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Original Paper

The Performance of the Modified $\Phi(\varrho z)$ Approach as Compared to the Love and Scott, Ruste and Standard ZAF Correction Procedures in Quantitative Electron Probe Microanalysis.

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Abstract

The recently introduced modified Gaussian $\Phi(\varrho z)$ approach is compared with three other correction procedures for quantitative electronprobe microanalysis. On the basis of results obtained for 441 published microanalysis data it is concluded that the modified $\Phi(\varrho z)$ approach and the Love-Scott correction model perform equally well and are both superior to the Ruste and ZAF correction models. Special attention has been paid to the new atomic number correction proposed by *Love* et al. It was found to be only marginally better than that of the $\Phi(\varrho z)$ approach.

1. Introduction

In quantitative electron probe microanalysis a number of corrections have to be applied to the measured intensity ratios between specimen and standard in order to convert them into concentration units. In the commonly accepted and widely used ZAF approach these corrections consist of three separate factors, *Z*, *A* and *F*, respectively.

The *Z*-factor (related to the atomic number effect) deals with the differences in x-ray generation between specimen and standard and is in fact split up in two separate factors R and S which treat the effects of electron backscattering (R) and x-ray generation (stopping power S) in the target. Most of the existing computer programs available today are based on the atomic number correction of *Duncumb* and *Reed* (1968) while a few employ the more rigorous but also much more complex *Philibert/Tixier* (1968) procedure. As the differences between the two models are reported to be very small (see e.g. *Beaman* and *Isasi* 1972) the former is usually preferred. Some years ago a new atomic number correction has been proposed by *Love* et al. (1978) with the aim to overcome a number of limitations in the Duncumb-Reed model mainly anticipated in the use of low electron energies and low or high overvoltage ratios. To our knowledge this new atomic number correction has not been compared yet in detail with that of *Duncumb* and *Reed* or that of *Philibert* and *Tixier* to show whether the aimed improvements are indeed achieved.

In calculating the *A*-factor an effort is made to calculate the differences in absorption of the generated x-rays between specimen and standard. The most extensively used method still seems to be the one based on the simplified *Philibert* (1963) model in which the surface ionisation is supposed to be zero. It has been shown on many occasions (see for example *Love* et al. 1974) that the validity of this model is very limited and

for strongly absorbing systems the full *Philibert* (1963) model is clearly preferred (*Ruste* and *Zeller* 1977, *Love* et al. 1975). Unfortunately this latter model seems to lead to somewhat less satisfactory results for medium to heavy element analysis (*Love* and *Scott* 1980, 1981) so it would be less advisable for application in a multipurpose program.

A very simple absorption correction model has been proposed by *Bishop* (1974). This model is based on the assumption that the ionisation is constant from the specimen surface up to a certain depth after which it falls abruptly to zero. The crucial parameter in this model is the mean depth of x-ray production for which *Love* and *Scott* (1978, 1980) developed a suitable expression based on the results of Monte-Carlo calculations. The resulting absorption correction seems to work surprisingly well as was shown by *Love* and *Scott* (1978, 1980) who used it in conjunction with their own atomic number correction (1980).

The fluorescence correction (*F*-factor), finally, in most correction procedures is based on the model of *Reed* (1965) and it is generally felt that the inaccuracies in the physical parameters used in it impose more limitations on the procedure than the model itself.

A completely new correction procedure has recently been put forward by *Brown* and coworkers (*Packwood* and *Brown* 1981, *Brown* and *Packwood* 1982). Their approach is mainly characterised by a serious effort to describe the so-called $\Phi(\varrho z)$-(ionisation as a function of mass depth ϱz) curves as accurately as possible. To this end equations have been developed which are indeed able to produce $\Phi(\varrho z)$ curves in close agreement with actually measured ones. Based on these equations a computer program was written and tested on a large number (about 500) of published microanalysis data with reported excellent results: a standard deviation of 4.8%, compared to 6.8% for the so-called "established" ZAF procedure and 5.4% for the *Love* and *Scott* program.

In a previous paper (*Bastin* et al. 1984) in which we described our experiences with a program written according to *Brown's* (1982) recommendations we have not been able to reproduce the excellent results originally claimed. After having made a number of alterations followed by a re-optimizing process carried out on the same file of microprobe analyses (about 450 measurements) used previously by *Love* et al. (1975, 1976) we were able to obtain results quite similar (r.m.s. value 5.4%) to those of *Love* et al. Hence, it would be very interesting to compare the performance of the two programs in more detail and also to compare them with the ZAF and *Ruste* programs. Special emphasis will hereby be laid on the atomic number

correction and, as far as possible, on the absorption correction.

2. The Correction Procedures

The performance of a new correction program is usually compared to the so-called "established" ZAF procedure which is taken to mean that the atomic number correction of *Duncumb* and *Reed*, the simplified *Philibert* absorption correction and *Reed's* correction for characteristic fluorescence are employed. This is, of course, not a very specific reference as many programs may still differ in a lot of details, like how the mass absorption coefficients are calculated or whether the critical excitation voltages are stored in data files or calculated through parameterisations etc.

Therefore, the ZAF program used in this case will be briefly discussed first. It is essentially the program purchased from TRACOR Northern and is suitable to work on-line in an automation system coupled to our JEOL Superprobe 733. It is written in Flextran which is an interpreter language and is consequently very easily accessed by the user. The expression for the ionisation potential used in the calculation of the stopping power is that of *Berger* and *Seltzer* (1964). Absorption edges, mass absorption coefficients and similar numerical data are all calculated through parameterisations the coefficients for which are stored in program lines.

For the purpose of the present comparison, however, these quantities are imposed on the program because it is forced to take the appropriate values from the file representing the 450 measurements.

