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Standard Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis[1]

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1. Scope

1.1 This guide is an introduction to mathematical procedures for correction of interelement (matrix) effects in quantitative X-ray spectrometric analysis.

1.1.1 The procedures described correct only for the interelement effect(s) arising from a homogeneous chemical composition of the specimen. Effects related to either particle size, or mineralogical or metallurgical phases in a specimen are not treated.

1.1.2 These procedures apply to both wavelength and energy-dispersive X-ray spectrometry where the specimen is considered to be infinitely thick, flat, and homogeneous with respect to the depth of penetration of the exciting X rays **(1)**.[2]

1.2 This document is not intended to be a comprehensive treatment of the many different techniques employed to compensate for interelement effects. Consult References 2 through 4 for descriptions of other commonly used techniques such as standard addition, internal standardization, etc.

2. Referenced Documents

2.1 *ASTM Standards:*

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[3]

3. Terminology

3.1 For definitions of terms used in this guide, refer to Terminology E 135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *absorption edge*—the maximum wavelength (minimum X-ray photon energy) that can expel an electron from a given level in an atom of a given element.

3.2.2 *analyte*—an element in the specimen whose concentration is to be determined.

3.2.3 *characteristic radiation*—X radiation produced by an element in the specimen as a result of electron transitions between different atomic shells.

3.2.4 *coherent (Rayleigh) scatter*—the emission of energy from a loosely bound electron which has undergone collision with an incident X-ray photon and has been caused to vibrate. The vibration is at the same frequency as the incident photon and the photon loses no energy. (See 3.2.7.)

3.2.5 *dead-time*—time interval during which the X-ray detection system, after having responded to an incident photon, cannot respond properly to a successive incident photon.

3.2.6 *fluorescence yield*—a ratio of the number of photons of all X-ray lines in a particular series divided by the number of shell vacancies originally produced.

3.2.7 *incoherent (Compton) scatter*—the emission of energy from a loosely bound electron which has undergone collision with an incident photon and the electron has recoiled under the impact, carrying away some of the energy of the photon.

3.2.8 *influence coefficient*—designated by α, a matrix correction factor for converting apparent concentrations to actual concentrations in a specimen. Other terms commonly used are alpha coefficient and interelement effect coefficient.

3.2.9 *mass absorption coefficient*—designated by μ, an atomic property of each element which expresses the X-ray absorption per unit mass per unit area, cm^2/g.

3.2.10 *primary absorption*—absorption of incident X rays by the specimen. The extent of primary absorption depends on the composition of the specimen and the X-ray source spectral distribution.

3.2.11 *primary spectral distribution*—the output X-ray spectral distribution usually from an X-ray tube. The X-ray continuum is usually expressed in units of absolute intensity per unit wavelength per electron per unit solid angle.

3.2.12 *relative intensity*—the ratio of an analyte X-ray line intensity measured from the specimen to that of the pure analyte element. It is sometimes expressed relative to the analyte element in a multi-component standard reference material.

3.2.13 *secondary absorption*—the absorption of the characteristic X radiation produced in the specimen by all the elements in the specimen.

3.2.14 *secondary fluorescence (enhancement)*—the generation of X rays from the analyte caused by characteristic X rays from other elements in the sample whose energies are greater than the absorption edge of the analyte.

3.2.15 *weight fraction*—a concentration unit expressed as a ratio of the mass of analyte to the total mass.

3.2.16 *X-ray source*—an excitation source which produces

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[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[3] *Annual Book of ASTM Standards*, Vol 03.05.

X rays such as an X-ray tube, radioactive isotope, or secondary target emitter.

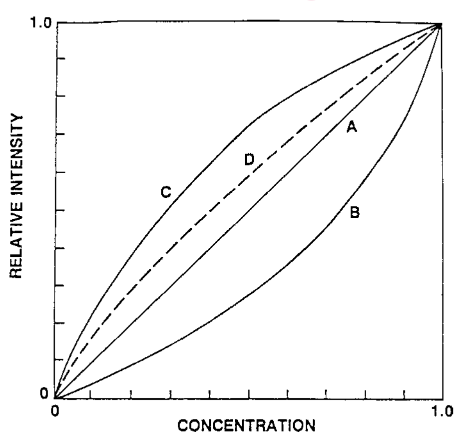
4. Significance and Use

4.1 Accuracy in quantitative X-ray spectrometric analysis depends upon adequate accounting for interelement effects. This guide is intended to serve as an introduction to users of X-ray fluorescence correction methods. For this reason, only selected mathematical models for correcting interelement effects are presented. The reader is referred to several texts for a more comprehensive treatment of the subject **(2-6).**

