THE FUNDAMENTAL ALGORITHM:
A NATURAL EXTENSION OF THE SHERMAN EQUATION
PART I: THEORY

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The fundamental algorithm between Ci and Ri in XRF analysis is deduced from Sherman's equation without any approximation, Its explicit expression is thus theoretically exact and it corrects completely for all matrix effects on the intensity Ri emitted by the analyte i in a given specimen. This powerful algorithm combines the practical flexibility of the influence coefficient concept and the theoretical exactness of the fundamental parameter method. In association with its innovative calibration procedure, the Fundamental Algorithm can be applied to the analysis of any sample type and offers maximum accuracy, limited only by the quality of sample preparation and the standards used.

1. Introduction

In 1955, Sherman [1] proposed an equation to calculate net X-ray intensities emitted by each element from a specimen of known composition when this one is irradiated by a polychromatic X-ray beam (see Table 1). This equation is of vital importance in XRF analysis for two main reasons. First, it enables to calculate what we measure. This feature is *unique* to X-ray spectrometry. No other analytical technique allows a such combination of theoretical physics and experimental results. Second, the Sherman equation can provide the *theoretical base* of all modern methods for the correction of matrix effects.

In 1982, for the first time, Rousseau presented the Fundamental Algorithm at the 31st Annual Denver X-Ray Conference, and three different papers [2-4] on this subject were published later (in 1984 and 1986) by the same author. The Fundamental Algorithm completely and accurately corrects all matrix effects that modify the measured net intensity emitted by an analyte *i* in a given specimen analyzed by X-ray fluorescence (XRF) spectrometry. It was directly deduced from the Sherman equation following an algebraic manipulation, with no approximation at all during the process of derivation. It is thus the same Sherman equation expressed in another form. Both expressions exactly represent the same relationship between net X-ray fluorescence intensity I_i and concentration C_i of the analyte *i*, but are expressed in

different ways. The Fundamental Algorithm is a realistic approach that considers the polychromatic incident radiation, 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 a *natural* extension of the Sherman equation.

In the 30-year period between the publications of Beattie and Brissey [5] in 1954 and Rousseau [2] in 1984, although both methods are based on the Sherman equation, mathematical methods were developed in response to modern needs for speed and accuracy in XRF analysis. The final answer to this development was the Fundamental Algorithm proposed by Rousseau. Presently, it incorporates all the theoretical knowledge on matrix effect corrections. Furthermore, it indissolubly links the classical fundamental parameter method [6] and the traditional influence coefficient concept [7-9], thus restoring a perfect complementarity between the two approaches and giving the analyst the ultimate method for mathematical matrix effect corrections.

The aim of this paper is to deduce the mathematical expression of the Fundamental Algorithm and to show its beauty, its physical sense and its practical utility. A further aim is to show that the Fundamental Algorithm is still the best expression of explaining all physical phenomena in XRF analysis and that, when combined with its innovative calibration procedure [3], it offers maximum accuracy in quantitative XRF

Table 1. Sherman's equation and definition of symbols.

$$I_i(\lambda_i) = g_i C_i \int_{\lambda_0}^{\lambda_{edge\,i}} \frac{I_0(\lambda)\mu_i(\lambda)}{\mu'_s(\lambda) + \mu''_s(\lambda_i)} \Big[1 + \sum_j C_j \delta_{ij}(\lambda)\Big] d\lambda \qquad (1)$$

where

$$\mu'_s(\lambda) = \sum_{n=1}^{N} C_n \mu_n(\lambda)\csc\phi'$$

$$\mu''_s(\lambda_i) = \sum_{n=1}^{N} C_n \mu_n(\lambda_i)\csc\phi''$$

$$\delta_{ij}(\lambda) = \frac{1}{2} D_j(\lambda) \cdot D_i(\lambda_j) \cdot k_j \lambda_j(\lambda) \frac{\mu_j(\lambda_j)}{\mu_i(\lambda)} P_{ij}(\lambda)$$

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

$$P_{ij} = \frac{1}{\mu'_s(\lambda)} \ln\Big[1 + \frac{\mu'_s(\lambda)}{\mu_s(\lambda_j)}\Big] + \frac{1}{\mu''_s(\lambda_i)} \ln\Big[1 + \frac{\mu''_s(\lambda_i)}{\mu_s(\lambda_i)}\Big]$$

i	Subscript for the analyte
j,k...,N	Subscripts for matrix elements (or compounds)
n	Subscript in summation term representing all elements (or compounds) in the specimen to be treated
s	Subscript for any specimen to be treated
λ_0	Minimum wavelength of the incident radiation
$\lambda_{edge\,i}$	Wavelength of the edge of considered line of analyte i
λ, λ_i	Incident wavelength, wavelength of the characteristic line i
$I_i(\lambda_i)$	Intensity of analyte i in a specimen for a given λ_i
$I_0(\lambda)$	Intensity of excitation source for a given λ
g_i	Proportionality constant, instrument dependent
C_i	Concentration or weight fraction of analyte i (% or fraction)
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_i will be emitted
ϕ', ϕ''	Incidence angle, emergent or take-off angle
$\mu_i(\lambda)$	Mass absorption coefficient of element i for a given λ
$\mu'_s(\lambda)$	Effective mass absorption coefficient of a specimen for incident λ
$\mu''_s(\lambda_i)$	Effective mass absorption coefficient of a specimen for emitted λ_i
D_j	Is unity when the incident wavelength λ can be absorbed by the element j, i.e. If $\lambda \le \lambda_{edge\,j}$; it is zero in all other cases
D_{ij}	Is unity when element j can enhance analyte i, i.e. if $\lambda_j \le \lambda_{edge\,i}$; it is zero in all other cases

analysis, limited only by the quality of sample preparation and the standards used.

2. Another Theoretically Valid Representation of the Sherman Equation

The quantitative XRF analysis is the only technique that enables to calculate completely from theory what we measure. Indeed, in 1955, Sherman [1] prophetically proposed a mathematical equation to calculate net X-ray fluorescence intensities emitted by each element in a specimen of a known composition when this one is irradiated by a polychromatic X-ray beam. Later, this equation was corrected by Shiraiwa and Fujino [10] who discovered a missing factor of 1/2 in the enhancement part of Sherman's equation. Equation (1) is the expression used to calculate the net intensity of the X-ray fluorescence radiation emitted

by an element i in a specimen containing several other elements j and bombarded by a polychromatic incident radiation. The tertiary X-ray fluorescence intensity will not be considered here because its value is usually very small and its mathematical treatment is complex and would not help in understanding the present approach.

In the equation (1), the contribution of δ_{ij} to intensity I_i by the enhancement of element j becomes a sum when there is more than one enhancing line from j, such as $K\alpha$ and $K\beta$, i.e.,

$$\delta_{ij} = \sum_j \delta_{ij} \qquad (2)$$

However, when a $K\alpha$ line may enhance the measured $L\alpha_1$ or the $L\beta_2$ line of the SAME element j, this contribution (at the most 2-3% of total intensity) is neglected because of the complexity of the calculation. For example, the $BaK\alpha$ line enhances the measured $BaL\alpha_1$ line when the tube voltage is > 40 kV. This omission is more or less compensated by the calibration procedure [3] owing to the use of a "comparison standard" approach. The enhancement effect of a $K\alpha$ line on the $L\alpha_1$ line of the same element can also be eliminated by reducing the tube voltage to a value lower than the binding energy of the K shell or simply by using the $K\alpha$ line rather than the $L\alpha_1$ line as the analytical line for the element to be determined.

