Review

Corrections for matrix effects in X-ray fluorescence analysis—A tutorial

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Abstract

This paper presents the basic concepts of the mathematical correction for matrix effects in X-ray fluorescence analysis. The emphasis is placed on the correction factor for matrix effects and its quantification. This correction factor is calculated using mathematical models proposed by Lachance–Traill, Claisse–Quintin and Rousseau, which can be applied in practice via an efficient calibration procedure. Each variable in these models is clearly identified so that specific numerical values can easily be substituted for calculation. This paper describes and emphasizes the application of the most effective existing models.
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Keywords: Quantitative XRF analysis; Correction for matrix effects; Sherman equation; Fundamental-parameters method; Influence coefficients; Fundamental algorithm; XRF calibration

Contents

1. Introduction

A previous paper [1] summarizes the main conclusions of an exhaustive study of the most popular analytical X-ray fluorescence (XRF) methods published during the last 50 years. Using these conclusions as a base, three optimized methods that cover the complete analytical range (0–100%) have been proposed.

To learn now how to apply these three optimized methods in practice, the author reviews in the first instance the most valid and useful XRF quantitative methods proposed since the last 50 years. These methods are covered from a historical point of view in order to present their contribution to the modern methods currently used. Then their most valid features are extracted for creating new modern fundamental-parameters (FP) methods that correspond to the modern analytical needs of XRF analysts. Thus, this first step will show that all the best features of XRF

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analytical methods published since 1954 are included in the three optimized methods proposed [1].

Then after the historical review, the basic concepts used to calculate the composition of unknown samples are described. They are: the correction of matrix effects and the calibration procedure. In XRF analysis, the calculation of sample compositions is based on the general relationship between the concentration (C_i) of the analyte i and the measured net intensity (I_i), which is simply expressed by

$$C_i = K_i \cdot I_i \cdot M_{is} \qquad (1)$$

where C_i=concentration of analyte i, K_i=calibration constant factor of i, I_i=measured net intensity of i and M_{is}=correction factor for matrix effects of specimen "s" on i.

Thus, in XRF analysis, the concentration of the analyte i can be visualized as being equal to the product of three terms: a calibration constant, the measured net intensity and a factor that corrects for the effects of the matrix composition on the analyte intensity. These effects, mainly *absorption* and *enhancement*, are called the *inter-element matrix effects*, or simply *matrix effects*, and those who need more information on the subject are invited to read the Ref. [1]. Also, bear in mind that the concentration C_i is the *weight fraction* of the element i in the original sample, not in the specimen, and for a given sample we always have:

$$\sum_{n=1}^{N} C_n = C_i + C_j + C_k + \ldots + C_N = 1.0 \text{ or } 100\% \qquad (2)$$

where concentration values can be expressed by a fractional number or in percentage (%), e.g., 0.1234 or 12.34%, which represents exactly the same thing.

Initially, the emphasis is placed on the correction factor M_{is} for matrix effects (absorption and enhancement) and its quantification. In order to gradually introduce the reader to the complex equations for the M_{is} correction factor, the first half of this paper is devoted to the analytical context involving a *monochromatic* excitation source [2]. Thus, only topics related to incident monochromatic sources will be presented. Even if this approach does not correspond to the most common instrumental reality, the correction factor for this context is expressed by mathematical models that are not only simpler and easier to understand, but more straightforward. This easier approach permits the analyst to focus on the essentials of what to know and facilitates the understanding of the subject. The second part of the paper deals with making the necessary adaptations to progress from monochromatic to *polychromatic* excitation sources.

The two most efficient methods for the correction of matrix effects are *influence coefficients* [1] and *fundamental parameters* [3]. Influence coefficients correct for both types of matrix effects: absorption and enhancement. The major part of this paper is devoted to these influence coefficients and their practical utilization. Indeed, their derivation is even extended from monochromatic to polychromatic incident radiation. The concept of the *multi-element influence coefficient* [1] is presented in combination with the modern *fundamental-parameters approach* [3], thus establishing a perfect synergy between the two approaches and giving the analyst a valuable method for

mathematical matrix effect corrections. In addition, *binary* and *empirical influence coefficients* [1] are discussed, and a number of different algorithms making use of such coefficients are presented. This paper also shows that the choice of the different types of influence coefficients is very much dependent on the nature of the specimens being analyzed, on their composition ranges and on the accuracy that the analyst wants to obtain.

Secondly, the emphasis is placed on the calibration factor, K_i, and its quantification. Naturally, the proposed theoretical formalism would be of less interest if it were not easily adaptable to practical analytical situations, being well known that any theory cannot account for all variations in all the instrumental parameters. This can easily be done by using the calibration procedure proposed by Rousseau [4], which allows one to match theoretical values to the experimental data obtained from every spectrometer.

Finally, the paper presents an experimental verification of the three proposed optimized methods. For experimental application examples, the previously published experimental data of Lachance–Willis [5], K. Mauser [6] and Rasberry–Heinrich [7] have been chosen. Since the concentrations of elements present in a specimen are quite difficult to quantify with any certainty, we can simplify the discussion if we assume that for all the methods presented hereafter that specimens are *homogeneous*, have *a flat and polished* surface and an *infinite thickness* with respect to the incident radiation and XRF emissions.

The aim of this paper is to explain how to use a given quantitative XRF method in practice, not to compare the proposed method to other valid ones, e.g. the Monte Carlo approach, which has already been done in a previous publication [27].

2. Historical review of the influence coefficient concept

To begin this review, one has to go as far back as 1954, when Beattie and Brissey [8] proposed their analytical XRF method based on the Sherman equation. This was one of the first methods proposed to have a theoretical basis. Unfortunately, their method contains eight significant approximations, which seriously delayed the development of modern methods in XRF spectrometry. In fact, it was only in 1984, 30 years later, that a new method [9] was proposed where all of these approximations were completely eliminated. It is these eight approximations that gave a bad reputation to the concept of the influence coefficient for the correction of matrix effects. They are:

1. A system of equations where N solutions are possible for the composition of a sample of N elements to be determined (*analyte*).
2. A forced normalization to 100% of the calculated concentrations of a sample.
3. Absorption correction factors are presumed to be constant values for a given concentration range.
4. A unique and effective wavelength is equivalent to the full polychromatic spectrum of the excitation source.
5. Enhancement is equivalent to a negative absorption.
6. Absorption correction factors are binary coefficients depending only on the analyte i and a matrix element j. The rest of the matrix composition is ignored.

7. Absorption correction factors can be calculated empirically from binary samples of known compositions.
8. The total effect of the matrix on the analyte i is equal to the sum of the effects of each element of the matrix, each matrix effect being calculated independently of each other.

A great contribution of Beattie and Brissey [8] is their proposal of the concept of *relative intensity*, which is defined as the ratio of the measured net intensity to the measured net intensity of the pure element. This definition was very useful for the development of future methods.

In 1955, the mathematician Jacob Sherman [10] from the Philadelphia Naval Shipyard (USA) was the first to publish a detailed demonstration of an equation enabling one to calculate theoretical net X-ray intensities emitted by each element from a specimen of known composition when it is irradiated by a poly-chromatic X-ray beam. Unfortunately, this equation has the form

$$I_i = f(C_i, C_j, C_k, \ldots, C_N)$$

which is not reversible for transformation to

$$C_i = f(I_i, I_j, I_k, \ldots, I_N)$$

which is required for the calculation of unknown sample compositions. I_x and C_x are the net intensity and the concentration of the N elements present in the sample, respectively. A factor of 1/2 in the part corresponding to the secondary fluorescent X-ray intensity (enhancement) and a factor of 1/4 in the part corresponding to the tertiary fluorescent X-ray intensity (third-element effect) were forgotten as demonstrated by Shiraiwa and Fujino [11]. Of course, these missing factors have been added to the initial Sherman equation. XRF spectrometry is the only analytical technique enabling one to calculate exactly what we are to measure. As we will see, this unique feature will allow us to develop powerful methods for the calculation of sample compositions.

In 1966, 12 years after Beattie and Brissey, Lachance and Traill [12] proposed a new method where the approximations 1 and 2 were eliminated. However, the six remaining approximations were still present in their method. It is important to note here that it is possible to eliminate the constraint of normalization to 100% when the Sherman equation is correctly used. A great contribution of Lachance and Traill is to have proposed a clear definition of the concept of the influence coefficient, which is a coefficient that quantifies the total matrix effect of an element j on the analyte i in a given specimen. This definition turned out to be very useful for the development of future methods.

In 1967, Claisse and Quintin [13] proposed a new method where the approximations 1 to 4 were not employed. The four remaining approximations are still present in their method. The great contribution of Claisse and Quintin is to have shown that the influence coefficient values vary with the concentration of the analyte i and the effective wavelength is an unnecessary and undesirable approximation. They also introduced the concept of the weighting factor for each wavelength of the excitation source spectrum. With regard to the calculation method of influence coefficients in the Claisse–Quintin algorithm, it has

been successively improved by Rousseau and Claisse [14] in 1974, by Tertian [15] in 1976 and by Rousseau [4] in 1984.

In 1968, in a revolutionary paper, Criss and Birks [16] proposed a new method, called *fundamental parameters* (FP), where all the approximations of Beattie and Brissey are excluded, except for approximation 2. These authors completely discarded the concept of the influence coefficient with all its vague approximations and focused only on the application of the Sherman equation in practice to calculate the composition of unknown samples without any approximation. The problem is that the Sherman equation allows only the calculation of intensities and not concentrations. To overcome this difficulty, the authors initiated the iteration process with measured relative intensities, *normalized to 1.0*, for calculating a first estimate of the sample composition. From this composition, a new set of theoretical intensities is calculated with the Sherman equation. These theoretical intensities are compared to the measured intensities. If the match is not within an allowed maximum error, the complete process is repeated. This iteration process is applied to the Sherman equation up to the point that the calculated intensities match closely the measured intensities. However, in practice, this method suffers from a few serious weaknesses, which are:

1. The condition of having to normalize to 1.0 the measured relative intensities for getting the first estimate of the sample composition may introduce a bias in the final results. It is preferable to use a solution that does not require any normalization for calculating sample compositions as showed by Lachance and Traill [12].
2. The Sherman equation was designed to calculate only theoretical X-ray intensities from the known composition of a sample, not concentrations. This means that we can *directly predict* a set of X-ray intensities, if the sample composition is very well defined and totals to 100%. In that sense, used in this way, the Sherman equation is a *continuous* function and converges *all the time* towards a specific set of calculated intensity values. Unfortunately, the Sherman equation cannot directly predict the composition of a sample that totals to 100% from a set of measured intensities. However, it is possible to use the Sherman equation to indirectly calculate sample compositions by iterations from the measured intensities. In this case, the Sherman equation becomes a *discontinuous* function because the measured intensities do not vary in a continuous way with sample compositions, but by *jumps*. This means that the equation converges with difficulty, or not at all, during the iteration process, if the first estimate of the sample composition is too far from the final and true composition; consequently, one cannot, generally speaking, use the normalized measured relative intensities as a first approximation to calculate by iterations the sample composition. This problem can be overcome by using another analytical method to calculate a first estimate as close as possible to the final composition.
3. The calibration procedure used by Criss and Birks [16], based on the reading of only a single standard similar to the unknowns is not efficient, as it may suffer from lack of

accuracy and therefore most of the time is not appropriate. It is preferable to use a calibration procedure that allows one to use more than a single standard [17]. With this procedure, graphics support for calibration lines is possible, while with Criss and Birks' procedure it is not. This feature is very useful to the XRF analyst for evaluating the quality of the calibration line.

The major contribution of Criss and Birks [16] is to have proposed to use the Sherman equation for the correction of matrix effects each time that the composition of an unknown sample has to be calculated. This approach is equivalent to calculating a new set of multi-element influence coefficients for every sample to be analyzed rather than to keep these coefficients constant for a series of unknown samples. It was a great step forward in the evolution of methods for the correction of matrix effects.

