
CONTRIBUTED PAPERS

RESOLVING APPARENT DIFFERENCES IN MATHEMATICAL EXPRESSIONS RELATING INTENSITY TO CONCENTRATION IN X-RAY FLUORESCENCE SPECTROMETRY

JAMES P. WILLIS¹ AND GERALD R. LACHANCE²

¹ Department of Geological Sciences, University of Cape Town, Rondebosch 7700, South Africa
² 1100 chemin St-Felix, Hammond, ON, Canada, K0A 2A0

In a recent study of three "popular expressions" relating concentration to intensity deemed "algebraically in perfect agreement" and "theoretically valid", these expressions were nevertheless qualified by such terms as "superfluous", "gives the analyst a false interpretation", "is in general invalid", "should not even exist!". The conclusions were based on assigning a primordial status to a fourth expression, "the Rousseau algorithm", which is deemed "THE Fundamental Algorithm" and which is then used to "verify the theoretical validity of..." the other algorithms, leading to categorically finding two expressions wanting. In particular, the correctness of the equation (2) in this paper (equation (4.51) in Lachance and Claisse [9]) has been called into question. The authors question the propriety of this approach and the validity of the conclusions that were reached.

INTRODUCTION

Analysts using other analytical techniques would be surprised that, some 50 years after XRF spectrometers became commercially available and used for quantitative compositional analysis, the correlation between concentration and emitted intensity still should be raised as a topic for conflict. This paper challenges the necessity for such conflict. A brief background is essential. In the quotations given below the underlining is that of the present authors.

Background

Prior to 1950 the basic problem as pointed out by v. Hamos [1] was: "This formula ... intensity emitted ... does not increase linearly with concentration. This is of extreme importance for quantitative analysis."

In 1955 the problem was succinctly expressed by Sherman [2] in some closing remarks of a 24-page paper: "The formulae in Section 4 may be considered as the rigorous solution to the direct problem under the assumption of a monochromatic incident beam. The inversion of the formulae to show c_i as explicit functions of the intensities or intensity ratios is clearly impossible in a rigorous sense."; "The restriction to a monochromatic beam is difficult to remove in an analytical sense."; "A suggestion is presented for a

useful extension to the treatment of a polychromatic incident beam."

The above quotations follow previous remarks by Sherman [2] in subsection 4.2: "it is to be noted that the increasing complexity of the formulae ... is due to two factors, namely: The final intensity is the resultant of a chain of radiative transfers ... This effect increases the order of integration. The change from a narrow beam or collimated beam to a broad or divergent beam. This effect changes the functions in the integrand from exponential ... to integroexponential...".

Steps for Solution of the Problem

In essence the task facing analysts in the development of practical/theoretical expressions relating intensity and concentration may be visualized under six components:

Firstly,

1) deriving expressions defining C_i .

Secondly, extending the analytical context:

2) from monochromatic to polychromatic incident excitation sources;

3) from absorption effect only to include the enhancement effect;

4) from binary systems to multi-element systems.

Thirdly, retaining:

- 5) the theoretical approach, i.e. based on XRF/physics principles;
- 6) explicitness, i.e. no approximation introduced in the derivation processes.

It is not surprising that the progression towards achieving this goal involved the contributions of a host of authors, that their contributions followed different paths, and that in many cases the contribution of one analyst "opened a door" for other analysts and further progress.

That a host of contributions are involved was pointed out by Jenkins [3] in 1979: "...around 50 different models have been proposed." but that "... only a handful are still in general use."

This corroborates listings of references to that effect by Lachance and Traill [4], Criss and Birks [5] and Rasberry and Heinrich [6].

Two Expressions are Examined

This paper will examine two expressions both of which were proposed after 1979 and which are germane to the apparent conflict.

One is equation (73) in Rousseau [8]:

$$I_i(\lambda_i) = g_i C_i \sum_{\lambda_k=\lambda_{\min}}^{\lambda_{\text{edge}i}} W_i(\lambda_k) \frac{1 + \sum_j C_j \delta_j(\lambda_k)}{1 + \sum_j C_j \beta_j(\lambda_k)} \quad (1)$$

The other is a mathematical expression (equation (4.51)) in Lachance and Claisse [9], namely,

$$P_i + S_i = P_{(i)} C_i - \sum_j A_j C_j + \sum_j E_{ij} C_j \quad (2)$$

where

P_i theoretical primary fluorescence emission

S_i theoretical secondary fluorescence emission

$P_{(i)}$ theoretical fluorescence emission from pure element "i"

C_i concentration (weight fraction) element "i", the analyte

A_{ij} absorption influence coefficient

C_j concentration (weight fraction) element "j", matrix element

E_{ij} enhancement influence coefficient

2fW

The purpose of this examination is to refute the claim by Rousseau that equation (2): "distorts the physical reality", "is a pure algebraic artifice", "does not tell to analysts the truth" and "should not even exist!"

