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Simple Model for Surface Ionization in Electron Probe Microanalysis

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A new model for surface ionization $\phi(0)$ was developed from a theoretical basis approximating the energetic distribution of backscattered electrons by a delta distribution in the interval $[1, U_0]$. The expression obtained is compared with other models and with a set of experimental data.

INTRODUCTION

A good description of depth distribution of primary ionizations is required in quantitative electron probe microanalysis (EPMA), in order to calculate certain correction factors. Such a distribution is commonly known as $\phi(\rho z)$, where ρz is the mass depth.

Several workers[1–3] have proposed models for $\phi(\rho z)$ which depend on different parameters. Particularly, the surface ionization $\phi(0)$ appears in every attempt to describe $\phi(\rho z)$ curves. Therefore, it is very important to develop an adequate expression for $\phi(0)$. On the other hand, since this parameter can be determined experimentally in a direct way, a large set of data is available for checking the models.

Considering the definition for $\phi(\rho z)$,[1] the surface ionization can be expressed as follows:

$$\phi(0) = 1 + \frac{\sum_{i=1}^{n} Q(U_i)/\cos\theta_i}{n_0\, Q(U_0)} \tag{1}$$

where n_0 is the number of incident electrons, n is the number of backscattered electrons that leave the specimen at angles θ_i with energies E_i, $Q(U)$ is the ionization cross-section, $U_i = E_i/E_c$ the overvoltage of the ith backscattered electron, E_c is the critical energy and U_0 is the incidence overvoltage. From this equation, it is clear that the surface ionization is greater than unity owing to the contribution of backscattered electrons. Taking into account their angular and energetic distribution, $\partial^2\eta/(\partial\theta\,\partial U)$, and integrating over all backscattering angles with a cosine law[4,5] for $\partial\eta/\partial\theta$, we have

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

Evaluation of Eqn (2) requires an analytical expression for the energy distribution $\mathrm{d}\eta/\mathrm{d}U$.[6] This spectrum exhibits a maximum close to U_0, which becomes sharper as the atomic number Z increases.

With the available expressions for $\mathrm{d}\eta/\mathrm{d}U$, it is possible to solve the integral in Eqn (2) by numerical or analytical calculations, although they generally result in very complicated expressions for $\phi(0)$.

The aim of this work was to obtain a simple and accurate expression for $\phi(0)$ and to compare it with other recently proposed models[4,7,8] and with a wide set of experimental data.[5,7]

DEVELOPMENT OF A NEW MODEL FOR $\phi(0)$

In order to find a simple expression for $\phi(0)$, the following approximation for $\mathrm{d}\eta/\mathrm{d}U$ in the interval $[1, U_0]$ is proposed:

$$\frac{\mathrm{d}\eta}{\mathrm{d}U} = \mathscr{K}\,\delta(U - \bar{U}) \tag{3}$$

where δ is the Dirac delta distribution, $\mathscr{K}$ is a normalization factor:

$$\mathscr{K} = \int_1^{U_0} \frac{\mathrm{d}\eta}{\mathrm{d}U}\,\mathrm{d}U \tag{4}$$

and $\bar{U}$ is the average overvoltage for backscattered electrons:

$$\bar{U} = \frac{\int_1^{U_0} U\frac{\mathrm{d}\eta}{\mathrm{d}U}\,\mathrm{d}U}{\int_1^{U_0} \frac{\mathrm{d}\eta}{\mathrm{d}U}\,\mathrm{d}U} \tag{5}$$

These assumptions are equivalent to replacing all backscattered electrons with energies greater than E_c by a monoenergetic beam with overvoltage $\bar{U}$. The surface ionization results:

$$\phi(0) = 1 + 2\mathscr{K}\frac{Q(\bar{U})}{Q(U_0)} \tag{6}$$

In order to find the values of $\mathscr{K}$ and $\bar{U}$, the spectral distribution given by del Giorgio *et al.*[9] was used:

$$\frac{\mathrm{d}\eta}{\mathrm{d}p} = \frac{\eta p}{\lambda^2}\,\mathrm{e}^{-p/\lambda} \tag{7}$$