As we had a special interest to use the other programs also on-line they were all written in Flextran within the basic framework given by the ZAF program with, of course, the necessary alterations according to the recommendations of the authors of the various programs. This would guarantee us full interchangeability of the programs within the main automation program. Only in one case *(Ruste)* could a copy of the original listing be used as reference; in the other cases this was either not made available (*Love* and *Scott*) or not suitable for reasons mentioned before *(Brown)*.

The *Love* and *Scott* program was entirely made according to the equations published in literature (*Love* et al. 1978, *Love* and *Scott* 1978) which means *Love* and *Scott's* new atomic number correction and *Bishops* (1974) absorption correction with *Love* and *Scott's* (1978) expression for the mean depth of x-ray production. The fluorescence correction was kept identical to that of the ZAF program; the same applies to the other programs that will follow. A correction for continuum fluorescence was not included.

In the *Ruste* program the *Philibert-Tixier* atomic number correction is employed with *Ruste's* (1977) expression for the ionisation potential and the so-called "full" *Philibert* absorption correction. In the latter a number of parameters have been made dependent on atomic number and energy in order to improve its performance for light (Z < 10) element work.

The modified Gaussian $\Phi(\varrho z)$ approach will now be discussed in rather more detail because it has only recently become available. According to *Brown* et al. (1981, 1982) $\Phi(\varrho z)$ curves can accurately be described by an equation of the type:

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

According to this equation the ionisation Φ as a function of mass depth (ϱz) is basically described by the Gaussian expression $\gamma \exp[-\alpha^2(\varrho z)^2]$ in which γ is a scaling factor and α gives the decay rate with the square of the mass depth ϱz. This is illustrated in Fig. 1 where two examples of $\Phi(\varrho z)$-curves have been calculated with equations (2)–(4). As the electrons travelling through the surface layers of the target are not yet fully efficient in producing x-rays, due to the collimation effect in the beam, a transient region is introduced to deal with this effect. This is the region mainly governed by β. As a result the ionisation will rise from its surface value $\Phi(0)$ to some peak value deeper in the specimen. In our previous paper (*Bastin* et al. 1984) we have shown that for the moment the optimum expressions for α, β and γ are:

$$\alpha = \frac{1.75 \times 10^5}{E_o^{1.25}(U_o-1)^{0.55}} \left[\frac{\ln(1.166E_o/J)}{E_c}\right]^{0.5} \quad (2)$$

$$\beta = 0.4\,\alpha\,\frac{Z^{1.7}}{A}(U_o-1)^{0.3} \quad (3)$$

$$\gamma = \frac{4.9\,\pi\,U_o}{(U_o-1)\ln U_o}(\ln U_o - 5 + 5\,U_o^{-0.2})\exp(0.001Z) \quad (4)$$

in which Z, A and J are the atomic number, atomic weight and ionisation potential for the matrix element in question. The expression for J we use is that of *Ruste*. E_0 is the accelerating voltage, E_c the critical excitation voltage and U_0 the overvoltage ratio (E_o/E_c) for the x-ray line in question. For a compound specimen (sp) the value of $(\alpha_i)_{sp}$ is obtained as follows (*Bastin* et al. 1984):

$$(\alpha_i)_{sp}^2 = \frac{\overline{A}}{\overline{Z}}\,\Sigma C_j\,\frac{Z_j}{A_j}\,\alpha_{ij}^2 \quad (5)$$

in which $\overline{A}$ und $\overline{Z}$ are the weight fraction averaged atomic weight and number of the specimen; A_j and Z_j those of the matrix element j and C_j its weight fraction.
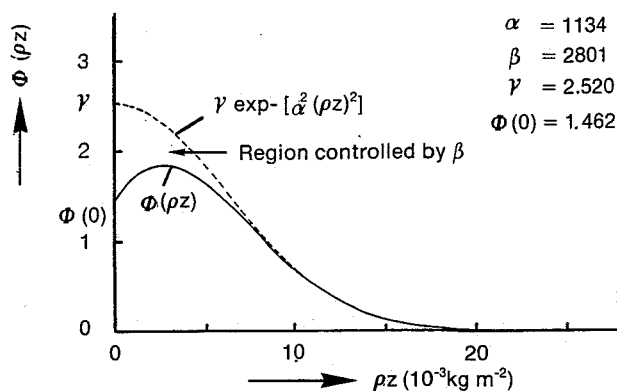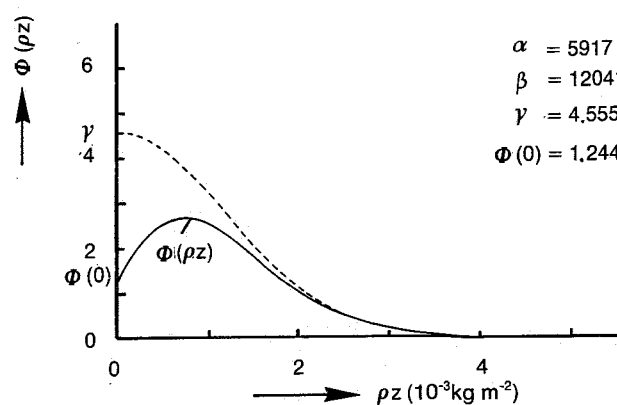

Fig. 1a △ 　　　　　　　　　　▽ Fig. 1b

$\alpha = 1134$
$\beta = 2801$
$\gamma = 2.520$
$\Phi(0) = 1.462$

$\alpha = 5917$
$\beta = 12041$
$\gamma = 4.555$
$\Phi(0) = 1.244$

Fig. 1　Two examples of $\Phi(\varrho z)$ curves (solid lines) calculated with equations (1)–(4): (a) Copper at 30 keV, (b) carbon at 10 keV. The dashed line gives the hypothetical undisturbed Gaussian distribution.