The examination is facilitated by the fact that both Rousseau and the authors are in agreement that Criss and Birks [5] is the **source** of the derivation of equations (1) and (2), namely, equations numbered 7 and 9 in Criss and Birks [5]. Thus both expressions can be traced back to Sherman, given that Sherman's contributions led to Shiraiwa and Fujino's contribution [10], which in turn led to Criss and Birks [5]. This sequence is recognized by Jenkins [3], p. 39, namely that "... Sherman published his classic work on the fundamental relationship between characteristic line intensity and concentration. His data were refined and improved by Shiraiwa and Fujino in the mid 1960's but a major problem remained the description of the spectrum of the exciting source radiation. This problem was finally overcome by Birks' group..."

Procedure

Each topic deals with a specific 'error' attributed to equation (2) by Rousseau. Four of the topics, namely: the **correct formulation** of equation (2); **summation over $\Delta\lambda$** for polychromatic excitation sources; the **choice of weighting factors**; and **defining I_i** (analyte intensity) as a function of $I_{(i)}$ (intensity of pure analyte); involve a minimum, if any, degree of interpretation.

The topics: **distortion** of physical reality and non respect of the **spirit** of Sherman, on the other hand, involve a degree of interpretation, namely, what constitutes a distortion and identifying or stating clearly what constitutes the spirit of Sherman.

†ã(1)

- quotations from Rousseau [7, 8];

- quotations from the published XRF literature, none from the authors' own publications;

- equations and data that are relevant to the topics, from Lachance and Claisse [9].

Notation and terminology

It is taken as given that it is very common when dealing with a number of references, especially if they cover a wide time span, for the authors to have used different symbols for identical definitions, and identical symbols for different entities. In this paper a common notation is used when designating identical entities, i.e. the symbols used in the original papers have been replaced for clarity reasons only.

CORRECT FORMULATION OF THE SO-CALLED 'LACHANCE IDENTITY'

The formulation (equation numbered 65) in Rousseau [8] of the so-called 'Lachance identity' is not correct. The equation as stated (incorrectly) by Rousseau is:

$$P_i + S_i = P_{(i)}C_i - P_i \sum_j \alpha_{ij}C_j + \sum_j \epsilon_{ij}C_j \quad (3)$$

where

α_{ij} absorption influence coefficient, Rousseau algorithm

ϵ_{ij} enhancement influence coefficient, Rousseau algorithm

whereas the correct mathematical expression, equation numbered 4.51 on p. 104 of Lachance and Claisse [9] and referred to by Rousseau as the 'Lachance identity', is equation (2), i.e.

$$P_i + S_i = P_{(i)}C_i - \sum_j A_{ij}C_j + \sum_j E_{ij}C_j \quad (2)$$

The two expressions are equivalent but their derivation is different, an important fact which Rousseau failed to recognize. Rousseau's derivation is given in [7], Section 11.4 titled: "*Deducing the Lachance Identity from the FA*", i.e. from the "*Fundamental Algorithm*" which led to equation (3). Given that equation (3) is derived from Criss and Birks [5] **after** its reformulation as the Fundamental Algorithm, wherein the influence coefficients are defined and expressed in terms of a and e influence coefficients, it therefore follows that these coefficients would be retained and appear in the formulation of equation (3).

However, the concept underlying the development of equation (2), recalled above, is different. The process involves deriving an expression for primary and secondary intensity (in arbitrary units, i.e. the incident spectrum is expressed in arbitrary units) directly and explicitly from the source, i.e. Criss and Birks [5]; hence, indirectly from Shiraiwa and Fujino [10] and Sherman [2]. The main goal was the derivation of a theoretical expression that did not relate to any one analytical algorithm, e.g. the Lachance-Traill [4], Broll-Tertian [11], de Jongh [12] or Rousseau [13] algorithms.