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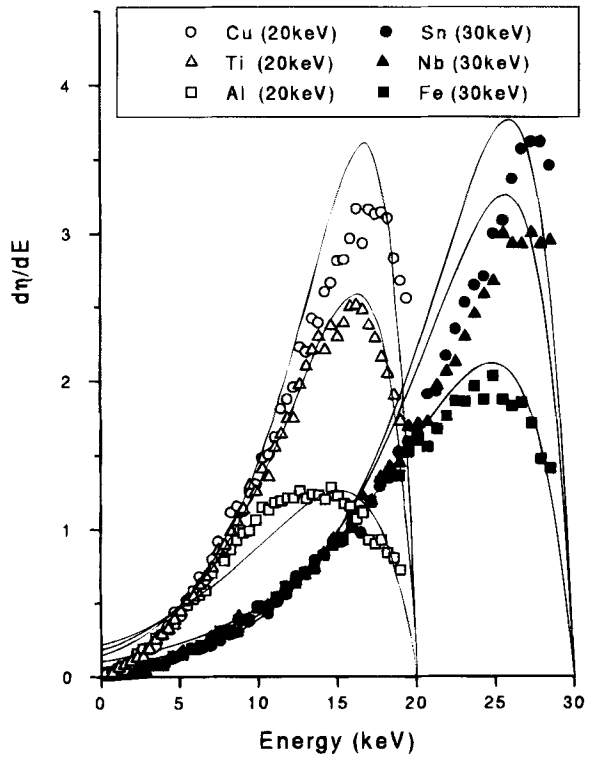

Figure 1. Comparison of the energy spectra of backscattered electrons given by del Giorgio *et al.*[9] (solid lines) and by the program PENELOPE[10] (symbols) for Al, Ti and Cu at 20 keV and for Fe, Nb and Sn at 30 keV.

where $p = 1 - U/U_0$ and $\lambda = 0.907/\sqrt{Z} + 0.00058Z - 0.01955$.

This distribution was derived from simplified Monte Carlo simulations. However, this model has shown to be appropriate when comparing it with Monte Carlo spectra obtained by means of the program PENELOPE.[10] This program avoids rough approximations such as the continuous slowing down of electrons, and includes very realistic descriptions for elastic and inelastic cross-sections (Fig. 1).

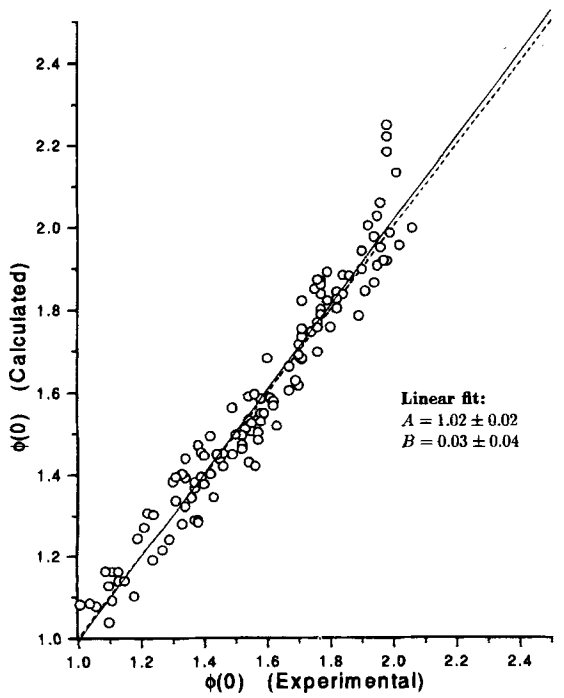

Figure 2. Comparison of experimental $\phi(0)$ values obtained by the tracer method with those predicted by Rehbach and Karduck.[8] Dotted line, $\phi(0)_{calc} = \phi(0)_{exp}$; solid line, linear fit.