In 1973, Willy de Jongh [18] proposed a new method where *all* approximations of Beattie and Brissey were overcome, except number 3. He assumed that the influence coefficients are constant values calculated from an average composition representative of the samples to be analyzed. This approximation is valid only for a very narrow range of concentrations. Otherwise, de Jongh succeeded to show us that *theoretical* and *multi-element* influence coefficients could be calculated from the Sherman equation and the normalization to 100% is not necessary when the Sherman equation is used correctly. But mainly, he showed us *how to calibrate* by proposing to plot the measured intensities as a function of the calculated intensities (he called it "apparent concentrations"). This was a very important contribution allowing one to adapt theory to the measured data obtained from each spectrometer.

In 1974, Rasberry and Heinrich (RH) [7] proposed a new *empirical* method, which is in complete disagreement with the Sherman equation. However, their method is valid only for the analysis of Cr–Fe–Ni alloys, i.e., specifically for stainless steels. They at least showed us what happens when we do not respect the Sherman equation. They also showed us empirically that the absorption and enhancement are two completely different matrix effects and their mathematical treatment must be done *separately* with two different and independent terms.

In 1981, Lachance [19] proposed a new method, called COLA, still using the concept of the binary influence coefficients. It was the last attempt at using this approximation in practice. It was justified at that time by the fact that no powerful and cheap computers were available for using the FP method. But soon after that, the first IBM-PCs appeared on the market and the FP method became more and more popular to the detriment of the COLA method. However, because of all the difficulties caused by the application of the FP method, its popularity started to decrease only from the early nineties.

In 1984, Rousseau [4,9] proposed the *fundamental algorithm* (FA) where the influence coefficients correcting for absorption and enhancement effects vary with the composition of every sample. This algorithm is totally in agreement with the Sherman equation and ignores completely all the approximations of Beattie and Brissey. With this method, the first estimate of the composition is calculated from the Claisse–Quintin algorithm, where there is no need to normalize the concentrations. This first estimate must be very close to the final composition, i.e., within 0.5% in relative difference. Then, the absorption and enhancement coefficients, the complex part of the Sherman equation that converges with difficulty, are directly calculated, only once, from this first estimation. Finally, the final sample composition, and a more accurate one, is calculated by applying an iteration process to the fundamental algorithm where the influence coefficients are kept constant. The calibration procedure associated with this method is the one proposed by de Jongh [18] in 1973. The whole method converges quickly, all the time, and can advantageously be compared to any other modern method in terms of ease of use and accuracy.

Finally, in 1985, Pella et al. [20] proposed an equation for calculating the intensities of the incident spectrum for every wavelength. It turned out to be the very last tool required allowing the easy application of any FP approach. Before that, the incident spectra had to be measured [21], which is much more complicated and difficult to carry out routinely.

There are few other modern models, which are more recent or subsequent to the fundamental algorithm. In 1983, Broll and Tertian (BT) [22] and, in 1995, Lachance and Claisse (LC) [23] proposed two equivalent algorithms. These two algorithms, as well as the fundamental algorithm, are different versions, algebraically equivalent, of the Sherman equation, where all the approximations of Beattie and Brissey are overcome. However, the BT and LC algorithms do not take into account the mathematical and physical principles proposed by Sherman. Indeed, the Sherman equation, or the fundamental algorithm, has the general form of a hyperbolic equation, whereas the algorithms of Broll–Tertian and Lachance–Claisse have the general form of a straight-line equation [24]. It is observed in practice that a hyperbolic equation converges more easily as compared to a straight-line equation. It is therefore more advantageous to use in practice an equation that has the shape of the fundamental algorithm rather than the other two. The BT and LC algorithms also combine the absorption and enhancement coefficients in a single entity, which are mathematically and physically completely different as demonstrated by Rasberry and Heinrich [7]. Therefore, since the BT and LC algorithms distort the mathematical and physical principles proposed by Sherman, they are invalid models and their use in practice should be discouraged.

At this time, in addition to the fundamental algorithm, there are at least two other FP methods [25,26] that solve the Sherman equation correctly. They use the Sherman equation within "standardless" software packages. Because they are proprietary products, the author does not know the details of their respective concentration calculation procedure, but knows from his tests that they use a valid approach for solving the Sherman equation. One of my favorite tests consists of measuring the *same* multi-element specimen 10 times. If, for a given FP method, the coefficient of variation (ratio of the standard deviation to the arithmetic mean in %) of the 10 calculated concentrations of the major element is of the same order of magnitude as the coefficient of variation of the 10 measured net intensities, then this means that the iteration

process converges always towards the same true concentration value, within the statistical counting error. We can assume in this case that the FP method solves the Sherman equation correctly. From this test, we can conclude that the two other FP methods are valid approaches to the problem of correcting for inter-element matrix effects. They are neither better nor worse than the whole fundamental algorithm method, but simply different and equivalent.

The present paper proposes three analytical methods that take into account all the above conclusions, which makes them extremely competitive with the most modern methods proposed today. For example, for the analysis of fused discs, each influence coefficient a_{ij} calculated in the Lachance–Traill algorithm takes into account the effect of the flux, the oxygen associated with the analyte and the element j on the analyte i, which represent 95% to 99% of the matrix composition. Thus, the a_{ij} coefficients are no longer binary coefficients, which was one of the severe approximations of Beattie and Brissey. The Claisse–Quintin algorithm also takes into account the effect of the whole matrix composition on the analyte i through the C_M factor, and the influence coefficients of the fundamental algorithm are accurately calculated for every sample composition. No true binary coefficients, or Taylor series, or intensity calculations, or normalization, or iterations on the complete Sherman equation are used with these methods, which are the main sources of error.

Being the synthesis of 30 years of research and development [3], the FA incorporates all the actual theoretical knowledge on matrix effect corrections. This powerful algorithm indissolubly unifies the traditional influence coefficient concept [4] and the classical fundamental-parameters method [6] into a single approach, giving the analyst an effective mathematical method for correcting matrix effects. When combined with its innovative calibration procedure [17], comparing measured intensities to calculated intensities, the FA method can be applied to the analysis of any type of sample and offers maximum accuracy in quantitative XRF analysis, limited only by the quality of the sample preparation and the standards used. Consequently, the FA method is still one of the most valid solutions to the Sherman equation, even if it was proposed more than 20 years ago.

Regarding the traditional FP approach, as proposed by Criss and Birks in 1968, the author has tried to demonstrate [27] that an iteration process starting with measured relative intensities is *not* a viable and valid alternative for calculating a first accurate estimate of the sample composition and should be avoided. Criss himself [28] recognized that another analytical method is necessary to convert the measured intensities into concentrations for getting an accurate first estimate of the sample composition. The author's solution to this problem is to use the CQ algorithm for calculating the first estimate of the sample composition and then the fundamental algorithm to calculate the final composition [1]. In addition to using two different algorithms with two different sets of influence coefficients, it uses two different sets of calibration data for calculating the sample composition [27]. This is the price one must pay to obtain results of high accuracy. Certainly, this solution is not the only valid one, but one thing is certain: the traditional FP approach should be superseded by new modern approaches that generate results of high accuracy.

3. Correction for matrix effects in the context of monochromatic excitation sources

In order to gradually introduce the reader to the complex equations for the matrix effect correction factor, M_{is}, this section is devoted to analytical contexts involving a *monochromatic* excitation source [2]. Thus, only topics related to incident monochromatic sources will be presented in this part. Even if this approach does not correspond to the most common instrumental reality, the correction factor for this context is expressed by mathematical models that are not only simpler and easier to understand, but more straightforward. This easier approach permits the analyst to focus on essentials of what to know and facilitates the understanding of the subject. Sections 4 and 5 of this paper deal with making the necessary adaptations to change from monochromatic to *polychromatic* excitation sources.

Fig. 1 is a schematic representation of the processes involved in primary and secondary X-ray fluorescence emission, i.e., the emitted X-ray intensity originates from primary (or direct) and secondary (or indirect) excitations (enhancement). Let us consider a flat, homogeneous, binary specimen containing the two elements i and j. Let us assume that a monochromatic excitation source of wavelength λ_k and intensity I_o strikes the specimen at an angle of ϕ' degrees. The sample composition "absorbs" or reduces the intensity $I_o(\lambda_k)$ before it reaches a given atom i and excites it. The primary fluorescence intensity $I_{iA}(\lambda_i)$ is emitted uniformly in every direction by the atom i and a fraction is emitted towards the crystal. It is also absorbed or reduced by the sample composition before it reaches the surface. This characteristic radiation emerges from the specimen at an angle of ϕ'' degrees. There is also another possible excitation source. If the energy of the intensity $I_j(\lambda_j)$ emitted by the atom j is high enough, or if the wavelength λ_j is shorter than the absorption edge of the analyte i, the same atom i absorbs λ_j and is excited again. The secondary fluorescence intensity $I_{iE}(\lambda_i)$ of atom i may increase $I_{iA}(\lambda_i)$ up to 30%. Thus, the measured intensity $I_i(\lambda_i)$ emitted by the element i is the sum of two components: I_{iA}, which is the *primary X-ray fluorescence emission* produced from direct excitation only, while I_{iE} is an additional characteristic X-ray radiation emitted due to indirect
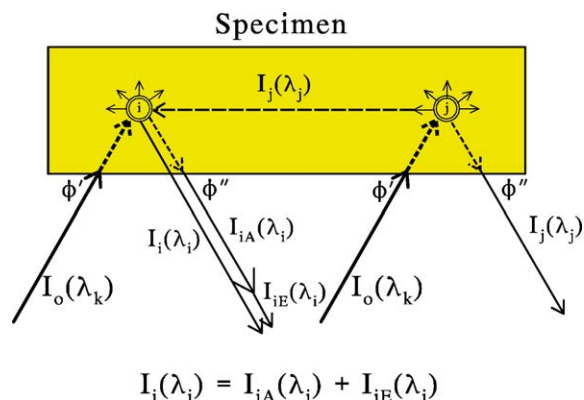

$$I_i(\lambda_i) = I_{iA}(\lambda_i) + I_{iE}(\lambda_i)$$

Fig. 1. Primary excitation of the analyte i and enhancement of 'i' by 'j' in an i–j binary specimen. A practical example would be i=Fe and j=Ni in a Fe–Ni alloy.

excitation, which is referred to as *secondary X-ray fluorescence emission* or *enhancement*. In order to clearly identify both types of excitation, the symbol I_{iA} is used to designate emissions involving *A*bsorption only, while I_{iE} is used to designate emissions due to *E*nhancement. The intensity that is measured experimentally is therefore the sum of each type of emission, i.e.,

$$I_i = I_{iA} + I_{iE} \tag{3}$$

If enhancement is not present, I_i is simply equal to I_{iA}.

