The theoretical derivation of fluorescent X-ray intensities from mixtures*

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Summary—A mixture of elements irradiated by a sufficiently energetic X-ray beam absorbs the incident X-rays and re-emits other X-rays, the wavelengths of which are characteristic of the elements in the sample, and the intensities of which may be correlated with their concentrations. The problem is to correlate I_{f_i}, the intensity of the X-ray spectrum emitted by an element of atomic number Z_i with c, μ, and τ (concentration, absorption coefficient, and emission coefficient, respectively) of the elements in the sample. The correlation is complicated by the fact that the fluorescent radiation from elements of higher Z will excite additional radiation from elements of lower Z.

Using integral methods, a mathematical analysis of the absorption–re-emission process yields explicit closed formulae, when the incident beam is monochromatic, for $I_{f_i}(c, \mu, \tau)$ in terms of logarithms and ψ-functions. A preliminary investigation suggests that the theory of means may offer a theoretical solution when the incident beam is polychromatic. Graphical methods make it possible to invert the formulae and express c in terms of I_{f_i}, which makes chemical analysis possible. The use of a reference sample of known composition in the same elements as the sample in question, makes it possible to derive a close approximation to the chemical analysis when the incident beam is polychromatic. A brief comparison of computed and measured intensities from samples of known composition shows a good agreement.

The report closes with appendices giving mathematical details, a numerical table of $\psi(x)$, $(0 \leq x \leq 1)$, and the fluorescence yields for some elements.

1. Introduction

The intensity of the characteristic X-ray spectrum emitted by an element in a mixture irradiated by a sufficiently energetic X-ray beam of fixed intensity is, in general, not simply a function of the concentrations and absorption coefficients of the various elements in the mixture. There is, in general, an additional dependency on the differences between the atomic numbers of the elements. This effect, often termed the "mutual enhancement effect," is due to the fact that the characteristic spectra of elements of higher atomic numbers are sufficiently energetic to excite the spectra of elements of lower atomic numbers. The added contribution to the intensity of the spectra of lower atomic number, or enhancement, may be highly significant. Indeed, under certain conditions, the enhancement may be greater than the intensity due to the primary incident beam.

By imposing certain conditions, which are really not too restrictive, it is possible to derive closed formulae correlating fluorescent X-ray intensity with composition of the mixture. Although some of the formulae are rather lengthy, the only functions involved are logarithms, with one exception. The exception is the Abel-Legendre χ function, which is easily tabulated. A short table of $\psi(\chi)$ is given in an appendix to this paper.

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* The views expressed by the author are his own and do not necessarily represent those of the Department of the Navy.

2. Preliminary considerations, conditions, and nomenclature

Consider a three-component mixture of elements, M, of atomic numbers Z_1, Z_2, Z_3 ($Z_1 < Z_2 < Z_3$) with concentrations c_1, c_2, and c_3, respectively, ($c_1 + c_2 + c_3 = 1$). (For a specific representation one may regard Z_1, Z_2, Z_3 as 24, 26, and 28, i.e., Cr, Fe, and Ni.)

Referring to Fig. 1, the incident beam enters the sample at a fixed entrance angle θ', while the fluorescent beam is measured at exit angle θ''. The angles are measured with respect to the normal to the surface of the mixture. The incident beam may be traced as follows. It is partly absorbed at depth l by an elementary thickness dl with emission of the characteristic spectra of Z_3, Z_2, and Z_1. The spectrum of Z_3 is emitted at l over all space angles, and is partly
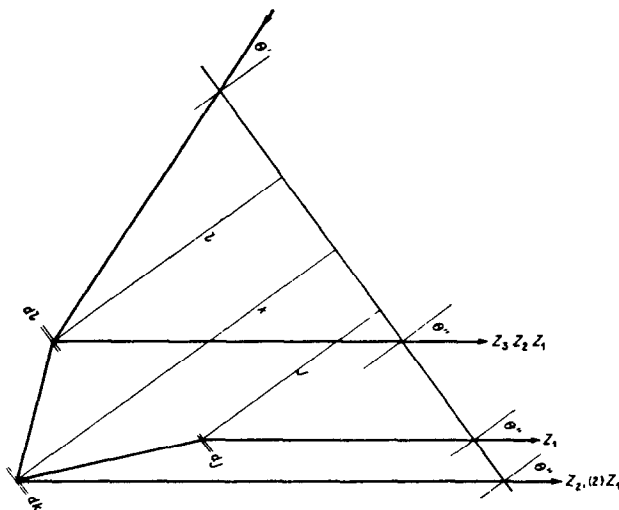

Fig. 1. Absorption and re-emission of X-rays.

absorbed at depth κ by an elementary layer $d\kappa$ with emission of the spectra of Z_2 and Z_1. In like manner, the spectrum of Z_2 emitted at l is partly absorbed at κ by an elementary layer $d\kappa$ with independent emission of the spectrum of Z_1. Similarly, the spectrum of Z_2 is emitted at κ over all space angles, and is partly absorbed at j by an elementary layer dj with emission of the spectrum of Z_1. The fluorescent spectra emitted at all layers are measured at angle θ''.

The following considerations are to be noted.

(1) The final intensities of the spectra of Z_3, Z_2, and Z_1 are the sums of one, two, and four components, respectively.

(2) The entrance and exit beams may be considered well collimated (in particular the window of the detector subtends a small angle at the radiator), and hence may be treated according to "narrow beam" theory.* However, the interior beams are distributed isotropically over all space angles and must be treated according to "broad beam" theory.

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* The change from a collimated beam to a broad or divergent beam, as in curved crystal spectrometers is discussed in Section 4(6).

(3) To obtain quantitative estimates for the intensities of the various spectra at the surface of an "infinitely thick" specimen, it is necessary to integrate the elementary contributions from dl, $d\kappa$, and dj over the interval $(0, \infty)$,* and, for the interior beams, over all space angles. It is to be anticipated that the depth effects will involve functions of $|l - \kappa|$ and $|j - \kappa|$.

In order not to involve the mathematical analysis with unnecessary difficulties, the following conditions are imposed on the problem·

(1) The intensities of the incident and fluorescent beams are to be measured only at the surface of the specimen.

(2) The range of atomic numbers (Z) will be limited from 22 to about 50 (Ti to Sn), so that only the κ spectra of the elements are involved.

(3) The κ spectrum of an element will be considered as consisting of only one line, $\kappa\alpha$.

(4) The incident beam is monochromatic with an energy not more than 50 kV, so that the photoelectric effect is the only interaction that need be considered

(5) Diffuse scattering will be neglected.

(6) The mixture will consist at most of three elements, or, the mixture will be analysed only for the elements of the three highest atomic numbers. While the nomenclature or symbolism used in papers on radiation transfer is not standardized, the following usage is rather common·

Z_i the atomic number or name of an element.

c_i the concentration of Z_i in the mixture; $\Sigma c_i = 1$.

θ' θ'' entrance and exit angles, respectively.

μ_{ij} the absorption coefficient of element Z_i for a beam of wavelength λ_j. The units of μ are cm²/g. μ is equal numerically to values tabulated as μ/ρ, or mass absorption coefficient. As is customary in radiation theory, length will be measured as mass/cm², or superficial density. Frequent use will be made of

μ_{ifj} the absorption coefficient of element Z_i for the fluorescent ($\kappa\alpha$) line of element Z_j.

ω_i the fluorescence yield of element Z_i, i.e , the ratio of the number of photons of X-radiation emitted by an atom to the number of photons absorbed from the exciting beam. ω_i is always less than 1 and independent of λ (5, 9).

r_i the "κ" jump for Z_i, i.e., the ratio of the absorption coefficients on the high-frequency and low-frequency sides of the κ discontinuity for Z_i. For elements considered in this paper. r_i is about 8 or 9 (5, 9).

I_i the intensity of a beam of wavelength λ_i measured as the rate of flow of photons.

μ', μ'' $\mu/\cos\theta'$ and $\mu/\cos\theta''$, respectively.

