

DEBATE ON SOME ALGORITHMS RELATING CONCENTRATION TO INTENSITY IN XRF SPECTROMETRY

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Willis and Lachance [9] debate the pertinence of a recent study done by Rousseau [2] of three "popular expressions" relating concentration to intensity in X-ray fluorescence (XRF) analysis. It should be pointed out that Willis and Lachance debate only the Lachance identity (Eqn 1) and its associated "new" Lachance-Traill algorithm (Eqn 2) and ignore the two other expressions, namely Claisse-Quintin and Broil-Tertian algorithms [2]. They also continue to ignore the fundamental character of the algorithm proposed by Rousseau [1]. The author would like to thank Willis and Lachance to give him the opportunity to debate six of his arguments in a rational and objective way. As a result the XRF analysts will be able to select the most reliable analytical methods, for getting the most accurate results, with full knowledge of the facts. Their choice of a method will not be based only on the reputation of its author... Finally the author discusses the validity of the four last conclusions that were reached by Willis and Lachance.

1. Introduction

First, the present author would like to explain the context in which the two papers in The Rigaku Journal [1, 2] have been published. He has a lot of respect for the pioneers who have contributed to the knowledge of XRF analysis particularly during the period 1954 (Beattie and Bressey [3]) to 1981 (COLA [4] from Lachance). During that period, innovative scientists such as Sherman, Birks, Norrish, Lachance, Claisse, Jenkins, Criss, Mantler, de Jongh, Raspberry-Heinrich, Willis, Tertian, and all the other great names that the author may have left out inadvertently, have contributed tremendously to the great success that quantitative analysis by XRF spectrometry is known for today. It is because of their groundwork that it was possible for the author to develop the Fundamental Algorithm [1] (FA), which is, he likes to remind himself, the synthesis [1] of 30 years of research and development in XRF analysis by those great men. As a consequence of this spectacular development, after 1981, all the knowledge, and also affordable personal computers, were available for developing powerful and accurate quantitative XRF methods based on fundamental parameters and theoretical multi-element influence coefficients. In 1982, at the Denver X-Ray Conference, the author presented his modest contribution to this evolution, and published it in 1984 in the X-Ray Spectrometry Journal [5, 6]. After 1982, a few other valid methods

have been proposed, like Uni Quant 5 [24], but the author considers that those proposed by Broil-Tertian [7] and Lachance-Claisse [8] in particular are a regressive step. It is the duty of any "specialist" in analytical XRF methods to evaluate newly proposed methods, otherwise who will do it! The author is just trying to make this wonderful science easier to understand, easier to apply and always more performing. When a new idea is of value to the analyst, he does not hesitate to promote it, as in his paper of 1987 on the COLA method [4]. Conversely, when an idea distorts physical reality, he does not hesitate to criticize it, no matter who is the author. It is the role of any diligent specialist to point out errors and highlight good ideas in order for knowledge to evolve and advance, and make the technique more efficient, more accurate and more popular.

The present paper is meant to be an objective response to the paper of Willis and Lachance [9]. Their reaction is quite understandable after the severe criticism [2] of the author regarding the analytical method proposed by Lachance and Claisse [8] in 1995. Let him explain why he did so.

In 1993, the author gave to Lachance, Claisse and Willis a private report, entitled *How to Manage the Future in XRF Analysis*, where he expressed all his strong reservations about the so-called "Lachance identity":

$$P_i + S_i = P_{(i)}C_i - P_i \cdot \left[\sum_j (\mathbf{a}_{ij} - \mathbf{e}_{ij}) \cdot C_j \right] \quad (1)$$

where

- P_i Theoretical primary intensity emitted by the analyte i in the specimen
- S_i Theoretical secondary intensity emitted by the analyte i in the specimen
- $P_{(i)}$ Theoretical primary intensity emitted by a pure specimen of the analyte i
- C_i Concentration of the analyte i in the sample to be analyzed
- α_{ij} Influence coefficient correcting for absorption effects of matrix element j on analyte i (see Ref. [1] for the mathematical definition)
- ϵ_{ij} Influence coefficient correcting for enhancement effects of matrix element j on analyte i (see Ref. [1] for the mathematical definition)
- C_j Concentration of the matrix element j in the sample

