Chapter Nine

Correction Models For Quantitative Analysis

9. Introduction

Raymond Castaing not only designed and built the first electron probe microanalyzer for his Ph.D. Dissertation (1951) at the University of Paris, but also laid much of the groundwork for quantitative chemical microanalysis. Although Castaing initially thought that the intensity of x-ray photons detected by the instrument should be simply and directly proportional to the concentration of the element in the sample producing the photons, he quickly discovered that the details of x-ray production, absorption and enhancement within the specimen are exceedingly complicated. Indeed, after almost 45 years of research, there is no universally accepted approach to calculating the concentration of an element from the x-ray intensities obtained on an "unknown" relative to a "standard" of known composition. In this chapter, we hope to introduce you to the most widely used correction procedures, and give you an appreciation for what is going on in the computer between the time the x-rays are collected and the “analysis” is printed.

The simple idea that the intensity of x-ray photons detected with energy and wavelength characteristic of element "i" in a sample of unknown composition can be compared with the intensity of the same x-rays in a standard of known composition, and thereby be used to determine the concentration of the element in the unknown material, is often referred to as Castaing's First Approximation. In its simplest form, the first approximation can be written as:

\[
\frac{C_i^u}{C_i^s} = \frac{I_i^u}{I_i^s}
\]

where \( C \) refers to concentration as weight fraction (or percent), \( I \) represents the intensity of x-ray photons collected, and \( s \) and \( u \) refer to standard and unknown respectively. Historically, the term on the right-hand-side of this equation (the ratio of x-ray intensities) defines what is known as the \textit{K-ratio or more precisely the “raw” k-ratio}. 

Sometimes this “raw” k-ratio is defined slightly differently when the standard is not a pure element, so that,
CHAPTER NINE
CORRECTION MODELS FOR QUANTITATIVE ANALYSIS

\[ K - \text{ratio} = \frac{\left( \frac{I_i^u}{I_i^s} \right) * C_i^s}{C_i^u} \]

eq. 9-2

But this is not often seen today, and therefore we assume that the “raw” k-ratio is simply the unknown intensity divided by the standard intensity. Where both intensities have been corrected for all instrument effects such as background, dead-time, beam drift, interferences and normalized to count time (usually counts per second).

9.1. The ZAF Correction Factor Approach

We can begin our discussion by recognizing that the production of x-rays is indeed proportional to the number of analyte atoms per unit volume within the specimen. If we let \( n \) be the number of characteristic analyte photons generated in the specimen per average primary electron, and \( x \) be a measure of the path length of the average electron traveling through the specimen, we can write the following proportionality:

\[
\frac{dn}{dx} \propto C \rho \left( \frac{N}{A} \right); \quad \text{grams of analyte} \cdot \text{grams of specimen} \cdot \text{grams of specimen} \cdot \text{no. of atoms of analyte}
\]

eq. 9-3

In this equation, \( C \) is the concentration of the analyte element, \( \rho \) is the density of the specimen, \( N \) is Avogadro's number and \( A \) is the atomic weight of the analyte element. The term on the right-hand-side of this equation is the number of analyte atoms per unit volume. It is important to realize that the concentration term in the first approximation, and in any "final" quantitative analysis, is based on the mass fraction concentration rather than on an atom fraction. In addition to equation (9-3), we learned earlier that the volume of specimen in which primary-beam electrons have energy in the range \( E_c \) to \( E_o \), is inversely proportional to the density of the specimen. Recognizing the role of density in determining the interaction volume, and accepting the proportionality presented in (9-3) it follows that the number of ionizable atoms is directly proportional to the mass fraction of that atom in the specimen.

Furthermore, it is also true that most of the matrix corrections (soon to be described) that are applied to intensities measured in a compound unknown (more than one element present) are properly formulated in terms of mass fractions. For example the average mass absorption coefficient is properly based on mass fraction summations of the pure element mass absorption coefficients because the mass absorption coefficients are mass normalized. The same can be said for average stopping power calculations, though this is not true for average backscatter loss factors which are not mass dependent, but rather atomic number dependent (Donovan, et. al., 2003).
The proportionality constant needed to turn equation (9-3) into an equation is a measure of the probability that once an electron encounters an analyte atom, the interaction will result in inner-shell ionization and the generation of a characteristic x-ray photon. The probability of a K-shell ionization is called the **K-shell ionization cross section**. It has the dimensions of area and is denoted by the symbol \( Q \). Recall that it is not sufficient just to produce an inner-shell ionization; the x-ray photon must escape from the atom, and its probability of doing so is called the **fluorescent yield**, \( \omega \). The product \( Q\omega \), therefore defines the probability that a primary-beam electron will actually produce an x-ray photon. Understanding these probabilities, we can now express (9-3) as an equation.