5. Description of Matrix Effects

5.1 Matrix effects in X-ray spectrometry are caused by absorption and enhancement of X rays in the specimen. Primary absorption occurs as the X rays from the source are absorbed by the specimen. The extent of primary absorption depends on the composition of the specimen, the output energy distribution of the exciting source, such as an X-ray tube, and the geometry of the spectrometer. Secondary absorption occurs as the characteristic X radiation produced in the specimen is absorbed by the elements in the specimen. When matrix elements emit characteristic X-ray lines which lie on the short-wavelength (high energy) side of the analyte absorption edge, the analyte can be excited to emit characteristic line radiation in addition to that excited directly by the X-ray source. This is called secondary fluorescence or enhancement.

5.2 These effects can be represented as shown in Fig. 1 using binary alloys as examples. When matrix effects are either negligible or constant, Curve A in Fig. 1 would be obtained. That is, a plot of analyte relative intensity (corrected for background, dead-time, etc.) versus analyte concentration would yield a straight line over a wide concentration range and would be independent of the other elements present in the specimen (Note 1). Linear relationships often exist in thin specimens, or in cases where the matrix effect is constant. Low alloy steels, for example, exhibit constant matrix effects in that the concentrations of the minor constituents vary, but the major constituent, that is, iron, remains relatively constant. In general, Curve B is obtained when the absorption by the matrix elements in the specimen of either the primary X rays or analyte characteristic X rays, or both, is greater than the absorption by the analyte alone. This secondary absorption effect is often referred to simply as absorption. The magnitude of the displacement of Curve B from Curve A in Fig. 1, for example, is typical of the strong absorption of nickel K_α X rays in Fe-Ni alloys. Curve C represents the general case where the matrix elements in the specimen absorb the primary X rays or characteristic X rays, or both, to a lesser degree than the analyte alone. This type of secondary absorption is often referred to as negative absorption. The magnitude of the displacement of Curve C from Curve A in Fig. 1, for example, is typical of alloys in which the atomic number of the matrix element (for example, aluminum) is much lower than the analyte (for example, nickel). Curve D in Fig. 1 illustrates an enhancement effect as defined previously, and represents in this case the enhancement of iron K_α X rays by nickel K_α X rays in Fe-Ni binaries.



Curve A—Linear calibration curve.
Curve B—Absorption of analyte by matrix. For example, R_{Ni} versus C_{Ni} in Ni-Fe binary alloys where nickel is the analyte element and iron is the matrix element.
Curve C—Negative absorption of analyte by matrix. For example, R_{Ni} versus C_{Ni} in Ni-Al alloys where nickel is the analyte element and aluminum is the matrix element.
Curve D—Enhancement of analyte by matrix. For example, R_{Fe} versus C_{Fe} in Fe-Ni alloys where iron is the analyte element and nickel is the matrix element.

FIG. 1 Interelement Effects in X-Ray Fluorescence Analysis

NOTE 1—The relative intensity rather than absolute intensity of the analyte will be used in this document for purposes of convenience. It is not meant to imply that measurement of the pure element is required, unless under special circumstances as described in 9.1.

6. General Comments Concerning Interelement Correction Procedures

6.1 Historically, the development of mathematical methods for correction of matrix effects has evolved into two approaches which are currently employed in quantitative X-ray analysis. When the field of X-ray spectrometric analysis was new, researchers proposed mathematical expressions which required prior knowledge of corrective factors called influence coefficients or alphas prior to analysis of the specimens. These factors were usually determined experimentally by regression analysis using reference materials, and for this reason are typically referred to as empirical or semi-empirical procedures (see 7.1.3, 7.2, and 7.8). During the late 1960s, another approach was introduced which involved the calculation of interelement corrections directly from first principle expressions such as those given in Section 8. First principle expressions are derived from basic physical principles, and contain physical constants and parameters, for example, which include absorption coefficients, fluorescence yields, primary spectral distributions, and spectrometer geometry. Fundamental parameter methods is a term commonly used to describe interelement correction procedures based on first principle equations (see Section 8).