(The author calls equation (1) an identity because the term P_i appears on both sides of the equation). At that time, Lachance (and also Claisse and Willis) completely ignored all the arguments of the author. At the very least, he had expected to hear from Lachance some arguments in favor of his approach for explaining why Rousseau could be wrong. Then, in 1995, Lachance and Claisse [8] published exactly the same equation (see Eqn 4.51 in Ref. [8]) again in their book, by ignoring all author's arguments of 1993. They even deduced the LachanceTraill (LT) algorithm [10] once more and associated it to a theoretical multi-element influence coefficient called m_{ij} :

$$C_i = R_i \left(1 + \sum_j m_{ij} C_j \right) \quad (2)$$

where

$$m_{ij} = \frac{P_i}{P_i + S_i} \cdot (\mathbf{a}_{ij} - \mathbf{e}_{ij}) = \frac{(\mathbf{a}_{ij} - \mathbf{e}_{ij})}{1 + \sum_j \mathbf{e}_{ij} C_j} \quad (3)$$

and where the relative intensity R_i is the ratio of the measured net intensity I_i emitted by the analyte i to the intensity $I_{(i)}$ of the pure analyte i . Equation (3) comes from Lachance [11]. Note that the same equation (3) had already been deduced 11 years ago by Rousseau [5]. Indeed, in 1984, he proposed the same expression in the following form:

$$C_i = R_i \left(1 + \sum_j \mathbf{a}_{ij}^* C_j \right) \quad (4)$$

where

$$\mathbf{a}_{ij}^* = \frac{\mathbf{a}_{ij} - \mathbf{e}_{ij}}{1 + \sum_j \mathbf{e}_{ij} C_j} \quad (5)$$

Note that equations (3) and (5) are the same. Lachance and Claisse use a different symbolism, but the meaning of each symbol is the same. It is akin to reinventing the wheel! Therefore, according to the author, their work does not contribute anything to progress in the knowledge of XRF analysis. In fact, it is a regressive step as demonstrated in Ref. [2]. Did the author was right to publicly reveal all his arguments of the Ref. [2] after having informed Lachance of all his reservations five years before? He does not know. It is to the reader to decide. Personally, the author considers that the Fundamental Algorithm [1] (Eqn 26) describes in a more realistic way than the "new" LT algorithm (Eqn 2) the physical reality in XRF analysis and its performance is better in practice. Furthermore, he thinks that it is a disservice to the XRF analyst community to continue to propose the LT algorithm with variable coefficients m_{ij} . This is what will be demonstrated hereafter.

Willis and Lachance [9] begin their paper with some statements about which we are all in agreement. The quoted statements of v. Hamos, Sherman, Jenkins, Lachance and Traill, Criss and Birks, Rasberry and Heinrich and Shiraiwa and Fujino are well known and largely accepted by all the XRF scientific community, including the author. Willis and Lachance give a long list of references about this more or less pertinent introduction, therefore this material will not be repeated here.

Willis and Lachance [9] contest the validity of six of author's arguments [2] about equations (1), (2) and (3). They are:

1. Correct formulation of the Lachance identity
2. Distortion of physical reality
3. Summation over the complete wavelength range of the polychromatic excitation source
4. Treatment of the weighting factor
5. Defining the intensity I_i of the analyte line as a function of the intensity $I_{(i)}$ of the pure analyte
6. Non respect of the spirit of Sherman

All these six arguments will be reconsidered to the light of the objections by Willis and Lachance. The author accepts to participate in this debate in the hope that it will reveal even more the true nature of the physical reality of quantitative analysis by X-ray spectrometry. It is also the hope

of the author that XRF analysts will find some benefits in practice, no matter who is right or wrong.

2. Correct Formulation of the Lachance Identity

Willis and Lachance [9] claim that the Lachance identity:

$$P_i + S_i = P_{(i)}C_i - \sum_j A_{ij}C_j + \sum_j E_{ij}C_j \quad (6)$$

has been stated incorrectly by the author [2] in the following form:

$$P_i + S_i = P_{(i)}C_i - P_i \cdot \sum_j \mathbf{a}_{ij}C_j + P_i \cdot \sum_j \mathbf{e}_{ij}C_j \quad (7)$$

where

$$A_{ij} = P_i \cdot \mathbf{a}_{ij} \quad (8)$$

and

$$E_{ij} = P_i \cdot \mathbf{e}_{ij} \quad (9)$$

Willis and Lachance **and** the author recognize that the two expressions are **exactly** equivalent but their derivation is different. So where is the problem? The only problem seems to be that Willis and Lachance simply prefer the derivation of Lachance and Claisse [8] rather than the one of Rousseau [1]. The author considers that their arguments for their preference are not convincing enough. It is like to say that a mother prefers her child rather than the child of another mother... Their preference is natural. For his part, the author finds the derivation of Lachance and Claisse laborious, introduces the unnecessary variables P_i , S_i , A_{ij} and E_{ij} and reveals nothing new as compared to the derivation by the author of the Fundamental Algorithm [1]; but what is worse, when the Lachance identity is rewritten in the form of the equation (7) or (1), it shows clearly that the variable P_i is expressed as a function of itself. This is just the type of equation that any mathematician tries to avoid. Finally, the Lachance identity is not particularly useful in practice. XRF analysts are really interested in calculating concentrations, and not intensities, which can actually be measured.

