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Evaluation of the Main Atomic Number, Absorption and Fluorescence Correction Models in Quantitative Microanalysis

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The principal $\mathscr{Z}\mathscr{A}\mathscr{F}$ correction models have been tested for a set of 471 experimental values from heavy element binary specimens ($Z > 12$) and another set of 116 determinations for oxides, both compiled by Love *et al.* New fluorescence correction models have been developed, based on a Gaussian distribution of ionizations. The atomic number, absorption and fluorescence correction models corresponding to this distribution are the best fitting ones.

INTRODUCTION

When a collimated electron beam enters a specimen, the intensity of characteristic radiation generated for line j of element i, may be written as

$$I_g^{ij} = n_0^{ij} \int_0^{\infty} \phi^{ij}(\rho z)\, \mathrm{d}(\rho z) \tag{1}$$

where $\phi^{ij}(\rho z)$ is the depth distribution of j characteristic production for element i (ρz is the mass depth), normalized with respect to the number n_0^{ij} of ionizations of the same type generated in an isolated layer of identical composition (Fig. 1).

If ψ is the take-off angle, the emerging intensity results:

$$I_e^{ij} = \frac{\Delta\Omega}{4\pi} n_0^{ij} \int_0^{\infty} \phi^{ij}(\rho z)\, \mathrm{e}^{-\chi\rho z}\, \mathrm{d}(\rho z) \tag{2}$$

where $\chi = \mu$ cosec ψ, μ is the mass absorption coefficient of the specimen to the observed radiation and $\Delta\Omega$ is the solid angle subtended by the detector. In order to avoid factors depending on the particular detector, geometry and atomic properties, this intensity is compared with that of a standard of known composition:

$$K = \frac{I_e}{I_e^0}$$

(henceforth the indices i and j are omitted in order to simplify the notation, and an index 0 will allways refer to the standard) As a rough approximation, we could say that this ratio corresponds to the value of the concentration C_i of the observed element in the specimen with respect to its concentration C_0 in the standard:

$$K = \frac{C_i}{C_0}$$

This approximation requires several corrections. Firstly, it should be noted that ionizations produced by incident electrons are not identically distributed in the sample and the standard; this effect, called the 'atomic number effect,' is corrected by a factor $\mathscr{Z}$. Secondly, radiation from the sample suffers an attenuation different to that from the standard, and an absorption correction factor $\mathscr{A}$ must be applied. Finally, there may exist an element excited by the incident electrons that emits photons with sufficient energy to ionize in turn the element of interest, thus giving an enhancement of primary radiation, also possible with photons from the continuum. The difference in this fluorescence enhancement between the specimen and standard is corrected by a factor $\mathscr{F}$. Then,

$$K = \frac{C_i}{C_0} \mathscr{Z}\mathscr{A}\mathscr{F}$$

$\mathscr{A}$ may take values very distant from unity, so that it is the most important factor; $\mathscr{Z}$ varies between 0.8 and 1.2 and $\mathscr{F}$ usually takes values very close to unity.

ABSORPTION CORRECTION

The behaviour of the absorption correction will be evaluated making use of the function

$$f(\chi) = \frac{\int_0^{\infty} \phi(\rho z)\, \mathrm{e}^{-\chi\rho z}\, \mathrm{d}(\rho z)}{\int_0^{\infty} \phi(\rho z)\, \mathrm{d}(\rho z)} \tag{3}$$

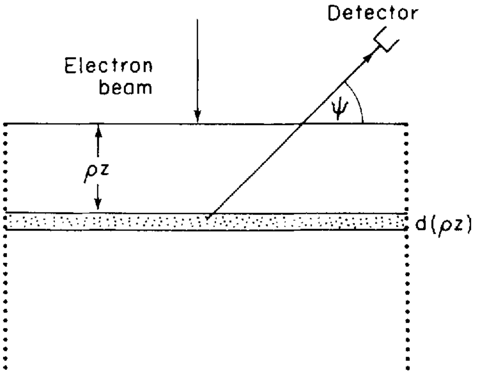

Figure 1. Characteristic x-ray production at depth ρz from a layer d(ρz).

