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

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ε1 NOTE—Editorial corrections were made throughout in April 2015.

## 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 Refs (**2-5**) for descriptions of other commonly used techniques such as standard addition, internal standardization, etc.

## 2. Referenced Documents

2.1 *ASTM Standards:*[3]

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

## 3. Terminology

3.1 For definitions of terms used in this guide, refer to Terminology E135.

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 to be determined by measurement.

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 that 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 that 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 (β, γ, δ and other Greek letters are also used in certain mathematical models), a correction factor for converting apparent mass fractions to actual mass fractions 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 primary spectral distribution.

3.2.11 *primary spectral distribution*—the output X-ray spectral distribution usually from an X-ray tube. The X-ray

[1] This guide is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.20 on Fundamental Practices.

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

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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 reference material.

3.2.13 *secondary absorption*—the absorption of the characteristic X radiation produced in the specimen by all 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 *X-ray source*—an excitation source which produces X-rays such as an X-ray tube, radioactive isotope, or secondary target emitter.

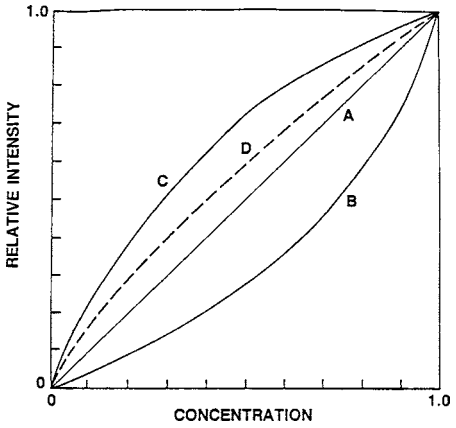
## 4. Significance and Use

4.1 Accuracy in quantitative X-ray spectrometric analysis depends upon adequate accounting for interelement effects either through sample preparation or through mathematical correction procedures, or both. 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 (**2-7**).

## 5. Description of Interelement 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 specimen absorbs the X -rays from the source. 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 that lie on the short-wavelength (high energy) side of the analyte absorption edge, the analyte can be excited to emit characteristic 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 mass fraction would yield a straight line over a wide mass fraction 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 composition is constant. Low alloy steels, for example, exhibit constant interelement effects in that the mass fractions of the minor constituents vary, but the major constituent, 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 $K$-$L_{2,3}$ ($K_\alpha$) 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 $K$-$L_{2,3}$ ($K_\alpha$) X-rays by nickel $K$-$L_{2,3}$ ($K_\alpha$) 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 interelement 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 principles expressions such as those given in Section 8. First principles 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 parameters method is a term commonly used to describe interelement correction procedures based on first principle equations (see Section 8).

6.2 In recent years, several researchers have proposed fundamental parameters methods to correct measured X-ray intensities directly for interelement 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) **(8).** For a binary specimen containing elements *i* and *j*, the LT equation is:

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

where:

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

The subscript i denotes the analyte and the subscript j denotes the matrix element. The subscript in $\alpha_{ij}^{LT}$ 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 $\alpha_{ij}^{LT}$ 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:

$$C_i = R_i \left(1 + \sum \alpha_{ij}^{LT} C_j\right) \tag{2}$$

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:

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

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

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

Therefore, six alpha coefficients are required to solve for the mass fractions $C_i$, $C_j$, and $C_k$ (see Appendix X1). Once the influence coefficients are determined, Eq 3-5 can be solved for the unknown mass fractions 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 mass fraction 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:

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

where: $\alpha_{ij}^{R}$ = influence coefficient obtained by regression analysis. A plot of $(C_i/R_i) - 1$ versus $C_j$ gives a straight line with slope $\alpha_{ij}^{R}$ (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 $\alpha_{ij}^{LT}$ (as determined from first principles 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 mass fraction 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 principles 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 parameters 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 that 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 parameters 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 mass 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 using X-ray spectrometric methods into three categories: (*1*) metals, (*2*) pressed minerals 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 to produce a glass disk, or when a powdered sample is mixed in a fixed sample-to-binder ratio and pressed to produce a briquette, physical and chemical differences among materials are correspondingly decreased and the magnitudes of the interelement effects are reduced and stabilized. Since enhancement effects are usually negligible in these systems, the LT equation is sufficiently accurate in many applications for making interelement 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 part sample + 6 parts flux dilutions or greater). For fused specimens, an equation can be written according to Lachance (**9**) as follows:

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

where:

$C_i$ = the analyte mass fraction in the fused specimen,

$C_f$ = the mass fraction of the flux (for example, $Li_2B_4O_7$),

$\alpha_{if}$ = 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, the alphas in fused systems can be modified by including the mass 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, $\alpha_{ij}^{M}$. The loss or gain in mass on fusion can also be included in the alpha terms (Note 2). Modified alphas have also been used for non-fused specimens in briquette form, such as minerals, to express the correction in terms of the metal oxides rather than the metals themselves.