As shown on p. 104 of reference [9], the concept was to reformulate equation (2) so as to be more amenable to quantitative analysis, namely by trans-

posing the term containing C_i from the right hand side of the equation to the left hand side:

$$P_{(i)}C_i = P_i + S_i + \sum_j A_{ij}C_j - \sum_j E_{ij}C_j \quad (4)$$

which can be further transformed to [9]

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

It is then shown in Lachance and Claisse [9] that the influence coefficients α_{ij} and ϵ_{ij} in the Rousseau algorithm can be defined as functions of A_{ij} , E_{ij} and P_i , while the influence coefficients a_{ij} , e_{ij} and m_{ij} in the Lachance-Traill algorithm given below (equations 4.57 and 4.58 in [9]) are functions of A_{ij} , E_{ij} , M_{ij} and $P_i + S_i$, not simply P_i alone as used in the definition for the Rousseau algorithm:

$$C_i = R_i \left[1 + \sum_j a_{ij}C_j - \sum_j e_{ij}C_j \right] \quad (5)$$

$$C_i = R_i \left[1 + \sum_j m_{ij}C_j \right]$$

Lachance and Claisse [9] found it gratifying that the weighting factor ($P_{i\lambda}$) used in the derivation of equation (2) is the monochromatic component of equation numbered 7 in Criss and Birks [5]. Also the influence coefficients a_{ij} , e_{ij} and m_{ij} subsequently derived from equation (4) for the L-T algorithm, are inversely proportional to equation numbered 9 in Criss and Birks [5], which is, therefore, the common source for the derivations of equations (1), (2) and (4).

PHYSICAL REALITY

If, ultimately, theoretical influence coefficients are to have any 'physical meaning', any mathematical expression deduced should retain the essence of the basic principles of X-ray physics as they pertain to X-ray fluorescence emission. Among the many 'errors' attributed by Rousseau to equation (2) as stated in [8] is: "...it distorts physical reality..." and "...and finally, as it will be explained below in section 4.2, it distorts the physical reality as proposed by Sherman."

The "specific error" claimed by Rousseau to have led to a distortion is expressed in the following quotations:

"The minus sign in the Lachance identity does not correctly translate the attenuation of I_i due to absorption by the matrix elements."

"Sherman himself represents again all absorption effects ... 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 then gives the analyst a false interpretation of the absorption phenomena."

It would therefore appear that the **distortion** rests on the premise that **division is allowed** and **subtraction is not allowed**, i.e. that subtraction in this instance would lead to a false interpretation of absorption.

The apparent conflict stems from Rousseau's statements concerning corrections for absorption effects: namely that such corrections "must be translated by a division" and "must not be translated by a subtraction", even if in both cases the expressions translate strong absorption by a decrease, and, in the context of light matrix elements, the expressions translate **weak** absorption by an **increase** in emitted intensity. There is no conflict if analysts interpret the two expressions as: "absorption effects may be expressed and quantified equally well by the resultant of **either a division or a subtraction**". This will be demonstrated later by means of a simple numerical example.

Divide or Subtract in Order to Quantify Absorption Effects

The principles of XRF emission clearly indicate that, generally, absorption leads to a **decrease** in emitted intensity but, in some analytical contexts, i.e. light elements (low absorption), leads to an **increase** in emitted intensity. If absorption is quantified in an equation and expressed by a **divisor**, this implies a division by a number greater than unity in the first case and a number less than unity in the case of low absorption. In the context of binary systems, if absorption is expressed by a **subtraction**, this implies subtracting a positive number in the first case and subtracting a negative number in the case of low absorption, which is equivalent to an addition.

In the situation that the emitted intensity increases due to the matrix element absorbing less than the analyte, some authors have used the terms "negative absorption" or "absorption in the opposite direction". The present authors, together with many others, including Rousseau, do not approve of this terminol-

ogy. It is important to try to avoid the use of "slang" or "loose" or "too simple" terminology and instead to opt for a proper description of the effect, namely: "if the matrix element absorbs more strongly than the analyte the result is a decrease in intensity (the absorption influence coefficient will be positive), but if the matrix element absorbs less strongly than the analyte element the result is an increase in intensity (the absorption influence coefficient will be negative)." There seems to be no obvious simple terminology that will be acceptable to all.

Simplified Numerical Example

At the heart of the apparent conflict is the interpretation of the absorption effects. The context is in defining emitted intensity and the effect of absorption, which can be defined in terms of a **divisor**, [...], i.e. $I_i = I_{(i)} C_i / [...]$, or in terms of **subtraction**, as in equation (2) using I for the intensity notation, i.e. $I_i = I_{(i)} C_i - \sum A_{ij} C_j$.

