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A Characteristic X-ray Fluorescence Correction for Thin-Film Analysis By Electron Microprobe

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The characteristic x-ray fluorescence correction in most thin film systems is negligible so no significant error usually results from its omission. Nevertheless, some cases exist where uncertainty about the size of the fluorescence correction may result in significant errors in the analytical results. Examples include films containing elements which would have a significant fluorescence contribution if present in bulk form, and film systems which might mistakenly be treated with bulk correction models because the films are thicker than the electron penetration depth.

Several characteristic fluorescence corrections for thin film systems are described in the literature..[1–5] Most, however, are limited in scope and application; use approximations; or only evaluate one-third or two-thirds of the triple integral in the fluorescence intensity equation with the remaining integrals to be evaluated by numerical methods.

de Boer[6] developed a comprehensive procedure to calculate the fluorescence correction for the x-ray fluorescence (XRF) analytical technique. He showed that the triple integral equations can be solved exactly for the general case of the exciting and excited element being in any layer. In XRF, however, the function describing the distribution of primary generated x rays is an exponential which is less commonly used to approximate the primary x-ray depth distribution function, $\phi(z)$, in electron probe microanalysis (EPMA).

Göhler and Hänisch[7] describe a solution for $\phi(z)$ models which have a $k_1e^{-k_2z} + k_3ze^{-k_2z}$ (linear– exponential) dependence.[8,9] They did not include the solution for the $k_3ze^{-k_2z}$ term, however, so their solution is equivalent to the solution of de Boer.

The two functional forms most commonly used to describe $\phi(z)$ in EPMA which are also applicable to film systems are the modified–gaussian model of Packwood and Brown[10] and the parabolic model of Pouchou and Pichoir (PAP).[11,12] Any treatment of fluorescence in thin film EPMA would have to consider these functional forms.

In this paper I develop the equations describing the total emitted characteristic x-ray fluorescence intensity for all geometries in a multilayer system and evaluate the resultant triple integral exactly in the case of the parabolic PAP and linear–exponential models and by numerical methods in the case of the modified–gaussian model. The solution for the modified–gaussian model is general and can be used for any functional form for $\phi(z)$. The solution for the linear–exponential models is shown to be a subset of the solution for the parabolic PAP model.

Fluorescence in a Multilayer Film System

There are n^2 possible exciter layer→ excited layer fluorescence interactions in an n-layer film system. Only three three basic geometries are necessary, however, to account for all of these interactions:

- Case A) The exciting element is in a layer below the excited element. Only upward directed primary radiation need be considered in the calculation of the fluorescence intensity.
- Case B) The exciting and excited element are in the same layer. If both elements are in the substrate, the equations are a subset of the general solution (Case B′). Case B′ includes the bulk specimen fluorescence correction. Both upward and downward directed primary radiation are included in the calculations.
- Case C) The exciter element is above the excited element; only downward directed primary radiation is considered. If the excited element is in the substrate, the solution is a simplified form of the general case (Case C′).

I will use case A to illustrate in detail the derivation of the characteristic x-ray fluorescence intensity; the derivations for the other cases are analogous.

Figure 1 shows the geometry of the generation of characteristic x-ray fluorescence in a multi-layered film system for case A. The x and y directions (plane of the surface of the specimen) are assumed to be of infinite dimensions and each layer homogeneous in composition. It is desired to find the total emitted characteristic fluorescence intensity, $I'^{sp}_{fA_k}$ in the direction ψ toward a detector with solid angle $\Omega/4\pi$ and detection efficiency P. ($\Omega/4\pi P$ cancels when the specimen intensity is divided by the standard intensity.) The secondary A k-line x rays (A_k) may result from fluorescence by several j-line x-rays of elements B (B_j) in any of the layers or substrate.

In the particular case illustrated in Figure 1, primary B_j x rays originating from point P_1 in a deep layer b excite secondary A_k x rays at point P_2 in a layer a nearer the surface. The thickness of a layer i is t_i. The mass absorption

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coefficient of primary B_j radiation in the layer i is denoted by μ_i and the mass absorption coefficient of the A_k secondary radiation in layer i times the cosecant of the x-ray takeoff angle, ψ, is designated by χ_i.

