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ABSTRACT

Knowledge of X-ray production as a function of depth by electrons ($\phi(\varrho z)$ curves) is important in quantitative electron probe microanalysis and other electron beam technologies. Extensive measurements of such curves have been made for electron energies between 6 and 30 keV and for many X-ray lines and matrix elements. Two experimental techniques based on measurements on sandwich or wedge shaped specimens have been used.

A number of expressions have been used to model $\phi(\varrho z)$ curves from a square function through complicated polynomial expressions. Recently, a Gaussian model has been proposed which accurately reflects the shape of the $\phi(\varrho z)$ curves and which can be linked to theoretical models. Generalizing the equation to the situation of non-normal electron incidence would appear possible.

Keywords: Electrons, X-ray generation, modeling, measurement, quantitative analysis, electron probe microanalysis, tracer.

INTRODUCTION

When an electron beam is incident on a solid target, interactions with the atoms of the target occur which lead to backscattering, scattering through small angles and energy loss by the electrons. The result is that energy is deposited and interactions occur within a volume of the target material. Depending on the target material and the electron energy, this volume may be more or less hemispherical or tear drop in shape, Figure 1, (Curgenven and Duncumb 1971). This shape for the interaction volume has been established in part experimentally (Shimizu et al 1975), but more generally using Monte Carlo calculations, for example Newbury and Yakowitz (1976) and Kotera et al (1981). In this paper, I will be concerned with the deposition of energy in a solid by electron beams of energy from a few keV to about 30 keV, primarily as a function of depth in the specimen and with respect to X-ray generation.

EXPERIMENTAL MEASUREMENTS OF $\phi(\varrho z)$ CURVES

Castaing and Descamps (1955) suggested the method for measurement of the $\phi(\varrho z)$ curves in which a so-called sandwich specimen is used. The thin layer of tracer element, deposited on a polished block of the matrix element, is chosen so that the atomic numbers match closely and no characteristic fluorescence occurs. The tracer layer is then covered with layers of different thickness of the matrix element (Figure 2). Measurement of a characteristic line intensity from the tracer layer element relative to the intensity from the same thickness of layer isolated in space under identical electron bombardment conditions yields the $\phi(\varrho z)$ curve. A typical curve is shown in Figure 3 in which the curve rises from a surface value greater than 1 to a maximum at some depth in the sample, then falls away steeply to zero. Other authors, for example Vignes and Dez (1968), Castaing and Henoc (1966) and Shimizu et al (1966), have made measurements of $\phi(\varrho z)$ curves where the tracer layer is similar in atomic number to the matrix but extensions have been made to use the method to measure both fluorescence and atomic number effects. (Brown(1966), Brown and Parobek (1972), Parobek and Brown 1978).

LIST OF SYMBOLS

a = Constant in equation of Büchner and Pitsch
A = Atomic weight
D = Constant in equation of Parobek and Brown equal to area under $\phi(\varrho z)$ curve
k = Value in Philibert expression for $\phi(\varrho z)$ related to randomization of electron paths
K = Constant in equation of Parobek and Brown
n = Constant used in exponential terms of the equations of Büchner and Pitsch as well as Parobek and Brown
N = Avogadro's number
q = Constant in the Gaussian equation for $\phi(\varrho z) = \frac{\gamma_o - \phi(0)}{\gamma_o}$
R = Value in Parobek and Brown equation equal to $\varrho z - \varrho z_a$
R_o = The value used by Philibert to describe the electron paths through surface layer
$a\varrho z$ = Electron absorption parameter
R_∞ = Same as R_o except at point of complete diffusion in the sample
U = The overvoltage ratio; electron energy divided by the absorption edge energy
z = Depth in the specimen
z_o = Depth of maximum in Andersen & Wittry expression for $\phi(\varrho z)$
z_a = Depth axis offset in Parobek and Brown equation
$\triangle z$ = Width of Gaussian in Andersen and Wittry equation
α = Constant in Gaussian related to the width of the Gaussian
β = Constant in Gaussian related to initial rise in $\phi(\varrho z)$
γ_o = Constant giving magnitude to Gaussian equation
ϱ = Density
η = Backscatter coefficient
ψ_A = Ionization cross section
$\phi(\varrho z)$ = X-ray generation as a function of depth relative to an isolated thin film
$\phi(O)$ = Value of $\phi(\varrho z)$ at the surface

