
CONTRIBUTED PAPERS

THE FUNDAMENTAL ALGORITHM: AN EXHAUSTIVE STUDY OF THE CLAISSE-QUINTIN ALGORITHM AND THE TERTIAN AND LACHANCE IDENTITIES PART II: APPLICATION*

DR. RICHARD M. ROUSSEAU

Geological Survey of Canada, 601 Booth St., Room 707, Ottawa, Ontario, K1A 0E8, Canada. e-mail: rousseau@gsc.nrcan.gc.ca

It was demonstrated in Part I that the Fundamental Algorithm between concentration and intensity in XRF analysis provides a solid theoretical foundation and can therefore be used to test the theoretical validity of any proposed algorithm or relation. In the present Part II, this property is used to study three popular expressions, namely the Claisse-Quintin algorithm and the Tertian and Lachance identities. For each expression, the main contributions and errors are explained, so as to highlight the former and avoid future repetition of the latter.

1. Introduction

The Fundamental Algorithm, as proposed by Rousseau [1] in 1984, provides a sound theoretical basis for testing existing algorithms or generating any new algorithm to meet specific needs. This feature will be used to verify the theoretical validity of three popular expressions used in XRF analysis, namely the Claisse-Quintin algorithm [2] and the Tertian [3] and Lachance [4] identities. Regarding the Claisse-Quintin algorithm [2], it will be demonstrated that its *canonical* form has been mathematically deduced further to a mathematical error but is in agreement with the fundamental theory only in cases where both matrix effects, absorption and enhancement, are present. For pure absorption cases only, this expression does not represent the physical reality and a more appropriate algorithm form for these cases is that proposed by Lachance and Traill [5]. Despite this, when the Claisse-Quintin algorithm is used with theoretical *binary* influence coefficients, it generates accurate analytical results for medium concentration ranges (0-40%), when the binary influence coefficients are calculated from theory according to the method proposed by Rousseau and Claisse [6] and when the term C_M , the matrix concentration, is used as proposed by Tertian [7].

Following publication of the paper by Criss and Birks [8] in 1968, introducing the fundamental parameter method, XRF scientists began to “juggle”

with the Sherman equation [9] in an attempt to extract new fundamental relations in XRF analysis. One such relation is that proposed by Tertian [3] in 1977, known as the “Tertian identity”. We will demonstrate that this identity calculates erroneous individual values for influence coefficients, does not help to better understand the physical phenomena in XRF analysis and is difficult to apply in practice. In other words, it is superfluous and of no interest. In 1988, Lachance [4] proposed another identity deduced from the Sherman equation. After a laborious algebraic manipulation, he deduced an identity that, algebraically, is perfectly in agreement with the Sherman equation. However, we will show that it distorts the physical reality as proposed by Sherman [9]. Furthermore, it reveals no new concept in XRF analysis and is of no practical interest. The aim of this paper is to show that the Fundamental Algorithm is a powerful tool for checking the theoretical validity of any new expression relating the measured net intensity I_i to the concentration C_i of the analyte i in a given specimen. Three expressions are studied. For each expression, the main contributions and errors are explained, so as to highlight their most important contributions, when errors are mentioned in order, the author likes to hope, to avoid future repetition. This paper is the second part of an overall paper entitled: “The Fundamental Algorithm: A Natural Extension of the Sherman Equation”. For this reason, the identification of equations begins with the number (40) rather than (1). We strongly recommend that the

*For part 1, see the issue of May 98, Vol. 15, No. 1, p13, of this Journal.

reader consults the first part before continuing with this paper.

2. The Algorithm of Claisse and Quintin

In 1967, Claisse and Quintin [2] proposed a generalization of the Lachance-Traill algorithm [5] for the correction of matrix effects in X-ray fluorescence analysis. They modified the Lachance-Traill algorithm to take into account the polychromaticity of the incident excitation X-ray beam. Note that their modification concerns cases of absorption only. For a polychromatic incident radiation, they showed that absorption influence coefficients vary with the concentration of each matrix element. Their approach is as follows.

Consider a polychromatic incident X-ray beam having an intensity distribution $I_0(\lambda_k)$ varying from λ_{\min} to $\lambda_{\text{abs edge } i}$ and divided into k intervals $\Delta\lambda_k$, small enough to make each interval practically monochromatic. Consider also a specimen S having N elements where i is the analyte. Summing the contribution of each interval $\Delta\lambda_k$ to the fluorescence intensity I_i of the analyte i in the specimen, the relative intensity R_i is

$$R_i = C_i \frac{\sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge } i}} W_i'(\lambda_k) \frac{1 + \sum_j C_j \delta_{ij}(\lambda_k)}{1 + \sum_j C_j \beta_{ij}(\lambda_k)}}{\sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge } i}} W_i'(\lambda_k)} \quad (40)$$

This equation is the same as the Sherman equation rewritten for relative intensity (see Eqn 19). The weighting factor W_i' associated to each incident wavelength λ_k is given by equation (15). The coefficient $\delta_{ij}(\lambda_k)$ is the enhancement influence coefficient in the case of a monochromatic incident source of wavelength λ_k . Its mathematical expression is given at Table 1 of Part 1. The coefficient $\beta_{ij}(\lambda_k)$ is the absorption influence coefficient in the case of a monochromatic incident source of wavelength λ_k . Its mathematical expression is given by equation (10). The coefficient $\beta_{ij}(\lambda_k)$ is the theoretical constant proposed by Lachance and Traill [5] (they called it "alpha coefficient") accounting for the matrix effects of element j on the intensity emitted by element i for a monochromatic incident excitation source. Since enhancement effects are much more difficult to evaluate than absorption effects, Claisse and Quintin initially ignored enhancement, i.e., they considered

that all coefficients $\delta_{ij}(\lambda_k)=0$. Thus, for a binary sample i - j , the equation (40) becomes

$$\frac{C_i}{R_i} = \frac{\sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge } i}} W_i'(\lambda_k)}{\sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge } i}} W_i'(\lambda_k) \frac{1}{1 + \sum_j C_j \beta_{ij}(\lambda_k)}} \quad (41)$$