If specifically I_i is sought using a **divisor**, then either of the following expressions is relevant:

$$I_i = \frac{I_{\lambda} C_i \mu_{ik}}{[\mu_s / \mu_i]} \quad \text{Or} \quad I_i = \frac{I_{(i)} C_i \mu_{ik}}{[1 + \sum \{ \dots \}_{ij} C_j]}$$

The 'divisor' in this context is any expression quantifying absorption effects. In Rousseau's [8] equation (73), equation (1) in this paper, the divisor in question is $[1 + \sum \beta_{ij} (\lambda_k) C_j]$ for monochromatic incident radiation or $[1 + \sum \alpha_{ij} C_j]$ for polychromatic incident radiation; for the Lachance-Claisse algorithm the corresponding symbols are $\alpha_{ij\lambda}$ and a_{ij} ; while in equation (7) in Criss and Birks [5] the divisor is μ_s , i.e. $[\mu_m (\lambda_k) \text{cosec } \epsilon + \mu_m (\lambda_i) \text{cosec } \psi]$ where ϵ and ψ are, respectively, the incident and take-off angles of the spectrometer.

The following numerical example using round numbers is introduced so that one can observe at a glance the essence of the topic under discussion, i.e. the interpretation of the **divisor** or the use of **subtraction**. The fact that actual experimental intensities are not used in no way compromises the conclusions that are reached.

Consider the following analytical context, where matrix element j is a strong absorber of analyte i radiation and matrix element k is a weak absorber of i radiation, and where C_i , C_j and C_k are weight fractions; $I_{(i)}$ = intensity from the pure analyte; I_i = analyte intensity from the specimen; $R_i = I_i / I_{(i)}$; and [...] is a **divisor** which can be expressed in terms of mass

attenuation coefficients or in terms of influence coefficients:

$$C_i=0.2 \quad C_j=0.4 \quad C_k=0.4 \quad I_{(i)}=20000 \quad I_i=2000$$

$$R_i=0.1 \quad [\dots]=2.0 \quad \mu_i=100 \quad \mu_j=400 \quad \mu_k=50$$

$$a_{ij}=\{3.0\} \quad \text{where } a_{ij} = (\mu_j - \mu_i) / \mu_i = (400 - 100) / 100$$

$$a_{ik} = \{-0.50\} \quad a_{ik} = (\mu_k - \mu_i) / \mu_i = (50 - 100) / 100$$

The mass attenuation coefficient for the specimen is, therefore:

$$M_s = \sum C_i \mu_i = 0.2 \times 100 + 0.4 \times 400 + 0.4 \times 50$$

$$= 20 + 160 + 20 = 200 \quad (N1)$$

Using a Divisor

The **divisor** [...], expressed in terms of a ratio of mass attenuation coefficients is equal to

$$[\mu_s / \mu_i] = [200 / 100] = [2.0]$$

Thus, using the **divisor** [...] expressed in terms of a ratio of mass attenuation coefficients, the relative intensity (equal to apparent concentration, $C_{i,app}$) can be calculated as

$$R_i = I_i / I_{(i)} = C_i / [\dots] = 0.2 / [2.0] = 0.1$$

$$= C_{i,app} \text{ (unit concentration)} \quad (N2)$$

and the emitted intensity is given by

$$I_i = I_{(i)} C_i / [\dots] = 20000(0.2) / [2.0] = 2000 \quad (N3)$$

The analytical expression, i.e. the expression for C_i , is given simply by (from equation (N2))

$$C_i = C_{i,app} [\dots] = 0.1 [2.0] = 0.2 \quad (N4)$$

Alternatively, the **divisor** [...] can be expressed in terms of influence coefficients [4] as

$$[\dots] = [1 + \{a_{ij}\} C_j + \{a_{ik}\} C_k]$$

$$= [1 + \{3.0\} 0.4 + \{-0.5\} 0.4] = [2.0] \quad (N5)$$

and then

$$I_i = I_{(i)} C_i / [\dots] = 20000(0.2) / [2.0] = 2000 \quad (N6)$$

and

$$C_i = C_{i,app} [1 + 1.2 + (-0.2)] = 0.1 [1 + 1.2 - 0.2] = 0.2 \quad (N7)$$

The results for intensity, (N3) and (N6), and concentration, (N4) and (N7), using a divisor expressed as a ratio of mass attenuation coefficients or in an influence coefficient formulation, respectively, are identical. However, the expression using influence coefficients has the advantage of identifying individually the two separate absorption effects, i.e. that due to matrix element 'j' and that due to matrix element 'k'.