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so that $\mathscr{A}$ is the ratio of $f(\chi_i)$ evaluated for the specimen and for the standard. For this purpose several expressions for $\phi(\rho z)$ are taken into account:

(a) Philibert[1] obtained $f(\chi)$ assuming an exponential attenuation of electrons [with the additional simplification $\phi(0)=0$]:

$$\phi(\rho z) \propto e^{-\sigma\rho z}(1-e^{-\sigma\rho z/h})$$

where σ is the Lenard coefficient,[2] which is essentially dependent on the energy of the incident electrons, and h is related to the mean ionization depth. This distribution produces

$$f(\chi)=\frac{1}{\left(1+\frac{\chi}{\sigma}\right)\left(1+\frac{h}{1+h}\cdot\frac{\chi}{\sigma}\right)}$$

This expression is one of the most commonly used in the computation programs for microanalysis, generally employing the parameters σ and h proposed by Heinrich:[3]

$$\sigma=\frac{4.5\times 10^5}{E_0^{1.65}-E_j^{1.65}}$$

$$h=1.2\frac{A}{Z^2}$$

where E_0 is the incident electron energy, E_j the excitation energy for the shell of interest and A and Z are the atomic weight and number, respectively.

(b) Bishop[4] suggested a uniform distribution function centred in the mean depth $\bar{z}$ of x-ray generation (square model); thus, the following expression is obtained:

$$f(\chi)=\frac{1-\exp(2\chi\rho\bar{z})}{2\chi\rho\bar{z}}$$

The value of $\bar{z}$ is assessed for the Philibert distribution:

$$\rho\bar{z}=\frac{2h+1}{h+1}\cdot\frac{1}{\sigma}$$

and with an expression obtained by Love and Scott[5] based on Monte Carlo simulations:

$$\rho\bar{z}=\frac{A}{Z}\cdot\frac{G(\eta)\ln U_0}{H(\eta)+\ln U_0}$$
$$\times(0.787\times 10^{-5}\,J^{0.5}\,E_0^{1.5}+0.735\times 10^{-6}\,E_0^2)$$

where G and H are polynomials, η is the electron backscattering coefficient, U_0 is the overvoltage E_0/E_j, and J is the mean excitation energy.

(c) Packwood and Brown[6] proposed the following expression for the distribution of characteristic x-ray production:

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

in which

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

where J is the mean excitation energy.

Tirira *et al.*[7] improved the parameter β and obtained better results than those given in previous publications[6,8] with the following expression:

$$\beta=109\,000\frac{Z^{1.5}}{(E_0-E_j)A}$$

and the original expressions for γ_0 and ϕ_0 were improved by theoretical calculations by Tirira and Riveros,[9] who arrived at

$$\gamma_0=\frac{U_0\ln U_0}{U_0-1}(1+\eta)$$

$$\phi_0=1+\eta\frac{U_0\ln U_0}{U_0-1}$$

Then, substituting in Eqn (3), we have

$$f(\chi)=\frac{R\left(\frac{\chi}{2\alpha}\right)-\frac{\gamma_0-\phi_0}{\gamma_0}R\left(\frac{\chi+\beta}{2\alpha}\right)}{1-\frac{\gamma_0-\phi_0}{\gamma_0}R\left(\frac{\beta}{2\alpha}\right)}$$

where $R(x)$ is as specified in the Appendix.

ATOMIC NUMBER CORRECTION

This factor may be expressed in terms of the ionization cross-section Q_j of the j shell of element i:

$$\mathscr{Z}=\frac{R_j\int_{E_0}^{E_j}Q_j/S\,\mathrm{d}E}{R_j^0\int_{E_0}^{E_j}Q_j/S_0\,\mathrm{d}E}$$

where S is the stopping power and R takes into account the loss of ionization caused by electron backscattering. Since Q_j/S varies smoothly with E, it is usual to replace the integrals by the integrands evaluated for a certain energy EM between E_j and E_0. Thus we obtain

$$\mathscr{Z}=\frac{R_i}{R_j^0}\cdot\frac{\bar{S}_0}{\bar{S}} \tag{4}$$

Different expressions exist for $\overline{EM}$ that may be chosen for the calculation of $\bar{S}_0$ and $\bar{S}$.

