

National Bureau of Standards, Washington, D. C. 20234, U. S. A.

Quantitative Electron Probe Microanalysis: Absorption Correction Uncertainty

By

H. Yakowitz and K. F. J. Heinrich

With 7 Figures

(Received February 27, 1967)

I. Introduction

*Castaing*¹ proposed that quantitative electron probe analysis could be carried out using pure elements as standards. This proposal is accepted, of choice or necessity, by most analysts; the accuracy of the procedure is, however, the subject of much debate. A recent publication by *Thomas*² in which several proposed correction procedures were applied to a great number of uncorrected data from diverse sources shows a disappointingly wide range of deviation of the calculated results with respect to the expected "true" values. Recognition of the complexity of the problem has lead numerous investigators³⁻⁵ to expand the theoretical treatment of quantitative analysis proposed by *Castaing*.

It is very difficult, however, to check on the correctness of theoretical models, unless the effects of uncertainty in the values of input parameters are recognized. Much of the existing confusion concerning the quantitative aspects of electron probe analysis is due to neglect of this important factor. Such input parameters include physical constants—X-ray mass attenuation coefficients, fluorescence yields, backscatter correction coefficients, among others—as well as data concerning the conditions of the measurement, such as the accelerating potential, the X-ray emergence angle, and the detector coincidence losses.

Most investigators propose correction procedures in which the effects of the generation and absorption of primary radiation, and those of production of secondary radiation, are taken into account separately. Therefore, we distinguish an atomic number correction, an absorption correction, and fluorescence corrections for X-rays excited by both characteristic and continuous radiation. Of these, the atomic number

correction is the most controversial. Before applying this correction, however, the experimental intensity ratios must be corrected for absorption of X-rays within the target, and this absorption correction is substantial for an element of low atomic number in the presence of other elements of high atomic number. Hence, the correction for X-ray absorption must be accurately applied before the effects of atomic number differences between the target components can be investigated experimentally.

The problem can be illustrated using the data on aluminum alloys presented by Clayton⁶. This author plotted experimental values of

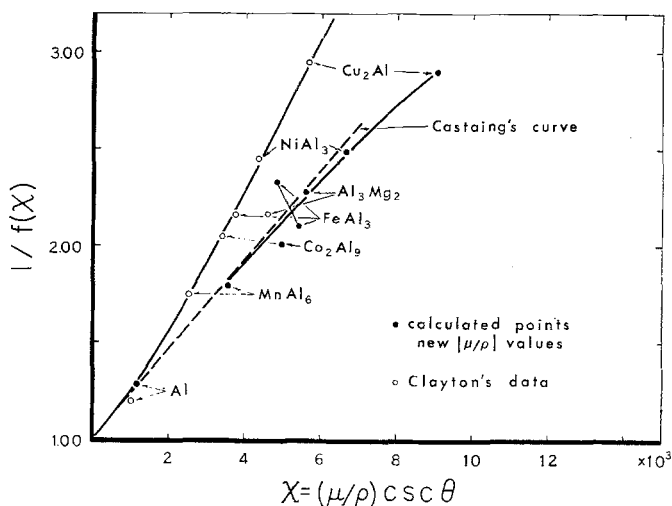


Fig. 1. Change in calculated compositions for Al in various alloys as a function of (μ/ρ) changes. New points agree with *Castaing's* curve for Al. Data from *Clayton*⁶

the inverse of the absorption function, $1/f(\chi)$, as a function of $\chi = (\mu/\rho) \csc \theta$, for aluminum and for six aluminum alloys (μ/ρ is the X-ray mass attenuation coefficient of the specimen for the measured radiation, and θ its angle of emergence). *Clayton* indicated the value of μ/ρ for Al K_α radiation in aluminum, but not those of the coefficients for Al K_α in the other elements. The deviation of the experimental data plotted this way from the data derived from *Castaing's* correction curve was interpreted to be an atomic number effect (Fig. 1). These data were also used by *Archard* and *Mulvey*⁷ who showed that the correction method developed by them is consistent with the $f(\chi)$ values of *Clayton*. *Archard* and *Mulvey* pointed out, however, that a revision with respect to the μ/ρ values employed would be desirable.

*Heinrich*⁸ has recently presented a revised tabulation of mass attenuation coefficients, indicating that lack of knowledge of these

coefficients is frequently the limiting factor in the accuracy of electron probe analysis. Applying *Heinrich's* values of mass attenuation coefficients to *Clayton's* data*, we redetermined the values of χ and of $1/f(\chi)$. A comparison with the original values of $1/f(\chi)$ obtained by *Clayton*, on Fig. 1, shows the uncertainty introduced into the presumed atomic number effect by the lack of knowledge of the mass absorption coefficients. In the present work, we propose to investigate the limits of accuracy of the *absorption correction*. We will show the effects of the uncertainty in the input *parameters* involved, upon the analytical error. As will be shown in the example for Al-Mg, there exists an additional error which lies with the model for $f(\chi)$.

II. Effect of Input Parameter Uncertainties on the Absorption Correction

According to *Beer's* law, the attenuation of X-rays generated within a target and emerging from it at the angle θ is:

$$\frac{J_0}{J} = \frac{\int_0^{z=\infty} \Phi(\varrho z) \exp(-\chi \varrho z) d(\varrho z)}{\int_0^{z=\infty} \Phi(\varrho z) d(\varrho z)} = f(\chi). \quad (1)$$

$\Phi(\varrho z)$ is the distribution in depth of the characteristic emission, viz. K_α or L_α , in a target subjected to normal electron incidence;

J is the X-ray counting rate observed by a detector at angle θ ;

J_0 is the counting rate which would be observed if there were no attenuation;

ϱ the density of the target material;

z the depth of X-ray generation within the target.

It is the purpose of the present communication to show how the analytical result is affected by uncertainties in the input parameters for absorption correction. For this purpose, the above form of the correction is assumed to be known. A critique of proposed forms of the absorption correction will be published at a later date.