α_{ij} is the quantity that describes α for element i-radiation in interaction with element j of the matrix. The values of β and γ are obtained by inserting the weight fraction averaged atomic number and weight into eq. (3) and (4). Normally the combined [ZA] -correction factor is calculated by multiplying eq. (1) with the absorption term $\exp(-\chi\varrho z)$ (in which $\chi = \mu/\varrho$ cosec Θ, μ/ϱ is the mass absorbtion coefficient and Θ is the take-off angle) for specimen (sp) and standard (st) and integrating the product for all mass depths between zero and infinity, followed by a division. For the purpose of this paper we have preferred to carry out the integration separately with and without the absorption term which gives us the [ZA] and [Z] factors, respectively. By a simple division the separate [A] factor then becomes available.

We have shown previously (*Bastin* et al. 1984) that the time consuming process of numerical integration of eq. (1) can be avoided by writing:

$$Z = \frac{[\gamma-(\gamma-\Phi(0)) \quad R(\frac{\beta}{2\alpha})]_{st}}{[\gamma-(\gamma-\Phi(0)) \quad R(\frac{\beta}{2\alpha})]_{sp}} \frac{\alpha_{sp}}{\alpha_{st}} \quad (6)$$

and:

$$ZA = \frac{[\gamma \; R(\frac{\chi}{2\alpha})-(\gamma-\Phi(0)) \quad R(\frac{\beta+\chi}{2\alpha})]_{st}}{[\gamma \; R(\frac{\chi}{2\alpha})-(\gamma-\Phi(0)) \quad R(\frac{\beta+\chi}{2\alpha})]_{sp}} \frac{\alpha_{sp}}{\alpha_{st}} \quad (7)$$

in which R is a fifth-order polynomial used in the approximation of the error function which comes in when the integrals are solved in closed form through a Laplace transformation.

R is described by:
$R = a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5$
with $t = 1/(1+px)$ and $p = 0.3275911$
$\quad a_1 = 0.254829592 \quad a_2 = -0.284496736$
$\quad a_3 = 1.421413741 \quad a_4 = -1.453152027$
$\quad a_5 = 1.061405429$

The input value for x is $\beta/2\alpha$, $\chi/2\alpha$ or $(\beta+\chi)/2\alpha$, respectively. Please note that Z and A are defined here by the relation $c = k Z A F$ (c is weight fraction, k is intensity ratio) in accordance with the original ZAF correction program of TRACOR.

3. Some Remarks on the Microanalysis Data Used

As it is not possible to judge the performance of any correction program from the results obtained in a few isolated analyses it is inevitably necessary to tackle the problem statistically: i.e. subject the program to as many reliable measurements as can be collected and treat the results statistically. The usual approach in this case is that for each given concentration for an analysis in the test file the intensity ratio k′ is calculated and compared to the measured k-ratio, which in fact means that the program is run backwards. 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 value (r.m.s.) are used as a final judgement of success.

A close inspection of the test file shows that the medium to heavy elements are very well represented whereas the reverse is true for the lighter elements. This is undoubtedly the result of the fact that, in order to avoid a double correction procedure, all measurements have been made with respect to pure element standards. This automatically excludes a number of elements like gases or alkalis and leaves practically only the elements Al and Si as representants of the lighter (Z < 22) elements, not to mention even lighter elements like C, N or O. We have stated before that this might have serious implications for any program optimized using this file when it comes to applying it to the very light elements.

Furthermore it is obvious that there is a heavy bias in the file towards high probe voltages. The vast majority of the measurements have been performed between 15 and 30 kV and there are only four(!) measurements below 10 kV. This is probably the result of the fact that most measurements (about 75%) are from before 1968, and the remainder from before 1972 and it is well-known that the older instruments were just not stable enough at low beam voltages to allow reliable measurements to be made.

In general we have the feeling that results obtained with modern instruments would show less scatter as the stability and exactness of e.g. probe voltage have undoubtedly been very much improved in the last decade.

Apart from this, with the tendency nowadays to work at substantially lower probe voltages (with 20 kV being almost the upper limit), there is some danger in optimizing a correction program with the present file. All these remarks serve to illustrate the bad need for new reliable measurements to set up a new data file. Nevertheless, as better data do not seem to be readily available and previous comparisons have been carried out with the same file, we have decided to do likewise.

4. Comparison of the Programs

In the next three sections the performance of the 4 correction programs will be compared. First an overall comparison is made which is, of course, a very straight-forward matter: all that matters is only the magnitude of the combined (ZAF) correction factor.