\[
\frac{dn}{dx} = C \bigg( \frac{N}{A} \bigg) Q \quad \text{or} \quad dn = C \bigg( \frac{N}{A} \bigg) \omega Q \, d(\rho x)
\]

eq. 9-4

The term \( d(\rho x) \) refers to an infinitesimal of the density normalized path length. \( Q \) has been empirically determined and is only a function of \( E \) and is not affected by the matrix composition of the specimen. \( \omega \), the fluorescent yield is a property of the analyte element, and is also not affected by the composition of the specimen.

With reference to Castaing's first approximation (9-1), we see our first evidence that if the standard and unknown have different compositions, the direct proportionality between x-ray intensity and composition might not hold true.

Equation (9-4) can be more appropriately written in terms of the energy of a primary-beam electron as it travels along a density-normalized path length.

\[
dn = \left( \frac{C \bigg( \frac{N}{A} \bigg) \omega Q}{\frac{dE}{d(\rho x)}} \right) \, dE
\]

eq. 9-5

Written in this manner, the number of photons generated is related to the energy loss of the primary electrons (dE) rather than path length. The expression in the denominator of the right-hand-side of equation (9-5) is called the **stopping power** of the specimen, and is denoted by the symbol \( S \).

\[
S \equiv \frac{-dE}{d(\rho x)}
\]

eq. 9-6

The stopping power is a measure of the rate of electron energy loss per unit of density normalized path length through the specimen. The stopping power for the hydrogen atom was first determined theoretically by Bethe in 1930. Since then, stopping power has been empirically determined by a number of experimental physicists. For a single element target it is commonly expressed in terms of \( Z \), \( A \), \( E_c \) and \( E_0 \) for that element. The important concept to
realize is that if we are interested in collecting x-rays produced by a particular element in either a standard or an unknown, the "stopping power" of interest is that of the entire specimen. In other words in order to calculate S we must first know the composition of specimen. If the composition of the specimen is known, or has been calculated, the stopping power is given by:

\[ S_j = \sum_j C_j \cdot S_{j(i)} \]

\[ \text{eq. 9-7} \]

In this, and all equations to follow in this chapter, \( C \) refers to mass fraction, \( i \) refers to the analyte element, \( j \) refers to all other elements present in the specimen and \( j(i) \) means all elements including \( i \). The summation is taken over all elements in the specimen.

The following eq. 9-8 is the commonly used equation for the total stopping power as derived by Berger and Seltzer (1964 -- what a combination of names!).

\[ S_{j(i)} = \frac{Z_j}{A_j} \ln \left[ \frac{0.583(E_{ej} + E_{ej})}{9.76(Z_j) + 58.8(Z_j^{0.19})} \right] \]

\[ \text{eq. 9-8} \]

The important point to note here is that because \( S \) is dependent on the composition of the material, including the analyte element, the generation of analyte x-rays depends not only on \( C_i \), but also on the other elements \( (j) \) in the specimen. Therefore, the simple first approximation (eq. 9-1) can strictly only hold if the unknown and standard have identical compositions. Since this scenario is nearly always impossible, a correction must be made to account for the different stopping powers in the standard and unknown. In other words, Castaing's first approximation must be modified to include the stopping power effects in both standard and unknown:

\[ \frac{I_u^i}{I_s^i} = \frac{C_u^i}{C_s^i} \cdot \frac{S_s^i}{S_u^i} \]

\[ \text{eq. 9-9} \]

In addition to differences in stopping power, a standard with a different mean atomic number (\( Z \)) may differ from an unknown in the production of backscattered electrons. Earlier in this course we developed the theory of BSE generation and many of you have subsequently utilized the intensity of the BSE signal to image phases of different atomic number. Although the generation of BSEs is clearly useful for imaging purposes, it is in fact detrimental to quantitative x-ray analysis because when high-energy electrons escape from the specimen, they no longer have the potential to generate characteristic x-rays. The higher the mean atomic number of the specimen, the more BSEs are generated, and this means that fewer high-energy electrons are available to produce x-rays. In terms of quantitative analysis, this means that if the standard and the unknown differ in mean atomic number (\( Z \)), the intensity of x-rays
generated will be affected by the backscattering process. We define the backscattering coefficient \( R \) as:

\[
R \equiv \frac{I \text{ (actually generated in specimen)}}{I \text{ (would be generated if no backscattering occurred)}}
\]

eq. 9-10

With this definition the backscatter coefficient, \( R \) denotes the fraction of the total "potential" intensity that is actually generated. Turning the equation around, \((1-R)\) defines the fraction of the potential intensity that is lost due to backscattering.