$I'^{sp}_{fA_k}$ is calculated after setting up the triple integral in the usual manner (e.g., Armstrong[4]) by

i) integrating over

a) all depths z of the production of B_j x rays,
b) all angles β of emission of the B_j x rays, and
c) all depths s of possible excitation of A_k x rays;

ii) multiplying by

a) a term $g = e^{\sum_{l=a-1}^{1} -\chi_l}$, accounting for x-ray absorption in the $a-1$ overlayers, and
b) a term D' which contains several constants:[4]

$$D' \;=\; \frac{1}{2} C_A \mu^A_{B_j} \frac{r_{A_k} - 1}{r'_{A_k}} \omega_{A_k} p_{A_k} \frac{\Omega}{4\pi} P \; ; \tag{1}$$

where

1) C_A is the weight fraction of element A in the layer a;
2) $\mu^A_{B_j}$ is the mass absorption coefficient of B_j radiation in pure element A;
3) r_{A_k} is the absorption jump ratio at the k-absorption edge and $\frac{r_{A_k}-1}{r'_{A_k}}$ is a generalized notation for the ratio of ionizing absorptions to total absorptions;
4) ω_{A_k} is the effective fluorescence yield of the k-shell; and
5) p_{A_k} is the relative weight of the A_k line of interest

iii) and finally summing over all lines j of all elements B in all layers l capable of exciting A_k x rays. Thus,

$$I'^{sp}_{fA_k} \;=\; g \sum_B \sum_j D' \int_{z=\delta_{b-1}}^{\delta_b} \int_{\beta=\pi/2}^{\pi} \int_{s=\delta_a}^{\delta_{a-1}} F'_{B_j}(z,\beta,s)\, \mathrm{d}s\, \mathrm{d}\beta\, \mathrm{d}z \tag{2}$$

where the integrand F'_{B_j} can be found by following the paths of primary and secondary x rays:

$$F'_{B_j}(z,\beta,s) = I^{sp}_{B_j}(z) \tan\beta e^{-[\mu_b(\delta_{b-1}-z) - \sum_{i=b-1}^{a+1} \mu_i t_i] \sec\beta} e^{-[\mu_a(s-\delta_a)\sec\beta + \chi_a(s-\delta_{a-1})]}. \tag{3}$$

The depth distribution of generated primary B_j x rays in the specimen, $I^{sp}_{pB_j}(z)$, is related to the $\phi^{sp}_{B_j}(z)$ distribution by

$$I^{sp}_{pB_j}(z) \;=\; \frac{C_B}{A_B} z_{B_j} \omega_{B_j} p_{B_j} Q_{B_j}(E_0) \phi^{sp}_{B_j}(z) \tag{4}$$

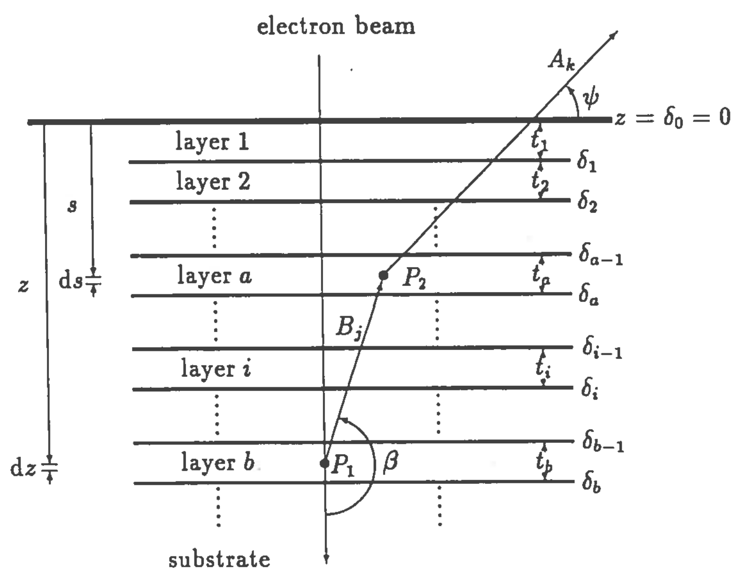

FIG. 1.- - Characteristic x-ray fluorescence in a multi-layer specimen.

where $Q_{B_j}(E_0)$ is the ionization cross section of the j-shell at the energy E_0, z_{B_j} is the number of electrons in the filled j-shell, and A_B is the atomic weight of B.

The function G'_{B_j} is defined here by

$$G'_{B_j}(z,\beta,s) \quad = \quad \frac{F'_{B_j}(z,\beta,s)}{\frac{C_B}{A_B} z_{B_j}\omega_{B_j} p_{B_j} Q_{B_j}(E_0)} \tag{5}$$

so

$$G'_{B_j}(z,\beta,s) \quad = \quad \phi^{sp}_{B_j}(z)\tan\beta e^{-[\mu_b(\delta_{b-1}-z)-\sum_{i=b-1}^{a+1}\mu_i t_i]\sec\beta} e^{-[\mu_a(s-\delta_a)\sec\beta+\chi_a(s-\delta_{a-1})]}. \tag{6}$$

The integral limits and integrand $G'_{B_j}(z,\beta,s)$ in Equations 2 and 6 are specific to each case of exciter layer–excited layer interaction and the evaluation of the triple integral has different solutions for each case.