Unfortunately it is much more difficult to assess directly the performance of the separate atomic number and absorption correction procedures as there is no absolute reference available. In some cases the results of Monte-Carlo calculations have been used as reference for the absorption correction (Love and Scott 1981) but although these are generally considered quite thrustworthy one should keep in mind that the Monte-Carlo method is also only a model and as such is no better than the validity of the underlying assumptions allow. We have tried, therefore, to assess the performance of the separate [Z] and [A] corrections through the analysis of the results for convenient cross-sections through the test file.
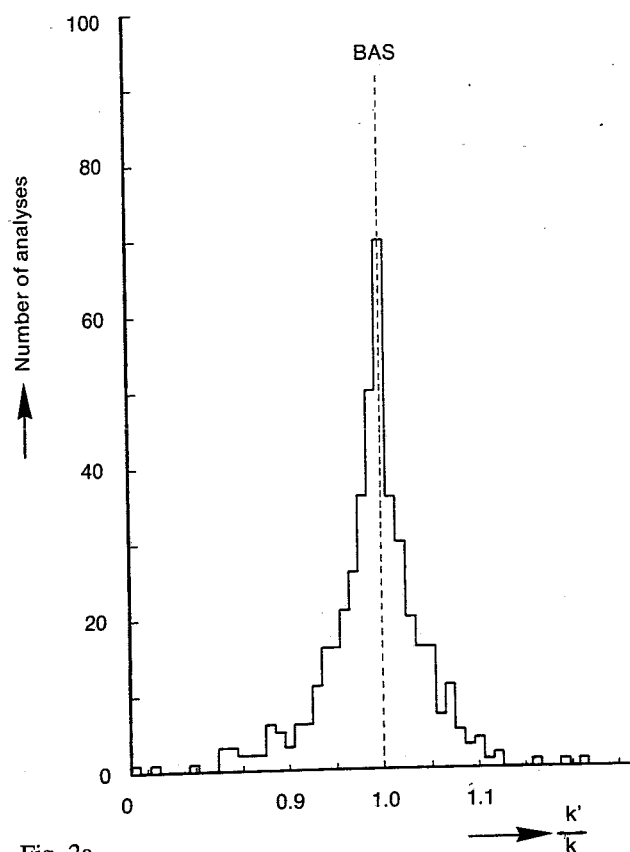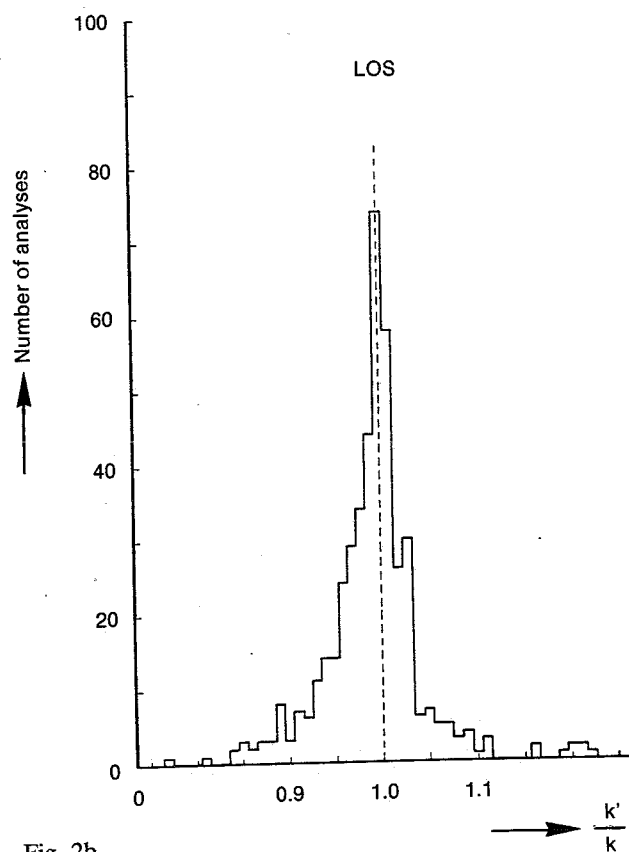
Fig. 2a

Fig. 2b

4.1. General performance

The over-all results obtained from 441 analyses for the various correction programs are represented in Figs. 2a–2d. It is obvious that both the *Love* and *Scott* (LOS) and the modified $\Phi(\varrho z)$ approach (which we will henceforth call shortly BAS) are by far superior to the other two programs, when the narrowness and the shape of the histograms are compared. This is underlined by the figures in Table 1 in which the r.m.s. values and the average k'/k values are given. It is also evident that the ZAF and Ruste programs show some positive bias (k'/k>1), whereas such an effect is much less present in the results of the other programs. A somewhat disappointing feature of the *Ruste* program is the development of a more pronounced tail towards higher k'/k values which is responsible for much of the increased bias. An inspection of the output revealed that this was essentially due to the malfunctioning of the absorption correction model for the Al and Si measurements, especially for probe voltages higher than 20 kV. This is undoubtedly the result of the use of a number of transient functions in the full *Philibert* cor-

Table 1   RMS values and averages obtained with the four correction programs

Program	Average	RMS (%)
BAS	0.9902	5.46
LOS	0.9929	5.56
ZAF	1.0145	6.30
RUSTE	1.0240	6.74