6.2 In recent years, several workers have proposed fundamental parameter methods to correct measured X ray intensities directly for matrix effects or, alternatively, proposed mathematical expressions in which influence coefficients are calculated from first principles (see Sections 7 and 8). Such influence coefficient expressions are referred to as fundamental influence coefficient methods.

7. Influence Coefficient Correction Procedures

7.1 *The Lachance-Traill Equation*:

7.1.1 For the purposes of this guide, it is instructive to begin with one of the simplest, yet fundamental, correction models within certain limits. Referring to Fig. 1, either Curve B or C (that is, absorption only) can be represented mathematically by a hyperbolic expression such as the Lachance-Traill equation (LT) **(7).** For a binary specimen containing elements *i* and *j*, the LT equation is:

$$C_i = R_i (1 + \alpha_{ij}^{LT} C_j) \quad (1)$$

where:
C_i = weight fraction of analyte *i*,
C_j = weight fraction of matrix element *j*,
R_i = the analyte intensity in the specimen expressed as a ratio to the pure analyte element, and
α_{ij}^{LT} = the influence coefficient, a constant.

The subscript i denotes the analyte and the subscript j denotes the matrix element. The subscript in α_{ij}^{LT} denotes the influence of matrix element *j* on the analyte *i* in the binary specimen. The LT superscript denotes that the influence coefficient is that coefficient in the LT equation. The magnitude of the displacement of Curves B and C from Curve A is represented by α_{ij}^{LT} which takes on positive values for B type curves and negative values for C type curves.

7.1.2 The general form of the LT equation when extended to multicomponent specimens is:

$$C_i = R_i (1 + \Sigma \alpha_{ij}^{LT} C_j) \quad (2)$$

For a ternary system, for example, containing elements *i*, *j* and *k*, three equations can be written wherein each of the elements are considered analytes in turn:

$$C_i = R_i (1 + \alpha_{ij}^{LT} C_j + \alpha_{ik}^{LT} C_k) \quad (3)$$

$$C_j = R_j (1 + \alpha_{ji}^{LT} C_i + \alpha_{jk}^{LT} C_k) \quad (4)$$

$$C_k = R_k (1 + \alpha_{ki}^{LT} C_i + \alpha_{kj}^{LT} C_j) \quad (5)$$

Therefore, six alpha coefficients are required to solve for the concentrations *i*, *j*, and *k* (see Appendix X1). Once the influence coefficients are determined, Eq 3-5 can be solved for the unknown concentrations with a computer using iterative techniques (see Appendix X2).

7.1.3 *Determination of Influence (Alpha) Coefficients from Regression Analysis*—Alpha coefficients can be obtained experimentally using regression analysis of reference materials in which the elements to be measured are known and cover a broad concentration range. An example of this method is given in X1.1.1 of Appendix X1. Eq 1 can be rewritten for a binary specimen in the form:

$$(C_i/R_i) - 1 = \alpha_{ij}^{R} C_j \quad (6)$$

where: α_{ij}^{R} = influence coefficient obtained by regression analysis. A plot of $(C_i/R_i) - 1$ versus C_j gives a straight line with slope α_{ij}^{R} (see Fig. X1.1 of Appendix X1). Note that the superscript LT is replaced by R because alphas obtained by regression analysis of multi-component reference materials do not generally have the same values as α_{ij}^{LT} (as determined from first principle calculations). This does not present a problem generally in the results of analysis if the reference materials bracket each of the analyte elements over the concentration ranges that exist in the specimen(s). Best results are obtained only when the specimens and reference materials are of the same type. The weakness of the multiple-regression technique as applied in X-ray analysis is that the accuracy of the influence coefficients obtained is not known unless verified, for example, from first principle calculations. As the number of components in a specimen increases, this becomes more of a problem. Results of analysis should be checked for accuracy by incorporating reference materials in the analysis scheme and treating them as unknown specimens. Comparison of the known values with those found by analysis should give acceptable agreement, if the influence coefficients are sufficiently accurate. This test is valid only when reference materials analyzed as unknowns are not included in the set of reference materials from which the influence coefficients were obtained.