Schmitz et al (1969) have proposed and used a wedge specimen to obtain $\phi(\varrho z)$ curves. (Figure 4(a)). These specimens are prepared by taper sectioning, at a shallow angle, a binary specimen made up of one element over top of a second element. In this case it is essential that the two elements be close in atomic number and that no characteristic fluorescence occurs. Measurement of the X-ray intensity from the top element as a function of distance across the wedge, and hence thickness of the element, yields the integral of the $\phi(\varrho z)$ curve. Differentiation of this integral curve yields the $\phi(\varrho z)$ curve itself as is illustrated in Figure 4(b). Table 1 summarizes the measurements of $\phi(\varrho z)$ curves which have been made to date. Most of the measurements have been made using normal electron incidence but in a few cases the electron beam has been inclined relative to the specimen normal.

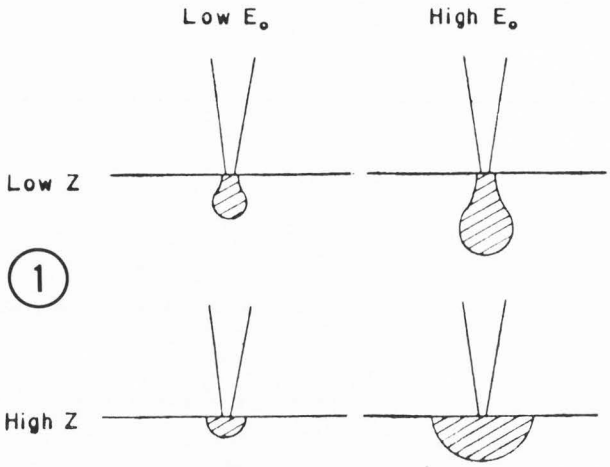


Fig. 1. Cross section through typical volumes of excitation by an electron beam.

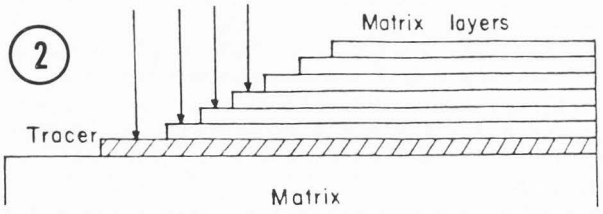


Fig. 2. Sandwich sample used by Castaing and Descamps (1955) to measure $\phi(\varrho z)$ curves.

