AN IMPROVED ABSORPTION CORRECTION FOR QUANTITATIVE ANALYSIS

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Résumé - On propose une correction nouvelle et polyvalente pour l'absorption. Elle est fondée sur une représentation approchée de la distribution en profondeur du rayonnement X caractéristique, sous la forme d'un profil quadrilatéral.

Abstract - A new and versatile correction for absorption is proposed which is based upon simplifying the x-ray depth distribution in a target to a quadrilateral profile.

1. INTRODUCTION

When carrying out analysis of ultra light elements (boron, carbon, nitrogen, oxygen and fluorine) very large mass absorption coefficients are involved. (For example a mass absorption coefficient of 37000 is given for C_K radiation in silicon (1)). Consequently the absorption correction factor tends to be large and its accuracy strongly influences the overall reliability of corrected microanalysis data. The usual way of reducing the magnitude of the absorption correction is to lower the probe voltage, thereby decreasing the depth to which electrons penetrate into the specimen. However, even if probe voltages of 10kV are used for light element work, it is found that the absorption correction factor, $f(\chi)$, may still be ~ 0.2 or less (i.e. 80% of the x-rays are absorbed). Reducing the probe voltage substantially below 10kV is generally not feasible because high beam currents are required to generate sufficient x-rays for analytical purposes and image quality is degraded. Moreover it is very inconvenient to operate at low kilovoltages because many other x-ray lines of interest may not be excited. Thus any absorption correction which can be considered to be universally applicable must perform accurately over the range $1 > f(\chi) > 0.2$.

2. THE ABSORPTION CORRECTION

The method most commonly used for correcting for absorption in the specimen is that of Philibert (2). Although based upon the physics of x-ray generation it includes several drastic approximations and is generally considered to be inappropriate for light element work (3).

An alternative approach to obtaining $f(\chi)$ has been by deriving, wholly empirically, analytical expressions to represent the generated x-ray distribution with depth in the target (hereafter referred to as the $\phi(\rho z)$ curve). The absorption correction factor is then given by

$$\frac{\int_0^\infty \phi(\rho z)\exp(-\chi\rho z)\,d\rho z}{\int_0^\infty \phi(\rho z)\,d\rho z} \qquad (1)$$

where $\chi = \mu/\rho \operatorname{cosec} \psi$, μ/ρ being the mass absorption coefficient and ψ the x-ray take-off angle. This $\phi(\rho z)$ curve fitting method is becoming increasingly popular because there are now a large number of data on x-ray depth distributions

which have been obtained experimentally using tracer techniques or Monte Carlo methods.

Before attempting to model a $\phi(\rho z)$ curve it is necessary to establish the most important parameters to include in an equation for $\phi(\rho z)$ and how accurately these parameters have to be defined. It is obviously unnecessary to describe $\phi(\rho z)$ exactly if approximations to the shape introduce insignificant errors in $f(\chi)$.

Bishop (4) showed that when $f(\chi) > 0.5$ the single most important parameter controlling the magnitude of the absorption correction was the mean depth of x-ray generation, $\overline{\rho z}$. His proposal was to use a simple rectangular profile to represent $\phi(\rho z)$ whereby the x-ray production remained constant until the mass depth was twice $\overline{\rho z}$ and then fell abruptly to zero. Love and Scott (5) developed the idea further, using an expression for $\overline{\rho z}$ derived from Monte Carlo calculations, and were able to show that their absorption correction model was significantly superior to that of Philibert, especially when χ is large. Such results indicated that it is probably not necessary to fit $\phi(\rho z)$ exactly although a slightly more realistic profile than the rectangle should lead to a markedly improved absorption correction.

3. THE QUADRILATERAL MODEL

Figure 1 shows a typical $\phi(\rho z)$ versus depth curve superimposed upon which is the profile we shall use in our new absorption correction. Point A of the quadrilateral is defined by the coordinates $(0, \phi(0))$. Point B is given by the maximum value of $\phi(\rho z)$, i.e. $\phi(\rho z_m)$ and by the corresponding mass depth, ρz_m. Point C $(\rho z_n, 0)$ lies close to the value for the x-ray range, ρz_r. Given a series of $\phi(\rho z)$ curves, points A and B are easily defined but locating C presents some difficulty because of the long tail which occurs, particularly for high atomic number elements. Also, in this form, the Quadrilateral model does not contain a term representing the mean depth of x-ray generation and, as indicated earlier, it is essential that this be included. Both these problems are overcome by representing ρz_n in terms of $\overline{\rho z}$ and the other three parameters $\phi(0)$, $\phi(\rho z_m)$ and ρz_m. Geometrical considerations reveal the following relationship.

$$\left[\rho z_m + \frac{\phi(\rho z_m)}{\phi(0)}\rho z_n\right]\overline{\rho z} = \frac{1}{3}\left[\rho z_m^2 + \frac{\phi(\rho z_m)}{\phi(0)}\rho z_n^2 + \frac{\phi(\rho z_m)}{\phi(0)}\rho z_m \rho z_n\right].$$

With this simple quadrilateral shape it is possible to derive directly an analytical expression for $f(\chi)$, viz

$$f(\chi) = 2[m(n-m)(m+kn)\chi^2]^{-1} \times [(n-kn-m)\exp(-\chi m) + km\exp(-\chi n) + \chi(mn-m^2) + kn - n - km + m] \quad (2)$$

where $k = \phi(\rho z_m)/\phi(0)$, $m = \rho z_m$ and $n = \rho z_n$.

Although this formula may appear complicated it is readily solved with the aid of a mini-computer and, unlike most other $\phi(\rho z)$ curve fitting techniques, lengthy numerical integration is not required.

