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Spectral Distribution of Backscattered Electrons: Application to Electron Probe Microanalysis

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The parameters ϕ_0 and γ_0 of the Gaussian model for the depth distribution of characteristic x-ray production $\phi(\rho z)$ were evaluated using an analytical expression for the energy distribution of backscattered electrons. The expressions obtained were compared with those which do not take into account this distribution. A test of the usefulness of both models was performed for microanalysis corrections.

INTRODUCTION

In quantitative electron probe microanalysis (EPMA), the concenration c_i of an element i in the specimen is related to the corresponding ratio K_i between the intensity of characteristic x-rays emerging from the sample and that from a standard of known composition:

$$K_i = \frac{c_i^s \int_0^\infty \phi_i^s(\rho z) \exp(-\mu_i^s \operatorname{cosec}\psi \rho z) \mathrm{d}(\rho z)}{c_i^{st} \int_0^\infty \phi_i^{st}(\rho z) \exp(-\mu_i^{st} \operatorname{cosec}\psi \rho z) \mathrm{d}(\rho z)} \quad (1)$$

where ψ is the take-off angle and μ_i is the mass absorption coefficient to the observed line of element i. Superscripts st and s refer to the standard and to the sample, respectively.

Packwood and Brown[1] developed a Gaussian model for $\phi(\rho z)$ from physical considerations:

$$\phi(\rho z) = \gamma_0 \exp[-(\alpha \rho z)^2]\left[1 - \left(\frac{\gamma_0 - \phi_0}{\gamma_0}\right) \exp(-\beta \rho z)\right] \quad (2)$$

which requires an accurate knowledge of the parameters α, β, ϕ_0 and γ_0. Tirira and Riveros[2] showed that the parameters γ_0 and ϕ_0 can be described by

$$\phi_0 = 1 + \frac{2}{Q(U_0)} \int_1^{U_0} Q(U) \frac{\mathrm{d}\eta}{\mathrm{d}U} \mathrm{d}U \quad (3)$$

and

$$\gamma_0 = \frac{2 \int_1^{U_0} Q(U) \mathrm{d}U}{Q(U_0) \int_1^{U_0} \mathrm{d}U} + \frac{2}{Q(U_0)} \int_1^{U_0} Q(U) \frac{\mathrm{d}\eta}{\mathrm{d}U} \mathrm{d}U \quad (4)$$

where U is the overvoltage, U_0 is the incidence overvoltage, $Q(U)$ is the ionization cross-section and $\mathrm{d}\eta/\mathrm{d}U$ is the energy distribution of backscattered electrons.

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Equations (3) and (4) were approximated by considering a backscattered electron distribution independent of the overvoltage U, in such a way that its integral between 1 and U_0 is equal to the fraction of backscattered electrons η:

$$\phi_0{}^a = 1 + \frac{\eta U_0 \ln(U_0)}{(U_0 - 1)} \quad (5)$$

$$\gamma_0{}^a = (1 + \eta) \frac{U_0 \ln(U_0)}{(U_0 - 1)} \quad (6)$$

These approximate expressions have the advantage of simplicity, giving very good results over a wide range of incidence overvoltages, as was shown in other papers.[3,4] It can be seen that for the limiting case $U_0 \to 1$, the parameters $\phi_0{}^a$ and $\gamma_0{}^a$ given by Eqns (5) and (6) take the value $1 + \eta$.

As U_0 approaches 1, the ionization distribution in a thick sample becomes a superficial one, producing the same intensity as in the thin isolated layer with respect to which the function $\phi(\rho z)$ is normalized; therefore, $\phi(0) = \phi_0$ would have to take the value 1.

Let us now consider the ideal problem of an infinite sample within which a pulse of monoenergetic electrons with an isotropic initial distribution of velocities is originated at a given point. The solution for this problem is a Gaussian spatial distribution[5] whose width increases when the mean electron energy decreases. The ionization distribution associated with such a distribution of electrons is the convolution of the electron distribution with the ionization cross-section at each energy.