It is also possible to obtain an expression for $\mathscr{Z}$ making use of the distribution function $\phi(\rho z)$. According to Eqn (1),

$$\mathscr{Z}=\frac{\int_0^\infty\phi(\rho z)\,\mathrm{d}(\rho z)}{\int_0^\infty\phi_0(\rho z)\,\mathrm{d}(\rho z)} \tag{5}$$

This expression will only be evaluated for the Gaussian distribution suggested by Packwood and Brown[6] with the improved coefficients mentioned above, yielding a 'Gaussian atomic number correction,' $\mathscr{Z}_\sigma$.

However, in Eqn (4) several parameters will be employed instead for the evaluation of the 'conventional' model $\mathscr{Z}_c$, taking into account various expressions[10,11] for the backscattering factor R with values for the electron backscattering coefficient η published by Bishop,[12] and for the stopping power S,[11,13,14] in which the models of Wilson[15] and Bloch[16] are used for the mean excitation energy. The corresponding expressions are given in the Appendix.

The parameters R and S for the specimen are obtained by computing a mean value from those corresponding to each element, weighted with the respective concentrations.

FLUORESCENCE CORRECTION

Fluorescence enhancement is taken into account by a factor $1+I_f/I_e$, where I_f is the secondary radiation emerging from the specimen and I_e the primary radiation, given by Eqn (2). In order to find I_f it is assumed that in a layer $d(\rho z)$ at depth ρz, the amount of radiation of element s capable of exciting the j shell of element i generated isotropically in all directions is $n_o^s\phi_s(\rho z)d(\rho z)$. The portion of these photons absorbed by the element i in the layer $d(\rho y)$ (see Fig. 2) between the directions θ and $\theta+d\theta$ is given by

$$\frac{1}{2}\sin\theta\,d\theta\exp(-\mu_s\rho y\sec\theta)C_i\mu_s^i\frac{d(\rho y)}{\cos\theta}$$

where μ_s^i and μ_s are the mass absorption coefficients of element i and the specimen to s radiation, respectively. Of these ionizations, only a fraction $(r_i-1)/r_i$ occurs in the j shell, and of all these, a fraction ω_i^j is converted into characteristic radiation. The portion of these photons that leaves the specimen towards the detector is $\exp[-\chi_i(\rho y+\rho z)]$, so the following equation is obtained:

$$I_f=\frac{1}{2}\cdot\frac{\Delta\Omega}{4\pi}\cdot C_i\cdot\frac{r_i-1}{r_i}\cdot\omega_i^j\mu_s^in_0^s\int\int\int\phi_s(\rho z)\,d(\rho z)$$
$$\times\exp(-\chi_i\rho z)\exp[(\mu_s\sec\theta+\chi_i)\rho y]\,d(\rho y)\tan\theta\,d\theta$$

It should be noted that in the ratio I_f/I_e, n_0 must be evaluated by using Bethe's[17] ionization cross-section. I_f depends on which expression is used for $\phi_s(\rho z)$. Four of them will be considered here:

(a) An expression given by Criss and Birks[18] obtained from $\phi(\rho z)=G\,\Sigma\,d_n\exp(-b_n\rho z)$, where G is the generated primary radiation and d_n and b_n are specific for each specimen and experimental conditions:

$$\mathscr{F}=1+\frac{1}{2}C_s\omega_s^k\frac{r_i-1}{r_i}\cdot\frac{A_i}{A_s}\cdot\frac{\mu_s^i}{\chi_i}\cdot\frac{E_j^i\ln U_0^s}{E_k^s\ln U_0^i}\cdot\frac{f_s(0)}{f_i(0)}\cdot$$
$$\times\frac{\sum_{n=1}^{3}\frac{d_n}{b_n+\chi_i}\left[\frac{\mu_s}{b_n}\ln\left(1+\frac{b_n}{\mu_s}\right)+\frac{\mu_s}{\chi_i}\ln\left(1+\frac{\chi_i}{\mu_s}\right)\right]}{\sum_{n=1}^{3}\frac{d_n}{b_n+\chi_i}}$$

