

SOME PROBLEMS WITH QUANTITATIVE ELECTRON PROBE MICROANALYSIS

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Abstract

The main lines of correction calculations are briefly reviewed, according to the ZAF scheme—where Z represents the atomic number effect, A the absorption, and F the fluorescence. The atomic number correction is discussed in detail and its importance in the case of thin specimens analysis is emphasized.

I. Introduction

Electron probe' microanalysis has been frequently considered as an absolute method, since it gives directly the mass concentration of an element A in a complex target ABC . . .:

$$C_A = (I_A/I(A)) \quad (1)$$

with the usual notation.

This relation is of course an approximate one, and the first question which arises is as follows: what kind of intensities are to be considered in relation (1) ?

A careful distinction has to be made between generated intensities and emerging intensities.

Let us call k_A the ratio of intensities of radiations (i.e., $K\alpha$) generated within both targets (specimen and standard)

$$k_A = (I_A/I(A)) \quad (2)$$

The theory has to derive the relation between k_A and C_A .

In Castaing's "first approximation", the relationship is simply:

$$k_A = C_A \quad (3)$$

while the Castaing "second approximation" takes the form

$$k_A = \frac{a_A C_A}{\sum_j \alpha_j C_j} \quad (4)$$

A more exact approximation which may be easily derived, is:

$$k_A = C_A \frac{(R/S)_{\text{specimen}}}{(R/S)_{\text{standard}}} \quad (5)$$

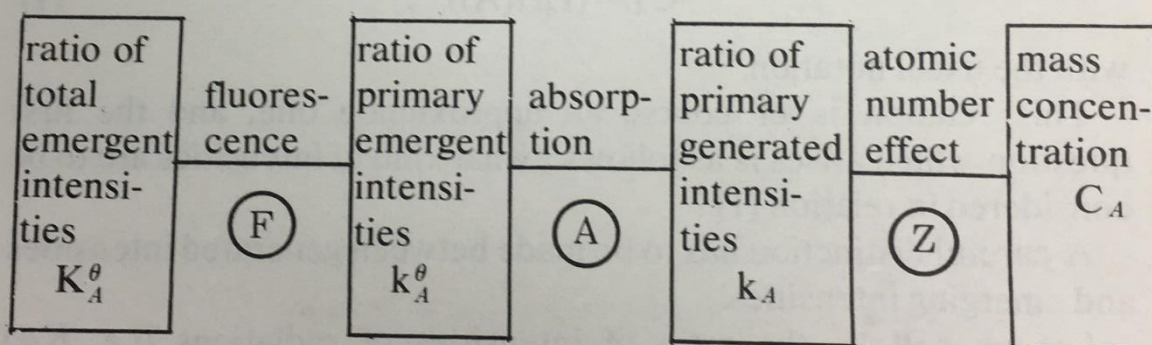
R is the "backscattering factor" (loss of ionizations due to electron backscattering) and S is the "stopping power factor". Both factors depend on the electron retardation law and the ionization cross-section of A atoms. Moreover, R depends on the number and energy distribution of backscattered electrons.

The second formula to be derived relates the ratio k_A of generated intensities to the ratio K_A^θ of the intensities J of the radiation emerging from the specimen and entering the spectrometer

$$K_A^\theta = (J_A/J(A)) \quad (6)$$

Two effects contribute to the difference between K_A^θ and k_A . First of all, radiation is absorbed inside the target and secondly, fluorescent radiation is emitted with the same wavelength as the primary. Relationships (3), (4), or (5) are only valid for primary emissions.

Thus, the essential features of the calculations may be summarized as follows:



The secondary emissions have to be subtracted from the total measured intensities ($K_A^\theta \rightarrow k_A^\theta$). The primary emergent intensities have then to be corrected for the absorption effect ($k_A^\theta \rightarrow k_A$) and finally the true concentration C_A is calculated from the ratio of primary generated intensities (atomic number effect).

This sequence may be expressed as the FAZ sequence. Conversely, by calculating the ratio of emergent intensities from the known (or assumed) concentrations, the ZAF sequence has to be followed. "Zafizing" is the usual method of calculation for

establishing theoretical calibration curves, K_A^θ versus C_A or K_A^θ/C_A versus C_A (or K_A^θ), or $K_A^\theta-C_A$ versus K_A^θ , while "Fazising" is generally employed for iterative calculations.

The importance of the order of the factors (namely FAZ or ZAF) should be noted. If the calculation stages are expressed as multiplicative factors, i.e.,

$$k_A^\theta = K_A^\theta \cdot f(C_i)$$

and so on . . . , the order of calculation is not significant. This is the case of many calculations, mainly with computers when iterative methods are used.

Nevertheless, experience seems to me to show that frequently one of the corrections is more significant than the others and its relative importance appears clearly when the right order of the sequence is respected. Generally speaking, every time the calculation cannot directly obey the general scheme, it is necessary to examine the physical significance of the processes involved, and the ZAF scheme remains the basis of such a critical investigation.

In developing general methods, homogeneous targets are assumed but in practice this assumption is often not justified. Analyses near boundaries (precipitates, diffusion, layers, . . .) are very frequent, and a "blind" calculation becomes impossible. Here again a clear understanding of the physical processes involved (as shown by the ZAF scheme) is absolutely essential.

I would suggest that the case of non-homogeneous targets has not yet received all the care it deserves. The correction calculation method must be generally verified by looking at homogeneous targets, although platings of A/B type are also very useful from this point of view and can give useful data in connection with absorption or fluorescence effect: $\phi(\rho z)$ function, ratio of secondary to primary emission, etc. . . .). But in practice, the "microprobist" has to deal with boundaries, precipitates, and so on, so that each new measurement often appears as a "particular case" and does not enter the general scheme of calculations for which programs are available.

From this point of view, the analysis of small particles embedded in a more or less amorphous matrix has not yet received sufficient attention. Such is the case for extraction replicas in metallurgy, foreign particles in biological tissues, The quantitative analysis of such specimens is very crucial in many fields of research; it has expanded widely with the developments of EMMA and similar

instruments combining electron microscopy and microanalysis. General methods of calculation (absorption, atomic number) are lacking for such specimens and no precise tests have been made to determine whether the corrections are negligible or not.

II. Discussion

A. ABSORPTION CORRECTION

The analytical expression for the $f(\chi)$ functions has been widely employed for some years, in spite of the drastic assumptions used in its derivation, even with the "effective σ " improvement suggested by Duncumb and Shields.

In the computer age however, the need for simple formulae is not as acute as during the slide rule period. It is thus to be hoped that the "collective model" on which the formula is based will be reconsidered in spite of the many difficulties likely to be encountered. The inaccuracies and the inadequacies of the physical laws involved (multiple scattering and diffusion, electron attenuation and retardation laws, etc.) have been pointed out in a series of papers by Cosslett and Thomas [11].