Expanding equation (N7) yields an expression in concentration units,

$$C_i = C_{i,app} + C_{i,app} \times 1.2 + C_{i,app} \times (-0.2) = 0.2 \quad (N8)$$

$$C_i = C_{i,app} + C_{i,abs j} + C_{i,abs k} = 0.2 \quad (N9)$$

i.e. $C_i = C_{i,app} + a$ correction for absorption effect due to presence of element j, $C_{i,abs j} + a$ correction for absorption effect due to presence of element k, $C_{i,abs k}$

Equation (N8) can be expressed in intensity units by multiplying each of the 'C' terms by the intensity emitted by the pure element, namely 20000, which leads to a value for the emitted intensity if no absorption effects were present

$$I_{(i)} C_i = I_{(i)} C_{i,app} + I_{(i)} C_{i,app} \times (1.2) + I_{(i)} C_{i,app} \times (-0.2) \quad (N10)$$

i.e.

$$I_{(i)} C_i = I_i + I_{i,abs j} + I_{i,abs k} \quad (N11)$$

$$= 2000 + 2000 \times (1.2) + 2000 \times (-0.2)$$

$$= 2000 + 2400 - 400$$

$$= 4000$$

The value 2400 for $I_{i,abs j}$ is given by

$$2000 \{3.0\} 0.4 \quad (N12)$$

and -400 for $I_{i,abs k}$ is given by $2000 \{-0.5\} 0.4$ (N13)

The measured emitted intensity I_i will be given by

$$I_i = I_{(i)} C_i - I_{i,abs j} - I_{i,abs k} \quad (N14)$$

$$= 4000 - 2400 - (-400) \quad (N15)$$

$$= 2000.$$

Clearly, the emitted intensity may be obtained by calculating the theoretical emitted intensity and subtracting the intensities absorbed by the matrix elements, in this example elements 'j' and 'k'.

Using Subtraction (Equation (2))

Using I_i and $I_{(i)}$ as the intensity symbols in equation (2) and defining I_i as

$$I_i = \frac{I_{(i)} C_i \mu_i^*}{C_i \mu_i^* + C_j \mu_j^* + C_k \mu_k^*} \quad (N16)$$

$$= \frac{20000 \times 0.2 \times 100}{0.2 \times 100 + 0.4 \times 400 + 0.4 \times 50} = 2000$$

and A_{ij} as

$$A_j = I_i \left(\frac{\mu_j^* - \mu_i^*}{\mu_i^*} \right) \quad \text{And} \quad A_{ik} = I_i \left(\frac{\mu_k^* - \mu_i^*}{\mu_i^*} \right) \quad (N17)$$

From equation (2)

$$I_i = I_{(i)} C_i - \sum_j A_{ij} C_j \quad (N18)$$

$$I_i = 20000 \times 0.2 - (I_i \times \{3.0\}) \times 0.4 - (I_i \times \{-0.5\}) \times 0.4$$

$$\begin{aligned}
I_i &= 20000 \times 0.2 - (2000 \times \{3.0\}) \times 0.4 - (2000 \times \{-0.51\}) \times 0.4 \\
&= 4000 - 2400 - (-400) \qquad \qquad \qquad (N19) \\
&= 2000.
\end{aligned}$$

Both (N14) and (N18), the latter being derived from equation (2), the 'Lachance identity', in which the quantification of absorption effects is represented by the **subtraction** of two terms representing corrections for the effects of matrix elements 'j' and 'k', can be expressed in words as: "The actual (measured) emitted intensity (2000) is equal to the 'apparent' emitted intensity (4000, no absorption effects) **minus** the intensity absorbed by matrix element 'j' (2400) **minus** the intensity absorbed by matrix element 'k' (-400)". In numerical terms both (N15) and (N19) give identical results.

To repeat statements made earlier, Rousseau [8] construes this as: "The minus sign in the Lachance identity does not correctly translate the attenuation of I_i due to absorption by the matrix elements." and "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 then gives the analyst a false interpretation of the absorption phenomena."

But, in reality, the theoretical emitted intensity is decreased by 2400, due to strong absorption by matrix element 'j', and is increased by +400, which is equal to minus (-400), due to the lower absorption by matrix element 'k' relative to analyte 'i'. That is the reality of the situation.

Thus, it is self-evident that equation numbered 73 in Rousseau [8], equation (1) in this paper, i.e. the Sherman equation "translated into mathematical language" and using division to correct for absorption effects, and equation (2), using subtraction to correct for absorption effects, both deliver the same message on the physical level, i.e. yield measured emitted intensities which are identical using either equation.

Theory and Experiment

"Physical reality" as it pertains to X-ray fluorescence spectrometry may be interpreted as the concordance of theory as expressed in terms of fundamental parameters on the one hand and experimentally measured emitted intensities on the other. This is a very basic concept in general science. Consider the following quotation relating to the field of cosmology [14]: "...a theory is just a model of the universe, or a restricted part of it, and a set of rules that

relate quantities in the model to observations that we make."

If one considers that the XRF analyst's "universe" is the "laboratory", one may visualize that:

-an equation is just a model of XRF theory, or a restricted part of it, and a set of algebraic rules that relate influence coefficients in the algorithms to intensities that we measure in the laboratory.