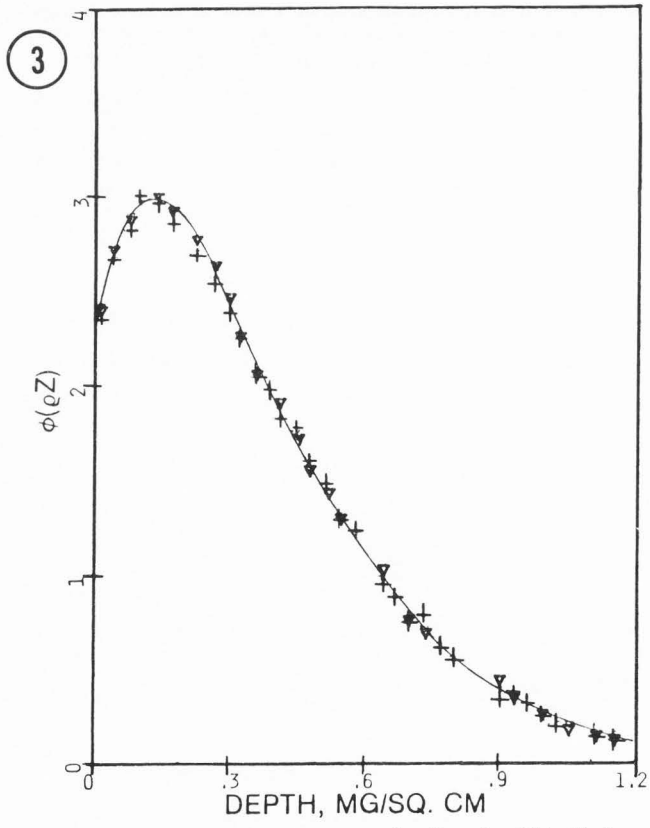
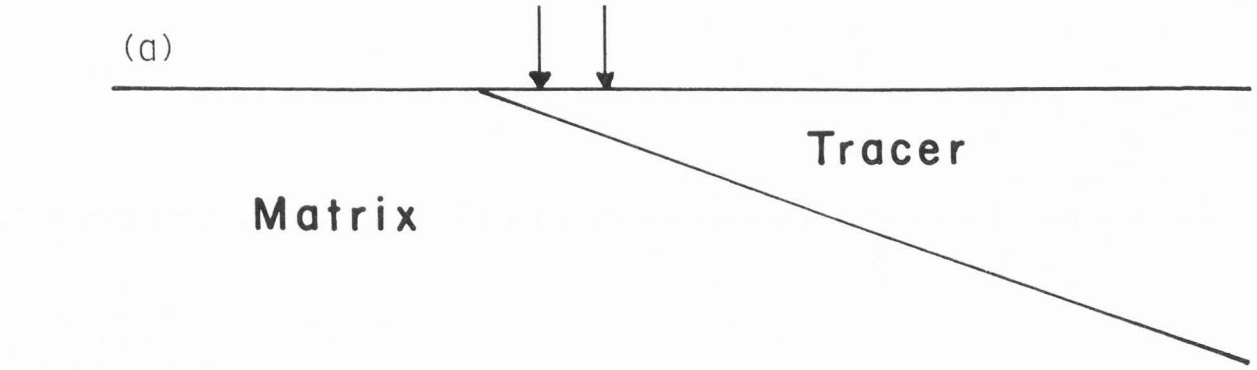


Fig. 3. $\phi(\varrho z)$ curve for a zinc tracer in silver for 25 keV electron energies. The two symbols represent data from two instruments with different X-ray take-off angles.

TABLE 1 Measured $\phi(\rho z)$ Curves

	Matrix	Tracer, line	Electron Energy, keV
Castaing & Descamps (1955)	Cu	ZnKα	29
	Au	BiLα	29
	Al	CuKα, ZnKα, CrKα, BiLα	29
Brown (1966)	Cu	ZnKα,NiKα,CoKα,FeKα,DyLαDyLβ	13.4,18.2,23.1,27.6
Castaing & Henoc (1966)	Al	MgKα	10,15,20,25,29
Vignes & Dez (1968)	Ti	VKα	17,20,24,29,35
	Ni	CuKα	17,20,24,29,35
	Pb	BiLα	29,33
Schmitz et al. (1969)	Cu	NiKα	20,25.5,30
Shimizu et al. (1966)	Cu	ZnKα	14.2,15.9,19.0,21.1,23.8,25.1, 26.5,28.5,30.0,31.7,33.1,34.7,37.0
Brown & Parobek (1972)	Al,Cu,Ag,Au	SiKα,CdLα,ZnKα,BiMα,BiLα	15,20,25,30
Parobek & Brown (1978)	Al,Ni,Ag,Au	SiKα	6,8,10
	Al,Ag,Ni	CuKα	12,15