Notwithstanding the rather pessimistic conclusions of these authors, this description offers nevertheless several advantages, the most important being that a good derivation of the $\phi(\rho z)$ distribution function would enable the Z and A factors to be calculated in a single step.

B. FLUORESCENCE CORRECTION

I should like to present only two short remarks about these corrections:

(a) *characteristic radiation*: the well known Castaing [8] formula, with or without the improvements or the simplifications due to several authors (Birks, Reed, Wittry, . . .), applies first of all to K-K excitation. The case of L-L, K-L, . . . excitations have perhaps not yet been analyzed with the careful attention required. For instance, in his general paper, Reed (1965) [17] finally gives a numerical application only in the case of K-K excitation. Furthermore, the absence of data on the fluorescence yield and the absorption jumps, together with the complexity of Coster-Kronig transitions, seem to frighten off fresh investigation in that field.

(b) *continuous spectrum*: I am afraid that people have too frequently claimed this correction to be negligible, without any

calculations to ascertain the validity of such an assumption. In the case of A/B interfaces, this fluorescence effect is known to be frequently quite important.

C. ATOMIC NUMBER EFFECT

With the assumption of a continuous energy loss law, the ratio of E_X quanta ($X = K, L_{III}, \dots$) produced in the specimen and the standard can be written as follows:

$$\frac{n_A}{n(A)} = C_A \frac{\bar{R}_A}{R(A)} \frac{\int_{E_0}^{E_X} \frac{\Psi_X^A(E)}{[dE/d\rho s]_{sp}} dE}{\int_{E_0}^{E_X} \frac{\Psi_X^A(E)}{[dE/d\rho s]_{st}} dE} \quad (7)$$

where $R(A)$ is relative to pure A standard, \bar{R}_A to the specimen (for element A). E is the mean electron energy, $\Psi_X(E)$ the ionization cross section of the A atoms for the X level, E_X the ionization energy for this level. $dE/d(\rho s)$ is the retardation equation of the electrons in the target, ρ its specific mass, s the length of the path traversed by the electrons in the target. The subscripts st and sp are respectively related to standard and specimen. By using a well known theorem, this expression can be simplified to:

$$\frac{n_A}{n(A)} = C_A \frac{\bar{R}_A}{R(A)} \frac{(dE/d\rho s)_{st,E'}}{(dE/d\rho s)_{sp,E''}} \quad (8)$$

Since the ratio of stopping powers $s = dE/d\rho s$ is rather insensitive to the energy E , the second factor on the righthand side may be calculated for some mean value of the energy, i.e., $E_1 = (E_0 + E_X)/2$. Whence, with the usual notation:

$$(n_A/n(A)) = C_A (\bar{R}_A/R(A)) (s(A)/\bar{s}_A) \quad (9)$$

or

$$(n_A/n(A)) = (\alpha_A C_A / \bar{\alpha}) \quad (10)$$

with

$$\alpha_A = s(A)/R(A) \text{ and } \bar{\alpha} = \bar{s}_A/\bar{R}_A$$

The "second approximation" assumes that

$$\bar{\alpha} = \sum \alpha_j C_j \quad (11)$$

This simplification can hardly be justified, but it works! Of course, the α 's depend on the incident energy E_0 . As used by Poole and Thomas, it has been very successful for the analysis of binary alloys or compounds.

For a more exact calculation, equation (7) is rewritten:

$$\frac{n_A}{n(A)} = C_A \frac{\bar{R}_A/\bar{S}_A}{R(A)/S(A)} \quad (12)$$

where

$$S(A) = \int_{E_0}^{E_X^A} \frac{\Psi_X^A(E) dE}{[dE/d\rho s]_A} \quad (13a)$$

and

$$\bar{S}_A = \int_{E_0}^{E_X^A} \frac{\Psi_X^A(E) dE}{[dE/d\rho s]_{\text{complex target}}} \quad (13b)$$

The R and S factors have to be calculated for the standard (pure element) and for the specimen (complex material).

As far as the S factor is concerned, an exact calculation can be carried out in both cases by calculating equation (13a) and (13b) with the help of some analytical laws for Ψ and $dE/d\rho s$.

D. CALCULATION OF S FACTOR¹

Let us consider a target containing elements A, B, C, ... of atomic masses A_i , ... atomic numbers Z_i , ... and mass concentrations C_i , ... such that $\sum_i C_i = 1$.

Let this target be bombarded with electrons of initial energy $E_0 = e \cdot V_0$; E_X is the ionization energy of the X level of atoms A. We shall study the element A.

¹ See Brit. J. Appl. Phys. (1968) ser. 2, vol. 1, 685.

If dn_X is the mean number of ionizations of the X level of the A atoms produced by the electrons along the path increment ds :

$$dn_X = C_A \rho \frac{N}{A} \Psi_A^X(E) ds$$

$$n_X = C_A \cdot \frac{N}{A} \int_{E_0}^{E_X} \frac{\Psi_A^X(E)}{dE/d\rho s} dE \quad (14)$$

assuming that $(dE/d\rho s)$ is defined and is continuous along the path and that dn_X might be integrated. N is Avogadro's number. Bethe (1930) [3] and Bethe, Rose, and Smith (1938) [4] have given the following expressions for Ψ and $dE/d\rho s$:

a. *Ionization Cross Section:*

$$\Psi_A^X(E) = \frac{\pi e^4}{E \cdot E_X} Z_X b_X \log \frac{4E}{B_X} \quad (15)$$

Z_X : number of electrons on X level

b_X : $b_K = 0.35$, $b_L = 0.25$

$B_X = 1.65 E_X$ according to Bethe, but Worthington and Tomlin (1956) [20] gave a better form for low excitation energy as $B_X = 4E_X$. We shall take the value of $4E_X$ for electron probe microanalysis, where the electron energy is quite small (< 40 keV); we then have $\Psi \rightarrow 0$ when $E \rightarrow E_X$.

The b_X value does not appear in the atomic number effect correction (see later).

If $U = \frac{E}{E_X}$, $U_0 = \frac{E_0}{E_X}$ (over-voltage ratio)

$$\Psi_A^X(U) = \pi e^4 \frac{Z_X b_X}{E_X^2} \cdot \frac{1}{U} \cdot \log U \quad (16)$$

b. *Retardation Equation:*

$$\frac{dE}{d\rho s} = - \frac{2\pi e^4 N}{U \cdot E_x} \sum_i C_i \cdot \frac{Z_i}{A_i} \log \frac{1.166 U E_x^A}{J_i} \quad (17)$$

J_i : mean ionization potential for the i atoms.

These equations suppose that the electron energy is high enough, i.e., $E > E_x^A$ in equation (15) and $U \cdot E_x^A > J_i$ for all the target atoms in equation (17).