NOTE 2—Under the action of heat and flux during fusion, the specimen will either lose or gain mass depending on the relative amounts of volatile matter and reduced species it contains. Therefore, the terms loss on fusion (LOF) and gain on fusion (GOF) are used to describe this behavior. It is common to see the term loss on ignition (LOI) used incorrectly to describe this behavior.

7.1.6.2 If the influence coefficient in the Lachance-Traill equation is calculated from first principles as a function of mass fraction assuming absorption only, it can be shown that $\alpha_{ij}^{LT}$ is not a constant but varies with matrix mass fraction depending on the atomic number of each matrix element. 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, $\alpha_{FeMg}$), the influence coefficient is nearly constant whereas, for others (for example, $\alpha_{FeCo}$), the influence coefficient exhibits a wide variation and even changes sign. In practice, this variation in $\alpha_{ij}^{LT}$ does not present problems when the specimen composition varies over a relatively small range, and enhancement effects are absent. This

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

| | $\alpha_{Fej}$ | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_{Fe}$ | 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. The values represent the effect of the element listed at the top of each column on the analyte Fe for each mass fraction of Fe listed in the first column.

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 $\alpha_{ij}^{LT}$ could lead to inaccurate results. For example, in the cement industry, low dilutions (for example, typically 1 part sample + 2 parts flux) have been employed to analyze cement and geological materials. Low dilutions are used to maximize the analyte intensity for trace constituents. At such low dilutions, it has been shown by Moore (**10**) that a modified form of Eq 1 gives more accurate results. This modified or exponential form of Eq 1 is also described in ASTM suggested 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 $\alpha_{ij}^{LT}$ with mass fraction, 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) (**11**) 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:

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

where:

$A_{ij}$ = a constant used when the significant effect of element $j$ on $i$ 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-Ni-Cr ternary alloys. These authors obtained the coefficients by regression analysis of data from 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 mass fractions 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($i$) that are in reasonably good agreement with those predicted from first principles calculations over a broad range of mass fraction. Further examination by several researchers of the accuracy of the RH equation for interelement effect correction in other ferrous as well as non-ferrous binary alloys reveal wide discrepancies when these coefficients are compared to those obtained from first principles calculations. Even modification of the enhancement term cannot overcome some of these limitations, as discussed by Tertian (**12**). For these reasons, the RH equation is not considered to be generally applicable, but it is satisfactory for making corrections in Fe-Ni-Cr alloys assuming availability of proper reference materials.

[4] Suggested Methods for Analysis of Metals, Ores, and Related Materials, 9th ed., ASTM International Headquarters, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, 1992, pp. 507-573.

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 **13**, **14** as follows:

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

where $\alpha_{ij}+\alpha_{ijj}\,C_j=\alpha_{ij}^{LT}$. The term $\alpha_{ij}+\alpha_{ijj}\,C_j$ allows for linear variation of $\alpha_{ij}^{LT}$ with composition. According to Claisse and Quintin (**13**) and Tertian (**14**), the interelement effect correction for ternary and more complex samples 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 (**13**) 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. The higher order term $\alpha_{ijk}\,C_j\,C_k$ is introduced to correct for the simultaneous presence of both $j$ and $k$. The term $\alpha_{ijk}$ is called a cross-product coefficient. Tertian (**15**) 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 it 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:

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

where $C_M$ = sum of all elements in the specimen except $i$. The binary coefficients, $\alpha_{ij}$ and $\alpha_{ijj}$, 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, $\alpha_{ijk}$, 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 (**16**) corrects for both absorption and enhancement effects over a broad range of mass fraction. The general form of the COLA expression is given as follows:

$$C_i = R_i\left(1+\sum_{j}\alpha'_{ij}\,C_j+\sum_{j}\sum_{k}\alpha_{ijk}\,C_j\,C_k\right) \quad (15)$$

The coefficient $\alpha'_{ij}$ can be computed from the equation:

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

where $\alpha_1$, $\alpha_2$, and $\alpha_3$ 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 ($\alpha_1$, $\alpha_2$, and $\alpha_3$) in Eq 16 are calculated from first principles using hypothetical binary samples. For example, in alloy systems, $\alpha_1$ 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 $\alpha_2$ is the range within which $\alpha'_{ij}$ 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, respectively). The $\alpha_3$ term expresses the rate with which $\alpha'_{ij}$ 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, respectively. Since $\alpha_3$ can take on positive, zero, or negative values, $\alpha'_{ij}$ can be computed for the entire composition range from $C_i = 1.0$ down to 0.0. The cross-product coefficients $\alpha_{ijk}$ 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, $\alpha_3$ 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 mass fraction of the fluxing agent is the major constituent and can be held relatively constant. In this case $\alpha_2$, $\alpha_3$, and $\alpha_{ijk}$ are very small and in practice are also equated to zero, so that $\alpha_{ij}$ reduces to $\alpha_{ij}^{LT}$. Hypothetical binary standards are used to calculate $\alpha_{ij}^{LT}$ 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 **(17).** This is believed to be due to the term $\alpha_3 (1 - C_j)$ in $\alpha'_{ij}$ in Eq 16 which allows for nonlinear variation in $\alpha'_{ij}$ 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 **(18, 19, 20)** is:

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

where:

$\alpha^*_{ij}$ = fundamental influence coefficient, which varies with composition and corrects for absorption, and
$\rho_{ij}$ = 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 **(20)**. The $\alpha^*_{ij}$ and $\rho_{ij}$ coefficients are computed from this estimated composition. A refined estimate of composition is obtained finally by applying the iterative process to Eq 17. The manner in which reference materials are used for purposes of calibration in this and other fundamental coefficient algorithms is discussed in 9.3.

7.6 *The Method of de Jongh:*

7.6.1 De Jongh's method **(21)** is similar to that of Lachance-Traill but with important differences. A series of equations can be written wherein the end result is expressed for an $n$ component system as follows:

$$C_i = (a_o + a_i I_i)\left(1 + \sum \alpha_{ij}^{dJ} C_j\right) \quad (18)$$

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 $\alpha_{ij}^{dj}$.

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 at an average composition for each element (for example, $\bar{C}_1, \bar{C}_2, \ldots \bar{C}_n$ where $j = 1, 2, 3, \ldots n$) 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 **(22, 23)** allows for variation of $\alpha_{ij}^{LT}$ in the Lachance-Traill equation to account for both absorption and enhancement effects. The term $\alpha_{ij}^{LT}$ in the LT equation is replaced by effective influence coefficients as follows:

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

where:

$\alpha_{ij}^{BT}$ = 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-principles expressions.

7.8 *Intensity Correction Equation*— This empirical procedure, developed by several researchers **(24, 25),** is similar to the general Lachance-Traill equation, except that X-ray intensity (count rate) is substituted for mass fraction to obtain the following equation:

$$R_i = \frac{C_i}{k_o + \sum_{k_{ij}} I_j} \quad (20)$$

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 interelement effect and is not severe. That is, the analyte X-ray intensity varies almost linearly with analyte mass fraction. The constant, $k_o$, and the coefficients, $k_{ij}$, are determined only from regression analysis of data from reference materials. However, the coefficients $k_{ij}$ should be differentiated from $\alpha_{ij}^{LT}$. 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 range of analyte mass fraction and requires a careful selection of the composition range of reference materials to obtain good accuracy.

## 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 **6** as 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 primary fluorescence contribution from a pure specimen of the analyte.

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 that 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 mass 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, $\lambda_i$,
$A$ = geometrical factor = $\sin\theta_1/\sin\theta_2$,
$\theta_1$ = incident angle of primary X radiation,
$\theta_2$ = emergence angle (take-off angle) of characteristic fluorescence radiation measured from the specimen surface,
$I_\lambda d\lambda$ = spectral intensity distribution of the primary radiation from the X-ray source,
$\lambda_o$ = short-wavelength limit of the primary spectral distribution, and
$\lambda a_i$ = the wavelength of the absorption edge of analyte element *i*.

8.3 For the pure specimen, $P_o$, Eq 22 takes the form:

$$P_o = qE_i \int_{\lambda_o}^{\lambda_{ai}} \left[ \frac{\mu_{i(\lambda)}\, I_\lambda d\lambda}{\mu_{i(\lambda)} + A\mu_{i(\lambda_i)}} \right] \tag{23}$$

8.4 The total secondary fluorescence contribution **(26)**, $S_i$, when each characteristic X-ray line *j* from the specimen can enhance the analyte *i*, is:

$$S_i = \sum_j S_{ij} \tag{24}$$

where $S_{ij}$ = sum of the contributions from several *j* elements which can enhance *i*. The expression for $S_{ij}$ is:

$$S_{ij} = 1/2\; q\; E_iC_i \int_{\lambda_o}^{\lambda_{aj}} \left(E_jC_j\,\mu_{i(\lambda_j)}\right) \left( \frac{\mu_j(\lambda)\, I_\lambda d\lambda}{\mu_{(\lambda)} + A\mu_{(\lambda_i)}} \right) \cdot L \tag{25}$$

where:

$E_j$ = excitation factor of enhancing element *j* for a given spectral line series,
$C_j$ = mass fraction of *j* in the specimen,
$\mu_i(\lambda_j)$ = mass absorption coefficient of analyte *i* in the specimen for characteristic wavelength $\lambda_j$ from element *j*,
$\lambda_{j(\lambda)}$ = mass absorption coefficient of element *j* in the specimen for incident wavelength, λ, and

$$L = \frac{ln\left[1 + \left(\mu_{(\lambda)}/\mu_{(\lambda_j)}\right)/sin\theta_1\right]}{\mu_{(\lambda)}/sin\theta_1} + \frac{ln\left[1 + \left(\mu_{(\lambda_i)}\right)/\left(\mu_{(\lambda_j)}\right)/\sin\theta_2\right]}{\mu_{(\lambda_i)}/\sin\theta_2} \tag{26}$$

where $\mu_{(\lambda j)}$ = mass absorption coefficient of the specimen for the characteristic wavelength, $\lambda_j$.

