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Experimental Determination of Mass Absorption Coefficients for Soft X-Rays

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INTRODUCTION

One of the most important corrections required in quantitative electron probe microanalysis, especially for soft X-rays, is that for absorption. Because a lack of direct measurements of mass absorption coefficients μ/ρ exists for many soft X-rays, there is a need for alternate techniques to determine the coefficients. Andersen showed that an empirical relation existed between the electron beam voltage E_p, which produced the maximum observed X-ray intensity, and the best-known values for μ/ρ in a variety of elemental and compound targets. Andersen qualitatively explained these results as due to the effect of attenuation by absorption eventually overcoming the increase in X-ray generation with increasing beam voltage, with the peak voltage (*i.e.*, the voltage corresponding to maximum observed X-ray intensity) being determined by the value of χ for the particular line in the target. In this paper, a quantitative basis is established for such empirical observations, and the theory developed is then used to determine indirectly the values of μ/ρ for a variety of soft X-rays.

THEORY

The basic ideas of the model have been presented by Kyser[2] but will be repeated here for completeness. The observed X-ray line intensity as a function of E_0 (with constant beam current) is assumed to be proportional to the product of the relative generation rate $(E_0-E_c)^n$ and the fraction $f(\chi)$ of X-rays generated that escape the target at a particular angle ϕ, where $\chi=(\mu/\rho)\csc\phi$. In practice, $E_0 \gg E_c$, where E_c is the threshold excitation potential for the X-ray line under study, and $1<n<2$. Hence, one can determine E_p, that value of E_0 which produces maximum observed intensity, by setting

$$\frac{d}{dE_0}[(E_0)^n f(\chi)] = 0 \tag{1}$$

and solving for E_p as a function of χ. Of course to perform this mathematical operation, one must have an analytical expression for $f(\chi)$.

A particular expression for $f(\chi)$ can be derived, based on assumptions originally proposed by Wittry.[3] A Gaussian distribution of X-ray generation with distance is used, namely

$$\Phi(\rho Z) = A \exp\left[-\left(\frac{\rho Z-\rho Z_0}{\rho \Delta Z}\right)^2\right] \tag{2}$$

The peak position of the Gaussian $\Phi(\rho Z)$ is located at ρZ_0, and the half-width is described by the parameter $\rho\Delta Z$. The associated $f(\chi)$ is then computed in the conventional manner by taking the Laplace transform of $\Phi(\rho Z)$ and normalizing:

$$f(\chi) = \frac{\exp\left[-(Z_0/\Delta Z)^2\right] \exp(u^2)[1 - \operatorname{erf}(u)]}{1 + \operatorname{erf}(Z_0/\Delta Z)} \tag{3}$$

where

$$u = \left[\frac{\chi \rho \Delta Z}{2} - \frac{Z_0}{\Delta Z}\right]$$

and

$$\operatorname{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-t^2}\, dt$$

Note that the product of χ and $\rho\Delta Z$, as well as the ratio $Z_0/\Delta Z$, appears in the argument u. The appropriate constants ρZ_0 and $\rho\Delta Z$ were determined by matching the Gaussian $\Phi(\rho Z)$ to a calculation for energy loss dE/dZ obtained via the Boltzmann transport equation of Brown.[4] The match was made at ρZ_0 and for $\rho Z > \rho Z_0$. The constants were determined for $E_0 = 30$ kV in a Cu target and are the same as those used by Wittry and Kyser[5] to describe the voltage dependence of cathodoluminescence in GaAs. The constants ρZ_0 and $\rho\Delta Z$ are then scaled with voltage E_0 in the same manner as the electron range R. The range R is assumed to have a voltage dependence described by the single exponent m. Thus

$$\rho Z_0 = 0.125R, \qquad \rho\Delta Z = 0.350R \tag{4}$$

where

$$R = 2.56 \times 10^{-3} (E_0/30)^m \text{ gm/cm}^2 \quad (E_0 \text{ in kV}).$$

The constant 2.56×10^{-3} gives the same range R in Cu at 30 kV as that obtained from Bethe's retardation law by integrating from the initial voltage E_0 to the voltage at which the retardation goes to zero. Of course, dE/dZ will approximate $\Phi(\rho Z)$ only when E_c is very small.