Let

$$\sum_i C_i \frac{Z_i}{A_i} = M \quad (18)$$

and

$$\prod_i \left[\left(\frac{1.166 E_x^A}{J_i} \right)^{C_i Z_i / A_i} \right] = W^M$$

or

$$\log W = \frac{1}{M} \sum_i C_i \cdot \frac{Z_i}{A_i} \log \frac{1.166 E_x^A}{J_i} \quad (19)$$

$$= \frac{1}{M} \sum_i C_i \frac{Z_i}{A_i} \log W_i^x \quad (20)$$

This leads to

$$\frac{dE}{d\rho s} = - \frac{2\pi e^4 N}{U E_x} \cdot M \log U \cdot W \quad (21)$$

and from (14)

$$n_x = C_A \frac{N}{A} \cdot \frac{Z_x b_x}{2N} \int_1^{U_0} \frac{\log U}{M \log U \cdot W} \cdot dU$$

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Let $(1/S) = n_X \cdot (A/N) \cdot (1/C_A)$, where $(1/S)$ is a function which can be used to represent the electron mass stopping effect in atomic number effect corrections.

Putting $X = U \cdot W$, we can integrate $(1/S)$ in terms of logarithmic integral (li) function and we get:

$$\frac{1}{S} = \frac{Z_X b_X}{2N} \cdot \frac{1}{M} \left\{ (U_0 - 1) - \frac{1}{W} \log W \times \right. \\ \left. \times \left[\text{li}(U_0 \cdot W) - \text{li}(W) \right] \right\} \quad (22)$$

The above equation allows the calculation of $(1/S)$ in any target.

In a target made of a pure element, it reduces to an already known equation (Archard, Mulvey, 1962) [1].

By assumption, we must have $U_0 \cdot W > 1$. If $W \rightarrow 1$, $(1/S)$ remains finite as can be seen in the series expansion:

$$\text{li } x = C + \log | \log x | + \sum_{s=1}^{\infty} \frac{(\log x)^s}{s \cdot s!}.$$

C = Euler's constant. The above expression allows the li function to be easily computed.

1. A Practical Way of Calculating $(1/S)$ for a Target of Known Composition

The terms $W_i^X = (1.166 E_X^A/J_i)$ can first be calculated. We have tabulated W_i^X for all elements of $3 \leq Z \leq 92$, taking the ionization energy E_X for the K level and L level from the tables of Bearden (1964) [2] and Blochin (1957) [6] (Fig. 1). We have used $J_i = 11.5 Z_i$ which might not be the best form for J (E_X and J_i in eV).

Afterwards one can calculate M (Eq. 18) and $\log W$ (Eq. 20).

The assumptions $U_0 \cdot W_i^X > 1$ involve a theoretical minimum value for U_0 , while in practical cases its value will always be greater. As a matter of fact, a small value of W_i^X is found for analysis of a light element in a heavy matrix, hence a low E_X and a high U_0 .

One can then calculate $(1/S)$. Practically, $(Z_X \cdot b_X / 2N)$ need not be calculated as this term vanishes in the correction coefficient. One then calculates a term $(1/S')$.

We have tabulated

$$(M/S') = U_0 - 1 - (1/W) \log W (\text{li } U_0 \cdot W - \text{li } W) \quad (23)$$