7.1.4 *Determination of Influence Coefficients from First Principles*—Influence coefficients can be calculated from fundamental parameter expressions (see X1.1.3 of Appendix X1). This is usually done by arbitrarily considering the composition of a complex specimen to be made up of the analyte and one matrix element at a time (for example, a series of binary elements, or compounds such as oxides). In this way, a series of influence coefficients are calculated assuming hypothetical compositions for the binary series of elements or compounds which comprise the specimen(s). The hypothetical compositions can be selected at certain well-defined limits. Details of this procedure are given in 9.3.

7.1.5 *Use of Relative Intensities in Correction Methods*—As stated in Note 1, relative intensities are used for purposes of convenience in most correction methods. This does not mean that the pure element is required in the analysis unless it is the only reference material available. In that case, only fundamental parameter methods would apply. If influence coefficients are obtained by regression methods from reference materials, then R_i can be expressed relative to a multi-component reference material. Eq 6 can be rewritten in the form for regression analysis as follows:

$$(C_i/R'_i) - 1 = \alpha_{ij}^{R'} C_j \quad (7)$$

where:
R'_i = analyte intensity in the specimen expressed as a ratio to a reference material in which the weight fraction of *i* is less than 1.0, and
$\alpha_{ij}^{R'}$ = influence coefficient obtained by regression analysis.

The terms R'_i and $\alpha_{ij}^{R'}$ can be related to the corresponding terms in Eq 6 by means of the following:

$$R'_i k_i = R_i \quad (8)$$

$$\alpha_{ij}^{R'} = \frac{\alpha_{ij}^{R}}{k_i} \quad (9)$$

where:
k_i = a constant.

7.1.6 *Limitations of the Lachance-Traill Equation*:

7.1.6.1 For the purposes of this guide, it is convenient to classify the types of specimens most often analyzed by X-ray analysts into three categories: (*1*) metals, (*2*) pressed minerals

TABLE 1 Alpha Coefficients for Analyte Iron in Binary Systems Computed Using Fundamental Parameters Equations[A]

	α_{Fej}															
C_{Fe}	O(8)	Mg(12)	Al(13)	Si(14)	Ca(20)	Ti(22)	Cr(24)	Mn(25)	Co(27)	Ni(28)	Cu(29)	Zn(30)	As(33)	Nb(41)	Mo(42)	Sn(50)
0.01	−0.841	−0.52	−0.39	−0.25	0.93	1.46	2.08	−0.10	−0.18	−0.44	−0.42	−0.36	−0.13	0.74	0.86	2.10
0.02	− 0.840	− 0.52	− 0.39	− 0.25	0.93	1.46	2.08	− 0.10	− 0.17	− 0.44	− 0.41	− 0.35	− 0.13	0.74	0.86	2.10
0.05	− 0.839	− 0.51	− 0.39	− 0.25	0.93	1.46	2.09	− 0.10	− 0.15	− 0.42	− 0.41	− 0.35	− 0.12	0.74	0.86	2.10
0.10	− 0.838	− 0.51	− 0.39	− 0.25	0.93	1.46	2.09	− 0.10	− 0.14	− 0.40	− 0.39	− 0.34	− 0.12	0.75	0.86	2.10
0.20	− 0.835	− 0.51	− 0.38	− 0.24	0.94	1.47	2.10	− 0.10	− 0.11	− 0.36	− 0.37	− 0.32	− 0.11	0.76	0.87	2.11
0.50	−0.832	−0.50	−0.37	−0.22	0.96	1.50	2.13	−0.10	−0.04	−0.27	−0.31	−0.28	−0.08	0.78	0.90	2.14
0.80	− 0.831	− 0.49	− 0.36	− 0.21	1.01	1.55	2.19	− 0.10	0.00	− 0.20	− 0.25	− 0.24	− 0.05	0.83	0.94	2.20
0.90	− 0.830	− 0.48	− 0.35	− 0.20	1.03	1.58	2.23	−0.10	0.01	− 0.18	− 0.23	− 0.23	− 0.04	0.85	0.96	2.25
0.95	− 0.830	− 0.48	− 0.35	− 0.20	1.05	1.60	2.26	− 0.10	0.02	−0.17	−0.23	−0.22	−0.03	0.86	0.98	2.28
0.98	− 0.830	− 0.48	− 0.35	− 0.20	1.06	1.62	2.29	− 0.10	0.02	− 0.17	− 0.22	− 0.22	− 0.03	0.87	0.98	2.30
0.99	−0.830	−0.48	−0.35	−0.20	1.06	1.62	2.29	− 0.10	0.02	− 0.16	− 0.22	− 0.21	− 0.02	0.87	0.99	2.31