We will see that the triple integral for a particular case cannot always be evaluated exactly for all functional forms of $\phi(z)$. The integrals with respect to s and β, however, can always be resolved exactly in terms of the exponential-integral function. I therefore introduce here the function $Y(z)$

$$G_{B_j} \quad = \quad \int_z \phi(z)\cdot Y(z)\mathrm{d}z \tag{7}$$

with

$$Y(z) \quad = \quad \int_\beta \int_s f(z,\beta,s)\cdot\, \mathrm{d}s\,\mathrm{d}\beta. \tag{8}$$

Evaluation of the Double Integral $Y(z)$

After rearranging and combining terms of the same variable in Equation 6, $Y(z)$ for case A can be written

$$Y(z) = Y(z)\!\uparrow\; = \int_{\pi/2}^{\pi} \tan\beta e^{-[\mu_b(\delta_{b-1}-z)-\sum_{i=b-1}^{a+1}\mu_i t_i]\sec\beta}\,\mathrm{d}\beta \int_{\delta_a}^{\delta_{a-1}} e^{-[\mu_a(s-\delta_a)\sec\beta+\chi_a(s-\delta_{a-1})]}\,\mathrm{d}s. \tag{9}$$

$Y(z)\!\uparrow$ indicates that only upward directed B_j primary radiation need be considered.

<u>1. Evaluation of the Integral With Respect to s</u>

The integral with respect to s in Equation 9 is of the form $\int_z c_1 e^{-c_2 s+c_3}\mathrm{d}s$ and is easily evaluated

$$\begin{aligned} Y(z)\!\uparrow \;=\; & -\int_{\pi/2}^{\pi} \sin\beta e^{(\mu_b z-\mu_b\delta_{b-1}+\sum_{i=b-1}^{a+1}\mu_i t_i+\mu_a t_a)\sec\beta} \frac{sec\beta}{\mu_a\sec\beta+\chi_a}\,\mathrm{d}\beta \\ & + e^{-\chi_a t_a}\int_{\pi/2}^{\pi} \sin\beta e^{(\mu_b z-\mu_b\delta_{b-1}+\sum_{i=b-1}^{a+1}\mu_i t_i)\sec\beta} \frac{\sec\beta}{\mu_a\sec\beta+\chi_a}\,\mathrm{d}\beta. \end{aligned} \tag{10}$$

<u>2. Evaluation of the Integral With Respect to β</u>

Both of the definite integrals in Equation 10 are of the form

$$H(c_1,c_2,c_3) \quad = \quad \int_{\pi/2}^{\pi} e^{c_1\sec\beta}\frac{sec\beta}{c_2\sec\beta+c_3}\sin\beta d\beta. \tag{11}$$

This type integral can be evaluated with the substitution $x = c_2\sec\beta$:

$$H(c_1,c_2,c_3) \quad = \quad \frac{1}{c_3}\left[\int_{-\infty}^{-c_2}\frac{e^{\frac{c_1}{c_2}x}}{x}dx + e^{-\frac{c_1}{c_2}c_3}\int_{-\infty}^{-c_2+c_3}\frac{e^{\frac{c_1}{c_2}u}}{u}du\right]. \tag{12}$$

where the second integral has been reduced to the same form as the first with the substitution $u = x + c_3$.

Integrals of the form

$$\int_{-\infty}^{x} e^{-t}/t\,dt$$

are defined as the exponential-integral function and are designated $\mathrm{Ei}(x)$. For $x \neq 0$, $\mathrm{Ei}(x)$ can be represented by the series expansion

$$\mathrm{Ei}(x) \quad = \quad \gamma + \ln[\mathrm{abs}(x)] + \sum_{k=1}^{\infty}\frac{x^k}{k\cdot k!}\,,\quad [x\neq 0] \tag{13}$$

where $\gamma = 0.5772158\ldots$ is Euler's constant.[13] The evaluation of Equation 11 is thus

$$H(c_1, c_2, c_3) \;=\; \frac{1}{c_3}\left[Ei(-c_1) - e^{-\frac{c_1}{c_2}c_3}\mathrm{Ei}\left(-c_1 + \frac{c_1}{c_2}c_3\right)\right] \tag{14}$$