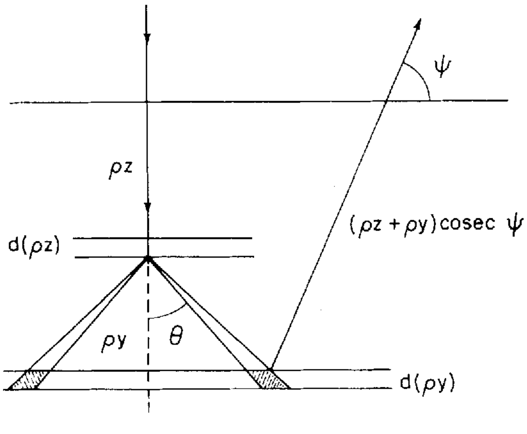

Figure 2. Generation and emission of secondary radiation.

Here ω_s^k is the fluorescence yield of element s of the k shell in question, A_i and A_s are the respective atomic weights and $f_l(\chi)$ is a function related to radiation absorption, here evaluated with the Gaussian distribution (see Appendix). The subscript l represents the element to which $\phi(\rho z)$ corresponds. This expression for $\mathscr{F}$ is almost independent of b_n and d_n, values for these coefficients are given in the Appendix.

(b) Reed[19] gave an expression in which an exponential attenuation for electrons $[\phi(\rho z)\propto e^{-\sigma\rho z}]$ is assumed, obtaining

$$\mathscr{F}=1+C_sJ(i)\left(\frac{U_0^s-1}{U_0^i-1}\right)^{1.67}\frac{\mu_s^i}{\chi_i}\left[\frac{\ln(1+x)}{x}+\frac{\ln(1+y)}{y}\right]$$

where $x=\chi_i/\mu_s$, $y=\sigma/\mu_s$ and $J(i)$ is a factor taking into account the fluorescence yields and the shells involved in the enhancement; this factor is tabulated in Reed's publications.

(c) If the Gaussian distribution for $\phi(\rho z)$ is used, the factor F becomes

$$\mathscr{F}=1+\frac{1}{2}C_s\cdot\frac{r_i-1}{r_i}\cdot\omega_s^k\cdot\frac{\mu_s^iA_i}{\chi_iA_s}\cdot\frac{E_j^i\ln U_0^s}{E_k^s\ln U_0^i}\cdot\frac{1}{f_i(\chi_i)}$$
$$\times\left\{\ln\frac{\chi_i+\mu_s}{|\chi_i-\mu_s|}f_s(\chi_i)+\frac{\gamma_0}{2\alpha}\bigg|_s\sqrt{\pi}\,S\left(1,\frac{p\mu_s}{2\alpha_s}\right)\right.$$
$$\left.-\frac{\gamma_0-\phi_0}{2\alpha}\bigg|_s\sqrt{\pi}\,S\left(1+\frac{p\beta_s}{2\alpha_s},\frac{p\mu_s}{2\alpha_s+p\beta_s}\right)\right\}$$

where $S(a,x)$ and p are given in the Appendix.

(d) A simplified expression for $\phi_s(\rho z)$ may be used; for example, taking $\phi_s(\rho z)\propto\delta(z-\bar{z})$, where δ is the Dirac delta function, i.e. assuming that all production of s radiation occurs at one single depth $\bar{z}$. In this way, the following expression for $\mathscr{F}$ is obtained:

$$\mathscr{F}=1+\frac{1}{2}C_s\omega_s^k\cdot\frac{r_i-1}{r_i}\cdot\frac{A_iE_j^i\ln U_0^s}{A_sE_k^s\ln U_0^i}\cdot\frac{f_s(\chi_i)}{f_i(\chi_i)}$$
$$\times\left\{\exp(-\chi_i\rho\bar{z})\left[\ln[(\chi_i+\mu_s)\rho\bar{z}]\right.\right.$$
$$\left.+\sum_{n=1}^{\infty}\frac{(-1)^n[(\mu_s-\chi_i)\rho\bar{z}]^n}{nn!}\right]$$
$$-\ln(\mu_s\rho\bar{z})-\sum_{n=1}^{\infty}\frac{(-1)^n(\mu_s\rho\bar{z})^n}{nn!}$$
$$\left.-\gamma[1-\exp(-\chi_i\rho\bar{z})]\right\}$$