In this equation, the ratio

$$\frac{1}{1 + \sum_j C_j \beta_{ij}(\lambda_k)} \quad (42)$$

has the following form

$$\frac{1}{1+x}$$

which can be expanded in series:

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + \dots \quad \text{For } x^2 < 1 \quad (43)$$

If this series expansion is used to transform ratio (42), equation (41) becomes

$$\frac{C_i}{R_i} = \frac{\sum W_i'}{\sum W_i' (1 - C_j \beta_{ij} + C_j^2 \beta_{ij}^2 - C_j^3 \beta_{ij}^3 + \dots)}$$

where, for simplicity, all summations are from $\lambda_k=\lambda_{\min}$ to $\lambda_{\text{abs edge } i}$, W_i' is used for $W_i'(\lambda_k)$, and β_{ij} is used for $\beta_{ij}(\lambda_k)$. If the numerator and the denominator of the ratio on the right-hand side are divided by $\sum W_i'$, then

$$\frac{C_i}{R_i} = \frac{1}{1 + \left[-C_j \frac{\sum W_i' \beta_{ij}}{\sum W_i'} + C_j^2 \frac{\sum W_i' \beta_{ij}^2}{\sum W_i'} - C_j^3 \frac{\sum W_i' \beta_{ij}^3}{\sum W_i'} + \dots \right]}$$

Again this equation has the general form

$$\frac{1}{1+x}$$

which can be approximated by the same series expansion (43). This gives then

$$\frac{C_i}{R_i} = 1 - \left[-C_j \frac{\sum W'_i \beta_{ij}}{\sum W'_i} + C_j^2 \frac{\sum W'_i \beta_{ij}^2}{\sum W'_i} - C_j^3 \frac{\sum W'_i \beta_{ij}^3}{\sum W'_i} + \dots \right] + \left[-C_j \frac{\sum W'_i \beta_{ij}}{\sum W'_i} + C_j^2 \frac{\sum W'_i \beta_{ij}^2}{\sum W'_i} - \dots \right]^2 - \left[-C_j \frac{\sum W'_i \beta_{ij}}{\sum W'_i} + \dots \right]^3 + \dots$$

Regrouping the terms leads to

$$\frac{C_i}{R_i} = 1 - \left[\frac{\sum W'_i \beta_{ij}}{\sum W'_i} \right] \cdot C_j + \left[\left(\frac{\sum W'_i \beta_{ij}}{\sum W'_i} \right)^2 - \left(\frac{\sum W'_i \beta_{ij}^2}{\sum W'_i} \right) \right] \cdot C_j^2 + \dots$$

which has the form of the well-known Claisse-Quintin algorithm for a binary sample, i.e.,

$$\frac{C_i}{R_i} = 1 + a_{ij} C_j + a_{ijj} C_j^2$$

Expanding function (41) for a multi-element sample containing elements i, j, k, ..., N with the same series (43), Claisse and Quintin [2] demonstrated that

$$\frac{C_i}{R_i} = 1 + \sum_j a_{ij} C_j + \sum_j a_{ijj} C_j^2 + \sum_j \sum_{k>j} a_{ijk} C_j C_k + \dots \quad (44)$$

where

$$\begin{aligned} a_{ij} &= \frac{\sum W_i \beta_{ij}}{\sum W'_i} \\ a_{ijj} &= a_{ij}^2 - \frac{\sum W_i \beta_{ij}^2}{\sum W'_i} \\ a_{ijk} &= 2 \cdot \left(a_{ij} \cdot a_{ik} \frac{\sum W_i \beta_{ij} \beta_{ik}}{\sum W'_i} \right) \end{aligned} \quad (45)$$

Despite their elegance, equations (45) cannot be used in practice to calculate influence coefficients. Indeed, these equations have been deduced after having used twice the series expansion (43), which converges only for values of $x^2 < 1$. But this convergence condition is

rarely met in practice [10]. Moreover, in the rare cases where the convergence condition is met, these equations for influence coefficients are valid only for a very narrow concentration range close to the origin ($C_j \approx 0$). A series like equation (43) can, in addition, must only be applied to functions that vary continuously for the indicated region of convergence. However, function (41) does not vary continuously with concentrations, as claimed by Sherman [11] himself. We must therefore conclude that equations (44) and (45) are the result of an invalid mathematical development.

For these reasons, we can therefore state that equations (44) and (45) are merely invalid for quantitative XRF analysis. Even Claisse and Quintin [2] recognized the disagreement between the theoretical and experimental data. They thought that the main errors were caused by insufficient knowledge of the spectral distribution of the excitation source, but this was not the case.

Another argument against the Claisse-Quintin algorithm is that, since equations (45) are invalid, it may be thought that at least the *canonical form* of equation (44) is theoretically valid if used with other equations for influence coefficients. Unfortunately, this is not the case. As it was demonstrated in Part I, section 11.2, without using any approximation or series, the form of equation (44) is perfectly in agreement with the Sherman equation (Eqn 40) only when absorption AND enhancement effects are present. When enhancement effects are absent, it is reduced to the Lachance-Traill algorithm (Eqn 28), with the coefficients of the two last higher order terms becoming zero (see Eqns 32). Note that the Fundamental Algorithm says exactly the same thing. When there is no enhancement, all coefficients $\epsilon_{ij} = 0$, and the Fundamental Algorithm becomes

$$C_i = R_i \frac{1 + \sum_j \alpha_{ij} C_j}{1 + 0} = R_i \left(1 + \sum_j \alpha_{ij} C_j \right)$$

which has the form of the Lachance-Traill algorithm.