[A] Data used by permission from G. R. Lachance, Geological Survey of Canada.

or powders, and (*3*) diluted samples such as aqueous solutions, fusions with borate salts, and oils. When a sample is fused in a fixed sample-to-flux ratio (for example, typically 1 + 6, or 1 + 12) to produce a glass disk, or when a powdered sample is mixed in a fixed sample-to-binder ratio and pressed, the magnitude of the matrix effects are correspondingly decreased and stabilized. Since enhancement effects are usually negligible in these systems, the LT equation is sufficiently accurate in many applications for making matrix corrections. It has also been shown that the LT equation is in agreement with first principles calculations when applied to fused specimens (that is, at least 1 + 6 dilutions or greater). For fused specimens, an equation can be written according to Lachance **(8)** as follows:

$$C_i = R'_i\,(1 + \alpha_{if}C_f)\left[\,1 + \left[\frac{\alpha_{ij}}{1 + \alpha_{if}\,C_f}\right]C_j + ...\right] \qquad (10)$$

where:

C_i = the analyte weight fraction in the fused specimen,
C_f = the weight fraction of the flux (for example, $Li_2B_4O_7$),
α_{if} = influence coefficient which describes the absorption effect of the flux on the analyte *i*, and
R'_i = the relative intensity of the analyte in the fused specimen to the intensity of the analyte in a fused reference material.

Various equations have been used in which the alpha correction defined above is modified by incorporating the effect of a constant term. For example, in fused systems the alphas can be modified by including the weight fraction of flux which remains essentially constant. That is, the term $\alpha_{ij}/(1 + \alpha_{if}C_f)$ in Eq 10 can be referred to as a modified alpha, α_{ij}^{M}. The loss on ignition (LOI) in fusions can also be included in the alpha terms. Modified alphas have also been used for non-fused pelletized specimens, such as minerals, to express the correction in terms of the metal oxides rather than the metals themselves.

7.1.6.2 If the influence coefficient in the Lachance-Traill equation is calculated from first principles as a function of concentration assuming absorption only, it can be shown that α_{ij}^{LT} is not a constant but varies with matrix concentration depending on the atomic number of the matrix elements. This is illustrated in Table 1, for example, for a selected series of binary specimens in which iron is the analyte. Note that in some cases (for example, α_{FeO}), the influence coefficient is nearly constant whereas, for others (for example, α_{FeCo}), the influence coefficient exhibits a wide variation and even changes sign. As long as the analyst is analyzing specimens in which enhancement effects are absent, this variation in α_{ij}^{LT} does not present problems in practice when the specimen composition varies over a relatively small range. This source of error is also minimized to some degree when type reference materials are used which reasonably bracket the composition of the specimen(s). However, it should be recognized that for some types of samples, which have a broad range of concentration, assumption of a constant α_{ij}^{LT} can lead to inaccurate results. For example, in the cement industry, low dilutions (for example, typically 1 + 3 sample-to-flux ratio) have been employed to analyze cement and geological materials. Low dilutions were used to maximize the analyte intensity, especially for elements with atomic numbers from 11 to 26. At such low dilutions, it has been shown by Moore **(9)** that a modified form of Eq 1 gives more accurate results. This modified or exponential form of Eq 1 is also described in ASTM methods (see E-2 SM 10-20, E-2 SM 10-26, and E-2 SM 10-34).[4] In 7.2-7.7, several equations will be described which take into account the variability in α_{ij}^{LT} with concentration, and are fundamentally more accurate than Eq 1 because they also include correction for enhancement effects.

7.2 *The Rasberry-Heinrich Equation*— Rasberry and Heinrich (RH) **(10)** proposed an empirical method to correct for both strong absorption and strong enhancement effects present in alloys such as Fe-Ni-Cr. The general expression can be written as follows:

$$C_i = R_i\left[1 + \sum_{j}^{n} A_{ij}\,C_j + \sum_{k}^{n}\frac{B_{ik}}{(1 + C_i)}\cdot C_k\right] \qquad (11)$$

where:

A_{ij} = a constant used when the significant effect of *j* and *i* is absorption; in such cases the corresponding B_{ik} values are zero (and Eq 11 reduces to the Lachance-Traill equation), and
B_{ik} = a constant used when the predominant effect of element *k* on *i* is enhancement; then the corresponding A_{ij} values are zero.