The distribution given by Eqn (2), which approximates such a convolution in the actual case, was constructed by taking the electron distribution at a mean energy and multiplying it by the ionization cross-section at this energy, i.e. the ionization distribution given by Eqn (2) is proportional to the electron distribution at a certain instant of its evolution.

Observing Eqn (2), it can be seen that the right-hand side becomes proportional to an instantaneous electron distribution for the ideal problem in the limiting case $\beta \to \infty$, the parameter γ_0 representing the ionizations in the surface layer of the ideal case. In the limiting case

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$U_0 \to 1$ for this ideal problem, the ratio of the ionizations produced within the layer where the pulse of electrons is deposited to those produced within an isolated layer must take the value 1, and therefore γ_0 would also have to take the value 1.

From these considerations, it can be seen that Eqns (5) and (6) overestimate the parameters ϕ_0 and γ_0 at low incidence overvoltages; we shall now see what we should expect for high U_0.

According to the available experimental spectra[6] of backscattered electrons, it can be seen that most backscattered electrons leave the sample with overvoltages close to U_0, approaching this value as the atomic number increases. On the other hand, for high overvoltages, the ionization cross-section is considerably lower than its maximum value, which occurs around $U = 2$. Therefore, when the incident beam is very energetic ($U_0 \gg 1$), most of the backscattered electrons escape with an overvoltage for which the ionization cross-section is substantially lower than its maximum value.

As a result, it can be seen that the greater the atomic number of the sample and the higher the incidence overvoltage, the greater is the overestimation of ϕ_0 and γ_0 by Eqns (5) and (6) because, as in these equations a distribution of backscattered electrons independent of the overvoltage is assumed, too high a weight is assigned to the region of low overvoltages, giving values greater than that predicted by Eqns (3) and (4).

In order to evaluate Eqns (3) and (4) without approximations, it is necessary to know the distribution $d\eta/dU$. According to a previous paper,[7] this distribution can be expressed as

$$\frac{d\eta(p)}{dp} = \frac{\eta p}{\lambda^2} \exp(-p/\lambda) \tag{7}$$

where

$$\lambda = AZ^{-0.5} + B \tag{8}$$

with $A = 0.907 \pm 0.012$ and $B = -0.012 \pm 0.006$. The variable p is related to the incident electron energy, E_0, and to the backscattered electron energy, E:

$$p = 1 - E/E_0 \tag{9}$$

The expression given in Eqn (7) for the spectrum of backscattered electrons has shown good agreement with the experimental results given by Darlington[6], except for high atomic numbers, for which the experimental spectra show a small shift in the position of the maximum towards U_0. This shift should be taken into account by means of a diminution of the corresponding λ values.

The integrals given by Eqns (3) and (4) were solved numerically by using Eqns (7), (8) and (9). Thus, expressions for ϕ_0 and γ_0 which take into account the spectral distribution of backscattered electrons were obtained; these expressions will be referred as ϕ_0^s and γ_0^s.

RESULTS

The parameter λ

In order to correct the deviations in the spectra of backscattered electrons for high atomic numbers mentioned in the Introduction, a term which increases λ values only for high atomic numbers was added to Eqn (8). For simplicity's sake, a function $aZ^n + b$ was chosen. The coefficients a, b and n were fitted in order to fulfil the following conditions: the average of the λ values corresponding to the best fittings to Darlington's[6] experimental gold spectra must agree with the corresponding value given by the corrected version of Eqn (8); $\lambda(Z)$ must be a decreasing function even for $Z = 92$; and the corrected expression for λ must give the same results as the uncorrected expression for $Z = 13$, since in the region of low and medium atomic numbers the calculated spectra agree with the experimental data. Finally, the most convenient expression was found to be linear in Z:

$$\lambda = \lambda_0 + 0.00058\ Z - 0.00755 \tag{10}$$

where λ_0 represents the uncorrected λ value.