and $Y(z)$ for case A is

$$Y(z)\uparrow \;=\; \frac{1}{\chi_a}\left[-\mathrm{Ei}(f_1z+g_1) - e^{a_1z+b_1}\left[\mathrm{Ei}(f_2z+g_2) - \mathrm{Ei}(f_2z+g_3)\right] + e^{b_2}\mathrm{Ei}(f_1z+g_4)\right] \tag{15}$$

with

$$\begin{array}{ll}
a_1 = \frac{-\chi_a}{\mu_a}\mu_b & g_1 = \mu_b\delta_{b-1} - \sum\mu_i t_i - \mu_a t_a \\
b_1 = \frac{\chi_a}{\mu_a}(\mu_b\delta_{b-1} - \sum\mu_i t_i) - \chi_a t_a & g_2 = -(\mu_b\delta_{b-1} - \sum\mu_i t_i)(\frac{\chi_a}{\mu_a} - 1) \\
b_2 = -\chi_a t_a & g_3 = g_2 + (\chi_a - \mu_a)t_a \\
f_1 = -\mu_b & g_4 = \mu_b\delta_{b-1} - \sum\mu_i t_i \\
f_2 = \mu_b(\frac{\chi_a}{\mu_a} - 1). &
\end{array}$$

The summations in the terms b_1 and $g_1 - g_4$ are over the i layers between layers b and a.

Solutions for the other geometries are:

<u>Case B.</u>

$$Y(z) \;=\; Y(z)\uparrow + Y(z)\downarrow \tag{16}$$

with

$$Y(z)\uparrow \;=\; \frac{1}{\chi_a}\left[-Ei(f_1z+g_1) + e^{a_1z+b_1}\left\{Ei(f_2z+g_2) - r_2\right\}\right] \tag{17}$$

$$Y(z)\downarrow \;=\; \frac{1}{\chi_a}\left[e^{b_2}Ei(f_3z+g_3) - e^{a_1z+b_1}\left\{Ei(f_4z+g_4) + r_1\right\}\right] \tag{18}$$

where

$$\begin{array}{lll}
a_1 = -\chi_a & f_1 = -\mu_a & g_1 = \mu_a\delta_{a-1} \\
b_1 = \chi_a\delta_{a-1} & f_2 = \chi_a - \mu_a & g_2 = (-\chi_a + \mu_a)\delta_{a-1} \\
b_2 = -\chi_a t_a & f_3 = \mu_a & g_3 = -\mu_a\delta_a \\
 & f_4 = \chi_a + \mu_a & g_4 = -(\chi_a + \mu_a)\delta_a
\end{array}$$

and r_1 and r_2 have the values

$$r_1 = \ln\left(1 + \tfrac{\chi_a}{\mu_a}\right) \quad \text{and} \quad r_2 = \ln\left(\mathrm{abs}\left[1 - \tfrac{\chi_a}{\mu_a}\right]\right).$$

<u>Case B′.</u>

$$Y(z)\uparrow + Y(z)\downarrow = \frac{1}{\chi_a}\left[-Ei(f_1z+g_1) + e^{a_1z+b_1}\left(Ei(f_2z+g_2) + r_1 - r_2\right)\right]. \tag{19}$$

For bulk specimens $b_1 = g_1 = g_2 = 0$ in Equation 19.

<u>Case C.</u>

$$Y(z)\downarrow \;=\; \frac{1}{\chi_a}\left[-Ei(f_1z+g_1) + e^{a_1z+b_1}\left[Ei(f_2z+g_2) - Ei(f_2z+g_3)\right] + e^{b_2}Ei(f_1z+g_4)\right] \tag{20}$$

with

$$\begin{array}{ll}
a_1 = \frac{-\chi_a}{\mu_a}\mu_b & g_1 = -(\mu_b\delta_b + \sum\mu_i t_i) \\
b_1 = \frac{\chi_a}{\mu_a}(\mu_b\delta_b + \sum\mu_i t_i) & g_2 = -(\mu_b\delta_b + \sum\mu_i t_i)(\frac{\chi_a}{\mu_a} + 1) \\
b_2 = -\chi_a t_a & g_3 = g_2 - (\chi_a + \mu_a)t_a \\
f_1 = \mu_b & g_4 = -(\mu_b\delta_b + \sum\mu_i t_i) - \mu_a t_a \\
f_2 = \mu_b(\frac{\chi_a}{\mu_a} + 1). &
\end{array}$$

<u>Case C′.</u>

$$Y(z)\downarrow \;=\; \frac{1}{\chi_a}\left[-Ei(f_1z+g_1) + e^{a_1z+b_1}Ei(f_2z+g_2)\right]. \tag{21}$$