If the word "equation" is substituted for "theory", subsequent text in [14] would roughly read:

- An equation is a good equation if it satisfies two requirements: It must accurately describe a large class of observations on the basis of a model that contains only a few terms, and it must make definite predictions about the data obtained in future measurements.
- Each time new data are observed to agree with the predictions, the equation survives, and our confidence is increased; but if some data are found to disagree, we have to abandon or modify the equation.

Abundant material and data have been reported in the literature [15, 16], some of which is presented in subsequent sections to confirm the validity of the concepts introduced in equation (2).

It is important at this point to remind the reader that equation (2) was developed so as to derive equation (4), both intermediate mathematical expressions in the process of defining influence coefficients for the Lachance-Trail algorithm [4], for very general analytical contexts, so that influence coefficients in the algorithm meet the following criteria:

- monochromatic and polychromatic excitation sources in the single equation;
- absorption and enhancement effects, and/or their combination in a single matrix effect; binary or multi element specimens;
- explicitly from fundamental principles of X-ray physics.

The Lachance and Claisse algorithm [9] is then expressed as (5), repeated below:

$$C_i = R_i \left[1 + \sum_j m_{ij} C_j \right] \qquad (5)$$

where

$$m_{ij} = (A_{ij} - E_{ij}) / (P_i + S_i) \qquad (6)$$

SUMMATION OVER $\Delta\lambda$ INTERVALS

The calculation of the primary and secondary emitted intensities must be carried out for a given exciting wavelength (λ), i.e. in the context of a

monochromatic excitation source, due to the fact that mass attenuation coefficients are functions of material and wavelength. It was established very early in the development of mathematical expressions relating concentration C to intensity I that, for polychromatic excitation sources, summation is involved. Referring to previous expressions in his presentation which had been derived for a monochromatic source, v. Hamos [1] states: "it was supposed that the primary beam of X-rays consists of a single wavelength. Practically the primary radiation, however, consists of several lines and the continuous spectrum. In order to calculate the secondary radiation produced in this case, we have to add the intensities excited by the different wavelength components of the primary radiation." It should be noted that v. Hamos refers to the incident beam as 'primary' X-rays, and to the intensity emitted by the characteristic lines of elements as 'secondary' radiation. Briefly stated, v. Hamos knew in the early 1940's that a summation was involved but lacked the method to do so.

It was only when Criss and Birks [5] proposed that the incident polychromatic excitation spectrum should be divided in narrow $\Delta\lambda$ intervals for the calculation of emitted intensity, i.e. in essence for a sequence of monochromatic sources, and that the summation should be carried out over the effective wavelength range, λ_{\min} to λ_{edge} , that a solution was found to the polychromatic problem. Thus it was not until the late 1960's that Criss and Birks provided the method that v. Hamos lacked in the 1940's.

Evidence That Lachance and Claisse Did Incorporate Summation over $\Delta\lambda$ Intervals

It is somewhat surprising when Rousseau initially points out that equation (2) was developed from the work of Criss and Birks [5], who proposed the concept of summation over $\Delta\lambda$ intervals, and then states: "The same development was repeated all over again by Lachance and Claisse ... on a more inductive basis.", and then alleges that, referring again to equation (2): "... does not explain the contribution of each incident (λ_k) to the total measured net intensity I_i ."

Should this truly be the case, Lachance and Claisse [9], who were obviously aware of the need for summation in the context of a polychromatic excitation source, would have compromised all subsequent mathematical expressions based on equation (2) had they omitted and failed to explain this step in their development of that equation.

The following are examples of where Lachance and Claisse did use the concept of summation over the effective wavelength range and explained (using both figures and tables) the contribution of each $\Delta\lambda$ interval to the total emitted intensity:

1. The definition in Lachance and Claisse [9] of primary and secondary emitted intensities, $P_{i\lambda}$ and $S_{ij\lambda}$: equations numbered 2.24 and 2.35, respectively.

$$P_{i\lambda} = G_i C_i \frac{I_{\lambda} \mu_{\lambda}}{\mu_s} \quad S_{ij\lambda} = G_j C_j \frac{I_{\lambda} \mu_{\lambda}}{\mu_s} e_{ij\lambda} C_j$$