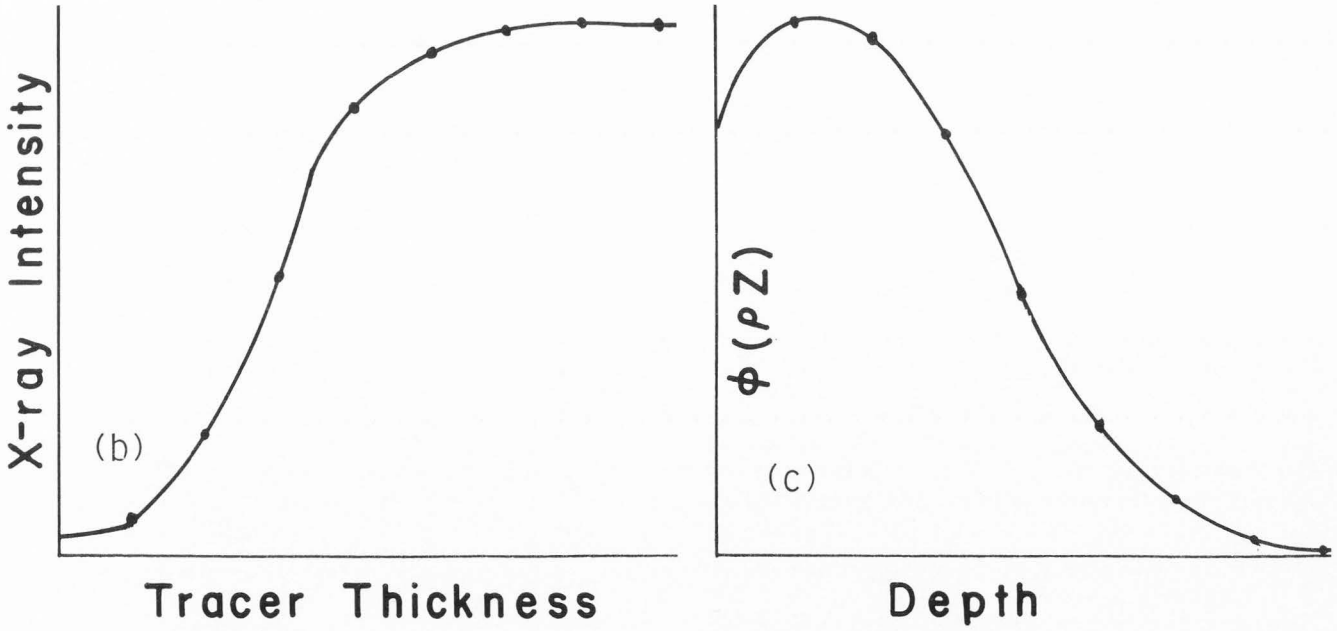


Fig. 4(a) Wedge specimen for determining $\phi(\rho z)$ curves.

Fig. 4(b) Total X-ray intensity as a function of thickness of the wedge which when differentiated yields (c) the $\phi(\rho z)$ curve.

Sufficient measurements of $\phi(\varrho z)$ curves have now been made to make some generalizations concerning the dependence of the characteristics of the curves with respect to the matrix and instrumental parameters. As would be expected, the depth of maximum production for the same characteristic line in any given matrix increases rapidly with an increase in electron energy (Figure 5). For a given matrix and electron energy, the depth of maximum production increases significantly with decreasing absorption edge energy (Figure 6). For a single X-ray line, at constant electron energy, the maximum production moves towards the surface with increasing atomic number and a significant change in shape occurs (Figure 7). Further, the area under the curves increases with atomic number. To properly model the $\phi(\varrho z)$ curves, these effects must be accounted for.

EXPRESSIONS FOR $\phi(\varrho z)$

Philibert (1963) was the first to derive an expression for $\phi(\varrho z)$ when he developed his absorption correction based on a calculation of the number of electrons crossing a thin layer as a function of depth in the specimen. He assumed a simple exponential variation of that number with depth and a constant cross section which led to

$$\phi(\varrho z) = R_\infty \frac{N}{A} \psi_A \exp(-\alpha \varrho z) \left[1 - \left(1 - \frac{R_o}{R_\infty}\right)\exp(-k\varrho z)\right] \quad (1)$$

To simplify the absorption correction and in view of the fact that little data were available for the value of R_o, R_o was set equal to 0 in the simplified absorption formula which implied a $\phi(\varrho z)$ expression

$$\phi(\varrho z) = \text{const}(e^{-\delta \varrho z} - e^{-(\sigma + k)\varrho z}) \quad (2)$$

For the purpose intended, which was a reasonably accurate absorption correction, this shape of $\phi(\varrho z)$ was accurate but it does have the limitations that at $\varrho z = 0$, $\phi(0) = 0$ which is far from the true value and in common with the more complex expression (1) has an exponential decay, which again is not strictly true.

An even more radical departure from the true $\phi(\varrho z)$ shape was proposed by Bishop (1974) who assumed a constant X-ray production to twice the mean depth of production, dropping to zero for greater depths. This model has been shown to give reasonable results in correction for X-ray absorption provided the absorption is not too large, Love et al. (1976).