In Fig. 1 both expressions for λ are plotted. Good agreement for low and medium atomic numbers can be observed; on the other hand, for $Z > 50$ the corrected expression is greater than the uncorrected expression (more than 10%), remaining a decreasing function of Z. The λ values obtained for the Darlington spectra were also plotted, showing a better agreement with the corrected λ values than with the uncorrected values.

Comparison of the parameters γ_0^a and ϕ_0^a with γ_0^s and ϕ_0^s

In order to evaluate the parameters ϕ_0 and γ_0, two tests were carried out. First, plots of these parameters *vs.* the incidence overvoltage were compared for both models, particularly observing the trend for high and low U_0. In

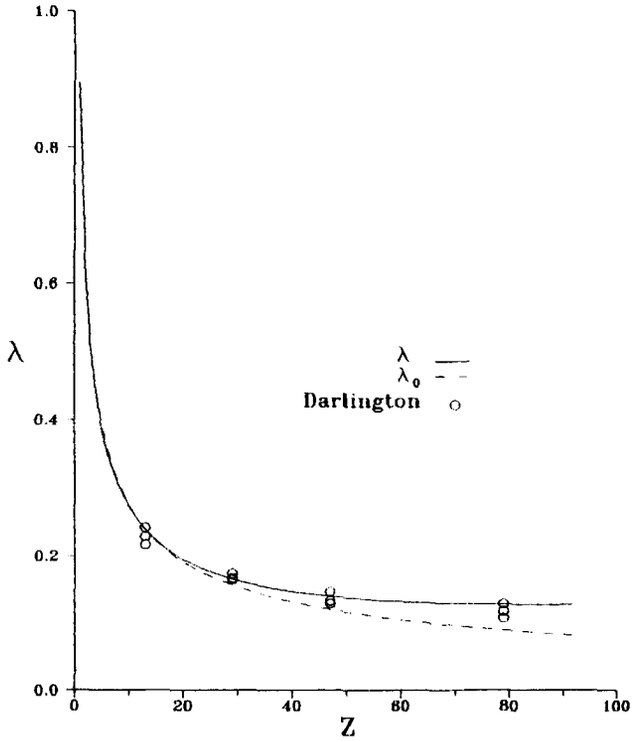

Figure 1. Original and corrected λ parameter as a function of the atomic number Z. The λ values obtained for Darlington spectra were also plotted.