The absorption correction procedure of *Philibert*⁴, modified by *Duncumb* and *Shields*⁵, is widely accepted as satisfactory. Its usefulness for the analysis of propagation of input errors can be considered evident. According to these authors, the absorption function $f(\chi)$ can be defined by

$$1/f(\chi) = (1 + \chi/\sigma) \left[1 + \left(\frac{h}{1+h} \right) \frac{\chi}{\sigma} \right] \quad (2)$$

* Except for the mass attenuation coefficient of Al for $Al K_\alpha$ which was assumed to be 408, in accordance with recent measurements of *Philibert* (unpublished), and of *Hughes* and *Woodhouse*⁶.

in which

$$\chi = (\mu/\rho) \csc \theta, \quad (2a)$$

$$h = 1.2 \bar{A}/\bar{Z}^2, \quad (2b)$$

\bar{A} being the mean atomic weight and \bar{Z} being the mean atomic number of the specimen respectively;

$$\sigma = \left[\frac{2.39 \cdot 10^5}{E^{1.5} - E_c^{1.5}} \right], \quad (2c)$$

E being the operating kilovoltage and E_c being the critical excitation kilovoltage respectively.

The value of $f(\chi)$ is used in the correction equation in the following manner:

$$C_i = k_i g \left(\frac{f(\chi)_{\text{std}}}{f(\chi)_{\text{unknown}}} \right) \quad (3)$$

in which

C_i is the true weight fraction of element i in the unknown;

k_i is the measured X-ray intensity for i in the unknown relative to the intensity for i in the standard;

g is a factor accounting for possible atomic number and fluorescence corrections.

Denoting the symbol $f(\chi)$ by f for the remainder of the discussion, use of the propagation of error formulae enables us to approximately obtain from Eqn. (3):

$$\frac{\Delta C}{C} = g \left[\left(\frac{\Delta f}{f} \right)_{\text{std}} - \left(\frac{\Delta f}{f} \right)_{\text{unknown}} + \frac{\Delta k}{k} \right] \quad (4)$$

where: Δf , ΔC etc. are small errors of unknown sign.

Errors in the measured intensity ratio, k , will not be considered here, and since atomic number and fluorescence effects are beyond the scope of this communication, g is presumed to be unity.

The problem is then to evaluate $(\Delta f/f)$, for both the specimen and the standard.

In order to accomplish this, we write the *Philibert-Duncumb* relation, Eqn. (2), as:

$$\frac{1}{f} = (1 + y) (1 + a y) \quad (5)$$

where: y is defined as (χ/σ) and a is defined as $h/(1 + h)$.

From Eqn. (5), the relative error in f is obtained by differentiation as:

$$\left(\frac{\Delta f}{f} \right) = [1 - f(1 - a y^2)] \left(-\frac{\Delta y}{y} \right) \equiv B \left(\frac{-\Delta y}{y} \right). \quad (6)$$

Substitution of (χ/σ) for y yields:

$$-\frac{\Delta y}{y} = \frac{\Delta \sigma}{\sigma} - \frac{\Delta \chi}{\chi}. \quad (7)$$

Substitution of the *Duncumb-Shields* expression⁵ for σ Eqn. (2c) leads to $(\Delta\sigma/\sigma)$ in terms of operating voltages:

$$\frac{\Delta\sigma}{\sigma} = - \frac{1.5 \Delta E}{E - E_c U^{-0.5}} \quad (8)$$

where: U is E/E_c .

Recalling that χ is equal to $(\mu/\varrho) \csc \theta$, we obtain for $(\Delta\chi/\chi)$:

$$\left(\frac{\Delta\chi}{\chi} \right) = + \frac{\Delta(\mu/\varrho)}{(\mu/\varrho)} - \cot \theta \Delta\theta. \quad (9)$$

Hence, if errors in θ and (μ/ϱ) are negligible, the effect of an error in the kilovoltage is:

$$\left(\frac{\Delta f}{f} \right)_{\theta, (\mu/\varrho)} = - B \left[\frac{1.5 \Delta E}{E - E_c U^{-0.5}} \right]. \quad (10)$$

Likewise, if the only error is in θ , then the result is:

$$\left(\frac{\Delta f}{f} \right)_{E, (\mu/\varrho)} = B \cot \theta \Delta\theta \quad (11)$$

and finally, if E and θ are correct, the effect of an error in μ/ϱ is given by:

$$\left(\frac{\Delta f}{f} \right)_{E, \theta} = - B [\Delta(\mu/\varrho)/(\mu/\varrho)]. \quad (12)$$

The quantity B (defined by Eqn. 6) is of great importance in the evaluation of the accuracy of electron probe microanalysis. Therefore, B was calculated for C ($Z = 6$), Al ($Z = 13$), Cu ($Z = 29$) and Au ($Z = 79$) using Eqn. (5) and the results are given in Table I. According to Eqn. (5), for a given material, f is determined by $y = \chi/\sigma$. Thus a curve of f versus y will represent a generalized (voltage independent) *Philibert-Duncumb* function for that substance. Fig. 2 shows such curves for carbon and for gold.

Table I. Value of $B = 1 - f(1 - a y^2)$ for Carbon, Aluminum, Copper, and Gold

y	B_C	B_{Al}	B_{Cu}	B_{Au}
0.067	0.081	0.072	0.068	0.065
0.333	0.337	0.301	0.267	0.262
0.667	0.560	0.496	0.452	0.433
1.0	0.721	0.638	0.577	0.536
2.0	1.03	0.909	0.810	0.735

The values of B for carbon and gold are plotted as a function of y in Fig. 3. A simplified expression for B can be obtained by noting that $a \ll 1$ and therefore

$$1/f \simeq (1 + y) \quad (13)$$

is a good approximation. It follows from this that $B \simeq 1 - f$. If f is fairly close to unity, it is sufficient for an estimate of the error in f , to assume that $f \simeq (1 + y)^{-1} \simeq 1 - y$, so that $B \simeq y$. Therefore, from Eqn. (6):

$$\frac{\Delta f}{f} \simeq -\Delta y = -\Delta(\chi/\sigma). \quad (14)$$

Thus, it is advisable to keep y and hence Δy as low as possible, in order to diminish the analytical error for a given set of input data.

