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Review of $\varphi(\rho z)$ Curves in Electron Probe Microanalysis

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Several workers have proposed different models for the ionization distribution function $\phi(\rho z)$, involving features related to the interaction of electrons with matter, e.g. ionization cross-section, stopping power, electron backscattering and mass absorption coefficients (MACs). A number of expressions have been developed for these parameters, on which the accuracy of the correction procedures depends. This paper presents a comparison among three of the more successful models for $\phi(\rho z)$: Packwood and Brown's Gaussian model, the quadrilateral model proposed by Sewell *et al.* and Pouchou and Pichoir's model.

In order to test these models, a set of 1547 measurements in binary samples of known composition has been compiled. Several models for the ionization cross-section have been tested, along with different expressions for the mean ionization potential J, in which the shell effect can be taken into account. In addition, two possibilities for both the MACs and the electron backscattering coefficient are available. In general, all the tested models showed similar performances. Finally, the advantages of the models related to basic principles over the mathematically optimized ones, in the shape of $\phi(\rho z)$ or in the parameters, are considered.

INTRODUCTION

Electron probe microanalysis (EPMA) can be performed in a fully empirical way, without considerations of the physical bases underlying the relationship between composition and relative characteristic x-ray intensities. More realistic analyses may be carried out through different correction models developed on the basis of several principles of the interaction of electrons with matter. From the different assumptions for these models, a set of algorithms arises, relating the concentration C wih the measured intensity ratio K:

$$K = C \times ZAF$$

where $K = I_{sp}/I_{st}$, I_{sp} and I_{st} are the intensities emerging from the sample and standard respectively, and ZAF is the combined correction for atomic number Z, absorption A and fluorescence F. Several constants and variables appear in these algorithms, the so-called 'parameters' of the model. The accuracy of the analytical procedure depends both on the model and on these parameters.

The use of empirical models is restricted by the necessity for by handling standards whose composition must be similar to that of the unknown sample. On the other hand, models developed upon physical bases are expected to achieve a wider range of validity; this range depends on their capability to describe the physical processes related to the interaction of electrons with the target. In addition, all these models will be expected to retain their validity when new advances in the description of the process of interaction of electrons with matter or in the precision of the electron probe instruments might occur.

Since 1980, special attention has been paid to the distribution of ionizations $\phi(\rho z)$ with the mass depth ρz, ρ being the target density. A great number of experimental data[1–5] and Monte Carlo simulations[6,7] show that the shape of the $\phi(\rho z)$ curves is almost independent of the incident electron energy and of the sample target. However, these variables may appear in the parameters of an algorithm that describes properly these curves. An appropriate description of $\phi(\rho z)$ will provide a better estimation of the combined ZA correction through the following expression:

$$ZA = \frac{[\int \phi(\rho z) \exp(-\mu\rho z \operatorname{cosec} \psi)\, \mathrm{d}(\rho z)]_{sp}}{[\int \phi(\rho z) \exp(-\mu\rho z \operatorname{cosec} \psi)\, \mathrm{d}(\rho z)]_{st}}$$

where ψ is the take-off angle and μ the mass absorption coefficient to the radiation of interest.

All the models developed upon physical bases involve partial aspects of the interaction of radiation with matter through different parameters, such as mass absorption coefficients, ionization cross-sections, mean ionization potential and electron backscattering spectrum. Several expressions have been proposed for these parameters, which may modify the performance of each model. A brief discussion about them will be given, together with some comments about the modification to some parameters when a multi-element instead of a pure sample is considered.

Mass absorption coefficients (MACs)

The accuracy of every correction model is largely conditioned by the set of MACs chosen. Two important regions may be established with regards to the photon energy $h\nu$:

(a) $h\nu > 1.6$ keV
(b) 0.1 keV $< h\nu <$ 1.6 keV

Several algorithms for MACs are available for the first region, some of which agree satisfactorily with the

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experimental data; these include the algorithms proposed by McMaster *et al.*[8] and by Heinrich (MAC30).[9] Other sets of coefficients are available and some of them show similar agreement with experimental data, such as those given by Scofield[10] and by Storm and Israel,[11] but they have the disadvantage of requiring the storage of very large files in the computer.

For the second energy region, the accuracy of these algorithms worsens, and the necessity to resort to MACs obtained by experimental procedures[12–14] arises. Therefore, if a model is expected to work for a wide range of elements, some of the algorithms mentioned above must be used for energies greater than 1.6 keV, along with more accurate experimental data for low energies.