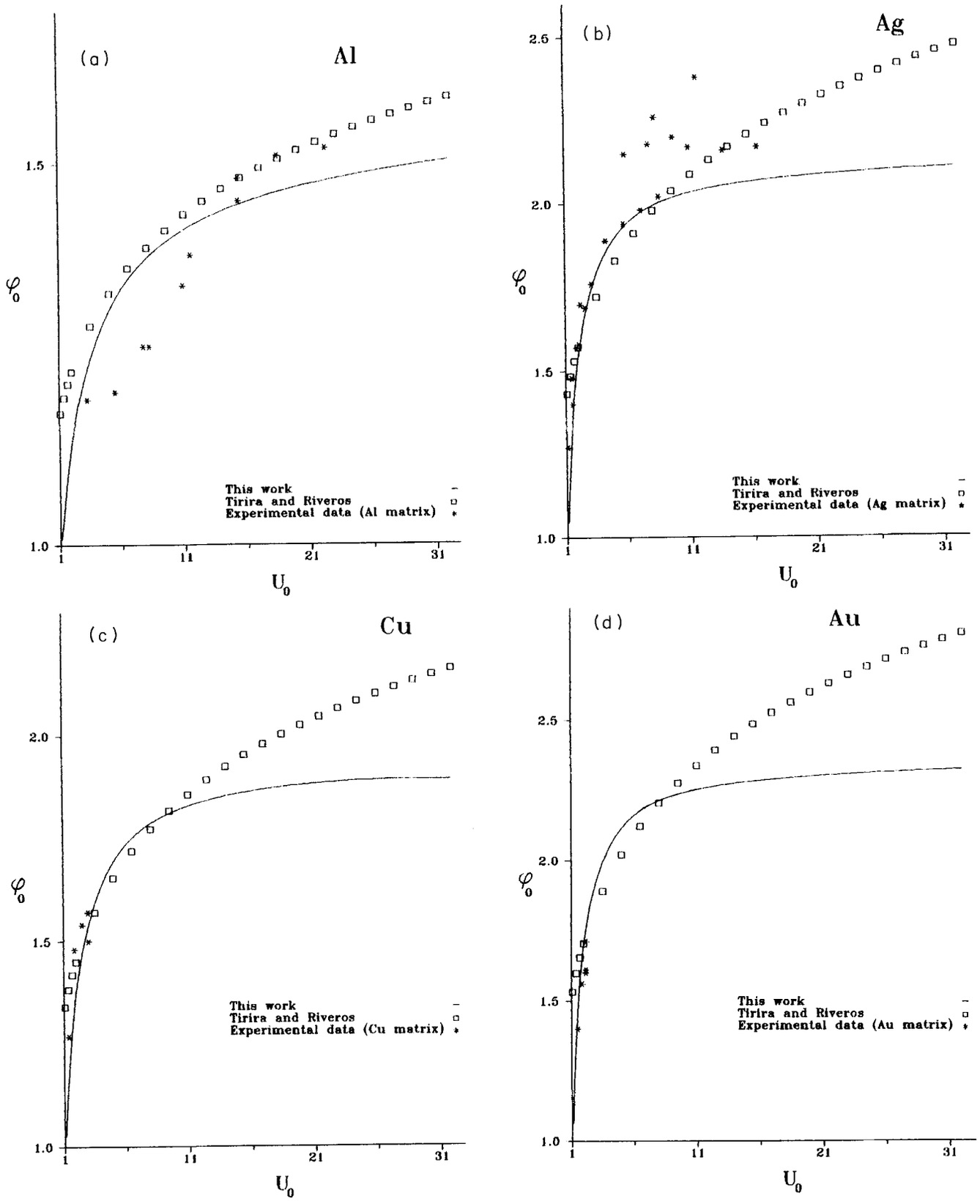

Figure 2. (a) ϕ_0^s and ϕ_0^a as a function of the incidence overvoltage U_0 for an aluminium matrix, (b) for a silver matrix, (c) for a copper matrix and (d) for a gold matrix. Some experimental data were also plotted.

addition, γ_0^a, ϕ_0^a, γ_0^s and ϕ_0^s values were compared with experimental data of ϕ_0 and γ_0.[1,8–13]

The first test gives the most important conclusions. Plots of ϕ_0 and γ_0 *vs.* U_0 for both models and four pure samples are shown in Figs 2 and 3. Here, the observations made in the Introduction can be verified: in the limiting case $U_0 \to 1$, ϕ_0^a and γ_0^a take the value $1 + \eta$, while ϕ_0^s and γ_0^s take the value 1, as expected. On the