The coefficient $D_i(\lambda_j) = 1$ if element j enhances element i, i.e., if wavelength λ_j is less than the wavelength of the K absorption edge of element i. If not, $D_i(\lambda_j) = 0$. The same applies to the coefficient $D_j(\lambda)$. All other terms have already been explained or can easily be interpreted.

The X-ray fluorescence intensity can be calculated from the full physical equation (1) using *fundamental parameters*, which include the X-ray tube spectrum, mass absorption coefficients, fluorescence yields and Coster-Kronig transition probabilities. In practice, the equations proposed by Pella et al. [11] are used to calculate up to 350 different intensities of the incident polychromatic spectrum emitted by the X-ray tube. Data from Heinrich [12] are used to calculate mass absorption coefficients by means of a method proposed by Springer and Nolan [13]. Modern values of X-ray fluorescence yields [14,15] and Coster-Kronig transition probabilities [16] are also used.

Equation (1) also requires as parameters the incidence and take-off angles for the instrument used to acquire X-ray intensities. A list of such angles for many commercial X-ray spectrometers has been published by Leyden and Bilbrey [17].

As can be seen from equation (1), the large number of fundamental parameters involved, and especially the polychromaticity of the incident radiation used to excite the fluorescence radiations, make this equation complex and difficult to handle. Furthermore, it has no clear relationship with the physical phenomena involved in XRF analysis. The Sherman equation will therefore be completely rewritten so as to facilitate its practical use and reveal information on the basic rules governing matrix effect corrections.

The first fundamental parameter needed to calculate the intensity from element i with equation (1) is the spectral distribution of the incident radiation. However, there is no analytical expression available to generate an incident spectrum in an essentially exact way, for any experimental conditions. Also, in order to be able to use the equations of the X-ray tube output proposed by Pella et al. [11], the integral over λ is replaced here by a finite sum of k values of wavelength intervals $\Delta\lambda_k$ with corresponding incident intensities $I_0(\lambda_k)$:

$$\int_{\lambda_{min}}^{\lambda_{edge\,i}} I_0(\lambda)d\lambda \rightarrow \sum_{k=\lambda_{min}}^{\lambda_{edge\,i}} I_0(\lambda_k)\Delta\lambda_k$$

By doing this, we ensure that equation (1) and the following equations remain basically the same, enabling to calculate the integral without having to express the intensity $I_0(\lambda)$ in an explicit form.

The total emitted intensity for the polychromatic incident source may be visualized as a sum of individual intensities, each being due to individual incident radiation λ_k, over the effective excitation range λ_{min} to $\lambda_{edge\,i}$. The concept of summing over a finite number of wavelength intervals was first proposed by Gilfrich and Birks [18] in 1968, and remains at the root of all "fundamental parameter" methods. These authors suggested dividing the polychromatic incident beam into a number of discrete wavelength intervals of 0.02 Å. The emitted intensity at the middle of each $\lambda + \Delta\lambda$ interval was then measured. 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.

Thus, if the integral in the equation (1) is replaced by a sum of k values of finite interval $\Delta\lambda$, we obtain:

$$I_i(\lambda_i) = g_i C_i \sum_{\lambda_k=\lambda_{\min}}^{\lambda_{edge\,i}} \frac{\mu_i(\lambda_k)I_0(\lambda_k)\Delta\lambda_k}{\mu_s'(\lambda_k) + \mu_s''(\lambda_i)} \times \left[1 + \sum_j C_j \delta_{ij}(\lambda_k) \right] \quad (3)$$

To simplify this equation, two new variables (β_{ij} and W'_i) will be introduced. To define these two variables, we need to consider the *effective mass absorption coefficients*. In this expression, the word "effective" designates the quantification of the TOTAL absorption of specific wavelengths 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. Thus, the following definitions:

$$\mu_i' = \mu_i(\lambda_k) \times \csc\phi'; \mu_j' = \mu_j(\lambda_k) \times \csc\phi' \quad (4)$$

$$\mu_i'' = \mu_i(\lambda_i) \times \csc\phi''; \mu_j'' = \mu_j(\lambda_i) \times \csc\phi'' \quad (5)$$

$$\mu_\sigma' = \sum_{n=i}^{N} C_n \mu_n' \quad (6)$$

$$\mu_s'' = \sum_{n=i}^{N} C_n \mu_n'' \quad (7)$$

$$\mu_i^* = \mu_i' + \mu_i''; \mu_j^* = \mu_j' + \mu_j''; \mu_s^* = \mu_s'\mu_s'' \quad (8)$$

where csc ϕ' and csc ϕ'' are the cosecants of the incident angle ϕ' and the take-off or emergent angle ϕ'', respectively. The specimen mass absorption coef-
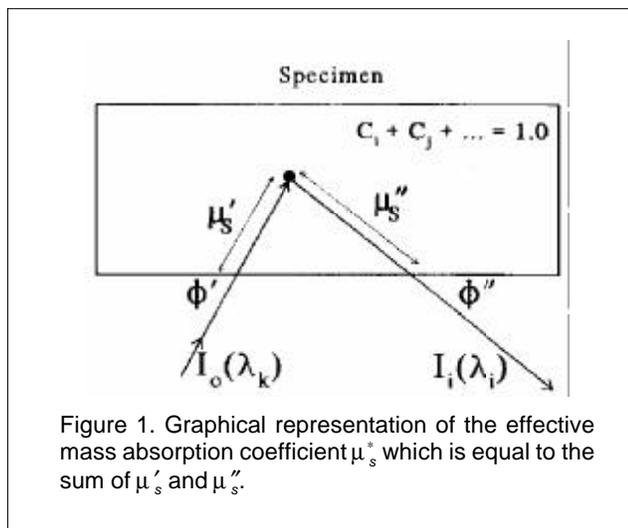

Figure 1. Graphical representation of the effective mass absorption coefficient μ_s^* which is equal to the sum of μ_s' and μ_s''.

ficients μ'_s and μ''_s are graphically represented by Fig. 1.