The Lachance identity is an intermediate step in the derivation process leading to the "new" LT algorithm (Eqn 2). The equivalent intermediate step for the derivation of the Fundamental Algorithm by Rousseau is the equation (16) in the Ref. [1]:

$$I_i(\mathbf{I}) = g_i C_i \sum_{I_k=I_{\min}}^{I_{\text{edge } i}} W_i'(\mathbf{I}_k) \frac{1 + \sum C_j \mathbf{d}_{ij}(\mathbf{I}_k)}{1 + \sum C_j \mathbf{a}_{ij}(\mathbf{I}_k)} \quad (10)$$

where

- I_i Net intensity of analyte i
- λ_i Wavelength of characteristic line of analyte i
- g_i Proportionality constant, instrument dependent
- C_i Concentration of analyte i in the sample
- W_i' Weighted factor for each incident wavelength λ_k
- λ_k Incident wavelength
- C_j Concentration of matrix element j in the sample
- δ_{ij} Influence coefficient correcting for enhancement effects of j on i for a monochromatic excitation source of wavelength λ_k
- β_{ij} Influence coefficient correcting for absorption effects of j on i for a monochromatic excitation source of wavelength λ_k

This equation allows one to calculate the intensity I_i , which is equal to $g_i \cdot (P_i + S_i)$. It is the Sherman equation [12] expressed in a modified form. Equations (6) and (10) have the same common source, the Sherman equation [12], as expressed by Criss and Birks [13]. Furthermore, contrary to the claim of Willis and Lachance, both expressions involve the use of P_i and S_i . That is essential; otherwise, they would not be equivalent! This is also true for the "new" LT algorithm and the Fundamental Algorithm. Thus, Lachance and Claisse [8] and Rousseau [1] derive two different, but equivalent, expressions from a common source. However, they follow two different routes for the derivation of these both expressions. The question now is to know which expression is most representative of physical reality? This subject will be discussed in Section 3.

In the meantime, how the intermediate expression (6) has been derived, or how it is formulated, is not the critical issue. What is important is the validity of the final result, i.e. the algorithm permitting one to calculate concentrations from measured intensities. It follows, therefore, that the Lachance identity (Eqn 6 or 7) is not of importance and does not deserve the prominence that Willis and Lachance assign to it.

3. Distortion of Physical Reality

To begin this section, the author takes the liberty to paraphrase the elegant first sentence of the same section in the paper of Willis and Lachance [9]. It represents very well the point of view of the author. The modified sentence becomes as follows: "In XRF analysis, theoretical influence coefficients have a physical meaning and any mathematical expression deduced for calculating them must not only be able to calculate representative values pertinent to an analytical context, but also must retain the essence of the basic physical principles as proposed by Sherman [12]."

As stated in their paper, Willis and Lachance [9] as well as the author recognize that the basic physical principles of XRF emission are very well described by the Sherman equation as rewritten by Criss and Birks [13]. The author recognizes also that the equation (6) is able to calculate representative numerical values pertaining to an analytical context. However, the question is to determine if the equation (6) of Lachance and Claisse [8] and the equation (10) of Rousseau [1] represent faithfully the physical principles as proposed by Sherman.

To find that out, let us consider only one aspect of the Sherman equation, i.e. how Sherman, Lachance and Claisse and Rousseau translate the absorption phenomena in mathematical language, in the case of a monochromatic excitation source of wavelength λ_k . In this case, for absorption effects only, Sherman wrote:

$$I_i = k_j \frac{C_i}{1 + \sum_j b_{ij} C_j} \quad (11)$$

For the same analytical context, the equation (10) of Rousseau becomes **exactly the same** as the Sherman equation, i.e.

$$I_i = k_j \frac{C_i}{1 + \sum_j b_{ij} C_j} \quad (12)$$

Finally, for the same analytical conditions, equation (6) of Lachance and Claisse becomes

$$I_i = I_{(i)} C_i - I_i \cdot \sum_j b_{ij} C_j \quad (13)$$

where

$$b_{ij} = \frac{m_j(I_k) \cos \epsilon c f'' + m_j(I_i) \cos \epsilon c f''}{m_i(I_k) \cos \epsilon c f'' + m_i(I_i) \cos \epsilon c f''} - 1 \quad (14)$$

