

We conclude that the calculated k-ratios agree very well with the measured ones within the experimental error, and that our new version also works well for oxygen. This substantiates the doubts we expressed earlier about measurements on coated, non-conductive specimens.

6. Discussion

We believe that we have shown that our new program is probably among the best currently available. However, caution has to be exercised in making too definite statements, because too much depends on uncertain input parameters like mass absorption

coefficients. The vast majority of experimental $\Phi(\rho z)$ data have been obtained using *Heinrich's* (1966) mass absorption coefficients. Hence, it follows that when $\Phi(\rho z)$ equations are fitted to these $\Phi(\rho z)$ data, the resulting correction program will perform best with this set of mass absorption coefficients or a similar one like that of *Frazer* (1967). If it should become apparent in the future that the new values of *Henke et al.* (1982) are indeed an improvement, then all existing $\Phi(\rho z)$ data would have to be corrected and, as a consequence, our $\Phi(\rho z)$ equations would have to be refitted.

In both cases, however, the same curve of *emitted* intensity vs. mass depth, which is the *measured* quantity in experimental $\Phi(\rho z)$ measurements, should be obtained. It is obvious, therefore, that under no circumstances can a particular absorption correction model operate with a variety of mass absorption coefficients for a specific case: the better the model is, the more selective it will be for the mass absorption coefficients.

We have not made any effort to compare items like the atomic number correction employed in the various programs because

(a) the reported differences, typically of the order of 0.5% (or less) in the r.m.s. values, are much too small to be very concerned with and it would require a data base of extremely accurate measurements to make statements of any value;

(b) the largest atomic number effects usually go with heavy absorption effects (e.g. Al-K α , Si-K α , O-K α radiations in heavy matrices) and this makes a separate test on the atomic number correction extremely difficult.

We consider the separation into atomic number and absorption effects artificial because the important physical quantity is the emitted intensity, which is represented by the combined Z and A factors. It is also possible that the malfunctioning of the atomic number correction is to a certain extent compensated by a malfunctioning of the absorption correction and the program in question may still turn out very good answers.

It appears more interesting to discuss the absorption correction models, especially the new "quadrilateral" model recently introduced (*Sewell et al.* 1985). It should provide an obvious improvement over the earlier models used by *Love and Scott*, simply because a slow evolution has taken place from a totally unrealistic rectangular model to a quadrilateral model which starts to look like a rudimentary $\Phi(\rho z)$ curve. The absorption correction of this model is based on 4 parameters (see Fig. 10): $\bar{\rho z}$ (the mean depth of x-ray production), ρz_m (the position of the maximum in the

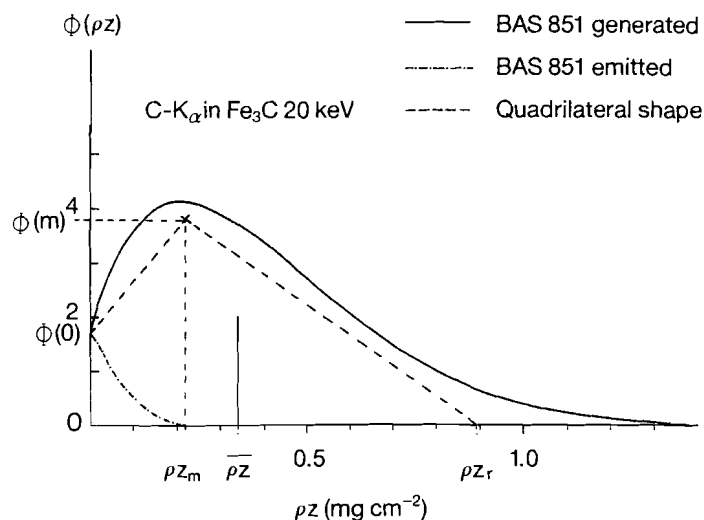


Fig. 10 Comparison between the $\Phi(\rho z)$ curve for C-K α in Fe_3C at 20 keV generated by our present version (BAS851) and the quadrilateral model (*Sewell et al.* 1985). Emitted intensity according to BAS851, assuming mass absorption coefficient: C-K α in C 2373; C-K α in Fe 13500. Take-off angle 40°.