The Claisse-Quintin algorithm therefore produces invalid equations for the binary influence coefficients. Its form, developed for absorption cases only, is theoretically invalid for the correction of this kind of matrix effects. Furthermore, it provides no mechanism for the correction of enhancement effects. We must thus conclude that this algorithm fails from

all standpoints to provide a valid solution for the correction of matrix effects.

Later, in 1980, Lachance and Claisse [12] tried to improve the Claisse-Quintin model by adding higher order terms to the equation (44). For the sake of accuracy, they suggested adding a term in C^4 as follows:

$$\frac{C_i}{R_i} = 1 + \sum_j a_{ij} C_j + \sum_j a_{ijj} C_j^2 + \sum_j a_{ijjj} C_j^4 + \sum_j \sum_{k>j} a_{ijk} C_j C_k + \dots \quad (46)$$

This equation cannot produce more accurate results because a complex function like the Sherman equation (Eqn 40) simply cannot be approximated by any kind of series expansion. As previously stated, series can only be applied to functions that vary continuously for the indicated region of convergence. As the Sherman equation does not vary continuously with concentrations, it cannot be expanded using a series. Sherman [11] himself said of his own equations: "they involve the use of hyperbolic curves in multidimensional spaces". No one has succeeded yet in approximating the Sherman equation accurately, for the relative intensity R_i , by using a series valid for both the region of convergence and for the entire concentration range. Many XRF scientists have failed to achieve this objective, including Tertian [13], de Jongh [14], Shiraiwa and Fujino [15], Rousseau [10] and Lachance and Claisse [12].

The Claisse-Quintin algorithm cannot be deduced from a series expansion, and the addition of higher order terms is mathematically incorrect. However, it can be deduced directly from the Sherman equation, as shown in Part I (see Eqn 31). The exact equation is

$$C_i = R_i \cdot \left[1 + \sum_j \alpha_{ij}^* C_j + \sum_j \alpha_{ijj}^* C_j^2 + \sum_j \sum_{k>j} \alpha_{ijk}^* C_j C_k \right] \quad (47)$$

where there is no higher order term greater than 2 and where the α^* influence coefficients are a function of the whole matrix composition, correct for all matrix effects, absorption and enhancement, and valid only for a given specimen. Their mathematical expressions are given by equations (30) and (32) of Part I. To make these equations easier to use in practice and also to overcome all the limitations of the original Claisse-Quintin algorithm, these coefficients can be approximated by theoretical *binary* influence coefficients.

These binary coefficients introduce two levels of approximation:

1. It is assumed 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.
2. The binary coefficient α_{ij}^* is a hyperbolic function [16] that represents the exact variation of the matrix effect of element j on analyte i , in a binary sample (C_i, C_j), as a function of concentration C_j . Assuming that the above first approximation introduces no error (which is false!), the exact binary hyperbolic function (α_{ij}^*) is approximated by a straight line as follows:

$$a_{ij}^* \approx a_{ij} + a_{ijj} C_j \quad (48)$$

where a_{ij} and a_{ijj} are the parameters of the approximated straight line.

To reduce the errors introduced by these two approximations for multi-element samples, Tertian [7] suggested replacing the term C_j in the last equation by C_M , where C_M is the concentration of the complete matrix composition, i.e.,

$$C_M = 1 - C_i = C_j + C_k + \dots + C_N \quad (49)$$

The "crossed" ternary coefficient a_{ijk} (that replaces the multi-element coefficient α_{ijk}^* in equation 47) is retained to compensate for the fact that the total inter-element correction cannot be strictly represented by a sum of binary matrix effects. In doing this, this coefficient improves the accuracy of the results. Combining all these modifications, the Claisse-Quintin algorithm, as amended, becomes

$$C_i = R_i \cdot \left[1 + \sum_j (a_{ij} C_j + a_{ijj} C_M) C_j + \sum_j \sum_{k>j} a_{ijk} C_j C_k \right] \quad (50)$$

Rousseau and Claisse [6] demonstrated how to calculate accurate and valid theoretical binary influence coefficients in the Claisse-Quintin algorithm for correcting all matrix effects, including the enhancement effects. The influence coefficient equations of equation (50) as proposed by Rousseau and Claisse [6] in 1974 were improved ten years later by Rousseau [17]. These coefficients are finally calculated by the following equations:

$$\begin{aligned}
a_{ij} &= \frac{1}{3} [-F_i(0.2,0.8) + 4F_i(0.8,0.2)] \\
a_{ij} &= \frac{5}{3} [-F_i(0.2,0.8) - F_i(0.8,0.2)] \\
a_{ijk} &= \frac{20}{7} [-F_i(0.3,0.35,0.35) - F_i(0.3,0.7,0)] \\
&\quad [-F_i(0.3,0,0.7)]
\end{aligned} \tag{51}$$

where for a ternary system (C_i, C_j, C_k), the variable $F_i(C_i, C_j, C_k)$ is defined by

$$F_i(C_i, C_j, C_k) = \frac{1}{C_j} \left(\frac{C_i}{R_i} - 1 \right) \tag{52}$$

where the ratio C_i/R_i is calculated by the Fundamental Algorithm when it is applied to a ternary system (C_i, C_j, C_k):

$$\frac{C_i}{R_i} = \frac{1 + \alpha_{ij} C_j + \alpha_{ik} C_k}{1 + \varepsilon_{ij} C_j + \varepsilon_{ik} C_k} \tag{53}$$

Note that: $F_i(C_i, 0, C_k) = \frac{1}{C_k} \left(\frac{C_i}{R_i} - 1 \right)$ (54)

Although both set of coefficients, the multi-element influence coefficients (Eqns 30 and 32) and the *binary* influence coefficients (Eqns 51) can be used in association with the Claisse-Quintin algorithm, they are two entirely different entities that are clearly not equivalent. The *multi-element* coefficients are calculated from the complete composition of a specific specimen, which is estimated fairly accurately from measured intensities. The binary coefficients are calculated for a given composition range, or series of samples, rather than for a given specimen. In other words, with binary coefficients it is assumed that they are CONSTANT for a given range of C_i and C_j rather than a VARIABLE dependent on the whole matrix composition. Multi-element coefficients are *exact*, while binary coefficients mean that some *approximations*, valid for a given concentration range, must be accepted in return for greater versatility [18].