In this paper, tests will be performed combining the algorithms by McMaster *et al.*[8] or MAC30[9] with the experimental data for low energies given by Henke *et al.*[13] or Bastin *et al.*[14]

Ionization cross-sections

Another parameter used in the development of the different correction models is the ionization cross-section. Several expressions have been developed, considering either the total cross-section Q or the cross-section for the nl shell Q_{nl}. As a function of the incident electron energy, this parameter varies strongly close to the critical excitation energy E_c, and very smoothly for energies over $2E_c$. The most widely used equation for Q_{nl} is that due to Bethe:[15]

$$Q_{nl} = \frac{\pi e^4}{EE_{nl}} Z_{nl} b_{nl} \ln\left(\frac{c_{nl}E}{E_{nl}}\right)$$

where E is the electron energy, E_{nl} the binding energy of an electron in the nl shell (elsewhere E_c) and Z_{nl} the number of electrons in the filled shell nl. The parameters b_{nl} and c_{nl} are often assumed to be constants for a particular sub-shell, but they could be a function of the atomic number Z. The previous equation is expected to be valid only when $E \gg E_{nl}$, but a satisfactory lower limit for E has not been defined. Although various simplifications and modifications have been made to Bethe's original expression, it is generally difficult to judge their validity for particular shells and ranges of energy and to select the most suitable parameters. In addition, it is often difficult to evaluate how good a model for cross-sections is, since in most ZAF correction models the cross-section term 'cancels out' when intensities from sample and standard are compared. In those models in which this cancellation does not occur [e.g. $\phi(\rho z)$ is used for combined ZA correction], variations due to the different expressions for Q_{nl} may be masked by experimental errors.

A detailed comparison of different expressions for Q_{nl} (theoretical, semi-empirical and experimental) has been presented by Powell,[16] and a discussion about their performances has recently been given by Argüello *et al.*[17]

Stopping power and mean excitation energy

All the models assume the electron energy loss within the target as a continuous process and describe it by means of expressions similar to that given by Bethe and Ashkin:[18]

$$\frac{dE}{d(\rho x)} = \frac{2\pi e^4 Z}{AE} \ln\left(\frac{1.166E}{J}\right)$$

where J is the mean excitation energy. This expression may be rewritten in terms of the variable $V = E/J$:

$$\frac{dE}{d(\rho x)} = \frac{Z}{AJf(V)}$$

In order to overcome unrealistic results at low energies, Love *et al.*[19] and Pouchou and Pichoir[20] proposed different expressions for $f(V)$, consistent with Bethe's law in the high-energy range, and more reliable at low energies.

Several models have been developed for the parameter J, the first of which was proposed by Bloch[21] on the basis of the Thomas–Fermi statistical model for the atom. Jensen,[22] by means of the Thomas–Fermi–Dirac model for the atom, developed a more complete expression. Another model was suggested later by Wilson,[23] taking into account experimental determinations of proton penetration in aluminium. A number of models have subsequently been proposed from measurements of stopping power or electron range[24–27] and also from microanalysis data, such as that suggested by Duncumb and da Casa.[28] This algorithm, however, worsens the performances of the models tested; this failure may be attributed to the fact that the model was developed through a fit for a particular set of microprobe analysis of binary compounds of known compositions and therefore it lacks physical meaning.

The following expressions for J (in eV) are the most successful in microanalysis:

$J/Z = 13.5$	Bloch
$J/Z = 9Z(1 + 0.5Z^{-2/3})$	Jensen
$J/Z = 11.5$	Wilson
$J/Z = 9.76 + 58.82Z^{-1.19}$ (for $Z \geqslant 12$)	Sternheimer
$J/Z = 9.0(1 + Z^{-2/3}) + 0.03Z$	Springer
$J/Z = 10.04 + 8.25\exp(-Z/11.22)$	Zeller
$J/Z = 22.4Z^{-0.172}$	Brizuela and Riveros

Care must be taken when the electron energy E_0 is not greater than approximately 1.5 times the binding energy E_c corresponding to the inner shells, since no contribution to the stopping power is due to these shells. This means that the parameter J varies with E_0, depending on which shells are able to contribute to ionizations. This shell effect is reflected by an overestimation of a few percent in the stopping power when Bethe's law is applied to low atomic number matrices, the discrepancy increasing for greater Zs. Livingston and Bethe[29] pointed out the importance of this effect, but it has not been taken into account in practice, although it has frequently been mentioned. When the k-shell effect appears, Bethe's law produces the following expression for the corrected mean ionization potential:

$$J' = \exp[\ln(J^2 J_k^{-1.81})/(Z - 1.81)]$$

where $J_k = 15.0008(Z - 0.3)^2$ and J corresponds to some of the expressions given above. This shell effect will be taken into account in the tests when $E_0 < 1.5E_k$, where E_k is the binding energy of the k shell. A detailed analysis of this consideration states that this energy relationship must be taken into account even when k lines are observed, a factor born in mind by Brizuela and Riveros.[27]