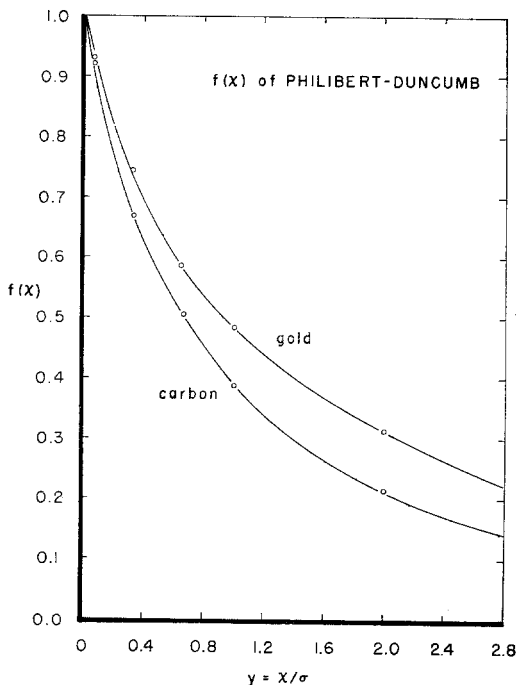


Fig. 2. General *Philibert-Duncumb* curves for f plotted as a function of $y = \chi/\sigma$ for C ($Z = 6$) and Au ($Z = 79$). Single curves may be plotted for any atomic number in this fashion

To perform accurate analyses, and particularly to observe atomic number effects, it is desirable to know f with an accuracy of 1% or better. Yet, errors in the values of input parameters are unavoidable; for instance, X-ray mass attenuation coefficients cannot, in general, be expected to be known with an accuracy better than 4%, particularly in the long wavelength region. If we introduce $B \simeq y$ in Eqn. (12):

$$\Delta f/f \simeq -y \frac{\Delta(\mu/\rho)}{\mu/\rho}. \quad (15)$$

It follows that, if $\frac{\Delta(\mu/\rho)}{\mu/\rho} = 0.04$, in order to maintain $\Delta f/f$ at one percent

or lower, y must be ≤ 0.25 . Consequently, to obtain an estimate of the absorption correction f with an error of 1% or less, the value of f must be greater than 0.8. [This result remains essentially unchanged if the original definition of $B = 1 - f(1 - a y^2)$ is substituted.] It should be remembered that to the effects of errors in μ/ρ , we must add those of errors in the emergence angle, in the operating voltage, and, last but not least, those in the model of the absorption correction. All of these effects increase with diminishing value of f (larger absorption correction). Thus, the proposed limitation is certainly not exaggerated.

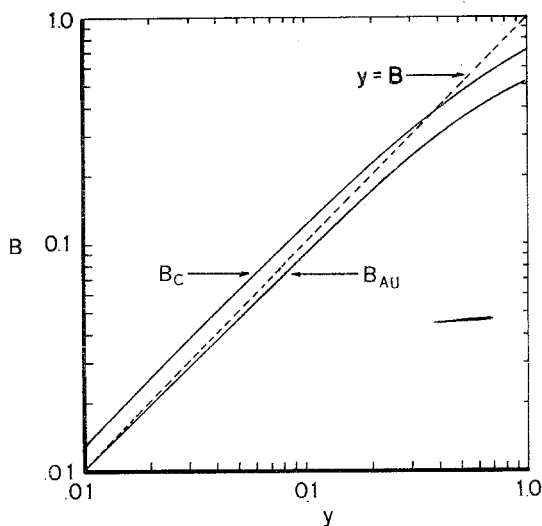


Fig. 3. Error coefficient, $B = 1 - f(1 - a y^2)$, for *Philibert-Duncumb* model plotted as a function of $y = \chi/\sigma$ for C ($Z = 6$) and Au ($Z = 79$) as well as log-linear approximation for calculation of B

Based on the foregoing discussion, we will investigate the effect of operational variables on y . The experimental variable with which the investigator will usually control y is the operating kilovoltage, E , since χ is predetermined, i. e., the material determines (μ/ρ) for the chosen analytical X-ray line and the equipment determines the value of θ . Solving Eqn. (5) for E in terms of y and χ , we obtain, according to *Duncumb* and *Shields*:

$$E = \left[\frac{(2.39 \cdot 10^5) y}{\chi} + E_c^{1.5} \right]^{2/3}. \quad (16)$$

We now let $y = 0.25$ be the maximum acceptable value and calculate the effect of such a limit. Eqn. (16) becomes:

$$E_{\max} = \left[\frac{6 \cdot 10^4}{\chi} + E_c^{1.5} \right]^{2/3} = \left[\frac{6 \cdot 10^4 \sin \theta}{(\mu/\rho)} + E_c^{1.5} \right]^{2/3}. \quad (17)$$

The importance of the role which the X-ray emergence angle, θ , plays in determining the accuracy of electron probe microanalysis is illustrated in Fig. 4, a plot of E_{\max} as a function of μ/ρ of the specimen for the chosen analytical line, at $\theta = 15^\circ$ and $\theta = 60^\circ$, respectively. The function represented in Fig. 4 is only slightly sensitive to changes in the critical excitation potential E_c . Fig. 4 shows that for every given μ/ρ , the operating voltage can be approximately doubled if the emergence angle is increased

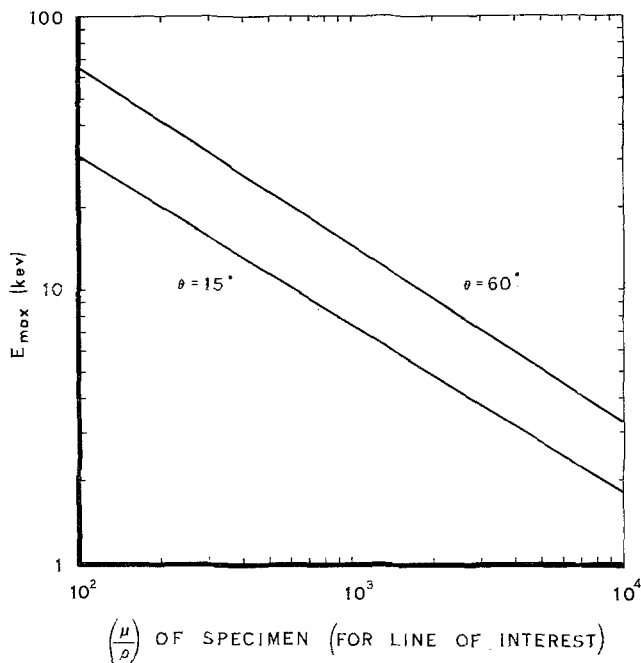


Fig. 4. Calculated value of E_{\max} (keV) from Eqn. (17) as a function of the mass attenuation coefficient of the sample for any line of interest at X-ray take-off angles of 15° and 60° respectively

from 15° to 60° . Such an increase in voltage results in higher counting rates, and frequently better stability and less contamination effects, although the spatial resolution of the analysis deteriorates.