From Fig. 1, in 1955, Sherman [10] demonstrated that the emitted X-ray fluorescence intensity originating from direct and secondary excitations, when the excitation source is *monochromatic*, is given by the following equation:

$$I_i(\lambda_i) = g_i C_i \frac{\mu_i(\lambda_k) \cdot I_o(\lambda_k) \cdot \Delta\lambda_k}{\mu_s'(\lambda_k) + \mu_s''(\lambda_i)} \left[1 + \sum_j \delta_{ij} C_j \right] \tag{4}$$

where the proportionality constant g_i is dependent upon the instrument used, the mass absorption coefficients for the specimen, μ_s, are calculated by

$$\mu_s'(\lambda_k) = \sum_{n=1}^{N} \mu_n(\lambda_k) \cdot C_n \cdot \csc\phi' \tag{5}$$

$$\mu_s''(\lambda_i) = \sum_{n=1}^{N} \mu_n(\lambda_i) \cdot C_n \cdot \csc\phi'' \tag{6}$$

where N is the number of elements in the specimen and where the enhancement contribution δ_{ij} for each matrix element j in concentration C_j is calculated from

$$\delta_{ij}(\lambda_k) = \frac{1}{2} D_j(\lambda_k) \cdot D_j(\lambda_k) \cdot k_j \mu_j(\lambda_k) \frac{\mu_i(\lambda_j)}{\mu_i(\lambda_k)} P_{ij}(\lambda_k) \tag{7}$$

$$k_j = \frac{r_j - 1}{r_j} \cdot \omega_j \cdot p_j \tag{8}$$

$$P_{ij}(\lambda_k) = \frac{1}{\mu_s'(\lambda_k)} \ln\left[1 + \frac{\mu_s'(\lambda_k)}{\mu_s(\lambda_j)} \right] + \frac{1}{\mu_s''(\lambda_i)} \ln\left[1 + \frac{\mu_s''(\lambda_i)}{\mu_s(\lambda_j)} \right] \tag{9}$$

and

$D_j(\lambda_k)$	1 if the incident radiation $\lambda_k \leq \lambda_{\text{abs edge}}$ of element j 0 in all other cases
$D_i(\lambda_j)$	1 if the fluorescence radiation $\lambda_j \leq \lambda_{\text{abs edge}}$ of analyte i 0 in all other cases
r_j	Jump ratio of element j for edge of considered line
ω_j	Fluorescence yield for considered line of element j
p_j	Probability that characteristic line λ_j will be emitted

The key point to observe in the above expressions is that the coefficient δ_{ij} depends on the full composition of the specimen and fundamental parameters (μ_s, ω_j and p_j).

To simplify Eq. (4), let us introduce the *effective mass absorption coefficients*, which are defined by

$$\mu_s^* = \mu_s'(\lambda_k) + \mu_s''(\lambda_i) \tag{10}$$

$$\mu_n^* = \mu_n'(\lambda_k) + \mu_n''(\lambda_i) \tag{11}$$

$$\mu_s^* = \sum_{n=1}^{N} \mu_n^* \cdot C_n \tag{12}$$

The word "effective" designates the quantification of the total absorption of specific wavelengths (λ_k and λ_i) by an element or a specimen in a given analytical context. It therefore takes into consideration not only the fact that it is the sum of absorption of the incident and emergent radiations but also their path-lengths in the specimen.

The definition (Eq. (12)) of the effective mass absorption coefficient μ_s^* yields

$$\begin{aligned} u_s^* &= C_i \mu_i^* + C_j \mu_j^* + C_k \mu_k^* + \ldots + C_N \mu_N^* \\ &= \mu_i^* \left[C_i + C_j \frac{\mu_j^*}{\mu_i^*} + C_k \frac{\mu_k^*}{\mu_i^*} + \ldots + C_N \frac{\mu_N^*}{\mu_i^*} \right] \end{aligned}$$

Now, bearing in mind that a given specimen of N elements:

$$\sum_{n=i}^{N} C_n = 1$$

we obtain

$$C_i = 1 - C_j - C_k - \ldots - C_N$$

and

$$\mu_s^* = \mu_i^* \left[1 + C_j \left(\frac{\mu_j^*}{\mu_i^*} - 1 \right) + C_k \left(\frac{\mu_k^*}{\mu_i^*} - 1 \right) + \ldots + C_N \left(\frac{\mu_N^*}{\mu_i^*} - 1 \right) \right].$$

Defining the variable

$$\beta_{ij}(\lambda_k) = \frac{\mu_j^*}{\mu_i^*} - 1 \tag{13}$$

where

$$\mu_i^* = \mu_i(\lambda_k) \cdot \csc\phi' + \mu_i(\lambda_i) \cdot \csc\phi''$$
$$\mu_j^* = \mu_j(\lambda_k) \cdot \csc\phi' + \mu_j(\lambda_i) \cdot \csc\phi''$$

gives

$$\mu_s^* = \mu_i^* \left[1 + \sum_j \beta_{ij} C_j \right] \tag{14}$$

Note that the variable $\beta_{ij}(\lambda_k)$, as we will see later, is defined as the *theoretical binary absorption influence coefficient* in the very special case of a monochromatic excitation source of wavelength λ_k. Furthermore, β_{ij} depends only on elements i and j and is not affected by the rest of the matrix composition. It is the same famous "alpha" coefficient proposed by Lachance and Traill [12] in 1966.

From Eq. (13), the coefficient $\beta_{ij}(\lambda_k)$ is the ratio of the difference between the mass absorption coefficient of element j and i relative to the mass absorption coefficient of element i. In other words, the coefficient $\beta_{ij}(\lambda_k)$ shows, in a relative way, how much greater or smaller the absorption of element j is compared to that of element i for the wavelength λ_k. It thus expresses a *relative* value. The relative absorption of element i compared to itself is therefore equal to zero, i.e., $\beta_{ii}=0$.

The coefficient $\beta_{ij}(\lambda_k)$ corrects for the absorption effects of the matrix element j on the analyte i and can be positive or negative. If Eq. (13) is rewritten in the following form:

$$\beta_{ij}(\lambda_k) = \frac{\mu_j^* - \mu_i^*}{\mu_i^*}$$

it is easier to determine when the influence coefficient $\beta_{ij}(\lambda_k)$ is positive or negative. The values for $\beta_{ij}(\lambda_k)$ depend on the elements i and j. For example, if Fe is determined in the presence of Mg (a lighter matrix element), then $\mu_i^* > \mu_j^*$ and $\beta_{ij}(\lambda_k)$ is negative. If Fe is determined in the presence of Ni (a heavier matrix element), then $\mu_i^* < \mu_j^*$ and $\beta_{ij}(\lambda_k)$ is positive.

In the following paragraphs, we will continue to modify the Sherman's equation to make it easier to understand and manipulate. Defining a second variable:

$$W_i'(\lambda_k) = \frac{\mu_i(\lambda_k)}{\mu_i^*} \cdot I_O(\lambda_k) \cdot \Delta\lambda_k \tag{15}$$

The combination of Eqs. (4), (14) and (15) leads to

$$I_i(\lambda_i) = g_i \cdot C_i \cdot W_i' \cdot \frac{1 + \sum_j \delta_{ij} C_j}{1 + \sum_j \beta_{ij} C_j} \tag{16}$$

This preliminary *modified Sherman equation* is already simpler and more revealing. Indeed, the intensity is still proportional to the concentration C_i but also to a ratio on the right-hand side. The numerator contains all the enhancement coefficients δ_{ij} of each element j, and the denominator all the absorption coefficients β_{ij}. Thus, I_i will *increase* with the enhancement effects and *decrease* with the absorption effects (if β_{ij} is positive). Furthermore, all these matrix effects are weighted by the factor W_i', which takes into account the polychromaticity of the incident spectrum. We will return to this subject later.

Because of the difficulty in determining the experimental constant g_i and for making the measured intensities independent of the instrument, the second important modification is to replace the absolute intensity I_i of element i by the *relative X-ray intensity*, R_i, which is defined as follows:

$$R_i = \frac{I_i(\lambda_i)}{I_{(i)}(\lambda_i)} \tag{17}$$

where $I_{(i)}$ is the intensity emitted by the pure element i. For a specimen composed only of the pure analyte i, $C_i=1$, all $C_j=0$, and the modified Sherman Eq. (16) becomes

$$I_{(i)}(\lambda_i) = g_i \cdot W_i' \tag{18}$$

The combination of Eqs. (16), (17) and (18) leads to

$$R_i = C_i \cdot \frac{1 + \sum_j \delta_{ij} C_j}{1 + \sum_j \beta_{ij} C_j} \tag{19}$$

Eq. (19) is still the same Sherman Eq. (4), except it calculates a relative intensity, R_i, rather than an absolute intensity I_i. Indeed, the intensity R_i is still proportional to the concentration C_i but also to a ratio on the right-hand side. The numerator contains all the enhancement coefficients δ_{ij} of each element j of the matrix, and the denominator contains all the absorption coefficients β_{ij} of each element j. Thus, here again the relative intensity R_i will increase with the enhancement effects and decrease with the absorption effect (if β_{ij} is positive). It is very important to note here that Eq. (19) respects the Sherman equation in every way: algebraically, mathematically and physically.

As analysts are interested in calculating concentrations rather than intensities which are measured, Eq. (19) must be reversed:

$$C_i = R_i \cdot \frac{1 + \sum_j \beta_{ij} C_j}{1 + \sum_j \delta_{ij} C_j} \tag{20}$$

which is the *fundamental algorithm* [3] in the case of monochromatic excitation sources. Eq. (20) is deduced from the Sherman Eq. (4) by algebraic manipulation without any approximation and is thus the same equation expressed in another form, namely that usually used for influence coefficient algorithms. It considers the direct excitation by the monochromatic incident radiation and the indirect (or secondary) excitation (enhancement), calculates influence coefficients for each sample to be analyzed and separately takes into account both matrix effects, *absorption* and *enhancement*. It can thus be considered as an extension of the Sherman equation.

The physical interpretation of the fundamental algorithm is simple and elegant. To a first approximation, Eq. (20) reveals that the concentration of the analyte i is proportional to its measured relative intensity, i.e., $C_i \approx R_i$, which is multiplied by a ratio correcting for all matrix effects. Indeed, the expression (13) of the coefficient β_{ij} contains only mass absorption coefficients (μ_i^* and μ_j^*). Therefore, we can affirm that the β_{ij} coefficient corrects for all absorption effects caused by element j on analyte i and the numerator of Eq. (20) corrects for all absorption effects of the matrix, each element j bringing its contribution to the total correction in a proportion C_j. If the numerator is greater than unity (it could be smaller when the matrix is less absorbent than the analyte), the intensity R_i is increased by a quantity equivalent to that absorbed by the matrix. Briefly then, the β_{ij} coefficient corrects for absorption effects and is defined by Eq. (13).

When some elements of the matrix are able to enhance the intensity of the analyte i, the corresponding coefficients δ_{ij} are different from zero and are essentially positive. In this case, the denominator is greater than unity and the intensity R_i is reduced by a quantity equivalent to that caused by the enhancement. Thus, the δ_{ij} coefficient defined by Eq. (7) corrects for enhancement effects.

Since the numerator of Eq. (20) corrects for all the absorption effects of the matrix on the analyte and the denominator corrects for all the enhancement effects, the form of Eq. (20) makes it

easier to understand the physical principles behind the complex equation of Sherman [10].

4. Application

Quantitative analysis by its very nature involves dealing with samples of *unknown* composition. The following numerical example illustrates how an iteration process may be used with Eq. (20) to calculate concentrations in unknowns when measured relative intensities and influence coefficients are known. For simplicity, the example will relate to a binary Fe–Ni system, the specimen SPLE-1, and for an incident monochromatic radiation of 0.71 Å (Table 1).