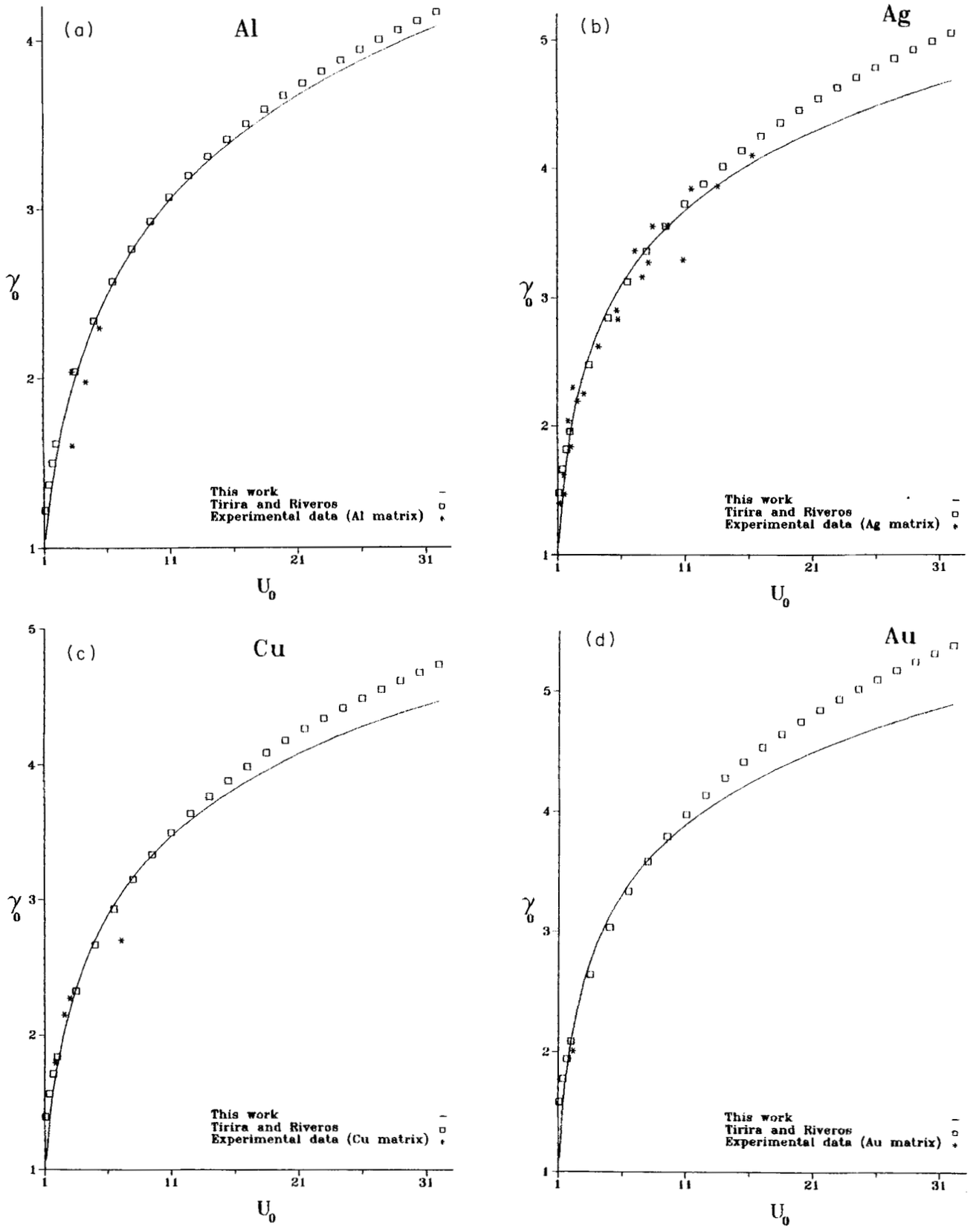

Figure 3. (a) γ_0^s and γ_0^a as a function of the incidence overvoltage U_0 for an aluminium matrix, (b) for a silver matrix, (c) for a copper matrix and (d) for a gold matrix. Some experimental data were also plotted.

other hand, these plots show how the expressions for ϕ_0^s and γ_0^s correct the overvaluation of ϕ_0^a and γ_0^a for high incidence overvoltages, as stated in the Introduction. Further this effect is more noticeable for high atomic numbers.

The differences between the approximated model and that proposed in this paper are much greater for ϕ_0 (Fig. 2) than for γ_0 (Fig. 3). This can be easily under-

stood from Eqns (3), (4), (5) and (6), since the relative difference between the two models for ϕ_0 as a function of U_0 is greater than the corresponding difference for γ_0.

In Figs 2 and 3 some experimental data are also plotted, showing a large dispersion; therefore, it is impossible to decide which of the models approaches them more closely. It just can be seen that in the plots of ϕ_0 *vs.* U_0 (Fig. 2), for very low U_0 values the experimental data take values lower than the corresponding values for $\phi_0{}^a$, as was discussed above.