The equation of the effective mass absorption coefficient can be transformed as follows:

$$\mu_s^* = \mu_s'(\lambda_k) + \mu_s''(\lambda_i)$$
$$= \sum_n C_n \mu_n(\lambda_k)\csc\phi' + \sum_n C_n \mu_n(\lambda_i)\csc\phi''$$
$$= \sum_n C_n \left[\mu_n(\lambda_k)\csc\phi' + \mu_n(\lambda_i)\csc\phi'' \right]$$
$$= \sum_n C_n \left[\mu_n^* \right] = C_i\mu_i^* + C_j\mu_j^* + C_k\mu_k^* + ... + C_N\mu_N^*$$
$$= \mu_i^* \left[C_i + C_j\frac{\mu_j^*}{\mu_i^*} + C_j\frac{\mu_k^*}{\mu_i^*} + ... + C_N\frac{\mu_N^*}{\mu_i^*} \right]$$

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

$$\sum_{n=i}^{N} C_n = 1 \quad (9)$$

we have

$$C_j = 1 - C_j - C_k - ... - c_N$$

then

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

Defining the following variable:

$$\beta_{ij}(\lambda_k) = \frac{\mu_j^*}{\mu_i^*} - 1 \quad (10)$$

where

$$\mu_j^* = \mu_j(\lambda_k)\csc\phi' + \mu_j(\lambda_i)\csc\phi'' \quad (11)$$

$$\mu_i^* = \mu_j(\lambda_k)\csc\phi' + \mu_i(\lambda_i)\csc\phi'' \quad (12)$$

this produces

$$\mu_s^* = \mu_i^* \left[1 + \sum_j C_j \beta_{ij}(\lambda_k) \right] \quad (13)$$

Note that the variable $\beta_{ij}(\lambda_k)$, as we will see later, is defined as the absorption influence coefficient in the case of a monochromatic incident source of wavelength λ_k. This coefficient corrects for the absorption effects of the matrix element j on the analyte i and can be positive or negative. If the equation (10) is rewritten in the following form:

$$\beta_{ij}(\lambda_k) = \frac{\mu_j^* - \mu_i^*}{\mu_i^*} \qquad (14a)$$

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 matrix composition. For example, if Fe is determinate in the presence of Mg, a *lighter matrix element*, then $\mu_i^* > \mu_j^*$ and $\beta_{ij}(\lambda_k)$ is *negative*. If Fe is determinate in the presence of Ni, a *heavier matrix element*, then $\mu_i^* < \mu_j^*$ and $\beta_{ij}(\lambda_k)$ is *positive*.

Furthermore, the coefficient $\beta_{ij}(\lambda_k)$ is the ratio of the *difference* between the mass absorption coefficients of elements *j* and *i* *relative* to the mass absorption coefficient of element *i*. In other words, the coefficient $\beta_{ij}(\lambda_k)$ shows how much grater or smaller the absorption of element *j* is compared to that of element *i*. It thus expresses a *relative* value. The relative absorption of element *i* compared to itself is therefore equal to zero. Indeed,

$$\beta_{ij}(\lambda_k) = \frac{\mu_i^* - \mu_i^*}{\mu_i^*} = 0 \qquad (14b)$$

In the following prargraphs, we will continue to modify Sherman's equation (1) so as to make it easier to understand and manipulate. Defining a second variable:

$$W_i(\lambda_k) = \frac{\mu_i(\lambda_k)}{\mu_i^*} I_0(\lambda_k)\Delta\lambda_k \qquad (15)$$

and combining equations (3), (8), (13) and (15) leads to

$$I_i(\lambda_i) = g_i C_i \sum_{\lambda_k=\lambda_{min}}^{\lambda_{edge\,i}} W_i(\lambda_k)\frac{1+\sum_j C_j\delta_{ij}(\lambda_k)}{1+\sum_j C_j\beta_{ij}(\lambda_k)} \qquad (16)$$

This equation is still the same Sherman equation (1) but in a severely modified form. It could be referred to as the "Modified Sherman Equation". In this form, the Sherman equation is already simpler and more revealing. 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* of the matrix, and the denominator contains all the absorption coefficients β_{ij} of each element *j*. Thus the reader can easily guess that intensity 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.

3. The Relative Intensity

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

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

where $I_{(i)}(\lambda_i)$ 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 Equation (16) becomes

$$I_{(i)} = g_i \sum_k W_i(\lambda_k) \qquad (18)$$

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

$$R_i = C_i \frac{\sum_k W_i(\lambda_k)\dfrac{1+\sum_j C_j\delta_{ij}(\lambda_k)}{1+\sum_j C_j\beta_{ij}(\lambda_k)}}{\sum_k W_i(\lambda_k)} \qquad (19)$$

or

$$R_i = C_i \frac{\sum_k W_i(\lambda_k)M_i(\lambda_k)}{\sum_k W_i(\lambda_k)} \qquad (20)$$

where in a given specimen, all matrix effects influencing the intensity of the analyte *i*, for each incident wavelength λ_k, can be calculated by the factor

$$R_i = C_i \frac{1+\sum_j C_j\delta_{ij}(\lambda_k)}{1+\sum_j C_j\beta_{ij}(\lambda_k)} \qquad (21)$$

The equation (20) reveals that the relative intensity R_i is a function of a ratio, that is the weighted mean of all matrix effects on the analyte *i* for a polychromatic incident source, where to each incident wavelength λ_k is given a weight $W'_i(\lambda_k)$.

Some analysts might be worried by the fact that the relative intensity R_i is defined as the ratio of I_i to $I_{(i)}$, the intensity of the pure analyte. In practice, the pure

specimen is not always available. In such situations, the calibration procedure [3] enables to determine the intensity of the pure analyte from multi-element standards. This intensity is simply equal to the slope of the calibration curve.

4. Deduction of the Fundamental Algorithm

Equation (19) of the relative intensity can be rewritten in the following form:

$$\frac{C_i}{R_i} = \frac{\sum_k W_i(\lambda_k)}{\sum_k W_i(\lambda_k)\frac{1+\sum_j C_j \delta_{ij}(\lambda_k)}{1+\sum_j C_j \beta_{ij}(\lambda_k)}}$$

The value of each term W_i at the numerator is not changed if, for each wavelength λ_k, it is multiplied by the ratio

$$\frac{1+\sum_j C_j \beta_{ij}(\lambda_k)}{1+\sum_j C_j \beta_{ij}(\lambda_k)}$$

which is equal to one. We have then,

$$\frac{C_i}{R_i} = \frac{\sum_k W_i(\lambda_k)\frac{1+\sum_j C_j \beta_{ij}(\lambda_k)}{1+\sum_j C_j \beta_{ij}(\lambda_k)}}{\sum_k W_i(\lambda_k)\frac{1+\sum_j C_j \delta_{ij}(\lambda_k)}{1+\sum_j C_j \beta_{ij}(\lambda_k)}}$$

In the last equation, the term

$$W_i(\lambda_k)\frac{1}{1+\sum_j C_j \beta_{ij}(\lambda_k)}$$

is present at the numerator and the denominator. If this expression is defined as a new weighting factor, $W_i(\lambda_k)$, and recalling the equation (15), we have:

$$\begin{aligned}W_i(\lambda_k) &= \frac{W_i(\lambda_k)}{1+\sum_j C_j \beta_{ij}(\lambda_k)}\\ &= \frac{\mu_i(\lambda_k)I_0(\lambda_k)\Delta\lambda_k}{\mu_s\left[1+\sum_j C_j \beta_{ij}(\lambda_k)\right]}\end{aligned} \qquad (22)$$