8.5 Substitution of Eq 22-26 in Eq 21 gives a first principles (fundamental parameters) expression from which relative intensities can be calculated.

8.6 With an X-ray tube source from which the primary radiation is polychromatic, it is necessary to know the spectral distribution, $I_\lambda d\lambda$ (intensity versus wavelength), or approximations must be made. To simplify the integral form of the tube spectrum, Criss and Birks **(27)** replaced the integrals in Eq 22, Eq 23, and Eq 25 with summations over small wavelength intervals such as 0.2 nm. Gilfrich and Birks **(28)** measured spectral distributions from several X-ray tubes (tungsten, molybdenum, and chromium targets) and tabulated values of $I_\lambda \Delta\lambda$, which have been used in several fundamental parameters expressions. In addition, algorithms have been proposed which can be used to calculate the spectral output distribution **(29, 30, 31).**

8.7 *Monochromatic Excitation*—A relatively simple fundamental parameter equation can be derived when the specimen is irradiated with X radiation of a single energy or wavelength, λ, (monochromatic excitation) **(32).** For example, such excitation sources are used in energy-dispersive spectrometers in the form of secondary target emitters or radioisotopes. In this case, Eq 21 can be rewritten for monochromatic excitation simply by replacing the integrals in Eq 22, Eq 23, and Eq 25, and the $I_\lambda d\lambda$ terms with the intensity of the incident radiation λ. The relative intensity for analyte *i* in a binary specimen containing an enhancing element *j* then becomes:

$$R_i = C_i\,(ABS)\left[1 + 1/2\;C_jE_j\;\mu_{i(\lambda_j)}\left(\frac{\mu_{j(\lambda)}}{\mu_{i(\lambda)}}\right)\cdot L\right] \tag{27}$$

where:

$$ABS = \frac{\mu_{i(\lambda)}\sin\theta_2 + \mu_{i(\lambda_i)}\sin\theta_1}{\mu_{(\lambda)}\sin\theta_2 + \mu_{(\lambda_i)}\sin\theta_1}$$

## 9. Computer Programs for Interelement Corrections

9.1 A common approach in fundamental parameters correction methods consists of the calculation by computer of relative X-ray intensities from first principles (see Eq 21-26) assuming

a hypothetical composition for the unknown specimen. These calculated intensities are compared with measured intensities, and successive adjustments of the unknown composition are made using available pure elements, compounds, or multi-element reference materials until the calculated and measured intensities are essentially the same. The final adjusted mass fractions are then assumed to be equal to the actual mass fractions in the unknown specimen. Relative intensities calculated from first principles using hypothetical compositions can also generate fundamental influence coefficients as mentioned in 7.1.4. A powerful feature of these methods is that even when pure elements or compounds are the only reference materials available, analysis of complex specimens is still possible. However, in practice, the best results are obtained when type reference materials are used in the analysis procedure.

9.2 *The NRLXRF Correction Procedure*— NRLXRF, a widely used fundamental parameters computer program for quantitative X-ray spectrometry, was developed at the Naval Research Laboratory by Birks, Gilfrich, and Criss **(33).** Another version of this program, XRF-11, was developed by Criss **(34)** for operation with minicomputers, as desktop computers were called at that time.

9.2.1 With such programs, a multi-element analysis of an unknown specimen can be performed when pure elements, chemical compounds, or multi-element reference materials are available. In this case, the measured intensities ($I_m$) of the materials with known compositions are used to adjust or rescale the calculated intensities of the unknown specimen ($I_u$). The rescaled, calculated intensities also are adjusted to match the measured intensities of the specimen in an iterative procedure. The final output composition for the unknown is reached when the calculated and measured intensities converge, that is, they agree within some predetermined limits. A schematic diagram that illustrates this procedure is shown in Fig. 2.