Consider an elementary slab of M of thickness dl at a distance l from a source of exciting monochromatic radiation of wavelength λ_j and of unit intensity (number of photons per unit of time). λ_j is less than the wavelength of the κ

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* For a thin sample the interval is $(0, t)$

absorption discontinuity of Z_i. Then the absorption by the elementary slab is $I(l)\mu_{\cdot j}\,dl$, where $I(l)$ is the intensity of the incident beam at l and $\mu_{\cdot j}$ is the absorption coefficient of M for λ_j. But $\mu_{\cdot j} = c_1\mu_{1j} + c_2\mu_{2j} + c_3\mu_{3j}$. Hence, the absorption by component Z_i in the elementary slab is $I(l)c_i\mu_{ij}\,dl$. It is well known that, under these conditions, the intensity of the fluorescent X-ray spectrum emitted by Z_i is $I(l)c_i\omega_i\left(1 - \dfrac{1}{r_i}\right) \cdot \mu_{ij}\,dl = I(l)\tau_{ij}\,dl$, where τ_{ij} may be considered as an emission coefficient corresponding to μ_{ij} as the absorption coefficient.

The intensity of the exciting beam at l will depend whether it is considered as a "narrow" or "broad" beam. If it is a *narrow beam* (i.e., subtending an elementary solid angle), propagated at an angle θ' with respect to l, then the intensity at l is $e^{-\mu l/\cos\theta'}$, the absorption is $(\mu_{ij}/\cos\theta') \cdot e^{-\mu l/\cos\theta'}\,dl$, and the fluorescent emission is $\tau'_{ij}e^{-\mu'l}\,dl$ (the primes indicate division of the symbol by $\cos\theta'$).

If the exciting beam is *broad*, isotropically distributed over all solid angles (spherical symmetry), the mean value of $I(l)$ is $\displaystyle\int_0^{\pi/2} e^{-\mu l/\cos\beta}\sin\beta\,d\beta$ and the corresponding emission will be measured by $\tau_{ij}\,dl\displaystyle\int_0^{\pi/2} e^{-\mu l/\cos\beta}(\sin\beta/\cos\beta)\cdot d\beta$. Substitution of $x = \sec\beta$ in the integral will transform it to $\tau_{ij}\,dl\displaystyle\int_1^\infty \frac{e^{-\mu lx}}{x}\,dx$. The functions $\displaystyle\int_1^\infty e^{-tx}x^{-n}\,dx$ are called integro-exponential functions (1, 4) of order n, and are usually written as $E_n(t)$. (The integral representation of $E_n(t)$ is valid only for $t > 0$.) Hence, the fluorescence intensity is $\tau_{ij}\,dl \cdot E_1(\mu l)$.

To summarize, the element of intensity of fluorescent radiation (1) for a *narrow* beam is $\tau'_{ij}e^{-\mu'l}\,dl$, and (2) for a broad beam is $\tau_{ij}E_1(\mu l)\,dl$.

3. Fluorescent intensity integrals

The integrals for the fluorescent beam intensities from M may now be written directly by reference to Fig. 1.

The following conditions will be recalled.

(a) The incident beam is monochromatic with wavelength λ_j sufficiently small to excite the spectra of Z_1, Z_2, Z_3. It is to be considered as of unit intensity at the surface of the specimen.

(b) The incident and exit (fluorescent) beams are narrow. The interior beams are broad.

(c) The atomic numbers are sufficiently far apart for the $\kappa\alpha$ lines of the elements of higher atomic numbers to be shorter than the absorption edges of the elements of lower atomic number.

(d) The specimen is "infinitely" thick.

$$I_{f3} = \tau'_3 \int_0^\infty dl \cdot e^{-(\mu' + \mu''_{f3})l} \tag{1}$$

$$I_{f2} = \tau'_2 \int_0^\infty dl \cdot e^{-(\mu' + \mu''_{f2})l} + \tau'_3\tau_{2f3} \int_0^\infty dl \int_0^\infty d\kappa \cdot e^{-(\mu'l + \mu''_{f3}\kappa)}E_1(\mu_{f3}\,|l - \kappa|) \tag{2}$$

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$$I_{f1} = \tau'_1 \int_0^\infty dl \, . \, e^{-(\mu' + \mu''_{f1})l} \tag{3}$$

$$+ \, \tau'_3 \tau_{1f3} \int_0^\infty dl \int_0^\infty d\kappa \, e^{-(\mu'l + \mu''_{f1}\kappa)} E_1(\mu_{f3} \, |l - \kappa|)$$

$$+ \, \tau'_2 \tau_{1f2} \int_0^\infty dl \int_0^\infty d\kappa \, e^{-(\mu'l + \mu''_{f1}\kappa)} E_1(\mu_{f2} \, |l - \kappa|)$$

$$+ \, \tau'_3 \tau_{2f3} \tau_{1f2} \int_0^\infty dl \int_0^\infty d\kappa \int_0^\infty dj \, e^{-(\mu'l + \mu''_{f1}j)} E_1(\mu_{f3} \, |l - \kappa|) \, . \, E(\mu_{f2} |\kappa - j|)$$

Except for the considerations discussed below, these integrals can be evaluated by direct computation, using the ordinary techniques of interchanging the order of integration (when E_1 is in the integrand), and integration by parts. However, the computation is rather lengthy, so the details of the computation will be reserved for Appendix I.

However, two difficulties arise in the reduction of the integrals, and these may be resolved as follows·

(1) Depending on the particular numerical value of the parameters, E_1 may occur in an integrand with a negative argument in the reduction of (3). The definition of $E_1(t) = \int_1^\infty \frac{e^{-tx}}{x} \, dx$ holds only for $t > 0$, since $E_1(t)$ has a logarithmic singularity at the origin ($t = 0$). However, the definition of $E_1(t)$ can be extended to negative values of t as follows. The exponential integral is defined as follows:

$$\mathscr{E}i(t) = \int_{-\infty}^t e^x x^{-1} \, dx, \tag{4}$$

which is valid for $t > 0$ provided that, when $t > 0$, $\mathscr{E}i(t)$ is interpreted in the sense of the Cauchy principal value

$$\mathscr{E}i(t) = \lim_{\delta \to 0} \left[\int_{-\infty}^{-\delta} e^x x^{-1} \, dx + \int_\delta^t e^x x^{-1} \, dx \right].$$

It follows from the definitions that

$$E_1(t) = \int_1^\infty \frac{e^{-tx}}{x} \, dx = \int_t^\infty \frac{e^{-x}}{x} \, dx = \int_{-t}^{-\infty} \frac{e^x}{x} \, dx = -\int_{-\infty}^{-t} \frac{e^x}{x} \, dx = -\mathscr{E}i(-t) \tag{5}$$

$$E_1(-t) = -\int_{-\infty}^t \frac{e^x}{x} \, dx = -\int_{-\infty}^{-t} \frac{e^x}{x} \, dx - \int_{-t}^t \frac{e^x}{x} \, dx \qquad (t > 0)$$

$$= \int_t^\infty \frac{e^{-x}}{x} \, dx + \int_{-t}^t \frac{e^{-x}}{x} \, dx$$

$$= \int_1^\infty \frac{e^{-tx}}{x} \, dx + \int_{-1}^1 \frac{e^{-tx}}{x} \, dx$$

$$E_1(-t) = E_1(t) + S(t) \qquad (t > 0) \tag{6}$$

Where $S(t)$ is defined in the sense of a principal value.

Most computations of (3) bring in, in the same formula, either the function $E_1(t)$ or $-\mathscr{E}i(-t)$, according as $t > 0$ or $t < 0$. It is therefore convenient to consider $E_1(t)$ as defined for all values of t, in spite of the fact that the positive branch $(t > 0)$ is not the analytic continuation of the negative branch $(t < 0)$. Tables of numerical values of $E_n(t)$ have been computed, but there is no need for them in the present application, since E_1 occurs only in an integrand, not in the final formula.

(2) The reduction of (3) makes frequent use of integrals of the form

$$\int \frac{\log\,(a + bx)}{x}\,dx.$$

These integrals are not expressible in terms of the commonly used transcendental functions. It is convenient, for present purposes, to define the Abel-Legendre ψ-function as follows:

$$\int \frac{\log\,(a + bx)}{x}\,dx = \frac{\log a \log x - \psi\left(-\dfrac{bx}{a}\right)}{\tfrac{1}{2}\log^2 bx + \psi\left(-\dfrac{a}{bx}\right)} \tag{7}$$

The ψ-function has been defined in other ways, the more usual ones being

$$\psi(x) = -\int_0^x \frac{\log\,(1 - t)}{t}\,dt$$

$$\psi(-x) = -\int_1^{1+x} \frac{\log t}{t(1 - t^{-1})}\,dt \qquad (x > 0)$$

$$\psi(x) = \sum_1^\infty \frac{x^n}{n^2} \qquad (|x| \le 1). \tag{8}$$

Some useful identities involving the ψ-function will be given in the Appendix I.