Eq 11 has given good results for analyses of Fe-NiCr ternary alloys. The coefficients were obtained by these authors by

[4] Methods for Analytical Atomic Spectroscopy, ASTM, 8th ed., 1987, pp 923–930, 949–955, and 992–996.

regression analysis of a series of Fe-Ni, and Fe-Cr, and Ni-Cr binaries, and a series of Fe-Ni-Cr ternary reference materials, which covered a broad range of concentrations from essentially zero to 0.99. For Fe-Ni binaries, the enhancement term $\left(\text{that is, } \frac{B_{ik}}{(1 + C_i)} \cdot C_k\right)$ gives values for the effect of Ni(*k*) on Fe(*i*) which are in reasonably good agreement with those predicted from first principle calculations over a broad range of concentration. Further examination by several workers of the accuracy of the RH equation for matrix correction in other ferrous as well as non-ferrous binary alloys reveal wide discrepancies when these coefficients are compared to those obtained from first principle calculations. Even modification of the enhancement term cannot overcome some of these limitations, as discussed by Tertian **(11).** For these reasons, the RH equation is not considered to be generally applicable but, however, quite satisfactory for making matrix corrections in Fe-Ni-Cr alloys assuming availability of proper reference materials.

7.3 *The Claisse-Quintin Equation*:

7.3.1 The Claisse-Quintin equation (CQ) can be described as an extension of the Lachance-Traill equation to include enhancement effects and can be written for a binary according to Refs **12, 13** as follows:

$$C_i = R_i\,[1 + \sum_{n-1} (\alpha_{ij} + \alpha_{ijj}\,C_j)\,C_j] \quad (12)$$

where $\alpha_{ij} + \alpha_{ijj}\,C_j = \alpha_{ij}^{LT}$. The term $\alpha_{ij} + \alpha_{ijj}\,C_j$ allows for linear variation of α_{ij}^{LT} with composition. According to Claisse and Quintin **(12)** and Tertian **(14)**, in ternary and more complex samples, the matrix correction is not strictly equal to a weighted sum of binary corrections. This phenomenon is referred to as a third element or cross-effect. For a ternary, the total correction for the interelement effects of *j* and *k* on the analyte *i* is given by Claisse and Quintin **(12)** as:

$$1 + (\alpha_{ij} + \alpha_{ijj}\,C_j)C_j + (\alpha_{ik} + \alpha_{ikk}\,C_k)\,C_k + \alpha_{ijk}\,C_j\,C_k \quad (13)$$

The binary correction terms for the effect of *j* on *i* and *k* on *i* are $(\alpha_{ij} + \alpha_{ijj}\,C_j)\,C_j$ and $(\alpha_{ik} + \alpha_{ikk}\,C_k)\,C_k$, respectively, while the higher order term $\alpha_{ijk}\,C_jC_k$ is introduced to correct for the simultaneous presence of both *j* and *k*. The term α_{ijk} is called a cross-product coefficient. Tertian **(14)** has discussed in detail the cross-effect and has introduced a term, ϵ, calculated from first principles to correct for it. The contribution of the cross-effect or cross-product term to the total correction is relatively small, however, compared to the binary coefficient terms, but can be significant.

7.3.2 The general form of the Claisse-Quintin equation for a multicomponent specimen can be written according to Ref **13** as:

$$C_i = R_i\,[1 + \sum_{j \neq 1} (\alpha_{ij} + \alpha_{ijj}\,C_M)\,C_j + \sum_j \sum_k \alpha_{ijk}\,C_j\,C_k] \quad (14)$$

where C_M = sum of all elements in the specimen except *i*. The binary coefficients, α_{ij} and α_{ijj}, can be calculated from first principles, usually at hypothetical compositions of $C_i = 0.20$ and 0.80, and $C_j = 0.80$ and 0.20, respectively. The cross-product coefficient, α_{ijk}, is calculated at $C_i = 0.30$, $C_j = 0.35$, and $C_k = 0.35$.