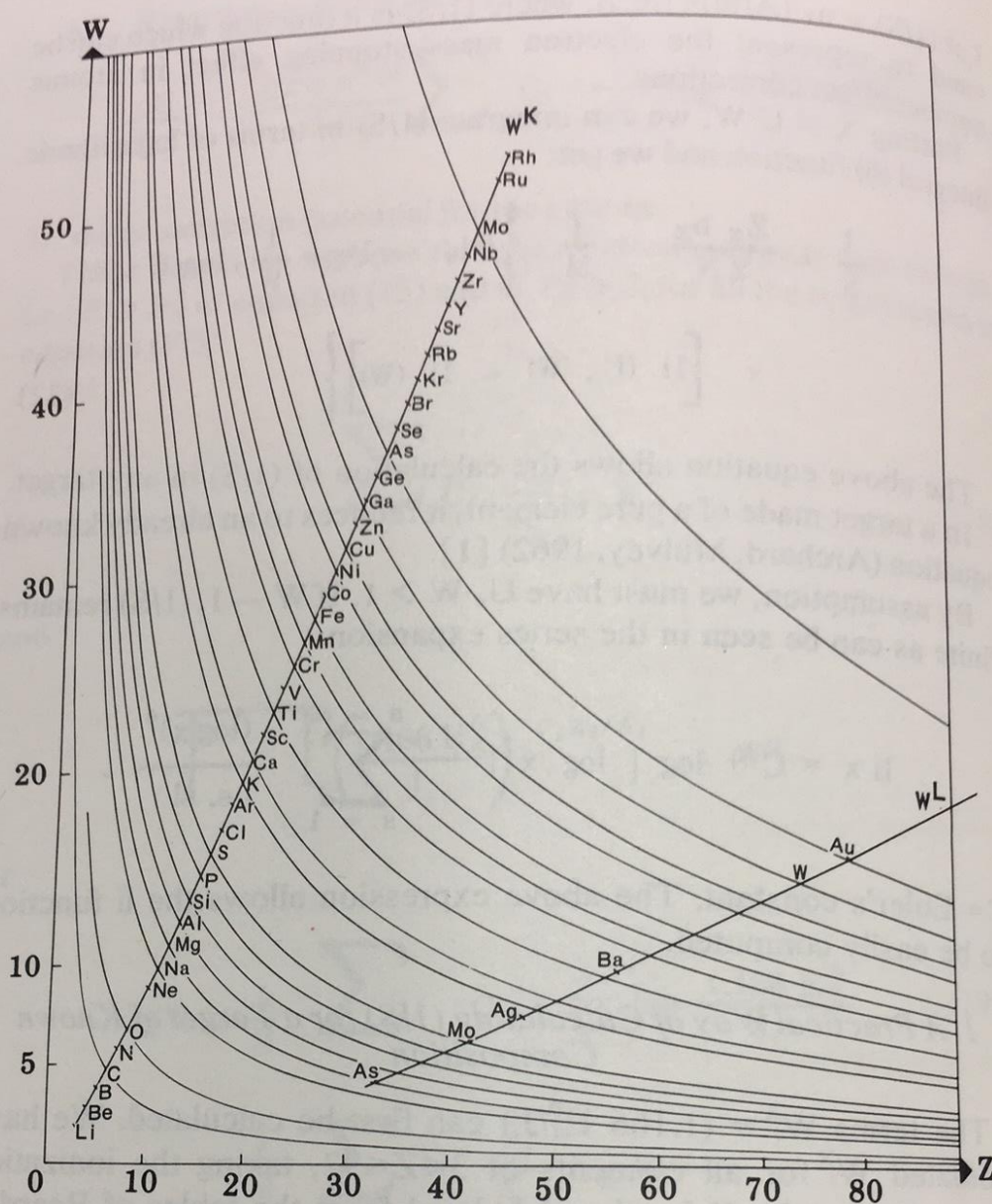


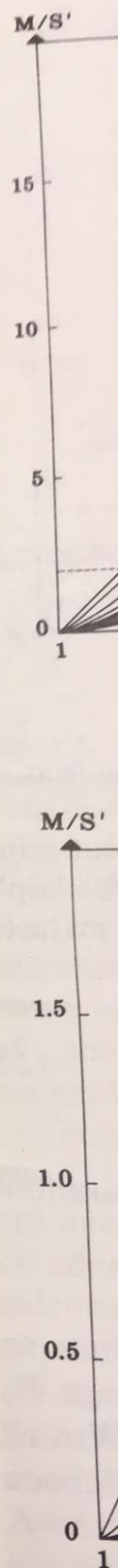
Figure 1. $W_i^X = (1.166 E_X / 11.5 Z_i)$.

for different values of W and U_o (Figs. 2,3,4) as the table of (M/S') values can be used for any target.

2. Applications

The "universal" curves (Figs. 2,3,4) give (M/S') from U_o and W values. W for an alloy can be calculated from W_A^X in pure specimens (Fig. 1), for the element analyzed, according to formula (20).

For instance, in copper-gold alloys where copper ($Cu K_\alpha$) is analyzed, and in copper-aluminium alloys where aluminium ($Al K_\alpha$) is analyzed, W variations have been plotted against copper



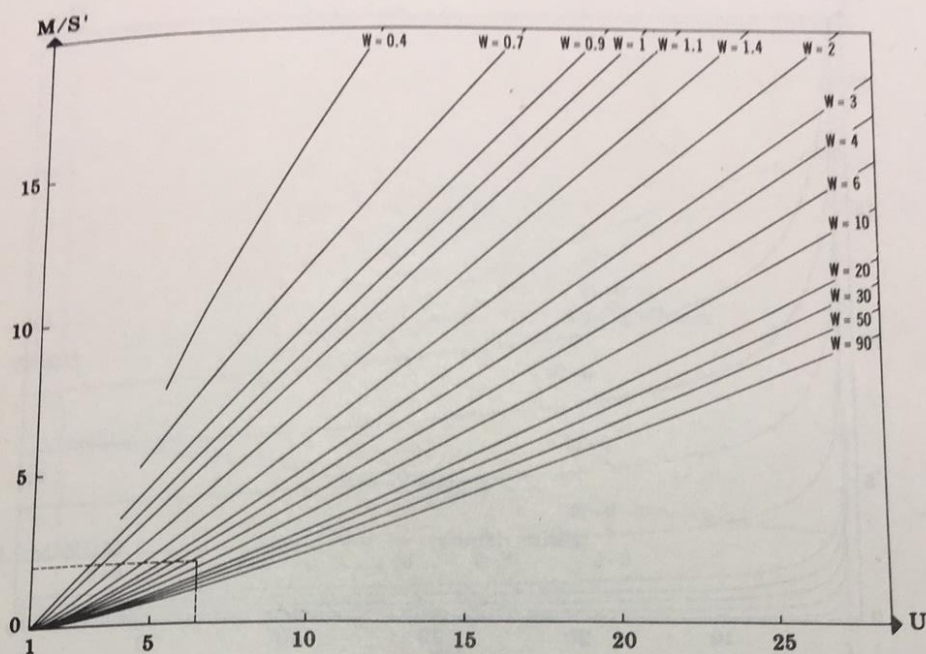


Figure 2. M/S' versus U for different W values, $1 < U < 30$.

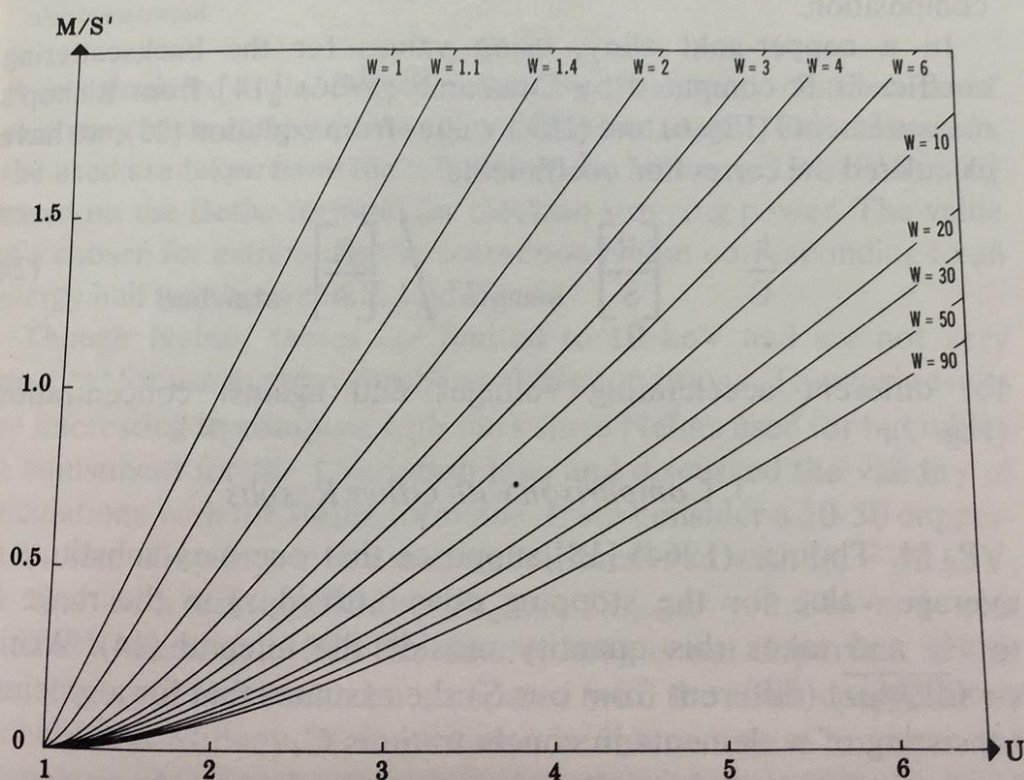


Figure 3. M/S' versus U for different W values, $1 < U < 6$.