Since the ψ-function remains in the final formulae, an abbreviated table of numerical values of $\psi(x)$, $(0 \le x \le 1)$ is presented in Appendix II.

4. Formulae for the fluorescent intensity

The intensity integrals in the previous paragraph may be evaluated by the use of the reduction formulae developed in Appendix I.

Since the explicit formulae are rather lengthy, they will be written in the following manner.

(1) The concentrations c_i will be implicitly contained in the absorption (or emission) coefficients, for example

$$\mu = c_1\mu_1 + c_2\mu_2 + c_3\mu_3$$

$$\tau'_i = \omega_i\left(1 - \frac{1}{r_i}\right)c_i\mu'_i \qquad\qquad \text{[reference 5, 9]}$$

(11) For a free element, the intensity is I_{f3}, $(c_1 = c_2 = 0)$.

(iii) For a binary mixture, Z_3, Z_2, the intensities are I_{f3} and I_{f2}, respectively. $(c_1 = 0)$.

(iv) For a three-component mixture Z_3, Z_2, Z_1, the intensities are I_{f3}, I_{f2}, and I_{f1}, respectively.

(v) The complete expression for I_{f1} involves a resolution of the general case into one of four exclusive cases, depending on certain functions of the absorption coefficients. In applying the formula, it is necessary to determine which one of the cases applies.

(1) Z_3 $\qquad I_{f3} = \dfrac{\tau'_3}{\mu' + \mu''_{f3}}$

*(2) Z_2. $\qquad I_{f2} = \dfrac{\tau'_2}{\mu' + \mu''_{f2}}$

$$+ \frac{\tau'_3 \tau_{2f3}}{\mu' + \mu''_{f2}} \left\{ \frac{1}{\mu'} \log \left(\frac{\mu'}{\mu_{f3}} + 1 \right) + \frac{1}{\mu''_{f2}} \log \left(\frac{\mu''_{f2}}{\mu_{f3}} + 1 \right) \right\}$$

Let

$$\mu' + \mu''_{f1} = A_1 \qquad \mu_{f2} + \mu_{f3} = c_1$$
$$\mu' + \mu_{f2} = A_2 \qquad \mu''_{f1} + \mu_{f2} = B_2$$
$$\mu' + \mu_{f3} = A_3 \qquad \mu''_{f1} + \mu_{f3} = B_3$$
$$\mu_{f2} - \mu''_{f1} = D_2 \qquad \mu_{f3} - \mu' = D_3$$

There are four cases depending on the signs of D_2 and D_3

	Case 1	Case 2	Case 3	Case 4
D_2	+	−	+	−
D_3	+	+	−	−

(3) Z_1 $\qquad I_{f1} = \dfrac{\tau'_1}{A_1}$

$$+ \frac{\tau'_2 \tau_{1f2}}{A_1} \left\{ \frac{1}{\mu'} \log \frac{A_2}{\mu_{f2}} + \frac{1}{\mu''_{f1}} \log \frac{B_2}{\mu_{f2}} \right\}$$

$$+ \frac{\tau'_3 \tau_{1f3}}{A_1} \left\{ \frac{1}{\mu'} \log \frac{A_3}{\mu_{f3}} + \frac{1}{\mu''_{f1}} \log \frac{B_3}{\mu_{f3}} \right\}$$

$$+ \frac{\tau'_3 \tau_{2f3} \tau_{1f2}}{\mu' \mu''_{f1}} \Big\{$$

$$+ \frac{1}{A_1} \left\{ \log \frac{A_3}{|D_3|} \log \frac{B_2}{A_2} - \log \frac{B_2}{|D_2|} \log \frac{B_3}{|D_3|} \right\}$$

$$+ \frac{1}{\mu''_{f1}} \log \frac{B_2}{|D_2|} \log \frac{B_3}{\mu_{f3}} + \frac{1}{\mu'} \log \frac{A_3}{|D_3|} \log \frac{A_2}{\mu_{f2}}$$

$$+ \frac{1}{\mu_{f2}} \log \frac{c_1}{\mu_{f3}} + \frac{1}{\mu_{f3}} \log \frac{c_1}{\mu_{f2}} + \text{(one of the following four cases)} \Big\}$$

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* This formula has been previously reported, without proof, by GILLAM and HEAL [7]

Case 1. $(D_2 > 0, D_3 > 0; \; D_2 + B_3 = D_3 + A_2 = \mu_{f2} + \mu_{f3} = c_1)$

$$-\frac{1}{\mu'}\left\{-\psi(1) + \log\frac{c_1}{D_3}\log\frac{c_1}{\mu_{f2}} + \psi\left(\frac{\mu_{f3}}{c_1}\right) + \psi\left(\frac{A_2}{c_1}\right)\right\}$$

$$-\frac{1}{\mu''_{f1}}\left\{-\psi(1) + \log\frac{c_1}{D_2}\log\frac{c_1}{\mu_{f3}} + \psi\left(\frac{\mu_{f2}}{c_1}\right) + \psi\left(\frac{B_3}{c_1}\right)\right\}$$

$$+\frac{1}{A_1}\left\{-\psi(1) + \log\frac{c_1}{D_2}\log\frac{c_1}{D_3} + \psi\left(\frac{A_2}{c_1}\right) + \psi\left(\frac{B_3}{c_1}\right)\right\}$$

Case 2. $(D_2 < 0, D_3 > 0, \; |D_2| + c_1 = B_3, \; D_3 + A_2 = \mu_{f2} + \mu_{f3} = c_1)$

$$-\frac{1}{\mu'}\left\{-\psi(1) + \log\frac{c_1}{D_3}\log\frac{c_1}{\mu_{f2}} + \psi\left(\frac{\mu_{f3}}{c_1}\right) + \psi\left(\frac{A_2}{c_1}\right)\right\}$$

$$-\frac{1}{\mu''_{f1}}\left\{\tfrac{1}{2}\log^2\frac{B_3}{|D_2|} - \tfrac{1}{2}\log^2\frac{|D_2|}{\mu_{f3}} + \tfrac{1}{2}\log^2\frac{c_1}{\mu_{f3}} + \psi\left(\frac{|D_2|}{B_3}\right) + \psi\left(\frac{\mu_{f2}}{c_1}\right)\right\}$$

$$+\frac{1}{A_1}\left\{\tfrac{1}{2}\log^2\frac{B_3}{|D_2|} - \tfrac{1}{2}\log^2\frac{|D_2|}{D_3} + \tfrac{1}{2}\log^2\frac{c_1}{D_3} + \psi\left(\frac{|D_2|}{B_3}\right) + \psi\left(\frac{A_2}{c_1}\right)\right\}$$

Case 3. $(D_2 > 0, D_3 < 0; \; D_2 + B_3 = \mu_{f2} + \mu_{f3} = c_1, |D_3| + c_1 = A_2)$

$$-\frac{1}{\mu'}\left\{\tfrac{1}{2}\log^2\frac{A_2}{|D_3|} - \tfrac{1}{2}\log^2\frac{|D_3|}{\mu_{f2}} + \tfrac{1}{2}\log^2\frac{c_1}{\mu_{f2}} + \psi\left(\frac{|D_3|}{A_2}\right) + \psi\left(\frac{\mu_{f3}}{c_1}\right)\right\}$$

$$-\frac{1}{\mu''_{f1}}\left\{-\psi(1) + \log\frac{c_1}{D_2}\log\frac{c_1}{\mu_{f3}} + \psi\left(\frac{\mu_{f2}}{c_1}\right) + \psi\left(\frac{B_3}{c_1}\right)\right\}$$

$$+\frac{1}{A_1}\left\{\tfrac{1}{2}\log^2\frac{A_2}{|D_3|} - \tfrac{1}{2}\log^2\frac{|D_3|}{D_2} + \tfrac{1}{2}\log^2\frac{c_1}{D_2} + \psi\left(\frac{|D_3|}{A_2}\right) + \psi\left(\frac{B_2}{c_1}\right)\right\}$$

Case 4. $(D_2 < 0, D_3 < 0; \; |D_2| + c_1 = B_3, |D_3| + c_1 = A_2, \mu_{f2} + \mu_{f3} = c_1)$

$$-\frac{1}{\mu'}\left\{\tfrac{1}{2}\log^2\frac{A_2}{|D_3|} - \tfrac{1}{2}\log^2\frac{|D_3|}{\mu_{f2}} + \tfrac{1}{2}\log^2\frac{c_1}{\mu_{f2}} + \psi\left(\frac{|D_3|}{A_2}\right) + \psi\left(\frac{\mu_{f3}}{c_1}\right)\right\}$$

$$-\frac{1}{\mu''_{f1}}\left\{\tfrac{1}{2}\log^2\frac{B_3}{|D_2|} - \tfrac{1}{2}\log^2\frac{|D_2|}{\mu_{f3}} + \tfrac{1}{2}\log^2\frac{c_1}{\mu_{f3}} + \psi\left(\frac{|D_2|}{\mu_{f3}}\right) + \psi\left(\frac{\mu_{f2}}{c_1}\right)\right\}$$

$$+\frac{1}{A_1}\left\{\psi(1) + \tfrac{1}{2}\log^2\frac{A_2}{|D_3|} - \tfrac{1}{2}\log^2\frac{|D_3|}{|D_2|} + \tfrac{1}{2}\log^2\frac{B_3}{|D_2|}\right.$$

$$\left. + \psi\left(\frac{|D_2|}{B_3}\right) + \psi\left(\frac{|D_3|}{A_2}\right)\right\}$$

The formula for I_{f2} will be said to represent the total intensity as the sum of a primary component and a mutual or enhancement component.