On the other hand, expressions have been proposed which better reflect the true shape of the $\phi(\varrho z)$ curve. Criss and Birks (1966) used a five term polynomial exponential expression to fit the $\phi(\varrho z)$ curves measured by Castaing and Descamps (1955); however extensive use of this formula has

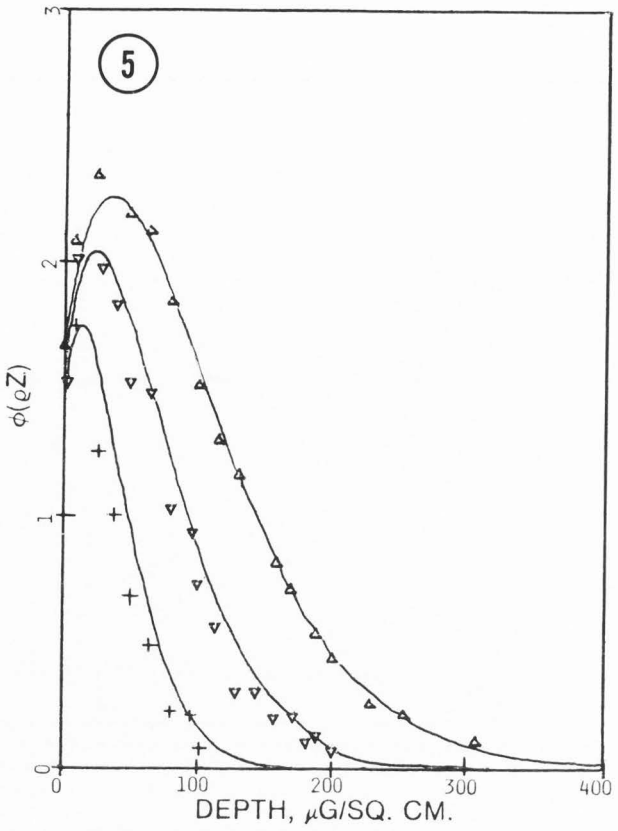


Fig. 5. $\phi(\varrho z)$ **curves for SiKα in Nickel at 6, 8 and 10 keV electron energy.**

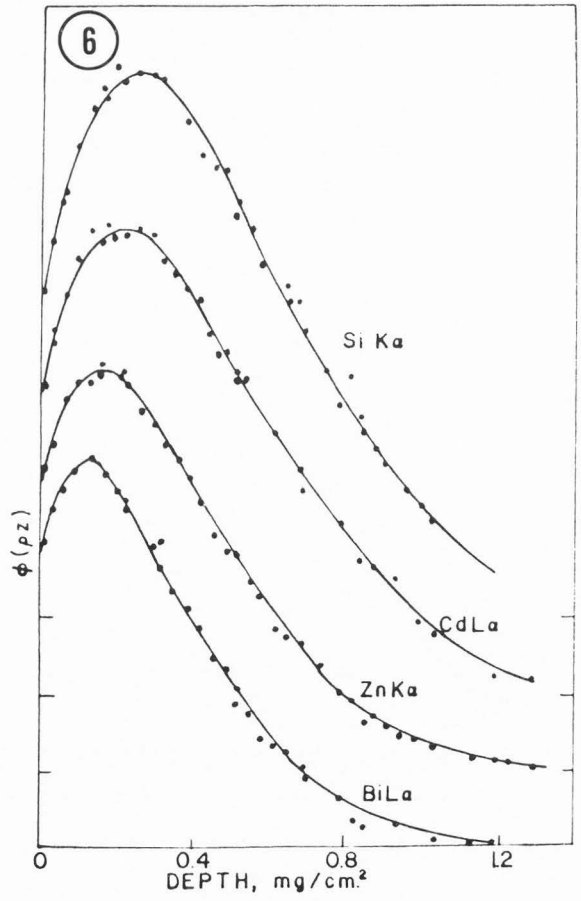


Fig. 6. $\phi(\varrho z)$ **curves showing the effects of absorption edge energy, matrix copper, 25 keV energy.**