On the other hand, at a given operating voltage, the effects of errors in input parameters and in the model decrease with increasing emergence angle. The situation arising in the analysis with very soft X-rays, discussed by *Duncumb* and *Melford*¹⁰ must now be considered. These authors propose a "thin film approximation" based on the fact that for very high values of χ (and hence y) all observed X-ray photons can be considered as being produced at the specimen surface (in terms of electron penetration); hence, the total emitted X-ray intensity tends to

$\Phi(0) \Delta(\varrho z)$, where $\Phi(0)$ is the relative emission of X-rays at zero depth, and $\Delta(\varrho z)$ is the effective thickness of the emitting layer. If this assumption is valid for both specimen and standard, the concentration can be calculated by

$$C = k \left(\frac{\Phi(0)_{\text{std}}}{\Phi(0)_{\text{alloy}}} \right) \left(\frac{\chi_{\text{alloy}}}{\chi_{\text{std}}} \right). \quad (18)$$

Eqn. (5) thus assumes the form $1/f = b \chi$ where b is a constant, and Eqn. (6) becomes $\Delta f/f = -\Delta \chi/\chi$.

Differentiation of Eqn. (18) yields:

$$\frac{\Delta C}{C} = \left[\frac{\Delta[\Phi(0)]_{\text{std}}}{\Phi(0)_{\text{std}}} - \frac{\Delta[\Phi(0)]_{\text{alloy}}}{\Phi(0)_{\text{alloy}}} \right] + \left[\frac{\Delta(\mu/\varrho)_{\text{alloy}}}{(\mu/\varrho)_{\text{alloy}}} - \frac{\Delta(\mu/\varrho)_{\text{std}}}{(\mu/\varrho)_{\text{std}}} \right] + [\cot \theta_{\text{std}} \Delta \theta_{\text{std}} - \cot \theta_{\text{alloy}} \Delta \theta_{\text{alloy}}]. \quad (19)$$

This equation indicates that an error in the mass attenuation coefficient produces a relative error of the same magnitude (with a change in sign) in the result, regardless of the X-ray emergence angle. The effect of errors in the emergence angle, however, diminishes with increasing emergence angle. The fact that the relative analytical error equals (with changed sign) that of the mass attenuation is crucial, if disappointing, in view of our poor knowledge of mass attenuation coefficients in the long wavelength region. Consequently, present claims of quantitative analysis of high accuracy in this X-ray region must be met with skepticism, unless standard and specimen are of similar composition.

III. Discussion and Experimental Values for the Al-Mg Binary System

In this section, we shall report on analyses of binary Al-Mg alloys, to illustrate the foregoing consideration. The Al-Mg system permits the absorption correction to be isolated so that experimental studies as well as theoretical calculations can be carried out.

In considering the corrections to be applied, atomic number effects can be ruled out since Al and Mg are adjacent in the periodic table and since their respective Z/A values are nearly equal. The Mg K_{α} lines will be excited by the Al K_{α} since the Mg K absorption edge lies at a lower energy level than the Al K_{α} line. Therefore, a fluorescence correction is required for Mg as well as an absorption correction. The magnitude of the correction to be applied is small since the absorption coefficients of both Al and Mg for Mg K_{α} are nearly equal and since the K-fluorescence yield from Al is very small. The *Philibert-Duncumb* relation was used to correct for absorption effects while *Castaing's* relation¹ was used to correct for fluorescence. The total correction calculated at all Mg compositions was one percent relative or less. Therefore, Mg in Al-Mg represents very nearly the ideal case in which the measured relative X-ray fluxes are equal to the concentrations across the entire range of compositions.

For Al, there will be no fluorescent X-ray excitation. However, a large absorption correction is needed because the mass attenuation coefficient (μ/ρ), of Mg for Al K_α is more than an order of magnitude greater than the μ/ρ of Al for Al K_α . The numerical value for μ/ρ of Al for Al K_α , written as μ/ρ (Al, Al K_α), was taken to be 408⁹. There are several reported values for μ/ρ (Mg, Al K_α) which are listed in Table II.

Table II. Mass Attenuation Coefficient of Mg and Al for Al K_α and Mg K_α According to Various Sources

Investigator	Reference	μ/ρ (Mg, Al K_α)	μ/ρ (Mg, Mg K_α)	μ/ρ (Al, Mg K_α)
Henke et al.	11	3797	—	—
Theisen	17	4100	340	643
Heinrich	8	4377	464	615
Philips	11	4050	350	500
Birks	18	4300	435	510
Allen	11	3900	—	—

Published values of μ/ρ (Mg, Mg K_α) and μ/ρ (Al, Mg K_α) are also given in Table II¹¹. The magnitude of the absorption correction for the Al-Mg system is not exceptional for the wavelength region under consideration; numerous other systems for which an even greater absorption correction is indicated (such as Mg in Cu-Mg) are of practical importance. For the calculation, *Heinrich's* values were used.