(a) Calculation of measured relative intensities R_{Fe} and R_{Ni} using Eq. (17):

$$R_{Fe} = \frac{209.9}{626.2} = 0.3352$$

$$R_{Ni} = \frac{438.4}{952.9} = 0.4601$$

(b) Calculation of the absorption influence coefficients β_{FeNi} and β_{NiFe} by substitution of effective mass absorption coefficients data in Eq. (13) for the incident radiation $\lambda_k = 0.71$ Å:

$$\beta_{FeNi} = \frac{45.81 \times 1.4142 + 89.98 \times 1.4142}{37.74 \times 1.4142 + 71.43 \times 1.4142} - 1 = 0.2438$$

$$\beta_{NiFe} = \frac{37.74 \times 1.4142 + 379.62 \times 1.4142}{45.81 \times 1.4142 + 58.94 \times 1.4142} - 1 = 2.9843$$

(c) Calculation of the enhancement influence coefficient δ_{FeNi} using Eqs. (7), (8) and (9): To calculate the coefficient δ_{FeNi}, an accurate first estimate of the sample composition must be known. We will explain later how to calculate this first estimate. For the moment, let us take the true composition of the sample for calculating the δ_{FeNi} coefficient. We have:

$$
\begin{aligned}
u_{Fe}^* &= \mu_{Fe}(\lambda_k)\mathrm{cosec}\phi' + \mu_{Fe}(\lambda_i)\mathrm{cosec}\phi'' \\
&= 37.74 \times 1.4142 + 71.43 \times 1.4142 \\
&= 154.39
\end{aligned}
$$

$$
\begin{aligned}
\mu_{Ni}^* &= \mu_{Ni}(\lambda_k)\mathrm{cosec}\phi' + \mu_{Ni}(\lambda_i)\mathrm{cosec}\phi'' \\
&= 45.81 \times 1.4142 + 89.98 \times 1.4142 \\
&= 192.03
\end{aligned}
$$

$$
\begin{aligned}
\mu_s^* &= C_{Fe}\mu_{Fe}^* + C_{Ni}\mu_{Ni}^* \\
&= 0.2263 \times 154.39 + 0.7711 \times 192.03 \\
&= 183.00
\end{aligned}
$$

$$
\begin{aligned}
\mu_s'(\lambda_k) &= [C_{Fe}\mu_{Fe}(\lambda_k) + C_{Ni}\mu_{Ni}(\lambda_k)]\mathrm{cosec}\phi' \\
&= [0.2263 \times 37.74 + 0.7711 \times 45.81] \times 1.4142 \\
&= 62.03
\end{aligned}
$$

$$
\begin{aligned}
\mu_s''(\lambda_i) &= [C_{Fe}\mu_{Fe}(\lambda_i) + C_{Ni}\mu_{Ni}(\lambda_i)]\mathrm{cosec}\phi'' \\
&= [0.2263 \times 71.43 + 0.7711 \times 89.98] \times 1.4142 \\
&= 120.97
\end{aligned}
$$

$$
\begin{aligned}
\mu_s(\lambda_j) &= C_{Fe}\mu_{Fe}(\lambda_j) + C_{Ni}\mu_{Ni}(\lambda_j) \\
&= 0.2263 \times 379.62 + 0.7711 \times 58.94 \\
&= 131.13
\end{aligned}
$$

$$
\begin{aligned}
P_{ij} &= \frac{1}{62.03} \times \ln\left(1 + \frac{62.03}{131.13}\right) + \frac{1}{120.97} \times \ln\left(1 + \frac{120.97}{131.13}\right) \\
&= 0.011648
\end{aligned}
$$

$$
\begin{aligned}
\delta_{ij} &= 0.5 \times (0.873 \times 0.420 \times 1.0) \times 45.81 \times \frac{379.62}{37.74} \\
&\times 0.011648 = 0.9838
\end{aligned}
$$

In the last equation, a factor of 1.0 is included to allow for the probability of the NiKα line being emitted in the Ni K series. This is not quite correct. The factor of 1.0 is an approximation. It should be around 0.878. We should also calculate an additional δ_{ij} coefficient to take into account the NiKβ line, which enhances Fe to a slightly different wavelength. The probability of the NiKβ line being emitted is equal to $1.0 - 0.878 = 0.122$. If we sum up both δ_{ij} coefficients, we get a new total value of δ_{ij} very similar to the one already calculated above. The approximation has no significant impact on the calculated value of δ_{ij} and the calculation is simpler.

(d) Calculation of sample composition by applying an iteration process to Eq. (20): For calculating concentrations C_i and C_j, the equations to be solved are:

$$C_i = R_i \frac{1 + \beta_{ij}C_j}{1 + \delta_{ij}C_j} \tag{21a}$$

Table 1
Data table for calculations

Analytical conditions

System: Fe–Ni   Analyte i=Fe   Matrix element j=Ni
Incident radiation: λ_k=0.71 Å (MoKα)
Instrument geometry: ϕ'=ϕ''=45°, cosec 45°=1.4142

Experimental data

Specimens	Concentrations		Analyte intensities (cps)	
	C_i (Fe)	C_j (Ni)	FeKα	NiKα
Pure-Fe	1.0	0	626.2	0
Pure-Ni	0	1.0	0	952.9
SPLE-1	0.2263	0.7711	209.9	438.4
SPLE-2	0.3431	0.6552		308.0
SPLE-3	0.3067	0.6931		345.4

Mass absorption coefficients (cm²/g)

	λ_k=0.71 Å	λ_j=1.659 Å	λ_i=1.937 Å
$\mu_i(\lambda)$	37.74	379.62	71.43
$\mu_j(\lambda)$	45.81	58.94	89.98

K absorption edge jump factor for Ni: 0.873
Fluorescence yield of Ni for the K shell: 0.420

Experimental data come from Ref. [5] and mass absorption coefficients from Ref. [29].
The FeKα intensities for the SPLE-2 and SPLE-3 specimens are left blank for the reader to calculate.

$$C_j = R_j(1 + \beta_{ji}C_i) \qquad (21b)$$

In Eq. (21a), the enhancement coefficient $\delta_{ij} \neq 0$ because the NiKα line (1.659 Å) is shorter than the K absorption edge of Fe (1.743 Å). Hence, a portion of the Ni radiation will be absorbed by Fe atoms leading to a secondary fluorescence component I_{FeE}. On the other hand, in Eq. (21b), the enhancement coefficient $\delta_{ji} = 0$ because the FeKα line (1.937 Å) is longer than the K absorption edge of Ni (1.488 Å). Hence, there is no absorption of the FeKα line by Ni atoms and the Fe radiation cannot enhance the NiKα radiation.

Since C_j is unknown, the iteration process is initiated by assuming in Eq. (21a) that C_j is equal to R_j, which leads to

$$C_i = 0.3352 \times \frac{1 + 0.2438 \times 0.4601}{1 + 0.9838 \times 0.4601} = 0.2566$$

This value is now substituted for C_i in Eq. (21b):

$$C_j = 0.4601 \times (1 + 2.9843 \times 0.2566) = 0.8124$$

This process is repeated, i.e., the last estimate of C_j is used to get a better estimate of C_i:

$$C_j = 0.3352 \times \frac{1 + 0.2438 \times 0.8124}{1 + 0.9838 \times 0.8124} = 0.2232$$

which is used in turn to get a better estimate of C_j:

$$C_j = 0.4601 \times (1 + 2.9843 \times 0.2232) = 0.7666$$

This process is repeated until convergence is reached, i.e., when the difference between two successive concentrations is minimal. If the above *iteration process* is continued, the following successive values are obtained:

$$C_i = 0.2268 \quad ; \quad C_j = 0.7715$$
$$C_i = 0.2264 \quad ; \quad C_j = 0.7710$$
$$C_i = 0.2268 \quad ; \quad C_j = 0.7710$$

The last iteration was not necessary. When the obtained values are compared to the chemical values: $C_i = 0.2263$ and $C_j = 0.7711$, we can conclude that the accuracy is excellent. If you add to this fact that the accurate calculated values were obtained only after four iterations, which demonstrates the high convergence level of the fundamental algorithm, all this proves the validity of the method in practice.

Although the calculation of sample compositions by hand is not practical, today's computers, once programmed, perform the above calculations in a fraction of a second, even for multi-element samples.

This simple numerical example illustrates very well what are the essential ingredients required to make the Sherman equation converge towards true values in practice: (a) the influence coefficients must be accurately calculated *before* starting the iteration process; (b) they must be kept *constant* during the iteration process; and (c) the used algorithm must respect the Sherman equation in every respect: algebraically, mathematically and physically.

5. Polychromatic excitation sources

Let us recapitulate quickly what has been presented so far:

(a) The concept of the influence coefficient, firstly proposed by Beattie and Brissey [8] but mainly developed by Lachance and Traill [12], has been integrated into the Sherman equation. By so doing, the Sherman equation, which is an equation that does not converge easily (or not all) in practice, becomes a powerful tool for calculating sample compositions.

(b) The concept of the relative intensity R_i as proposed by Beattie and Brissey [8] has been integrated to the Sherman equation.

(c) Eq. (13) proposed by Lachance and Traill [12] for calculating the *theoretical binary absorption influence coefficients* has been integrated to the Sherman equation to facilitate the calculation of concentrations.

(d) A detailed derivation of the *theoretical binary enhancement influence coefficient* was presented and integrated to the Sherman equation.

(e) All of the above has been combined into a fairly simple comprehensive algorithm, the fundamental algorithm, relating concentration to intensity.

(f) When an iteration process is applied to the fundamental algorithm for calculating sample compositions, the equation system converges all the time and there is no need to normalize the measured intensities. However, the first estimate of the sample composition must be accurately know, within 0.5% relative, before starting the iteration process. Also, the influence coefficients calculated from this first estimate composition must be accurately known before starting the iteration process and they must be kept constant during the calculation of concentrations by iterations.

All of the above was done, we must remember, in the analytical context of a *monochromatic* excitation source. However, many if not most X-ray fluorescence spectrometers use X-ray tubes that generate a *polychromatic* radiation as the excitation source. Thus, the next part of this paper will deal with making the necessary adaptations to change from monochromatic to polychromatic excitation. Although the above derivations are related to incident monochromatic sources, it will be demonstrated that the basic formalism of the fundamental algorithm is equally valid and the same for polychromatic excitation sources.

To pass from a monochromatic to a polychromatic excitation source, the total emitted intensity for an incident polychromatic source must be visualized as a sum of individual intensities, each one being due to each individual incident radiation λ_k over the effective excitation range $\lambda_{\min}$ to $\lambda_{\text{edge } i}$.

The concept of summing over a finite number of wavelength intervals $\Delta\lambda$ was first proposed by Gilfrich and Birks [21] in 1968, and remains the basis of all fundamental-parameters approaches. Fig. 2 is a schematic presentation of how Gilfrich and Birks suggested dividing the incident polychromatic beam into a number of discrete wavelength intervals of 0.02 Å. The next step was to experimentally measure the emitted intensity at the middle of each $\lambda + \Delta\lambda$ interval. For example, the intensities emanating

from a W target tube operated at 45 kV were found to be (measured in arbitrary units) equal to 15.5, 36.6, 56.8, 76.6, …, 2.7 for the intervals 0.29, 0.31, 0.33, 0.35, …, 2.59 Å, respectively. This informed us that the sum must take into account the fact that the intensities for the intervals 0.31, 0.33 and 0.35 are 2.36, 3.66 and 4.94 times more intense than the one at 0.29 Å. More important still was the knowledge that the intensity of the Lα characteristic line of W (to be added to the 1.47 Å interval) is 38.2 times more intense than the one at the 0.29 Å interval, etc. Nowadays, in practice, the equations proposed by Pella et al. [20] are used to calculate up to 350 different intensities of the incident polychromatic spectrum emitted by the X-ray tube. There is no more need to measure them. Thus, recalling Eq. (3), we have

$$I_i = \sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge } i}} \{I_{iA} + I_{iE}\}_{\lambda_k} \tag{22}$$

For example, let us consider the steps involved in the calculation of I_{Fe} in the presence of Ni for the above experimental context. For Fe, the effective wavelength interval is from 0.29 to 1.73 Å, which can be divided into 73 monochromatic intervals of 0.02 Å. Each individual intensity has then to be calculated for the 73 monochromatic incident wavelengths λ_k and summed. For Ni, the effective wavelength interval is from 0.29 to 1.47 Å because only these wavelengths are shorter than the wavelength of the Ni absorption edge (1.488 Å). This region can be divided into 60 monochromatic intervals of 0.02 Å. Sixty incident wavelengths λ_k will then produce enhancement because they can excite Ni which in turn enhances Fe.

6. Correction for matrix effects in the context of polychromatic excitation sources

The combination of Eqs. (16) and (22) leads to

$$I_i = g_i C_i \sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge } i}} \left\{ W_i'(\lambda_k) \cdot \frac{1 + \sum_j C_j \delta_{ij}(\lambda_k)}{1 + \sum_j C_j \beta_{ij}(\lambda_k)} \right\}_{\lambda_k} \tag{23}$$

where $W_i'(\lambda_k)$ is given by Eq. (15), the enhancement coefficient $\delta_{ij}(\lambda_k)$ is given by Eqs. (7), (8) and (9), and the absorption coefficient $\beta_{ij}(\lambda_k)$ is given by Eq. (13).

