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Comparison of $\Phi(\rho z)$ Curve Models in EPMA

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Abstract. Several authors have proposed different models for the ionization distribution function $\Phi(\rho z)$. This paper presents a comparison of three of the most successful models for $\Phi(\rho z)$: Packwood and Brown's Gaussian model including Bastin et al.'s and Riveros et al.'s versions, the quadrilateral model proposed by Sewell et al. and Pouchou and Pichoir's model. In general, all the tested models showed similar performances. Finally the advantages of the models related to basic principles over the mathematically optimized ones are considered.

Key words: EPMA, ZAF correction models, ionization distribution function.

In electron probe microanalysis (EPMA), concentration determinations may be carried out through different correction models relating the concentration C to the measured intensity ratio k:

$$k = C \cdot \mathrm{ZAF}, \tag{1}$$

where $k = I_{sp}/I_{st}$, I_{sp} and I_{st} are the intensities emerging from sample and standard respectively, and ZAF is the combined correction for atomic number Z, absorption A and fluorescence F. The combined ZA correction is usually expressed through $\Phi(\rho z)$, the distribution of ionizations with mass depth ρz, ρ being the target density. After a description of three of the most successful models for $\Phi(\rho z)$, a mutual comparison of them will be performed using a compilation of 680 microanalyses published by Bastin et al. [1]. This set was chosen because of its advantages with respect to other data sets, because it includes: absorption effects which are somewhat stronger (11% of data with ZA > 50% and 30% with ZA > 20%), greater range of experimental conditions and average experimental errors between 2% and 3%. On the other hand, mass absorption coefficients (MACs) will be assessed, combining the algorithms by McMaster et al. [2] or MAC30 [3] with the experimental data for low energies given by Henke et al. [4] or Bastin et al. [1].

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Ultralight elements are not included in the present test because their analysis involves serious problems, as pointed out by Bastin and Heijligers [5], the most important being: shift and shape alteration of characteristic lines due to chemical effects, experimental inconveniences, and inaccurate knowledge of MACs.

Gaussian Model (Packwood and Brown)

Packwood and Brown [6] proposed a Gaussian model for $\Phi(\rho z)$ assuming 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:

$$\Phi(\rho z) = \exp[-\alpha^2(\rho z^2)] \cdot [\gamma_0 - (\gamma_0 - \Phi_0)\exp(-\beta\rho z)], \tag{2}$$

in which the assessment of the parameters α, β, γ_0 and Φ_0 has been described by Packwood and Brown in their original paper. As these original parameters did not produce successful results, modifications were proposed by Bastin et al. [1, 5, 7] and by Riveros and co-workers [8–10], providing better performances.

Modifications by Bastin et al.

Bastin et al. [7] optimized the expressions for the original parameters using a set of 430 microanalyses compiled by Love et al. [11]; they found limitations to their first version of the parameters and produced new expressions [1] (Table 1: BASTIN 86) for β and γ_0 based on experimental data and Monte Carlo simulations for $\Phi(\rho z)$.

Recently, Bastin and Heijligers [5] proposed a drastic change in the $\Phi(\rho z)$ parameterizations (Table 1: BASTIN 89). In their previous model, independent equations had been developed on physical bases for the parameters. Now, a new mathematical optimization has forced the parameters α, β, γ_0 and Φ_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 [12]. The equation for Φ_0 was also taken from these authors.

Modifications by Riveros and co-workers.

Bearing in mind the physical meaning of each parameter of the Gaussian distribution, Riveros and co-workers [8–10] derived new expressions for them, without mathematical optimizations for a particular set of microanalysis data. More careful calculations were performed for the parameters Φ_0 and γ_0 [8], especially for the mean free path length of electrons and for the contribution of backscattered electrons to the surface ionizations. The obtained expressions depend on the spectral energy distribution of backscattered electrons $d\eta/dU$, U being the overvoltage. However, good results are produced when approximating $d\eta/dU$ by a constant function proportional to the total fraction of backscattered electrons η (Table 1: GAUSS 1). Expressions involving $d\eta/dU$ have also been evaluated using the expression proposed by del Giorgio et al. [13] (Table 1: GAUSS 2) [10]. The parameter β was assessed by relating the mean depth of diffusion to the value for which the transient function approaches unity [9].