Backscattered electron spectrum

The backscattered electron spectrum $d\eta/dE$ is involved in the different correction models when assessing the loss of ionizations. This spectrum depends to a great extent on the average atomic number of the specimen, and has a smooth variation with the electron energy. In most models, $d\eta/dE$ is taken as a constant value proportional to the total fraction of backscattered electrons η. The best known models for η in EPMA are the expression proposed by Tomlin,[30] fitted for the experimental data given by Bishop,[31] and that developed by Love and Scott[32] from Monte Carlo simulations:

$$\eta = \frac{\ln Z}{6} - a \qquad \text{Tomlin}^{30} \text{ and Bishop}^{31}$$

$$\eta = \eta_{20}\left[1 + \frac{G(Z)}{\eta_{20}} \ln\left(\frac{E_0}{20}\right)\right] \qquad \text{Love and Scott}^{32}$$

where η_{20} and $G(Z)$ are both polynomials in Z.

An expression for the differential spectrum $d\eta/dE$ was given by del Giorgio *et al.*[33] from Monte Carlo simulations; however, no significant variation in the performance of the correction models is obtained:

$$\frac{d\eta(p)}{dp} = \frac{\eta p}{\lambda^2} \exp(-p/\lambda)$$

where $\lambda = 0.907Z^{-0.5} - 0.012$ and $p = 1 - E/E_0$.

Parameter averaging

When analysing multi-element specimens, parameters such as atomic number, atomic weight, electron backscattering coefficient, mean ionization potential and MAC must be chosen to be representative of the sample. For this purpose, average values should be taken, weighing them by means of mass concentrations or atomic fractions. According to the definition, MACs must be mass-averaged; since incident electrons interact with the atoms in the specimen, the remaining parameters should be atomic-averaged. However, most correction models achieve better performances by mass-averaging all the parameters. Frequently, the averaging expressions have no physical basis, and they often vary from one correction model to another. Further, in some models,[20,34] the atomic number of a multi-element sample is obtained by means of different mass-averaging expressions, depending on which parameter of $\phi(\rho z)$ is evaluated.

Tested models and data set chosen

This paper provides a review of the three most successful models for the function $\phi(\rho z)$ up to now: the quadrilateral model (LOSII) proposed by Sewell *et al.*,[35] the PAP model developed by Pouchou and Pichoir[20] and the Gaussian model of Packwood and Brown,[36] considering the modifications to the parameters suggested by Bastin and co-workers[14,34] and by Riveros and co-workers.[37–39]

In order to test the performances of these models, a set of microanalyses on binary standards of known composition must be considered. The set of 1547 measurements in this paper involves data published in different previous publications;[7,40–54] only those data strongly deviating from the general behaviour of all models have been excluded from the compilation.*

Ultralight elements are not included in the present test because their analysis involves different problems, the most important being the following:

—shift and shape alteration of characteristic lines are strongly dependent on the structural and chemical state of elements in the sample;

—experimental conditions (detection system, take-off angle, stability and correctness of voltage and of beam current, preparation and contamination of the specimen, etc.) must be carefully taken into account;

—MACs must be known more precisely and form a coherent set of values; in addition, background and dead-time corrections must be carefully carried out.

Therefore, any compilation to test ultralight elements must include data measured under similar experimental conditions. At the same time, the set of MACs considered should be carefully obtained from determinations independent of the models tested.

An extensive discussion about all important topics to bear in mind when determining ultralight element intensities, as preliminary steps to the use of the correction models, was given by Bastin and Heijligers.[34] They, and also Pouchou and Pichoir,[55] performed different tests when considering the analysis of ultralight elements with varying success for the different elements. In these tests they included MACs obtained through the $\phi(\rho z)$ model proposed. Whether this choice is right or not is open to debate.