7.4 *The Algorithm of Lachance (COLA)*:

7.4.1 The comprehensive Lachance algorithm (COLA) proposed by Lachance **(15)** corrects for both absorption and enhancement effects over a broad range of concentration. The general form of the COLA expression is given as follows:

$$C_i = R_i\,(1 + \sum_j \alpha'_{ij}\,C_j + \sum_j \sum_k \alpha_{ijk}\,C_j\,C_k) \quad (15)$$

The coefficient α'_{ij} can be computed from the equation:

$$\alpha'_{ij} = \alpha_1 + \frac{\alpha_2\,C_M}{1 + \alpha_3\,(1 - C_M)} \quad (16)$$

where α_1, α_2, and α_3 are constants. The concept of cross-product coefficients as given by Claisse and Quintin (see Eq 14) is retained and included in Eq 15. The three constants (α_1, α_2, and α_3) in Eq 16 are calculated from first principles using hypothetical binary samples. For example, in alloy systems, α_1 is the value of the coefficient at the $C_i = 1.0$ limit (in practice computed at $C_i = 0.999$; and $C_j = 0.001$). The value for α_2 is the range within which α'_{ij} will vary when the concentration of the analyte decreases to the $C_i = 0.0$ limit (in practice, computed from two binaries where $C_i = 0.001$ and 0.999; and $C_j = 0.999$ and 0.001). The α_3 term expresses the rate with which α'_{ij} is made to vary hyperbolically within the two limits stated. In practice, it is generally computed from three binaries where $C_i = 0.001$, 0.5, and 0.999; and $C_j = 0.999$, 0.5, and 0.001. Since α_3 can take on positive, zero, or negative values, α'_{ij} can be computed for the entire composition range from $C_i = 1.0$ down to 0.0. The cross-product coefficients α_{ijk} are calculated at the same levels as in Eq 14.

7.4.2 For multi-element assay of alloys, all coefficients in Eq 15 are calculated. For oxide specimens such as cements and powdered rocks, α_3 is very small and in practice is usually equated to zero. Eq 15 then reduces to the Claisse-Quintin Eq 14. For fused specimens, another simplification can be made because the concentration of the fluxing agent is the major constituent and can be held relatively constant. In this case α_2, α_3, and α_{ijk} are very small and in practice are also equated to zero, so that α_{ij} reduces to α_{ij}^{LT}. Hypothetical binary standards are used to calculate α_{ij}^{LT} where C_i is taken at the mid-range of the analyte concentration (for example, $C_i = 0.5$ and $C_j = 0.5$) in the specimen.

7.4.3 A significant improvement was obtained using COLA rather than the CQ equation for the analysis of iron in a series of Fe-Ni alloys **(16).** This is believed to be due to the term α_3 $(1 - C_j)$ in α'_{ij} in Eq 16 which allows for nonlinear variation in α'_{ij} with composition rather than a linear variation described by the CQ relation. For this reason, the COLA equation is more accurate in alloy analyses than the CQ equation when the contribution of the $\alpha_3(1 - C_j)$ term becomes significant.

7.5 *The Algorithm of Rousseau*—The algorithm of Rousseau **(17, 18, 19)** is:

$$C_i = R_i\,\frac{1 + \sum_j \alpha^*_{ij}\,C_j}{1 + \sum_j \rho_{ij}\,C_j} \quad (17)$$

where:

α^*_{ij} = fundamental influence coefficient which varies with composition and corrects for absorption, and

ρ_{ij} = fundamental influence coefficient which varies with composition and corrects for enhancement.

In this method a first estimate of the composition of the unknown specimen is calculated using the Claisse-Quintin relation (Eq 14) and fundamental coefficients **(19).** From this estimated composition, the α^*_{ij} and ρ_{ij} coefficients are computed. A refined estimate of composition is obtained finally by applying the iterative process to Eq 17. The manner in which reference materials are used in this and in other fundamental coefficient algorithms for purposes of calibration is discussed in 9.3.

7.6 *The Method of de Jongh*:

7.6.1 De Jongh's method **(20)** is similar to that of Lachance-Traill but with some important differences. A series of equations can be written wherein the end result is expressed for an *n* component system as follows:

$$C_i = (a_o + a_i I_i)(1 + \Sigma\, \alpha_{ij}^{dJ} C_j) \tag{18}$$

where:
a_o = intercept,
a_i = slope, and
I_i = net intensity measured in counts per unit time.