rection model. These are namely devised in order to obtain good results for very light elements (Z<10) with apparent success in this case (*Love* et al. 1981). On the other hand they should provide a link with the good results obtained with the simple *Philibert* model for elements with Z>24. As the elements Al and Si are evidently halfway between those limits it would seem that they are not properly dealt with in the model for higher voltages. We would not, therefore, recommend the use of this model in a general-purpose program although it should be remembered that the program has never been designed with this aim by the authors.
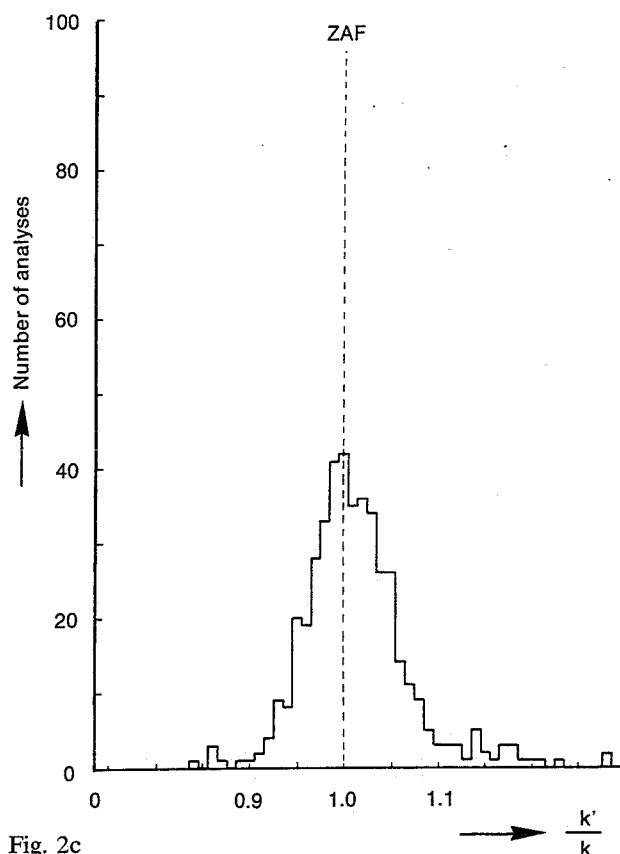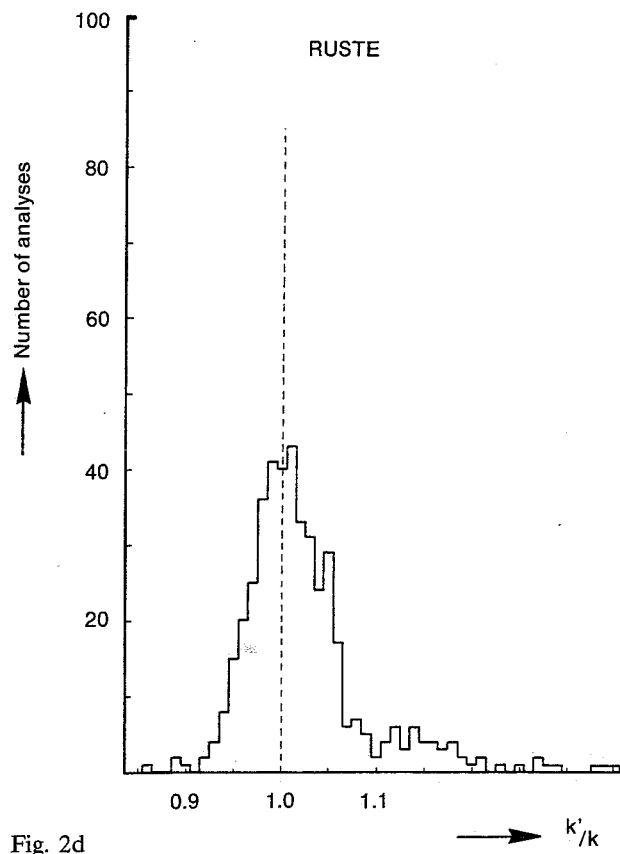
Fig. 2c

Fig. 2d

Fig. 2   Histograms representing the general performance of the four correction models for 441 analyses: (a) Modified $\Phi(\varrho z)$ approach (BAS), (b) *Love* and *Scott* Model (LOS), (c) conventional ZAF approach (ZAF), (d) Ruste and Zeller approach (RUSTE).

Considering the performance of the BAS and LOS programs in more detail it is apparently very difficult to decide in favour of either of them as is also reflected by the very small differences in r.m.s. values in Table 1.

Perhaps one could say that the histogram of the BAS program is slightly more symmetric although it is somewhat doubtful whether the quality of the microprobe measurements in the test file would allow such a statement, certainly in view of the critical remarks made before. In our opinion it is very doubtful if any correction program now or in the future would be able · to produce an r.m.s. value below 5% with the existing file which we feel contains a number of analyses with gross errors.

4.2. The atomic number correction

As the atomic number correction proposed by *Love* and *Scott* has been claimed to offer some improvements over the existing methods (*Love* et al. 1978) it

seemed very interesting to compare it with the atomic number corrections of the other programs. In this case the *Ruste* program has partly been excluded as it has been reported before that the *Philibert-Tixier* correction yields essentially the same results (within 1% relative) as the *Duncumb-Reed* correction. According to our experience this is indeed the case, at least for the measurements contained in the file (Z>13) but this does not necessarily apply to lighter elements as the application of *Ruste's* expression for J will certainly give rise to differences for very light elements.

For the comparison a cross-section through the file has been made according to three criteria:
– The difference in atomic number between the two elements had to be larger than 10.
– The absorption correction factor had to lie between 0.9 and 1.1.
– The Z-factor had to be larger than the A-factor.

This selection led to a number of 163 analyses which were submitted to the three programs. The results are represented in Fig. 3 and Table 2. It is apparent that
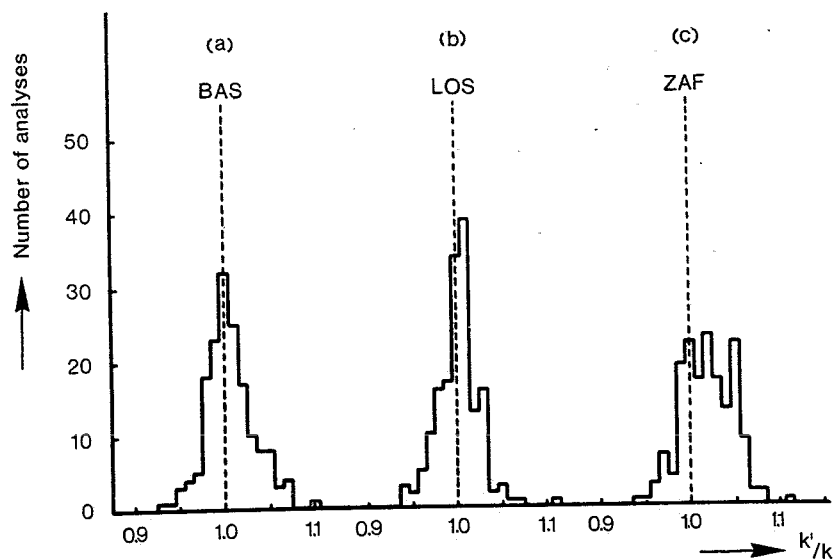
Fig. 3 Performance of the atomic number corrections of three different correction models. The results are based on a selection of 163 analyses which depend for their correction mainly on this effect. See also Table 2. (a) Modified $\Phi(\varrho z)$ approach (BAS), (b) Love and Scott Model (LOS), (c) Duncumb-Reed Model (ZAF).

the BAS and LOS programs are superior to the *Duncumb-Reed* procedure and that the ZAF program, as we have it, exhibits a similar bias as the histogram of the total file.