As an example, Fig. 1 shows a comparison between the Gaussian $\Phi(\rho Z)$ and that given by Duncumb and Melford[6] for C$K\alpha$ in Fe_3C at 20 kV which was obtained with Monte Carlo calculations. For the Gaussian curve, an exponent of $m = 1.68$ in the electron range (Eq. (4)) has been used, based on the work of Andersen.[7] This is very close to the value of 1.70 which Wittry and Kyser[5] found necessary to use for interpreting the voltage dependence of cathodoluminescence in GaAs. This example was chosen since it represents a soft X-ray in a mid

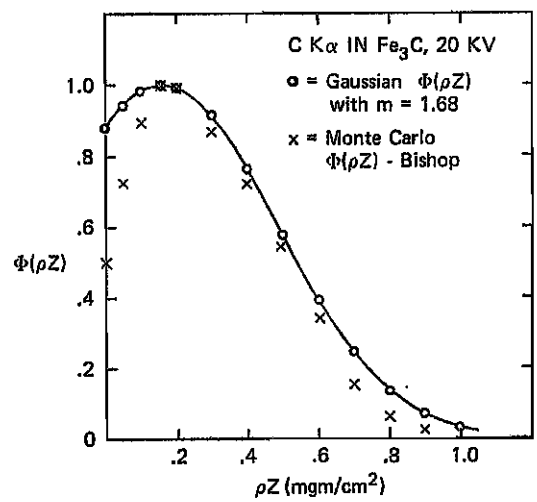

Fig. 1. Comparison of $\Phi(\rho Z)$ for C$K\alpha$ in Fe_3C.

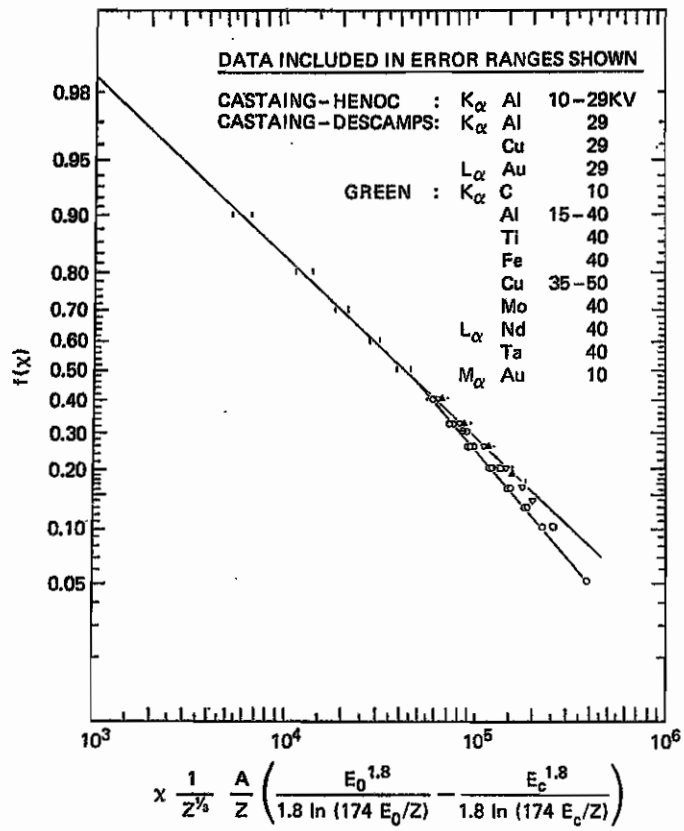

Fig. 2. $f(\chi)$ versus $\chi\cdot(\overline{\rho Z})^*$ for the experimental data listed (after Andersen and Wittry[81]).

atomic number matrix, and the Monte Carlo $\Phi(\rho Z)$ should approximate dE/dZ well. The deviation between these two curves of $\Phi(\rho Z)$ is significant for $\rho Z<\rho Z_0$, which is expected from the manner in which the Gaussian $\Phi(\rho Z)$ was initially matched to the Boltzmann calculations described previously. This is particularly important, since the observed X-ray intensity is proportional to the Laplace transform of $\Phi(\rho Z)$. When χ is very large, as it often is for soft X-rays, the shape of $\Phi(\rho Z)$ for small ρZ can be very important.