9.3 *Fundamental Influence Coefficient Correction Procedures*—Computer programs have also been developed for the methods of Claisse-Quintin, De Jongh, Lachance (COLA), Rousseau, and Broll and Tertian. One example of a computer program that employs the fundamental influence coefficient approach is called NBSGSC and is applicable to the analysis of minerals, both as pressed powders and as fused specimens, and alloys **(35).** A schematic diagram of this program is given in Fig. 3. Reference materials also are used in these procedures. The calibration step is performed, generally, as follows:

9.3.1 First, a calibration plot of calculated relative intensity ($R_i^S$) (that is, corrected for interelement effects) versus the corresponding measured X-ray intensity is obtained for each analyte from reference materials. Ideally, this should be a straight line with a zero intercept. Extrapolation of this straight line to $R_i^S = 1.0$ gives the expected measured intensity of the pure analyte (that is, 100 %).

9.3.2 The measured intensities of the analytes in the specimens are used to obtain the calculated relative intensities of the analytes ($R_i^U$) from the above calibration plot.

9.3.3 From these values of $R_i^U$, the composition of the unknown specimen is computed (using an influence coefficient equation) in an iterative loop until some convergence criteria are met and the final results are obtained.

9.4 *SAP3 Computer Program*—Nielson and Sanders **(36)** developed a rather unique fundamental parameters computer program (SAP3) by using monochromatic X-ray source excitation in an energy-dispersive X-ray spectrometer. Their approach makes use of measured incoherent and coherent scattered primary X-rays from the specimen along with characteristic X-ray intensities. This method is applicable, for the most part, to the analysis of samples in which the major constituents are of low atomic number such as botanical and geological materials. An important feature of this approach is that additional information about the specimen matrix, such as the total mass of low atomic number elements in the specimen (for example, carbon, hydrogen, oxygen and nitrogen) can be obtained from the intensity of scattered primary X-rays.

9.5 *CORSET and QUAN Computer Programs:*

9.5.1 *Polychromatic Excitation; Use of Equivalent Wavelengths*—As an alternative to using a measured or calculated X-ray tube spectrum, an approximation can be made which involves the concept of equivalent wavelengths. In general, algorithms have been developed which consider only

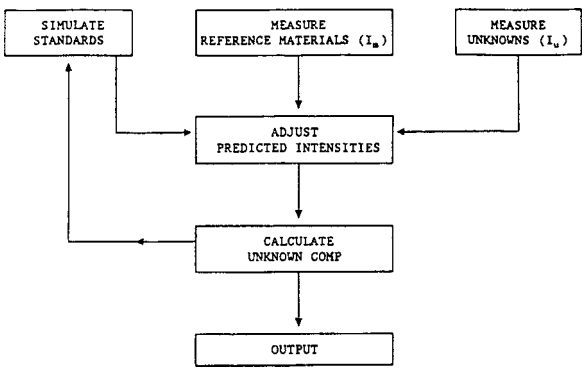



**FIG. 2 NRLXRF Correction Scheme**

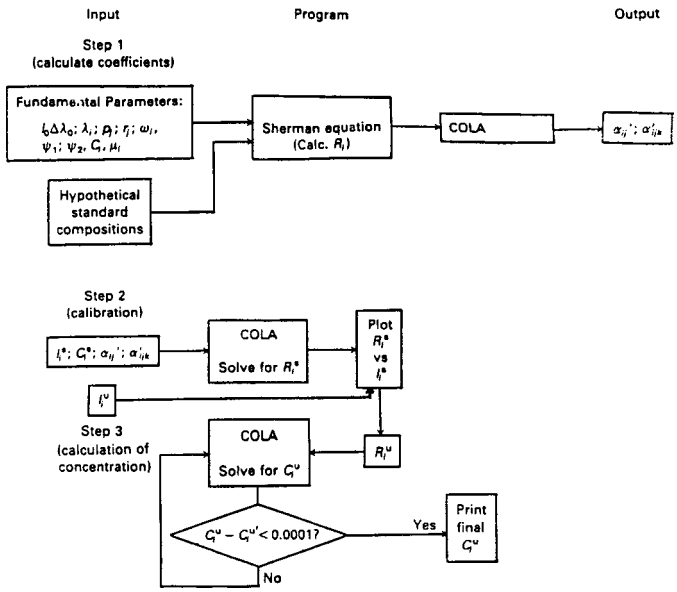



**FIG. 3 Schematic Diagram of the NBSGSC Program**

selected regions (wavelengths) of an X-ray tube spectrum which are most effective in exciting a particular analyte X-ray line **(37),** hence, the term equivalent or effective wavelength, $\lambda_e$. Since, in a multi-component specimen, different wavelengths must be selected, corrections based on this approach must employ a sliding scale of wavelengths. For example, in situations where characteristic lines from the X-ray tube target contribute very little to the excitation of the analyte in the specimen, $\lambda_e$ is taken to be equal to two-thirds the energy of the absorption edge value of the excited analyte(s). Such corrections then work essentially like the monochromatic excitation model, but where a different $\lambda_e$ is used for each analyte in place of a single monochromatic wavelength. Although pure element reference materials can be used for analysis of unknown specimens with this model, it is recommended that reference materials similar in composition to the unknown be measured whenever possible for best results.