Similarly, the formula for I_{f1} will be considered to represent the total intensity as the sum of a primary component, a mutual component due to Z_2, a mutual component due to Z_3, and a third-order component.*
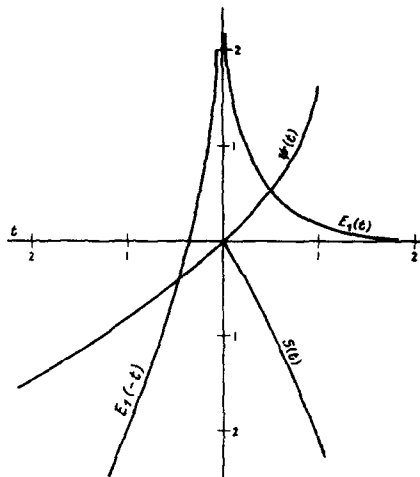

Fig 2. Graphs of functions

4.1. Thin specimen

If the specimen is thin, thickness t, in g/cm², the interval of integration becomes $(0, t)$ and the formula for the intensity of the radiation from Z_2 in a mixture $Z_2 Z_3$ may be written as follows·

$$F_1 = \mu' + \mu''_{f2}$$

$$G_1 = \mu_{f3} - \mu' \qquad\qquad H_1 = \mu_{f3} + \mu'$$

$$G_2 = \mu_{f3} - \mu''_{f2} \qquad\qquad H_2 = \mu_{f3} + \mu''_{f2}$$

$$K_1(t) = \log \frac{|G_1|}{\mu_{f3}} + E_1(G_1 t) \qquad L_1 = \log \frac{H_1}{\mu_{f3}} + E_1(H_1 t)$$

$$K_2(t) = \log \frac{|G_2|}{\mu_{f3}} + E_1(G_2 t) \qquad L_2 = \log \frac{H_2}{\mu_{f3}} + E_1(H_2 t)$$

$$M = e^{-\mu' t} + e^{-\mu''_{f2} t} \qquad\qquad N = E_1(\mu_{f3} t)$$

$$I_{f2} = \frac{\tau'_2}{F_1}(1 - e^{-F_1 t})$$

$$+ \frac{\tau'_3 \tau_{2f3}}{F_1}\left\{ \frac{1}{\mu'}[e^{-F_1 t}\kappa_1 + L_1 - MN] \right.$$

$$\left. + \frac{1}{\mu''_{f2}}[e^{-F_1 t}\kappa_2 + L_2 - MN] \right\}$$

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* Graphs of $E_1(t)$, $E_1(-t)$, $S(t)$, $\psi(t)$ are shown in Fig 2.

4.2. *Remarks*

It is to be noted that the increasing complexity of the formulae as one proceeds from I_{f3} to I_{f1} is due to two factors, namely:

(1) The final intensity is the resultant of a chain of radiative transfers (mutual or enhancement effect). This effect increases the order of integration.

(2) The change from a narrow or collimated beam to a broad or divergent beam. This effect changes the functions in the integrand from exponential, e^{-x}, to integro-exponential, where E_1 and E_2 apply to absorption and transmission effects respectively.

As an example of the latter effect one may consider the formula for I_{f3}. Then, if the incident and emergent beams are cones with 90° half-angle around the axes of symmetry, that is, full π geometry,

$$I_{f3} = \tau \int_0^\infty E_1(\mu\kappa) E_2(\mu_f\kappa)\, d\kappa$$

$$= \frac{\tau}{2}\left[\frac{1}{\mu}\left(1 - \frac{\mu_f}{\mu}\log\left(1 + \frac{\mu}{\mu_f}\right)\right) + \frac{1}{\mu_f}\log\left(1 + \frac{\mu_f}{\mu}\right)\right]$$

The similarity of this explicit expression to that obtained for the mutual effect in a binary system is to be noted.

If the cones subtend arbitrary half-angles, γ and β respectively, then

$$I_{f3} = \int_0^\gamma d\eta \int_0^\beta d\xi\, \frac{\tau\cos\xi}{\mu\cos\xi + \mu_f\cos\eta}\sin\eta\sin\xi$$

Although this integral can be reduced by elementary methods, the explicit formula is cumbersome and lengthy.

The extension of the analysis to I_{f2} and I_{f1}, using divergent incident or emergent beams, may well be left for another occasion.

5. Comparison with experiment

Strictly speaking, one cannot compare fluorescent intensities computed for monochromatic excitation with measured intensities excited by a polychromatic beam. There is, however, a certain amount of regularity in a practical sense. For example, fluorescent radiation intensities computed for a series of mixtures of the same elements for a range of wavelength of incident radiation are, for any one element, proportional to each other (linear on a logarithmic scale), if the variations in concentrations are not too great. Hence, it is better to make comparisons with a reference mixture of similar composition, not at all necessarily closely similar, than with the extreme case of comparison with the intensity of the radiation from the free element. A close study of wavelength effects is made difficult by the unreliability or lack of precision in the available estimates of the fluorescence yields for the various elements (see Appendix III).

In some instances a comparison of computed and observed results may be expected to show agreement to a reasonable extent. If one were to use the white beam from a tungsten target tube, operated at about 50 KVP, the presence of the tungsten L-spectrum will result in a high concentration of energy in the region

around 1 0 to 1·2 A. Hence, for mixtures of elements from iron to zinc, computed intensities for an incident beam of assumed wavelength 1 0 to 1 2 should show reasonable agreement with observed values.

The following comparison of computed and observed intensities is to be considered as indicating the reasonableness of the formulae rather than proving them. (The experimental conditions were excitation at 50 KVP for the incident beam with $\theta' = 30°$, $\theta'' = 60°$. The total count for each measurement was at least 150,000.)

5.1. *Binary Mixtures*

Table 1. ZnO—Fe_2O_3. Computed for incident beam at $\lambda = 1\ 20$.
Intensity ratio of $\kappa\alpha$ line. $\theta' = 30°$, $\theta'' = 60°$

c_2	c_3	Zn		Fe			
		Computed	Observed	Computed			Observed
				Primary	Mutual	Total	
0 95	0 05	0 029	0 033	0 923	0·040	0 963	0 965
0·90	0 10	0·059	0 066	0 851	0 075	0 926	0 932
0 85	0 15	0·091	0·100	0 782	0 106	0 888	0 890
0 80	0·20	0·124	0 136	0 717	0 134	0·851	0 856
0·50	0 50	0·362	0·377	0 388	0 220	0·608	0 600
0 20	0·80	0·695	0·685	0 137	0·161	0 298	0 296
0·15	0·85	0·764	0·744	0 101	0 133	0·234	0 235
0 10	0 90	0 837	0·825	0 066	0 098	0 164	0·164
0 05	0·95	0 916	0 906	0 032	0 054	0 087	0·088

It should be noted that at lower concentrations the contribution of the mutual component to the total intensity is more significant than that from the primary one. A computation for the limiting value for other mixtures, i.e., $c_1 \rightarrow 0$

$$\omega_2 \frac{\mu_{2i}}{\mu_{1i}} \left\{ \frac{\mu_{1f2}}{\mu'_{1i}} \log \left(\frac{\mu'_{1i}}{\mu_{2f2}} + 1 \right) + \frac{\mu_{1f2}}{\mu''_{2f1}} \log \left(\frac{\mu''_{2f1}}{\mu_{2f2}} + 1 \right) \right\},$$

indicates that the ratio of mutual to primary component in some instances may approach 3·5.