Recently, Andersen and Wittry[81] have evaluated the experimental data available on the absorption correction. Figure 2 is their compilation of experimentally determined $f(\chi)$ values plotted against an argument, the argument being the product of χ and the " effective mean depth of ionization," $(\overline{\rho Z})^*$. A special scale for $f(\chi)$ was constructed which permitted $f(\chi)$ to be plotted as nearly a straight-line function. The scale does not affect the dependence of $f(\chi)$ on $(\overline{\rho Z})^*$, and was only used by them as a plotting aid. The scale assumes a Gaussian $\Phi(\rho Z)$ using the same parameters given previously, although the analytical expression given in their appendix contains minor errors which did not affect their plot. Note there is a split in their data for $f(\chi)$ <0.5. Andersen and Wittry obtained better results in their evaluation by using the lower curve for targets with atomic number $Z<26$.

The justification for using the Gaussian $\Phi(\rho Z)$ and its associated $f(\chi)$ lies in the fact that it is in agreement with the values of $f(\chi)$ predicted by the Andersen-Wittry plot. Figure 3 shows the voltage dependence of $f(\chi)$ for Fe$L\alpha$ in Fe. The Andersen-Wittry curve splits at low $f(\chi)$, but note that the Gaussian $f(\chi)$ has essentially a constant deviation of ≈ 0.03 from the lower Andersen-Wittry curve. The same behavior is present in a similar plot of $f(\chi)$ for Cu$L\alpha$ in Cu. This suggests that the excessive X-ray generation predicted by the Gaussian $\Phi(\rho Z)$ for $Z<Z_0$

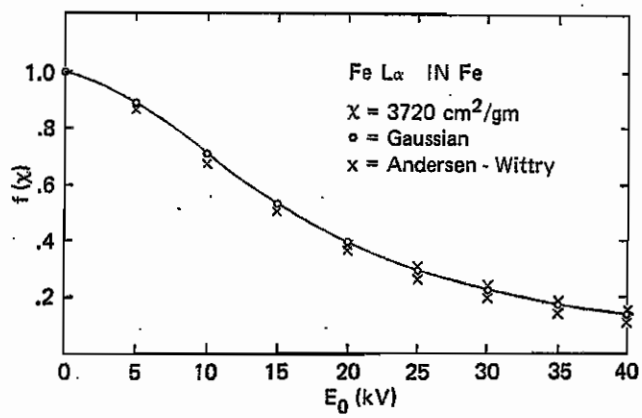

Fig. 3. Comparison of $f(\chi)$ for $FeL\alpha_{1,2}$ in Fe between Eq. (3) with $m=1.68$ and Fig. 2.

is not entirely negligible. A modification to $\Phi(\rho Z)$, and hence $f(\chi)$, is presented in the appendix to take account of this excessive generation. The modification is sufficiently small to be neglected in the following theory, but does provide even better agreement with the lower Andersen-Wittry curve in Fig. 3.

The agreement between the Gaussian and Andersen-Wittry $f(\chi)$ for mid-Z targets is not surprising when one considers that the Gaussian $\Phi(\rho Z)$ gives a mean depth of generation $(\overline{\rho Z})_G=2\rho Z_0=0.25R$. An an example, for $\chi(\text{Fe}, \text{Fe}L\alpha)=3720$ cm²/gm and $5<E_0<30$ kV, $(\overline{\rho Z})^*/(\overline{\rho Z})_G$ is approximately constant. This suggests that atomic number dependence could be included in the Gaussian $\phi(\rho Z)$ and $f(\chi)$ by scaling ρZ_0 and $\rho\Delta Z$ as $A/Z^{4/3}$, the same way that $(\overline{\rho Z})^*$ is linearly scaled. However, the voltage dependence of $(\overline{\rho Z})_G$ and $(\overline{\rho Z})^*$ is not identical. The latter appears to scale as $(E_0)^{1.6}$, whereas the former scales with the range R.