2. Figure 3.1 in [9] provides a schematic example of the intensity of the continuum emitted from an X-ray tube (and characteristic lines from the target element) divided into $\Delta\lambda$ intervals.
3. Tables numbered 11.1.7 to 11.1.9 in [9] provide comprehensive listings of λ and $I_{\lambda}\Delta\lambda$ for W, Cr and Rh target X-ray tubes, respectively, at 45 kV.
4. The symbols and formulation used for the summations, namely, $\Sigma(\dots)\Delta\lambda$, appear in the following: equations numbered 3.30, 3.12, 3.31, and 3.42, which define P_i , S_i , $P_{(j)}$ and P_i+S_i , respectively, and equations 3.32 and 3.44 which define A_{ij} and E_{ij} . For example, equation numbered 3.30 defines the primary emitted intensity for a polychromatic excitation source: $P_i = \Sigma_{\lambda} P_{i\lambda} \Delta\lambda$.
5. Tables numbered 3.7 to 3.9 in [9] list values for the seventeen $\Delta\lambda$ intervals (the effective wavelength range for analyte Mo at 45 kV) for tungsten and rhodium target X-ray tubes and for A_{ij} and E_{ij} , i.e. for the contexts of absorption (element Y) and enhancement effects (elements Ag and Sn). The last row in each of these tables is the sum of the individual values for each of the seventeen $\Delta\lambda$ intervals.
6. Tables numbered 4.2 to 4.5 in [9] relate to ten $\Delta\lambda$ intervals (the effective wavelength range for analyte Ag at 45 kV), in this case to illustrate the effect of different X-ray target tubes, different instrument geometries and different concentrations of the analyte on the individual values and their summation. The headings of the six columns in Table numbered 4.2 are explained in detail immediately following the tabulation.

7. Tables numbered 4.6, 4.7 and 4.9 in [9] also relate to analyte Mo at 45kV as in (5.) above, but in this case, the tube target element is Rh, hence two of the seventeen Al intervals include the intensities of the two characteristic lines of Rh. It is pointed out in the text that the two characteristic lines of rhodium account for more than 50% of the total emission for molybdenum in this context. The last row in each of these tables is the sum of the individual values for each of the seventeen $\Delta\lambda$ intervals.
8. Figure 4.1 in [1] shows the plot of the primary emitted intensity for Mo in the binary Mo-Y and pure Mo for each effective $\Delta\lambda$ interval. A plot of the relative intensities for each interval is also shown along with the relative intensity generated by the summation data from Table numbered 4.6.

From the above, the statement/allegation from Rousseau "... does not explain the contribution of each incident (λ_k) to the total measured net intensity I_i " is clearly incorrect and unjustified.

WEIGHTING FACTORS

An error imputed by Rousseau [8] to the equation (2) is that: "*Contrary to equation (73), the Lachance identity by itself says nothing about the weighting factor W_i ...*".

The words **by itself** and weighting factor W_i are germane to this allegation. It is a fact that the weighting factor W_i was not used in the derivation of equation (2). However, this should not be interpreted to mean that no weighting factor was used. Instead of using the factor W_i (λ_k) proposed by Rousseau [8, 13], the weighting factor used in the derivation of equation (2) in [9] is the weighting factor proposed by Broil and Tertian [10], namely $P_{i\lambda}$. This is shown in [9], equations numbered 3.25 and 3.37, i.e. intermediate steps in the derivation of equation (2). For example equation numbered 3.25 defines $A_{ij\lambda}$ as a product involving $P_{i\lambda}$, namely:

$$A_{ij\lambda} = P_{i\lambda} \left(\frac{\mu_j^* - \mu_i^*}{\mu_i^*} \right) \quad (7)$$

Equation numbered 3.37 is similar but relates to the enhancement term $E_{ij\lambda}$:

$$E_{ij\lambda} = P_{i\lambda} (e_i + e_j) \quad (8)$$

The relation between the two weighting factors $P_{i\lambda}$ and $W_{i\lambda}$ is given in [9], equation numbered 4.46, namely:

$$P_{i\lambda} = C_i W_{i\lambda} \quad (9)$$

It is noted that $P_{i\lambda}$ is the monochromatic component of equation numbered 7 in Criss and Birks [5], i.e. an equation that had been proposed 15 years earlier in the context of defining theoretical primary fluorescence emissions (absorption only).

The use of the weighting factor $P_{i\lambda}$ is well documented in tables numbered 4.2 to 4.7 referred to earlier in points numbered (6.) and (7.) in the previous section.

EMITTED INTENSITY AS A FUNCTION OF THAT EMITTED BY THE PURE ELEMENT

In "Section 4.2 Comments on the Lachance Identity," Rousseau [8] 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.*"

Strictly speaking, Sherman [2] never calculated I_i as a function of $I_{(i)}$, the reason being that Sherman, p. 295, states: "Instead of measuring intensity ... as counts per second, it is advantageous to represent intensity by the reciprocal of the counting rate, i.e. time (t) required for the counter to reach a predetermined fixed count."