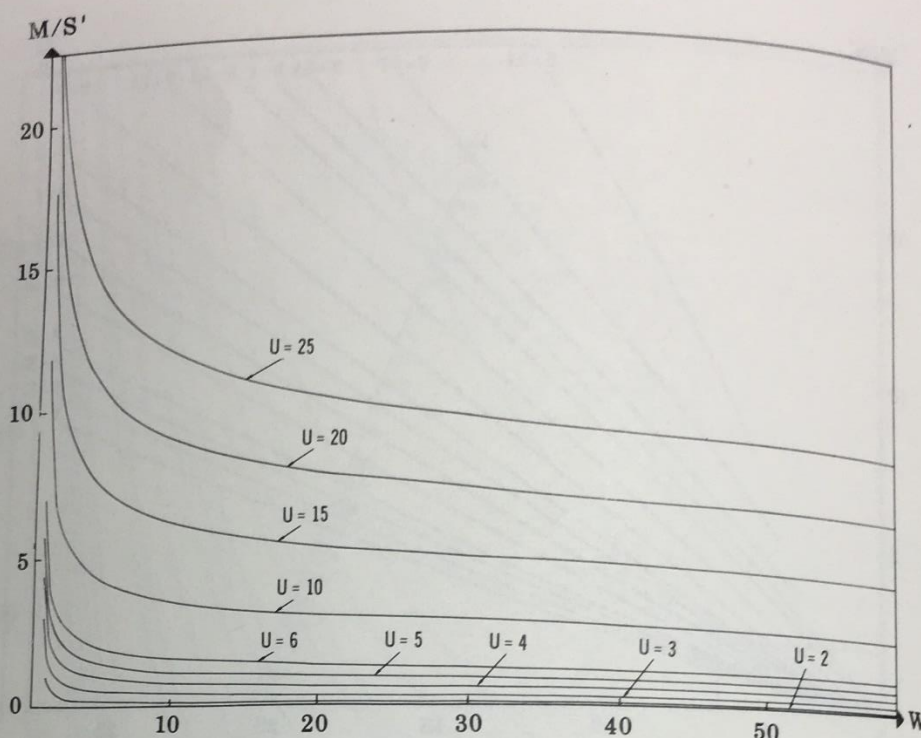


Figure 4. M/S' versus W for different U values.

concentration (Fig. 5). Generally, W is not a linear function of composition.

In a copper-gold alloy, using values for the backscattering coefficient R computed by Duncumb (1966) [14] from Bishop's measurements (Fig. 6) and $(1/S')$ values from equation (23), we have calculated the correction coefficients

$$\frac{k}{C} = \left[\frac{R}{S} \right]_{\text{sample}} / \left[\frac{R}{S} \right]_{\text{standard}} \quad (24)$$

for different accelerating voltages and against concentrations (Fig. 7).

3. Comparison with Other Results

P. M. Thomas (1964) [18] supposes that one may substitute an average value for the stopping power $(dE/d\rho z)$ in the range E_0 to E_X and takes this quantity outside the integral (14). Writing $s = (dE/d\rho z)$ (different from our S) she assumes that for a specimen consisting of n elements in concentrations C_i

$$\left(\frac{s}{R} \right) = \sum_i C_i \left(\frac{s}{R} \right)_i \quad (25)$$

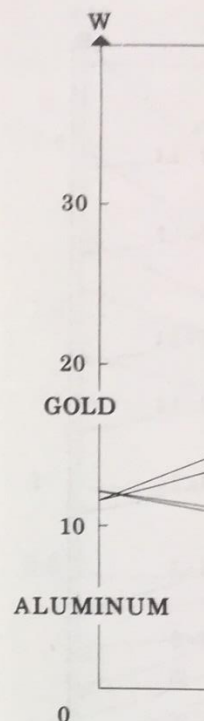


Figure 5. W versus composition for Gold and Aluminum. The curves for Gold and Aluminum also been traced.

R is calculated from the backscattered electrons backscattered coefficient. The values she used are based on the measurements of Bishop (1966) [14] of s chosen for the energy half value.

Though Neuman's calculations are practical for use in electron probe analysis, they are interesting and an adjustment in the calculations would be of value. We find with Thomas's method that the k/c values of Archard and Neuman are in good agreement.

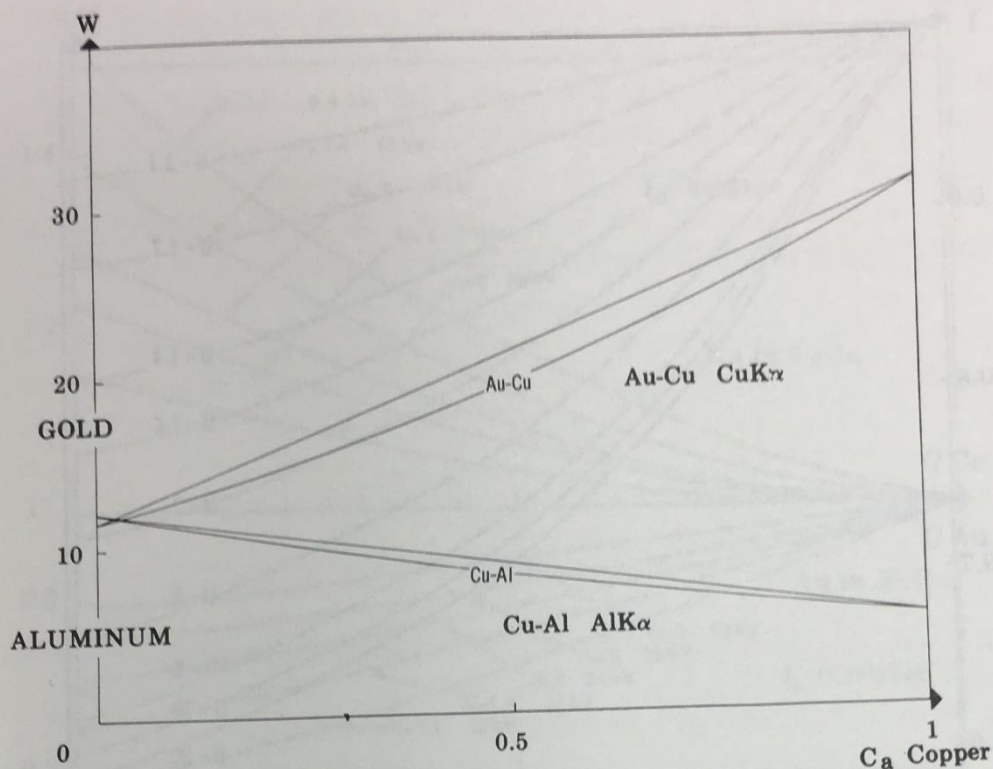


Figure 5. W versus copper concentration in copper-gold alloy (copper analyzed) and in copper-aluminium alloy (aluminium analyzed). A linear approximation has also been traced.