The binary influence coefficients (Eqns 51) of the Claisse-Quintin algorithm (50) are considered to be constant for a given series of samples when applied to samples with a medium concentration range (0-40%), for example, for the case of oxides in pressed powder pellets. In this case, the calculation method alone

introduces a theoretical mean relative error of 0.04% on the calculated concentrations [19].

For better accuracy, and for a specific composition range, Lachance and Claisse [20] suggested the selection of a more limited and representative set of reference binary and ternary compositions to calculate the binary influence coefficients (by Eqns 51). This improvement has no effect or is only marginal, because the two severe basic approximations used for the calculation of binary coefficients are still present. Recalibration using standards with the specific composition range will have a greater impact on improving the accuracy of the analytical results. If more accuracy is required, a better strategy is to use the Fundamental Algorithm method. With this method, the Claisse-Quintin algorithm is used to calculate an initial estimate of composition, which is then used for subsequent treatment by the Fundamental Algorithm to obtain the final and more accurate composition of the sample (see Part I).

To conclude, the major contributions of Claisse and Quintin, in addition to having proposed the form of a powerful and original algorithm, are as follows:

1. Mathematical equations for influence coefficients must take full account of the polychromaticity of the incident radiation where each incident wavelength λ_k has a weight equal to $W_i'(\lambda_k)$. Naturally, the spectral distribution of the incident radiation must be known, but this is no longer a problem today.
2. Binary influence coefficients are not constants, but are values that vary with the concentration of each matrix element j (see Eqn 48), thereby enabling to use them for a larger concentration range.

3. The Tertian Identity

In 1977, for the first time, Tertian [3] presented an equation that has been published later (in 1983) by Broil and Tertian [21]. In this last paper, the authors proposed the basis of a new approach using multi-element influence coefficients in an algorithm in the form of the Lachance-Traill algorithm. The Broil and Tertian method is as follows.

Broil and Tertian chose the Lachance-Traill algorithm rather than the Fundamental Algorithm as the basic algorithm to correct for matrix effects. This choice is not reprehensible by itself, since both algorithms are equivalent, as demonstrated in Part 1. The following equation:

$$C_i = R_i \left(1 + \sum_j \alpha_{ij}^* C_j \right) \quad (55)$$

where

$$\alpha_{ij}^* = \frac{\alpha_{ij} - \varepsilon_{ij}}{1 + \sum_j \varepsilon_{ij} C_j} \quad (56)$$

is the well-known Lachance-Trail algorithm [7] where the α_{ij}^* multi-element coefficients correct for all the matrix effects, absorption and enhancement, of every element j on the analyte i in a given specimen. As such, from the point of view of accuracy in the correction for matrix effects, equation (55) is no better or no worse than the Fundamental Algorithm. It is simply another, equivalent way of expressing the same thing. The fact to combine the coefficients α_{ij} and ε_{ij} in a single coefficient α_{ij}^* does not increase the accuracy of the results, nor does it increase calculation speed. However, in practice, the main drawback of equation (56) is that it introduces an additional calculation step by merging the α_{ij} and ε_{ij} coefficients, and the analyst loses important information on the unknown sample because the coefficient values correcting for absorption and enhancement effects are combined in a single number.

Furthermore, the Lachance-Trail algorithm was initially developed on the assumption of a monochromatic incident radiation when there is no enhancement. The Fundamental Algorithm, which is a *natural* development from the Sherman equation, is more realistic by taking account of the polychromatic incident radiation and enhancement, and by considering *separately* both types of matrix effects, absorption and enhancement.

The equation presented in 1977 by Tertian [3], and that is referred to as the ‘‘Tertian identity’’, is:

$$C_i = R_i \left[1 + \sum_j \left(\alpha_{ij} - \varepsilon_{ij} \frac{C_j}{R_j} \right) C_j \right] \quad (57)$$

where α_{ij} and ε_{ij} are the usual multi-element coefficients of the Fundamental Algorithm correcting for absorption and enhancement effects, respectively, and that are valid for a given specimen only. Keeping in view that the Fundamental Algorithm is

$$C_i = R_i \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \varepsilon_{ij} C_j} \quad (58)$$

these two last equations have been directly deduced from the Sherman equation. Furthermore, they are mathematically equivalent, as shown in Part 1. However, although they are equivalent on the algebraic level, they do not deliver the same message on the physical level.

The physical interpretation of the Fundamental Algorithm is simple, clear, obvious and elegant. Indeed, the Fundamental Algorithm reveals that the measured relative intensity R_i , having been *reduced* by the absorption effects (when α_{ij} is positive), is increased by the sum of each coefficient α_{ij} (the contribution of each coefficient α_{ij} being in a proportion C_j), to become proportional to the concentration C_i of the analyte. Furthermore, while some matrix elements may enhance the analyte i , the intensity R_i is increased by the enhancement effects of the matrix. Again, to make it proportional to C_i , its value must be reduced by using the coefficients ε_{ij} that are always positive and different from zero for enhancement cases. The contribution of each coefficient ε_{ij} to the sum is in a proportion C_j , the concentration of the enhancing element j . Consequently, the denominator value is greater than unity and the intensity R_i is reduced by a quantity equivalent to that caused by the enhancement. It is thus easy to understand the physical interpretation of equation (58), even for people unfamiliar with the subject.

Furthermore, the mathematical equations of a_{ii} and e_{ii} show that they are a weighted mean of the absorption and enhancement effects, respectively, when a weighting factor $W_i(\lambda_k)$ is associated with each incident wavelength λ_k . This important feature does not explicitly appear in the equations proposed by Broll and Tertian.