3. Evaluation of the Integral with Respect to z

The triple integral for case A is now given by

$$G_{B_j} = \int_{\delta_{b-1}}^{\delta_b} \phi_{B_j}^{sp}(z) \times \frac{1}{\chi_a}\left[-\mathrm{Ei}(f_1z+g_1) - e^{a_1z+b_1}\left[\mathrm{Ei}(f_2z+g_2) - \mathrm{Ei}(f_2z+g_3)\right] + e^{b_2}\mathrm{Ei}(f_1z+g_4)\right] dz. \tag{22}$$

G_{B_j} can be evaluated exactly (in terms of the exponential–integral function) when $\phi(z)$ has certain functional forms including exponential, polynomial and linear–exponential. For such $\phi(z)$ models, Equation 22 can be written as linear combinations of integrals of the form

$$\int_z z^n e^b \mathrm{Ei}(fz+g)dz \quad \text{and} \quad \int_z z^n e^{az+b}\mathrm{Ei}(fz+g)dz \quad ; \; n = 0, 1, 2.$$

3a. Indefinite integrals of the form $s_n = \int z^n e^b \mathrm{Ei}(fz+g)\mathrm{d}z$.

The indefinite integrals are found by integrating by parts:

$$s_n = \int z^n e^b \mathrm{Ei}(fz+g)\mathrm{d}z = \frac{e^b}{(n+1)f^{n+1}}\left[u^{n+1}\mathrm{Ei}(u) - e^u \mathrm{E}_n(u)\right] - T_n + C, \; n = 0, 1, 2\ldots \tag{23}$$

where $u = fz+g$; T_n is given by

$$T_0 = 0 \quad \text{and} \quad T_n = \sum_{r=1}^{n} \frac{n!}{(n-r)!r!}\cdot\left(\frac{g}{f}\right)^r s_{n-r}, \quad \text{for } n = 1, 2, \ldots \;;$$

and $\mathrm{E}_n(u)$ denotes the exponential–polynomial

$$\mathrm{E}_n(u) = \sum_{r=0}^{n}(-1)^r \frac{n!u^{n-r}}{(n-r)!}.$$

Equation 23 evaluated at $u = 0$ ($z = -g/f$) contains terms of $0^{n+1}\mathrm{Ei}(0)$ ($\mathrm{Ei}(0)$ is undefined). With Equation 13 and l'Hospital's rule, these terms can be shown to be equal to zero. Thus,

$$\lim_{u\to 0} s_n = \frac{e^b(-1)^{n+1}n!}{(n+1)f^{n+1}} - T_n + C \tag{24}$$

where T_n has the same values as in Equation 23.

3b. Integrals of the form $s_n' = \int z^n e^{az+b}\mathrm{Ei}(fz+g)\mathrm{d}z$.

The indefinite integrals are found by integrating by parts:

$$s_n' = \int z^n e^{az+b}\mathrm{Ei}(fz+g)\mathrm{d}z = \frac{e^{\frac{-ag}{f}+b}}{a^{n+1}}\left[e^{\frac{a}{f}u}\mathrm{E}_n\left(\frac{a}{f}u\right)\mathrm{Ei}(u) - (-1)^n n!\mathrm{Ei}\left[\left(\frac{a}{f}+1\right)u\right] - T_n'\right] + C \tag{25}$$

where $u = fz+g$ and T_n' is given by

$$T_0' = 0 \quad \text{and}$$

$$T_n' = \sum_{r=1}^{n} e^{(\frac{a}{f}+1)u}(-1)^{n-r}\left(\frac{a}{a+f}\right)^r \mathrm{E}_{r-1}\left[\left(\frac{a}{f}+1\right)u\right]\frac{n!}{r!} + \frac{a^{n+1}}{e^{\frac{-ag}{f}+b}}\frac{n!}{(n-r)!r!}\cdot\frac{g^r}{f^r}s_{n-r}', \text{ for } n = 1, 2\ldots$$

Equation 25 evaluated at $u = 0$ ($z = -g/f$) contains multiple terms of $\mathrm{Ei}(0)$. With Equation 13 and l'Hospital's rule s_n' can be shown to have finite values as $u \to 0$. Thus,

$$\lim_{u\to 0} s_n' = \frac{e^{\frac{-ag}{f}+b}}{a^{n+1}}\left[(-1)^n n!\ln\left(\frac{a}{f}+1\right) - T_n'\right] + C \tag{26}$$

now with

$$T_0' = 0 \quad \text{and} \quad T_n' = \sum_{r=1}^{n}(-1)^{n+1}\left(\frac{a}{a+f}\right)^r\frac{n!}{r} + \frac{a^{n+1}}{e^{\frac{-ag}{f}+b}}\frac{n!}{(n-r)!r!}\cdot\left(\frac{g}{f}\right)^r s_{n-r}', \quad \text{for } n = 1, 2, \ldots$$