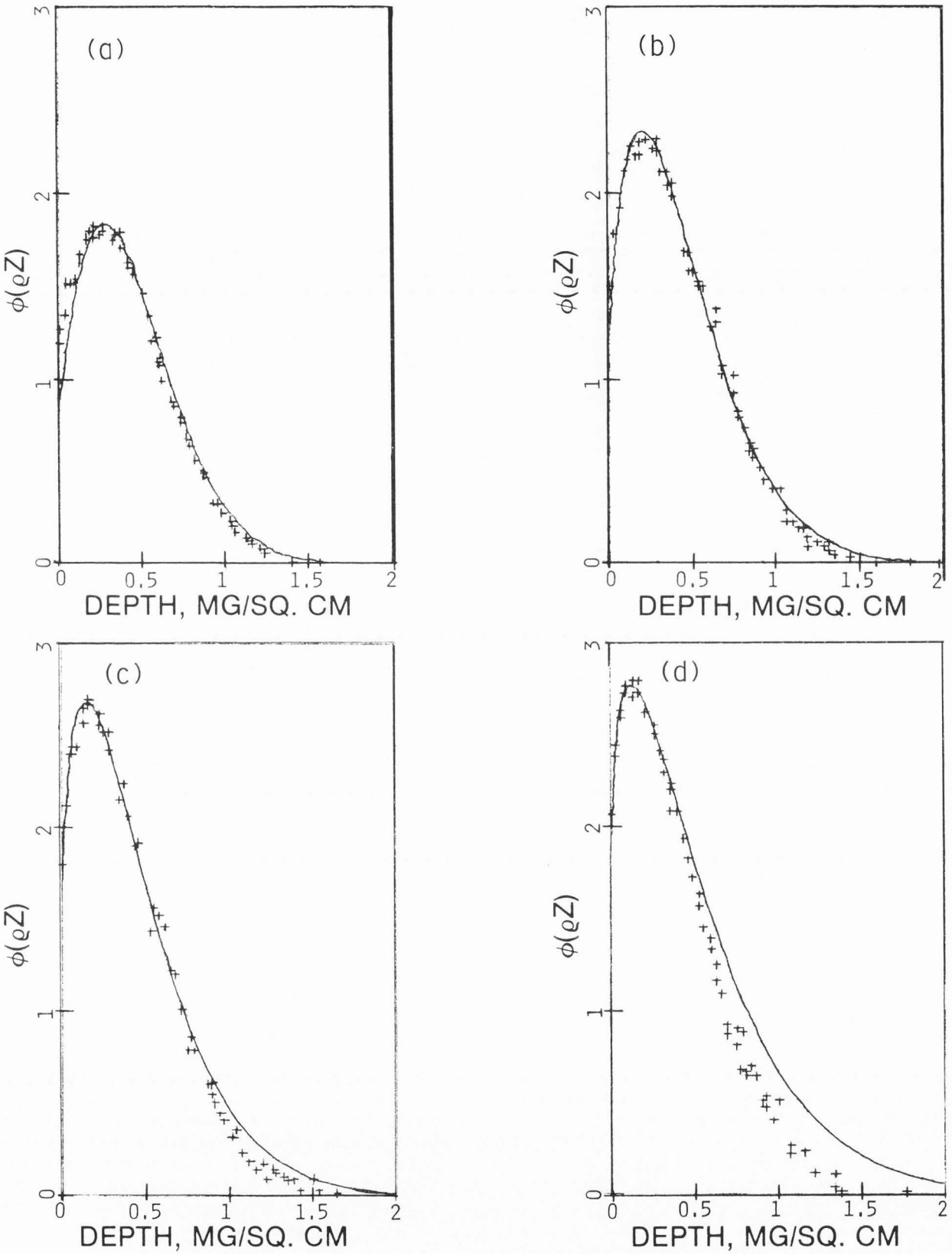


Fig. 7. $\phi(\varrho z)$ curves for CdLα at 25 keV electron energy. Matrices are (a) Al, (b) Cu, (c) Ag and (d) Au.

never been made. Andersen and Wittry (1968) proposed a Gaussian expression for $\phi(\varrho z)$ in which the maximum of the Gaussian is centered at the maximum in the $\phi(\varrho z)$ curve, i.e.

$$\phi(\varrho z) \propto \exp\left[-\left(\frac{z-z_o}{\triangle z}\right)^2\right] \tag{3}$$

This leads to a non-zero value of $\phi(\varrho z)$ at the surface, yet it is a curve which is symmetric about the maximum value and this is not in agreement with the measured curves. The consequence is that in any fitting to experimental data agreement between observed and measured $\phi(0)$ values is poor.