Notice that the intensity in the denominator of equation (9-10) is what we have been considering so far (i.e., eq. 9-9). Recognizing that standard and unknown may have different backscattering coefficients, we must further modify equation (9-9) as follows):

\[
\frac{I_u^i}{I_i^i} \cdot \frac{R_s^i}{R_i^i} = \frac{C_u^i}{C_i^i} \cdot \frac{S_s^i}{S_i^i}
\]

eq. 9-11

By placing the "R-ratio" on the left-hand-side of the equation, we can now treat the intensities as those actually generated within the specimen.

The "stopping power" and "backscatter" corrections deal with the fundamental generation of primary characteristic x-ray photons by the analyte elements present in both the unknown specimen and the reference standard. They are both function of the mean atomic number of the target. They can be thought of as correction factors for the \( Z \) effect.

Note that although it is traditional to calculate the average backscatter loss in a compound specimen based on the mass fractions of the elements present, because backscatter is actually a function of \( Z \) (and weakly of beam energy), a rigorous calculation of backscatter loss requires a calculation based on "\( Z \)" fraction, plus a correction for screening of the nuclear charge by inner orbital electrons in higher \( Z \) atoms. See Donovan, et. al., 2003. This discrepancy is only significant in cases where the atomic number correction is very large, for example the analysis of Si in PbSiO₃ or ThSiO₄ using SiO₂ as a primary standard.

In chapter 3 we learned that x-rays, once generated within the specimen might be absorbed as they travel through the specimen. Therefore, the x-ray intensity we actually measure may not be that actually produced by inner-shell ionization. In addition to the atomic number effects, we also must correct for x-ray absorption. This correction is known as the \( A \) factor.
X-rays produced by other elements within the specimen may have energies sufficiently high to cause secondary fluorescence of analyte atoms. This effect will obviously serve to increase the intensity we measure above that predicted by the first approximation. We must therefore also apply a correction for the fluorescence taking place within the specimen. This correction factor is known as the \( F \) factor.

The ZAF correction factor approach was designed to consider all of the above failings of the first approximation sequentially and to calculate correction factors for two specimens so that when the measured intensities are multiplied by these factors, the resulting "corrected intensities" are truly proportional to concentration. The correction factors for stopping power (S) and backscattering (R) are dependent mainly on the mean atomic number and are often lumped together into a "Z" factor. The absorption and fluorescence factors are denoted by "A" and "F" respectively. These conceptual corrections can be applied to the first approximation to yield the following:

\[
\begin{align*}
\frac{I_i^u}{I_i^s} \cdot \frac{Z_i^u}{Z_i^s} \cdot \frac{A_i^u}{A_i^s} \cdot \frac{F_i^u}{F_i^s} &= \frac{C_i^u}{C_i^s} \\
\end{align*}
\]

eq. 9-12

Over the years, numerous equations have been presented for each of the "factors" in the ZAF approach. In all cases, these equations are simply fits to empirical data, and one always worries about extrapolating such equations outside the system for which they were determined. One also has to worry about which of the numerous equations for each factor is truly the "best". The following table summarizes the most widely used equations for the correction factors.

### Summary of Formulae for ZAF Correction Factors

**I. Stopping Power**

\[
S_i = \sum_j C_j S_j(i)
\]

\[
S_j(i) = \frac{Z_j}{A_j} \ln \left[ \frac{0.583(E_{c,i} + E_0)}{9.76(Z_j) + 58.8(Z_j^{-0.19})} \right]
\]

Berger and Seltzer (1964)

**II. Backscattering Factor**

\[
R_i = \sum_j C_j R_j(i) \quad - \text{note approximation of average backscatter loss using mass fraction averaging}
\]
R_j(i) = R_1 - R_2 \ln [ R_3 Z_j + 25] \quad \text{Yakowitz (1975)}

R_1 = 8.73 \times 10^{-3} U_{0,i}^3 - 0.1669 U_{0,i}^2 + 0.9662 U_{0,i} + 0.4523

R_2 = 2.703 \times 10^{-3} U_{0,i}^3 - 5.182 \times 10^{-2} U_{0,i}^2 + 0.302 U_{0,i} - 0.1836

R_3 = (0.887 U_{0,i}^3 - 3.44 U_{0,i}^2 + 9.33 U_{0,i} - 6.43)/U_{0,i}^3

(R values are polynomial fits in terms of "overvoltage", U_{0,i}.)