The term $W_i'(\lambda_k)$ has been introduced because the sum of individual intensities involves a prorating or a weighting factor $W_i'(\lambda_k)$ for each $\Delta\lambda_k$ interval. This term is equal to the incident intensity $I_o(\lambda_k)\Delta\lambda_k$ weighted by the ratio of the mass absorption coefficient of the element i, for the incident wavelength λ_k, relative to the effective mass absorption coefficient of the element i, for the same incident wavelength λ_k.

For a specimen composed only of the pure analyte i, $C_i = 1$, all $C_j = 0$, and Eq. (23) becomes

$$I_{(i)} = g_i \sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge } i}} \{W_i'(\lambda_k)\}_{\lambda_k} \tag{24}$$

where $I_{(i)}$ is the intensity emitted by the pure element i. The combination of Eqs. (17), (23) and (24) leads to

$$R_i = C_i \frac{\displaystyle\sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge } i}} \left\{ W_i'(\lambda_k) \cdot \frac{1 + \sum_j C_j \delta_{ij}(\lambda_k)}{1 + \sum_j C_j \beta_{ij}(\lambda_k)} \right\}}{\displaystyle\sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge } i}} \{W_i'(\lambda_k)\}_{\lambda_k}} \tag{25}$$

Reversing this equation and after some algebraic manipulations, we obtain the *fundamental algorithm* in the context of a polychromatic excitation source:

$$C_i = R_i \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j} \tag{26}$$

which is the generalization of Eq. (20) developed for the context of an incident monochromatic source and where

$$\alpha_{ij} = \frac{\sum_k W_i(\lambda_k) \beta_{ij}(\lambda_k)}{\sum_k W_i(\lambda_k)} \tag{27}$$

$$\varepsilon_{ij} = \frac{\sum_k W_i(\lambda_k) \delta_{ij}(\lambda_k)}{\sum_k W_i(\lambda_k)} \tag{28}$$

The new *weighting factor*, $W_i(\lambda_k)$, present in the two previous equations is defined by

$$W_i(\lambda) = \frac{\mu_i(\lambda_k) \cdot I_O(\lambda_k) \cdot \Delta\lambda_k}{\mu_i^* \cdot [1 + \sum_j C_j \cdot \beta_{ij}(\lambda_k)]} \tag{29}$$

The physical interpretation of the fundamental algorithm (Eq. (26)) derived in the context of a polychromatic excitation source is exactly the same as the one of Eq. (20) derived for a monochromatic context. It is amazing to realize that, after so many algebraic manipulations, that no matter the selected approach (monochromatic or polychromatic excitation) used for
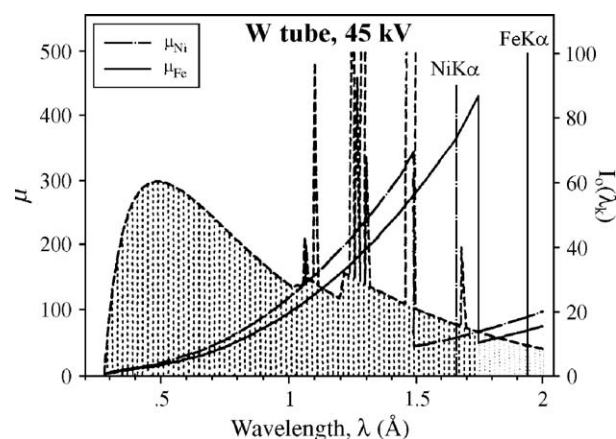

Fig. 2. A schematic representation of the excitation of Fe in a Fe–Ni binary mixture using a W tube operated at 45 kV. The incident polychromatic beam is divided into a number of discrete wavelength intervals of 0.02 Å. Wavelengths longer than the $Fe_{K\,abs\,edge}$ at 1.743 Å cannot excite FeK radiation. The figure is from Ref. [5].

deriving a new algorithm from the Sherman equation, that as long as we respect the Sherman equation algebraically, mathematically and physically, we always end up with the mathematical form of the fundamental algorithm.

The *fundamental algorithm* (Eq. (26)) was proposed in 1984 by Rousseau [9] to correct for all inter-element matrix effects that modify the measured net intensity emitted by an analyte i in a given specimen. The FA was deduced from the Sherman equation by algebraic manipulation without any approximation and is thus the same equation expressed in another form, namely the one usually used for influence coefficient algorithms. Also, Rousseau derived new theoretical expressions for the *multi-element influence coefficients* α_{ij} and ε_{ij} for the fundamental algorithm in the context of incident polychromatic sources. He showed that the multi-element absorption influence coefficient, called α_{ij}, is the *weighted mean* of all absorption effects caused by element j on analyte i in a given specimen, where each incident wavelength λ_k is weighted by a weight $W_i(\lambda_k)$. This is mathematically expressed by Eq. (27) where $\beta_{ij}(\lambda_k)$ is the absorption influence coefficient in the context of an incident monochromatic source, as previously shown. Similarly, the enhancement influence coefficient, called ε_{ij}, is the *weighted mean* of all enhancement effects caused by element j on analyte i in a given specimen, where each incident wavelength λ_k is weighted by a weight $W_i(\lambda_k)$. This is mathematically expressed by Eq. (28) where $\delta_{ij}(\lambda_k)$ is the enhancement influence coefficient in the context of an incident monochromatic source, as previously shown.

In physics, the validity of a new theory is confirmed if it reveals new facts. First, let us take a closer look at Eqs. (27) and (28) of the α_{ij} and ε_{ij} coefficients. They have exactly the same mathematical form as the equation of a weighted mean [9]. Thus, by analogy, the α_{ij} and ε_{ij} coefficients can be considered as the *weighted means* of all absorption and enhancement effects, respectively, caused by element j on analyte i, where to each incident wavelength λ_k is given a weight $W_i(\lambda_k)$, which can be seen as the product of two terms:

$$W_i(\lambda_k) = \left[\frac{\mu_i(\lambda_k)}{\mu_i^*} I_o(\lambda_k) \Delta\lambda_k \right] \cdot \left[\frac{1}{1 + \sum_j C_j \beta_{ij}(\lambda_k)} \right]$$

The first term takes into account the polychromaticity of the incident spectrum by giving a weight to each value of the incident intensity $I_o(\lambda_k)\Delta\lambda_k$, while the second weights for each binary combination of elements i and j by the total absorption effect of the matrix, i.e., it takes into account the type of matrix composition in which the analyte i is determined, which makes physical sense.

Second, these considerations concerning W_i lead to the two following important conclusions:

- The α_{ij} and ε_{ij} coefficients are not constant for a binary system i–j and vary not only with the concentrations of element j but also with the nature and concentration of all other elements in the matrix.
- The total matrix effect on the analyte i is not equal to the sum of the binary effects of every element j of the matrix, each

effect being calculated independently of each other. In other words, each element j contributes to the total matrix effect on the analyte i, but the individual contribution of each element j cannot be isolated and cannot be calculated independently of all the other matrix elements.

Since the α_{ij} and ε_{ij} coefficients depend on the total matrix composition and since the sample composition is unknown prior to the analysis, they must be calculated for each sample from an accurate first estimate of the sample composition, which is calculated using the Claisse–Quintin algorithm [1]:

$$C_i = R_i \Big[1 + \sum_j (a_{ij} + a_{ijj} C_M) \cdot C_j + \sum_j \sum_{k>j} a_{ijk} C_j C_k \Big] \quad (30)$$

where C_M is the total matrix concentration and a_{ij}, a_{ijj} and a_{ijk} are *constant* binary (a_{ij} and a_{ijj}) and ternary (a_{ijk}) influence coefficients. Then, from this estimated composition, all α_{ij} and ε_{ij} coefficients, the complex parts of the Sherman equation, are calculated only once. With these calculated coefficients now used as constants, the final composition of the sample (and a more accurate one) is calculated by applying an iteration process to the fundamental algorithm.

The fundamental algorithm, in association with the CQ algorithm, can be applied to any type of sample with a large concentration range (0–100%), such as elements in alloys. In this case, the concentration calculation method by itself introduces a theoretical mean relative error of only 0.05% [1,30] on the calculated concentrations. Rousseau and Bouchard [31] demonstrated the experimental validity of the whole fundamental algorithm method by analyzing 28 standards for 15 elements with wide concentration ranges. The experimental conditions are listed, as well as all measured net intensities. Rousseau and Bouchard [31] used only two standards (high and low) per analyte, different for each case, to obtain the intercepts and the calibration slopes, which are tabulated along with the mean absolute errors.

7. Concept of binary influence coefficients

The definition of explicit expressions for the calculation of theoretical multi-element influence coefficients has been a milestone achievement in the search for efficient solutions for the correction of matrix effects. These explicit expressions have been defined in terms of fundamental and instrumental parameters in the context of incident polychromatic sources and for multi-element systems, provided the compositions of the specimens are known or closely estimated. The concept underlying influence coefficients has evolved towards a new generation of coefficients calculated for each sample composition, thereby extending the range of application and increasing the accuracy of results.

The only inconvenience of this approach is that an estimate of the composition of the unknown sample must be known before calculating its final composition. An elegant way to solve this problem is to use *binary influence coefficients* that are constant for a given concentration range rather than changing with the composition of every sample.

Binary influence coefficients are based on the hypothesis that the total matrix effect on the analyte i is equal to the sum of the effects of each element j of the matrix, each effect being calculated independently of each other. Of course, this hypothesis is an approximation, but when used in appropriate analytical contexts, it can generate accurate results. With this approach, a valid set of binary influence coefficients can be calculated for a given composition range rather than for a given sample composition. Thus, with the binary coefficient approach, the coefficient a_{ij} is assumed to be a *constant* for a given range of C_i and C_j rather than to be a *variable* that changes with the composition of each matrix.

The binary coefficients can be used in any theoretically valid algorithm, i.e., in agreement with the Sherman equation. Among all the proposed algorithms, two are more generally favored for their accuracy and their solid theoretical foundation. These are the Lachance–Traill and Claisse–Quintin algorithms. Let us examine them in more detail.

8. Lachance–Traill algorithm

The mathematical model of Lachance and Traill [12] is

$$C_i = R_i\left(1 + \sum_j a_{ij}C_j\right) \tag{31}$$

where R_i is the ratio of the measured net intensity I_i to the measured net intensity of the pure analyte i. For accurate results, the binary influence coefficient a_{ij} must be calculated using the expression [1]

$$a_{ij} = \frac{\alpha_{ij} - \varepsilon_{ij}}{1 + \varepsilon_{ij}C_{jm}} \tag{32}$$

where α_{ij} and ε_{ij}, defined by Eqs. (27) and (28), are calculated for the special case of a binary standard having a composition (C_{im}, C_{jm}), where C_{im} is the mid-value of the calibration range of the analyte i and

$$C_{jm} = 1 - C_{im} \tag{33}$$

In the Lachance–Traill model, the binary coefficients represent the correction of the *total* matrix effect and are treated as constants, i.e., their values do *not* vary with the sample composition.

The influence coefficients a_{ij} of the Lachance–Traill algorithm are considered as *constant* (it is an approximation) when applied to samples with a limited concentration range (0–10%), such as oxides in rock samples prepared as fused discs. In this case, the method introduces a theoretical mean relative error of 0.02% [1,30] on concentrations calculated by Eqs. (31) and (32). For a concentration range greater than 10%, the concentrations calculated by this approach are unacceptable.

9. Claisse–Quintin algorithm

The Claisse–Quintin model [13] is an expanded version of the Lachance–Traill algorithm that accounts for the fact that binary influence coefficients are not constant but vary with the concentration of each matrix element j. For this reason, this

algorithm uses two additional influence coefficients to correct for matrix effects:

$$C_i = R_i\left[1 + \sum_j (a_{ij} + a_{ijj}C_M)C_j + \sum_j \sum_{k>j} a_{ijk}C_jC_k\right] \tag{34}$$

where C_M is the matrix concentration and is equal to

$$C_M = 1 - C_i = C_j + C_k + \ldots + C_N \tag{35}$$

This term C_M has been proposed by Tertian [15] to replace the term C_j in the original equation, in order to reduce the errors introduced by the approximations of the algorithm.