A change in the incident wavelength will introduce a significant change in the value of the fluorescent spectrum. The primary component of Z_2 is constant for all λ less than the absorption discontinuity for Z_3 (ratio from mixture to free element), but the mutual component ratio decreases markedly with increase in wavelength of the incident beam.

Attempts to compute the (relative) intensity of the incident spectrum from comparison of computed values at various wavelengths with observed ratios by the method of least squares (multiple regression) were unsuccessful, since the inverse matrix is of the order of 10^{-6} compared with the absorption coefficients.

5.2. *Three-component Mixtures*

Table 2. ZnO—NiO—Fe$_2$O$_3$. Computed for incident beam at $\lambda = 1\cdot20$.
Intensity ratio of Fe—$\kappa\alpha$.

Composition $(c_1 c_2 c_3)$	112	121	211
Primary component	0·1870	0·1968	0·4127
Mutual component			
Ni	0·0561	0·1217	0·0935
Zn	0·0974	0·0407	0·0907
Third-order process	0·0331	0·0267	0·0221
Total	0·374	0·386	0·619
Experimental values	0·362	0·374	0·629

Table 3. Cr—Fe—Ni. Complete analysis of alloys (metal). Incident beam: $\lambda = 1\cdot2$.

(a) *Inconel*

Element	Concentration	Component or process	Intensity ratios	
			Computed	Observed
Ni	0·79	Primary	0·605	0·597
Fe	0·065	Primary	0·0424	
		Mutual	0·0445	
		Total	0·087	0·083
Cr	0·145	Primary	0·1003	
		Mutual Fe	0·0082	
		Mutual Ni	0·1078	
		Third-order process	0·0164	
		Total	0·233	0·227

(b) *Alloy Type* 310

Element	Concentration	Component or process	Intensity ratios	
			Computed	Observed
Ni	0·205	Primary	0·088	0·095
Fe	0 550	Primary	0·3341	
		Mutual	0·0428	
		Total	0·377	0·384
Cr	0·245	Primary	0·1956	
		Mutual Fe	0·1234	
		Mutual Ni	0·0210	
		Third-order process	0 0207	
		Total	0·361	0·365

6. Effect of a polychromatic incident beam

Even a cursory examination of the formulae in Section 4 will show that the extension to a polychromatic beam introduces great difficulties for a rigorous solution. The following discussion is to be considered as only an introduction to the problem.

For Z_3

$$(1) \qquad I_{f3} = \tau'_3/\mu'_i + \mu''_{f3},$$

which may be expanded to show c_i explicitly.

$$(2) \qquad I_{f3}(c_1 c_2 c_3) = \frac{c_3 \omega'_3 \mu'_{3i}}{c_1(\mu'_{1i} + \mu''_{1f3}) + c_2(\mu'_{2i} + \mu''_{2f3}) + c_3(\mu'_{3i} + \mu''_{3f3})}$$

The expression for free Z_3, i.e., $c_1 = c_2 = 0$, becomes

$$(3) \qquad I_{f3}(001) = \frac{\omega'_3 \mu'_{3i}}{\mu'_{3i} + \mu''_{3f3}}$$

A linear expression in c_i may be obtained by dividing (3) by (2).

$$(4) \qquad Q = \frac{I_{f3}(001)}{I_{f3}(c_1 c_2 c_3)} = 1 + \left(\frac{c_1}{c_3}\right)\frac{\mu'_{1i} + \mu''_{1f3}}{\mu'_{3i} + \mu''_{3f3}} + \left(\frac{c_2}{c_3}\right)\frac{\mu'_{2i} + \mu''_{2f3}}{\mu'_{3i} + \mu''_{3f3}}$$

Instead of measuring intensity of a beam, with a Geiger counter, as counts per second, it is advantageous to represent the intensity by the reciprocal of the counting rate, i.e., time required for the counter to reach a predetermined fixed count.

Let
$$T_3 = \frac{1}{I_{f3}}$$

Then

$$(5) \qquad Q = \frac{T_{f3}(c_1 c_2 c_3)}{T_{f3}(001)} = 1 + \left(\frac{c_1}{c_3}\right)\frac{\mu'_{1i} + \mu''_{1f3}}{\mu'_{3i} + \mu''_{3f3}} + \left(\frac{c_2}{c_3}\right)\frac{\mu'_{2i} + \mu''_{2f3}}{\mu'_{3i} + \mu''_{3f3}}$$

or

$$(6) \qquad T_{f3}(c_1, c_2, c_3) = u_0 + \left(\frac{c_1}{c_3}\right) u_1 + \left(\frac{c_2}{c_3}\right) u_2$$

where u_i depends on the absorption coefficients of the elements in the mixture and the counting rate of the free element, parameters which are independent of the composition of the mixture.

The problem for the analysis involving a polychromatic incident beam of an arbitrary spectrum is to derive good linear approximations, similar to formula (6), which will present Q, the ratio of the intensity of the spectrum of Z_3 in a mixture to the intensity of the spectrum from free Z_3, which will be explicitly independent of the spectrum of the incident beam.

One may rephrase equation (3) for a polychromatic beam as

$$(7) \qquad I_{f3} = \int_{\lambda_0}^{\lambda_c} I_0(\lambda)\omega'_3 \frac{\mu'_{3s}(\lambda)}{M_{33}(\lambda) + \dfrac{c_1}{c_3} M_{13}(\lambda) + \dfrac{c_2}{c_3} M_{23}(\lambda)} \, d\lambda$$

$$(8) \qquad I_{f3}(r_{13}, r_{23}) = \int_{\lambda_0}^{\lambda_c} I_0(\lambda)\omega'_3 \frac{\mu'_{3s}(\lambda)}{M_{33}(\lambda)} \frac{1}{1 + r_{13}\dfrac{M_{13}(\lambda)}{M_{33}(\lambda)} + r_{23}\dfrac{M_{23}(\lambda)}{M_{33}(\lambda)}} \, d\lambda$$

where (λ_0, λ_c) is the range of wavelength in the polychromatic beam capable of exciting the spectrum of Z_3.

$I_0(\lambda)$ is the intensity (number of photons) in the incident beam of wavelength λ.

$$M_{13} = \mu'_{1s} + \mu''_{1f3}; \qquad M_{23} = \mu'_{2s} + \mu''_{2f3}$$

$$r_{13} = c_1/c_3; \qquad r_{23} = c_2/c_3$$

$$(9) \qquad I_{f3}(0, 0) = \int_{\lambda_0}^{\lambda_c} \frac{I_0(\lambda)\omega'_3\mu'_{3s}(\lambda)}{M_{33}} \, d\lambda$$

If

$$(10) \qquad f = 1 + r_{13}\frac{M_{13}}{M_{33}} + r_{23}\frac{M_{23}}{M_{33}} = 1 + r_{13}u_1 + r_{23}u_2$$

$$(11) \qquad p = I_0(\lambda)\omega'_3 \frac{\mu'_{3s}(\lambda)}{M_{33}}$$

Then

$$(12) \qquad Q = \frac{\displaystyle\int_{\lambda_0}^{\lambda_c} p \, d\lambda}{\displaystyle\int_{\lambda_0}^{\lambda_c} \frac{p}{f} \, d\lambda} = \left(\frac{\displaystyle\int_{\lambda_0}^{\lambda_c} pf^{-1} \, d\lambda}{\displaystyle\int_{\lambda_0}^{\lambda_c} p \, d\lambda} \right)^{-1}$$

That is, Q is the harmonic mean of f with respect to p as a weight or distribution function.

There is no loss of generality if Q were to be normalized in the sense that $\int p \, d\lambda = 1$. Hence,

$$(13) \qquad Q = (\int pf^{-1})^{-1}.$$

By definition, a mean of f with respect to p of order r is

$$(14) \qquad \mathscr{M}_r(f, p) = \left(\frac{\int pf^r}{\int p} \right)^{1/r} \qquad (r \neq 0)$$

or in normalized form

$$(15) \qquad \mathscr{M}_r(f, p) = (\int pf^r)^{1/r}.$$

The properties of power means have been extensively investigated. Some of the applicable properties are

$$(16) \qquad \mathscr{M}_r(ku) = k\mathscr{M}_r(u) \qquad (k = \text{const})$$

$$(17) \qquad \mathscr{M}_r(u) \geqslant \mathscr{M}_s(u) \qquad (r > s)$$

If $\mathscr{A}(u)$ is the arithmetic mean, i.e., $r = +1$, and $\mathscr{H}(u)$ the harmonic mean ($r = -1$), it follows that

$$(18) \qquad \mathscr{A}(u) \geqslant \mathscr{H}(u) \qquad (u \neq 0)$$

with equality only if the set $\{u\}$ is constant.