Heinrich (1981) has proposed offsetting the axes with respect to both depth and $\phi(\varrho z)$ value. The result of shifting the depth origin is that the simplified Philibert expression has a non-zero value at the surface, while offsetting the ϕ axis removes the long tail associated with the exponential decay. Both shifts should have a beneficial effect on the agreement with measured curves.

Reuter (1972) returned to the more complete equation of Philibert (1963) in an attempt to relate that equation to more recent data of electron energy loss and $\phi(0)$ while improving the derivation by taking into account the change in ionization cross section with energy, i.e.

$$\psi = U^{-0.7} \ell n\, U \tag{4}$$

To evaluate ψ, Reuter assumed that electron energy and hence U decreases with depth in a manner derived from Bethe's Law. For R_∞ he used the value 3 and set

$$R_o = \phi(0) = 1 + 2.8\left(1 + \frac{0.9}{U}\right)\eta \tag{5}$$

with the backscatter coefficient η obtained from a fit to coefficients measured by Heinrich (1966).

The electron transmission was based on fits to experimental data which showed a linear dependence at shallow depths with an exponential dependence where complete diffusion occurs. The agreement of this approach with measured $\phi(\varrho z)$ curves was good for relatively low atomic number elements and K lines but less satisfactory for L lines of higher atomic member elements.

Büchner and Pitsch (1971) used the data from measurements of Schmitz et al. (1969) using wedge samples in which the integral of $\phi(\varrho z)$ is obtained. They found that the integral curves could be accurately described by

$$1 - \exp(-(a\varrho z)^n) \tag{6}$$

where a and n are empirical fitting constants. On differentiating this expression, $\phi(\varrho z)$ is obtained, i.e.

$$\phi(\varrho z) = a\, n\, (a\varrho z)^{n-1} \exp(-(a\varrho z)^n). \tag{7}$$

This equation shares the same limitation as the $\phi(\varrho z)$ equation implied from the simplified Philibert absorption correction in that the value for $\phi(0)$ is 0. The fit to the tail of the experimental $\phi(\varrho z)$ curves is much more satisfactory however.

Parobek and Brown (1978) fitted a similar equation to measured $\phi(\varrho z)$ curves for electron energies from 6 to 15 keV

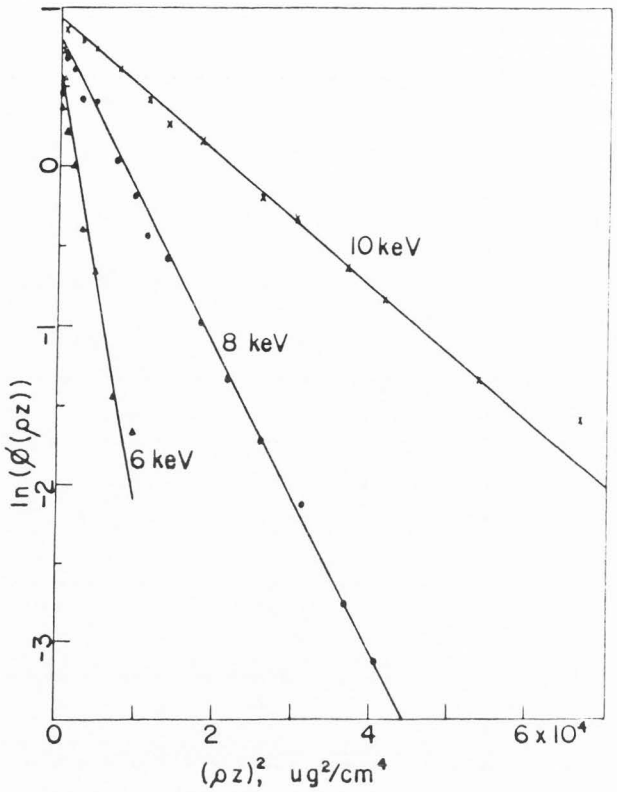


Fig. 8. Curves of Figure 5, plotted to show the Gaussian behaviour of $\phi(\varrho z)$ curves. + is for 6 keV, ∇ is for 8 keV, and △ 10 keV electron energies. All arrows are for silicon Kα in nickel.