III. Absorption Factor

f(\chi) = [1 + 3 \times 10^{-6} (E_{0,0}^{1.65} - E_{c,i}^{1.65}) \chi + 4.5 \times 10^{-13} (E_{0,0}^{1.65} - E_{c,i}^{1.65})^2 \chi^2]^{-1}

\chi = (\mu/\rho)_{i \cdot \text{specimen}} \cdot \cosec \Psi \quad \text{Heinrich, Yakowitz and Vieth (1972)}

(\mu/\rho)_{i \cdot \text{specimen}} = \sum_j C_j (\mu/\rho)_{i-j}

IV. Fluorescence Factor

\Omega_i = \sum_j \Omega_{j-i}

\Omega_{j-i} = 0.5 C_j \frac{(\mu/\rho)_{j-i}}{(\mu/\rho)_{j \cdot \text{spec}}} \frac{(r_i - 1)}{r_i} \omega_j \frac{A_i}{A_j} \frac{(U_{0,j} - 1)^{1.67}}{(U_{0,i} - 1)^{1.67}} \left[ g(u) + g(v) \right] \Lambda_{j-i}

(\mu/\rho)_{j \cdot \text{specimen}} = \sum_j C_j (\mu/\rho)_{j-j} \quad \text{Reed (1965)}

g(u) = \ln(1 + u)/u; \quad u = \cosec \Psi \left[ (\mu/\rho)_{i \cdot \text{specimen}} / (\mu/\rho)_{j \cdot \text{specimen}} \right]

g(v) = \ln(1 + v)/v; \quad v = 4.5 \times 10^5 / [E_{0,0}^{1.65} \times (\mu/\rho)_{j \cdot \text{specimen}}]

U_{0,i} = E_0/E_{c,i} \text{ for } E_0/E_{c,i} \leq 10; \text{ if } E_0/E_{c,i} > 10, \text{ set } U_{0,i} = 10; \text{ all terms in keV.}

Note that each of the four correction factors is composition-dependent, and hence evaluation of a factor for a given specimen (standard or unknown) requires a summation of the factors for each element in the specimen multiplied by the weight fraction of that element. For a standard this means that even if only a single element in that standard is used in an analysis, the full composition of the standard must be used to calculate the Z, A and F factors for the analyte element. The consequences for unknowns are even more severe. Note that in order to
calculate the correction factors for an unknown, a composition must be used. This means that the procedure must be iterative. In practice, software begins with a "first approximation" composition as calculated from equation (9-1). This first approximation composition is then used to calculate the correction factors. By repeating the entire process until a desired degree of convergence occurs, the final composition is refined. In practice, two to four iterations generally are sufficient. The closer the standard is the unknown, the fewer iterations needed, although modern computers are fast enough so that this is not generally a consideration.

More important, is the accuracy of the correction factors. Once again, they are all largely fits to experimental data, and may in fact not be generally valid for all compositional ranges or combinations of elements. Recognizing not only that the correction factors are not perfect, but the magnitude of correcting the first approximation can be as large as 500%, it makes some sense to minimize the influence of the correction factors by making the ratios of correction factors in the unknown and the standard as close to unity as possible. For example, the difference between two ZAF corrections as determined for apatite and silicate suggest we shouldn’t use fluorine in apatite as a standard for fluorine in mica (even assuming that the differences in peak shape and shift are not significant). Once again, this is strong justification for selecting standards as close as possible to the unknowns.

However, this needs to be balanced against the fact that it is almost impossible to “know” the actual composition (accuracy) of compound standards. Metallic elements and simple oxide are generally pure enough that a composition of 99.99% or so can be assigned with some confidence. But a standard such as a glass for complicated material not constrained by stoichiometric considerations, requires special treatment.

So it boils down to what do you trust more: the compound standard composition (that may be close to your unknown composition) or the matrix correction procedures that you will have to rely on if extrapolating from a pure metal or oxide standard?

The PAP Approach

A major shortcoming of the ZAF approach is related to the absorption correction factor. As noted above, several versions of this factor have been presented over the years (e.g., Duncomb and Shields, 1964; Heinrich, 1969). The different versions are simply empirical fits to different sets of measured absorption data. They are all based on an absorption equation developed by J. Philibert in 1963.