R is calculated from Brandt's data on the energy distribution of electrons backscattered from pure element targets. The values of s she used are taken from the tabulations by Nelms (1956, 1958) [16] based on the Bethe formula for electron stopping power. The value of s chosen for estimating the correction is that corresponding to an energy half way between E_0 and E_X .

Though Nelms' tables are limited to 10 keV and are not very practical for use in micro-probe analysis conditions, Thomas' results are interesting to compare with ours since Nelms used for her tables an adjustment for the J variation law, and discussed the validity of calculations with the Bethe formulae. If we consider a 50-50 copper-aluminium alloy in which aluminium is analyzed with $E_0 = 10$ keV, we find with our method $(1/S)_{\text{spec.}}/(1/S)_{\text{stand.}} = 1.144$ and with Thomas's method 1.137. The discrepancy is not important in this case. Figure 7 might also be compared with the same computed by Archard and Mulvey. It should also be interesting to compare the k/c values obtained here with some others deduced from direct

ELECTRON PROBE

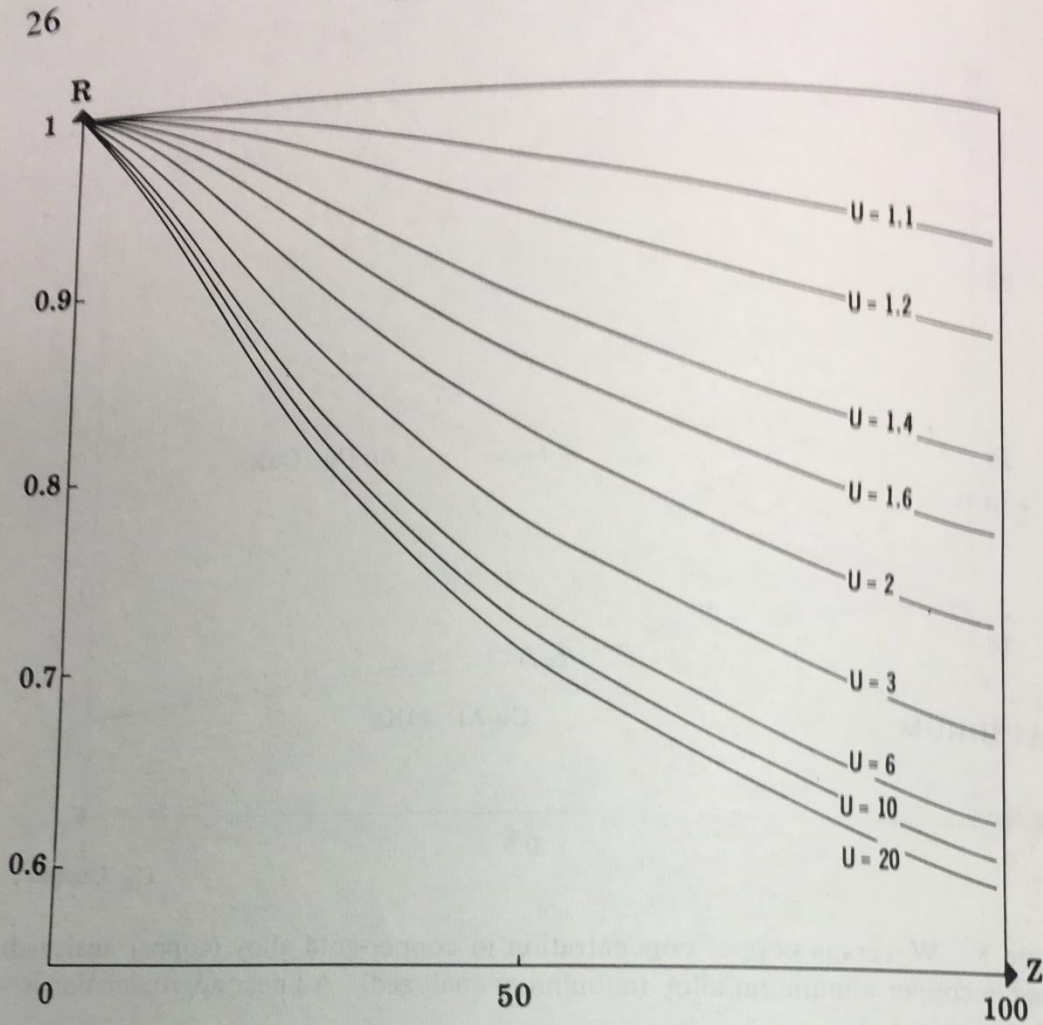


Figure 6. R versus Z for different U values according to Duncumb.

calculation of x-ray production by Monte Carlo methods according to Green (1962) [15] and Bishop (1965) [5].

The analytical forms show that approximation using a "mean atomic number" in order to have the same calculation with a mixed target as in pure elements is generally physically unfounded and can lead to important relative errors.

The validity of the present calculation is limited, especially in cases of small over-voltage: by approximation inherent in the Bethe formulae; by the values of the coefficients we used; and particularly because we neglect straggling by taking the mean electron energy as parameter (cf. Cosslett, 1964 [9], 1965 [10] and Brown, 1965 [7]). Since the atomic number effect is more important when the over-voltage is low the present model would need to be refined, using for instance the Walske (1952 and 1956) [19] calculations for extending the validity of Bethe's formula, or adjusting coefficient and parameter values with experimental measurement (Duncumb and da Casa).