The remaining parameter to be determined is the value of the exponent n which describes the relative X-ray generation rate with voltage in Eq. (1). Initial use of the value $n=1.63$ proposed by Green[9] did not result in reasonable agreement between theory and experiment. Figure 4 shows experimental results reported by Duncumb and Melford[6] for $CK\alpha$ in diamond

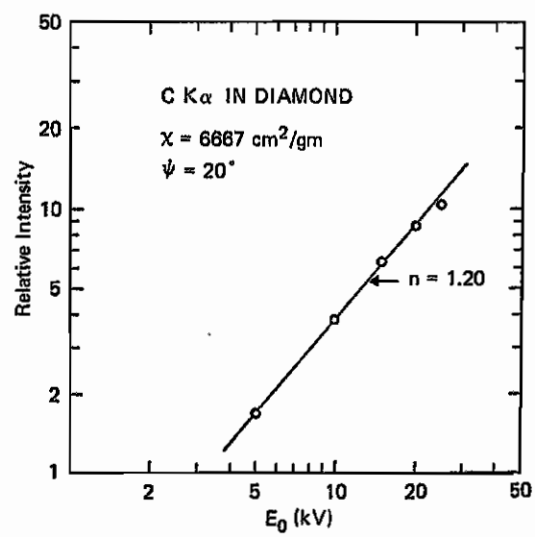

Fig. 4. Generated intensity versus voltage for $CK\alpha$ in diamond after an absorption correction was made to the data of Duncumb and Melford with Fig. 2.[6]

after an absorption correction was made with the aid of the Andersen-Wittry plot and lower curve. The exponent $n=1.20$ over a wide range of voltage. Experimental results obtained by the author for Fe$L\alpha$ in Fe and Cu$L\alpha$ in Cu after an absorption correction was made in the same manner yield $n=1.2$ also. Calculations of R/S' versus E_0 based on the atomic number correction theory of Philibert and Tixier[10] and the backscatter coefficient calculations of Duncumb and Reed[11] also result in $n\simeq 1.2$ for Ti$L\alpha$ through Zn$L\alpha$ when $E_0 \gg E_c$. Recently Shiraiwa and Fujino[12] have shown that the exponent n in Eq. (1) appears to vary continuously from 2.3 for hard X-rays and $(E_0/E_c)\cong 1$ to 1.0 for soft X-rays and $(E_0/E_c)\gg 1$. While the value of 1.20 cannot be accepted as a universal constant, it does appear that for soft X-rays and large overvoltages, n is significantly less than 1.63.

The maximizing operation indicated in Eq. (1) is performed in the following manner:

$$\frac{d}{dE_0}[(E_0)^n f(\chi)] = \left\{(E_0)^n \frac{d}{dE_0} f(\chi) + f(\chi)\frac{d}{dE_0}(E_0)^n\right\} = 0 \tag{5}$$

where

$$\frac{d}{dE_0} = \left(\frac{du}{dE_0}\right)\frac{d}{du} = \left[\frac{\chi}{2}(\rho\Delta Z)\frac{m}{E_0}\right]\frac{d}{du}$$

Approximation: Let $\operatorname{erf}(u)\cong 2/\sqrt{\pi}\, u (u \ll 1)$. Then

$$E_p \cong \left\{\frac{\left(\frac{n}{m}\right)(30)^m \sqrt{\pi}}{(0.35)(2.56\times 10^{-3})\chi}\right\}^{1/m} \tag{6}$$

Equation (6) shows the dependence of E_p on n, m, and the constants in Eq. (4) used to describe the range R. For the values $n=1.20$, $m=1.68$,

$$\chi\,(\mathrm{cm^2/gm}) \cong \left(\frac{2230}{E_p}\right)^{1.68} \tag{7}$$

A more exact solution, obtained with the aid of a digital computer, differs from the approximate solution only in the numerator constant:

$$\chi\,(\mathrm{cm^2/gm}) = \left(\frac{2660}{E_p}\right)^{1.68} \tag{8}$$

Without an atomic number correction to $f(\chi)$, Eq. (8) is intended to apply only to a mid-Z target. Wittry[13] has shown that if one uses the principle of scaling $\Phi(\rho Z)$ with the electron range, and utilizes a special property of the Laplace transform, then the exponent relating E_p and χ should be just that in the voltage dependence of the range, namely m. However, that conclusion requires an assumption that the exponents n and m are very nearly the same, and his theory does not allow the calculation of the numerator constant in Eq. (8) as the present theory does.