From MINKOWSKI's inequality it follows that

$$(19) \qquad \mathscr{A}(1 + u) = 1 + \mathscr{A}(u)$$

$$(20) \qquad \mathscr{H}(1 + u) \geqslant 1 + \mathscr{H}(u)$$

From these inequalities it follows that

$$(21) \quad \mathscr{A}(1 + r_{13}u_1 + r_{23}u_2) = 1 + r_{13}\mathscr{A}(u_1) + r_{23}\mathscr{A}(u_2)$$
$$> \mathscr{H}(1 + r_{13}u_1 + r_{23}u_2)$$

and

$$(22) \quad r_{13}\mathscr{A}(u_1) + r_{23}\mathscr{A}(u_2) > \mathscr{H}(1 + r_{13}u_1 + r_{23}u_2)$$
$$-1 > r_{13}\mathscr{H}(u_1) + r_{23}\mathscr{H}(u_2)$$

or

$$(23) \quad Q \geqslant 1 + r_{13}\mathscr{H}(u_1) + r_{23}\mathscr{H}(u_2).$$

Since u_1, u_2 do not depend on composition, but only on the absorption coefficients of the elements and the spectrum of the incident beam, any particular case can be analysed or computed to see how far (17) departs from equality.

The advantage of (17) over the representation of Q as an integral is that the theory of means is a much more powerful mode of attack than integration. The question of analyticity of distribution of u_i does not enter the problem, for the set $\{u_i\}$ may be arbitrary to any extent (except that $u \neq 0$), and (17) will still hold This problem of suitable approximation in particular instances cannot be answered in general but must be considered for each particular set of elements in a mixture.

In general, it may be expected that, over significantly important ranges of r_{ij}, for many mixtures the resultant inequality (17) will be practically indistinguishable from equality.

As an experimental check on the formulae the following test was made. Assuming a binary mixture, then

$$Q_3 = 1 + r_{13}M_{13}/M_{33}$$

It is also assumed that the K and L branches of the absorption curve of Z_3 and Z_1 are parallel, particularly with respect to $Z\ _1 e$, the empirical formulae for the absorption coefficients are

(1) on the K branch $\mu = aZ^m\lambda^n$

(2) on the L branch $\mu = bZ^m\lambda^n$

Then
$$\frac{M_{13}}{M_{33}} = \left(\frac{Z_1}{Z_3}\right)^m \frac{\lambda^n + \lambda_{f3}{}^n}{\lambda^n + \dfrac{b}{a}\lambda_{f3}{}^n}$$

Then, for a fixed Z_3, if for various $Z_i < Z_3$ mixtures are made so that $r_{13} \dfrac{M_{13}}{M_{33}}$ is constant, the resultant Q_3 will be constant, i.e., the measurement of Z_3 will take the same time for a fixed count.

Experiment proved that there was reasonable constancy, but only if the concentrations were computed on an atomic basis, that is, if

$$c_1 = \text{const} \times \frac{A_1}{Z^{2\cdot75}}$$

where A_1 is the atomic weight of Z_1. This will have no effect on the usual mode of analysis, since the exponent of Z does not enter explicitly into the formulae.

Some of the experimental data are given below as examples of the order of precision. The numbers are seconds for the counter to record $N = 2^{17}$ counts for Z_3 mixed with various Z_i. The mixtures were made of oxides.

Z_1 \ Z_3	Sr	As	Zn
Ti	235	150	117
Cr	245	148	118
Fe	256	155	121
Zn	259	151	
As	254		

There is no relation between columns, constancy is to be expected only within each column.

7. The inverse problem

The formulae in Section 4 may be considered as the rigorous solution to the direct problem under the assumption of a monochromatic incident beam. The inversion of the formulae to show c_i as explicit functions of the intensities or intensity ratios is clearly impossible in a rigorous sense.

Various approximations and graphical methods may be devised, but this problem is not the subject of this paper.

8. Summary and remarks

Under assumptions of a monochromatic incident beam and a one-line fluorescent spectrum, formulae have been derived for the intensities of the fluorescent spectra of three-element mixtures.

A suggestion is presented for a useful extension to the treatment of a polychromatic incident beam.

The restriction to a one-line fluorescent spectrum is theoretically a trivial one. For example, referring to the real K spectrum, it is only necessary to repeat the analysis for the β line with proper allocation of ω. The extension to L spectra

is similar. If the absorption coefficients and the location of the absorption discontinuities are known, it is only necessary to repeat the analysis for each added line.

The restriction to a monochromatic beam is difficult to remove in an analytical sense, since the incident spectrum has no analytical properties correlated with the absorption properties of the mixture.

The restriction of the mixture to no more than three components is a practical one. As may be anticipated, the formulae, in closed form, for many components, become increasingly lengthy and laborious to compute. As a practical consideration, it is questionable whether it is necessary to consider any usual mixture as containing more than four major components (elements). With the increase of the number of components, it becomes more important to develop a good analytic approximation to the exact closed form.

APPENDIX I
Reduction of the intensity integrals

All necessary formulae for the evaluation of the fluorescent intensity integrals are computed in this appendix. In reducing the various integrals, principal parts will be used whenever necessary. There seems to be no essential value in a general specification of the range of the parameters for which the formulae are valid. In any particular application, the formula to be used must be such that the following two conditions hold,

(1) the argument of a logarithmic term is positive, and

(2) the argument of a ψ-term is ≤ 1.

Care should be taken in the use of formulae involving E_1 terms, since the sign of arguments depends on concentration of Z_i as well as on the wavelengths of the various beams.

It will be noted that formulae have not been computed for the limiting case where the argument of an E_1 function vanishes. The computation is rather lengthy and the reduction is of no practical interest, since even small changes in concentration will make the arguments non-vanishing.

It will be noted that logarithms, when they occur in formulae, are all natural logarithms

1. *Definitions*

(1)
$$E_1(t) = \int_1^\infty \frac{e^{-tx}}{x}\,dx \qquad (t > 0)$$

(2)
$$S(t) = \int_{-1}^1 \frac{e^{-tx}}{x}\,dx \qquad (t > 0)$$

(3)
$$E_1(-t) = E_1(t) + S(t) \qquad (t > 0)$$

(4)
$$\psi\left(-\frac{bx}{a}\right) = \log a \log x - \int \frac{\log (a + bx)}{x}\,dx$$

$$\psi\left(-\frac{a}{bx}\right) = -\tfrac{1}{2} \log^2 bx + \int \frac{\log (a + bx)}{x}\,dx$$

$$\psi(x) = \sum_1^\infty \frac{x^n}{n^2}$$

2. *Useful Identities Involving $\psi(x)$*

(5) $$\psi(1) = \tfrac{1}{6}\pi^2 \qquad \psi(0) = 0 \qquad \psi(-1) = \tfrac{1}{12}\pi^2$$

(6) $$\psi(-x) = -\tfrac{1}{6}\pi^2 + \psi\left(\frac{1}{1+x}\right) - \log(1+x)\log x + \tfrac{1}{2}\log^2(1+x)$$

(7) $$\psi(-x) = -\tfrac{1}{2}\log^2(1+x) - \psi\left(\frac{x}{1+x}\right)$$

(8) $$\psi(x) + \psi(1-x) = \tfrac{1}{6}\pi^2 - \log x \log(1-x)$$

(9) $$\psi(-x) + \psi\left(-\frac{1}{x}\right) = -\tfrac{1}{6}\pi^2 - \tfrac{1}{2}\log^2 x$$