9.5.2 The main advantage of using this approach, rather than the more rigorous polychromatic integrated tube spectrum approach, was that computer programs such as CORSET **(38)** and QUAN **(39)** were developed to perform rapidly and efficiently in minicomputers (desktop computers) with limited memory. However, advances in computer technology overcame this limitation so that the effective wavelength approach no longer offers any significant advantages in multi-element analysis over the more rigorous methods that employ an integrated tube spectrum.

9.6 *Monte Carlo Correction Methods*— Gardner and Doster **(40)** developed Monte Carlo computer programs to determine and correct for interelement effects. Although this technique is not widely used in X-ray fluorescence analysis, there appear to be several advantages in using this approach, especially in situations where a wide-angle specimen-source-detector geometry is used, or when specimens lack infinite thickness, or when dealing with heterogeneous (layered) specimens.

## 10. Conclusion

10.1 In principle, although fundamental parameter methods do not require the use of reference materials to correct for interelement effects in specimens, they are, in fact, used in practice as described in Sections 8 and 9. For best accuracy, reference materials of the same type as the specimens should be used in the correction procedure. This will compensate considerably for uncertainties in the fundamental parameters (for example, fluorescence yields, mass absorption coefficients, etc.). Also, differences in specimen volume excited by X-rays as compared to that in the reference material can lead to bias, especially when wavelength-dispersive X-ray spectrometers are used. The use of type standards will eliminate this potential source of error.

10.2 Even though there has been only limited intercomparison of fundamental influence coefficient methods with other fundamental parameters methods in the literature, comparable results can be expected when the same reference materials are used **(17).**

10.3 To obtain satisfactory results when using empirical or semi-empirical correction procedures, appropriate reference materials must be available over the analyte mass fraction range of interest. As the number of different types of materials to be analyzed increases and the elemental composition varies considerably, it becomes less likely that appropriate reference materials will be available. In such situations, fundamental parameters correction methods are more attractive and efficient to use, because these methods are applicable to a wide range of sample types and only a limited number of type reference materials are required for good accuracy. It is also possible to perform analyses when only pure elements or compounds are available, although the results obtained typically are less accurate. With increasing availability of computer programs, fundamental parameters correction procedures became easier to use. Nevertheless, both empirical and fundamental correction procedures have roles to play in quantitative X-ray analysis, and ultimately, the analyst must decide which approach is best suited for the analytical problem at hand.

## 11. Keywords

11.1 fundamental parameters; influence coefficients; interelement effects; X-ray fluorescence

# APPENDIXES

**(Nonmandatory Information)**

## X1. INFLUENCE COEFFICIENTS

X1.1 This section uses graphical methods for obtaining influence coefficients in the Lachance-Traill equation for purposes of illustration only. In practice, these coefficients are calculated using computer programs.

X1.1.1 *Regression Method For Obtaining Influence (Alpha) Coefficients from Reference Materials*—Consider a series of binary alloy reference materials consisting of nickel and iron. Assume nickel is the analyte, *i*, and iron is the matrix element, *j*. For various mass fractions of nickel and iron, the following relative intensities for nickel were obtained on a commercial X-ray spectrometer **(11).**

The Lachance-Traill equation can be applied to the data in Table X1.1 to correct for the X-ray absorption of the nickel $K\text{-}L_{2,3}$ ($K\alpha$) radiation by iron. Accordingly, Eq 1 is as follows:

**TABLE X1.1 XRF Data for Ni and Fe in Binary Fe-Ni Alloys**

| $C_{Ni}$ | $C_{Fe}$ | $R_{Ni}$ |
|---|---|---|
| 0.0329 | 0.9549 | 0.0125 |
| 0.3599 | 0.6315 | 0.1720 |
| 0.4820 | 0.5100 | 0.2553 |
| 0.6552 | 0.3431 | 0.4073 |
| 0.6931 | 0.3067 | 0.4515 |
| 0.7711 | 0.2263 | 0.5483 |
| 0.8964 | 0.1018 | 0.7595 |
| 0.9322 | 0.0659 | 0.8321 |
| 0.9516 | 0.0462 | 0.8782 |

$$C_{Ni} = R_{Ni}\left(1+\alpha_{NiFe}C_{Fe}\right) \quad \text{(X1.1)}$$

and rearranging:

$$\left[\frac{C_{Ni}}{R_{Ni}}\right] - 1 = \alpha_{NiFe}C_{Fe} \quad \text{(X1.2)}$$

A plot of $(C_{Ni}/R_{Ni}) - 1$ versus $C_{Fe}$ will give a straight line the slope of which is $\alpha_{NiFe}$. As shown in Fig. X1.1, the value obtained for $\alpha_{NiFe}$ is 1.71.