DESCRIPTION OF THE CORRECTION MODELS CONSIDERED

Gaussian model (Packwood and Brown)

On the basis of a careful analysis of experimental determinations of $\phi(\rho z)$, Packwood and Brown[36] proposed in 1981 a Gaussian model for the distribution of ionizations in a bulk target. This model assumes a random walk for the incident electrons within the sample; the resulting normal distribution is modified close to the surface by a transient function taking into account the variation of x-ray production with depth. The corresponding equation is

$$\phi(\rho z) = \exp[-\alpha^2(\rho z)^2]\{\gamma - [\gamma - \phi(0)] \exp(-\beta\rho z)\}$$

in which the assessment of the parameters α, β, γ and $\phi(0)$ was given by Packwood and Brown in their original paper. These original parameters did not produce

* The complete data set used in this review is available on request from the authors.

successful results after testing them on a set of analyses of specimens of known composition. Therefore, modifications were proposed by Bastin and co-workers[14,34,56] and by Riveros and co-workers,[37–39] providing better performances.

Modifications by Bastin *et al.*

From Packwood and Brown's original equations for the parameters of the Gaussian distribution, Bastin *et al.*[56] in 1984 optimized the expressions using a set of 430 microanalyses for binary alloys compiled by Love *et al.*[57] in 1975. Subsequently, they found limitations to their first version of the parameters and produced new expressions[14] (BASTIN 86) for β and γ based on experimental data and Monte Carlo simulations for $\phi(\rho z)$. The resulting expressions are the following:

$$\gamma = \begin{cases} 1 + \dfrac{U_0 - 1}{0.3384 + 0.4742(U_0 - 1)} & \text{for } U_0 \leqslant 3 \\ \dfrac{5\pi(U_0 + 1}{U_0 \ln(U_0 + 1)} & \text{for } U_0 > 3 \\ \times\ [\ln(U_0 + 1) - 5 + 5(U_0 + 1)^{-0.2}] & \end{cases}$$

$$\beta = \alpha \frac{Z}{A^n}$$

with $n = Z/(0.4765 + 0.5473Z)$ and

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

The expression for $\phi(0)$ is that given by Love *et al.*,[58] while J is that of Zeller and Coulon.[26]

Recently, Bastin and Heijligers[34] proposed a drastic change in the $\phi(\rho z)$ parameterizations (BASTIN 89). In their previous model, independent equations had been developed on physical bases for the Gaussian parameters. Now, a new mathematical optimization forced the parameters α, β, γ and $\phi(0)$ to cooperate in a consistent way in order to provide a specified value for the total generated intensity in the specimen, by means of the atomic number correction of Pouchou and Pichoir.[20] The corresponding expressions for the parameters are the following.

The equation for $\phi(0)$ is that used by Pouchou and Pichoir:[20]

$$\gamma = \begin{cases} 3.98352U_0^{-0.0516861} & \\ \quad \times (1.276233 - U_0^{-1.25558Z^{-0.1424549}}) & \text{for } U_0 \leqslant 6 \\ 2.814333U_0^{0.262702Z^{-0.1614454}} & \text{for } U_0 > 6 \end{cases}$$

For $Z \leqslant 9$, this expression must be multiplied by $E_c/(-0.041878 + 1.05975E_c)$.

$$\alpha = \frac{2.1614 \times 10^5 Z^{1.163}}{E_0^{1.25}(U_0 - 1)^{0.5}A} \left[\frac{\ln(1.166E_0/J)}{E_c}\right]^{0.5}.$$

In order to obtain the value of β the following relationship is used:

$$R(\beta/2\alpha) = [\gamma - 2\alpha F/\sqrt{\pi}]/[\gamma - \phi(0)]$$

where $R(\beta/2\alpha)$ is the fifth-degree polynomial used in the approximations of the erfc$(\beta/2\alpha)$ function and F is the value of the integral $\phi(\rho z)$ distribution calculated with the atomic number correction of Pouchou and Pichoir.[20]

The simplest way to obtain the β-value from this relationship is to cut the function $R(\beta/2\alpha)$ into nine different regions and to fit these regions with much simpler geometric functions. Care must be taken near the transition points from some function to another, where the prediction may become poor. More details about this procedure are given in the original paper.[34]

Modifications by Riveros and co-workers

Bearing in mind the physical meaning of each parameter of the Gaussian distribution, Riveros and co-workers[37–39] derived new expressions for them in 1987, without mathematical optimization for a particular set of microanalysis data. However, the parameter α was not modified from that given by Packwood and Brown, which was derived under the assumption of a random walk for the electrons within the sample.