Equations for calculating accurate and valid theoretical binary influence coefficients in the Claisse–Quintin algorithm were first proposed by Rousseau and Claisse [14], then improved 10 years later by Rousseau [4]. These equations are:

$$a_{ij} = \frac{1}{3}[-F_i(0.2, 0.8, 0) + 4F_i(0.8, 0.2, 0)]$$

$$a_{ijj} = \frac{5}{3}[F_i(0.2, 0.8, 0) - F_i(0.8, 0.2, 0)]$$

$$a_{ijk} = \frac{20}{7}[F_i(0.3, 0.35, 0.35) - F_i(0.3, 0.7, 0)] - F_i(0.3, 0, 0.7)$$

where

$$F_i(C_i, C_j, C_k) = \frac{1}{C_j}\left(\frac{C_i}{R_i} - 1\right)$$

and

$$\frac{C_i}{R_i} = \frac{1 + \alpha_{ij}C_j + \alpha_{ik}C_k}{1 + \varepsilon_{ij}C_j + \varepsilon_{ik}C_k}$$

Note: if $C_j = 0$, then $F_i(C_i, 0, C_k) = \frac{1}{C_k}\left(\frac{C_i}{R_1} - 1\right)$.

The "crossed" coefficients a_{ijk} are included to compensate for the fact that the total matrix effect correction cannot be strictly represented by a sum of binary matrix effect corrections. By so doing, these coefficients improve the accuracy of results.

The influence coefficients of the Claisse–Quintin (CQ) algorithm are considered as constant when applied to samples with a medium concentration range (0–40%), such as oxides in cement samples prepared as pressed powder pellets. In this case, the algorithm introduces a theoretical mean relative error of 0.04% [1,30] on the calculated concentrations. For a concentration range as large as 0–100%, e.g., in the case of alloy analysis, the CQ algorithm introduces a mere 0.3% relative error [1,30]. The choice of this algorithm for calculating an accurate first estimate of the sample composition, which is needed for the application of the fundamental algorithm, is thus perfectly justified.

10. Empirical influence coefficients

Empirical influence coefficients are based on the observation that the magnitude of matrix effects (absorption and enhancement) of any element j on analyte i, in a given sample, can be quantified by an overall factor usually denoted as an *empirical influence coefficient* e_{ij} ("e" for empirical).

Empirical influence coefficients are derived by calculating the best possible fit between measured intensities and concentrations of a given set of reference materials, which cover the analyte concentration ranges of interest. The values are usually calculated using multiple regression analysis techniques to solve a series of simultaneous equations. The effectiveness of empirical coefficients depends on the availability of reference materials that *closely* match the composition ranges of the unknowns. As the number of analytes increases, so must the number of reference materials that are required. In fact, to avoid any divergent solution of the respective simultaneous equations, a minimum of $2(N+1)$ reference materials must be used, where N is the number of elements to be determined, if all the coefficients are unknown, or the number of remaining coefficients to be calculated, if some of them are already known. Furthermore, the preparation of reference materials must be absolutely identical to the preparation of samples to be analyzed, which means that they must reproduce the same "preparation defaults" as the unknowns. However, the preparation and measurement of an adequate number of reliable reference materials can be long and tedious.

This statistical approach is very sensitive to any experimental error in the data and can easily and frequently yields inaccurate empirical coefficients with no physical meaning. Also, the calculated coefficients can *only* be applied to unknowns with composition and sample preparation similar to the reference materials used. Thus, empirical coefficients are liable to be less accurate over an extended composition range, depend on the compositions of reference materials used, and consequently their range of application is limited. The use of empirical coefficients, with all their potential problems, must then be limited as much as possible or they should be used only when software packages for calculating accurate theoretical coefficients are simply not available.

The only remaining possible advantage of using empirical coefficients is that they only have to be calculated once, as long as there is no change in the sample preparation, concentration range of analytes and instrumental conditions, and without the need to resort to complex theory for concentration calculations.

Two algorithms can be used for calculating concentrations with empirical coefficients. There are:

$$C_i = C_{oi} + m_i I_i \left(1 + \sum_j g_{ij} I_j\right) \tag{36}$$

and

$$C_i = C_{oi} + m_i I_i \left(1 + \sum_j e_{ij} C_j\right) \tag{37}$$

where C_i=concentration of the analyte i, C_{oi}=background equivalent concentration, C_j=concentration of a matrix element j, I_i=net intensity of the analyte i peak, I_j=net intensity of the matrix element j peak, m_i=reciprocal of slope of the calibration line of analyte i, g_{ij}=empirical coefficient correcting matrix effect of j on i in an intensity model and e_{ij}=empirical coefficient correcting matrix effect of j on i in a concentration model.

Table 2
Compositions of calibration reference materials and checked reference materials used as "unknowns"

Steel samples	Concentration (%)				
	Cr	Fe	Ni	Mo	Total
Calibration reference materials					
303	17.21	70.80	8.14	0.55	96.70
309	22.07	62.60	12.41	0.10	97.18
310	24.60	53.00	19.70	0.22	97.52
316	16.50	67.90	10.45	2.15	97.00
321	17.68	68.60	10.01	0.33	96.62
Checked reference materials					
330	18.30	42.90	35.46	0.15	96.81
347	17.71	69.10	9.59	0.28	96.68
430	16.55	82.00	0.18	0.04	98.77
431	15.91	80.50	2.12	0.17	98.70

Data come from Ref. [6].

Eq. (36) was proposed by Lucas-Tooth and Pyne [32] in 1964. It is an algorithm based on measured intensities. This algorithm assumes that the matrix effect of an element j on the analyte i is proportional to its intensity. This assumption does not correspond to physical reality because, in general, measured intensities are modified by matrix effects and are not directly proportional to concentrations. Thus, the g_{ij} coefficients have no physical meaning, but they can easily be calculated by multiple regressions during the calibration step. The only advantage of this algorithm is that the concentrations can directly be calculated from measured intensities without the need to resort to an iteration process. The C_{oi} symbol is supposed to represent a background equivalent concentration, but in this algorithm, it does not have any analytical meaning at all. It is simply a number, negative or positive, in order to improve the accuracy of results.

Eq. (37) is the Lachance–Traill algorithm [12]. This algorithm assumes that the matrix effect of an element j on the analyte i is proportional to its concentration C_j. This assumption is a better approximation in agreement with the physical reality. The concentrations C_j required for matrix corrections are obviously not known for an unknown sample. In this case, we need to resort to an iteration process for solving the set of equations. In this algorithm, the C_{oi} concentration is the intercept with the concentration axis (X-axis). Generally, it is a negative concentration value. Theoretically, the C_{oi} concentration is zero when the intensity I_i has been exactly corrected for background, line overlaps and blank. However, with empirical coefficients, it is wise to include the C_{oi} in the regression analysis of a set of reference materials because it takes into account any systematic error made in background and line overlap corrections.

Only the algorithm proposed by Lachance and Traill is recommended for use with empirical coefficients. All other proposed algorithms, such as the one of Rasberry and Heinrich [7] or Lucas-Tooth and Pyne [32], etc., are *not* recommended because of their extremely limited application range or lack of accuracy.

To demonstrate the problems that are met in practice with empirical coefficients, let us consider the experimental data of

Table 3
List of the nine models used to calculate the Cr concentration

No.	Model $i=$Cr	Intercept	S (%)
1	$C_i=m_iI_i$	$=0$	0.63
2	$C_i=m_iI_i(1+g_{iFE}I_{Fe})$	$=0$	0.21
3	$C_i=C_{oi}+m_iI_i(1+g_{iFe}I_{Fe})$	$\neq0$	0.15
4	$C_i=C_{oi}+m_iI_i(1+g_{iFe}I_{Fe}+g_{iNi}I_{Ni})$	$\neq0$	0.05
5	$C_i=C_{oi}+m_iI_i(1+g_{iFe}I_{Fe}+g_{iNi}I_{Ni}+g_{iMo}I_{Mo})$	$\neq0$	0.00
6	$C_i=m_iI_i(1+g_{iFe}I_{Fe}+g_{iNi}I_{Ni}+g_{iMo}I_{Mo})$	$=0$	0.08
7	$C_i=C_{oi}+m_iI_i(1+\sum_j a_{ij}C_j)$	$\neq0$	0.19
8	$C_i=C_{oi}+m_iI_i(1+\sum_j a_{ij}C_j+e_{iFe}C_{Fe})$	$\neq0$	0.10
9	$C_i=C_{oi}+m_iI_i(1+\sum_j \alpha_{ij}^*C_j)$	$\neq0$	0.13

For each model, with or without the intercept (C_{oi}), the standard deviation (S) is calculated for the given set of reference materials. The definitions of the empirical coefficients g_{ij} and e_{ij} were given above. The definitions of the theoretical coefficients a_{ij} and α_{ij}^* are given below. Data come from Ref. [6].

Tables 2, 3 and 4. Here, the chromium is determined in four steel samples containing four analytes (Cr, Fe, Ni and Mo) and the calibration is accomplished with five reference materials. However, just five reference materials are insufficient for analyzing with empirical coefficients a set of samples containing four analytes. Indeed, reminding ourselves that N is the number of analytes, in this case $N=4$, the minimum requirement to avoid the indetermination of the equation system is $2(N+1)=2(4+1)=10$ reference materials. However, the number of reference materials has been voluntarily reduced to five because it is frequent in practice that the analyst does not have access to the minimum required number of reference materials. In this case, the best algorithm to use in association with empirical coefficients, the Lachance–Traill one, becomes useless. Because of the lack of reference materials, we have no other choice but to calculate the concentrations with the Lucas-Tooth and Pyne algorithm. This algorithm can tolerate a smaller number of reference materials by allowing one to reduce the number of empirical coefficients to matrix elements with a *major* influence only. The Lachance–Traill algorithm will be used with *theoretical* coefficients (or a mixture of theoretical and empirical coefficients) only for comparison.

In Table 2, note that the Cr concentration range in calibration reference materials (16.5–24.6%) almost covers one of the unknown samples (15.91–18.3%), which is an essential condition with empirical coefficients, i.e., any extrapolation must be absolutely avoided. Furthermore, the total of the given concentrations in each calibration reference material should be close to 100%. However, such is not the case for the five given

calibration reference materials, which is another potential source of errors. It is evident that this experimental verification is a severe test for checking empirical coefficients.

Table 3 shows nine different methods (or models) which use the two algorithms with their coefficients and with or without the intercept (C_{oi}). The empirical coefficients are calculated during the calibration step by regression analysis using the method of *least squares fitting*. The objective is to obtain the best fit of a given algorithm to experimental data. The quality of the best fit of each algorithm is checked by the minimum standard deviation (S), which is calculated from the following formula:

$$S = \sqrt{\frac{\sum(C_{given}-C_{calculated})^2}{n-1}} \qquad (38)$$

where C is the given and calculated Cr concentration in each calibration reference material and n is the number of reference materials used.

However, the best fit is not typically the most appropriate criterion for selecting the best calibration procedure. It is preferable to select a number of reference materials not used for calculation of the calibration coefficients, calculate the composition of these reference materials as unknowns and compare the results with the given (chemical) values. Also, analyze some of your typical unknowns with your calibration procedure and a different analytical technique and compare the results.

Table 4 gives the results of four reference materials analyzed as unknowns. The absolute average error (%) is given for each model. From the study of results in Table 4, we observe that:

1. With empirical models nos. 1 to 6, the standard deviation for calibration reference materials is improved when the number of coefficients used increases. It becomes zero for model no. 5, but the absolute average error for the checked reference materials is the highest (1.52%). This last model is a good example of overcorrection for calibration reference materials ($S=0.0\%$), but one that gives the worst results for unknowns. The results are acceptable only for the empirical model no. 6, where the absolute average error is 0.29%.
2. The three theoretical models 7 to 9 use the Lachance–Traill algorithm in association with different types of *theoretical* coefficients. The calculation of all theoretical coefficients is based on fundamental parameters, not on regression analysis.