using a least squares criterion and offsetting the ϱz axis to give a non-zero value for $\phi(0)$. The $\phi(\varrho z)$ equation then becomes

$$\phi(\varrho z) = D\, K\, n\, (KR)^{n-1} \exp(-(KR)^n) \tag{8}$$

in which $R = \varrho z - \varrho z_a$. The functional dependence of the four parameters D, K, n and z_a on the matrix atomic number and weight, the electron energy and the absorption edge energy was established from appropriate plots. Later, Brown and Robinson (1979) using the same equation and a SIMPLEX optimizing procedure obtained values of the parameters for $\phi(\varrho z)$ curves measured at electron energies from 15 to 30 keV. With these equations, the $\phi(\varrho z)$ curve could be predicted for any characteristic line in any matrix for electron energies from a few to greater than 30 keV.

The disadvantage of the above empirical equation is that it cannot be extrapolated to other measurement conditions and the only path to improvement is through more accurate $\phi(\varrho z)$ curves obtained either by measurement or through theoretical calculations. Packwood and Brown (1981) showed that a plot of $\ell n(\phi(\varrho z))$ versus the square of depth yielded straight lines for all measured $\phi(\varrho z)$ curves (Figure 8). The implication is that $\phi(\varrho z)$ are Gaussian. On this basis, they proposed that the $\phi(\varrho z)$ curves could be modelled by

$$\phi(\varrho z) = \gamma_o \exp(-\alpha^2(\varrho z)^2)(1 - q \exp(-\beta\varrho z)) \tag{9}$$

where

$$q = \frac{\gamma_o - \phi(0)}{\gamma_o}.$$

Again a SIMPLEX procedure was used to establish the optimum values of the parameters γ_0, α and β in fits to approximately 100 measured $\phi(\varrho z)$ curves.

A simple theoretical derivation of the parameters for the Gaussian equation can also be carried out assuming a randomization of the electron paths from an initially collimated electron beam. On this basis, Packwood and Brown (1981) showed that the derived dependence of these parameters matched the observed dependence obtained from the measured curves. Later (Brown and Packwood 1982) the parameters were modified slightly to improve the results of application of the Gaussian expression to the analysis of specimens of known composition. The real advantage of the Gaussian expression over earlier equations is that it can be tested and improved at three levels; through better and more extensive $\phi(\varrho z)$ curves, through improved theoretical derivations of the parameters themselves, and through improvements obtained in the analysis of standard specimens and preparation of error histograms.

PROBLEMS TO BE SOLVED

One of the major unsolved effects in the prediction of $\phi(\varrho z)$ curves is how such curves change as the electron incidence angle deviates from 90°. As mentioned previously, some limited measurements have been made, either intentionally or accidentally. For example, Castaing and Descamps' (1955) measurements were made with an electron incidence angle of 80° to the specimen surface. The Gaussian expression would appear to offer a possible solution to such prediction since the value of a α is certain to be changed only by a geometrical factor, γ_0 should be unchanged, β should be related to α and $\phi(0)$ values should be modified to take into account changed backscatter coefficients.

The extension of predictions of $\phi(\varrho z)$ curves to very low electron energies and to low X-ray energies is also of great practical interest because of the microanalysis of carbides, nitrides and oxides. Several factors seem to alter significantly the $\phi(\varrho z)$ curves. Very large overvoltage ratios are inevitable in the measurement of the low energy characteristic X-ray lines. As a consequence, $\phi(0)$ values appear to have less z dependence than might be expected on the basis of backscattering coefficients and the total X-ray production increases at a rate much less than 1.6 power of the overvoltage.

CONCLUSIONS

The modeling of $\phi(\varrho z)$ curves has reached the point where much experimental data and theoretical calculations can be used in improving our understanding. At the same time, the expressions for $\phi(\varrho z)$ can provide a sensitive test for the accuracy of calculations by such techniques as Monte Carlo and transport equation methods.

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