" $\Phi(\rho z)$ " curve), h (the ratio between $\Phi(m)$ and $\Phi(0)$) and ρz_r (the fictitious end of the $\Phi(\rho z)$ curve).

The parameter $\bar{\rho z}$ is considered (*Sewell et al.* 1985) the dominant factor in the absorption correction, even to the extent that the ranking order of different models was judged to follow closely the averaged error in calculated-to-measured $\bar{\rho z}$ values. It has further been argued on several occasions by these authors that it is not necessary to have the real $\Phi(\rho z)$ curve for an accurate absorption correction. Although this may apply to cases of light to medium absorption, such a statement does not become true by repeating it. This can clearly be seen in Fig. 10 where the quadrilateral shape is compared to the $\Phi(\rho z)$ curve generated by our program for the case of C-K α radiation in Fe_3C at 20 keV. It is difficult to see how a parameter like $\bar{\rho z}$, which is located far beyond the point from where the last photon is able to reach the surface, can dominate the absorption correction. It is evident, in our opinion, that in this case the first part of the curved $\Phi(\rho z)$ curve, roughly up to the maximum, is the sole determining factor – that is, the shape factor is dominant for cases of heavy absorption, a view which has been put forward by *Bishop* (1974) already. Anyway, it seems difficult to us for any artificial model to find the correct parameterization, especially where parameters like ρz_r , without any physical significance, are involved.

A few final remarks on the quadrilateral model have to be made concerning the computational complexity. It has been suggested (Sewell et al. 1985) that parameters like ρz_m and ρz_r are expressed in terms of the mean depth $\overline{\rho z}$.

This is true for ρz_m ; for ρz_r , however, it is the other way around: $\overline{\rho z}$ is expressed in quadratic terms of ρz_m and ρz_r , which means that ρz_r has to be solved as one of the roots of a quadratic equation. It is obvious that this further contributes to the considerable complexity already present in this new model. One could wonder if all this effort would not be better spent in trying to find the real $\Phi(\rho z)$ curve.

7. Conclusions

(1) The new version of our correction program, based on improved equations for the Gaussian $\Phi(\rho z)$ approach, is probably among the best of the currently available correction programs, provided that the proper mass absorption coefficients are used. Its performance is excellent both for medium to heavy elements (r.m.s. value 2.99%) as for very light elements like carbon (r.m.s. value 4.1%). In both cases it must be taken into account that due to the presence of very heavy absorption cases the experimental error is correspondingly larger, which makes the results all the more remarkable.

(2) The new correction program by Sewell et al., based on the quadrilateral absorption model, will perform rather well for medium to heavy elements, provided that the authors' choice of mass absorption coefficients is followed. The performance for very light elements like carbon is much less satisfactory. A new optimization using heavy absorption cases, might produce an improvement.

(3) The Love and Scott versions based on the rectangular absorption model cannot be recommended for cases of significant absorption.

(4) The ZAF and Ruste models are the least satisfactory of the models evaluated here.

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Appendix

Numerical details on the data base used in the comparison of the performances of various correction programs. 681 binary systems AB.

- Column 1: Analysis number
- Column 2: Atomic number of component A
- Column 3: Atomic number of component B
- Column 4: Mass absorption coefficient element of A-radiation in element A
- Column 5: Mass absorption coefficient of element A-radiation in element B
- Column 6: Critical excitation voltage (keV) element A-radiation
- Column 7: Weight fraction of element A
- Column 8: k-ratio of element A-radiation
- Column 9: Accelerating voltage (keV)
- Column 10: Take-off angle (deg)
- Column 11: Type of element A-radiation; 0= $K\alpha$, 1= $L\alpha$, 2= $M\alpha$