(9a) $$\psi(x) + \psi(-x) = \tfrac{1}{2}\psi(x^2)$$

3. *Table of Integrals*

(Elementary Forms) $k, l > 0$

(R1) $$k\int_1^\infty \frac{dx}{x(k+lx)} = \log\left(\frac{k}{l}+1\right)$$

(R2) $$k\int_1^\infty \frac{dx}{x(k-lx)} = \log\left|\frac{k}{l}-1\right|$$

(R3) $$k\int_{-1}^1 \frac{dx}{x(k+lx)} = \log\frac{|k-l|}{(k+l)}$$

(R4) $$k\int_{-1}^1 \frac{dx}{x(k-lx)} = \log\frac{(k+l)}{|k-l|}$$

(R5) $$\int_{-1}^1 \frac{\log(k+lx)}{x}\,dx = \psi\left(\frac{l}{k}\right) - \psi\left(-\frac{l}{k}\right) \qquad (k>l)$$

$$k > l, \quad m > n, \quad k, l, m, n > 0, \quad \Delta = kn - lm$$

(R6, i) $$n\int_{-1}^1 \frac{\log(k+lx)}{m+nx}\,dx = \log\frac{\Delta}{n}\log\frac{m+n}{m-n} + \psi\left(-\frac{l}{\Delta}(m-n)\right)$$
$$- \psi\left(-\frac{l}{\Delta}(m+n)\right), \quad (\Delta > 0)$$

(R6, ii) $$= \tfrac{1}{2}\log^2\frac{l}{n}(m+n) - \tfrac{1}{2}\log^2\frac{l}{n}(m-n)$$
$$+ \psi\left(-\frac{\Delta}{l(m+n)}\right) - \psi\left(-\frac{\Delta}{l(m-n)}\right)$$

(R7) $$m\int\frac{\log(k+lx)}{x(m+nx)}\,dx = \int\frac{\log(k+lx)}{x}\,dx - n\int\frac{\log(k+lx)}{m+nx}\,dx$$

$$\text{(R8)} \quad m\int_1^\infty \frac{\log\,(k + lx)}{x(m + nx)}\,dx = \tfrac{1}{2}\log^2\frac{l}{n}\,(m + n) - \tfrac{1}{2}\log^2 l + \psi\left(-\frac{\Delta}{l(m + n)}\right)$$
$$-\,\psi\left(-\frac{k}{l}\right)$$

$$E_1(ax)\,.\,(a,\,b,\,p > 0)$$

$$\text{(R9)} \quad p\int_0^\infty e^{-px}\,dx = 1$$

$$\text{(R10)} \quad p\int_0^\infty e^{-px}E_1(ax)\,dx = \log\left(\frac{p}{a} + 1\right)$$

$$\text{(R11)} \quad p\int_0^\tau e^{px}E_1(ax)\,dx = e^{p\tau}E_1(a\tau) - E_1\{(a - p)\tau\} - \log\left|\frac{p}{a} - 1\right|$$

$$\text{(R12)} \quad \int_0^\infty E_1(ax)E_1(bx)\,dx = \frac{1}{b}\log\left(\frac{b}{a} + 1\right) + \frac{1}{a}\log\left(\frac{a}{b} + 1\right)$$

$$\text{(R13)} \quad p\int_0^\infty e^{-px}E_1(ax)E_1(bx)\,dx = -\psi(1) + \log\frac{p + a + b}{a}\log\frac{p + a + b}{b}$$
$$+\,\psi\left(\frac{p + a}{p + a + b}\right) + \psi\left(\frac{p + b}{p + b + a}\right)$$

$$S(ax)$$

$$\text{(R14)} \quad p\int_0^\infty e^{-px}S(ax)\,dx = \log\frac{|\,p - a\,|}{p + a}$$

$$\text{(R15)} \quad p\int_0^\infty E_1(ax)S(bx)\,dx = \psi\left(\frac{b}{p + a}\right) - \psi\left(-\frac{b}{p + a}\right)$$
$$-\,\psi\left(-\frac{p - b}{a}\right) + \psi\left(-\frac{p + b}{a}\right)$$

$$\text{(R16)} \quad p\int_0^\infty e^{-px}S(ax)S(bx)\,dx = \psi\left(\frac{b}{p - a}\right) - \psi\left(-\frac{b}{p - a}\right) - \psi\left(\frac{a}{p + b}\right)$$
$$+\,\psi\left(\frac{a}{p - b}\right) - \psi\left(\frac{b}{p + a}\right) + \psi\left(-\frac{b}{p + a}\right) + \psi\left(-\frac{a}{p + b}\right) - \psi\left(-\frac{a}{p - b}\right)$$

$$E_1(-ax)$$

$$\text{(R17)} \quad p\int_0^\infty e^{-px}E_1(-ax)\,dx = \log\left|\frac{p}{a} - 1\right|$$

$$\text{(R18)} \quad p\int_0^\infty e^{-px}E_1(ax)E_1(-bx)\,dx = \tfrac{1}{2}\log^2\frac{p + a}{b} - \frac{1}{2}\log^2\frac{b}{a} + \psi\left(\frac{b}{p + a}\right)$$
$$-\,\psi\left(-\frac{p - b}{a}\right)$$

(R19) $\quad p\displaystyle\int_0^\infty e^{-px}E_1(-ax)E_1(-bx)\,dx = \psi(1) - \frac{1}{2}\log^2\frac{p-a}{b} + \frac{1}{2}\log^2\frac{p-b}{a}$

$$- \frac{1}{2}\log^2\frac{b}{a} + \psi\left(\frac{a}{p-b}\right) + \psi\left(\frac{b}{p-a}\right)$$

(R20) $\quad p\displaystyle\int_0^\infty e^{-px}E_1(a\,|t-x|)\,dx = e^{-pt}\log\frac{p+a}{|p-a|} - e^{-pt}E_1\{(a-p)t\} + E_1(at)$

For thin specimens

(R21) $\quad \displaystyle\int_1^\infty \frac{e^{-\kappa t}}{(l+mt)}\,dt = \frac{1}{m}\left\{e^{\frac{\kappa l}{m}}E_1\left[\frac{\kappa}{m}(l+m)\right]\right\}$

(R22) $\quad \displaystyle\int_0^\tau e^{pt}E_1(at)\,dt = \frac{1}{p}\left\{-\log\left|\frac{p}{a}-1\right| + e^{p\tau}E_1(a\tau) - E_1[(a-p)\tau]\right\}$

(R23) $\quad \displaystyle\int_0^\tau e^{-pt}E_1(at)\,dt = \frac{1}{p}\left\{\log\left(\frac{p}{a}+1\right) - e^{-p\tau}E_1(a\tau) + E_1[(a+p)t]\right\}$

(R24) $\quad \displaystyle\int_0^t e^{-px}E_1[a(t-x)]\,dx = \frac{1}{p}\left\{-e^{-pt}\log\left|\frac{p}{a}-1\right| + E_1(at)\right.$

$$\left.- e^{-pt}E_1\{(a-p)t\}\right\}$$

(R25) $\quad \displaystyle\int_t^\tau e^{-px}E_1[a(x-t)]\,dx = \frac{1}{p}\left\{e^{-pt}\log\left|\frac{p}{a}+1\right| - e^{-p\tau}E_1(a(\tau-t))\right.$

$$\left.+ e^{-pt}E_1[(a+p)(\tau-t)]\right\}$$

4. Computation of Reference Integrals

$$\Delta = kn - lm$$

(R8) $\quad \displaystyle\lim_{u\to\infty}\int_1^u \frac{\log(k+lx)}{x}\,dx = -\psi\left(-\frac{k}{l}\right) - \frac{1}{2}\log^2 l + \lim_{u\to\infty}\frac{1}{2}\log^2 lu$

$$\lim_{u\to\infty}\int_1^u\frac{\log(k+lx)}{m+nx}\,dx = -\psi\left(-\frac{\Delta}{l(m+n)}\right) - \frac{1}{2}\log^2\frac{l}{n}(m+n)$$

$$+ \lim_{u\to\infty}\frac{1}{2}\log^2 lu\left(1+\frac{m}{nu}\right)$$

$$\lim_{u\to\infty}m\int_1^u\frac{\log(k+lx)}{x(m+nx)}\,dx = -\psi\left(-\frac{k}{l}\right) - \frac{1}{2}\log^2 l + \psi\left(-\frac{\Delta}{l(m+n)}\right)$$

$$+ \frac{1}{2}\log^2\frac{l}{n}(m+n) + \frac{1}{2}\lim_{u\to\infty}\left\{\log^2 lu - \log^2 lu\left(1+\frac{m}{nu}\right)\right\}$$

but

$$\lim_{u\to\infty}\left\{\log^2 lu - \log^2 lu\left(1+\frac{m}{nu}\right)\right\} = \lim_{u\to\infty}\left\{-2\log lu\log\left(1+\frac{m}{nu}\right) - \log^2\left(1+\frac{m}{nu}\right)\right\}$$

$$= 0$$

since
$$\log\left(1 + \frac{1}{u}\right) = O\left(\frac{1}{u}\right).$$

(R10)
$$p \int_0^\infty e^{-px} E_1(ax)\, dx = p \int_0^\infty dx\, e^{-px} \int_1^\infty dt\, \frac{e^{-axt}}{t}$$

$$= p \int_1^\infty \frac{dt}{t} \int_0^\infty dx\, e^{-(p+at)x} = p \int_1^\infty \frac{dt}{t(p+at)}$$