where $\gamma=0.577216$ is Euler's constant. The value of $\bar{z}$ used here corresponds to the expression

$$\bar{z}=\frac{\int_0^\infty z\phi(\rho z)\,d(\rho z)}{\int_0^\infty\phi(\rho z)\,d(\rho z)}$$

in which $\phi(\rho z)$ is the Gaussian distribution.

PROCEDURE FOR EVALUATION OF THE DIFFERENT CORRECTION MODELS

The procedure usually followed in order to evaluate the accuracy of the correction models consists in studying

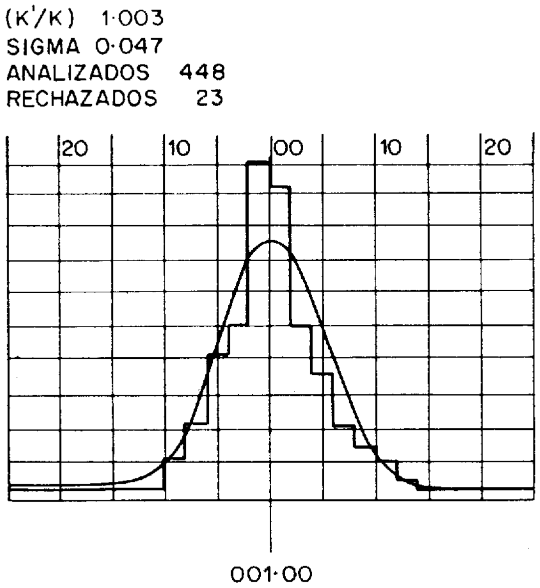

Figure 3. Histogram from samples with observed $Z > 11$ showing the results for the mean value of K'/K and standard deviation σ. Symmetry is calculated as the ratio of counts with $K'/K > 1$ to those with $K'/K < 1$.

the distribution of quotients between calculated intensity ratios K' and experimental K for a large set of specimens of known composition. The values of K'/K are arranged so as to construct a histogram in which dispersion represented by the standard deviation σ, closeness of its mean value to unity and symmetry (ratio of counts with $K'/K > 1$ to those with $K'/K < 1$) are taken as evaluation criteria (see Fig. 3).

As mentioned above, the absorption correction presents the greatest variations, so the accuracy of its determination is very important. Although it has been the most studied, the existing models for the computation of $f(\chi)$ are not adequate for the whole range of possible values of χ, and fail especially in the high absorption region $[f(\chi) < 0.5]$, making difficult the determination of light elements ($Z \leq 12$) because they emit low-energy lines and therefore are not very piercing. In addition, in this energy range ($E < 1.2$ keV) the mass absorption coefficients are subject to considerable errors (about 10%). Owing to these difficulties, the efficiency of models was computed separately. For heavy elements 471 binary specimen data compiled by Love *et al.*[20] were used; for light elements the same workers[21] collected a set of binary oxide measurements in which the element of interest was oxygen.

Most of published evaluations for heavy elements reject 41 data from the original list, for according to Love *et al.*[22] their behaviour is anomalous with respect to the general trend when any parameter (e.g. overvoltage, take-off angle or concentration) is changed. In this work, the whole list of data was considered, and after applying the $\mathscr{X}\mathscr{A}\mathscr{F}$ correction a histogram was constructed, from which those values deviating from the general trend (more than 3σ from mean value) were excluded, assuming that the errors were exclusively experimental, so that the distribution of counts was a normal one.

When testing the behaviour of models on oxides, the complete list of binary oxides was considered, whereas in preceding works only those data measured with a JEOL JXA-50A microprobe ($\psi = 35°$) were taken into account, since the corresponding values for the same set of specimens obtained with a Cambridge Microscan I ($\psi = 20°$) were considered to be wrong.