In fact it is surprising to note how much the general shapes of the histograms in Fig. 3 resemble those of Fig. 2. Considering the BAS and LOS programs in more detail it could be said that the performance of the latter is sligthly better in this respect and this can partly be attributed to a somewhat better functioning of the LOS program for very low overvoltages $(1.2 < U_o < 1.4)$. In general, however, the differences are probably within the experimental error of the measurements. Furthermore, it is to some extent questionable in how far the artificial separation of the total correction factor into 3 (in fact 4) separate factors is justified. From a purely formal point of view it could be argued that the only correct Z-factor is obtained by the integration of $\Phi(\varrho z)$ curves in specimen and standard as is done in the $\Phi(\varrho z)$ approach. Nevertheless, at the moment no final judgement can be made which of the two programs is the best in this respect. The only conclusion seems to be that they are both better than the *Duncumb-Reed* approach. It should, however, be stressed that these conclusions are only valid for the elements in the file, i.e. atomic numbers larger than 13.

As one of the claims made by *Love* et al. (1978) was a better performance of their atomic number correction for either high or low overvoltage ratios, we found it interesting to investigate this feature in more detail. As we had already seen that the LOS program performed better than most other programs at low overvoltage ratios we focused attention on the former case.

Table 2 RMS values obtained for 163 selected analyses which depend for their correction mainly on the atomic number correction

Program	RMS (%)
BAS	2.73
LOS	2.41
ZAF	2.87

To this end a number of analyses of uranium-compounds with an increasing atomic number for the lighter element have been selected (see Figs. 4a–4c). As the differences for the heavy element in these examples can hardly be made visible (mutual difference <1%, differences between extremes max. 2%) these have been left out. Although the general appearance of the *Duncumb-Reed, Ruste* and BAS curves is quite similar for overvoltages up to 50 in the case of C and N, the *Love* and *Scott* curve shows a peculiar bend upwards for very high overvoltages. By definition this would mean that the amount of x-rays generated per electron in the standard, divided by that generated in the specimen would sharply increase at very high overvoltages. At first sight it seems difficult to understand why this should be the case, certainly as all other programs show some kind of saturation (see Fig. 4). The strange effect disappears as the atomic number of the lighter element reaches the values of 12–14, probably because then the overvoltage in the range of probe voltages used is no longer sufficient to show it. However, it would seem that this effect would not play
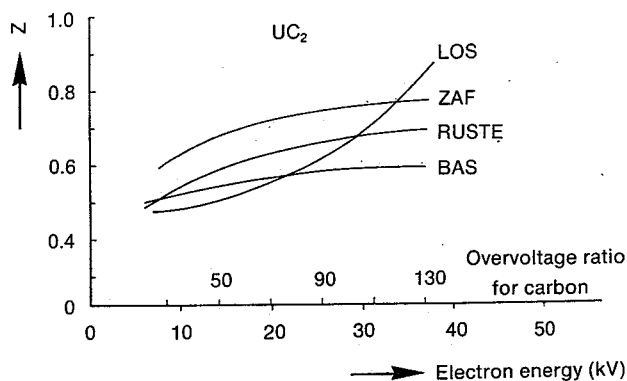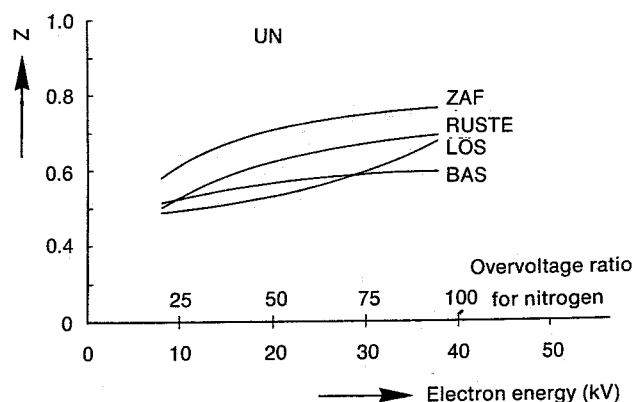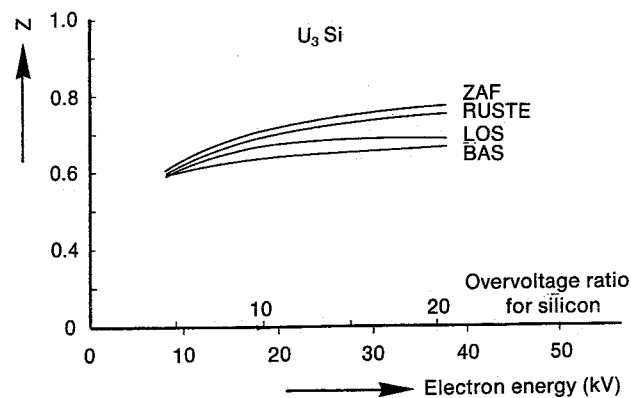
Fig. 4a

Fig. 4b

Fig. 4c

Fig. 4 Differences in atomic number corrections (Z) for the lighter element in the four correction models for three selected binary uranium-compounds. The inner horizontal scale gives the overvoltage ratio for the lighter element. (a) UC_2, (b) UN, (c) U_3Si.

an important role in microanalysis as nobody would probably attempt to measure carbon with probe voltages higher than 20 kV. Below this value the results for the *Love and Scott* and BAS programs are not greatly different and it has been observed on many occasions that the differences between the BAS and *Love and Scott* results are smaller than the differences of either of them with the other two corrections.