More careful calculations were performed for the parameters $\phi(0)$ and γ,[37] specially for the mean free path of electrons and for the contribution of backscattered electrons to the surface ionizations, providing

$$\phi(0) = 1 + \frac{2}{Q(U_0)} \int_1^{U_0} Q(U) \frac{d\eta}{dU}\, dU \tag{3}$$

$$\gamma = \frac{2\int_1^{U_0} Q(U)\, dU}{Q(U_0)\int_1^{U_0} dU} + \frac{2}{Q(U_0)} \int_1^{U_0} Q(U) \frac{d\eta}{dU}\, dU \tag{4}$$

Appropriate results are obtained when the spectral energy distribution $d\eta/dU$ is approximated by a constant function proportional to η and Bethe's ionization cross-section is chosen, arriving in this case at the following expressions:

$$\phi(0) = 1 + \frac{\eta U_0 \ln U_0}{U_0 - 1} \tag{5}$$

$$\gamma = (1 + \eta) \frac{U_0 \ln U_0}{U_0 - 1} \tag{6}$$

These approximate expressions have the advantage of simplicity, showing very good results for a wide range of experimental conditions. In this paper, Eqns (3) and (4) were also evaluated using the expression for $d\eta/dU$ proposed by del Giorgio *et al.*[33] combined with Bethe's ionization cross-section.

On the other hand, the parameter β was assessed by relating the mean depth of diffusion to the value for which the transient function approaches unity,[38] obtaining the following expression for this parameter:

$$\beta = \frac{1.1 \times 10^5 Z^{1.5}}{(E_0 - E_c)A}$$

while Packwood and Brown's original expression for α is maintained:

$$\alpha = 2.14 \times 10^5 \frac{Z^{1.16}}{AE_0^{1.25}} \left[\frac{\ln(1.166E_0/J)}{E_0 - E_c}\right]^{0.5}$$

The model for J proposed by Brizuela and Riveros[27] is considered. However, any model for J which is physi-

cally meaningful may be used in this expression without significant variations in the results.

Quadrilateral model LOSII (Sewell *et al.*)

This model for $\phi(\rho z)$ was presented[35] with the purpose of obtaining, for a wide range of experimental conditions, a better estimate of the absorption correction model separate from the atomic number correction, as considered in the traditional ZAF models.

In this model, $\phi(\rho z)$ was approximated by means of two straight lines, determined by the surface ionization $\phi(0)$, position and height of the peak of the $\phi(\rho z)$ curve, ρz_m and ϕ_m, and ρz_r, a value related to the electron range in the sample. The resulting function is

$$\phi(\rho z) = \begin{cases} [\phi_m - \phi(0)] \dfrac{\rho z}{\rho z_m} + \phi(0) & 0 \leqslant \rho z \leqslant \rho z_m \\ \phi_m \dfrac{\rho z_r - \rho z}{\rho z_r - \rho z_m} & \rho z_m \leqslant \rho z \leqslant \rho z_r \end{cases}$$

where

$$\rho z_m = \overline{\rho z}[0.29 + (0.662 + 0.443 U_0^{0.2}) Z^{-0.5}]$$

$$\overline{\rho z} = \frac{(\rho s_m \ln U_0)}{[(2.4 + 0.07Z) \ln U_0 + 1.04 + 0.48\eta]}$$

$$\rho s_m = \frac{(0.773 \times 10^{-5} J^{0.5} E_0^{1.5} + 0.735 \times 10^{-6} E_0^2)}{C_i Z_i / A_i}$$

$$\rho z_r = \alpha\{1 + [1 + 2\rho z_m/(\alpha h)]^{0.5}\}$$

$$\alpha = 0.5(3\overline{\rho z} - \rho z_m)$$

where $h = \phi_m/\phi(0)$* can be expressed as $h = \alpha_1 - \alpha_2 \exp(-\alpha_3 U_0^x)$, with $\alpha_1 = 2.2 + 1.88 \times 10^{-3} Z$, $\alpha_2 = (\alpha_1 - 1) \exp \alpha_3$, $\alpha_3 = 0.01 + 7.19 \times 10^{-3} Z$ and $x = 1.29 - 1.25\eta$. These parameters were derived from tracer and Monte Carlo determinations of $\phi(\rho z)$,[7] as well as an optimization exercise over a set of microanalyses;[35] for this purpose, the atomic number correction proposed by Love *et al.*[19] using Bloch's model[21] for J and Reed's fluorescence correction[59] were used. The database used was criticized by Bastin *et al.*,[14] because in a very few cases (*ca.* 3%) the ZA correction is greater than 50%.

In 1989, Scott and Love[60] proposed a slight modification to the backscattering factor R in the Z correction without improving the previous performance of the model, as reported in their work.