EXPERIMENTAL PROCEDURE

The experimental data presented here were obtained with a conventional electron probe microanalyzer and a take-off angle of 52.5°. The target current was electronically maintained constant as the electron accelerating voltage E_0 was varied in small increments. The target current was used as a feedback signal to control a specially constructed magnetic condenser lens

power supply. The instrument was equipped with a liquid nitrogen cooled objective lens to minimize contamination of the target. This facilitated long-term repetitive measurements on the same spot. The electron beam was focused at each E_0 by precalibration of the magnetic objective lens. Lateral wander of the beam was minimized during refocus by proper alignment of the electron optics. This ensured that X-ray focus was maintained. The X-ray spectrometer was set to the appropriate emission line and not scanned during a series of increments in E_0. A background intensity was not measured at each E_0 since (a) the intensity could not be duplicated with the required accuracy if the spectrometer were changed; (b) the background intensity is almost constant under the condition of constant target current with varying E_0, and (c) the line to background ratio was large for the elements studied. The Ti$L\alpha_{1,2}$ and V$L\alpha_{1,2}$ lines were measured with a lead stearate crystal in second order. The remaining lines, Cr$L\alpha_{1,2}$ through Zn$L\alpha_{1,2}$, were obtained with a RAP crystal in first order. The high voltage power supply for the electron gun was calibrated with an electrostatic voltmeter, and the triode bias resistor and emission current were monitored. The bias voltage was kept small.

Pure elemental standards of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn were used. The nearby $L\beta_1$ lines were of negligible intensity because of extreme absorption, especially at the higher voltages. No correction was made for variation with E_0 of X-ray production due to backscattered electrons, since for $(E_0/E_c) \gg 1$ this variation is small.[11] The basic data consisted of X-ray counts versus E_0, and a 5-point smoothing routine with a digital computer and plotter was used to enable accurate determination of E_p for each standard measured.

EXPERIMENTAL RESULTS

Several examples of observed intensity versus E_0 are shown in Fig. 5. The general trend is that the longer emission wavelengths peak at lower E_0 and decrease more rapidly on either side of E_p. Listed in Table 1 are the observed values of E_p and the associated values of χ and μ/ρ calculated from Eq. (8). The values of E_p are believed to be accurate within ± 0.25 kV. Note that the peak voltage E_p increases in a smooth fashion with increasing atomic number, except for the cases of Co$L\alpha$ and Ni$L\alpha$. This behavior was repeated in several experimental runs,

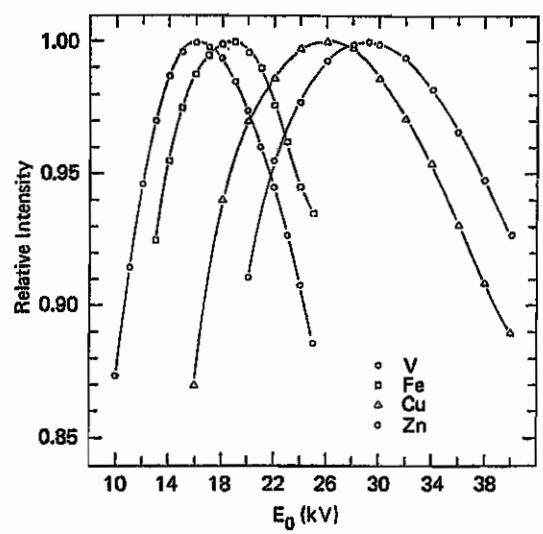

Fig. 5. Observed intensity versus voltage for V, Fe, Cu, and Zn$L\alpha_{1,2}$ in V, Fe, Cu, and Zn respectively. The data has been digitally smoothed before plotting.

Table 1. Observed peak voltages and χ, μ/ρ calculated from Eq. (8).

$L\alpha_{1,2}$ line	E_c (keV)	Target	E_p (keV)	χ (cm²/gm)	μ/ρ (cm²/gm)
Ti	0.454	Ti	13.80	7,000	5,550
V	0.512	V	16.20	5,250	4,165
Cr	0.574	Cr	17.20	4,800	3,810
Mn	0.639	Mn	17.50	4,600	3,650
Fe	0.708	Fe	19.00	4,000	3,175
Co	0.779	Co	18.50	4,200	3,330
Ni	0.853	Ni	17.70	4,500	3,570
Cu	0.933	Cu	26.00	2,400	1,910
Zn	1.022	Zn	29.00	2,000	1,590