Table 4
Results for Cr concentrations in steel samples using nine different calibration procedures

Models	1	2	3	4	5	6	7	8	9
S (%)	0.63	0.21	0.15	0.05	0.00	0.08	0.19	0.10	0.13
Steel sample	Cr (%)	Absolute deviation (%)							
330	18.30	−0.26	+0.53	−1.85	−3.39	−0.59	+0.70	−0.07	+0.12
347	17.71	+0.60	+0.15	−0.10	−0.14	−0.05	+0.13	+0.05	+0.01
430	16.55	+1.75	+0.59	−0.41	−1.34	+0.27	+0.03	+0.14	−0.06
431	15.91	+1.67	+0.57	−0.39	−1.22	+0.24	+0.13	+0.12	−0.04
Average error (%)		1.07	0.46	0.69	1.52	0.29	0.25	0.10	0.06

Data come from Ref. [6].

They are calculated before the calibration from physical values like absorption coefficients and fluorescence yields. They are not calculated during the calibration from data, concentrations and intensities, of a minimum set of $2(N+1)$ reference materials. They do not require a minimum of reference materials and there is no need to reduce the number of correction coefficients to use. The accuracy of results depends on the method used to calculate theoretical coefficients. For the three models, the standard deviation for the calibration reference materials varies from 0.19% to 0.13%, but the error for the checked reference materials is greatly improved (from 0.25% to 0.06%). Model no. 7 uses *fixed* theoretical multi-element coefficients calculated for an average composition as proposed by de Jongh [18]. They are valid only for a narrow composition range of the given set of calibration reference materials. The model no. 8 uses mixed coefficients, i.e., theoretical for all the matrix elements (except Fe) and empirical for the predominant element (Fe). It is the model using empirical coefficients that gives the best results. Model no. 9 uses *variable* theoretical multi-element coefficients as proposed by Broll and Tertian [22]. They are calculated for each individual reference material and unknown sample. It is the most reliable way for calculating any type of theoretical multi-element coefficients (Rousseau [3], Broll–Tertian [22], Lachance–Claisse [23]) and getting accurate results.

From this experimental verification, we can conclude that empirical coefficients based on an appropriate number of carefully selected and precisely analyzed reference materials can give acceptable results (see model no. 6). However, the optimized strategy with empirical coefficients is to mix them with theoretical coefficients. Use appropriate reference materials to optimize *empirically* the matrix effect corrections of only the element(s) with *major* influence on the analyte. For example, in steel samples, you can correct empirically the matrix effect of Fe on Cr, but for the correction of the effects of the rest of the matrix elements on the analyte (Cr), use theoretical coefficients.

An easier and much more practical solution to these problems is to calculate theoretical coefficients. They can be calculated for any combination of elements and any experimental conditions, within a few fractions of second! With the dramatic increase in the power of computers during the past few years, a better understanding of the theory of X-ray excitation and an increasingly accurate knowledge of fundamental constants, theoretical approaches are being applied with rapidly increasing frequency. Three important reasons in favor for the theoretical approaches are that they: (1) require only a few reference materials (even one is sufficient) for calibration, (2) enable the analyst to determine wider concentration ranges and (3) increase the accuracy of results. Thus, there is no longer a need for the use of simpler empirical approaches with their associated severe limitations.

11. Calibration and routine analysis

Before doing quantitative XRF analysis, it is necessary to calibrate the instrumentation. Although in many cases the analysis of samples with a limited composition range may allow for the use of empirical calibration curves comparing uncorrected (for matrix effects) net intensities to concentrations, it is usually preferable to work with a general-purpose calibration procedure that is applicable to a larger variety of matrix types covering wide concentration ranges. Furthermore, with theoretical FP models (such as the FA), a special calibration procedure must be used, because it is well known that any theory cannot account for all variations in all the instrumental parameters. The proposed calibration procedure succeeds in matching theory with the experimental data obtained from *every* spectrometer. Since it has already been very well explained in Ref. [27], I will not repeat it here, except for the main conclusions.

Let us define the following symbols:

I_i	Measured net intensity of the analyte i
$I_{(i)}$	Net intensity of the pure analyte i
R_i	Theoretical relative intensity
I_{iM}	Measured *gross* intensity of the analyte i in any drift monitor
C_i	Concentration of the analyte i
M_{is}	Correction factor for matrix effects of specimen "s" on i
m_i	Slope of the calibration line
b_i	Intercept on the Y-axis of the calibration line

The equation used to plot any calibration line in association with any FP model is

$$\frac{I_i}{I_{iM}} = m_j \cdot \frac{C_i}{M_{is}} + b_i \tag{39}$$

where the *measured* relative intensity I_i/I_{iM} (Y-axis) is plotted as a function of the *calculated* (or theoretical) relative intensity $R_i=C_i/M_{is}$ (X-axis). C_i is the concentration of the analyte i in a standard and the term M_{is} is calculated from the Sherman equation [3] or any theoretically valid algorithm [1]. The slope of the line represents the net intensity of the pure element i (see Eq. (16) in Ref. [27]). Thus, this calibration procedure represents very well the physical reality because we are consistently comparing *measured* relative intensities (I_i/I_{iM}) to *calculated* relative intensities ($R_i=C_i/M_{is}$). This is the best way to get a true calibration straight-line. This feature makes the calibration lines *robust*, i.e., they can be extrapolated by a factor of two or three, thus protecting the analyst from errors when the concentrations of samples to be analyzed exceed the calibration range of standards. In addition, incorrect standards will be shown clearly as outliers in the calibration line. Fig. 3 shows an example of the type of calibration straight line represented by Eq. (39).

In Eq. (39), the intercept b_i is theoretically zero, unless I_i has not been perfectly corrected for background, line overlaps, etc. Therefore, a significant intercept value indicates the presence of systematic errors and one must try to discover the cause of it and correct for it.

The calibration slope m_i allows the theory to be adapted to the experimental data of each spectrometer. It represents the
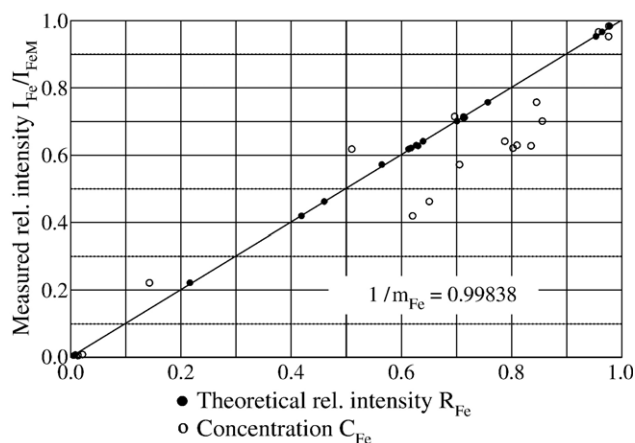
Fig. 3. Fe calibration graph using NIST alloy standards. The graph of measured relative intensities as a function of the concentration C_{Fe} gives scattered points (O). On the other hand, the plot of the same measured relative intensities as a function of the theoretical relative intensities calculated by the fundamental algorithm lines up each point (●) on the calibration line. Data come from Ref. [31].

Table 5
Sample compositions and relative intensities for Cr–Fe–Ni specimens (W tube, 45 kV, geometry 63/33)

Specimens	Concentration, C				Relative intensity, R		
Fe–Ni	Cr	Fe	Ni	Total	Cr	Fe	Ni
Binaries							
971		0.0462	0.9516	0.9978		0.0789	0.8782
972		0.0659	0.9322	0.9981		0.1104	0.8321
974		0.1018	0.8964	0.9982		0.1621	0.7595
983		0.2263	0.7711	0.9974		0.3172	0.5483
986		0.3067	0.6931	0.9998		0.4007	0.4515
987		0.3431	0.6552	0.9983		0.4373	0.4073
1159		0.5100	0.4820	0.9920		0.5907	0.2553
126B		0.6315	0.3599	0.9914		0.6958	0.1720
809B		0.9549	0.0329	0.9878		0.9659	0.0125
Fe–Cr binaries							
4061	0.0353	0.9627		0.9980	0.0617	0.8970	
4062	0.0608	0.9372		0.9980	0.1004	0.8270	
4065	0.1214	0.8766		0.9980	0.1817	0.6974	
4173	0.1900	0.8080		0.9980	0.2587	0.5739	
4181	0.2503	0.7477		0.9980	0.3326	0.4748	
4183	0.3194	0.6786		0.9980	0.4023	0.4048	
4184	0.3658	0.6322		0.9980	0.4476	0.3579	
Fe–Ni–Cr ternaries							
5074	0.2525	0.6838	0.0498	0.9861	0.3258	0.4511	0.0203
5181	0.1988	0.6945	0.0996	0.9929	0.2651	0.4971	0.0416
5324	0.2696	0.5280	0.1927	0.9903	0.3311	0.3529	0.0821
5321	0.1988	0.5919	0.2002	0.9909	0.2582	0.4343	0.0898
7271	0.1879	0.7159	0.0829	0.9867	0.2536	0.5298	0.0343
161	0.1688	0.1501	0.6429	0.9618	0.2072	0.1460	0.4367
1189	0.2030	0.0140	0.7260	0.9430	0.2263	0.0125	0.5630

Data come from Ref. [7].

experimental average intensity of the pure analyte determined from a set of multi-element standards. Depending on the analytical context, this measured value might be substantially different from the theoretical value. It is this difference that compensates to a large extent for all the theoretical limitations of the Sherman equation. The obtained slope value is the required factor allowing one to adapt theory to a particular set of experimental data and makes truly meaningful the equal sign in Eq. (39). In other words, it is equivalent to *rescaling* the theoretical calculations by a factor, the slope of the calibration line, to match reality.

Other great advantages of this calibration procedure comparing "apples" to "apples" are as follows. It is truly *matrix independent* because it can place on a straight line any type of matrix compositions containing the analyte. It enables each analyte to be calibrated over wide concentration ranges and requires only a few good standards.

To apply the proposed calibration procedure in practice, rearranging Eq. (39) for C_i leads to

$$C_i = \frac{1}{m_i} \cdot \left(\frac{I_i}{I_{iM}} - b_i \right) \cdot M_{is} \tag{40}$$

The interpretation of Eq. (40) makes physical sense. Firstly, if there are some errors in the background calculation, b_i is

Linear algorithm

$$C_i = K_i \cdot I_i = \frac{1}{I_{(i)}} \cdot I_i = R_i$$

Lachance-Trail algorithm

$$C_i = R_i \left(1 + \sum_j a_{ij} C_j \right)$$

Claisse-Quintin algorithm

$$C_i = R_i \left[1 + \sum_j \left(a_{ij} + a_{ijj} C_M \right) C_j + \sum_j \sum_{k>j} a_{ijk} C_j C_k \right]$$

Fundamental Algorithm (proposed by Rousseau)

$$C_i = R_i \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j}$$

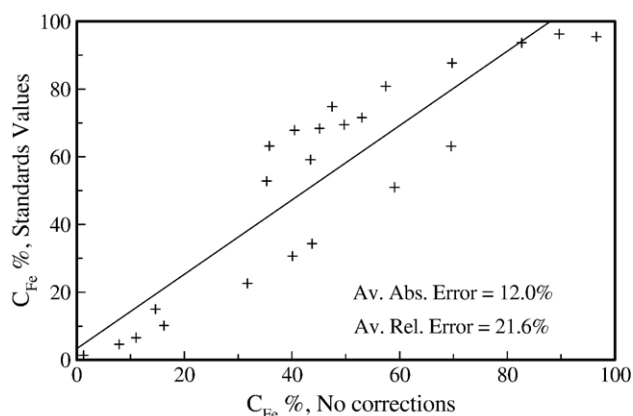Fig. 4. A comparison of some algorithms using influence coefficients.