PAP model (Pouchou and Pichoir)

With the purpose of obtaining an expression for $\phi(\rho z)$ which simplifies EPMA calculations, Pouchou and Pichoir[20] searched for a function that should accomplish the following requirements; predict the total generated radiation; take the $\phi(0)$ value at the surface; and vanish with a zero slope at a certain depth related to the electron range.

They eliminated Gaussian profiles in order to avoid numeric integrations, selecting two parabolic branches smoothly joined for $\phi(\rho z)$. The resulting curve is given by:

$$\phi(\rho z) = \begin{cases} A_1(\rho z - R_m)^2 + B_1 & \text{for } 0 \leqslant \rho z \leqslant R_c \\ A_2(\rho z - R_x)^2 & \text{for } R_c \leqslant \rho z \leqslant R_x \end{cases}$$

where A_1, A_2 and B_1 are expressed in terms of $\phi(0)$, R_m is the maximum of the function $\phi(\rho z)$, R_x is the electron range and R_c is the crossover point of the parabolae. This ensemble of parameters is derived from physical considerations and from fittings to experimental and simulated data for $\phi(\rho z)$, experimental analyses of binary and stratified specimens of known composition and measurements of electron range. The expressions for these parameters involve extensive calculations and can be found in the original paper.[20]

Pouchou and Pichoir[20] gave alternative procedures for low overvoltages, since, as they pointed out, the method breaks down in these cases, because no realistic value for R_c can be obtained. In such cases an additional degree of freedom can be introduced in the distribution by suppressing the parametric relationship between R_c and R_x. This feature suggests that, despite the good results obtained in EPMA, two parabolae may not be enough to fit completely the function $\phi(\rho z)$.

RESULTS AND DISCUSSION

The procedure usually followed in order to evaluate the performance of the different models for $\phi(\rho z)$ in microanalysis consists in studying the distribution of ratios between calculated intensity ratios K' and experimental K ratios for a large set of specimens of known composition. The values of K'/K are arranged so as to construct a histogram in which the dispersion represented by the root mean square error (rms) σ, the closeness of its mean value to unity, the symmetry with respect to unity (ratio of counts with $K'/K > 1$ to those with $K'/K < 1$), and the symmetry with respect to the mean value (real symmetry) are taken as evaluation criteria. Samples whose K'/K ratio departs from the mean value more than three times the rms error are rejected. By means of this criterion, it has been found that most rejected data are discarded by all models, without showing any systematic trend, that is, they are not grouped by a high ZAF correction, overvoltage, etc. For this reason, the number of rejected data is an additional factor which somewhat qualifies a model.

In this paper, for the sake of simplicity, only Reed's fluorescence correction factor[59] will be used. All other models for this factor produce similar results despite their complexity, as shown by Ugarte *et al.*[61]

Gaussian model

Modifications by Bastin *et al.* Bastin *et al.* claimed an rms error of 2.99 around a mean value of 1.001 when testing the BASTIN 86 model in their compilation of 680 analyses,[14] in which data with $U_0 \leqslant 1.5$ were rejected. They later tested the BASTIN 89 model on a data file of

* It must be noted that separate evaluation of ϕ_m and $\phi(0)$ is not necessary in the assessment of the absorption correction factor.

877 measurements[34] (the previous set of 680 data supplemented with 197 metal analyses in borides), obtaining an rms error of 2.44% around a mean value of 0.9955. It should be noted that for the subset with 197 analyses, an rms error of *ca.* 1.6% is obtained, and most correction factors for these data are not important: only in 7% of them is the ZA correction greater than 10%, but none of them is above 15%.

Table 1 shows that the BASTIN 89 model produces a better performance than BASTIN 86, although symmetries are still very poor. At the same time, it is less sensitive to the use of different physically meaningful expressions for parameters such as mean ionization potential, MACs, surface ionization $\phi(0)$ and cross-section on which the model depends.

Several sets of MACs have been tested, and it can be seen that the rms error worsens in BASTIN 86 when the set of MACs given by Henke *et al.*[13] is chosen for low energies, as pointed previously by Riveros *et al.*[62]

Some of the most important results obtained in this paper with this model are shown in Table 1. Average values for $\bar{Z}$, $\bar{A}$ and $\bar{\eta}$ have been taken following Pouchou and Pichoir.[20]

Modifications by Riveros and co-workers. As can be seen from Table 2, performances are not strongly improved when avoiding the approximation of uniform backscattered distribution of electrons. A more accurate set of data is required in order to decide if any improvement appears.