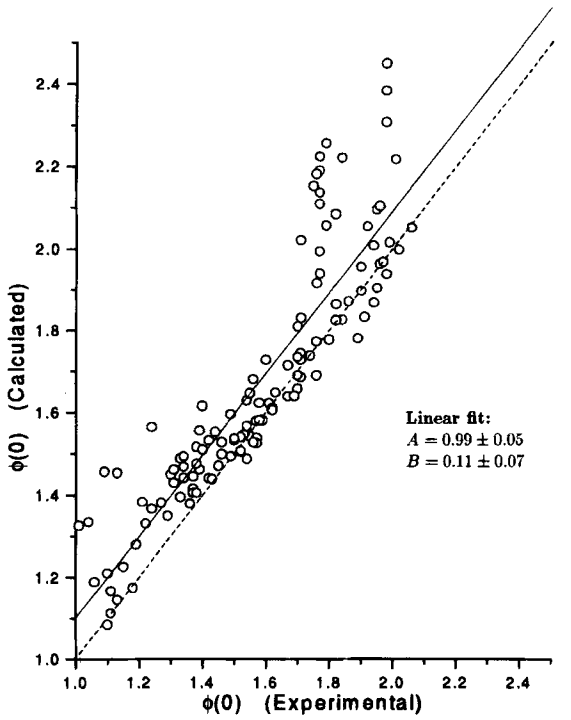

Figure 3. Comparison of experimental $\phi(0)$ values obtained by the tracer method with those predicted by Tirira and Riveros.[4] Dotted line, $\phi(0)_{calc} = \phi(0)_{exp}$; solid line, linear fit.

The expressions obtained for $\mathscr{K}$ and $\bar{U}$ are

$$\mathscr{K} = \eta\left(1 - \frac{p_c/\lambda + 1}{e^{p_c/\lambda}}\right) \tag{8}$$

$$\bar{U} = U_0\left\{1 - \lambda\left[2 - \frac{(p_c/\lambda)^2}{e^{p_c/\lambda} - (p_c/\lambda) - 1}\right]\right\} \tag{9}$$

where $p_c = 1 - 1/U_0$.

A remarkable feature of this model is that it can be easily evaluated with different expressions for the cross-section, owing to its explicit dependence on $Q(U)$. In the present assessments, the expression given by Pouchou and Pichoir[3] was used.

DATA ANALYSIS AND DISCUSSION

The accuracy of the present model was tested by comparing its results with those from other expressions and with experimental values.

The experimental data used here were obtained by the tracer method and compiled by August and Wernisch[5] and Merlet.[7] From the total set of data, those for which secondary fluorescence effects could be important were excluded: magnesium (Kα) on an aluminium substrate,[11] silicon (Kα) and bismuth (Mα) on silver.[2,12] In addition, two groups of data corresponding to silicon (Kα) on aluminium[12,13] were discarded because severe discrepancies arise between both groups.

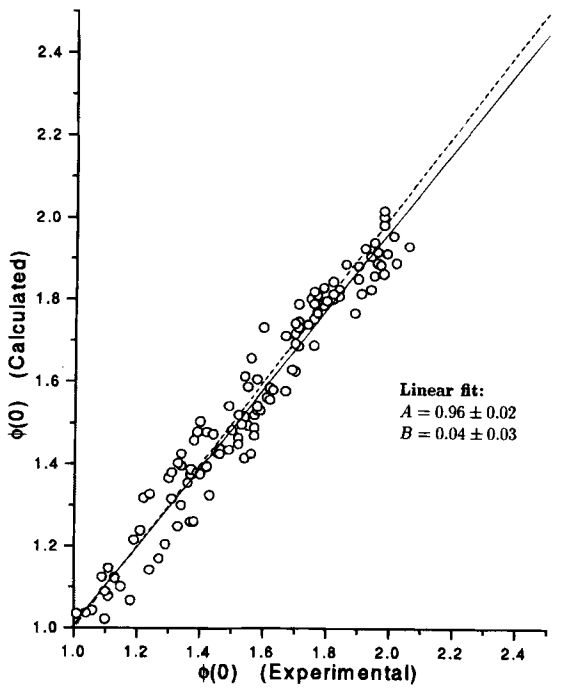

Figure 4. Comparison of experimental $\phi(0)$ values obtained by the tracer method with those predicted by Merlet.[7] Dotted line, $\phi(0)_{calc} = \phi(0)_{exp}$; solid line, linear fit.