Let us represent the term in parentheses in equation (57) by the resultant or effective coefficient α_{ij}^* (to use Broll and Tertian's term), i.e.,

$$\alpha_{ij}^* = \alpha_{ij} - \varepsilon_{ij} \frac{C_j}{R_j} \quad (59)$$

Broll and Tertian [21] explain the physical meaning of this coefficient as follows: ‘‘the coefficient α_{ij}^* is the difference of two terms, where α_{ij} accounts for absorption effects and can be, according to the case, positive or negative; and where $(\varepsilon_{ij} C_j / R_j)$, always positive, accounts for enhancement effects if present. Both terms include third element effects. Coefficient

α_{ij}^* of course reduces to α_{ij} when enhancement is absent.”

It is unfortunate that Broil and Tertian have not provided any further explanation on, for example, why coefficient ϵ_{ij} has to be multiplied by the ratio C_i/R_i or why the same ratio appears on both sides of the equation (57). The fact of expressing a variable (C_i/R_i) as a function of itself does not help understand the physical phenomena in XRF analysis. Compared with the Fundamental Algorithm, the Tertian identity reveals little about the physical properties of Sherman's equation, or at least, nothing new. On the physical level, the utility of equation (57) is thus highly questionable.

Let us now consider in more detail the effective coefficient a_{ij}^* correcting for the total effect of the matrix on the analyte i . Since the Sherman equation, Fundamental Algorithm, Tertian identity and Lachance-Trail algorithm are all equivalent, the equation

$$\alpha_{ij}^* = \frac{\alpha_{ij} - \epsilon_{ij}}{1 + \sum_j \epsilon_{ij} C_j} \quad (60)$$

deduced from the Fundamental Algorithm in Part I (see Eqn 29) must also be equivalent to equation (59) as proposed by Tertian. Tertian [22] claims that equation (60) is false, but in fact this is not the case, as demonstrated by Lachance [23] and the present author in Part I. To check whether or not equations (59) and (60) are equivalent, let us combine equations (59) and (58) as follows:

$$\alpha_{ij}^* = \alpha_{ij} - \epsilon_{ij} \cdot \frac{C_i}{R_i} = \alpha_{ij} - \epsilon_{ij} \cdot \frac{1 + \sum_j \alpha_{ij} C_j}{1 + \sum_j \epsilon_{ij} C_j}$$

or

$$\alpha_{ij}^* = \frac{\alpha_{ij} \cdot (1 + \sum_j \epsilon_{ij} C_j) - \epsilon_{ij} \cdot (1 + \sum_j \alpha_{ij} C_j)}{1 + \sum_j \epsilon_{ij} C_j}$$

or

$$\alpha_{ij}^* = \frac{(\alpha_{ij} - \epsilon_{ij}) + \alpha_{ij} \cdot (\sum_j \epsilon_{ij} C_j) - \epsilon_{ij} \cdot (\sum_j \alpha_{ij} C_j)}{1 + \sum_j \epsilon_{ij} C_j} \quad (61)$$

Since the second term $\alpha_{ij} \cdot (\sum_j \epsilon_{ij} C_j)$ and the third term $\epsilon_{ij} \cdot (\sum_j \alpha_{ij} C_j)$ of the numerator are not equal, equations

(59) and (60) are thus NOT equivalent, although the two equations (57) and (58) are equivalent, as shown in Part I, for the simple following reason: the individual values of the coefficient α_{ij}^* as calculated by Tertian (Eqn 61) are wrong, although their sum gives the correct value for the ratio C_i/R_i (Eqn 57). Indeed, combining equations (55) and (61) leads to

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

or

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

or

$$\frac{C_i}{R_i} = 1 + \sum_j \left(\frac{\alpha_{ij} - \epsilon_{ij}}{1 + \sum_j \epsilon_{ij} C_j} \right) \cdot C_j + 0 \quad (62)$$

Thus, this last equation shows that Tertian, when calculating the ratio C_i/R_i , obtains the correct value because the right-hand side of this last equation is equivalent to the Fundamental Algorithm or the Sherman equation. On the other hand, when he calculates the individual value of each coefficient α_{ij}^* , he uses equation (61) which introduces two new terms (similar to B-B as in Eqn 35) and the calculated value of α_{ij}^* is different from that calculated by equation (60). The individual values of the coefficient α_{ij}^* are therefore wrong, although their sum gives the correct value for the ratio C_i/R_i (Eqn 62). This has already been shown by Lachance [23] in 1989, using numerical data for a ternary sample. The only case where equations (59) and (60) are equivalent is for binary samples. Similarly, equation (60) becomes equivalent to equation (61) only in cases of binary samples. This is also shown with numerical data in the new book by Lachance and Claisse [20] (page 114).

Some other comments on equation (59) of the effective coefficient α_{ij}^* as proposed by Tertian are as follows:

1. The equation (59) is not expressed only in term of fundamental coefficients (α_{ij} and ϵ_{ij}).
2. It unnecessarily combines the correction of two completely different matrix effects, absorption and enhancement, in a single coefficient α_{ij}^* .
3. Compared with the Fundamental Algorithm, the equation (59) reveals no new "vision" of X-ray physics.
4. The physics is not highlighted.
5. The equation (59) introduces an error into the calculation of the numerical value of α_{ij}^* .