Exact Solutions for Certain $\phi(z)$ Models

The functions $S_n(\delta_1, \delta_2, b, f, g)$ and $S_n'(\delta_1, \delta_2, a, b, f, g)$ are defined here by

$$S_n(\delta_1, \delta_2, b, f, g) = \int_{\delta_1}^{\delta_2} z^n e^b \mathrm{Ei}(fz+g)\mathrm{d}z = s_n|_{\delta_1}^{\delta_2} \tag{27}$$

and

$$S_n'(\delta_1, \delta_2, a, b, f, g) = \int_{\delta_1}^{\delta_2} z^n e^{az+b}\mathrm{Ei}(fz+g)\mathrm{d}z = s_n'|_{\delta_1}^{\delta_2}. \tag{28}$$

1. Parabolic PAP $\phi(z)$ Model

The parabolic PAP model is given by

$$\begin{aligned}\phi(z) &= A_1(z-R_m)^2+B_1 && \text{for } z\le R_c \\ \phi(z) &= A_2(z-R_x)^2 && z>R_c.\end{aligned} \tag{29}$$

The integral with respect to z for case A can now be expressed as

$$G_{B_j}=\int_{\delta_{b-1}}^{\delta_b}(d_2z^2+d_1z+d_0)\times\frac{1}{\chi_a}\left[-\mathrm{Ei}(f_1z+g_1)-e^{a_1z+b_1}\left[\mathrm{Ei}(f_2z+g_2)-\mathrm{Ei}(f_2z+g_3)\right]+e^{b_2}\mathrm{Ei}(f_1z+g_4)\right]\mathrm{d}z \tag{30}$$

with

$$\begin{aligned}d_2=A_1,\quad d_1=-2A_2R_m,\quad &\text{and } d_0=R_x^2+B_1 && \text{for } z\le R_c\\ d_2=A_2,\quad d_1=-2A_2R_x,\quad &\text{and } d_0=R_x^2 && \text{for } z>R_c.\end{aligned}$$

The integral G_{B_j} is expressed in terms of S_n and S_n' for case A as

$$G_{B_j}=\sum_{n=0}^{2}d_n\left[-S_n(\delta_{b-1},\delta_b,0,f_1,g_1)-S_n'(\delta_{b-1},\delta_b,a_1,b_1,f_2,g_2)+S_n'(\delta_{b-1},\delta_b,a_1,b_1,f_2,g_3)+S_n(\delta_{b-1},\delta_b,b_2,f_1,g_4)\right]. \tag{31}$$

This is an exact solution of the triple integral G_{B_j} in terms of the exponential–integral function. Solutions for cases B and C are analogous.

2. Heinrich Exponential Model

The exponential model of Heinrich is given by

$$\phi(z)=\alpha\beta e^{-\beta z}+(1-\alpha)\beta^2ze^{-\beta z} \tag{32}$$

so G_{B_j} can be expressed in terms of S_n' by

$$\begin{aligned}G_{B_j} \;=\; &\sum_{n=0}^{1}d_n\cdot\left[-S_n'(\delta_{b-1},\delta_b,-\beta,0,f_1,g_1)-S_n'(\delta_{b-1},\delta_b,a_1-\beta,b_1,f_2,g_2)\right.\\ &\left.+\,S_n'(\delta_{b-1},\delta_b,a_1-\beta,b_1,f_2,g_3)+S_n'(\delta_{b-1},\delta_b,-\beta,b_2,f_1,g_4)\right]\end{aligned} \tag{33}$$

with $d_1=(1-\alpha)\beta^2$ and $d_0=\alpha\beta$.

3. PAP Simplified Exponential Model

G_{B_j} for the PAP simplified exponential model,

$$\phi(z)=Ae^{-\alpha z}+(Bz+\phi_0-A)e^{-\beta z}, \tag{34}$$

can be expressed in terms of the function S_n' in a similar manner.

Solution for Modified Gaussian $\phi(z)$ Models

When the x-ray depth distribution function $\phi(z)$ is a modified–gaussian,

$$\phi(z)=\gamma_0e^{-\alpha^2z^2}-(\gamma_0-\phi_0)e^{\alpha^2z^2-\beta^2},$$

the integrals in equations of type 22 are of the form

$$\int_z e^{-(bz+c)^2}Ei(f_nz+g_m)\mathrm{d}z$$

which cannot be solved in closed form. This type integral can be easily approximated, however, with numerical integration techniques.