- i Analyte
- j Matrix element

- C_i Concentration of analyte i in the sample
- C_j Concentration of matrix element j in the sample
- I_i Net intensity of analyte i
- k_i or $I_{(i)}$ Intensity of pure analyte i
- λ_k Incident wavelength
- β_{ij} Influence coefficient correcting for absorption effects of j on i for a monochromatic excitation source of wavelength λ_k
- $\mu_x(\lambda_y)$ Mass absorption coefficient of the element x calculated for the wavelength y
- ϕ', ϕ'' Incident and take off angles of X-ray beams

The three equations (11), (12) and (13) have been written using the same symbolism in order to facilitate comparison. Note also that these three equations are all equivalent to the LT algorithm as proposed by Lachance and Traill [10] in 1966, i.e.

$$C_i = \frac{I_i}{I_{(i)}} \left(1 + \sum_j b_{ij} C_j \right) \quad (15)$$

It is not surprising then, that all the numerical examples supplied by Willis and Lachance [9] show perfect agreement. Let us find out now if all these versions of the Sherman equation (Eqns 12 and 13) say the same thing on the mathematical and physical plans. In order to do that, let us look at it from the point of view of a mathematician and that of a physicist. According to the mathematician, the absorption effects in the equation (12) of Rousseau has the general form of a hyperbola equation, i.e.

$$Y = \frac{a}{1+x} \quad (16)$$

while the equation (13) of Lachance and Claisse has the general form of a straight-line equation, i.e.

$$Y = b-cx \quad (17)$$

Both equations are illustrated by the plots of Figures 1 and 2. The mathematician is forced to conclude that the same variable (x) when expressed as a **division** and as a **subtraction** cannot vary in the same way, even if the parameters a , b and c can be selected in a such way to give the same numerical values.

The physicist would say that a **subtraction** is not equivalent to a **division**. Even if the final result is the same, the involved physical processes

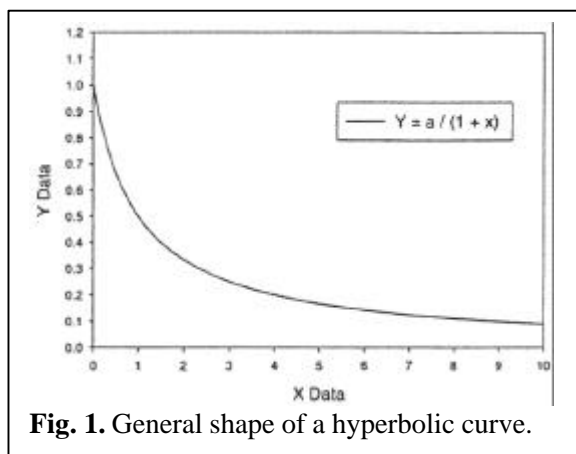


Fig. 1. General shape of a hyperbolic curve.

are different. For illustrating it, let assume that there are five light bulbs hanging from the ceiling of a room. By removing one light bulb from the ceiling, the light intensity is reduced. This phenomenon is the equivalent to a subtraction (5-1=4, only four light bulbs are still in place). The light intensity can also be reduced by a dimmer. By turning the knob, for a constant voltage (V), an increase of the resistance (R) reduces the current (i), which has the effect of also reducing the intensity of the light. This phenomenon is the equivalent of a division, after the Ohm law ($i = V/R$). It is true that in both instances the net result is the same, in spite of the fact that the two physical phenomena used for reducing the light intensity are completely different.

The physicist is forced to conclude that in physics, a subtraction is not equivalent to a division. Similarly to the above example, using current and resistance, in XRF analysis the analyte intensity decreases (or increases) when the matrix absorbs more (or less) strongly than the analyte. The absorption phenomena are then better represented by a division. Just remember, for example, the Beer-Lambert law ($I = I_0 / \exp(\mu x)$), and the Sherman equation ($I_i = k_i C_i / \mu_s^*$).

The author is forced to conclude in agreement with the mathematician and the physicist that equation (6) of Lachance and Claisse does not describe properly, or that it distorts, physical reality as described by the Sherman equation. Such is not the case with equation (10) of Rousseau, which completely respects the Sherman equation. Thus, it is both confusing and unnecessary to propose a new equation for calculating intensities. A considerable amount of work has already been

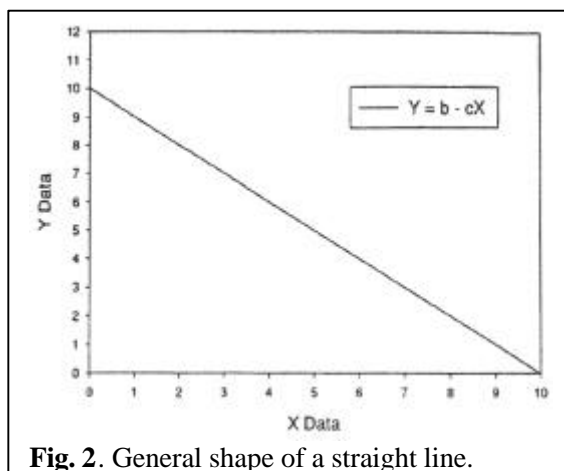


Fig. 2. General shape of a straight line.