We obtain

$$\frac{C_i}{R_i} = \frac{\sum_k\left\{W_i(\lambda_k)\left[1+\sum_j C_j \beta_{ij}(\lambda_k)\right]\right\}_k}{\sum_k\left\{W_i(\lambda_k)\left[1+\sum_j C_j \delta_{ij}(\lambda_k)\right]\right\}_k}$$

If in the last equation the square brackets are removed in both the numerator and denominator, and each term is divided by $\sum_k W_i(\lambda_k)$, we finally obtain

$$C_i = R_i\frac{1+\sum_j \alpha_{ij}C_j}{1+\sum_j \varepsilon_{ij}C_j} \qquad (23)$$

with

$$\alpha_{ij} = \frac{\sum_k W_i(\lambda_k)\beta_{ij}(\lambda_k)}{\sum_k W_i(\lambda_k)} \qquad (24)$$

and

$$\varepsilon_{ij} = \frac{\sum_k W_i(\lambda_k)\delta_{ij}(\lambda_k)}{\sum_k W_i(\lambda_k)} \qquad (25)$$

The reader must realize that equation (23) is exactly the same as equation (1) proposed by Sherman in 1955. Equation (23) has been obtained after a long algebraic manipulation from the equation (1), without any approximation. The only difference is that equation (23) allows us to calculate the concentration C_i from the measured relative intensity R_i, which is corrected for matrix effects by the ratio on the right-hand side of the equation. Henceforth, if we accept the fundamental nature of the Sherman equation, equation (23) can be referred to as the "*Fundamental Algorithm*", where equations (24) and (25) are the fundamental explicit equations used to calculate the coefficients correcting for absorption and enhancement effects, respectively. We will see why in the next section.

5. Physical Interpretation

As it stands, the Fundamental Algorithm (Eqn 23) contains all that is needed to calculate a sample composition from X-ray intensities and also provides a complete and accurate correction for all matrix effects. This relation is theoretically exact since it has been deduced from the Sherman equation without any approximation during the process of derivation. Moreover, if we accept the fundamental nature of the Sherman equation in XRF, it follows that equation (23), being derived directly from the Sherman equation, must also be recognized as fundamental. Thus, equation (23) can be considered the unique fundamental and theoretically exact algorithm linking concentration and intensity in XRF analysis.

The physical interpretation of the Fundamental Algorithm (Eqn 23) is quite simple and elegant. To a

first approximation, equation (23) 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. In fact, the coefficient α_{ij}, calculated from the β_{ij} and W_{ij} coefficients, includes all mass absorption coefficients μ_s^* (when there is no enhancement) of the Sherman equation. Therefore, we can affirm that the α_{ij} coefficient corrects for all absorption effects caused by element j on analyte i and the numerator of the ratio corrects thus 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 lower if the matrix is less absorbent than the analyte), the intensity R_i will be increased by a quantity equivalent to that absorbed by the matrix. Briefly then, the α_{ij} coefficient corrects for absorption effects and its only acceptable theoretical definition is given by equation (24).

Now, if some elements of the matrix are able to enhance the analyte i, the corresponding coefficient ε_{ij}, deducted from δ_{ij}, will be different from zero and always positive. Therefore, we can affirm that the ε_{ij} coefficient corrects for all enhancement effects causes by element j on analyte i and the denominator of the ratio corrects thus for all enhancement effects of the matrix, each element j bringing its contribution to the total correction in a proportion C_j. In this case, the denominator will be greater than unity and the intensity R_i will be reduced by a quantity equivalent to that caused by the enhancement. Thus, the ε_{ij} coefficient corrects for enhancement effects and its only acceptable theoretical definition is given by equation (25).

Since the numerator of the Fundamental Algorithm corrects for all absorption effects of the matrix on the analyte and since the denominator corrects for all enhancement effects, the form of this equation makes it easier to understand the physical principles behind the complex equation of Sherman.

Note that the concentration C_i of the analyte i does not appear in the ratio of the Fundamental Algorithm. At the numerator, the α_{ij} coefficient is equal to zero because the coefficient β_{ij} expresses a difference between the mass absorption coefficients μ_j^* and μ_i^* as a ratio to μ_i^* (therefore $\beta_{ii} = \mu_i^* - \mu_i^* / \mu_i^* = 0$). At the denominator, the ε_{ii} coefficient is also equal to zero because an element cannot enhance itself, except in the case (rare in most analytical situations) where a

Kα line can enhance significantly the Lα_1 line of the same element. However, as explained previously, such a situation can be ignored.

Now that we have a better understanding of the Fundamental Algorithm, let us take a closer look at the α_{ij} and ε_{ij} equations. First, we should remember that in statistics, if each value x_i is associated with a weighting factor $w_i > 0$, then the weighted mean $\bar{x}$ is calculated by

$$\bar{x} = \frac{\sum_i w_i x_i}{\sum_i w_i} \tag{26}$$

Equations (24) and (25) have precisely the same form as the equation above. So, by analogy, we can say that α_{ij} and ε_{ij} are 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 $W_i(\lambda_k)$. But weighted by what and what is included in the W_i factor? Equation (22) for the weighting factor $W_i(\lambda_k)$ can be seen as the product of two terms:

$$W_i(\lambda_k) = \left[\frac{\mu_i(\lambda_k)}{\mu_i^*} I_0(\lambda_k) \Delta \lambda_k \right] \cdot \left[\frac{1}{1 + \sum_j C_j \beta_{ij}(\lambda_k)} \right]$$

The first term gives a weight to each value of the incident intensity $I_0(\lambda_k) \Delta \lambda_k$. The second term weights for each binary combination of elements i and j by the total absorption effect of the matrix. The weighting factor W_i then takes into account the polychromaticity of the incident spectrum and the matrix type of elements i and j, which makes physical sense.

These considerations concerning W_i lead to the two following important conclusions:

1. The α_{ij}, and ε_{ij} coefficients are not constants 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.

2. 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 other matrix elements.

Concerning the quantitative aspect of the α_{ij} and ε_{ij} coefficients, their expressions allow the calculation of all the values needed to correct adequately for matrix effects in a given sample. Thus it is no longer necessary to use empirical or approximate influence coefficients.

6. The Practical Application of the Fundamental Algorithm

When a series of values of the α_{ij} and ε_{ij} coefficients is calculated for a given specimen, these values are valid only for this specific specimen since they depend on the full matrix composition. Any other specimen with the same series of elements, but in different proportions, will need a new set of coefficient values to correct accurately for matrix effects.

Since the α_{ij} and ε_{ij} coefficients depend on the total matrix composition, the composition of each sample must be calculated in the following way: an initial estimate of the composition must be calculated using the Claisse-Quintin algorithm [8]:

$$C_i = R_i \left[1 + \sum_j \left(a_{ij} + a_{ij} j C_m \right) C_j + \sum_{k>j} a_{ijk} C_j C_k \right] \quad (27)$$

where C_m is the concentration of the total matrix, and a_{ij}, a_{ijj}, and a_{ijk} are binaries (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 part of Sherman's equation, are calculated once only. With these calculated coefficients now used as constants, the final (and more accurate) composition of the sample is calculated by applying an iteration process to the Fundamental Algorithm.