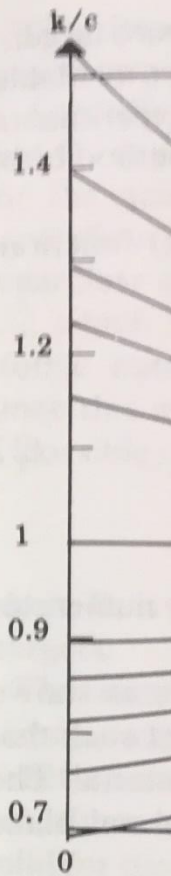


Figure 7

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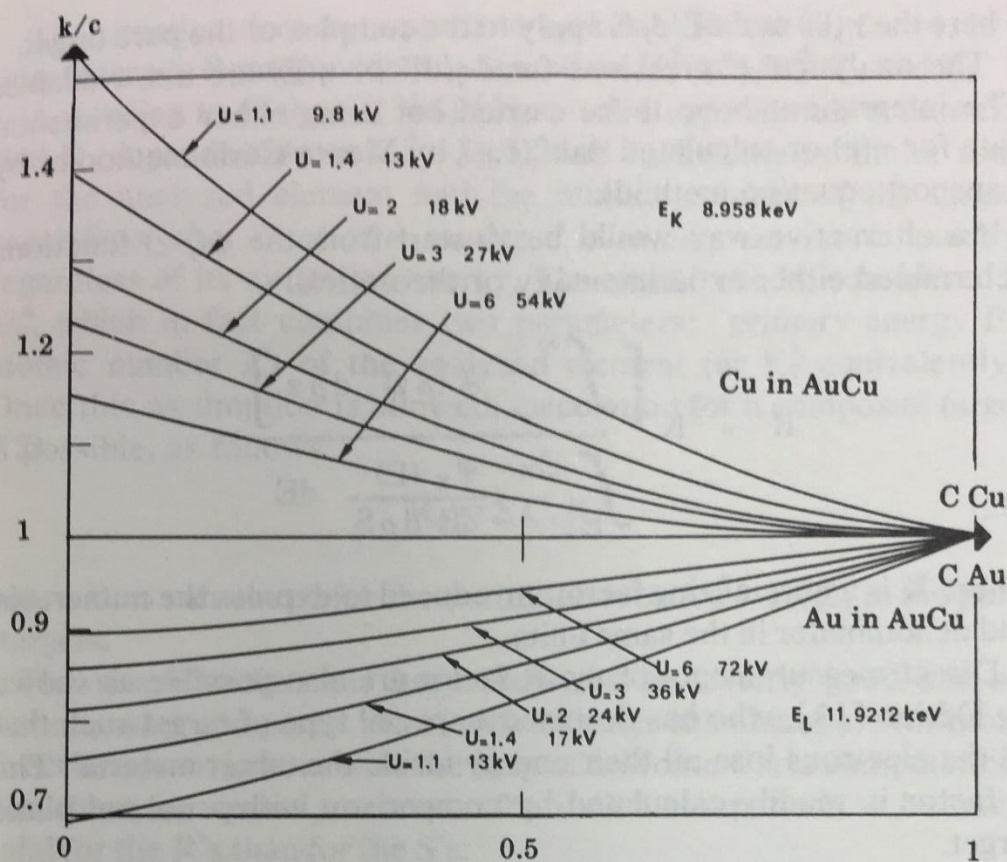


Figure 7. The atomic number effect correction factor versus concentration.

E. CALCULATION OF THE R FACTORS

The R factors can be computed for pure elements by using analytical expressions for Ψ and $dE/d\rho s$, provided that the energy distribution of electrons backscattered from these pure targets is known.

$$1 - R(A) = \frac{\int_{E_0}^{E_X^A} \eta(E) \frac{\Psi_X^A(E)}{dE/d\rho s} dE}{\int_{E_0}^{E_X^A} \frac{\Psi_X^A(E)}{dE/d\rho s} dE} \quad (26)$$

with

$$\eta(E) = \int_E^{E_0} \frac{d\eta}{dE} dE$$

where the $\eta(E)$ and $dE/d\rho S$ apply to the complex or the pure target.

The analytical expressions for $d\eta/dE$ or $\eta(E)$ are not available. The integrations have to be carried out using either experimental data for $\eta(e)$ or calculated data (e.g., by Monte Carlo method or by transport equation method).

An alternative way would be to start from the $\phi(\rho z)$ functions determined either experimentally or theoretically.

$$R = K \frac{\left[\int_0^\infty \phi(\rho z) d\rho z \right]}{\int_{E_0}^{E_x} \frac{\Psi_x(E)}{dE/d\rho S} dE} \quad (27)$$

where K is a normalizing factor introduced to express the numerator and denominator in the same units.

Direct measurements of the R factor are also possible as shown by Dérian [13], who has designed a special type of target such that all the electrons lose all their energy inside the target material. The R factor is readily calculated by comparison with a normal plane target.

Dérian applied this method to the determination of R in pure targets of Al, Cu, and Ag for a series of over-voltage ratios $U_0 = E_0/E_K$. As these values are in good agreement with Duncumb's evaluations (based on equation (27) and $\eta(E)$ derived from Bishop experimental and theoretical results) one may be confident in the latter. Other calculations of the R factor (by Green, from older experimental data, by Brown from its T.E.P. calculation) seem to give figures which are too low.

We are finally faced with the calculation of \bar{R}_A , i.e., the R factor for A element in a complex target. This seems a priori to be a formidable task, as this factor like the S factor, must be dependent on U_0 , on all the Z_i , C_i , and E_X^A , or equivalently on U_0 , all the Z_i , C_i , and $E_0 (= E_X^A U_0)$.

Let us look again at the calculation of the S factor. The case of A radiation in pure A is very simple (E_X^A is a Z_A function). $S(A)$ depends only on U_0 and Z_A . But the case of A radiation emitted from an otherwise pure B target is more complicated. Three variables have to be considered: $U_0^A = E_0/E_X^A$, E_X^A , Z_B . In other words, the S factor depends on W and $U_0^A = E_0/E_X^A$ but W depends on Z_A and Z_B .

For a complex target, we have to calculate a mean \bar{W} depending on the Z_i of the components, but a simple relation like $\bar{S}_A = \sum_i C_i S_i$ does not hold, and is even meaningless.

The situation for a pure B target.

According to that R_A depends on the analytical expression regardless of U_0^A , which in atomic number. Once this assumption is possible, as

where R_i is calculated for i targets.

The simplification by Bishop, who compared direct ones with indirect ones. But, there is, a problem valid for the R factor.

It would be a reliable parameter for target material. Tables of R_A are reasonable, since, i.e., in the case of Z_B , J_B , and E_X^A electron energy.

F. T.

If we want to calculate R in a thin target, the range in target or a thin foil takes a different value.

For such a case, the energy on the target concentration. We write the result for the massive target.

If we assume that the R factor can be neglected

The situation does not appear to be better for the R_A factor. In a pure B target, R must evidently depend on $U_o^A = E_o/E_X^A$, Z_A and Z_B .

According to Bishop (1966) [5], a valid approximation assumes that R_A depends only on $U_o^A = E_o/E_X^A$ and Z_B , i.e., the excitation ratio for the analyzed element and the atomic number of the target, *regardless the Z of the analyzed element*, or more exactly, regardless of its excitation energy. The quantity to be considered is U_o^A , which in fact combines two parameters: primary energy E_o , atomic number Z_A of the analyzed element (or E_X^A equivalently). Once this assumption is allowed, calculation for a composite target is possible, as follows:

$$\bar{R}_A = \sum_i C_i R_i \quad (28)$$

where R_i is calculated for the excitation ratio $U_o^A = E_o/E_X^A$ in the pure i targets.

The simplification has been shown to be a fairly good one by Bishop, who compared the results of such calculations with more direct ones carried out with the help of a Monte Carlo computation. But, there is, a priori, no reason for such a comparison to be more valid for the R's than for the S's.

It would be interesting to look at the possibility of W being a more reliable parameter, because W is determined by the properties of the target material and of the excited A atoms. We should then need tables of R_A versus W and $U_o^A = E_o/E_X^A$. This suggestion seems reasonable, since W depends essentially on the target properties, i.e., in the case of a pure B target (A emission in otherwise pure B) Z_B , J_B , and E_X^A (i.e., Z_A), all quantities on which the backscattered electron energy and number might be dependent.