The next stage is to test the performance of the model over a range of χ values. Initially we will make the assumption that all four parameters ($\phi(0)$, $\phi(\rho z_m)$, ρz_m and $\overline{\rho z}$) can be defined exactly. This has been done using the Monte Carlo $\phi(\rho z)$ curve for aluminium K radiation at 30keV shown in figure 1, although any representative $\phi(\rho z)$ profile is suitable for evaluation purposes. Values for $f(\chi)$ obtained using the Quadrilateral model are compared with those obtained from the Monte Carlo $\phi(\rho z)$ curve for a range of χ values between 100 and 100,000. In figure 2 the results are plotted as $f(\chi)_{QUAD}/f(\chi)_{MC}$ versus log χ. When the ratio of the $f(\chi)$ values is unity it may be adjudged that the Quadrilateral model is performing perfectly. Also shown, for the purposes of comparison, are the equivalent results obtained from the Philibert and Bishop absorption models, both of which have been adjusted to give the correct mean depth of x-ray generation. It is evident that

the Quadrilateral model gives by far the best f(X) data and errors in excess of 5% relative do not occur until χ exceeds 20,000. In contrast a 5% error criterion is exceeded when $X > 3{,}000$ for the Bishop model and $X > 1000$ for the Philibert model. This ranking order of performance will remain the same for other analytical conditions although much higher χ values can be tolerated as the probe voltage is reduced. This is illustrated in figure 3 where 5% errors are not exceeded until $X > 7500$ (simplified Philibert) and $X > 30{,}000$ (Bishop); for the Quadrilateral model errors are less than 1% up to $X = 100{,}000$. Quite clearly then the simple quadrilateral shape is perfectly adequate to describe the $\phi(\rho z)$ curve with the necessary degree of accuracy and it merely remains to derive appropriate equations for $\overline{\rho z}$, $\phi(0)$, $\phi(\rho z_m)$ and ρz_m.

As with all absorption corrections, the Quadrilateral model depends sensitively on the value of $\overline{\rho z}$ and figure 4 illustrates the effect of a 10% error in its value on the aluminium data at 30keV. A 5% error in the absorption correction now occurs at $X = 780$ compared with $X = 20{,}000$, the value obtained when $\overline{\rho z}$ was correct. Thus any analytical expression for $\overline{\rho z}$ must represent the mean depth with the utmost accuracy possible. An expression has already been developed specifically to describe the mean depth of x-ray generation (6). However, in view of the importance of getting the value exactly right it is being re-evaluated using new $\phi(\rho z)$ curves from tracer experiments and Monte Carlo calculations.

Fortunately the Quadrilateral model is much less sensitive to errors in the other three parameters and performance is not seriously degraded provided that these can be specified to within 10% of the 'true' values. Various formulae for $\phi(0)$ already exist (7,8,9) and one of these may be suitable for incorporation in the Quadrilateral model. Furthermore, current work suggeststhat $\phi(\rho z_m)$ can be represented as

$$f(\phi(0),\ U_o,\ Z)$$

and ρz_m as

$$f(\overline{\rho z},\ \eta)$$

where U_o is the overvoltage ratio, Z the mean atomic number of the target and η the backscatter coefficient.

When the four parameters on which the Quadrilateral model is based have been precisely defined in terms of appropriate equations we shall be reporting upon the performance of our absorption correction, when applied to a wide range of experimental microanalysis data.

Acknowledgements

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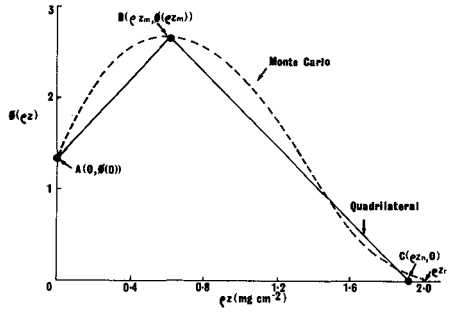

Fig.1. Quadrilateral profile superimposed upon Monte Carlo $\phi(\rho z)$ curve for aluminium Kα radiation at 30 keV.

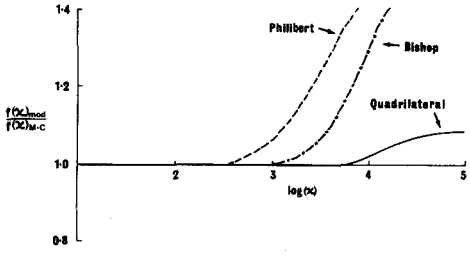

Fig.2. $f(\chi)$ values calculated for aluminium at 30 keV using the different correction models ($f(\chi)$mod) compared with Monte Carlo calculations ($f(\chi)_{M-C}$).

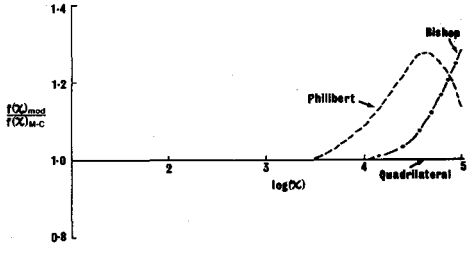

Fig.3. As Fig.2. but the calculations carried out for aluminium at 10 keV.

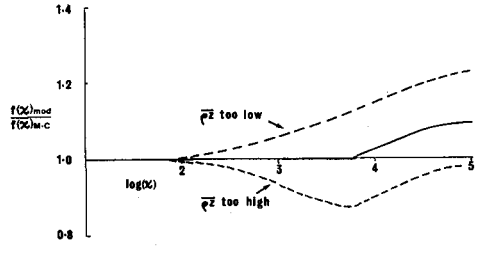

Fig.4. $f(\chi)$ values calculated for aluminium at 30 keV using the Quadrilateral model; —— $\overline{\rho z}$ value correct; --- 10% error in ρz.