Briefly, equation (59) is in general invalid (except for binary samples), little original and without elegance. In the Broll and Tertian method, the intensities of the unknown are compared with those of a "comparison standard" whose the composition is fairly close to that of the unknown, or at least not significantly different. This practice is particularly appropriate for industrial applications. The mathematical approach is as follows. Writing equation (55) for a given unknown sample

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

where $R_i = I_i / I_{(i)}$ is the relative intensity of the analyte i in the unknown. Writing the same equation for a fairly similar standard gives

$$C_i^* = R_i^* \left(1 + \sum_j \alpha_{ij}^* C_j^* \right) \quad (62)$$

where $R_i^* = I_i^* / I_{(i)}$ is the relative intensity of the analyte i in the standard. The ratio of the two last equations gives

$$\frac{C_i}{C_i^*} = \frac{I_i}{I_{(i)}} \cdot \frac{I(i)}{I_i^*} \cdot \frac{1 + \sum_j \alpha_{ij}^* C_j}{1 + \sum_j \alpha_{ij}^* C_j^*}$$

or

$$C_i = C_i^* \cdot \frac{I_i}{I_{(i)}} \cdot \frac{I(i)}{I_i^*} \cdot \frac{1 + \sum_j \alpha_{ij}^* C_j}{1 + \sum_j \alpha_{ij}^* C_j^*} \quad (63)$$

where I_i , C_i , C_j , ..., are variables that belong to the unknown and I_i^* , C_i^* , C_j^* , ..., to the standard. The α_{ij}^* coefficients are calculated from the known compo-

sition of the selected multi-element standard. The Broll and Tertian method comprises the following steps. To calculate the composition of a sample of N elements, N expressions similar to equation (63) are written. The α_{ij}^* coefficients are first calculated for the known composition of the selected comparison standard and then introduced in both the numerator and the denominator of equation (63). If the unknown and the standard have a fairly similar composition, this will be sufficient and a correct analyse of the unknown will be achieved by means of the usual iteration process, which converges rapidly. When the unknown composition is rather different from that of the selected standard, equation (63) will yield a first approximation of the unknown composition, thus permitting the calculation of a new set of α_{ij}^* values more appropriate for the numerator. Repeating again this operation once or twice gives a correct analysis. Otherwise, in extreme cases, it is better to change the standard for another one having a closer composition to the unknown. This method, by suitably dividing the composition ranges and selecting the appropriate corresponding standards, enables day-to-day applications to be reduced to ordinary Lachance-Traill operations, using constant coefficients. This approach will usually work very well in particular for routine analyses of samples with a limited composition range. Other cases require the procedure mentioned above to be repeated.

Regarding the present method, the following reservations must be mentioned:

The "comparison standard" algorithm (63) is the equivalent of calibrating with only one standard. Indeed, equation (62) can be written in the following form:

$$I_i = I_{(i)}^* \cdot \frac{C_i^*}{1 + \sum_j \alpha_{ij}^* C_j^*}$$

This last equation has the general form of a straight-line equation passing by the origin, i.e.,

$$Y_i = m_i X_i$$

when the measured net intensity I_i^* (Y-axis) is plotted on a calibration graph as a function of the ratio $C_i^* / (1 + \sum_j \alpha_{ij}^* C_j^*)$ (X-axis). In this case, the slope m_i is equal to the intensity of the pure element i , i.e.,

$$m_i = I_{(i)}$$

Equation (62) can also be written in the form

$$\frac{I}{I_{(i)}} = \frac{1}{I_{(i)}^*} \cdot \frac{C_i^*}{1 + \sum_j \alpha_{ij}^* C_j^*}$$

and combining the last two equations with equation (63) leads to

$$C_j = \frac{1}{m_i} \cdot I_i \cdot \left(1 + \sum_j \alpha_{ij}^* C_j\right) \quad (64)$$

Thus, the unknown composition is calculated from this last equation where the calibration slope, m_i , is calculated from a SINGLE standard. This is not the most reliable way of calibrating. At the opposite, the calibration procedure [17] used jointly with the Fundamental Algorithm is more “robust” and protects the analyst from unexpected errors.

Equation (63) requires the compositions of the unknown and the standard to be fairly similar. If this condition is really respected, the last ratio on the right-hand side becomes superfluous, and accurate unknown compositions can be calculated with only

$$C_i = C_i^* \cdot \frac{I_i}{I_i^*}$$

On the other hand, if the unknown composition is rather different from that of the standard, the standard must absolutely be replaced by another one having a composition closer to the one of unknowns to be analyzed. On which criteria should the most appropriate standard be selected? By a program comparing and matching the intensities of standards in a database? What happens when the program cannot find a good match? Does this mean that the operator must stop the routine analyses and read a new standard similar to the unknown? Or if the program finds a good match but the standard has not been read for a long period, how can a potential drift during this period be corrected? What happens if a standard really similar to the unknown is not available? It is thus clear that the calibration procedure selected by Broil and Tertian suffers from many weaknesses. On the other hand, none of these potential problems are found in the calibration procedure [17] used by the Fundamental Algorithm. It is thus a more “universal” calibration procedure.

Briefly, the Fundamental Algorithm methodology is more universal and less cumbersome to apply. Generally speaking, the approach of Broil and

Tertian can be considered a step back in terms of ease of use, rather than an improvement compared to the Fundamental Algorithm. Although both methods are comparable in terms of accuracy, we do not encourage analysts to use the Broil and Tertian method, even in its improved version [24].

To conclude, the Tertian identity does not impress XRF scientists by its originality. It is incomplete, with little physical sense, it does not help to better understand the physical phenomena in XRF analysis, it is difficult to apply in practice and, most important, it allows one to calculate wrong individual values for the effective influence coefficients α_{ij}^* . In other words, it is superfluous and of no interest.

4. The Lachance Identity

In 1988, for the first time, Lachance [4] presented an equation that is referred to as the “Lachance identity”. It was deduced, following a laborious and skillful algebraic manipulation, from the Sherman equation (see Part 1, section 11.4). The same development was repeated all over again by Lachance and Claisse [20] on a more inductive basis. This equation is

$$P_i + S_i = P_{(i)} C_i - P_i \sum_j \alpha_{ij} C_j + P_i \sum_j \varepsilon_{ij} C_j \quad (65)$$

where

$$I_i = P_i + S_i \quad (66)$$

and

$$I_{(i)} = P_{(i)} \quad (67)$$

The symbol P_i designates the *primary* fluorescence intensity, the major part of I_i involving absorption only, while S_i designates the *secondary* fluorescence intensity, the part due to enhancement. The sum of both is the *measured net* Xray fluorescence intensity I_i . $P_{(i)}$ is the intensity of the element i emitted by a pure specimen. It is also known as $I_{(i)}$. The Lachance identity can also be deduced from the Fundamental Algorithm (see Part I). Both expressions are thus equivalent, and consequently the Lachance identity is theoretically valid.