The fundamental principles involved with any absorption equation

Figure 9-1  Illustration of absorption of x-rays generated at some depth within the specimen
can be understood by assuming the production of x-rays from any finite depth within the interaction volume and then examining the absorption of those x-rays as they travel along a path to the surface defined by the take-off angle. As the beam electrons are scattered within the specimen and have their energies reduced from $E_0$ to $E_c$, they generate a certain number of x-ray photons at each depth level in the specimen (i.e., at depth $z$ below the surface there is a certain intensity of radiation, $\partial I$, that is produced). Adsorption is proportional to the path length the x-rays must traverse to get out of the sample. There are two important parameters illustrated in Figure 9-1: one is the absorption along the density-normalized path length ($\rho Z$ cosec $\psi$), and the other is the variation of $\partial I$ with respect to depth within the specimen. The function $\phi(\rho Z)$ is used to describe the latter parameter.

The function $\phi(\rho Z)$ is defined as:

$$\phi(\rho Z) = \frac{dI}{d(\rho Z)}$$

eq. 9-13

Nowadays, the function $\phi(\rho Z)$ can be calculated by combining Monte Carlo simulations of electron paths (c.f., Chapter 2) with equations predicting the generation of x-rays (c.f., eq. 9-5). The form of $\phi(\rho Z)$ as a function of depth within a specimen is illustrated in Figure 9-2. The initial increase in x-ray generation below the surface is due to electron scattering, which effectively increases the path length of electrons within layer $d(\rho Z)$. As density-normalized depth increases, the production of x-rays decreases.

Figure 9-2 Schematic illustration of the function $\Phi(\rho Z)$ vs. depth.
For any finite depth interval \((\rho Z + \phi(\rho Z))\)

\[
\delta I = \int \frac{[(\rho \xi) + \delta(\rho \xi)]}{(\rho \xi)} \phi(\rho \xi) + d(\rho \xi)
\]

\[\text{eq. 9-14}\]

The total intensity generated is given by the integral

\[
I_{\text{generated}} = \int_0^\infty \phi(\rho \xi) + d(\rho \xi)
\]

\[\text{eq. 9-15}\]

But the intensity generated at each depth is subject to absorption according to Beer's law such that,

\[
\frac{dI_{\text{emergent}}}{dI_{\text{generated}}} = \exp \left\{ -\frac{\mu(\rho)}{\rho \xi} \phi(\rho \xi) \right\}
\]

\[\text{eq. 9-16}\]

and

\[
dI_{\text{emergent}} = \phi(\rho \xi) \exp \left\{ -\frac{\mu(\rho)}{\rho \xi} \phi(\rho \xi) \right\} d(\rho \xi)
\]

\[\text{eq. 9-17}\]

Finally, the ratio of emergent to generated intensities is given by

\[
\frac{I_{\text{emergent}}}{I_{\text{generated}}} = \frac{\int_0^\infty \phi(\rho \xi) \exp \left\{ -\frac{\mu(\rho)}{\rho \xi} \phi(\rho \xi) \right\} d(\rho \xi)}{\int_0^\infty \phi(\rho \xi) d(\rho \xi)} = f(X)
\]

\[\text{eq. 9-18}\]
The function \( f(\chi) \), where \( \chi = \left( \frac{\mu}{\rho} \right) \cdot \text{cosec} \Psi \), is the parameter used in the ZAF "F" factor. In order to evaluate \( f(\chi) \), we need to know the depth distribution of x-ray generation. Prior to 1991, there was no satisfactory theoretical derivation for \( \phi(\rho z) \), and \( f(\chi) \) needed to be experimentally determined. The most commonly used experimental approach to measuring absorption is the so-called "tracer method" in which a thin layer composed of the element of interest is sandwiched between offset layers of the absorbing material.

This cleverly designed experimental technique allows for relatively precise determination of, for example, the absorption of V K\( \alpha \) x-rays by titanium. Drawbacks to this technique are, however, significant. First of all, it only indirectly measures \( \phi(\rho z) \) at point 2 thru 4. More importantly, it only provides absorption data for two elements at a time. For a complete description of absorption of V K\( \alpha \) x-rays, the experiment would have to be repeated for all elements capable of absorbing vanadium x-rays. The matrix of all possible combinations of elements poses a formidable experimental task. For this reason, only a fraction of the many combinations of elements have actually been measured with this technique. The approach has been to measure a relatively few number of element pairs (usually relatively heavy metals) and then extrapolate the data to different compositions.