done on this subject: Sherman [12], Shiraiwa and Fujino [14], Criss and Birks [13], G. Pollai, M. Mantler and H. Ebel [15], Rousseau [1], etc. It would be valuable to propose new equations if, and only if, they are fully in agreement with the previous ones and propose something new. Without such an approach, the present approach of Lachance and Claisse [8] is likely to cause confusion and introduce further divergence about the correct use of the fundamental physical concepts in XRF analysis. Therefore, their approach is not particularly useful and indeed its use should be discouraged.

4. Summation over the Complete Wavelength Range of the Polychromatic Excitation Source

The calculation of X-ray intensities by the Sherman equation requires an explicit equation for calculating the spectral distribution of the polychromatic excitation source. However, there is no analytical expression available to generate an incident spectrum in an essentially exact way, for any experimental conditions. To overcome this problem, the integral over λ is replaced by a finite sum of k values of narrow wavelength intervals $\Delta\lambda_k$ with corresponding incident intensities $I_0(\lambda_k)$:

$$\int_{I_{\min}}^{I_{\text{edge}i}} I_0(I) dI \rightarrow \sum_{k=I_{\min}}^{I_{\text{edge}i}} I_0(I_k) \Delta I_k \quad (18)$$

where the summation is carried out over the effective wavelength range, i.e. from λ_{\min} to λ_{edge} of the analyte i . The concept of summing over a finite number of wavelength intervals was first proposed by Gilfrich and Birks [16] in 1968, and continues to be at the root of all Fundamental-Parameters

methods.

There are plenty of instances as evidence in the book of Lachance and Claisse [8] that they incorporated the summation over $\Delta\lambda$ intervals in the derivation process of equation (6) and the subsequent equation (2). However, that is not the real problem, but they rather omitted to explain the physical impact of the summation term Σ_{λ} on the m_{ij} coefficient (Eqn 3) in the "new" LT algorithm. They also failed to explain that the α_{ij} and ε_{ij} coefficients are the weighted means of all absorption and enhancement effects, respectively, caused by element j on analyte i , where to each incident wavelength $\Delta\lambda$ is given a weight $W_i(\lambda_k)$. It is this physical interpretation that seems important to the author. See the Ref. [1] for more information.

5. Treatment of the Weighting Factor

The treatment of the weighting factor is not just a matter of which symbol is used in the Lachance identity (Eqn 6) to represent it. Lachance and Claisse [8] use the symbol $P_{i\lambda}$ to represent the weighting factor, while Rousseau [1] uses the symbol $W_i(\lambda_k)$. Both symbols are equivalent but do not deliver the same message on the physical plan. And this is what is much more important in this instance, i.e. the interpretation of the message.

The concept of the weighting factor W_i was introduced by Rousseau [5] in 1984 to define the influence coefficients α_{ij} and ε_{ij} and its interpretation is as follows:

The equations (24) and (27) of the α_{ij} and ε_{ij} coefficients reveal explicitly that they 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 $W_i(\lambda_k)$. Rousseau ascribes great importance to this concept because it reveals something new that was **concealed** in the Sherman equation; in practice, this interpretation makes physical sense and it leads to two important conclusions on the correction for matrix effects [1]. The interpretation of this important concept was completely ignored by Lachance and Claisse [8].

Indeed, the equivalent equations used by Lachance and Claisse to define the α_{ij} and ε_{ij} coefficients are equations (8) and (9) rewritten in the following form:

$$\mathbf{a}_{ij} = \frac{A_{ij}}{P_i} \quad (8)$$

and

$$\mathbf{e}_{ij} = \frac{E_{ij}}{P_i} \quad (9)$$

As opposed to the **equivalent** equations (24) and (27) of Rousseau, the two last equations of Lachance and Claisse do not **explicitly** reveal that the coefficients α_{ij} and ε_{ij} are weighted means. Lachance and Claisse content themselves only defining individually each variable A_{ij} , E_{ij} and P_i for numerical calculations. They do not interpret their ratios. Of course, it is important to define each variable individually but the author considers that it is also important to interpret the meaning of the above ratios, which represent the **weighted means** (see Eqn 26 of Ref. [1]) of all absorption and enhancement effects, respectively, caused by element j on analyte i . Lachance and Claisse mention nothing in their book about this important feature of the α_{ij} and ε_{ij} coefficient definitions and failed to explain their interpretation. The important expression "weighting factor" is not even included in the index of the book. Another related problem of Lachance and Claisse [8] is that they use and define too many unnecessary variables, such as P_i , S_i , A_{ij} , E_{ij} , M_{ij} , a_{ij} , e_{ij} , m_{ij} , etc., which confuse students unnecessarily when the method is taught (author's opinion based on his personal teaching experience).