To apply this method in practice, a commercial software package known as CiROU was developed by one of the authors (R.M.R.). For more information on this program, please contact the author.

The Fundamental Algorithm method has the following clear advantages:

1. Since the numerator of equation (23) corrects for all the absorption effects of the matrix on the analyte and since the denominator corrects for all the enhancement effects, the form of equation (23) makes it much easier

to understand the physical principles behind the complex equation of Sherman. Consequently, its great beauty lies in its perfect symmetry.

2. For the first time, it enabled to deduce the concept of influence coefficients directly from the Sherman equation without any approximation. It proposes the fundamental, unique and explicit equations for calculating the α_{ij}, ε_{ij} coefficients, only in terms of fundamental parameters.

3. The equations of the α_{ij}, ε_{ij} coefficients reveal that they are the weighted means of all absorption and enhancement effects, respectively, caused by element j on analyte i in a given specimen. They also introduce a weighting factor for each incident wavelength λ_k of the incident spectrum.

4. Empirical coefficients are no longer required. The Fundamental Algorithm uses only theoretical influence coefficients that are in full agreement with the treatment of physics as proposed by Sherman. They are calculated for each sample composition, increasing the accuracy in so doing.

5. This method also uses a fully theoretical approach to calculate all the required parameters. For example, the method uses equations proposed by Pella et al. [11] to calculate up to 350 different intensities of the incident spectrum emitted by the X-ray tube. It uses data from Heinrich [12] to calculate mass absorption coefficients by a method proposed by Springer and Nolan [13]. It also uses modern values of X-ray fluorescence yields [14, 15] and Coster-Kronig transition probabilities [16].

6. The method can be used in practice to calculate the composition of any sample type, of any composition, i.e., for concentration ranges varying from 0 to 100%. It introduces a theoretical mean relative error of 0.05% only. An experimental verification of this method done by Rousseau and Bouchard [4] on different types of alloy has confirmed its accuracy and versatility.

7. In contrast to the fundamental parameter method, it directly calculates concentrations

rather than intensities, and the calculation technique has been optimized.

8. Normalization of calculated concentrations is no longer required. Since the complex part of Sherman's equation is calculated once only, the calculation time is greatly reduced.

9. It allows deduction of other theoretically valid algorithms, such as the Lachance-Traill [7] or the Claisse-Quintin [8] algorithms. In other words, it can be the source of all modern methods to correct for matrix effects.

10. It takes advantage of 30 years of research and development on mathematical models for matrix effect corrections (see section 8).

However, this theoretical approach needs to be adapted to the experimental data of each spectrometer, since theory cannot account for all the instrumental parameters. It is done through a smart calibration procedure that compares the measured intensities to the calculated intensities [3].

7. Limitations of the Fundamental Algorithm

As pointed out by Criss [19], it is assumed for the calculation of influence coefficients in the Fundamental Algorithm that the incident radiation is parallel, the X-rays travel effectively in straight line within the specimen until they are absorbed, only one level of enhancement can occur, there is no scattering of X-ray fluorescence intensities, and all measured fluorescence X-rays exit the specimen at the same angle. Clearly, the mathematical model proposed by Sherman is not strictly correct: it is even imperfect. Furthermore, there are many effects that the model does not address at all. For example, it does not account for the X-ray tube current, various solid angles, the reflectivity of the analyzing crystal and the detector efficiency. The l/r^2 dependence of intensity on distance from the target is also ignored. No mathematical model can account perfectly for all the subtleties of instrument response and X-ray interactions within the specimen. However, experience shows that the model performs very well in practice and all these approximations or ignored effects can be compensated by using an appropriate calibration procedure as explained below.

Another practical problem common to all purely fundamental approaches is the inevitable uncer-

tainties affecting the fundamental and instrumental parameters. With the Fundamental Algorithm this problem is largely compensated by using every fundamental or instrumental parameter as a ratio. For example, consider the absorption influence coefficient for a monochromatic incident radiation of wavelength λ_k:

$$\beta_{ij}(\lambda_k) = \frac{\mu_j(\lambda_k)\csc\phi' + \mu_j(\lambda_i)\csc\phi''}{\mu_i(\lambda_k)\csc\phi' + \mu_i(\lambda_i)\csc\phi''} - 1$$

Even in the case where the individual errors on each parameter are high, the practical error introduced by their ratio is found to be negligible.

Furthermore, there are two other potential sources of errors when using fundamental calculations because two other effects are deliberately neglected, namely (a) the occurrence of tertiary X-ray fluorescence, which in severe cases might represent 2-4% of total intensity, and (b) the modification of measured intensities by contributions due to the scattering of both the incident and the fluorescence X-ray radiations inside the specimen. These contributions may also increase the measured intensity by 2-4% over that predicted theoretically. Fortunately, these two effects, together with the others mentioned previously, are largely compensated by the calibration procedure [3]. The slope of the calibration line represents the average intensity of the pure analyte calculated from a number of standard specimens. Depending on the analytical context, this calculated value might be fairly different from the measured value. It is this difference that compensates to a large extent for all the theoretical limitations mentioned above. Thus, the calibration procedure [3] enables the theory to be "adapted" to the experimental data generated by each spectrometer. In practice, the calibration procedure will inevitably generate different values of the pure analyte intensity for the same set of experimental data produced by different spectrometers. In other words, it is equivalent to *rescaling* the theoretical calculations by a factor, the slope of the calibration line, to match reality.

The calibration procedure associated with the Fundamental Algorithm enables each analyte to be calibrated over wider ranges of concentration and require only a handful of good standards. However, the complete composition of each standard is needed because the analyte line intensity is affected by the concentration of all the elements present in the

specimen. If only 98% or 99% of the composition of a standard is certified, it will have limited capability for accurately calculating all the corrections for matrix effects, because the matrix composition is not well known.

The Fundamental Algorithm does not correct for instrumental and physical effects. Instrumental effects, such as background, overlaps and dead time, must be reduced to a strict minimum by careful selection of measurement conditions. When instrumental effects are unavoidable, it is necessary to make specific corrections for background, overlaps and dead time before treating matrix effects. The Fundamental Algorithm does not also correct for physical effects, such as variations of particle size, mineralogical or surface effects, but only for variations in the chemical composition of the samples or standards, i.e., for elemental interactions. However, these limitations can easily be overcome by an appropriate sample preparation.