Table III. Errors in the value of *Philiberti-Duncumb's* "f" for Al K_α
Due to Input Parameter Errors:

$$\frac{\mu}{\rho} \text{ (Al, Al } K_\alpha) = 408 \pm (2\%); \quad \frac{\mu}{\rho} \text{ (Mg, Mg } K_\alpha) = 4377 \text{ (10\%);}$$

$$\frac{\mu}{\rho} \text{ (alloy, Al } K_\alpha) = 2392 \pm (9.3\%); \quad \Delta\theta = +0.5^\circ; \quad \Delta E = +0.25 \text{ kV}$$

[calculated according to Eqns. (10)–(12)]

Material	θ	E	y	Pct. $\left(\frac{\Delta f}{f}\right)_{\theta, E}$	Pct. $\left(\frac{\Delta f}{f}\right)_{(\mu/\rho), E}$	Pct. $\left(\frac{\Delta f}{f}\right)_{(\mu/\rho), \theta}$
Al	15°	5	0.061	0.15	0.25	0.67
Al	15°	10	0.196	0.44	0.71	0.88
Al	15°	20	0.577	1.0	1.62	0.95
50-Al-Mg	15°	5	0.357	3.35	1.17	3.24
50-Al-Mg	15°	10	1.15	7.16	2.50	3.08
50-Al-Mg	15°	20	3.38	9.3	3.25	1.9
Al	60°	5	0.018	0.05	0.013	0.21
Al	60°	10	0.058	0.14	0.04	0.29
Al	60°	20	0.172	0.40	0.11	0.38
50-Al-Mg	60°	5	0.106	1.21	0.07	1.17
50-Al-Mg	60°	10	0.341	3.21	0.19	1.38
50-Al-Mg	60°	20	1.01	6.56	0.39	1.34

In order to show the effect of various errors on the value of f , according to the *Philibert-Duncumb* model, Eqn. (2), at several voltages, a 50 Al-50 Mg alloy was assumed available for the determination of Al at 5, 10 and 20 kV respectively. Two X-ray take-off angles, 15° and 60° , were considered. As to the errors, we assume a value of $\Delta\theta = 0.5^\circ$ for both sample and standard, and a value of $\Delta E = 0.25$ kV. The estimated errors for μ/ρ (Mg, Al K_α) = 4377 and μ/ρ (Al, Al K_α) are 10% and 2% respectively. The results of substitution into Eqns. (10)–(12) are given

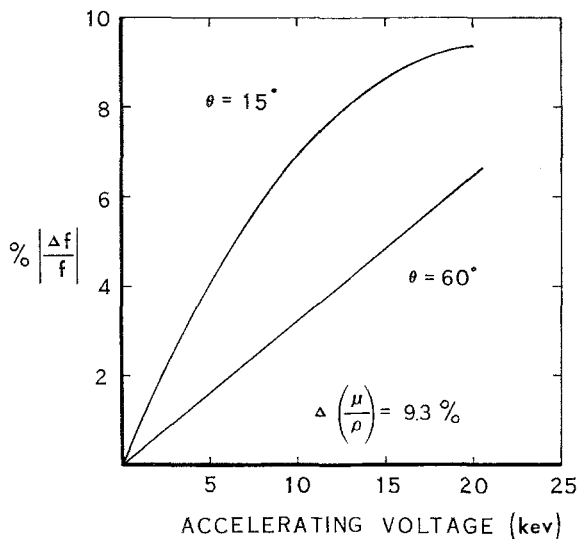


Fig. 5. Effect of input parameter errors at X-ray take-off angle of 15° and 60° on f in the *Philibert-Duncumb* model for Al in 50 Al-50 Mg alloy

Fig. 5a. Effect of 9.3% error on μ/ρ (Alloy, Al K_α)

in Table III for both take-off angles and each error type, i. e. (μ/ρ) , θ , and E , separately. Fig. 5a-c give the same information graphically, Fig. 6 provides a plot of the cotangent of θ in radians as a function of the magnitude of θ . When multiplied by $B \Delta\theta$, the error due to uncertainties in the emergence angle can be obtained.

It is apparent that better (μ/ρ) values are necessary to improve the accuracy; however, going to lower voltage at high take-off angles should give acceptable results (a 1 to 2% relative error). The 0.5 take-off angle error is not serious at the 60° angle. The voltage error can be minimized by calibration of the power supply; it is not too serious at 60° .

Another implication is that sample preparation effects are more apparent at low take-off angles. Extreme care is thus required when working with instruments having low X-ray take-off angles. This should

not imply that having a high take-off angle permits one to relax specimen preparation criteria. *Picklesimer*¹² performed an experiment designed

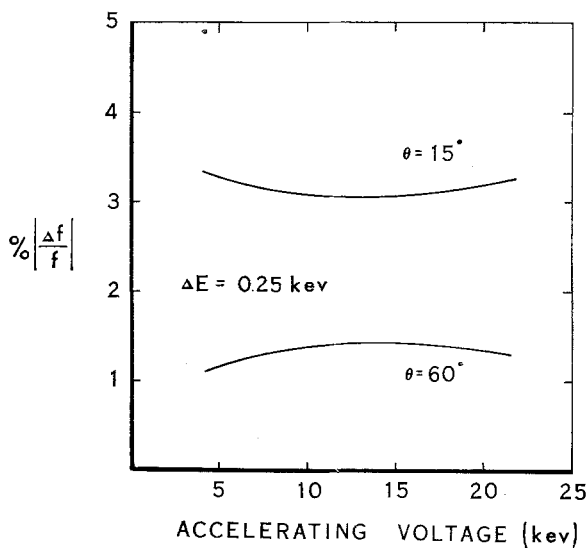


Fig. 5b. Effect of 0.25 keV error in operating voltage

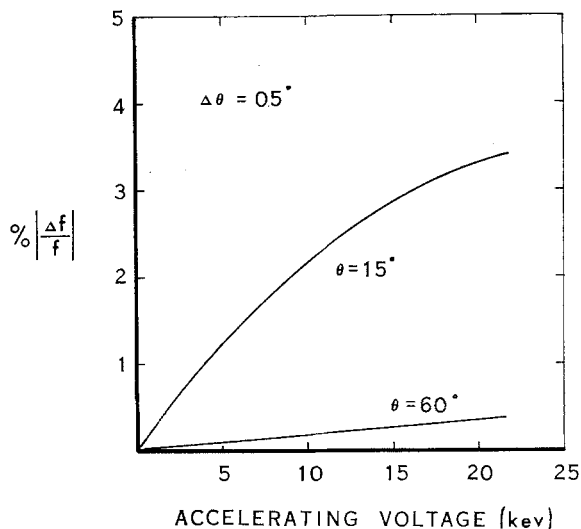


Fig. 5c. Effect of 0.5° error in take-off angle

to quantitatively show the effect of specimen preparation as a function of emergence angle on a 50-50 Cu-Ni alloy in the heavily etched, lightly

etched, as polished, and from 3/0 Al_2O_3 papers conditions respectively. He used instruments with X-ray take-off angles of 15.5° and 35° . There was little effect on the results in the first three named conditions of surface preparation for both values of θ . After grinding on 3/0 paper, no change was observed with θ of 35° ; however, a 2 to 3% variation occurred when using a 15.5° emergence angle. After grinding on 3/0 paper "there were 2 to 4 micron steps" between scratches. Only the relatively