Table 1. Performance of the tested correction models. "Sym 1" and "Sym $\langle k'/k \rangle$" indicate the symmetry of the histogram around unity and mean value, respectively. The bold lines show the best results obtained with each model

Model	Mac references	Rejected data	U_0 range	Average	RMS	Sym 1	Sym $\langle k'/k \rangle$
	[5]	23	$U_0 > 1$	0.094	2.61	0.685	1.040
Gaussian	[5]	23	$U_0 > 1.5$	0.994	2.57	0.691	1.030
BASTIN 89	[2, 5]	24	$U_0 > 1$	0.990	2.25	0.451	0.964
	[3, 5]	**27**	$\boldsymbol{U_0 > 1}$	**0.993**	**2.19**	**0.536**	**1.028**
	[5]	**39**	$\boldsymbol{U_0 > 1}$	**1.003**	**2.79**	**1.462**	**1.180**
Gaussian	[5]	25	$U_0 > 1.5$	1.003	2.72	1.469	1.184
BASTIN 86	[3, 5]	20	$U_0 > 1$	0.999	3.63	1.129	1.143
	[2, 5]	22	$U_0 > 1$	0.997	3.39	1.092	1.317
	[2, 5]	**31**	$\boldsymbol{U_0 > 1}$	**0.999**	**2.51**	**0.870**	**0.949**
Gaussian	[2, 5]	20	$U_0 > 1.5$	0.998	2.39	0.826	0.937
GAUSS 2	[2, 4]	66	$U_0 > 1$	0.995	2.78	0.689	1.040
	[3, 5]	29	$U_0 > 1$	1.002	2.62	1.093	0.943
	[3, 4]	66	$U_0 > 1$	0.998	2.89	0.875	0.974
	[2, 5]	**64**	$\boldsymbol{U_0 > 1}$	**1.001**	**2.53**	**0.875**	**0.839**
Gaussian	[2, 4]	80	$U_0 > 1$	0.995	2.61	0.656	0.987
GAUSS 1	[3, 5]	54	$U_0 > 1$	1.005	2.66	1.133	0.830
	[3, 4]	66	$U_0 > 1$	0.999	2.60	0.858	0.949
	[2, 4]	21	$U_0 > 1$	0.994	2.49	0.721	1.053
	[2, 5]	58	$U_0 > 1$	0.994	2.51	0.737	1.152
LOS II	[2, 5]	58	$U_0 > 1.5$	0.994	2.52	0.788	1.126
	[5]	61	$U_0 > 1$	0.998	2.70	1.056	1.142
	[3, 5]	60	$U_0 > 1$	0.997	2.49	1.006	1.168
	[3, 4]	**20**	$\boldsymbol{U_0 > 1}$	**0.997**	**2.51**	**0.970**	**1.095**
	[2, 5]	29	$U_0 > 1.5$	0.994	2.24	0.573	1.017
	[2, 5]	**45**	$\boldsymbol{U_0 > 1}$	**0.994**	**2.28**	**0.586**	**0.991**
	[2, 4]	53	$U_0 > 1$	0.991	2.67	0.524	1.090
PAP	[3, 5]	46	$U_0 > 1$	0.996	2.37	0.668	0.933
	[3, 4]	51	$U_0 > 1$	0.993	2.88	0.605	1.042
	[5]	43	$U_0 > 1$	0.999	2.37	0.846	0.996

The parameter α has not been modified from that given by Packwood and Brown, but the model for the mean ionization potential J, proposed by Brizuela and Riveros [14], is considered, taking into account shell effects. Parameters are atomically averaged except for $d\eta/dU$ which is mass averaged, according to del Giorgio et al. [13].

Quadrilateral Model (Sewell, Love, Scott)

In this model, $\Phi(\rho z)$ was approximated by means of two straight lines, determined by the surface ionization Φ_0, the 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 involved parameters were derived from tracer and Monte Carlo determinations of $\Phi(\rho z)$, as

well as from an optimization over a set of microanalyses [15]; using the Z-correction proposed by Love et al. [16], Bloch's model for J [17] and Reed's fluorescence correction [18]. The resulting function is:

$$\Phi(\rho z) = [\Phi_m - \Phi_0] \cdot (\rho z / \rho z_m) + \Phi_0 \qquad \text{for} \qquad 0 < \rho z < \rho z_m, \tag{3}$$

$$\Phi(\rho z) = \Phi_m \cdot (\rho z_r - \rho z)/(\rho z_r - \rho z_m) \qquad \text{for} \qquad \rho z_m < \rho z < \rho z_r, \tag{4}$$

(See Table 1 section LOS II for data).

PAP Model (Pouchou and Pichoir)

With the purpose of obtaining an expression for $\Phi(\rho z)$ which simplifies EPMA calculations, Pouchou and Pichoir [12] searched for a function consisting in two parabolae, that should accomplish the following requirements: predict the total generated radiation, begin with the $\Phi(0)$ value at the surface and vanish with a zero slope at a certain depth related to the electron range. The resulting curve is given by:

$$\Phi(\rho z) = A_1 \cdot (\rho z - R_m)^2 + B_1 \qquad \text{for} \qquad 0 < \rho z < R_c, \tag{5}$$

$$\Phi(\rho z) = A_2 \cdot (\rho z - R_x)^2 \qquad \text{for} \qquad R_c < \rho z < R_x, \tag{6}$$