8. Origin of the Fundamental Algorithm

The Fundamental Algorithm (FA) is the synthesis of 30 ears of research and development on the correction of matrix effects in XRF analysis. A list of XRF scientists and a brief description of their main contributions to the Fundamantal Algorithm, together with the publication year, is presented below. The ideas mentioned have been incorporated in the Fundamental Algorithm in one way or another, and have helped make the FA the most efficient method of correcting for matrix effects. They are:

1955 Sherman's equation [1]

1966 Lachance and Traill [7] (LT):

    Concept of the influence coefficient

    Absorption influence coefficients $\left(\beta_{ij} = \mu_j^*/\mu_i^* - 1\right)$ for a monochromatic incident source

    Unique solution for each calculated sample composition

    During the concentration calculation, there is no need for normalization

1967 Claisse and Quintin [8] (CQ):

    Generalization of the LT method for matrix effect corrections

    Introduce the weighting factor for each incident λ_k

    Influence coefficients vary with concentrations

1968 Gilfrich & Birks [18]: the first measured incident spectrum

    Criss & Birks [6]: the fundamental parameter method

    Show how to use Sherman's equation in practice

1970 Rousseau's Master's thesis [20]:

    For the first time, proposes the FA for a monochromatic incident excitation source

1973 de Jongh [21]:

    Theoretical multi-element influence coefficients can be calculated

    Calibration: measured intensities versus calculated intensities (or *apparent concentration*)

    Ignores one analyte during the analytical process

1974 Rousseau and Claisse [8]:

    Proposes a new method to calculate theoretical binary influence coefficients in the CQ algorithm

1976 Tertian [22]:

    Introduces the C_M factor in the CQ algorithm

1980 Criss [23]:

    Proposes calculation of an initial estimate of the sample composition for calculating the α_{ij} and ε_{ij} coefficients once

1982 Rousseau:

First public presentation of the FA at the 31st Annual Denver X-Ray Conference

1984 Rousseau [2]:

First publication on the Fundamental Algorithm

1985 Pella, Feng and Small [11]:

Calculated intensities for the incident spectrum

9. A Physical Demonstration of the Fundamental Algorithm

A more "physical" demonstration of the Fundamental Algorithm is as follows. In 1966, Lachance and Traill [7] proposed the following definition of the absorption influence coefficient for a monochromatic incident source of wavelength λ_k:

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

where

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

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

The $\beta_{ij}(\lambda_k)$ coefficient corrects for the absorption effect of the matrix element j on the analyte i when the incident X-ray source is monochromatic. In 1984, Rousseau [2] generalized this definition for a polychromatic incident source:

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

where

$$W_i(\lambda_k) = \frac{\mu_i(\lambda_k)}{\mu_i^*} \cdot \frac{I_0(\lambda_k)\Delta\lambda_k}{1 + \sum_j C\beta_{ij}(\lambda_k)}$$

is the weighting factor of each wavelength λ_k of the incident X-ray spectrum. The α_{ij} coefficient is the weighted mean of all the absorption effects caused by matrix element j on analyte i in a given specimen when it is bombarded by a polychromatic incident spectrum. The value of the α_{ij} coefficient is unique and fundamental for a given set of experimental conditions and for a given specimen. Note that the

coefficient $\beta_{ij}(\lambda_k)$ is a binary coefficient depending only on elements i and j. On the other hand, the coefficient α_{ij} is a multi-element coefficient depending on the full matrix composition including element j.

If there is no enhancement, the concentration C_i is calculated by the following algorithm:

$$C_i = R\left(1 + \sum_j \alpha_{ij}C_j\right)$$

which has the same form as the Lachance-Traill algorithm [7]. In the general case where both matrix effects, absorption and enhancement are present, this latter algorithm becomes

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

which is the Fundamental Algorithm where

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

The ε_{ij} coefficient is the weighted mean of all the enhancement effects caused by matrix element j on analyte i in a given specimen when it is bombarded by a polychromatic incident spectrum. The value of the ε_{ij} coefficient is unique and fundamental for a given set of experimental conditions and for a given specimen.

As demonstrated, the Fundamental Algorithm is the generalization of the Lachance-Traill algorithm when the specimen is bombarded by a polychromatie incident spectrum and where both matrix effects, absorption and enhancement, are present. The α_{ij} and ε_{ij} coefficients are multi-element coefficients depending on the full matrix composition of each specimen.

10. Why the Fundamental Algorithm is so Fundamental

To earn the label "fundamental", an algorithm must have so many attributes that for many years such a possibility was believed to be a figment of the imagination, or an impossible dream...

First, let us define the meaning of the word "fundamental" by giving an example. The *fundamental unit of time* is the second (s) which is defined as the time interval equal to 9,192,631,770 periods of

the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium-133 atom. Although arbitrary, this is the modem convention selected by the scientific community to measure the length of time, in terms of which all other derived units can be expressed. In other words, a fundamental concept is the basic raw material, or the foundations, on which is built any theory. Another important point is that this definition must be UNIQUE. If the second were to be defined in different ways, by different lengths of time, confusion would obviously result. As a consequence, the minute, hour, day, week, etc. are all different units of time, but they are not fundamental. They are simply multiples or derived units of the fundamental value (the second).

By analogy, the same argumentation can be applied to algorithms relating concentrations and intensities in XRF analysis. Many XRF algorithms are theoretically valid, but only ONE can be fundamental. It should be noted that there is no consensus among XR.P scientists on this point. Not all of them agree on the number of such algorithms, nor on the criteria for selecting THE ONLY fundamental algorithm. Indeed, some support the existence of many fundamental algorithms. However, the rules given here will demonstrate, the authors like to hope, the existence of one *true* and unique fundamental algorithm.

The algorithm proposed by Rousseau (Eqn 23) is fundamental because:

> 1. It is a solid theoretical foundation based on all concepts and knowledge accumulated to date on quantitative XRF analysis. To confirm this, the reader is invited to review sections 4, 5, 8, 9 and 11.

> 2. It is in full agreement with the treatment of the physical process as proposed by Sherman and can be applied to the analysis of any sample type.

> 3. Its shape makes it much easier to understand the physical principles behind the complex equation of Sherman.

> 4. It proposes explicit equations to calculate influence coefficients correcting for both matrix effects, absorption and enhancement, only in terms of fundamental parameters. These equations are the fundamental definitions of the influence coefficients

correcting for matrix effects in XRF analysis and therefore permit the establishment of a sound theoretical basis for the concept of correcting influence coefficients.

5. These equations have finally enabled to understand the complete physical mechanism of matrix effect correction. In particular, for the first time the α_{ij} and ε_{ij} coefficient equations have shown that influence coefficients are merely the weighted means of all absorption and enhancement effects, respectively, caused by element *j* on analyte *i*, where the weighting factor $W_i(\lambda_k)$ is associated with each incident wavelength λ_k.

6. It can be used to deduce ALL the other theoretically valid algorithms. It must serve as the basic reference for testing the validity of any other algorithm. It must be the source for generating any new algorithm or relation to meet specific needs (see the next section).

Only the Rousseau algorithm has ALL these features. It is thus not too strong a statement to claim that the Rousseau algorithm is THE Fundamental Algorithm rather than A fundamental algorithm among others.

11. Deduction of Other Algorithms from the FA

One of the nice properties of the Fundamental Algorithm (FA) is that any other proposed and theoretically valid algorithm can be directly deduced from it. To illustrate this fact, two popular algorithms are considered, i.e., those of Lachance and Traill [7] (LT) and Claisse and Quintin [8] (CQ). Even the identities proposed by Tertian [24] in 1983 and Lachance [25] in 1988 can be deduced from the FA.