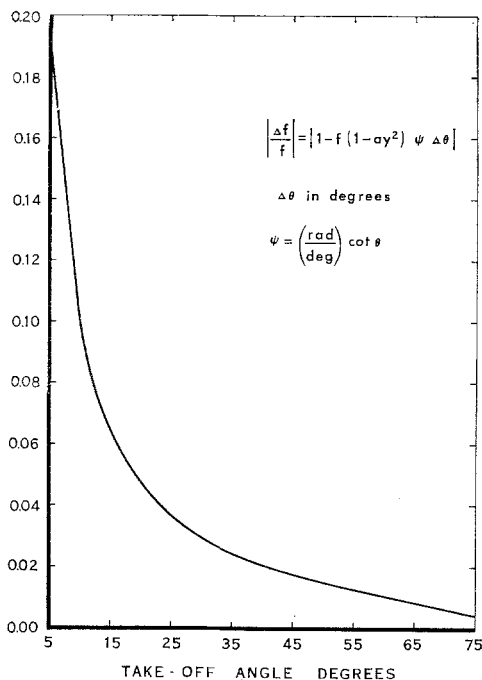


Fig. 6. Effect of errors in take-off angle on f in the *Philibert-Duncumb* model as a function of nominal take-off angle

high energy K_α lines of Cu and Ni were used; the f values for the alloy are 0.96 and 0.91 at 35° and 15.5° respectively. Therefore even for cases where $f \geq 0.91$, i. e., very low absorption of the line of interest, low X-ray emergence angles may lead to difficulty if 2–4 micron steps are encountered¹². In yet another study, it was shown experimentally that the less energetic (softer) the X-ray line under study, the worse the effect of a non-flat sample examined at a given voltage¹³.

At this point, we will examine theoretical and experimental models for f , again using Al in Al–Mg as an example. The experimental data of *Goldstein et al.* on Al–Mg¹⁴ can then be used for purposes of comparison.

Consider an alloy containing 50.0% Al and 50.0% Mg. We shall compare the experimental values for f of *Green*¹⁵, those of *Castaing-Henoc*¹⁶ and the equation of *Philibert-Duncumb*⁵ for determining k values for Al and Mg at 10, 15 and 20 kV; furthermore, the calculations of *Bishop* will be used at 10 kV as well. Values of f vs. χ at 10, 15 and 20 kV are shown as Fig. 7. The discrepancies at low f values are apparent.

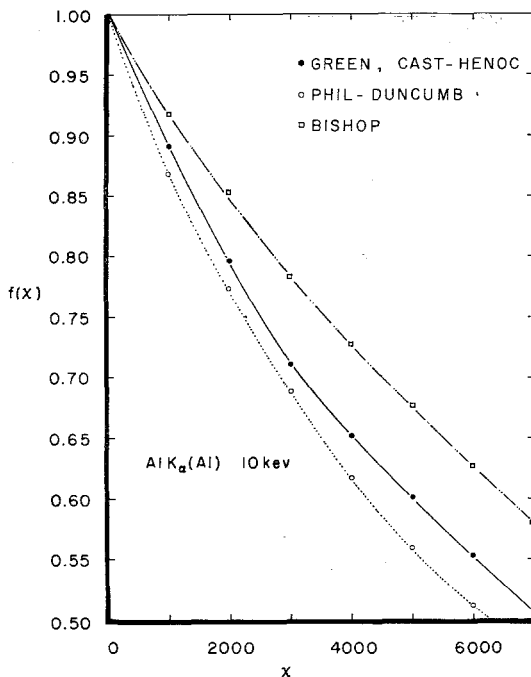


Fig. 7. Values of f for Al in an Al matrix according to *Bishop* (theoretical), *Philibert-Duncumb* (semi-empirical), *Green* (empirical) and *Castaing-Henoc* (empirical)

Fig. 7a. f vs. χ at 10 keV

To show the interaction of uncertainties in both (μ/ρ) and the model, the f values for each model and each (μ/ρ) value in Table II were computed with $\theta = 52.5^\circ$. The results are listed in Table IV. As expected, the discrepancies are greatest at the lowest f values.

Using Table IV, the expected k value for the two constituents was calculated from Eqn. (3). For Mg, the calculated fluorescence correction using *Castaing's* method is 1.1, 1.2 and 1.3% at 10, 15 and 20 kV respectively. The " k " values of Table V for Mg have been multiplied by the appropriate factor for comparison with the measured values. The results are shown in Table V along with the experimental k values of *Goldstein et al.* which are estimated to be good to $\pm 1.5\%$ relative.

The alloys were splat-cooled and carefully checked for homogeneity prior to analysis¹⁴. Chemical analysis is claimed to be accurate to 0.4% relative. Examination of Table V shows that for Mg, all results at all voltages are within experimental error; the choice of model or mass attenuation coefficient makes little difference because f is 0.8 or greater. However, for Al, almost all results are outside the limits of $\pm 1.5\%$ relative.