Figure 9-3 Schematic diagram illustrating the “tracer” method for measuring absorption. The circles are a schematic representation of the interaction volume. Grayed regions represent the area of generation of vanadium x-rays.
In 1991, Jean-Louis Pouchou and Françoise Pichoir (hereafter known as PAP) pointed out the failings of the traditional ZAF approach based on the Philibert model. They noted that especially for low-Z elements, the Philibert model failed to predict recent tracer data and greatly underestimated the $\phi(\rho z)$ distribution. An example provided by PAP is shown in Figure 9-4 which shows the depth distribution of Mg K$\alpha$ x-ray generation in aluminum (i.e., absorption of Mg by Al). The Philibert model clearly does not reproduce the measurements. In contrast, the new model presented by PAP provides an excellent fit.

The simplified Philibert model corresponds to a very crude representation of the depth distribution of x-ray generation $\phi(\rho z)$ by means of a linear combination of two exponentials, i.e.,

$$f(\chi) = [1 + a_1\gamma\chi + a_2\gamma^2\chi^2]^{-1}$$

eq. 9-19

where $a_1$ and $a_2$ are constants and $\gamma = (E_0^{1.65} - E_{c,i}^{1.65})$ (see the equations above for the ZAF "A" factor). The primary goal of the PAP model is to provide a more accurate calculation of x-ray generation within the specimen. The authors accomplish this by developing a better representation for the total intensity generated within the interaction volume:

$$F = \int_0^\infty \phi(\rho z) + d(\rho z)$$

eq. 9-20

The PAP calculation is performed in two steps:

1. Calculation of the area of the distribution, equivalent in principle to that of an atomic number correction.

2. Direct calculation of the generated intensity, based on the distribution $\phi(\rho z)$ defined by its area and by the parameters of form adopted for the mathematical representation.
With the PAP approach, the distinction between separate Z and A factors is lost. In the most simple terms, \( \phi(\rho z) \) is mathematically expressed by means of two parabolic branches, equal in value and slope at a certain depth level. The equations defining the parabolic branches are complicated and need not be reproduced here. The bottom line is that the PAP model appears to be clearly superior in reproducing experimental tracer data, especially for relatively low-Z elements. For example, an uncertainty analysis based on the difference between calculated and measured tracer data results in a standard deviation of approximately 4% for the traditional ZAF approach and 1-2% for the PAP approach.

Once the \( \phi(\rho z) \) distribution has been calculated, the PAP method incorporates the traditional fluorescence factor based on the equations and data provided by Reed (1965). These are the same equations as listed above for the Fluorescence Factor.

Like the ZAF approach, the PAP correction is an iterative model. It relies on the first approximation concentrations for the initial input. Depending on the similarity of the standard and unknown, two to four iterations are usually required to achieve acceptable convergence.

We can summarize the theoretical approach with the following equation:

\[
\begin{pmatrix}
C^u_i \\
C^s_i
\end{pmatrix} = \begin{pmatrix}
I^u_i \\
I^s_i
\end{pmatrix} \begin{pmatrix}
R^u_i \\
R^s_i
\end{pmatrix} \begin{pmatrix}
S^u_i \\
S^s_i
\end{pmatrix} \begin{pmatrix}
f(\chi)^u_i \\
f(\chi)^s_i
\end{pmatrix} \begin{pmatrix}
(\Omega_e + 1)^u_i \\
(\Omega_e + 1)^s_i
\end{pmatrix}
\]

In the traditional ZAF correction procedure, the R and S factors (backscatter and stopping power, respectively) are grouped together as the "Z factor", i.e.,

\[
C = K \cdot Z \cdot A \cdot F
\]

where K refers to the "K-ratio", Z the atomic number factor, A the absorption factor and F the fluorescence factor. In the PAP approach, R, S and \( f(\chi) \) are treated together and calculated as \( \phi(\rho z) \), i.e.,

\[
C = K \cdot \phi(\rho z) \cdot F
\]

The PAP software is now distributed with all Cameca microprobes, and to our knowledge all Cameca users have chosen to base their analyses on this model. Cameca's only current competition (for microprobes) is JEOL, which does not provide the PAP software. Users of the new JEOL "SuperProbe" either use a traditional ZAF package or a modified ZAF that incorporates a \( \phi(\rho z) \)-type of calculation.

On-line computers were first integrated with electron microprobes in 1975. Prior
to that time, all correction procedures (i.e., ZAF corrections) had to be run on a mainframe computer after the analyses were completed. Between 1975 and 1988, microprobes were equipped with an on-line minicomputer, but that generation of computers lacked the memory and speed required to perform a ZAF correction. During that period of time, and continuing today in many labs, the correction of x-ray data was accomplished with a very simple empirical model known as the Bence-Albee approach. Since many important geological papers include microprobe analyses made with the Bence-Albee technique, and some of you may end up in labs in which it is still used, we believe it useful to describe the technique and its limitations.