For the oxygen lines, the mass absorption coefficients proposed by Ruste and Gantois[23] were used, except for Pb, where their value differs considerably from the experimental values, and was therefore replaced with one suggested by Robinson.[24]

In the evaluation of Eqn (4) for the conventional $\mathscr{X}$ factor, EM was chosen as the arithmetic mean value of E_j and E_0 for its simplicity and accuracy, i.e. $EM = (E_0 + E_j)/2$.

RESULTS AND DISCUSSION

As considered above, the $\mathscr{A}$ factor is the most important correction, so it has to be evaluated first. For this purpose, some models for $\mathscr{X}$ were utilized ($\mathscr{X}_G$ and some conventional ones) and also the fluorescence correction factor suggested by Reed.[19]

When evaluating $\mathscr{X}_G$, a certain dependence on the stopping power of both the sample and the standard appeared in the parameters α and α_0; in the case of the specimen this parameter was averaged using mass concentrations and also atomic fractions, and noticeable differences were found in the results.

The parameters R and S were also tested for atomic fractions, but the best results were always obtained when mass concentrations were used.

Table 1 shows that every model worsens on passing from heavy to light elements. In this range, conventional models of $\mathscr{A}$ do not behave well, since they show a marked tendency to overestimate K (generally symmetries greater than 3 and mean values greater than 1), except for model 10; this trend is opposite to that observed with heavy elements. On the other hand, $\mathscr{A}_G$ [absorption correction using the Gaussian expression for $\phi(\rho z)$] gives symmetries smaller than *ca* 2.

For heavy element analysis, the best fitting models were the Gaussian and Philibert's simplified models. This was to be expected because, if absorption was moderate, the same values for $f(\chi)$ were assessed with the respective models of $\phi(\rho z)$ (see Fig. 4). For high absorption ($\chi > 1000$ cm^2 g^{-1}), the values for $f(\chi)$ were different, and the performances of the two models were different for light elements.

Bishop's square model, in spite of its roughness, showed good results, particularly model 10, whose symmetry for light elements was 1.69.

Next, the different atomic number correction models were evaluated, with Reed's factor $\mathscr{F}$ and $\mathscr{A}_G$ (using Wilson's mean excitation energy), since the latter showed the best behaviour for both sets of specimens. Table 1 shows that for heavy elements, $\mathscr{X}_G$ with mass averaging was the best fitting model. The other models gave similar results among themselves, except those for the Love stopping power, with worse symmetry (models 16 and 17).

For oxide determinations, the histograms showed much greater asymmetry; the models utilizing Love's