Fig. 5. Given Fe concentrations in Fe–Cr–Ni alloys plotted against concentrations calculated from uncorrected Fe intensities (in %). Note the large absolute and relative errors.
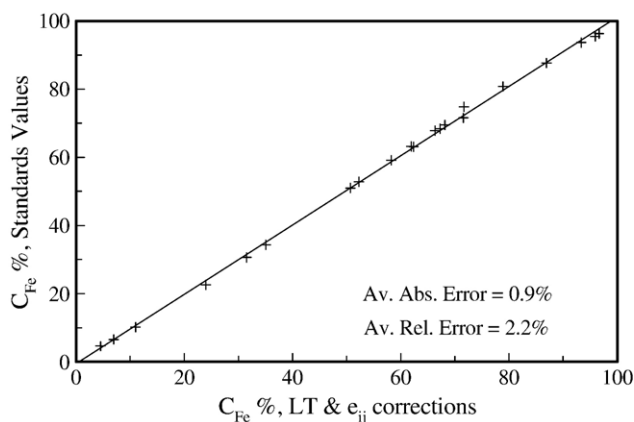
Fig. 6. Given Fe concentrations in Fe–Cr–Ni alloys plotted against concentrations calculated using the Lachance–Traill algorithm (LT) and empirical influence coefficients calculated by multiple regression analysis (CiREG [33] program). Note that absolute and relative errors are still unacceptably large.

Fig. 8. Given Fe concentrations in Fe–Cr–Ni alloys plotted against concentrations calculated using the Claisse–Quintin algorithm (CQ) and theoretical binary influence coefficients (CiROU [33] program). Note the smaller absolute and relative errors.

different from zero and subtracted from the measured net intensity I_i *before* being corrected for matrix effects by the M_{is} factor. Secondly, the concentration is proportional to the *true* net intensity, corrected for the instrumental drift, so that *only* the true net intensity is corrected for matrix effects by the M_{is} factor. Thirdly, the true net intensity is corrected for the imperfections of theory by the calibration slope m_i before being corrected for matrix effects.

Thus, Eq. (40) is in perfect agreement with the basic physical rules of XRF spectrometry. For accurate results, it is imperative, however, that any theoretical model for calculating the M_{is} factor respects the underlying physics in XRF analysis.

An experimental verification of this analytical method is given in Ref. [31], where 15 different analytes were determined in many different types of alloys, covering large concentration ranges.

12. Experimental verification

Fig. 4 shows the main types of algorithms discussed above that use influence coefficients. The concentration and the

measured relative intensity data for a set of Cr–Fe–Ni specimens are given in Table 5. Figs. 5–9 compare given concentrations for Fe in a set of Cr–Fe–Ni specimens to the values calculated by the different algorithms [1] in Fig. 4, which are the linear algorithm, the Lachance–Traill (LT) algorithm (used in association with empirical and binary constant influence coefficients), the Claisse–Quintin (CQ) algorithm and the fundamental algorithm (FA).

It can be observed that there is a progressive improvement in the fit of the data in Figs. 5–9. The data fit for the LT algorithm is not as good as the CQ or Fundamental algorithm because the Fe concentration range is much too large (1–96%). Here, the LT algorithm is used beyond its application range. Otherwise, it should give excellent results in analytical contexts involving limited concentration ranges (0–10%). On the other hand, there is little improvement between the results from the CQ algorithm and the FA, which is normal. Remember that the CQ algorithm is used in association with the FA for calculating each sample composition. At first, the CQ algorithm calculates an accurate first estimate of the composition of a sample, while the FA
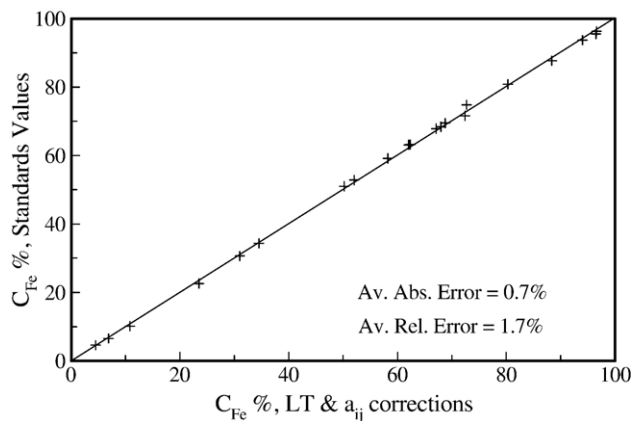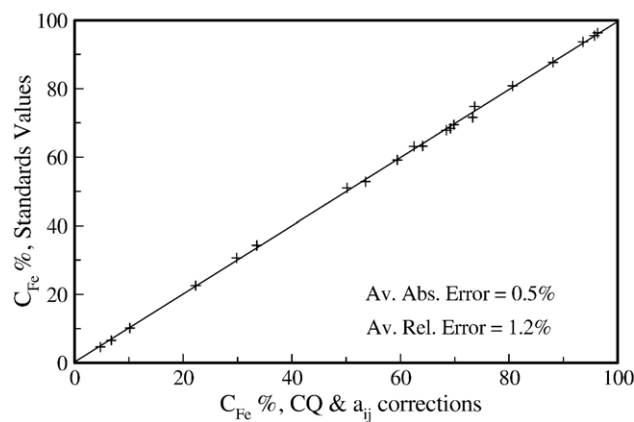

Fig. 7. Given Fe concentrations in Fe–Cr–Ni alloys plotted against concentrations calculated using the Lachance–Traill algorithm (LT) and theoretical binary influence coefficients (CiLT [33] program). Note the very considerable improvement in absolute and relative errors.
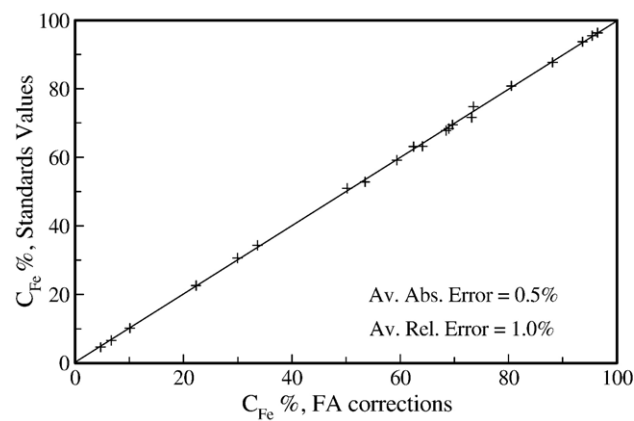

Fig. 9. Given Fe concentrations in Fe–Cr–Ni alloys plotted against concentrations calculated using the fundamental algorithm (FA) and theoretical multi-element influence coefficients (CiROU [33] program). Note the very small absolute and relative errors.

calculates from it the final composition. In order to make the FA method viable and valid, the first composition estimation must be very close to the final result, i.e., inside of 0.5% relative. This is what we observe for these samples.

The two last ternary specimens of Table 5, i.e., numbers 161 and 1189, have a low total of 96.18% and 94.30%, respectively, which means that we cannot accurately correct for matrix effects because 3.82% and 5.70% of the specimen composition, respectively, are unknown elements. Therefore, the data points of these two specimens has been omitted from Figs. 6–9 because the low totals would distort the average errors introduced by the different algorithms for the calculation of matrix effect corrections. On the other hand, Fig. 5 represents the plot of the Fe concentration (in %) as a function of the Fe relative intensity (in %). The data of the two low total specimens have been included in this figure to illustrate the effects of the matrix composition on the Fe peak intensities. In this case, the unknown elements do not introduce any additional errors.

13. Conclusion

In this paper, the fundamental algorithm (FA) relating C_i and R_i is deduced from Sherman's equation without any approximation. This expression is thus theoretically exact and corrects fully for all matrix effects affecting the intensity R_i emitted by the analyte i in a given specimen. The derivation of the FA was extended from monochromatic to polychromatic excitation sources. It was shown that the FA firmly combines the classical fundamental-parameters approach and the traditional influence coefficient concept, thus establishing a perfect synergy between the two approaches and giving the analyst one of the most valuable methods for mathematical matrix effect corrections. When combined with its innovative calibration procedure [17], comparing measured intensities to calculated intensities, the FA method can be applied to the analysis of any type of sample and offers maximum accuracy in quantitative XRF analysis, limited only by the quality of the sample preparation and the standards used.

The influence coefficients α_{ij} and ε_{ij} deduced at the same time as the FA correct for absorption and enhancement effects, respectively. They are calculated from fully explicit equations, in terms of fundamental parameters only. These equations are the fundamental definitions of coefficients correcting for matrix effects in XRF analysis and permit the establishment of a sound theoretical basis for the concept of the influence coefficient. There is therefore no justification for further use of empirical or semi-empirical coefficients in theory or in analytical practice.

The rewriting of Sherman's equation in the form proposed illustrates clearly and simply all the physical concepts hidden behind so many parameters. In particular, it shows that the α_{ij} and ε_{ij} coefficients are merely the weighted means of all absorption and enhancement effects for all incident wavelengths when a weighting factor W_i is associated with each.

Another useful aspect of the new formalism is that it provides a precise measure of the importance of the matrix effect of each element j on the analyte i and the contribution of each element j to the total matrix effect. In other words, we can accurately quantify all matrix effects caused by element j on

analyte i and thus retain a maximum physical meaning. From a theoretical point of view, it also discredits the all-too-common assumption that the correction for total matrix effect is equal to the sum of the binary corrections, each correction being calculated independently from each other.

In addition, the concept of binary and empirical influence coefficients was discussed, and some algorithms making use of such coefficients were presented. The accuracy obtainable using the different algorithms is very much dependent on the nature of the specimens being analyzed and the concentration range of each analyte. Examples were given and compared for the system Cr–Fe–Ni that is subject to severe absorption and enhancement effects. As a general rule, it is best to make use of an algorithm that corrects for both effects, absorption and enhancement, and in which the magnitude of the influence coefficients can be made to vary with the concentration of the matrix elements. Influence coefficients, except in special and specific circumstances (e.g., limited concentration ranges), are *not* constant, and should not be treated as such if the best results are to be obtained.

It is extremely important to remember that influence coefficients *do not* correct for particle size, mineralogical or surface effects (physical effects). Influence coefficients correct *only* for *matrix effects*, i.e., variations in the chemical composition of unknown samples and reference materials.

Naturally, this new formalism would be of less interest if it were not easily adaptable to practical analytical situations. This can easily be done by using the calibration procedure proposed by Rousseau [4] and the calculation method of sample compositions described in Section 8.

Finally, the new formalism is a powerful, accurate and prolific tool for use, for example, in calculating such varied parameters as the *basic*, *modified* and *hybrid influence coefficients* (after the terminology of Lachance [34]), which can be applied to many kinds of samples (alloy, rock, ore, cement, etc.), to check the accuracy of a given algorithm when it is applied to a specific series of samples, to calculate the influence coefficients correcting for volatile products lost during the preparation of fused discs, and so on. Briefly, its use can be only of benefit to the work of any XRF analyst.

The fundamental algorithm is not the only valid solution for calculating sample compositions with the Sherman equation. Some other approaches have also been proposed [25,26]. But in the future, the author believes the ultimate solution will be the one which can eliminate any iteration process and directly calculate the sample composition from a multi-variable analysis method [35], without normalization of intensities or concentrations, respecting at the same time the constraint that the sum of all concentrations must be equal to 100%.

Now, what about the future? With the advent of the 21st century, it is time more than ever to promote modern FP methods. Within the next few years, the author believes traditional FP methods will be abandoned altogether in favor of algorithms using theoretical influence coefficients. To my knowledge, there are presently only three commercial products [25,26,33] on the market which are able to solve correctly the Sherman equation. The author invites the instrument manufacturers to concentrate their efforts on developing new software packages based on

modern FP approaches to supersede obsolete software, and stop trying to promote methods which no longer correspond to modern analytical needs of XRF analysts.

Acknowledgments

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