(R9, R1)

(R11)
$$p \int_0^\tau e^{px} E_1(ax)\, dx = p \int_0^\tau dx\, e^{px} \int_1^\infty dt\, \frac{e^{-axt}}{t}$$

$$= p \int_1^\infty \frac{dt}{t} \int_0^\tau dx\, e^{(p-at)x} = p \int_1^\infty \frac{e^{(p-at)\tau}}{t(p-at)}\, dt - p \int_1^\infty \frac{dt}{t(p-at)}$$

$$= \int_1^\infty dt\, \frac{e^{(p-at)\tau}}{t} + \int_1^\infty a\, dt\, \frac{e^{(p-at)\tau}}{p-at} - p \int_1^\infty \frac{dt}{t(p-at)}$$

$$= e^{p\tau} \int_1^\infty dt\, \frac{e^{-a\tau t}}{t} - \int_1^\infty \frac{e^{-(a-p)\tau t}}{t}\, dt - p \int_1^\infty \frac{dt}{t(p-at)}$$

(def. E_1 and R_2)

(R12)
$$\int_0^\infty E_1(ax) E_1(bx)\, dx = \int_1^\infty \frac{dt}{t} \int_0^\infty e^{-btx} E_1(ax)\, dx = \frac{1}{b} \int_1^\infty \frac{dt}{t^2} \log\left(\frac{bt}{a} + 1\right)$$

(R13)
$$\int_0^\infty e^{-px} E_1(ax) E_1(bx)\, dx = p \int_1^\infty \frac{dt}{t} \int_0^\infty dx\, e^{-(p+bt)x} E_1(ax)$$

$$= p \int_1^\infty \frac{\log\left(\dfrac{p+a}{a} + \dfrac{b}{a}t\right) dt}{t(p+bt)} = \tfrac{1}{2} \log^2 \frac{p+b}{a} - \tfrac{1}{2} \log^2 \frac{b}{a} + \psi\left(-\frac{a}{p+b}\right)$$

$$- \psi\left(-\frac{p+a}{b}\right)$$

(R10, R8)

To obtain (R13), use identities in ψ (5, 6, and 7).

(R15)
$$p \int_0^\infty e^{-px} E_1(ax) S(bx)\, dx = p \int_{-1}^1 \frac{dt}{t} \int_0^\infty e^{-(p+bt)} E_1(ax)\, dx$$

$$= p \int_{-1}^1 \frac{\log\left(\dfrac{p+a}{a} + \dfrac{b}{a}t\right)}{t(p+bt)}\, dt$$

(R10, R6,i)

(R17, 18, 19) Combine appropriate forms for $E(-ax) = E(ax) + S(ax)$ and reduce by the use of the identities in $\psi(x)$.

(R20)
$$J = \int_0^\infty e^{-px} E_1(a\,|t - x|)\,dx$$

$$= \int_0^t e^{-px} E_1(at - ax)\,dx + \int_t^\infty e^{-px} E_1(ax - at)\,dx$$

$$aJ = \int_0^{at} e^{-\frac{p}{a}x} E_1(at - x)\,dx + \int_{at}^\infty e^{-\frac{p}{a}x} E_1(x - at)\,dx$$

$$y = at - x \qquad\qquad y = x - at$$

$$J = \frac{1}{a} e^{-pt}\left\{\int_0^{at} e^{\frac{p}{a}y} E_1(y)\,dy + \int_0^\infty e^{-\frac{p}{a}y} E_1(y)\,dy\right\}$$

(R11, R10)

5. *Reduction of Intensity Integrals*

The evaluation of the intensity may be reduced to combinations of the following forms.

(J1)
$$\int_0^\infty dl\,e^{-pl}$$

(J2)
$$\int_0^\infty dl \int_0^\infty d\kappa\, e^{-(pl+gk)} E_1\{a\,|l - \kappa|\}$$

(J3)
$$\int_0^\infty dl \int_0^\infty d\kappa \int_0^\infty d\jmath\, e^{-(pl+g\jmath)} E_1\{a\,|l - \kappa|\}\cdot E_1\{b\,|k - \jmath|\}.$$

The first typical integral (J1) is elementary, and is evaluated in R9.
The second typical integral (J2) may be written as

$$J2 = \int_0^\infty dl\,e^{-pl} \int_0^\infty d\kappa\, e^{-gk} E_1\{a\,|l - \kappa|\}.$$

The inner integral is evaluated in R20. The second integration may be evaluated by the use of the reduction forms for $E(ax)$ and $E(-ax)$.

The third typical integral (J3) may be written as

$$J3 = \int_0^\infty d\kappa \int_0^\infty dl\,e^{-pl} E_1\{a\,|l - \kappa|\} \int_0^\infty d\jmath\,e^{-g\jmath} E_1\{b\,|k - \jmath|\}$$

which. on reducing by use of R20. becomes

$$J3 = \frac{1}{pg} \int_0^\infty d\kappa \left\{e^{-p\kappa} \log\frac{p + a}{|p - a|} - e^{-p\kappa} E_1\{(a - p)k\} + E_1(ak)\right\}$$

$$\times \left\{e^{-g\kappa} \log\frac{g + b}{|g - b|} - e^{-g\kappa} E_1\{(b - g)k\} + E_1(b\kappa)\right\}$$

Expansion of the product in the integrand will reduce J3 to a sum of nine integrals, the values of which are given in R9 to R13 and R17 to R19. The resultant expressions may then be reduced to simpler forms, depending on the particular

combinations of the parameters. The sign of the arguments of the E_1-function will depend not only on the particular elements, Z_i and the wavelength of the incident beam, but also on the concentrations of the elements in the mixture.

APPENDIX 2

$$\psi(x) = \sum \frac{x^n}{n^2}$$

χ	0·00	0 01	0 02	0 03	0 04	0 05	0 06	0 07	0·08	0 09
0 0	0 0	0 01003	0 02010	0 03023	0·04041	0 05064	0 06092	0 07126	0·08166	0 09211
0 1	0 10262	0 11318	0 12381	0·13449	0 14523	0 15603	0 16690	0 17783	0 18882	0 19988
0 2	0 21100	0 22219	0 23345	0 24478	0 25618	0 26765	0 27920	0 29082	0 30251	0 31428
0 3	0 32613	0 33806	0 35007	0 36216	0 37434	0·38661	0 39896	0 41140	0·42393	0 43656
0 4	0 44928	0 46210	0 47502	0·48804	0·50117	0 51440	0 52774	0 54119	0 55476	0 56844
0 5	0 58224	0 59616	0 61022	0 62440	0 63887	0 65316	0 66775	0 68248	0 69736	0 71239
0 6	0 72767	0 74294	0 75846	0 77416	0 79003	0 80608	0 82233	0 83878	0 85543	0 87229
0 7	0 88943	0 90670	0·92425	0 94206	0 96013	0 97847	0 99710	1 01603	1 03528	1·05486
0 8	1 07482	1 09510	1·11581	1·13694	1 15852	1 18058	1 20317	1 22632	1 25009	1·27453
0 9	1 29971	1 32573	1·35268	1 38068	1 40993	1·44064	1 47680	1 50790	1·54580	1 58863
1·0	1·64493									

APPENDIX 3

$$\omega(K)$$

	Ref. [5]	*	Ref. [8]
24 Cr	0 22	0·241	0 27
26 Fe	0·28	0 303	0·34
27 Co	0 31	0·336	(0·38)
28 Ni	0 34	0 368	0·42
29 Cu	0 37	0 400	0 46
30 Zn	0 40	0 432	0 49
33 As	0 49	0 523	(0·58)
34 Se	0·52	0·551	0 60
35 Br	0 54	0 578	0 63
38 Sr	0 62	0 650	0 71
42 Mo	0·71	0·727	0 77
47 Ag	0 79	0 796	0 83
50 Sn	0·83	0·827	0 86

* Arend's formula—$\omega(k) = \dfrac{0.957Z^4}{0.984 \times 10^6 + Z^4}$

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