Equation (65) is similar in type to equation (35), where the variable P_i is expressed as a function of itself. As was the case for the Tertian identity, it is not particularly useful in practice, teaches us nothing new, is a pure algebraic artifice and finally, as it will

be explained below in section 4.2, it distorts the physical reality as proposed by Sherman.

4.1. Another Way to Deduce the Lachance-Trail Algorithm

The Lachance identity, which is equivalent to the Sherman equation and also to the Fundamental Algorithm, can be used to deduce, another time, the popular Lachance-Trail algorithm. Is this really necessary? Consider any way the deduction. Recalling equation (65):

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

it can be modified algebraically as follows:

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

hence

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

or

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

Knowing that the relative intensity

$$R_i = \frac{I_i}{I_{(i)}} = \frac{P_i + S_i}{P_{(i)}} \quad (68)$$

hence

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

$$C_i = R_i \left\{ 1 + \sum_j A_{ij} C_j - \sum_j E_{ij} C_j \right\} \quad (69)$$

With

$$A_{ij} = \frac{P_i}{P_i + S_i} \alpha_{ij} \quad \text{and} \quad E_{ij} = \frac{P_i}{P_i + S_i} \varepsilon_{ij} \quad (70)$$

Defining the variable

$$N_{ij} = A_{ij} - E_{ij} \quad (71)$$

Finally, we get

$$C_i = R_i \left\{ 1 + \sum_j N_{ij} C_j \right\} \quad (72)$$

which is the well-known Lachance-Trail algorithm. This last algorithm (72) has the same form and the same meaning as equation (55):

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

where the multi-element influence coefficient α_{ij}^* calculated by

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

is simply the combination (or the sum) of the coefficients A_{ij} and E_{ij} after they have been modified by equation (38). Furthermore, the Lachance-Trail algorithm itself is a derivative of the Fundamental Algorithm. It is thus not surprising that all these equations are equivalent, since they were all deduced from the same source: the Sherman equation. The question is then: why waste so much energy deducing an algorithm that has already been deduced so well, so often and by so many?

Lachance and Claisse [20] claim (page 105) that the coefficients A_{ij} and E_{ij} , as defined by equations (70), are fundamental influence coefficients. This statement cannot be correct since, in both equations (70), the coefficients α_{ij} and ε_{ij} are multiplied by the term $P_i/(P_i+S_i)$. Only the coefficients α_{ij} and ε_{ij} as defined by equations (24) and (25) are fundamental. The reader is invited to read again the discussion on the word 'fundamental' in Part I, section 10.

4.2. Comments on the Lachance Identity

The Lachance identity is given by equation (65). It was proposed more than ten years ago, and even after all this time, it is still difficult to justify its existence. Some comments and observations are presented below to corroborate this opinion.

1. The Lachance identity does not respect the spirit of the Sherman equation which shows how to CALCULATE the MEASURED NET INTENSITY $I_i(\lambda_i)$ emitted by the analyte i in a GIVEN specimen when bombarded by an incident POLYCHROMATIC X-ray radiation. It is marvelously translated into mathematical language by the following equation (Eqn 16):

$$I_i(\lambda_i) = g_i C_i \sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge}i}} W_i'(\lambda_k) \frac{1 + \sum_j C_j \delta_{ij}(\lambda_k)}{1 + \sum_j C_j \beta_{ij}(\lambda_k)} \quad (73)$$

The physics behind the Sherman equation is *simple* to understand and *elegant*. The measured net intensity I_i increases with δ_{ij} and decreases with β_{ij} for each incident wavelength λ_k able to excite the analyte i , each one having a weighting factor W_i' . We can calculate the measured TOTAL net intensity I_i by summing the contribution of each λ_k to the intensity I_i .

Equation (73) tells us that if a matrix element j enhances the analyte i , its intensity I_i will be increased by the fraction $C_j \delta_{ij}$. Furthermore, each matrix element j absorbs a fraction $C_j \beta_{ij}$ of the emitted intensity I_i and this intensity will be reduced by the TOTAL fraction $\sum_j C_j \beta_{ij}$ before reaching the specimen surface. Note that each coefficient β_{ij} may be positive or negative, depending on whether or not the matrix element j is heavier than the analyte i . Finally, Sherman said one more important thing. The total matrix effect (absorption and enhancement) of each matrix element j on I_i occurs for each incident wavelength λ_k able to excite the analyte i . Each of the incident wavelengths λ_k does not have the same importance. Some wavelengths λ_k have more effect on i than others. This fact is taken in consideration by giving a weighting factor to each λ_k . Eventually, the SUM ($\sum \lambda_k$) of each intensity I_i , that is produced by each λ_k and modified by each element j of the matrix, is equal to the TOTAL intensity I_i emitted by the analyte i . This simple equation is a wonderful translation of the spirit of the Sherman equation which, by the way, was proposed more than 40 years ago, in 1955.

The intensity I_i is calculated as a function of fundamental parameters ONLY and not as a function of other intensities, such as the intensity $I_{(i)}$ of the pure, or even as a function of itself.

2. Sherman never suggested calculating the measured net intensity I_i emitted by a specimen A as a function of the intensity $I_{(i)}$ emitted by another specimen B. Physically speaking, it is very difficult to visualize. The Lachance identity (Eqn 65) gives the false impression that the pure intensity $I_{(i)}$ is absolutely necessary to calculate the XRF fluorescence intensity I_i . This characteristic creates confusion when new XRF analysts or students learn quantitative XRF analysis.

3. Sherman never suggested calculating the measured net intensity I_i as a function of I_i itself (or the part P_i of it). Indeed, after equation (66), P_i is the major component of I_i . The intensity I_i in the Lachance identity is thus expressed in terms of itself.