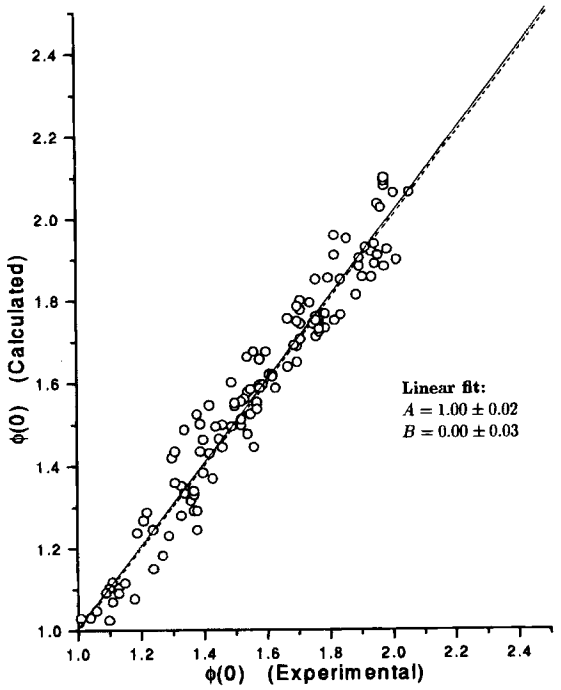

Figure 6. Comparison of experimental $\phi(0)$ values obtained by the tracer method with those predicted by this work. Dotted line, $\phi(0)_{calc} = \phi(0)_{exp}$; solid line, linear fit.

The models for $\phi(0)$ considered in this work are those given by Tirira and Riveros,[4] Merlet[7] and Rehbach and Karduck.[8] In addition, a numerical evaluation of Eqn (2) was performed using the spectral distribution given by del Giorgio *et al.*[9]

Tirira and Riveros[4] obtained an expression for $\phi(0)$ from Eqn (2) by approximating $d\eta/dU$ by a constant value and supposing that all the backscattered electrons have enough energy to produce ionizations. Merlet[7] developed an expression for $d\eta/dU$ and obtained a formula for $\phi(0)$, performing an optimization of certain parameters to achieve better agreement between calculated and experimental values. The model proposed by Rehbach and Karduck[8] is a fit to Monte Carlo data.

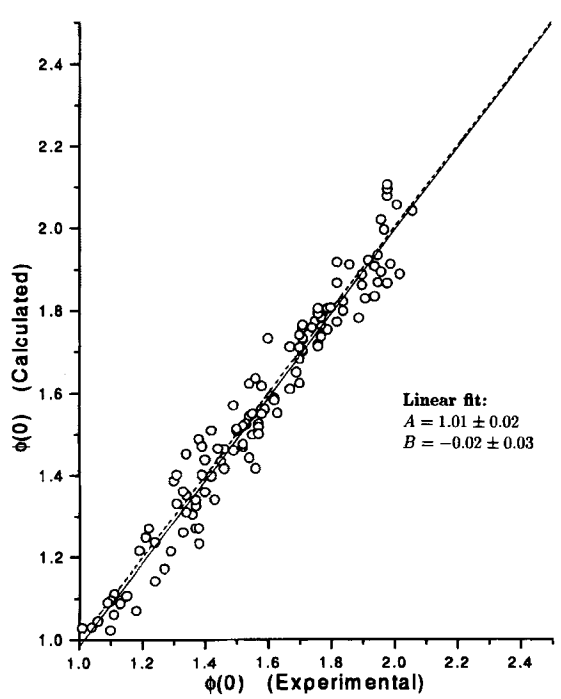

Figure 5. Comparison of experimental $\phi(0)$ values obtained by the tracer method with those obtained by integrating Eqn (2) using the spectral distribution of backscattered electrons given by del Giorgio *et al.*[9] Dotted line, $\phi(0)_{calc} = \phi(0)_{exp}$; solid line, linear fit.