The terms a_o, a_i, and I_i are instrument-dependent parameters and considered separate from the physical parameters manifested in α_{ij}^{dj}.

7.6.2 For a series of specimens containing *n* elements in which the concentrations of each analyte vary over a range, de Jongh's method requires that the influence coefficients be calculated about an average composition for each element (for example, $\bar{C}_1$, $\bar{C}_2$, ... $\bar{C}_n$ where j = 1, 2, 3, ... *n*) in the specimens. Both absorption and enhancement effects are treated by this method. An interesting feature of the method is that one element can be arbitrarily eliminated from the correction procedure so there is no need to measure it. For example, in ferrous alloys, iron is often the major constituent and is usually determined by difference, and therefore, can be eliminated from the correction procedure. For details on the mathematical procedure used to eliminate a component from the analysis, refer to the original publication.

7.7 *Method of Broll & Tertian*— The expression of Broll and Tertian **(21, 22)** allows for variation of α_{ij}^{LT} in the Lachance-Traill equation to account for both absorption and enhancement effects. The term α_{ij}^{LT} in the LT equation is replaced by effective influence coefficients as follows:

$$\alpha_{ij}^{LT} = \alpha_{ij}^{BT} - h_{ij}\left[\frac{C_i}{R_i}\right] \tag{19}$$

where:
α_{ij}^{BT} = influence coefficient which varies with composition and corrects for absorption, and

the term $h_{ij}(C_i/R_i)$ accounts for enhancement and third element effects. These so-called effective coefficients are calculated from first-principle expressions.

7.8 *Intensity Correction Equation*— This empirical procedure, developed by several workers **(23, 24),** is similar to the general Lachance-Traill equation, except that X-ray intensity is substituted for concentration to obtain the following equation:

$$R_i = \frac{C_i}{k_o + \Sigma_{k_{ij}} I_j} \tag{20}$$

where:
I_j = the X-ray intensity corrected for background of the matrix element *j*,
k_o = a constant for the system, and
k_{ij} = influence coefficient, a constant.

This procedure is limited in the sense that it applies to specimens in which absorption is the predominant matrix effect and is not severe. That is, the analyte X-ray intensity varies almost linearly with analyte concentration (for example, metals in oil). The constant, k_o, and the coefficients, k_{ij}, are determined only from regression analysis from reference materials. The coefficients k_{ij} should, however, be differentiated from α_{ij}^{LT}. Eq 20 has been applied successfully in cases where the unknown specimen composition can be bracketed quite closely with reference materials of similar composition. In general, this procedure applies over a small analyte concentration range and to obtain good accuracy requires a more careful selection of the composition range of reference materials.

8. First Principle Equations

8.1 The relative intensity from an analyte *i* for a given X-ray spectral line in a specimen can be described according to Ref 5as follows:

$$R_i = \frac{P_i + S_i}{P_o} \tag{21}$$

where:
P_i = the primary fluorescence contribution as a result of the effect of the incident X-ray beam from the source on the analyte *i*,
S_i = secondary fluorescence or enhancement effect on analyte *i*, and
P_o = the pure specimen.

8.2 For the case when the X-ray source is polychromatic (for example, an X-ray tube), an equation for P_i can be written as follows:

$$P_i = qE_iC_i \int_{\lambda_o}^{\lambda_{ai}} \left[\frac{\mu_{i(\lambda)}\, I_\lambda d\lambda}{\mu_{(\lambda)} + A\mu_{(\lambda_i)}}\right] \tag{22}$$

where:
q = factor which depends on spectrometer geometry,
E_i = excitation factor of element *i* for a given spectral line series (*K*, *L*, ...),
C_i = concentration of analyte *i* in specimen, usually expressed as weight fraction.
$\mu_{i(\lambda)}$ = mass absorption coefficient of element i in the specimen for incident wavelength, λ,
$\mu_{(\lambda)}$ = mass absorption coefficient of the specimen for incident wavelength, λ,
$\mu_{(\lambda_i)}$ = mass absorption coefficient of the specimen for the characteristic wavelength, λ_i,
A = geometrical factor = $\sin\theta_1/\sin\theta_2$,
θ_1 = incident angle of primary X-ray radiation,
θ_2 = emergence angle (take-off angle) of characteristic fluorescence radiation measured from the specimen surface,