6. Defining the Intensity I_i of the Analyte Line as a Function of the Intensity I_{ii} of the Pure Analyte

When discussing the Lachance identity (Eqn 6) of Lachance and Claisse [8], the author [1] states that: "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." This statement is correct. It was in reference to the equations of page 289 of the Sherman paper [12], rather than to the ones of page 295. Indeed, on page 289, Sherman calculates **absolute** net intensities as a function of fundamental parameters, intensities of the incident source and the specimen composition. On the other hand, on page 295, he calculates **intensity ratios**, not absolute net intensities, which is obvi-

ously not the same thing.

7. Non Respect of the Spirit of Sherman

Again here, there is a large gap between what the author intended to explain and what Willis and Lachance have understood. The author assumes that his explanations were not clear enough. Let us try again.

Based on equation (10), which is the Sherman equation [12] expressed in a modified form, Sherman clearly states that the emitted X-ray intensity is:

- Calculated explicitly from fundamental parameters, intensities of the excitation source and specimen composition. Not from $P_{(i)}$, P_i , or (P_i+S_i) intensities;
- Proportional to the concentration C_i of the analyte;
- Proportional to a ratio where 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 (or increase) with the absorption effects if β_{ij} is positive (or negative);
- All these matrix effects are weighted by the factor W_i' , which takes into account the polychromaticity of the incident spectrum.

In the light of equation (10), the author considers that these conditions represents the "spirit of Sherman", involve no degree of interpretation, are objective and are not a subjective exercise. Any new expression proposed for calculating X-ray intensities must respect these preliminary requirements to be theoretically valid. Any new mathematical expression deduced for calculating X-ray intensities must not only be able to calculate representative values pertaining to an analytical context, but also must respect the hyperbolic nature of the Sherman equation to be in agreement with physical reality. An examination of the literature done by Rasberry and Heinrich [17] based on 42 publications confirms that the relation between intensity and concentration can be adequately represented by a hyperbolic function. Furthermore, Sherman himself stated that [18]:

"The theoretical correlation of the intensity of the fluorescent spectra, excited by a

polychromatic beam, from a multicomponent mixture and the concentration of an element in the mixture involves integral harmonic **means** and the use of **hyperbolic** curves in multidimensional spaces. The computational labor involved makes the relations too complicated for general use."

That being said, the author is forced to conclude that the word **linear** does not quite fit the "spirit of Sherman" and this statement is objective. However, it does not mean that linearity is eliminated from the calibration procedure. On the contrary, efficient calibration procedures have been developed with success by Rousseau, Willis and Duncan [19] where linearity continues to be the main objective.

8. The "New" Lachance-Trail Algorithm

The LT algorithm (Eqn 2) has been deduced yet another time from the Lachance identity [8] (Eqn 6). If the Lachance identity distorts physical reality, the chances are good that the subsequent equation derived from it will also be compromised with regard to experimental reality. When the foundations are fragile, the rest of the edifice is liable to be fragile as well. Let us see.

Lachance and Claisse [8] deduced from the Lachance identity (Eqn 6) a "new" (already deduced by Rousseau [5], 11 years ago) effective influence coefficient m_{ij} , which is used in association with the LT algorithm:

$$C_i = R_i \left[1 + \sum_j (a_{ij} - e_{ij}) C_j \right] \quad (19)$$

where .

$$m_{ij} = a_{ij} - e_{ij} \quad (20)$$

and

$$a_{ij} = \frac{P_i \cdot \mathbf{a}_{ij}}{P_i + S_i} \quad (21)$$

$$e_{ij} = \frac{P_i \cdot \mathbf{e}_{ij}}{P_i + S_i} \quad (22)$$

The α_{ij} and ϵ_{ij} coefficients are fundamental influence coefficients correcting for absorption and enhancement effects, respectively. The coefficients a_{ij} and e_{ij} are fractions of the influence coefficients α_{ij} and ϵ_{ij} , respectively, when the secondary intensity S_i is different from zero. The coefficients a_{ij} and e_{ij} are equal to α_{ij} and ϵ_{ij} , respectively, when the secondary intensity S_i is equal to zero. Thus, we can say that the coefficients a_{ij} and

e_{ij} are some "kind" of absorption and enhancement influence coefficients, respectively.