where A_1, A_2 and B_1 are expressed in terms of Φ_0; R_m, the maximum of the function $\Phi(\rho z)$; R_x, the electron range and R_c, the crossover point of the parabolae. These parameters were derived from physical considerations, from experimental and simulated data for $\Phi(\rho z)$, from experimental analyses of specimens of known composition and from measurements of the electron range. The authors gave alternative procedures for low overvoltages; in such cases an additional degree of freedom can be introduced in the distribution by suppressing the parametric relation between R_c and R_x. This feature suggests that 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 quotients between calculated intensity ratios k' and experimental k-ratios for a large set of specimens of known composition. Samples whose k'/k-ratio deviate from the mean value more than three times the relative root mean square (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 indicated by a high ZAF correction, overvoltage, etc. In the present paper, Reed's fluorescence correction factor [18] is used and for each model, average values for Z, A and η have been taken following the original papers.

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 [1], in which

data with incident overvoltage is lower than 1.5 were rejected. They later tested the BASTIN 89-model upon a data file of 877 measurements [5] (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 around 1.3% is obtained, and most correction factors for these data are relatively unimportant: only in 7% of them the ZA correction is larger than 10% (none of them is above 15%).

According to Bastin et al., better performances in the BASTIN 86-model are obtained when selecting $U_0 > 1.5$ but no significant variation for the whole set of microanalyses was found. It can be seen that in this case, 39 data are rejected, whilst the test discards 25 for the subset with $U_0 > 1.5$. It must be emphasized that from the 50 samples with $U_0 < 1.5$, only in 14 the k'/k values lie three times the rms error beyond the mean value and the 36 left remain close to the mean value. As it can be seen from Table 1, the BASTIN 89 model does not modify substantially the performance of the BASTIN 86 model.

It can also be seen that the rms error deteriorates in BASTIN 86, when the set of MACs chosen is different from that suggested by Bastin et al. in their compilation of microanalyses. Although they suggest the use of their own set of MACs, in BASTIN 89 the algorithms by McMaster et al. [2] and MAC30 [3] produce better results.

Modifications by Riveros and co-workers

Performances are not strongly improved when avoiding the approximation of uniform backscattered distribution, except in the number of rejected data (see Table 1). Significant improvements could only be evidenced with a more accurate data set. The use of different expressions for J based on either experimental data of the stopping power or theoretical assessments does not modify significantly the performance of the model.

Quadrilateral Model (Sewell, Love, Scott)

Sewell et al. [15] quoted an rms error of 2.94% around a mean value of 0.994 when testing this model on their compilation of 554 data. Bastin et al. [1] tested the original quadrilateral model on the data set used in this paper obtaining an rms error of 4.33% around 0.990, considering the MACs proposed by them.

According to the present evaluation (see Table 1) results worsen when the complete set of MACs proposed by Bastin are used, as well as when the model chosen for J is different from that given by Bloch [17], except when Wilson's model [19] for J is used (both models have a similar origin). Bishop's model [20] for η was chosen in this test, since it slightly improves the performances produced when the model given by Love et al. [21] is used. No improvement is introduced if the range of overvoltages is limited.

PAP Model (Pouchou and Pichoir)

Pouchou and Pichoir [22] have recently evaluated their model in a set of 826 analyses, quoting an rms error of 1.91% around 0.998. They have used the MAC30

algorithm if 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 have used the absorption coefficients of Henke and replaced some values 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 the ZA correction is larger than 20%.

When this model is tested upon Bastin's data base, the best results are obtained replacing the MAC values by those given by McMaster et al. [2] for energies larger than 1.6 keV (see Table 1). No substantial variation is observed for different sets of MACs, J or η formulae or when limiting the range of overvoltages to $U_0 > 1.5$.

Final Comments

- For low energies, in most correction models, MACs proposed by Bastin et al. [1] produce better performances than those given by Henke et al. [4]. On the other hand, for high energies the best results are obtained with the algorithms of McMaster et al. [2] and MAC30 [3], with slight differences between them. Only for the Gaussian model BASTIN 86 important improvements are achieved when using MACs proposed by these authors. This behavior may be due to the fact that these MACs were obtained by means of the function $\Phi(\rho z)$ proposed by them.
- The correction models LOSII and Gaussian-BASTIN 86 strongly depend on the expression for J taken, while PAP and Gaussian models BASTIN 89 and GAUSS are quite insensitive to the model for J used.
- Except for MACs, the parameters should be atomically averaged, since the incident electrons interact with atoms; however, the only models in which most of the parameters are atomically averaged are GAUSS 1 and 2. A remarkable case is the PAP model, in which the parameter Z is averaged in several different ways.
- The limitation $U_0 > 1.5$ does not improve the performance of the different models over the whole data set.
- The better performances of each model are set bold in Table 1. There is no significant variation in the rms error, while in those models in which a better performance in the rms error is observed, the values for the average worsen.
- Finally, it should be emphasized that provided the models are closely related to basic principles (which means 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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