Table 1. Evaluation of the different Z and A factors using Reed's F

						Heavy elements				Light elements			
Method	Model for $\phi(\rho z)$	Parameters	Atomic number correction model	Mean excitation energy	Averaging	Rejected data	$\overline{K'/K}$	Symmetry	$\sigma_0(\%)$	Rejected data	$\overline{K'/K}$	Symmetry	$\sigma_0(\%)$
1	Philibert simplified[1]	σ and h by Heinrich[3]	S: Bethe[17] R: Springer[10]	Duncumb–Dacasa	Mass	15	1.007	0.82	5.93	18	1.057	3.64	12.10
2			Gaussian	Wilson	Mass	41	1.004	0.96	4.56	—	—	—	—
3		σ and h by Love *et al.*[20]	S: Bethe R: Springer	Duncumb–Dacasa	Mass	13	0.982	0.40	4.60	14	1.058	4.05	9.19
4			Gaussian	Wilson	Mass	29	0.988	0.54	4.66	15	1.086	8.10	9.54
5	Bishop	$\overline{\rho z}$ by Philbert, σ and h by Heinrich[3]	S: Bethe R: Springer	Duncumb–Dacasa	Mass	21	0.980	0.41	4.62	—	—	—	—
6			Gaussian	Wilson	Mass	19	0.985	0.58	4.89	1	1.069	8.10	8.40
7		$\overline{\rho z}$ by Philbert,[1] σ and h by Leve *et al.*[22]	S: Bethe R: Springer	Duncumb–Dacasa	Mass	16	0.987	0.51	4.68	—	—	—	—
8			Gaussian	Wilson	Mass	14	0.993	0.72	4.82	3	1.057	5.05	7.90
9		$\overline{\rho z}$ by Love *et al.*[5]	S: Love[11] R: Love[11]	Bloch	Mass	18	0.989	0.57	4.51	1	1.041	2.89	7.33
10			S: Love R: Love	Bloch	Atomic	—	—	—	—	1	1.009	1.69	7.84
11			Gaussian	Wilson	Mass	16	0.994	0.74	4.92	1	1.071	6.00	7.74
12	Gaussian	Tirira *et al.*[9]	Gaussian	Wilson	Mass	23	1.004	1.01	4.77	0	1.023	2.03	6.83
13			Gaussian	Wilson	Atomic	22	1.005	1.17	4.87	0	1.004	1.12	7.18
14			S: Bethe R: Springer	Wilson	Mass	23	1.004	1.01	4.79	11	0.975	0.58	7.48
15			S: Bethe R: Love	Wilson	Mass	19	1.000	0.94	4.96	2	0.983	0.73	6.80
16			S: Love R: Springer	Bloch	Mass	22	1.010	1.67	4.89	2	0.998	0.96	6.46
17			S: Love R: Love	Bloch	Mass	24	1.001	1.81	4.86	0	1.005	1.26	6.39
18			S: Livingston[14] R: Springer	Wilson	Mass	20	1.000	0.97	4.84	3	0.970	0.63	7.45
19			S: Livingston[14] R: Love	Wilson	Mass	20	1.000	1.00	4.96	2	0.978	0.70	6.88

stopping power and $\mathscr{Z}_G$ with atomic averaging were the best fitting ones.

In order to evaluate the different $\mathscr{F}$ models, only 191 data were chosen from the list of 471, since in the remainder this correction was insignificant. $\mathscr{Z}$ and $\mathscr{A}$ corrections were evaluated for the Gaussian expressions (using Wilson's J and mass averaging). The results for different $\mathscr{F}$ are shown in Table 2. As this is the smallest correction, it was expected that the different models would produce almost the same fitting; thus it was observed that a model as rough as $\phi_s \propto \delta(z-\bar{z})$ fitted data as accurately as Packwood and Brown's distribution,[6] which adjusted the experimental data for radiation

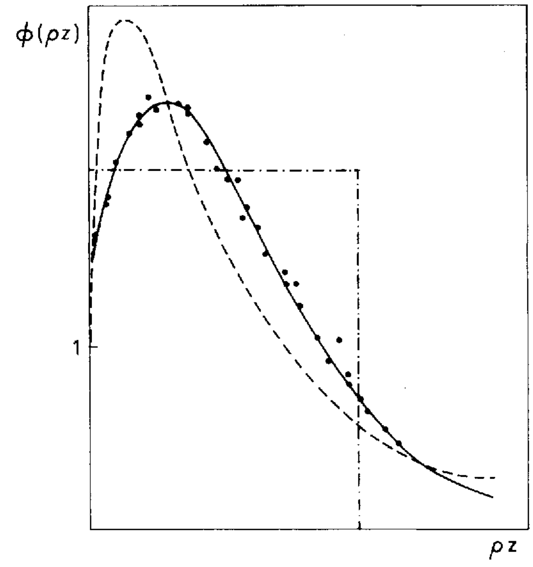

Figure 4. Comparison of the different models for the depth distribution of characteristic production with experimental data for copper (25 keV). ——, Gaussian; – – – –, Philibert's simplified expressions;[1] – · – · –, Bishop.

Table 2. Fluorescence correction models with Gaussian $\mathscr{Z}$ and $\mathscr{A}$ factors

Model	$\overline{K'/K}$	Symmetry	$\sigma(\%)$	Rejected data
$\delta(z-\bar{z})$	0.998	0.77	5.73	12
Gaussian	0.996	0.67	5.68	14
Criss and Birks[18]	0.995	0.67	5.64	14
Reed[19]	0.992	0.63	5.83	13

distribution to a great extent. Every model improved the results corresponding to Reed's model, the most frequently used one.