### 9.2. The Bence-Albee Technique

Equation (9-21) can be simply expressed as

\[ C = K \cdot \alpha \]

where \( C \) is the concentration of the unknown, \( K \) is the K-ratio, and \( \alpha \) is a correction factor. If standard and unknown were exactly of the same composition, \( \alpha \) would equal unity. If, relative to the standard, fluorescence in the unknown dominates, \( \alpha \) would be less than unity, and if absorption in the unknown dominates, \( \alpha \) would be greater than unity.

The actual meaning of alpha can be understood by considering a binary metal alloy composed of elements A and B. Figure 9-5 illustrates the relationship of \( K \) to \( C \) for different values of \( \alpha \). Alpha = 1 corresponds to a linear (1:1) variation of \( K \) with concentration. If fluorescence of element A dominates, the K-ratio will be greater than that predicted by the concentration of A. On the other hand, if absorption of A plays the dominant role, the K-ratio will be less than that predicted by the concentration of A in the binary alloy.

The analytical form of an equation describing curves such as shown in Figure 9-5 is as follows:
The term "\( K^{A}_{AB} \)" is read as "the K-ratio for element A in alloy AB". Notice that the term \( \alpha^{A}_{AB} \) is a constant.\(^{1}\) The problem with this assumption was later realized by others to be inadequate over a range of binary element concentrations. Rivers (unpublished, 1979) wrote a software (PRMAIN) incorporating a two coefficient (linear fit to alpha-factors as a function of binary composition) Bence-Albee correction at UC Berkeley and later, Armstrong published a even more rigorous three coefficient (polynomial fit) to the correction factors (Armstrong, 1988).

If alpha is indeed a constant over all values of \( C^{A} \), then a plot of \( C^{A}/K^{A}_{AB} \) vs \( C^{A} \) should be linear. The correction required for element A in the binary system AB changes from 1 in pure A (\( C^{A} = 1 \)) to a maximum difference from 1 when \( C^{A} = 0 \). The factor \( \alpha^{A}_{AB} \) is defined as \( C^{A}/K^{A}_{AB} \) in the limit where \( C^{A} \to 0 \). \( \alpha^{A}_{AB} \) is a measure of the affect of element B in the mixture of A and B on the x-ray intensity of A. Such plots can be measured experimentally by collecting x-ray intensities from binary alloys and fitting the data to equations of the form 9-22. Alternatively, they could be calculated by running a ZAF program backwards, i.e., knowing the actual composition, calculate what the observed x-ray intensities would be in a binary alloy.

Ziebold and Ogilvie (1964) demonstrated that such empirical correction factors (alphas) determined for x-rays generated in binary metal alloys could indeed be described by such linear expressions. The linear relationship shown in Figure 9-5 is equivalent to:

\[
\frac{(1 - K^{A}_{AB})}{K^{A}_{AB}} = \alpha^{A}_{AB} \frac{(1 - C^{A}_{AB})}{C^{A}_{AB}}
\]

\text{eq. 9-22}

\( \alpha^{A}_{AB} \) is a constant. \( K^{A}_{AB} \) is read as "the K-ratio for element A in alloy AB". Notice that the term \( \alpha^{A}_{AB} \) is a constant.\(^{1}\) The problem with this assumption was later realized by others to be inadequate over a range of binary element concentrations. Rivers (unpublished, 1979) wrote a software (PRMAIN) incorporating a two coefficient (linear fit to alpha-factors as a function of binary composition) Bence-Albee correction at UC Berkeley and later, Armstrong published a even more rigorous three coefficient (polynomial fit) to the correction factors (Armstrong, 1988).