The $\phi(0)$ values calculated with the present approximation and with the other models are plotted against experimental data in Figs 2–6. The dispersion of the points around a straight line of slope 1 shows the accuracy of the model considered. In order to give a measure of this accuracy, a linear fit was performed for each model; the resulting values for the slope A and the intercept B show the closeness of the model to a straight line of slope 1 and intercept 0.

From the analysis of Figs 2–6 it can be observed that the Tirira and Riveros model overestimates in general the value of $\phi(0)$, especially for overvoltages less than 2

Table 1. Mean values and root mean square errors for the distribution of ratio between calculated and experimental values, $\phi(0)_{calc}/\phi(0)_{exp}$, for the surface ionization

Model for $\phi(0)$	Mean value	σ
Rehbach and Karduck[8]	1.004	0.042
Tirira and Riveros[4]	1.064	0.086
Merlet[7]	0.990	0.040
Integral expression[a]	0.992	0.039
This work	1.004	0.042

[a] The integral expression was evaluated with the spectral distribution given by del Giorgio *et al.*[9]

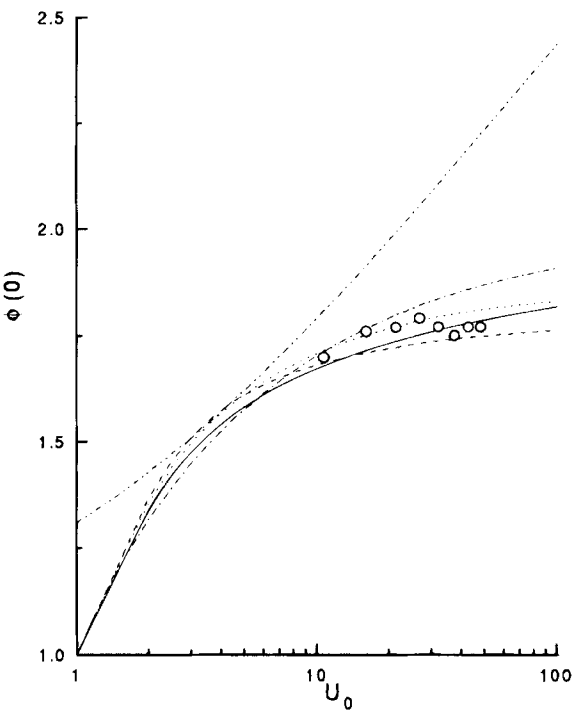

Figure 7. Variation of the $\phi(0)$ values for Cu Lα in a Co matrix obtained with the analytical expressions of Rehbach and Karduck[8] (—·—), Tirira and Riveros[4] (—··—), Merlet[7] (···), del Giorgio *et al.*[9] (——) and this work (— —). The circles represent experimental values.[7]

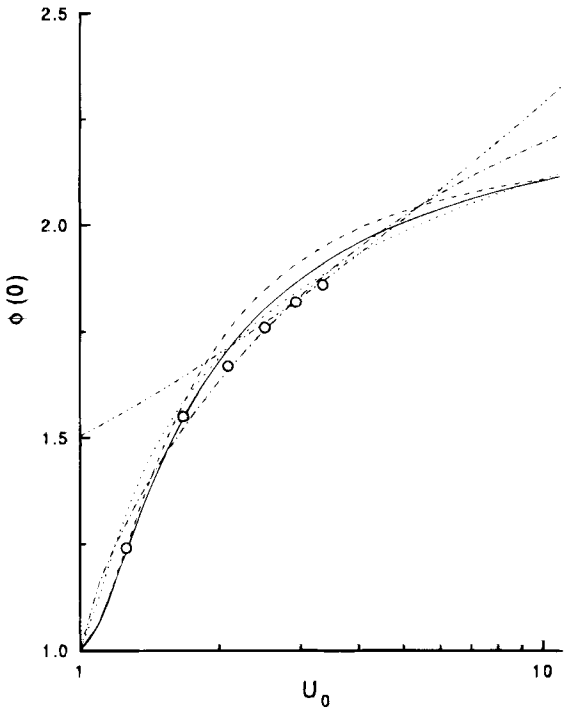

Figure 9. Variation of the $\phi(0)$ values for Au Lα in a Pt matrix obtained with the analytical expressions of Rehbach and Karduck[8] (—·—), Tirira and Riveros[4] (—··—), Merlet[7] (···), del Giorgio *et al.*[9] (——) and this work (——). The circles represent experimental values.[7]