In conclusion, it may be said that it is convenient to choose the $\mathcal{F}$ expression which simplifies numerical calculations, since the differences are very small compared with the errors in $\mathcal{Z}$ and $\mathcal{A}$ corrections.

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APPENDIX

When dealing with Gaussian $\phi(\rho z)$, $R(x)$ appearing in $f(\chi)$ is related to the complementary error function:

$$R(x)=\sum_{i=1}^{5}\frac{a_i}{(1+px)^i}$$

and the constants have the following values: $a_1=0.254829592$, $a_2=-0.284496736$, $a_3=1.421413741$, $a_4=-1.453152027$, $a_5=1.061405429$ and $p=0.3275911$

The expressions for R involved in the atomic number correction are as follows:

Springer:

$$R=\sum_{i=0}^{4}c_i(E_j/E_0)^i$$

where the coefficients c_i are tabulated in Ref. 10;

Love *et al.*:

$$R=1-\eta[I(U_0)+\eta G(U_0)]^{1.67}$$

where $I(U_0)$ and $U_0G(U_0)$ are polynomials[11] in ln U_0.

The corresponding expressions for S are as follows:

Love *et al.*:

$$\bar{S}=\frac{Z}{A\left[1+16.05\left(\dfrac{J}{E_j}\right)^{0.5}\left(\dfrac{U_0^{0.5}-1}{U_0-1}\right)^{1.07}\right]}$$

Bethe:

$$\bar{S}=7.85\times10^4\frac{Z\ln(1.166\,EM/J)}{EMA}$$

Livingston: the same expression as Bethe's, but taking into account shell effects.

Fluorescence correction due to Criss and Birks involves the following function:

$$f_l(\chi)=\frac{\gamma_0}{2\alpha}\bigg|_l\sqrt{\pi}\,R\left(\frac{\chi}{2\alpha}\right)_l-\frac{\gamma_0-\phi_0}{2\alpha}\bigg|_l\sqrt{\pi}\,R\left(\frac{\beta+\chi}{2\alpha}\right)_l$$

in which $R(x)$ has just been specified. The corresponding coefficients for $\phi(\rho z)$ were fitted by the authors: $d_1=-0.47800911$, $d_2=14.857378$, $d_3=-13.08157$, $b_1=2301.5987\ \mathrm{cm}^2\,\mathrm{g}^{-1}$, $b_2=3951.1108\ \mathrm{cm}^2\,\mathrm{g}^{-1}$ and $b_3=5389.2626\ \mathrm{cm}^2\,\mathrm{g}^{-1}$.

$S(a,x)$ involved in the Gaussian fluorescence correction model is as follows:

$$S(a,x)=\sum_{n=1}^{5}\frac{a_n}{a^n}\left[\ln\left(1+\frac{1}{x}\right)-\sum_{j=1}^{n-1}\frac{1}{j(1+x)^j}\right.$$
$$+\frac{1}{\left(1+x\dfrac{\chi_i}{\mu_s}\right)^n}\ln\frac{|\chi_i-\mu_s|}{\mu_s\left(1+\dfrac{1}{x}\right)}$$
$$\left.+\sum_{j=1}^{n-1}\frac{1}{(1+x)^j j\left(1+x\cdot\dfrac{\chi_i}{\mu_s}\right)^{n-j}}\right]$$

The coefficients p and a_n appeared above in $R(x)$.

The following expression is obtained for the mean depth when dealing with the Gaussian $\phi(\rho z)$:

$$\rho\bar{z}=\frac{\gamma_0-(\gamma_0-\phi_0)\left[1-\dfrac{\beta\sqrt{\pi}}{2\alpha}\displaystyle\sum_{n=1}^{5}\frac{a_n}{(1+p/2\cdot\beta/\alpha)^n}\right]}{\alpha\sqrt{\pi}\left[\gamma_0-(\gamma_0-\phi_0)\displaystyle\sum_{n=1}^{5}\frac{a_n}{(1+p/2\cdot\beta/\alpha)^n}\right]}$$