In physics, when two variables are subtracted it is because they are of the same nature. For example, we can subtract a speed value from another speed value, a distance from another distance, an energy value from another energy value, an intensity from another intensity, etc. We cannot simply subtract a distance value from a speed value, for example, i.e. we cannot subtract two variables of different nature, even if they are dimensionless; now a_{ij} and e_{ij} are two variables of a different nature, mathematically and physically, correcting for absorption and enhancement effects, respectively. Therefore, Lachance and Claisse, by proposing equation (19), are not respecting this fundamental reality.

Another way to interpret this fact is by assuming that the enhancement is equivalent to a **negative absorption**. The present author, together with many others, including Lachance, Claisse and Willis, does not support this interpretation about the enhancement. It is important then, to try to avoid the use of the "new" LT algorithm (Eqn 19) that favors such a conclusion.

In practice, there is another consequence of regrouping in one entity the α_{ij} and ϵ_{ij} coefficients rather than to keep them separated, as in the Fundamental Algorithm (see Eqn 26), in a ratio. In practice, not only there is no benefit in using the "new" LT algorithm rather than the Fundamental Algorithm, but one also loses something. By using equation (19) we lose the *mathematical robustness*, i.e. equation (19) requires more iterations than the Fundamental Algorithm before getting to the final result (the convergence process is slower) and this equation is also more sensitive to any error in measured intensities [20].

Furthermore, Lachance and Claisse did not suggest any method to calculate the first estimate of the sample composition and no calibration procedure either: their "new" (?) Fundamental-Parameters method is incomplete. More comments regarding this approach are presented in Ref. [2].

Lachance [21, 22] (and also Claisse [8] and Willis [9]) bases many of his conclusions on simple numerical examples, which are, most of the time, very far from the practical reality of XRF analysts. The validity of such an approach (and also conclusions) is questionable because it does

not allow one to check realistically if the spirit of Sherman is faithfully respected throughout. Furthermore, Lachance's numerical examples would be more convincing for XRF analysts if they were included calibrations, calculations for the first estimate of sample compositions, and explained how well the iteration process converges toward the final results. All these important steps are essential to any Fundamental-Parameters method. For example, the Fundamental Algorithm uses an outstanding calibration procedure [19] and an effective method for calculating the first estimate of sample compositions [1].

Consequently, the author does not anticipate a long future for the "new" LT algorithm for the following reasons. When Lachance and Traill [10] proposed the initial LT algorithm in 1966, they also proposed an equation to calculate theoretical influence coefficients. They called them "alpha" coefficients. These alpha coefficients have very specific properties: they are calculated from theory for a specific analytical context, using binary standards, assuming that the incident tube spectrum is monochromatic and they are calculated **only** to correct for absorption effects. The enhancement effects are not taken into account. The proposed equation was:

$$C_i = R_i \left(1 + \sum_j b_{ij} C_j \right) \quad (23)$$

where the "alpha" coefficient β_{ij} is defined by the equation (14). In 1984, Rousseau [5] generalized the **same** coefficient β_{ij} to a polychromatic excitation source as follows:

$$a_{ij} = \frac{\sum_k W_i(\lambda_k) b_{ij}(\lambda_k)}{\sum_k W_i(\lambda_k)} \quad (24)$$

where to each incident wavelength λ_k is given a weight $W_i(\lambda_k)$. This coefficient still does not correct for the enhancement effects. The question is then how to modify the resulting LT algorithm:

$$C_i = R_i \left(1 + \sum_j a_{ij} C_j \right) \quad (25)$$

to take into account the enhancement effects? The answer is **not** the "new" form of the LT algorithm (Eqn 19). Indeed, the new equation must incorporate all the mathematical and physical properties of the magnificent equation (25) for the correction of absorption effects, but must also integrate the correction for the enhancement effects while remaining respectful and faithful to the spirit of Sherman (see Section 7). The Fundamental Algo-

rithm as proposed by Rousseau [5] in 1984 fulfills all these conditions:

$$C_i = R_i \frac{1 + \sum_j \mathbf{a}_{ij} C_j}{1 + \sum_j \mathbf{e}_{ij} C_j} \quad (26)$$

where

$$\mathbf{e}_{ij} = \frac{\sum_k W_i(\mathbf{I}_k) \mathbf{d}_{ij}(\mathbf{I}_k)}{\sum_k W_i(\mathbf{I}_k)} \quad (27)$$

is the influence coefficient correcting for the enhancement effects. The equations that define the symbols $W_i(\lambda_k)$ and $\delta_{ij\lambda_k}$ are given in Ref. [1]. It should be noted that when the matrix elements j do not enhance the analyte i , all the coefficients ϵ_{ij} are equal to zero and the Fundamental Algorithm becomes the famous LT algorithm (Eqn 25). Indeed, the reader should look at the Fundamental Algorithm as a generalization of the LT algorithm to correct for enhancement effects. The author finds it gratifying to have succeeded in combining, in such an elegant way, the exceptional qualities of the LT algorithm in a context of pure absorption to an efficient correction for enhancement effects, without physically assuming that an enhancement effect is equivalent to a negative absorption. However, the author does agree with Willis and Lachance [9] that the beauty is purely in the eye of the beholder, and different, and therefore subjective, for each person...