Simpson's Rule of numerical integration for n intervals requires evaluating the integrand at the integral limits and at 2n-1 interior points. Evaluation of the integrand for the interior points poses no problems, but when a boundary of layer a coincides with a boundary of layer b for any geometry, some of the Ei function terms in equations of type 22 may contain zero argument.

Case A. If there are no intervening layers between layers a and b, then the summation terms in Equation 15 are eliminated and the arguments of the exponential-integral terms $\mathrm{Ei}(f_2z+g_2)$ and $\mathrm{Ei}(f_1z+g_4)$ are both 0. $Y(z)\uparrow$ at the layer a–layer b boundary, however, now has the simplified form

$$Y(z)\uparrow=-\int_{\pi/2}^{\pi}\sin\beta e^{\mu_at_a\sec\beta}\frac{\sec\beta}{\mu_a\sec\beta+\chi_a}\,\mathrm{d}\beta+e^{-\chi_at_a}\int_{\pi/2}^{\pi}\sin\beta\frac{\sec\beta}{\mu_a\sec\beta+\chi_a}\,\mathrm{d}\beta. \tag{35}$$

with solution

$$Y(z)\uparrow \quad = \quad \frac{1}{\chi_a}\left[-\mathrm{Ei}(g_1) + e^{b_1}\left\{\mathrm{Ei}(g_2) - r_2\right\}\right] \tag{36}$$

where $b_1 = -\chi_a t_a$, $g_1 = -\mu_a t_a$, and $g_2 = (\chi_a - \mu_a)t_a$.

The arguments of the Ei functions in Equation 36 are independent of z and non-zero. For the other cases:

Case B. At the upper interval endpoint

$$Y(z)\downarrow \quad = \quad \frac{1}{\chi_a}\left[e^{b_1}Ei(g_1) - Ei(g_2) + r_1\right] \tag{37}$$

where $b_1 = -\chi_a t_a$, $g_1 = -\mu_a t_a$, and $g_2 = -(\chi_a + \mu_a)t_a$.

Case B at the lower interval endpoint is equivalent to case A.

Cases A′, C′ and Bulk Specimens. These geometries are equivalent. The Ei(0) terms occur at the layer a boundary nearest the specimen surface.

$$Y(z)\downarrow \quad = \quad \frac{1}{\chi_a} r_1 \tag{38}$$

Case C. This is equivalent to case B downward directed radiation.

Accuracy of Numerical Integration

The choice of the number of numerical integration intervals for a desired accuracy can be made with the aid of the exact solution of the triple integral, G_{B_j}, derived for the parabolic PAP model. A hypothetical sample of a 300 μg/cm^2 film of gallium arsenide (GaAs) on GaAs substrate was modeled. The operating potential was 30 keV and the takeoff angle, ψ, was 40 deg for the calculations. The mass absorption coefficients are those of Heinrich.[14] Integration was done with the exact formula (Equation 31 for case A, etc.) and with Simpson's rule for numerical integration (Equation 22 for case A, etc.) with the number of Simpson intervals variable. Four exciter–excited layer fluorescence geometries are present in this system. The results are listed in Table 1.

For better than 1% accuracy only 4 Simpson intervals (2n+1=9 evaluations of equations of type 15-21 and 36-38) are needed for the calculation of the fluorescence of Ga when As is in the film. When the exciting element As is in the substrate, 4-8 intervals are needed.

The k-ratio Equation for Thin Film Microanalysis

The k-ratio for A_k radiation is (neglecting continuum fluorescence):

$$k_{A_k} \quad = \quad \frac{I'^{sp}_{pA_k} + I'^{sp}_{fA_k}}{I'^{A}_{pA_k}}. \tag{39}$$

For a layer containing A extending from δ_{a-1} to δ_a in a multilayer film system this is (from Equations 1-6)

$$k_{A_k} \quad = \quad gC_A \frac{\omega_{A_k,e}\int_{\delta_{a-1}}^{\delta_a}\phi^{sp}_{A_k}(z)e^{-\chi_a}dz + \frac{1}{2}\sum_B\sum_j G_{B_j}\mu^A_{B_k}\frac{r_{A_k}-1}{r'_{A_k}}C_B\frac{A_A}{A_B}\frac{z_{B_j}}{z_{A_k}}\frac{Q_{B_j}(E_0)}{Q_{A_k}(E_0)}\omega_{B_j}p_{B_j}\omega_{A_k,B_j}}{\omega_{A_k,e}\int_0^\infty \phi^A_{A_k}(z)e^{-\chi^A_{A_k}}\mathrm{d}z}. \tag{40}$$

Table 1. - - Evaluation of the triple integral G_{B_j} of Equation 31 by exact and numerical integration for the hypothetical sample described in the text.