11.1 Deducing the LT Algorithm from the FA

The Lachance-Traill (LT) algorithm [7] can easily be deduced from the Fundamental Algorithm as follows:

$$C_i = R_i \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j} \qquad \text{where} \qquad R_i = \frac{I_i}{I_{(i)}}$$

$$C_i = R_i \left[1 - 1 + \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j} \right]$$

$$C_i = R_i \left[1 + \frac{-1 - \sum_j \varepsilon_{ij} C_j + 1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j} \right]$$

$$C_i = R_i \left[1 + \sum_j \left(\frac{\alpha_{ij} - \varepsilon_{ij}}{1 + \sum_j \varepsilon_{ij} C_j} \right) C_j \right]$$

$$C_i = R_i \left(1 + \sum_j \alpha_{ij}^* C_j \right) \qquad (28)$$

where

$$\alpha_{ij}^* = \frac{\alpha_{ij} - \varepsilon_{ij}}{1 + \sum_j \varepsilon_{ij} C_j} \qquad (29)$$

Equation (28) is the well-known LT algorithm, where the α_{ij}^* coefficient corrects for all matrix effects, absorption and enhancement, of any element j on the analyte i in a given specimen (or in a given matrix). Provided that the α_{ij}^* coefficient is used, the LT algorithm corrects for both types of matrix effects as accurately as the Fundamental Algorithm. However, as such, equation (29,) is of no practical interest. The fact of combining coefficients α_{ij} and ε_{ij} in a single coefficient α_{ij}^* does not contribute to increase the accuracy of the results or the calculation speed. Thus, in practice, the drawback of equation (29) is that it introduces an extra calculation step by merging α_{ij} and ε_{ij}.

11.2 Deducing the CQ Algorithm from the FA

The Claisse-Quintin (CQ) algorithm [8] can easily be deduced from the Fundamental Algorithm as follows:

$$C_i = R_i \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j} \qquad \text{where} \qquad R_i = \frac{I_i}{I_{(i)}}$$

$$C_i = R_i \left[1 + \sum_j \alpha_{ij} C_j \right] \cdot \left[1 - 1 + \frac{1}{1 + \sum_j \varepsilon_{ij} C_j} \right]$$

$$C_i = R_i \left[1 + \sum_j \alpha_{ij} C_j \right] \cdot \left[1 - \frac{\sum_j \varepsilon_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j} \right]$$

$$C_i = R_i \left[\begin{array}{l} 1 + \sum_j \alpha_{ij} C_j - 1 - \sum_j \left(\dfrac{\varepsilon_{ij}}{1 + \sum_j \varepsilon_{ij} C_j} \right) C_j \\[2em] - \dfrac{\left(\sum_j \alpha_{ij} C_j \right) \left(\sum_j \varepsilon_{ij} C_j \right)}{1 + \sum_j \varepsilon_{ij} C_j} \end{array} \right]$$

$$C_i = R_i \left[1 + \sum_j \alpha_{ij}^* C_j - \frac{\left(\sum_j \alpha_{ij} C_j \right) \left(\sum_j \varepsilon_{ij} C_j \right)}{1 + \sum_j \varepsilon_{ij} C_j} \right]$$

where

$$\alpha_{ij}^* = \alpha_{ij} - \frac{\varepsilon_{ij}}{1 + \sum_j \varepsilon_{ij} C_j} \qquad (30)$$

If the third term of the right bracket is expanded, we obtain the CQ algorithm:

$$C_i = R_i \left[1 + \sum_j \alpha_{ij}^* C_j + \sum_j \alpha_{ijj}^* C_j^2 - \sum_j \sum_{k>j} \alpha_{ikj}^* C_j C_k \right] \qquad (31)$$

with

$$\alpha_{ijj}^* = - \frac{\alpha_{ij} \cdot \varepsilon_{ij}}{1 + \sum_j \varepsilon_{ij} C_j}$$

and (32)

$$\alpha_{ijk}^* = - \frac{\alpha_{ij} \cdot \varepsilon_{ik} + \alpha_{ik} \cdot \varepsilon_{ij}}{1 + \sum_j \varepsilon_{ij} C_j}$$

Although the three equations of influence coefficients α^* (Eqns 30 and 32) are of no practical interest because of their complexity, at least this demonstration proves that the "canonical" form of the CQ algorithm (Eqn 31) is theoretically valid when both matrix effects, absorption and enhancement, have to be corrected.

One surprising conclusion from equations (32) is that α_{ijj}^* and α_{ijk}^* become zero when there is no enhancement ($\varepsilon_{ij} = \varepsilon_{ik} = 0$). Thus, the second-order terms disappear and the CQ algorithm becomes the LT algorithm. A detailed indepth study of this subject will be presented in Part II of this paper.

11.3 Deducing the Tertian Identity from the FA

The identity as proposed by Tertian [24] is

$$C_i = R_i \left[1 + \sum_j \left(\alpha_{ij} - \varepsilon_{ij} \frac{C_i}{R_i} \right) \cdot C_i \right] \qquad (33)$$

This equation and the Fundamental Algorithm have been directly deduced from the Sherman equation. We must therefore ensure that they are equivalent. The Fundamental Algorithm (Eqn 23) can be written in the following form:

$$\frac{C_i}{R_i}\left(1+\sum_j \varepsilon_{ij}Cj\right) = 1+\sum_j \alpha_{ij}C_j$$

or

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

or

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

or

$$\frac{C_i}{R_i}=1+\sum_j \left(\alpha_{ij}-\varepsilon_{ij}\cdot\frac{C_i}{R_i}\right)\cdot C_j \tag{34}$$

which is the Tertian identity. Equations (23) and (33) are then equivalent on the algebraic level but are far from delivering the same message on the physical level. Thus, the term C_i/R_i appears on both sides of equation (34). General equations of type

$$A=A+B-B \tag{35}$$

are not very useful in practice, teach nothing new, are pure algebraic artifices and finally make no physical sense.

In contrast to the Fundamental Algorithm, the Tertian identity cannot easily be physically interpreted. Indeed, it is difficult to decipher the physical meaning of the term

$$\varepsilon_{ij}\cdot\frac{C_i}{R_i} \tag{36}$$

This leads us to conclude that the Tertian identity (Eqn 33), even if correct on the algebraic level, reveals nothing new on physical phenomena in XRF analysis and as such is of no interest.