X1.1.2 *Solving Simultaneous Equations to Obtain Influence (Alpha) Coefficients:*

X1.1.2.1 For more complex systems, simultaneous equations may be solved to obtain the influence coefficients. This approach is recommended only if the relative intensities are calculated from first principles. The procedure can be illustrated for a simple system as follows: For example, in the Fe-Ni-Cr alloy system the Lachance-Traill correction can be applied in the following form:

$$C_{N\,i} = R_{Ni}\ \left(1+\alpha_{NiCr}C_{Cr}+\alpha_{NiFe}C_{Fe}\right) \quad \text{(X1.3)}$$

where:

$i$ = analyte, Ni, and
$j$ and $k$ = matrix elements, Fe and Cr, respectively.

X1.1.2.2 The data from two reference materials that will be used to illustrate this procedure are given in Table X1.2.

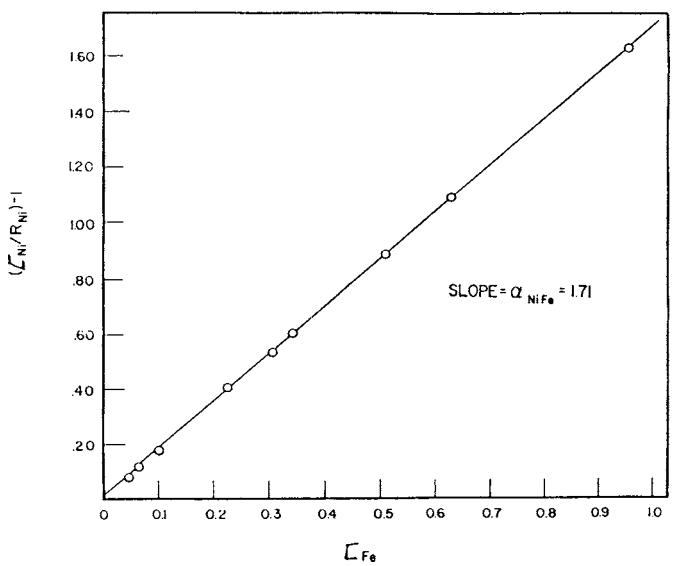



**FIG. X1.1 Determination of the Alpha Coefficient for the Effect of Iron on the Analyte Nickel from Fe-Ni Binary Alloys Using the Lachance-Traill Correction Procedure**

**TABLE X1.2 XRF Data for Example of Simultaneous Equations**

| $C_{Ni}$ | $C_{Cr}$ | $C_{Fe}$ | $(C_{Ni}/R_{Ni}) - 1$ |
|---|---|---|---|
| 0.0498 | 0.2525 | 0.6838 | 1.4532 |
| 0.6429 | 0.1688 | 0.1501 | 0.4722 |

Writing two simultaneous equations following the form of Eq X1.2, $\alpha_{NiCr}$ and $\alpha_{NiFe}$ can be obtained as follows:

$$1.4532 = 0.2525\alpha_{NiCr}+0.6838\alpha_{NiFe} \quad \text{(X1.4)}$$

$$0.4722 = 0.1688\alpha_{NiCr}+0.1501\alpha_{NiFe} \quad \text{(X1.5)}$$

Eliminating the $\alpha_{NiCr}$ term by multiplying Eq X1.4 by $\frac{0.2525}{0.1688} = 1.4959$ and subtracting it from Eq X1.3 gives $\alpha_{NiFe}$ as follows:

$$1.4532 = 0.2525\alpha_{NiCr}+0.6838\alpha_{NiFe} \quad \text{(X1.6)}$$

$$0.7063 = 0.2525\alpha_{NiCr}+0.2245\alpha_{NiFe}$$

$$0.7468 = 0.4593\alpha_{NiFe}$$

$$\alpha_{NiFe} = 1.63$$

Substitution of $\alpha_{NiFe} = 1.63$ in Eq X1.4 and solving for $\alpha_{NiCr}$ yields $\alpha_{NiCr} = 1.34$.

X1.1.2.3 Note that the values of $\alpha_{NiFe}$ obtained in X1.1.1 and X1.1.2 differ. This difference is due primarily to the use of fewer reference materials in the X1.1.2.2 example. It is not uncommon, however, to see relative differences in alpha coefficients on the order of 5 % to 10 % in the literature.