An interesting feature of the *Ruste* correction is the fact that the results slowly approach those of the *Duncumb-Reed* correction with increasing atomic number to become almost identical for Z = 26 (Fe). This is the result of the expressions for J which become comparable for the *Berger and Seltzer* and *Ruste* equations for these atomic numbers.

As a final remark it can be stated that in general the atomic number correction of the BAS program is somewhat less kV-dependent than that of the other programs and this is most noticeable at low overvoltage ratios ($U_o < 1.5$).

4.3. The absorption correction

Quite contrary to the atomic number correction it is much more difficult to assess the performance of the absorption correction. Of course, when the values in the histograms of Fig. 3 are subtracted from those in Fig. 2, it follows that the r.m.s. value of the BAS program is somewhat more favourable than that of the LOS program and that they both perform significantly better than the other programs. However, because in analyses with substantial absorption corrections usually also appreciable atomic number effects are present, it is very difficult to separate these effects and to decide in favour of one of the programs. An exception can only be made for those analyses in which combinations of elements with atomic numbers differing by two (for Z>21) or one (for Z<21) are involved and the heavy element has been measured, like the Ni-Fe and Al-Mg systems. Unfortunately, these are really too few in number to base definite conclusions on. Nevertheless, in order to demonstrate some features of the various absorption corrections and to appreciate the magnitude for the corrections involved we have chosen a number of analyses of Al in a Mg-9.1 wt% Al alloy, made at two different take-off angles (see Fig. 5). While examining these figures one has to realise that in this heavily absorbing system the absorption correction factor for Al can increase up to about 15 at 40 keV for a take-off angle of 20° and still about 7 for a take-off angle of 52.5°. In practice this means that the measured k-ratio has to be multiplied with 15 in order to correct for absorption.
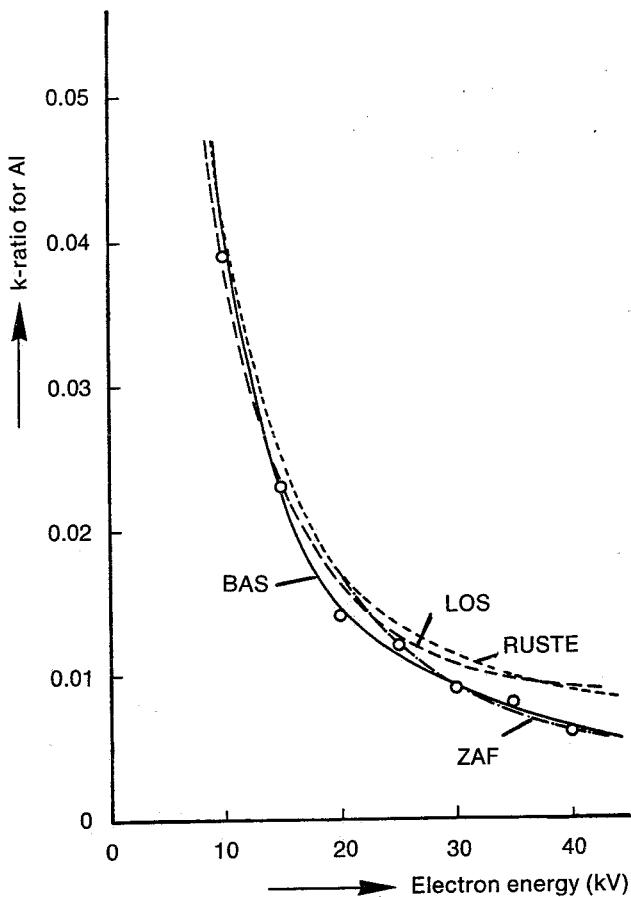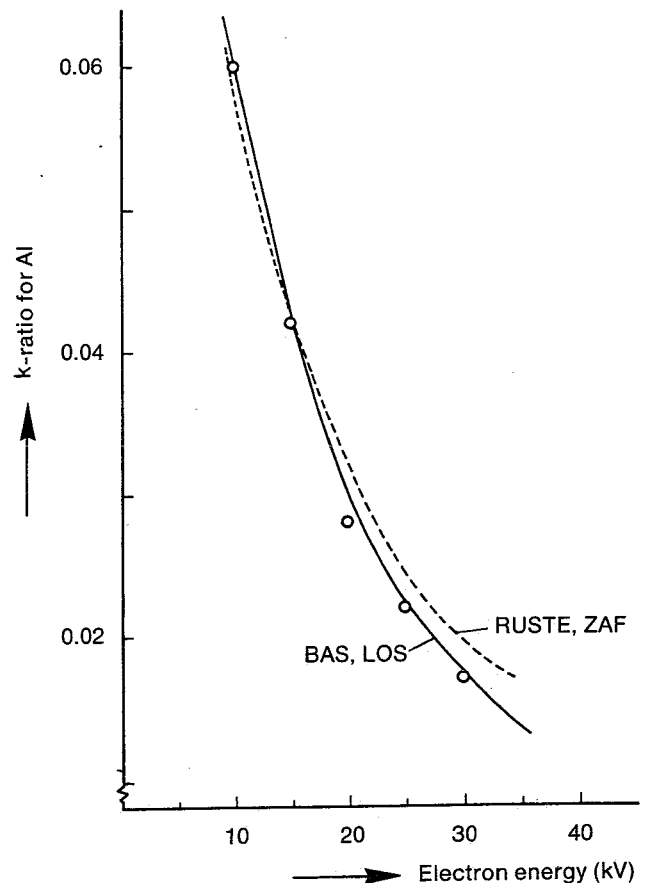
Fig. 5a   Fig. 5b

Fig. 5   The performance of the absorption correction in a selected series of Al measurements in a Mg-9.1 wt% Al alloy for two different take-off angles: (a) 20°, (b) 52.5°. The open circles represent the experimental data according to *Thoma* (1970).