	$G_{B_j} \times 10^6$			
Integration Method	1x1	1x2	2x1	2x2
exact (Equation 31)	0.3743	0.3942	1.708	4.272
numerical, n=2 intervals	0.3738	0.4099	1.710	4.252
" n=4 "	0.3741	0.3980	1.708	4.268
" n=6 "	0.3742	0.3959	1.708	4.270
" n=8 "	0.3742	0.3951	1.708	4.271

1x1=Fluorescence of Ga Kα in the film by As Kα in the film

1x2=Fluorescence of Ga Kα in the film by As Kα in the substrate

2x1=Fluorescence of Ga Kα in the substrate by As Kα in the film

2x2=Fluorescence of Ga Kα in the substrate by As Kα in the substrate

ω_{A_k,B_j} represents the effective fluorescence yield of A_k radiation after ionization by B_j x-rays which may differ from the fluorescence yield $\omega_{A_k,e}$ after electron ionization (Coster-Kronig transitions may differ). The transition probability, p_{A_k}, cancels in Equation 40. Because the B_j and A_k primary intensities are implicitly contained in this equation, the calculation of $K \rightarrow L$ and $L \rightarrow K$ fluorescences are simplified as in the method of Henoc et al.[15] This equation is strictly applicable, however, only to $\phi(z)$ models in which the primary x-ray intensity is a parameter of the model.[9,11,16]

Alternatively, a method based on Reed's[17] fluorescence correction procedure can be used. For this method we need an approximation for the ratio of generated (unattenuated) primary intensities of B_j and A_k x rays in the specimen. Reed's approximation is

$$\frac{I^{sp}_{pB_j}}{I^{sp}_{pA_k}} = \frac{C_B}{C_A}\frac{\omega^j_B}{\omega^k_A}\frac{p_{B_j}}{p_{A_k}}\frac{A_A}{A_B}\frac{(U_{B_j}-1)^{1.67}}{(U_{A_k}-1)^{1.67}}P_{kl} \ , \tag{41}$$

where U_{B_j} and U_{A_k} are the overvoltage ratios for B_j and A_k radiation, and P_{kl} is a factor accounting for the ratio of primary intensities when B_j and A_k are from different shells. This formula is for bulk specimens. For thin film specimens we can assume B_j and A_k intensities from theoretical bulk specimens having the same $\phi(z)$ distributions as for the thin film specimen. From Equation 4 the intensity for the theoretical bulk B_j radiation is

$$I^{sp}_{pB_j} = \frac{C_B}{A_B} z_{B_j}\omega_{B_j}p_{B_j}Q_{B_j}(E_0)\int_0^\infty \phi^{sp}_{B_j}(z)\mathrm{d}z \tag{42}$$

with a similar equation for the A_k x-ray intensity. Multiplying the numerator and denominator of the second term of equation 40 by the B_j and A_k theoretical intensities of Equation 42 and substituting Reed's approximation of Equation 41 we obtain

$$k_{A_k} = gC_A\left[\frac{\int_{\delta_{a-1}}^{\delta_a}\phi^{sp}_{A_k}(z)e^{-\chi_a}\mathrm{d}z}{\int_0^\infty \phi^A_{A_k}(z)e^{-\chi^A_{A_k}}\mathrm{d}z} + \frac{\frac{1}{2}\sum_B\sum_j G_{B_j}\mu^A_{B_k}\frac{r_{A_k}-1}{r'_{A_k}}C_B\omega_{B_j}p_{B_j}\frac{A_A}{A_B}\frac{(U_{B_j}-1)^{1.67}}{(U_{A_k}-1)^{1.67}}P_{kl}\frac{\int_0^\infty\phi^{sp}_{A_k}(z)dz}{\int_0^\infty\phi^{sp}_{B_j}(z)dz}}{\int_0^\infty \phi^A_{A_k}(z)e^{-\chi^A_{A_k}}\mathrm{d}z}\right] .$$

Reed's method does not account for differing effective fluorescence yields from x-ray or electron excitation.

Conclusion

Exact equations for the calculation of the characteristic x-ray fluorescence intensity in homogeneous thin film systems were derived. The equations were substituted into the k-ratio equation showing that the fluorescence correction for thin film systems can be calculated directly without the need to use approximations for the ratio of generated intensities. The equations in this paper and the iteration procedure described in a previous paper[18] were incorporated into a computer program to calculate the compositions of thin film systems from experimental k-ratio data.

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