It is important to remind the reader that the Fundamental Algorithm was developed to be applied to very general analytical contexts by meeting the following criteria:

- Combines the treatment of monochromatic and polychromatic excitation sources in a single algorithm;
- Corrects for both matrix effects, absorption and enhancement, for binary, ternary or any multi-element specimens;
- Is deduced explicitly from fundamental principles of X-ray physics and respects them completely;
- Uses an efficient calibration procedure [19] that allows one to adapt theory to the experimental data of each spectrometer;
- Uses an efficient approach for calculating the first estimate [1] of the sample composition.

9. Conclusion

In the past, many mathematical models, or al-

gorithms, using "alpha" coefficients were proposed for the correction of matrix effects. They were all approximations to a physical equation called the Sherman equation [12]. Then in 1968, Criss and Birks [13] showed how to apply this equation to quantitative XRF analysis, in a method that they called "Fundamental Parameters". Like anything else in science, these concepts have greatly evolved since the last four decades. Today, many approximate algorithms from the very beginning can be directly deduced from the Sherman equation, without doing any approximation during the derivation process [1]. They are all equivalent to the Sherman equation; they are all the same equation as the Sherman equation, except they express the Sherman equation in a different mathematical form. Now, which form is the best one for describing all the physical phenomena implied in quantitative XRF analysis? Which form performs the best in practice for calculating the composition of a sample? Based on the evidence, the author must conclude that it is the Fundamental Algorithm [1] (FA). The FA is the same Sherman equation expressed in another mathematical form. It is a Fundamental-Parameters method that combines the practical aspect of influence coefficients and the theoretical correctness of the Sherman equation.

However, there is a major difference between the Sherman equation and the FA. The Sherman equation enables one to calculate only Xray intensities from which the sample composition can be possibly deduced, i.e. it is an indirect calculation process. It was the major contribution of Criss and Birks [13] in 1968. On the other hand, the FA calculates directly the sample composition without having to calculate the intensities first. In practice, the consequences of that critical difference are: The FA is more robust mathematically than the Sherman equation. It always converges during the calculation process and requires less iterations to get the final sample composition.

In the light of these comments on method evolution and Fundamental Parameters, the four last conclusions of Willis and Lachance [9] are clearly incorrect and cannot be justified. The author sees the situation as equivalent to a competition of the Olympic Games. All participants to a race could be excellent athletes, in very good shape, but only one participant will receive the golden medal for the race. If somebody is not

ready to accept this rule, it is better for him or her to not participate. In this particular case, it means that

- authors who have submitted papers for publication in XRF analysis,
- editors of journals who have accepted to publish them,
- teachers who have taught the proposed analytical methods
- and instrument manufacturers who have used these methods in practice

must be aware that, in spite of the excellence of their work, the proposed methods will eventually become obsolete and replaced by something better. The author apologizes if his enthusiast for the Fundamental Algorithm has let imply something different.

In future, the use of the "new" LT algorithm (Eqn 2) will inevitably cease for all the reasons mentioned above and will be replaced by the Fundamental Algorithm (Eqn 26), which is in agreement with physical reality. However, the LT algorithm associated with *theoretical binary influence coefficients* as proposed by Rousseau [23] can be applied with accuracy to the determination of limited concentration ranges (0-10%) (e.g. oxides diluted in fused discs).

In order to obtain accurate results with the Fundamental Algorithm some rules must be respected. Although the calibration procedure [19] of the Fundamental Algorithm requires only a little number of reference materials, a few, nevertheless, must be used in practice. For best accuracy, reference materials of a type similar to the unknown samples should be used. Also, the preparation of samples and reference materials must be identical. Thus, that will compensate considerably for all the imperfections of theory and the uncertainties in the fundamental parameters (e.g., fluorescence yields, mass absorption coefficients, etc.).

Finally, the present author, together with Lachance, Claisse and Willis, does not believe that XRF spectrometry is in a sad state and considers that the door is still open to valid criticism. He is also convinced that the topic of mathematical algorithms relating concentration to intensity in X-

ray fluorescence spectrometry should remain open to further valid developments.

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