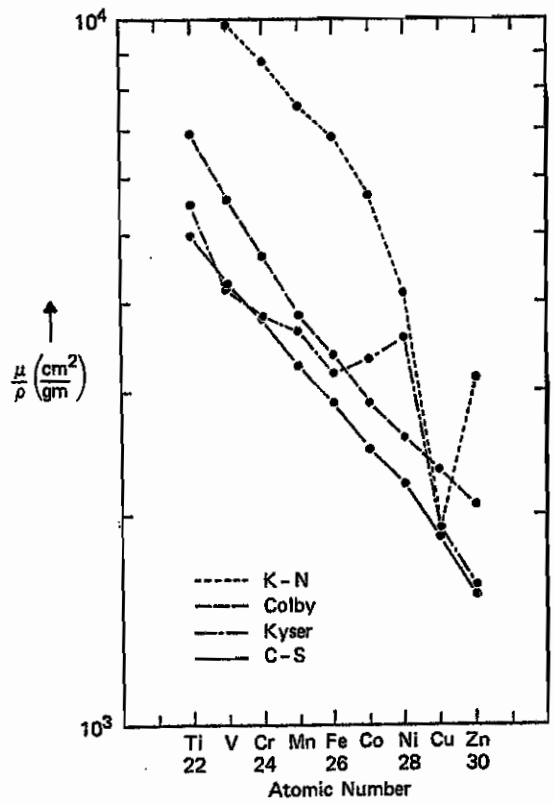

Fig. 6. Comparison of μ/ρ for self-absorption of $L\alpha_{1,2}$ between Kyser, Kaman-Nuclear (K-N),[14] Colby,[15] and extrapolation of Cooke and Stewardson[16] (C-S).

and is not considered to be instrumental error.

Figure 6 shows a comparison of μ/ρ values from this work and several other sources commonly used for reference in quantitative analysis. Since the values obtained from these sources are extrapolated or interpolated over large ranges in wavelength λ and atomic number Z, they are subject to large errors.

As a test of the theory, one can correct the observed intensities shown in Fig. 5 for absorption with Eqs. (3) and (13) using the appropriate parameters for n and m described and the values of μ/ρ calculated from E_p and Eq. (8). The calculations can be arbitrarily matched at

E_p. These theoretical curves of intensity versus voltage match the experimental curves within 5% relative.

As a further test of the theory, quantitative analysis of a well-characterized specimen was performed in which the absorption correction was extreme. A 60% Cu-40% Au standard supplied by the U.S. National Bureau of Standards was measured. At E_0=25 kV, $k_{CuL\alpha}$=0.385, and $k_{AuM\alpha}$=0.288 using elemental standards. Utilizing a popular computer correction program[16] with μ/ρ (Cu$L\alpha$, Cu)=2297, μ/ρ (Cu$L\alpha$, Cu)=7075 gave C_{Cu}=0.512, C_{Au}=0.366. Before applying the present theory to this data, we deduced a new value for μ/ρ (Cu$L\alpha$, Au) by measuring E_p in the 60/40 alloy to obtain an effective μ/ρ which is the weight fraction average of μ/ρ (Cu$L\alpha$, Cu) and μ/ρ (Cu$L\alpha$, Au). Using the previously deduced value of μ/ρ (Cu$L\alpha$, Cu)=1910, we then calculated μ/ρ (Cu$L\alpha$, Au)=5810. Using these new μ/ρ values in MAGIC III and using an absorption correction given by Eq. (3) for Cu$L\alpha$ yielded C_{Cu}=0.596, C_{Au}=0.388. This improved analysis required changes in *both* μ/ρ and the $f(\chi)$ formula for Cu$L\alpha$.

DISCUSSION

The Gaussian $\Phi(\rho Z)$ and its associated $f(\chi)$ is used in this analysis because it represents the true shape of $\Phi(\rho Z)$ better than the model originally proposed by Philibert,[17] at least for small values of ρZ. Of course this is the region most critical for soft X-rays suffering large absorption. The formulation of Philibert has already been shown to be inaccurate for soft X-rays and large values of E_0.[6]

In principle, this technique could be applied to an unknown compound sample when measuring a soft X-ray to yield an " effective " χ-value. This χ-value and a appropriate formula for $f(\chi)$ could then be used in quantitative analysis *without* iterating to a χ-value from tables of μ/ρ for various emission lines and elemental absorbers, which is the standard practice now. As shown in this study, such standard tables and $f(\chi)$ formulae may lead to an erroneous result when absorption is very high.