4. Contrary to equation (73), the Lachance identity by itself says nothing about the weighting factor W_i' and does not explain the contribution of each incident wavelength λ_k to the total measured net intensity I_i .

5. The minus sign in the Lachance identity does not correctly translate the attenuation of I_i due to absorption by the matrix elements. Indeed, the attenuation of I_i in a given specimen obeys to the Beer-Lambert law:

$$I_i = I_0 \exp[-\mu_s \rho_s t_s]$$

where the absorption effects are represented by a *division*, not by a subtraction. Furthermore, Sherman himself represents again all absorption effects on I_i , in equation (73), by a division. Thus, the attenuation of I_i in a given specimen must not be translated by a subtraction, physically speaking, but must be translated by a division. The Lachance identity thus gives the analyst a false interpretation of the absorption phenomena.

6. The Lachance identity was proposed 45 years too late! If it had been proposed in the early fifties (before the Sherman equation), its would have been more successful. Why reinvent the wheel when Sherman did such a good job, when his equation is so elegant? The Lachance identity is thus superfluous, and it is unfortunate that so much energy has been spent on an approach of such poor quality, rather than on the Sherman equation itself.

To conclude, the Lachance identity definitely suffers from a lack of physical and mathematical rigor, is incomplete, partial, does not tell to analysts the truth about an important part of the physical reality, and too many equivalent equations, along with too many new variables (P_i , S_i , $P_{(i)}$, A_{ij} , E_{ij} , N_{ij} , a_{ij} , e_{ij} , m_{ij} , etc.), create confusion among beginners. For all these reasons, the Lachance identity is NOT a fundamental expression as claimed by Lachance and Claisse [20] (page 104). It is not even an algorithm; it should not even exist!

5. Conclusion

It has been demonstrated that the Claisse-Quintin algorithm is the result of a mathematical error, although it can generate accurate analytical results when theoretical binary influence coefficients as proposed by Rousseau [17] are used for medium composition ranges (0-40%). The Tertian and Lachance identities, such as equation (35), are merely mathematical artifices that are not plausible physical representations.

This exhaustive study of three popular expressions in XRF analysis clearly illustrates that the Fundamental Algorithm is still the best expression for explaining all physical phenomena in XRF analysis, and it now incorporates all the theoretical knowledge on matrix effect corrections. This study shows the beauty of the Fundamental Algorithm, its physical sense and its practical utility.

The Fundamental Algorithm is the most “robust” method for the mathematical correction of matrix effects because it is physically and mathematically in agreement with the Sherman equation. Furthermore, in practice, it gives the analyst the ultimate method for mathematical matrix effect corrections and, when associated with its innovative calibration procedure [17], provides maximum accuracy in quantitative XRF analysis, limited only by the quality of sample preparation and the standards used.

Acknowledgments

The author is very grateful to Dr. Jacques A. Boivin from the “Centre de recherche minérale”, Québec city, Canada, for the review of the manuscript.

References

- [1] R. M. Rousseau, *X-Ray Spectrometry*, **13**, 115, (1984).
- [2] F. Claisse and M. Quintin, *Can. Jour. of Spectrosc.*, **12**, 129, (1967).

- [3] R. Tertian, 4^{ième} Colloque International sur les Méthodes Analytiques par Rayonnements X, Strasbourg, France, Preprints, p. 113, (1977).
- [4] G. R. Lachance, *Advances in X-Ray Analysis*, **31**, 471, (1988).
- [5] G. R. Lachance and R. J. Traill, *Can. Jour. of Spectrosc.*, **11**, 43, (1966).
- [6] R. Rousseau and F. Claisse, *X-Ray Spectrometry*, **3**, 31, (1974).
- [7] R. Tertian, *Advances in X-Ray Analysis*, **19**, 85, (1976).
- [8] J. W. Criss and L. S. Birks, *Anal. Chem.*, **40**, 1080, (1968).
- [9] J. Sherman, *Spectrochimica Acta*, **7**, 283, (1955).
- [10] R. Rousseau, Ph. D. Thesis # 3001, Laval University, Québec, QC, Canada, (1975).
- [11] J. Sherman, *ASTM Special Technical Publication No. 157*, 27, (1954).
- [12] G. R. Lachance and F. Claisse, *Advances in X-Ray Analysis*, **23**, 87, (1980).
- [13] R. Tertian, *X-Ray Spectrometry*, **2**, 95, (1973).
- [14] W. K. de Jongh, *X-Ray Spectrometry*, **2**, 151, (1973).
- [15] T. Shiraiwa and N. Fujino, *X-Ray Spectrometry*, **3**, 64, (1974).
- [16] S. D. Rasberry and K. F. J. Heinrich, *Anal. Chem.*, **46**, 81, (1974).
- [17] R. M. Rousseau, *X-Ray Spectrometry*, **13**, 121, (1984).
- [18] R. M. Rousseau, *Advances in X-Ray Analysis*, **32**, 69, (1989).
- [19] R. M. Rousseau, *X-Ray Fluorescence Analysis in the Geological Sciences, Advances in Methodology, Short Course Vol. 7, GAC-MAC Annual Meeting, Montréal, QC, Canada*, 141, (1989).
- [20] G. R. Lachance and F. Claisse, *Quantitative X-Ray Fluorescence Analysis, Theory and Application*, John Wiley & Sons, (1995).
- [21] N. Broll and R. Tertian, *X-Ray Spectrometry*, **12**, 30, (1983).
- [22] R. Tertian, *X-Ray Spectrometry*, **15**, 177, (1986).
- [23] G. R. Lachance, *X-Ray Fluorescence Analysis in the Geological Sciences, Advances in Methodology, Short Course Vol. 7, GAC-MAC Annual Meeting, Montréal, QC., Canada*, 55, (1989).
- [24] N. Broll, P. Caussin and M. Peter, *X-Ray Spectrometry*, **21**, 43, (1992).