Several models for the ionization cross-section have been considered in the case of the non-uniform backscattered distribution; the model showing the best performances is that of Bethe,[15] as pointed by Argüello *et al.*[17]

Atomic average was chosen for multi-element samples, except for the distribution of backscattered electrons, where mass average was taken, as suggested by del Giorgio *et al.*[33]

Table 1. Gaussian model: parameters by Bastin *et al.*

Average $\langle K'/K \rangle$	Rms σ (%)	Symmetry around 1	Symmetry around $\langle K'/K \rangle$	MAC	Rejected data	Range for U_0
0.994	2.25	0.585	1.053	McMaster Bastin	53	>1.5
0.994	2.30	0.616	1.033	McMaster Bastin	53	>1
0.996	2.21	0.693	1.061	MAC30 Bastin	63	>1
0.994	2.42	0.613	1.012	McMaster Henke	34	>1
0.995	2.39	0.687	1.046	MAC30 Henke	35	>1
1.001[a]	3.19	1.266	1.129	McMaster Bastin	61	>1
1.003[a]	3.17	1.307	1.053	MAC30 Bastin	67	>1
1.001[a]	3.63	1.282	1.147	McMaster Henke	44	>1
1.001[a]	3.71	1.312	1.084	MAC30 Henke	42	>1

[a] BASTIN 86.

Table 2. Gaussian model: parameters by Riveros and co-workers

Average $\langle K'/K \rangle$	Rms σ (%)	Symmetry around 1	Symmetry around $\langle K'/K \rangle$	MAC	Rejected data	Range for U_0
1.002	2.49	1.019	0.870	McMaster Bastin	68	>1
1.003	2.51	1.143	0.852	MAC30 Bastin	67	>1
1.001	2.64	0.897	1.003	McMaster Henke	71	>1
1.003	2.65	1.127	0.866	MAC30 Henke	69	>1
1.006[a]	2.62	1.277	0.807	McMaster Bastin	74	>1
1.008[a]	2.61	1.522	0.812	MAC30 Bastin	67	>1
1.005[a]	2.56	1.188	0.824	McMaster Henke	90	>1
1.007[a]	2.57	1.425	0.800	MAC30 Henke	82	>1

[a] Uniform distribution of backscattered electrons assumed.

The use of different expressions for J based on either experimental data for the stopping power or on theoretical assessments does not modify sensitively the performance of the model, and the model given by Brizuela and Riveros[27] was used. On the other hand, the performance worsens when the model for J proposed by Duncumb and da Casa[28] is used.

Quadrilateral model LOSII (Sewell *et al.*)

Sewell *et al.*[35] quoted an rms error of 2.94% around a mean value of 0.994 when testing this model on their compilation of 554 data. Later, Scott and Love[60] assessed a new expression for the backscattering factor R, reporting an rms error of 3.1% on the same data base. Bastin *et al.*[14] tested the original quadrilateral model on the data set used in this work obtaining an rms error of 4.33% around 0.990, considering the MACs proposed by them.

Table 3 shows the performances obtained in this work using this correction model, in which mass average has been taken for $\bar{Z}$, $\bar{A}$ and $\bar{\eta}$. The results

Table 3. Quadrilateral model (LOSII)

Average $\langle K'/K \rangle$	Rms σ (%)	Symmetry around 1	Symmetry around $\langle K'/K \rangle$	MAC	Rejected data	Range for U_0
0.998	2.37	0.839	1.118	McMaster Bastin	81	>1
0.999	2.34	1.079	1.140	MAC30 Bastin	81	>1
0.999	2.36	0.937	1.077	McMaster Henke	41	>1
0.999	2.33	0.976	1.048	McMaster Henke	38	>1.5
1.000	2.32	1.130	1.76	MAC30 Henke	40	>1

Table 4. PAP model: Pouchou and Pichoir

Average $\langle K'/K \rangle$	Rms σ (%)	Symmetry around 1	Symmetry around $\langle K'/K \rangle$	MAC	Rejected data	Range for U_0
0.998	2.28	0.864	1.039	McMaster Bastin	67	>1
0.998	2.25	0.837	1.028	McMaster Bastin	50	>1.5
1.000	2.32	0.936	0.967	MAC30 Bastin	64	>1
0.999	2.34	0.872	1.008	McMaster Henke	61	>1
1.000	2.37	0.945	0.957	MAC30 Henke	56	>1

worsen when the model chosen for J is different from that given by Bloch, except when Wilson's model for J is used; this was to be expected, since both models have a similar origin.

Bishop's model[31] for η was chosen in this test, since it slightly improves the performances produced when the model given by Love and Scott[32] is used.

No improvement is introduced on limiting the range of overvoltages considered, as can be seen from Table 3.