In order to carry out the second test, $\phi_0{}^a$ and $\phi_0{}^s$ values were plotted against the corresponding experimental values (Fig. 4). A similar plot for γ_0 was not performed because this parameter is less sensitive to the differences between both models, as was stated above. This test gave moderate results (r.m.s. 6.5% for both models with respect to experimental data), since errors in the experimental data may mask the improvement introduced when considering the distribution of backscattered electrons. For example, according to data published by Packwood and Brown,[1] for the Si Kα line in a silver matrix, a unique ϕ_0 value of 2.17 is given for incidence energies of both 30 and 20 keV.

Application to microanalysis

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 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 depart from the mean value by more than three times the r.m.s. error are rejected.

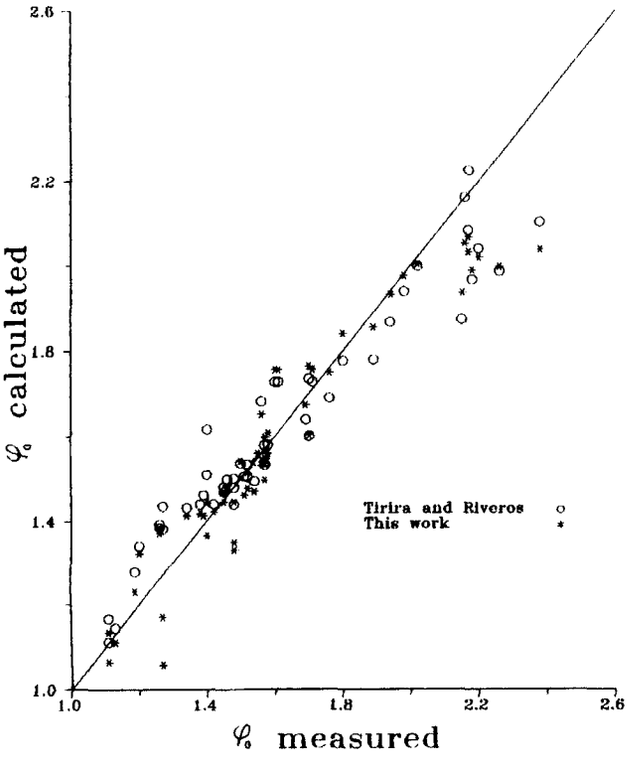

Figure 4. $\phi_0{}^s$ and $\phi_0{}^a$ *vs.* experimental ϕ_0 values.

In order to evaluate the application of Eqn (7) for the distribution of backscattered electrons to microanalysis, a set of 680* experimental determinations compiled by Bastin *et al.*[14] was used. For mass absorption coefficients the expression proposed by McMaster *et al.*[15] was used, since this was obtained from experimental measurements without mathematical optimization for microanalysis (which would reduce its reliability to the set of samples for which the optimization was performed). On the other hand, as was stated by McMaster *et al.*, this expression is not valid for low energies; therefore, we used the coefficients chosen by Bastin *et al.*[14] for energies lower than 1.6 keV, some of those tabulated by Henke *et al.*[16] and the remainder given by Bastin *et al.*[17] since the latter measured mass absorption coefficients for low energies.

The expression for β developed by Tirira *et al.*[3] was used, whereas for the parameter α the expression proposed by Packwood and Brown[1] was chosen; for the fluorescence correction factor the model given by Reed[18] was used; finally, the model for the mean excitation energy developed by Brizuela and Riveros[19] from measurements of the stopping power, which takes into account shell effects, was used. Further, it is necessary to choose the backscattering coefficient η for normalizing the spectra; an expression for η has been derived previously[7] as an intermediate result; it shows the same deviations as the original expression for $d\eta/dU$ does for high atomic numbers. We considered it unnecessary to optimize η (as was done with $d\eta/dU$ by means of λ), since a number of workers[20–23] carried out measurements of η from which analytical expressions were fitted. For these reasons, the expression fitted by Reed[24] from experimental data was used. However, the performance of the expression for η given by del Giorgio *et al.*[7] was also tested; all the results are given in Table 1. As expected, this expression produces worse results, although the r.m.s. error is still below 3%.