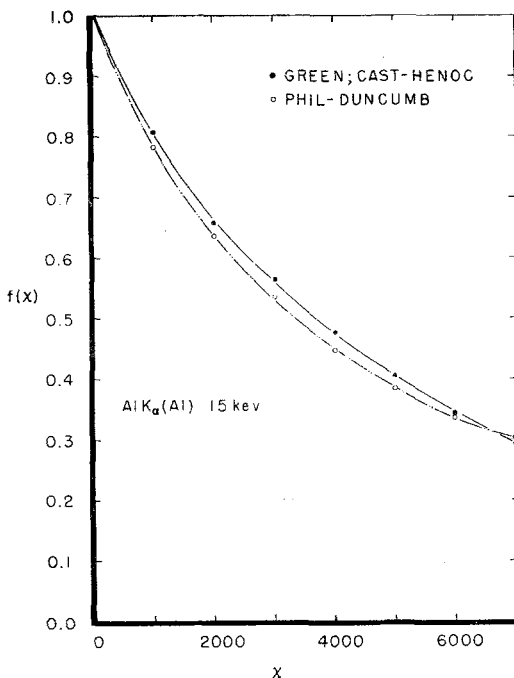


Fig. 7b. f vs. x at 15 kV

The discrepancies, as expected, increase with increasing voltage. This confirms our conclusions concerning input parameter errors.

In fact, since one can take B as being equal to y (Fig. 3) [or more accurately $B \simeq (1 - f)$], when f drops below 0.8, no valid conclusion as to the right model and the right (μ/ρ) combination can be made in spite of the fact that aluminum is the material for which the most extensive study of f vs. x is presently available. For other materials whose f vs. x relationships are less well-known, it is even more imperative to keep f above 0.8.

IV. Conclusions

1. Error analysis of the X-ray absorption correction indicates that serious analytical errors can result from uncertainties in input parameters.

2. In order to reduce the effects of these errors, the ratio χ/σ should be kept to 0.25 or less.

3. In consequence, the value of the absorption function $f(\chi)$ should be 0.8 or greater.

4. Keeping $f(\chi)$ above 0.8 has the added advantage of minimizing the effects of discrepancies between the various models for $f(\chi)$.

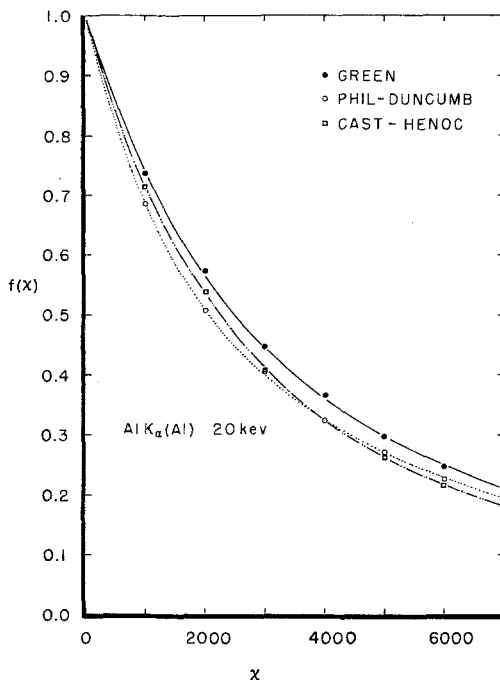


Fig. 7c. f vs. χ at 20 keV

5. To achieve these conditions experimentally, instruments should be capable of giving stable, high count rates at low overvoltage ratios and have high X-ray emergence angles.

6. To further improve the accuracy of microprobe analysis, particularly of low atomic number elements, more accurate experimental determinations of mass attenuation coefficients and of the function $f(\chi)$ are required.

7. By plotting the ratio χ/σ against $f(\chi)$, as determined by the *Philibert-Duncumb* model, a single generalized curve is obtained.

Summary

The accuracy of the X-ray absorption correction for quantitative microprobe analysis is affected by uncertainties in the input parameters

Table IV

Kilo-voltage	Source for $\frac{\mu}{\rho}$ (Mg, Al K α)	Henke et al.	Theisen	Heinrich	Philips	Birks	Allen
	Source for f						

Values of f_{Al} for a 50 Al-Mg Alloy

10	Bishop	0.806	0.793	0.782	0.795	0.785	0.801
10	Green, Castaing-Henoc	0.740	0.723	0.710	0.725	0.714	0.734
10	Philibert-Duncumb	0.715	0.700	0.686	0.704	0.691	0.711
15	Green, Castaing-Henoc	0.592	0.572	0.559	0.578	0.563	0.586
15	Philibert-Duncumb	0.560	0.559	0.525	0.542	0.528	0.552
20	Green	0.487	0.473	0.446	0.469	0.451	0.479
20	Castaing-Henoc	0.450	0.425	0.404	0.431	0.411	0.430
20	Philibert-Duncumb	0.434	0.412	0.404	0.420	0.405	0.428

Values of f_{Mg} for a 50 Al-Mg Alloy

10	Bishop	0.947	0.943	0.953	0.949
10	Green, Castaing-Henoc	0.923	0.921	0.935	0.930
10	Philibert-Duncumb	0.908	0.904	0.919	0.914
15	Green, Castaing-Henoc	0.876	0.869	0.889	0.881
15	Philibert-Duncumb	0.841	0.832	0.856	0.850
20	Green	0.800	0.790	0.820	0.810
20	Castaing-Henoc	0.808	0.798	0.815	0.815
20	Philibert-Duncumb	0.773	0.761	0.799	0.785

(mass attenuation coefficients, X-ray emergence angle, and operating voltage), as well as by inaccuracies in the proposed absorption correction models. If the mass attenuation coefficient is known within 5%, then to keep the error of this correction below 1%, the absorption function, $f(\chi)$, must be equal to or higher than 0.8. Experimental conditions leading to small absorption corrections are discussed, and the advantages of high X-ray emergence angles are demonstrated. As an illustration, the analysis (theoretical and experimental) of several aluminum-magnesium alloys is discussed.