PAP model (Pouchou and Pichoir)

Pouchou and Pichoir[20] evaluated their model in a set of 826 analyses, quoting an rms error of 1.91% around 0.998. They used the MAC30 algorithm when the emitter is not a very light element, correcting some values of MACs corresponding to situations in which the line is close to an absorption edge or to particular resonance situations which are ignored by the MAC30 algorithm. For very low energies they used the absorption coefficients of Henke and replaced some value by other measurements made by Bastin and Heijligers.

It should be pointed out that this set of 826 analyses does not present matrix effects as important as those appearing in Bastin's 680 data base, since only in a 15% of them is the ZA correction greater than 20%.

No substantial variation is observed when different sets of MACs are used, as can be seen in Table 4. The same occurs when the parameters J and η are different from those proposed in the original model of Berger[24] and Love and Scott,[32] respectively. On the other hand, no remarkable variation appears when limiting the range of overvoltages to $U_0 > 1.5$.

As suggested by Pouchou and Pichoir,[20] different mass-averaging expressions for the parameter Z appear in the different parameters of the model.

CONCLUSION

Some final comments may be given on the light of the results obtained.

For low energies, in most correction models, MACs proposed by Bastin *et al.*,[14] derived from their model for $\phi(\rho z)$, produce better performances than those given by Henke *et al.*[13] This may be due to the fact that experimental errors of MACs in this region are, nowadays, greater than the uncertainties inherent to the correction models. On the other hand, for high energies the results obtained with the algorithms of McMaster *et al.*[8] and MAC30[9] are very similar.

The correction models LOSSII and Gaussian–BASTIN 86 depend strongly on which expression is taken for J, whereas the PAP and Gaussian models BASTIN 89 and Riveros are insensitive to the model for J used.

The models for η given by Bishop[31] and Love and Scott[32] may be used alternatively, since no significant variation in the rms error or in the symmetries occurs.

Different methods for parameter averaging appear in the different models, most of them without physical justification. A remarkable case is the PAP model, in which the parameter Z is averaged in several different ways when assessing the total intensity generated in a sample. This feature is also observed for BASTIN 89, since the same assessment is performed.

The limitation $U_0 > 1.5$ does not improve the performance of the different models over the whole data set. A similar comment may be given if high overvoltages are avoided ($U_0 > 20$). This suggests that the performances of these models do not depend on the

Table 5. Comparison of the different models

Model	Average $\langle K'/K \rangle$	Rms σ (%)	Symmetry around 1	Symmetry around $\langle K'/K \rangle$	MAC	Model for J	Rejected data
Bastin *et al.*[86]	1.001	3.19	1.266	1.129	McMaster Bastin	Zeller	61
Bastin *et al.*[89]	0.996	2.21	0.693	1.061	MAC30 Bastin	Zeller	63
Riveros and co-workers[a]	1.006	2.62	1.277	0.807	McMaster Bastin	Brizuela Riveros	74
Riveros and co-workers[b]	1.002	2.49	1.019	0.870	McMaster Bastin	Brizuela Riveros	68
Love–Scott II	0.999	2.36	0.937	1.077	McMaster Henke	Bloch	41
Pouchou and Pichoir	1.000	2.32	0.936	0.967	McMaster Bastin	Berger	64

[a] Uniform energy distribution for backscattered electrons.
[b] Energy distribution for backscattered electrons by del Giorgio *et al.*[33]

overvoltage, although this might be due to the experimental errors of the data, which may be too high if we search for evidence for this dependence.

An additional comment regarding the accuracy of the experimental determination at low overvoltages may be given. All the models considered here involve the ionization cross-section, a rapidly increasing function of the overvoltage when $1 < U_0 < 2$, which applies to most elements and shells. This requires a very high accuracy in the accelerating voltage measurements when U_0 lies in this interval, since small errors in this value may produce important variations in the assessment of the cross-section, and therefore in the calculated intensity. This might explain the differences appearing in several analyses of the data file with the same elements, in which slight variations in the experimental conditions or concentrations produce K'/K values either very close to unity or very separated from it.

The best performances of each model are given in Table 5. The variations found among the different models are not significant, since all models produce an rms error which agrees with the experimental uncertainties of the data set chosen.

Finally, it should be emphasized that provided the models are closely related to basic principles, with no optimizations in the shape of $\phi(\rho z)$ or in the parameters, any advance in the description of the process of interaction of electrons with matter will be reflected in advances in the performance of the models. On the other hand, if $\phi(\rho z)$ or the parameters are developed through optimizations, every advance will need new optimizations in the models.

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