F. THIN FILMS AND EXTRACTION REPLICAS

If we want the relative concentrations of two elements, A and B, in a thin target, i.e., a target whose thickness is very much less than the range in terms of beam energy (for instance an extraction replica or a thin foil for electron microscopy), the atomic number effect takes a different form.

For such an analysis, we use a probe with constant intensity and energy on the same point of the target to measure the apparent concentration $K_A = (J_A/J(A))$ of A and that of B, and we generally write the result as the ratio K_A/K_B . The standards are supposed to be the massive pure elements as usual.

If we assume that the effect of backscattering in the specimen can be neglected in this case (since we are calculating a ratio) and that

the effects of fluorescence and absorption can be neglected in the specimen and corrected in the standard, we have with the same symbols as above:

$$\text{in the specimen} \quad dn_x = C_A \frac{N}{A} \Psi_A^x(E) d\rho s$$

$$\text{in the massive standard,} \quad n_x = \frac{N}{A} \int_{E_0}^{E_x^A} \frac{\Psi_A^x(E)}{dE/d\rho s} dE$$

and with the analytical expressions for Ψ and $dE/d\rho s$:

$$dn_x = C_A \frac{N}{A} \cdot \frac{\pi e^4}{E_0 E_x^A} \cdot Z_x b_x \log U_0^A d\rho s$$

$$n_x = \frac{N}{A} \cdot \frac{Z_x b_x}{2N} \int_1^{U_0^A} \frac{\log U}{M_A \log U \cdot W_A^x} \cdot dU$$

with

$$U_0^A = \frac{E_0}{E_x^A}, \quad M_A = \frac{Z_A}{A_A}, \quad W_A^x = \frac{1.166 E_x^A}{J_A}$$

R_A is the backscattering factor of standard A for the over-voltage ratio U_0^A , and,

$$\frac{1}{S'_A} = \int_1^{U_0^A} \frac{\log U}{M_A \cdot \log U W_A^x} \cdot dU$$

We can write as a first approximation:

$$k_A = \frac{dn_x}{n_x} = C_A \cdot \frac{\pi e^4 2N}{E_0} \cdot \frac{\log U_0^A}{E_x^A} \cdot \frac{d\rho s}{R_A / S'_A}$$

If we put

If $P_A > P_N$
greater than

Example:

- Analysis of $(P_{Al}/P_{Ni}) =$
- Analysis of aluminium

In both cases, the result was less than expected, which would be due to the correction.

If the specimen is sufficiently thick, the bulk target correction is less than negligible.

Experiment

Ni and martensitic transformation following

30

20

Without compositional analysis, the results are in favour of the electron probe

If we put

$$P_A = \frac{\log U_o^A}{E_X^A R_A / S_A'} \quad (29)$$

$$\frac{K_A}{K_B} = \frac{C_A}{C_B} \cdot \frac{P_A}{P_B} \quad (30)$$

If $P_A > P_B$, the measured concentration in A against that of B is greater than the real concentration.

Example:

- Analysis of very thin precipitates of Ni+Al in a carbon replica (P_{Al}/P_{Ni}) = 0.63 at 30 keV, 0.55 at 20 keV.
- Analysis of low copper concentrations in a thin foil of an aluminium-copper alloy (P_{Al}/P_{Cu}) = 0.67 at 30 keV.

In both cases the measured value of the aluminium concentration was less than the true value. The effect is just the opposite of what would be observed in a bulk target, and it is far greater.

If the specimen is not thin enough, or if the voltage is not sufficiently high, the effect must lie between those characteristic of a bulk target and of a thin foil; however, it seems difficult to calculate the correction or even to determine whether the factor is greater or less than one, and the absorption effect in the specimen is no more negligible.

Experimental Results:

Ni and Al containing precipitates were extracted from a semi-martensitic stainless steel. Experimental results are given in the following table:

	N_i/A_i (exp ^{al})	N_i/A_i (corrected)
30 kV	3.27	2.1
20 kV	4.25	2.35

Without corrections, experimental results would indicate Ni_2Al composition. After correction for atomic number effect, the results are in favor of Ni Al. This determination has been confirmed by electron diffraction (Ni_3Al was a possible precipitate).

This thin film correction has also been studied by Duncumb from both theoretical and experimental viewpoints.

III. Conclusion

As it has been tentatively shown, the expressions used for the correction calculations depend on a lot of drastic assumptions and on the validity of some physical laws involved (ionization cross-sections, continuous retardation law). The validity of the expressions used for these laws is known to be not very good, and probably limited to some more or less wide range of atomic numbers. Moreover, the validity of Bethe retardation law is generally questionable since it neglects energy straggling. This last effect probably modifies appreciably the energy loss distribution as a function of depth and, consequently, the ionization distribution with depth (the so-called $\phi(\rho z)$ function).

These limitations affect to the same extent the other approaches which would seem more accurate: Monte Carlo computation, resolution of Boltzmann transport equation. These approaches suffer basically from the same inaccuracies; moreover, they give numerical solutions and no analytical expressions for the Z and A corrections. One has perhaps to get rid of the feeling that analytical expressions are necessary and to convince oneself of the convenience of working with tables, the results of numerical methods being collected in these tables. Probably these numerical methods will give more and more accurate results through more realistic models of the electron behavior in massive targets. For everyday calculations, however, analytical expressions which would need only a limited quantity of input data seem to be desirable. It is hoped that such better expressions will be available in the future; in combination with tables they will permit corrections to be readily carried out in most of the common cases.

In conclusion, the need for more reliable data concerning the basic parameters (μ/ρ , $W_{K,L}$, J , ...) as well as for the physical law involved (Ψ , dE/dps , multiple scattering, backscattering), must be stressed.

Experiments on composite targets (measurement of backscattered electron energy distribution, direct measurement of R factor, etc...) will enable a better check of the suggested computation of the Z effect to be made. The case of non-metallic specimens, such as complex oxides, would perhaps deserve specially careful

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- [1] Archard
Acade
- [2] Bearden
- [3] Bethe, F
- [4] Bethe, F
(1938)
- [5] Bishop,
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- [12] Dasher
- [13] Dérian
- [14] Duncu
and
- [15] Green
- [16] Nelms
- [17] Reed,
- [18] Thoma
- [19] Walsk
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- [20] Worth

measurements. Finally, theoretical computations, based on the Monte Carlo model, the resolution of Boltzmann transport equation, the invariant imbedding method (Dashen [12]) or the older "collective" model, could perhaps be carried out with more refined basic laws. The case of thin films and extractions replica also requires careful attention.

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