and greater than 20. Tirira and Riveros noticed this and recommended the use of the spectrum $d\eta/dU$ for overvoltages below 2. Although the model presented in this work shows slightly better values for the parameters A and B and their errors, it is difficult to decide which approximation for $\phi(0)$ is the best given the uncertainties involved.

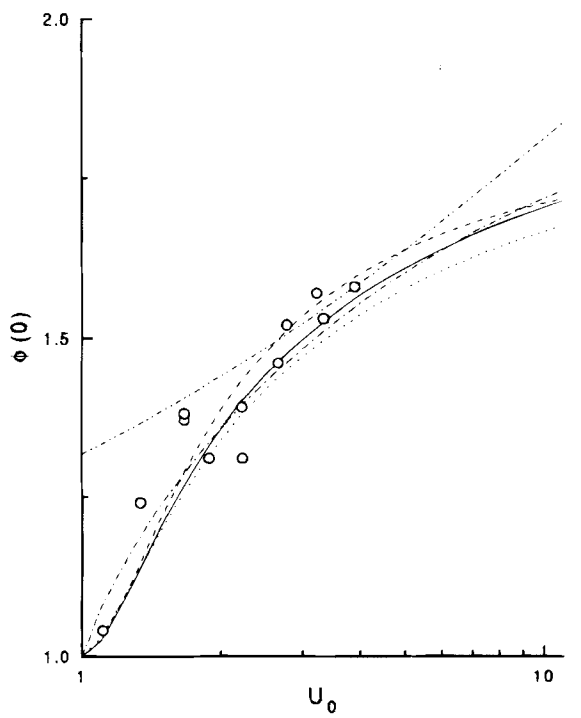

Figure 8. Variation of the $\phi(0)$ values for Cu Kα in an Ni matrix obtained with the analytical expressions of Rehbach and Karduck[8] (—·—), Tirira and Riveros[4] (—··—), Merlet[7] (···), del Giorgio *et al.*[9] (——) and this work (——). The circles represent experimental values.[7,14]

In order to obtain a better estimation of the accuracy of each model, the mean value of the ratio between calculated and experimental values, $\phi(0)_{calc}/\phi(0)_{exp}$, was assessed for each model, along with its root mean square error σ. The results are shown in Table 1.

From the analysis of Table 1, it can be seen that all the models assessed behave in a similar way, except for that given by Tirira and Riveros,[4] which presents the greatest deviation. The predictions of Eqn (2) with the spectral distribution given by del Giorgio *et al.*[9] present a slightly smaller deviation from experimental data.

In Figs 7–9, $\phi(0)$ vs U_0 curves are presented, comparing all the considered models for several characteristic lines in different matrices. These plots also show that the analyzed expressions behave in a very similar way, except for the expression of Tirira and Riveros,[4] validity of which is limited to a range of overvoltages.

CONCLUSION

The model for surface ionization proposed in this work has the advantage of simplicity and shows good agreement with experimental data. This model is not a fit to experimental data and involves no mathematical optimization. For this reason, it is expected to predict $\phi(0)$ properly for samples and experimental conditions different from those considered in this work.

Another advantageous feature of the new model is its capability of assessing $\phi(0)$ with different expressions for the distribution of backscattered electrons and for the ionization cross-section. By choosing more realistic models for $d\eta/dU$ and $Q(U)$, better results for $\phi(0)$ might be obtained.

Finally, uncertainties in the experimental values seem to be too large to decide which of the different models considered in this work has a better performance. For this reason, smaller errors in experimental determinations are necessary.

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