



Standard Guide for Correction of Inter-element Effects in X-Ray Spectrometric Analysis¹

This standard is issued under the fixed designation E1361; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{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*:

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.

Current edition approved Nov. 15, 2014. Published April 2015. Originally approved in 1990. Last previous edition approved in 2007 as E1361 – 02 (2007). DOI: 10.1520/E1361-02R14E01.

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.

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

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.

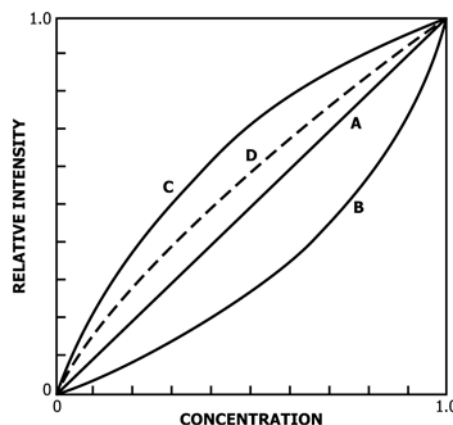
4. Significance and Use

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



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

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_{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 $K-L_{2,3}$ (K_{α}) X-rays by nickel $K-L_{2,3}$ (K_{α}) X-rays in Fe-Ni binaries.

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.

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:

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

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
- 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:

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

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 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:

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

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 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-Trail 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:

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

where:

C_i = the analyte mass fraction in the fused specimen,

C_f = the mass fraction of the flux (for example, $\text{Li}_2\text{B}_4\text{O}_7$),

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, 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, α_{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-Trail equation is calculated from first principles as a function of mass fraction assuming absorption only, it can be shown that α_{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, α_{FeMg}), the influence coefficient is nearly constant whereas, for others (for example, α_{FeCo}), the influence coefficient exhibits a wide variation and even changes sign. In practice, this variation in α_{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

C_{Fe}	$\alpha_{\text{Fe}j}$															
	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	−0.25	−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.