In fact, we hardly know of any other physical measurement in which the measured value has to be multiplied by 10 or 15 in order to get the final result! This goes only to show how large a demand is being made on the correction procedure. One has, however, to bear in mind that such factors are not uncommon in analyses of very light elements. e.g. C in the Si-C and B-C systems for probe voltages as low as 10–15 kV already. Hence, the importance of Fig. 5 goes probably far beyond the importance of the actual Al measurements represented here at very high voltages; probably nobody would measure Al at such high probe voltages. It is clear that for a take-off angle of 52.5° the BAS and LOS programs perform almost equally well, while the ZAF and *Ruste* programs are definitely inferior. These differences become much more pronounced for an even lower take-off angle of 20° (Fig. 5a). Strange enough the ZAF program is second best

here for very high probe voltages. Most probably this must be regarded as a pure coincidence because the correct absorption correction procedure can only be expected when the proper $\Phi(\varrho z)$ curve for the system is used, be it a measured or a calculated one, and it is well-known that the simplified *Philibert* model, used in ZAF, does not give a very realistic representation of the actual $\Phi(\varrho z)'$ curves. Fortunately, in this system several $\Phi(\varrho z)$ curves have been measured (*Castaing and Hénoc* 1966) and Fig. 6 shows the comparison between the measured and calculated $\Phi(\varrho z)$ curve at 25 keV. In view of the very good agreement it is not surprising that the BAS program performs so well in this system.

It is only fair to say that for several other examples the LOS program performs somewhat better than BAS but as a general conclusion it can be stated that they are both superior for heavily absorbing systems.
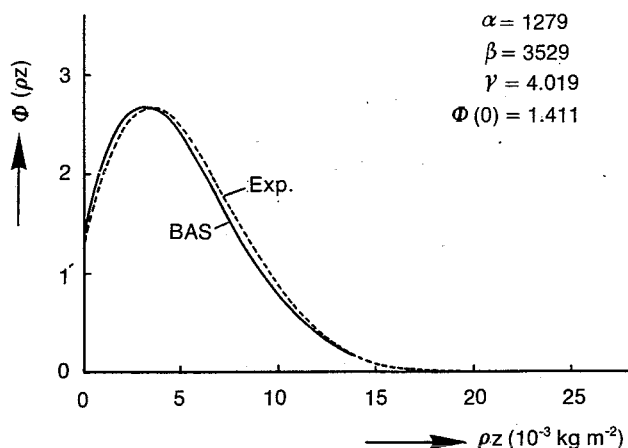
$$\alpha = 1279$$
$$\beta = 3529$$
$$\gamma = 4.019$$
$$\Phi(0) = 1.411$$

Fig. 6 Comparison between the measured (*Castaing* and *Hénoc* 1966) and calculated $\Phi(\varrho z)$ curve for a Mg tracer in Al at 25 keV.

It would therefore be tempting to test them both on a number of analyses of very light elements like C, N or O. Such a test, however, has to wait until a sufficient number of reliable measurements have been performed on these elements. At the moment, work to this effect on carbon is in progress in our laboratory. The measurements are being made in a number of binary carbides at various probe voltages. Preliminary results indicate that the BAS program shows very promising results in this respect as does the LOS program. So perhaps they are both a genuine step forward to the ultimate goal: one universal program suitable for both light and heavy element work.

As far as the $\Phi(\varrho z)$ approach for very light elements is concerned, there is, of course, a lack of measured $\Phi(\varrho z)$ data for the light elements. This prevents a comparison of calculated and measured $\Phi(\varrho z)$ data. In this connection it is interesting to note that the shape and magnitude of the $\Phi(\varrho z)$ curve for carbon at 10 keV (Fig. 1b) as calculated by the present BAS program agrees very well with the results of Monte-Carlo calculations (*Love* et al. 1980). The shape of this curve as calculated by a predecessor of the present program (*Parobek* and *Brown* 1978) has previously been criticized in this respect. Strange enough the shape of the curve for copper at 30 keV (Fig. 1a) has remained more or less the same and differs considerably from the shape predicted by the Monte-Carlo simulations. There seems, however, to be substantial disagreement between the measured $\Phi(\varrho z)$ data for Cu at 30 keV as indicated in the same paper by *Love* et al. (1980). Our calculation agrees closely with one of the measured $\Phi(\varrho z)$ curves while the Monte-Carlo calculations of

Love et al. agree closely with the other one. Hence, it seems that no final conclusion can be drawn on this issue!

5. Conclusions

An evaluation of the performance of four correction programs for quantitative electronprobe microanalysis has shown that the BAS program, based on a modified $\Phi(\varrho z)$ approach, and the *Love* and *Scott* program are the most satisfactory and hence, are probably among the best programs for elements with atomic numbers larger than 13. An evaluation for very light elements has to wait for sufficient data to be collected, although preliminary results indicate that they both perform very well in this respect too. It has also been shown that the new atomic number correction by *Love* et al. gives results which are not greatly different from those generated by the BAS program. The differences can only be expected to be prominent for practical conditions which are hardly ever encountered in microprobe analysis (e.g. overvoltage ratios larger than 100 for carbon). The results of the *Ruste* and ZAF programs were found to be almost identical in this respect (differences smaller than 1% relative for the majority of cases) with the exception of very light elements. This is most probably the result of the use of different expressions for the ionisation potential. The general performance of the *Ruste* and ZAF programs was found to be similar for the medium to heavy elements. A somewhat disappointing feature of the *Ruste* program was its functioning for elements like Al and Si at higher (>20) probe voltages where it was found less satisfactory than the ZAF program.

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