11.4 Deducing the Lachance Identity from the FA:

The Lachance identity [25] can easily be deduced from the Fundamental Algorithm as follows:

$$C_i = R_i \frac{1+\sum_j \alpha_{ij}C_j}{1+\sum_j \varepsilon_{ij}C_j} \qquad \text{where} \qquad R_i = \frac{I_i}{I_{(i)}}$$

$$C_i = R_i\left[1-1+\frac{1+\sum_j \alpha_{ij}C_j}{1+\sum_j \varepsilon_{ij}C_j}\right]$$

$$= R_i\left[1+\frac{-1+\sum_j \varepsilon_{ij}C_j+1+\sum_j \alpha_{ij}C_j}{1+\sum_j \varepsilon_{ij}C_j}\right]$$

$$C_i = R_i+\left[\frac{R_i}{1+\sum_j \varepsilon_{ij}C_j}\right]\cdot\left[\sum_j \alpha_{ij}C_j - \sum_j \varepsilon_{ij}C_j\right]$$

where the relative intensity $\qquad R_i = \frac{I_i}{I_{(i)}} = \frac{P_i+S_i}{P_{(i)}}$

Where P_i primary fluorescence intensity

$\qquad S_i$ secondary fluorescence intensity (enhancement)

$\qquad P_{(i)}$ primary intensity of element i in a pure specimen

Therefore,

$$P_{(i)}C_i = (P_i+S_i)+\left[\frac{P_i+S_i}{1+\sum_j \varepsilon_{ij}C_j}\right] \\ \left[\sum_j \alpha_{ij}C_j - \varepsilon_{ij}C_j\right] \tag{37}$$

Lachance [25] demonstrated that the Sherman equation can be written in the following form:

$$P_i = \frac{P_i+S_i}{1+\sum_j \varepsilon_{ij}C_j} \tag{38}$$

Introducing equation (38) into equation (37) leads to

$$P_{(i)}C_i = (P_i+S_i)+P_i\left[\sum_j \alpha_{ij}C_j - \varepsilon_{ij}C_j\right]$$

or

$$P_i+S_i = P_{(i)}C_i - P_i\cdot\sum_j \alpha_{ij}C_j + P_i\cdot\sum_j \varepsilon_{ij}C_j \tag{39}$$

By introducing an equation (Eqn 38) equivalent to the Sherman equation into another equation (Eqn 37) also equivalent to the Sherman equation, we keep going in circles like a dog chasing its tail. We are not moving forward.

The last equation is an identity because the intensity P_i appears on both sides of the equation. Although this equation was deduced by skillful algebraic manipulation, it will be shown in Part II of the paper that it is of no interest from the practical, theoretical and even from the educational standpoints.

For the sake of brevity, it is not possible here to compare all the algorithms proposed in the literature with the Fundamental Algorithm. However, one thing is certain: if a proposed algorithm is not equivalent to the Fundamental Algorithm, its form cannot be theoretically correct and its application to practical situations will produce more or less accurate analytical results. This is the case, for example, of the Rasberry-Heinrich algorithm [26] as demonstrated by Rousseau [2].

However, from the four examples given, it should be home in mind that the FA form not only enables the theoretical validity of any proposed algorithm (or identity) to be tested, but also gives an explicit equation for each influence coefficient, in terms of fundamental parameters only. It then becomes possible to compare equations for coefficients from one algorithm with those from another. This is the subject of Part II of this paper, which is an exhaustive study of the Claisse-Quintin algorithm and the Tertian and Lachance identities.

Another useful feature of the Fundamental Algorithm is that it provides a solid theoretical foundation upon which the derivation of other algorithms, developed to meet specific needs, can be based. Also, because the Fundamental Algorithm clearly proposes equations that account for absorption and enhancement effects, it facilitates the writing of computer programs.

12. Conclusion

The Fundamental Algorithm 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 coefficients α_{ij} and ε_{ij} correct for absorption and enhancement effects, respectively. They are calculated from fully explicit equations, in terms of fundamental parameters only. These equations are the definitions of coefficients correcting for matrix effects in XRF analysis and permit the establishment of a sound theoretical basis for the concept of correcting influence coefficients. 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 averages 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.

Naturally, this new formalism would be of less interest if it were not easily adapted to practical analytical situations. This can easily be done by using the calibration procedure proposed by Rousseau [3] and the calculation method of sample compositions described in section 6.

Finally, the new formalism is a powerful, accurate and prolific tool for use, for example, in calculating such varied parameters as the basic, hybrid and modified influence coefficients (after the terminology of Lachance), 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 glass discs, and so on. Briefly, its use can be only of benefit to the work of any XRF analyst.

13. References

[1] J. Sherman, *Spectrochimica Acta*, **7**, 283, (1955).

[2] R. M. Rousseau, *X-Ray Spectrometry*, **13**, 115, (1984).

[3] R. M. Rousseau, *X-Ray Spectrometry*, **13**, 121, (1984).

[4] R. M. Rousseau and M. Bouchard, *X-Ray Spectrometry*, **15**, 207, (1986).

[5] H. J. Beattie and R. M. Brissey, *Anal. Chem.*, **36**, 980, (1954).

[6] J W. Criss and L. S. Birks, *Anal. Chem.*, **40**, 1080, (1968).

[7] G. R. Lachance and R. J. Traill, *Can. Jour. of Spectrosc.*, **11**,43, (1966).

[8] F. Claisse and M. Quintin, Can. *Jour. of Spectrosc.*, **12**, 129,(1967).

[9] R. M. Rousseau and F. Claisse, *X-Ray Spectrometry*, **3**, 31, (1974).

[10] T. Shiraiwa and N. Fujino, *X-Ray Spectrometry*, **3**, 64,(1974).

[11] P. A. Pella, L. Feng and J. A. Small, *X-Ray Spectrometry*, **14**, 125, (1985).

[12] K. F. J. Heinrich, 11th International Congress on X-Ray Optics and Microanalysis, London, Ont., Canada, 67, (August 1986).

[13] G. Springer and B. Nolan, *Can. Jour. of Spectrosc.*, **21**, 134,(1976).

[14] W. Bambinek, B. Crasemann, R. W. Fink and al., *Reviews of Modem Physics*, **44**, 716, (1972).

[15] W. Hanke, J. Wernisch and C. Pohn, *X-Ray Spectrometry*, **14**, 43, (1985).

[16] T. R Schreiber and A. M. Wims, *X-Ray Spectrometry*, **11**,42, (1982).

[17] D. E. Leyden and D. B. Bilbrey, *Advances in X-Ray Analysis*, **29**, 493, (1986).

[18] J. V. Gilfrich and L. S. Birks, *Anal. Chem.*, **40**, 1077,(1968).

[19] J. W. Criss, Workshop on Quantitative Techniques and Errors in XRF, 45th Annual Denver X-Ray Conference, (August 1996).

[20] R. Rousseau, Master thesis # 1635, Laval University, Quebec, Canada, (1970).

[21] W. K. de Jongh, *X-Ray Spectrometry*, **2**,151, (1973).

[22] R. Tertian, *Advances in X-RayAnalysis*, **19**, 85, (1976).

[23] J. W. Criss, *Advances in X-Ray Analysis*, **23**, 93, (1980).

[24] N. Broil and R. Tertian, *X-Ray Spectrometry*, **12**, 30, (1983).

[25] G. R. Lachance, *Advances in X-Ray Analysis*, **31**, 471, (1988).

[26] S. D. Rasberry and K. F. J. Heinrich, *Anal. Chem.*, **46**, 81, (1974).

Editor's note:

Dr. R. M. Rousseau's paper consists of Part I: Theory and Part II: Application. We reget that for reasons of space, we were unable to carry both of them together this time. Part II will appear serially in the next November '98 issue.