Zusammenfassung

Die Genauigkeit der Röntgenstrahl-Absorptionskorrektur für die quantitative Mikrosondenanalyse ist von Fehlern der benützten Parameter (Massenabschwächungskoeffizienten, Austrittswinkel und Arbeitsspannung) und auch von Ungenauigkeiten in der Form der Korrektur beeinflusst. Wenn der Abschwächungskoeffizient mit 5% Genauigkeit bekannt ist, so muß die Absorptionsfunktion, $f(\chi)$, 0,8 oder größer sein, um den Korrekturfehler unter 1% zu halten. Die zur Verminderung der Absorptionskorrektur nötigen Arbeitsbedingungen werden angegeben und die Vorteile eines großen Austrittswinkels nachgewiesen. Die theoretische und experimentelle Analyse von Aluminium-Magnesium-Legierungen wird als Erläuterungsbeispiel verwendet.

Table V

Kilovoltage	Source of $\frac{\mu}{\rho}$ (Mg, Al K α)	Henke	Theissen	Heinrich	Philips	Birks	Allen	k Value Measured by Goldstein et al.
	k value computed							
Values for k_{Al} Calculated for a 50 Al-Mg Alloy								
Compared to Measured Values								
10	Bishop	0.422	0.416	0.410	0.417	0.411	0.420	0.387
10	Green, Castaing-Henoc	0.394	0.385	0.378	0.386	0.381	0.391	
10	Philibert-Duncumb	0.387	0.379	0.371	0.381	0.374	0.385	
15	Green, Castaing-Henoc	0.331	0.320	0.312	0.323	0.315	0.328	0.311
15	Philibert-Duncumb	0.324	0.312	0.303	0.313	0.305	0.319	
20	Green	0.292	0.283	0.267	0.281	0.270	0.287	0.245
20	Castaing-Henoc	0.271	0.256	0.243	0.259	0.247	0.259	
20	Philibert-Duncumb	0.270	0.256	0.251	0.261	0.252	0.266	
Values for k_{Mg} Calculated for a 50 Al-Mg Alloy								
Compared to Measured Values								
10	Bishop		0.499	0.502	0.502	0.504		0.506
10	Green, Castaing-Henoc		0.494	0.501	0.500	0.503		
10	Philibert-Duncumb		0.492	0.500	0.498	0.503		
15	Green, Castaing-Henoc		0.487	0.499	0.495	0.502		0.495
15	Philibert-Duncumb		0.485	0.495	0.495	0.502		
20	Green		0.476	0.493	0.488	0.501		0.499
20	Castaing-Henoc		0.480	0.495	0.491	0.501		
20	Philibert-Duncumb		0.471	0.490	0.487	0.497		

Résumé

L'exactitude de la correction d'absorption dans l'analyse quantitative par sonde électronique est diminuée à conséquence des erreurs des paramètres utilisés (coefficients d'absorption massique, angle d'émergence du rayonnement analysé, et tension d'accélération des électrons) et du modèle de correction. Si le coefficient d'absorption est connu à 5% près, pour éviter des erreurs plus grandes que 1%, il faut que la fonction d'absorption $f(\chi)$ soit 0,8. On indique les conditions expérimentales conduisant à une faible correction d'absorption et on démontre les avantages d'un angle d'émergence élevé. L'analyse théorique et expérimentale des alliages aluminium—magnésium est utilisée à manière d'exemple.

References

- ¹ *R. Castaing*, Thesis, University of Paris (1951), publ. O. N. E. R. A. No. 55.
- ² *P. M. Thomas*, U. K. At. Energy Auth. Rept. AERE-R 4593, pp. 16 (1964).
- ³ *D. B. Wittry*, ASTM Spec. Tech. Publ. 349 (1963), p. 128.
- ⁴ *J. Philibert*, X-ray Optics and X-ray Microanalysis. (Proc. Third Int'l. Symp., Stanford Univ.—*H. H. Pattee*, *V. E. Cosslett*, and *A. Engström*, eds.) New York: Academic Press. 1963. p. 379.
- ⁵ *P. Duncumb* and *P. K. Shields*, The Electron Microprobe. (Proc. Symp. Electrochem. Soc., Washington, D. C. 1964—*T. D. McKinley*, *K. F. J. Heinrich*, and *D. B. Wittry*, eds.) New York: Wiley. 1966. p. 284.
- ⁶ *D. B. Clayton*, Brit. J. Appl. Physics 14, 117 (1963).
- ⁷ *G. D. Archard* and *T. Mulvey*, Brit. J. Appl. Physics 14, 626 (1963).
- ⁸ *K. F. J. Heinrich*, The Electron Microprobe. (Proc. Symp. Electrochem. Soc., Washington, D. C. 1964—*T. D. McKinley*, *K. F. J. Heinrich*, and *D. B. Wittry*, eds.) New York: Wiley. 1966. p. 296.
- ⁹ *G. D. Hughes* and *G. D. Woodhouse*, Optique des Rayons X et Microanalyse. (Proc. Fourth Int'l. Symp., Orsay—*R. Castaing*, *P. Deschamps*, and *J. Philibert*, eds.) Paris: Editions Scientifiques Hermann. 1966. p. 202.
- ¹⁰ *P. Duncumb* and *D. A. Melford*, Tube. Inv. Res. Labs. Tech. Rept. 195, pp. 27 (1965).
- ¹¹ *H. M. Stainer*, U. S. Bur Mines Inf. Circ. IC-8166, pp. 124 (1963).
- ¹² *M. L. Picklesimer* and *G. Hallerman*, U. S. Atomic Energy Comm. Rept. ORNL-TM-1591, pp. 46 (1966).
- ¹³ *H. Yakowitz*, ASTM Spec. Tech. Publ. In Press.
- ¹⁴ *J. I. Goldstein*, *F. J. Majeske*, and *H. Yakowitz*, Advances in X-ray Analysis 10, 431 (1961).
- ¹⁵ *M. Green*, Thesis, University of Cambridge (1962).
- ¹⁶ *R. Castaing* and *J. Hénoc*, Optique des Rayons X et Microanalyse. (Proc. Fourth Int'l. Symp., Orsay—*R. Castaing*, *P. Deschamps*, and *J. Philibert*, eds.) Paris: Editions Scientifiques Hermann. 1966. p. 120.
- ¹⁷ *R. Theisen*, Quantitative Electron Microprobe Analysis. New York: Springer-Verlag. 1965. p. 32.
- ¹⁸ *L. S. Birks*, Electron Probe Microanalysis. New York: Interscience. 1963. p. 202.