The spectra of backscattered electrons were developed for pure samples, however an expression taking into account multi-element effects was suggested:[7] although the most rigorous method would be to average the spectra from each element, a tentative approximation is to calculate the spectrum for a pure sample with an average atomic number. Moreover, this should be an atomic average, since the number of scattering centres (atoms) per unit volume is the magnitude involved.

From Table 1, it can be seen that the suggested approximation does not give very good results, especially regarding the mean value and the symmetry with respect to unity; as can also be observed, the calculated

* Although Bastin *et al.* refer to 681 data, in fact there are only 680, because data Nos 57 and 58 are identical.

Table 1. Performance of the parameters ϕ_0 and γ_0 in a set of 680 microanalysis measurements by approximating this distribution by means of the backscattering coefficient (a) and by considering the spectral distribution of backscattered electrons (s)[a]

ϕ_0 and γ_0	η	Backscattering average	σ	$\langle K'/K \rangle$	Symmetry with respect to 1	Real symmetry	Rejected
s	Ref. 24	1, atomic	0.034	0.982	0.36	0.90	36
s	Ref. 24	1, mass	0.026	1.007	1.74	0.91	51
s	Ref. 24	2, mass	0.025	1.000	0.87	0.87	56
a	Ref. 24	mass	0.025	1.001	0.88	0.84	64
s	Ref. 7	2, mass	0.029	1.002	1.17	0.97	46
Bastin *et al.*[14]			0.028	1.004	1.73	1.28	41
PAP			0.027	0.999	1.05	1.14	39
Quadrilateral			0.027	1.000	1.17	1.17	24

[a] 1 refers to the assumption of spectra for pure samples with average atomic numbers, and 2 refers to the average of spectra from each element. Two models for the coefficient η used to normalize the spectral distribution were tested. Three well known correction models were also compared (last three rows).

K' values are generally below the experimental values when the atomic average is considered, whereas the opposite occurs with the mass average. Further, although the histogram is narrower in the second case, this occurs at the expense of rejecting a larger number of samples.

For these reasons, the approximation was avoided and the averages of spectra were taken. This average of spectra is a mass average, since the results are much better than those for the atomic average, in contrast to the expected behaviour.[7] A considerable improvement in the results can be seen from Table 1, since both the mean value and the symmetry with respect to unity improve.

It can be observed from Table 1 that although $\phi_0{}^a$ and $\gamma_0{}^a$ in addition to $\phi_0{}^s$ and $\gamma_0{}^s$ produce fairly similar results, a smaller number of samples are rejected in the latter case. Finally, in order to allow a global comparison, three well known correction models[14,25,26] are included in Table 1 using all the parameters as in the original papers and the evaluation criteria mentioned above. All models gave similar results, uncertainties being masked by experimental errors.

CONCLUSIONS

This paper shows the good performance of the proposed expression[7] for the energy distribution of backscattered electrons in microanalysis. This good performance is especially noted in the trends of $\phi_0{}^s$ and $\gamma_0{}^s$ for high and low incidence overvoltages, retaining the good results given by $\phi_0{}^a$ and $\gamma_0{}^a$ when they are tested with the set of samples compiled by Bastin *et al*,[14] whose main feature is high absorption. A set of data with smaller experimental errors might be of help for revealing the improvements introduced by $\phi_0{}^s$ and $\gamma_0{}^s$.

The comparison with experimental data for ϕ_0 and γ_0 gives good results when the energy distribution of backscattered electrons is taken into account and also when it is not considered. On the other hand, these comparisons do not favour any of both models, for two reasons: the errors in the experimental data for ϕ_0 and γ_0 are too large to appreciate any differences, and we do not have experimental values for either low or high incidence overvoltages, which are precisely the regions where introduced modifications are important.

The complete solution of Eqns (3) and (4) using an analytical expression for the spectrum of backscattered electrons has great importance, since in this way physical aspects are taken into account more carefully. A comparison with more accurate experimental data for ϕ_0 and γ_0 over a wider range of incidence overvoltages would be of interest, in order to study the error introduced when using Eqns (5) and (6) instead of solving Eqns (3) and (4) without approximations.

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