This formulation is intended to apply presently to a soft X-ray with $E_c \leq 1$ kV in a mid-atomic number matrix. Present plans include a further study of the atomic number dependence in the Gaussian $\Phi(\rho Z)$ and $f(\chi)$. The anomalous behavior of E_p for Co$L\alpha$ and Ni$L\alpha$ is not explained at present, and further theoretical study is also in progress here.

CONCLUSIONS

New self-absorption coefficients for Ti$L\alpha_{1,2}$ through Zn$L\alpha_{1,2}$ are presented based on a Gaussian model for X-ray generation with distance. The shape parameters of the Gaussian $\Phi(\rho Z)$ are scaled with the electron range, and a new formulation for $f(\chi)$ is used to obtain a relation between E_p and χ, where E_p is the beam voltage which produces maximum observed intensity. It was found necessary to use an exponent n=1.20 in the relation describing X-ray generation rate with voltage E_0 for such soft X-rays. An improved analysis of a known Cu–Au alloy is obtained using this formulation, compared to a widely used correction procedure for absorption.

Acknowledgments

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APPENDIX

Modification to Gaussian $f(\chi)$

The Gaussian $\Phi(\rho Z)$ can be modified to provide a better match with Monte Carlo and transport equation calculations by subtracting an exponential component:
Let

$$\Phi'(\rho Z) = \Phi_1(\rho Z) - \Phi_2(\rho Z) \tag{9}$$

where

$$\Phi_1 = A_1 \exp\left[-\left(\frac{\rho Z - \rho Z_0}{\rho \Delta Z}\right)^2\right], \qquad \Phi_2 = A_2 \exp\left(\frac{-b\rho Z}{\rho Z_0}\right)$$

and $F(\chi)$ is the Laplace transform of $\Phi(\rho Z)$. Then

$$f'(\chi) = \left\{\frac{F_1(\chi) - F_2(\chi)}{F_1(0) - F_2(0)}\right\} \cong \left\{f_1(\chi) - \frac{F_2(\chi)}{F_1(0)}\right\} \tag{10}$$

$$\text{for} \quad F_2(0) \ll F_1(0)$$

Now

$$F_2(\chi) = \left\{\frac{A_2}{\chi + \dfrac{b}{\rho Z_0}}\right\} \cong \left(\frac{A_2 \rho Z_0}{b}\right) \tag{11}$$

$$\text{for} \quad b \gg \chi \rho Z_0$$

Then

$$f'(\chi) = \left\{f_1(\chi) - \frac{\left(\dfrac{A_2}{A_1}\right)\left(\dfrac{Z_0}{\Delta Z}\dfrac{1}{b}\right)}{\dfrac{\sqrt{\pi}}{2}\left[1 + \operatorname{erf}\left(\dfrac{Z_0}{\Delta Z}\right)\right]}\right\} \tag{12}$$

where $f_1(\chi)$ is given by Eq. (3).

The parameter values which seem to give the best match are $A_2/A_1 = 0.4$, $b = 4$. Then

$$f'(\chi) \cong [f_1(\chi) - 0.029] \tag{13}$$

It is interesting to compare the maximum value of Φ' to its value at the surface:

$$\Phi'(0) = [\Phi_1(0) - \Phi_2(0)] = \left\{A_1 \exp\left[-\left(\frac{Z_0}{\Delta Z}\right)^2\right] - A_2\right\} \tag{14}$$

Then

$$\left\{\frac{\Phi'(0)}{\Phi'_{\max}(\rho Z)}\right\} = \frac{A_1}{A_1}(0.88 - 0.4) = 0.48 \tag{15}$$

This can be compared with calculations based on a formula due to Hoff and Everhart[18] who measured the distribution of energy loss with depth in Si and fitted a third degree polynomial to it. This calculation yields $\lambda(0)/\lambda_{\max} = 0.51$ where their $\lambda(y)$ is proportional to $\Phi(\rho Z)$. Note that the ratio in Eq. (15) is independent of beam voltage especially. This arises because both Z_0 and ΔZ are scaled with E_0 in the same manner.

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