X1.1.3 *Determination of $\alpha_{ij}^{LT}$ from First Principles*—If the excitation source is monochromatic and enhancement effects are absent (that is, absorption only), $\alpha_{ij}$ can be calculated from first principles yielding a simple expression involving mass absorption coefficients and is:

$$\alpha_{ij}^{LT} = \mu_j(\lambda_o)+A\cdot\mu_j(\lambda_i) - 1 \quad \text{(X1.7)}$$

where:

$\lambda_o$ = monochromatic wavelength of the source,
$\lambda_i$ = wavelength of the characteristic line for analyte $i$,
$\mu_j(\lambda_o)$ = mass absorption coefficient of matrix element $j$ for wavelength $\lambda_o$,
$\mu_i(\lambda_o)$ = mass absorption coefficient of analyte element i for wavelength $\lambda_o$,
$\mu_j(\lambda_i)$ = mass absorption coefficient of matrix element $j$ for wavelength $\lambda_i$,
$\mu_i(\lambda_i)$ = mass absorption coefficient of analyte element $i$ for wavelength $\lambda_i$, and
$A$ = geometric constant that includes the incident and takeoff angles of the particular spectrometer used (see 8.2).

NOTE X1.1—Even when the excitation source is *not* monochromatic (for example, X-ray tube), it is often useful to approximate the spectral output distribution of the X-ray source by a single wavelength for each analyte in the specimen to allow simple calculation of $\alpha_{ij}$. This concept of a single wavelength most efficient for exciting a particular analyte in the specimen is referred to as an equivalent or effective wavelength and is discussed in Ref (**37**) and 9.5. For multicomponent specimens irradiated by polychromatic X-rays, influence coefficients can be obtained from first principles using relative intensities calculated from Eq 21.

## X2. CALCULATION OF THE UNKNOWN SPECIMEN COMPOSITION WHEN THE INFLUENCE (ALPHA) COEFFICIENTS ARE KNOWN

X2.1 Considering a ternary system composed of elements *i, j* , and *k*, three simultaneous equations can be solved for the respective mass fractions as follows:

$$C_i = R_i\left(1+\alpha_{ij}C_j+\alpha_{ik}C_k\right) \quad \text{(X2.1)}$$

$$C_j = R_j\left(1+\alpha_{ji}C_i+\alpha_{jk}C_k\right) \quad \text{(X2.2)}$$

$$C_k = R_k\left(1+\alpha_{ki}C_i+\alpha_{kj}C_j\right) \quad \text{(X2.3)}$$

These linear equations can be solved for the unknown mass fractions when the alpha coefficients have been previously determined from reference materials or calculated from fundamental parameters expressions. Sets of linear equations can be solved by: (*1*) elimination, (*2*) determinants, (*3*) matrix inversion, or (*4*) iteration. Iteration is a more common approach and involves making successively closer estimates of each mass fraction.

X2.2 The iterative procedure can be illustrated for the Fe-Ni-Cr alloy system using the following data:

| $R_{Ni}$ | $\alpha_{NiFe}$ | $\alpha_{NiCr}$ |
|---|---|---|
| 0.0549 | 1.21 | 0.80 |
| $R_{Fe}$ | $\alpha_{FeCr}$ | $\alpha_{FeNi}$ |
| 0.4699 | 1.46 | −0.459 |
| $R_{Cr}$ | $\alpha_{CrFe}$ | $\alpha_{CrNi}$ |
| 0.3391 | −0.352 | −0.370 |

X2.2.1 For the first iteration, the *C*'s inside the brackets can be equated to the *R*'s. The calculated *C*'s are then used in the next iteration to calculate a different set of *C*'s. The procedure can be repeated indefinitely; but generally, when a comparison of results indicates no appreciable change from those of the preceding iteration, convergence has been met, and the results from the last iteration may be considered the final mass fractions. These calculations can be performed by a computer utilizing, for example, the "DO LOOP" in Fortran language. The computer program may be written so that when succeeding iterations produce results that do not differ by more than 0.001 in the mass fraction, the results are printed out as final values. For example:

X2.2.1.1 *First Iteration:*

$$C_{Fe} = 0.4699\left[1+0.0549(-0.459)+0.3391(1.46)\right] = 0.6907 \quad \text{(X2.4)}$$

$$C_{Ni} = 0.0549\left[1+0.4699(1.21)+0.3391(0.80)\right] = 0.1010$$

$$C_{Cr} = 0.3391\left[1+0.4699(-0.352)+0.0549(-0.370)\right] = 0.2761$$

X2.2.1.2 *Second Iteration:*

$$C_{Fe} = 0.4699\left[1+0.1010(-0.459)+0.2761(1.46)\right] = 0.6381 \quad \text{(X2.5)}$$

$$C_{Ni} = 0.0549\left[1+0.6907(1.21)+0.2761(0.80)\right] = 0.1132$$

$$C_{Cr} = 0.3391\left[1+0.6907(-0.352)+0.1010(-.370)\right] = 0.2439$$

X2.2.1.3 *Third Iteration gives:* $C_{Fe} = 0.6133$, $C_{Ni} = 0.1081$, $C_{Cr} = 0.2488$, and

X2.2.1.4 *Fourth Iteration gives:* $C_{Fe} = 0.6178$, $C_{Ni} = 0.1067$, $C_{Cr} = 0.2523$, etc.

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