For those of you well versed in petrology, Figure 9-5 and equation 9-22 are identical to those used to define the partitioning of an element between two minerals. A plot of the mole fraction of an element in one mineral along the ordinate and the mole fraction of the same element in another mineral along the abscissa will produce a smooth curve defining a constant \( K_{D} \).
By empirically determining alpha factors in a number of binary metal alloys, Ziebold and Ogilvie were able to make corrections for a number of metal alloy systems. They also extended the approach to multicomponent systems by arguing that the alpha factor for a ternary system, ABC, can be defined as the weighted average of two of the three binary alpha factors. In other words, for the ternary system ABC,

$$\alpha_{ABC} = \left( \frac{\alpha_{AB}^A C_{ABC}^B + \alpha_{AC}^A C_{ABC}^C}{C_{ABC}^B + C_{ABC}^C} \right)$$

eq. 9-24

Bence and Albee (1968) extended the empirical correction factor approach by using binary oxides (e.g., SiO₂, MgO, Al₂O₃, etc.) instead of pure metals. They, along with Albee and Ray (1970) published "measured" alpha factors for 36 elements. The alpha factors were listed in matrix form and could easily be put into a data table in a simple computer algorithm. It turns out that the "empirical" alpha factors were actually measured for only a few oxide pairs. The rest were calculated using a ZAF routine. In essence, they simply combined the Z, A and F factors calculated for binary oxides into a single "alpha factor". In this regard, a shortcoming of the Bence-Albee approach is that the "empirical correction factors" are not independent of the many assumptions, approximations and failings of the ZAF method.

For multiple element minerals, the Bence-Albee method calculated what they called the "beta factor", which is simply the concentration-weighted average of the binary oxide alpha factors, i.e.,

$$\beta_{A,B,C,...,N}^A = \frac{C_{A,B,C,...,N}^A \alpha_{AA}^A + C_{A,B,C,...,N}^A \alpha_{AB}^A + C_{A,B,C,...,N}^C \alpha_{AC}^A + \cdots + C_{A,B,C,...,N}^N \alpha_{AN}^A}{C_{A,B,C,...,N}^A + C_{A,B,C,...,N}^B + \cdots + C_{A,B,C,...,N}^N}$$

eq. 9-25

In this form, the correction factor $\alpha$ is the actual factor used to convert measured intensity ratios to actual concentrations. The concentration of oxide "A" in an unknown is then calculated from the following equation:
The big advantage to the Bence-Albee approach was that the numerical calculations are simple enough to perform on a calculator or crude computer such as existed on most microprobes until a few years ago.

An unfortunate aspect of the original Bence-Albee paper was that they actually suggested that since the alpha factors were based on binary oxide pairs, oxides could be effectively used as standards. This was very appealing because it implied that the only standards a lab needed were pure, homogeneous oxides. For example, Bence and Albee implied (and many individuals believed) that analysis of minor amounts of Ti in pyroxene could accurately be done using pure TiO₂ as the standard. In actual fact, such blind faith in the accuracy of the correction procedure, produced many poor analyses. It is especially suspect for low-Z elements such as fluorine, sodium and magnesium. If you are ever in a situation where you have to use the Bence-Albee method, it is absolutely critical to have standards that are very close to the unknowns you are analyzing.

Back in the "dark ages", one had to know a great deal about the various correction procedures. In some cases, they actually had to be done by hand calculation! Nowadays, with high-speed, on-line computers and extremely sophisticated software, the complicated task of transforming raw x-ray intensities into meaningful analyses is almost transparent to the operator. For example, a complete, 13-element analysis may only require only a few seconds to perform a complete correction. And the accuracy over a wide range of compositions is generally recognized as very good- though there are certain situations that you can still get into trouble.

Although our confidence in state-of-the-art correction procedures justifiably is high, such confidence should not breed complacency on the part of the analyst. At the risk of sounding like a broken record, we remind you that even the most sophisticated correction procedure does not guarantee complete accuracy, and the shortcomings of all corrections, can be minimized by intelligent selection of standards and strict attention to other compositionally dependent corrections such spectral interferences, element volatility and peak shape-shift changes.

Let us conclude these lecture notes, by urging you to use them frequently in your future work with electron-beam instruments. In these notes, we have striven to give you the information required to understand and make the most out of two extremely valuable tools, namely the EMPA and the SEM. We emphasize that these sophisticated and very expensive instruments are only tools for doing scientific research. The scientific importance of the data collected by these instruments is primarily governed by the nature of the scientific problem being addressed. Modern electron-beam instruments have enormous capabilities. Our instruments are clearly "state-of-the-art", however, they rely ultimately on the operator who controls the quality of the data they produce. They also rely on all operators to take good care
of them -- not only to prolong their useful life, but to also insure that they retain their reproducibility and accuracy.

Furthermore, the ultimate quality of any data produced by these instruments requires good judgment and practice by the operator. All aspects -- from sample preparation, coating, instrument-parameter-selection, tuning of x-ray spectrometers, standard selection, focusing and a host of other operator-controlled features ultimately control the quality and the relevance of the data collected. We have provided you with essentials, but it is up to you to utilize this knowledge so as to maximize the quality of your data.