It follows that one must not look in Sherman [2] for mathematical expressions using the symbols I_i =(a function of $I_{(i)}$), but instead look for expressions that use symbols of the type t_i =(a function of $t_{(i)}$). Thus, on p. 295, Sherman defines the following:

#2: an expression for the emitted intensity by a specimen which is equivalent to the notation I_i .

#3: an expression for the emitted intensity by the 'free' element, i.e. the pure element, $I_{(i)}$.

#4: divides #3 by #2 in order to obtain a linear expression in the concentration of element i, i.e. the reciprocal of the familiar, in modern terminology, $I_i/I_{(i)}$ or R_i .

In current notation, Sherman equates t to N/I , where N is the "predetermined fixed count". This leads to #5, an expression that defines Q

$$Q = t_i/t_{(i)} = 1 + (C_j/C_i)(\mu_j/\mu_i) + (C_k/C_i)(\mu_k/\mu_i) \quad (10)$$

Mathematical expression #6 defining ξ is obtained by cross-multiplication, namely

$$t_i = u_0 + u_1(C_j/C_i) + u_2(C_k/C_i) \quad (11)$$

where $u_0 = t_{(i)}$

$$u_1 = t_{(i)} (\mu_j/\mu_i)$$

$$u_2 = t_{(i)} (\mu_k/\mu_i)$$

Equation (11) is therefore equivalent to:

$$t_i = t_{(i)} + t_{(i)}(\text{ratio Conc} \times \text{ratio macs}) + t_{(i)}(\text{ratio } \dots) \quad (12)$$

In a previous publication, Sherman [17] expresses the same concept textually: "This relation then follows: $T_{f2}(\text{mixture}) = \text{const} \times T_{f2}(\text{free element}) + \text{const} (c_1/c_2)$."

Expressed in words, the intensity of the fluorescent beam of an element in a binary mixture, measured by the time for a fixed count, is linearly proportional to the intensity of the fluorescent beam from the free element, measured by the time for the fixed count, and the ratio of the concentrations of the elements (the concentration of the element sought (c_2) is in the denominator. This relation is easily extended to multicomponent mixtures." Note: Sherman uses the symbol T for expressing time.

Not only does Sherman define intensity emitted by a specimen as a function of the intensity emitted by the pure element [equation (11) above], but the intensity for the pure expressed as $t_{(i)}$ is present in every term on the right hand side of the equal sign, i.e. equal to the number of components present in the system under consideration. A serious drawback to this type of expression is that the concentration of the analyte C_i occurs in as many terms as there are matrix elements.

From the above, the statement from Rousseau given at the beginning of this section is clearly unjustified.

RESPECTING THE SPIRIT OF THE SHERMAN EQUATION

If, in the earlier treatment of physical reality it was considered a topic that involved a degree of interpretation, it is even more so if one addresses **the spirit of Sherman** in his overall contribution to XRF spectrochemical analysis. The "distortion" of physical reality could be reduced to a divide or subtract option to quantify a decrease in intensity due to the absorption effect, which is clear enough. In dealing with what constitutes the **spirit** of Sherman in some tangible description, the authors considered the following:

Is there something throughout Sherman's contributions [2, 17] that can be quantified in some manner. As a matter of fact the more general question arises: Is there something in the contributions of many, if not all, analysts that is traceable and shared

with Sherman. An examination of the literature would indicate that the word **linear** can fit such a role.

In the case of v. Hamos [1], this concept was expressed in a negative manner, i.e. "This formula shows that the ... intensity emitted ... does not increase **linearly** with the concentration. This is of extreme importance for quantitative analysis."

In the case of Sherman, the word appears textually. Sherman [2] states, p. 295: "A **linear** expression in c_i may be obtained by..." (Sherman does not capitalize C).

It should be noted that the words in bold in the above are the authors' choice, they do not appear as such in the original text.

Expressing Linearity

Thus, analysts seek **linearity**, i.e. mathematical expressions that will **linearize** the scatter when measured (experimental) intensities are plotted versus concentrations for a suite of standards. If expressions are found that do so to a satisfactory level as expressed by an acceptably small standard deviation, then it is reasonable to assume that a similar degree of accuracy will be reflected in samples submitted for analysis. This implies that the unknowns are treated exactly as the reference materials used to verify the validity of the mathematical expression, i.e. the algorithm under consideration. In many cases, the concept of linearity is illustrated in diagrams by plotting before and after data, by plots of corrected versus uncorrected, etc.

A second way of showing how successful an algorithm is in linearizing experimental data is by tabulating the "true" versus "found" concentrations in adjacent columns, and quantifying the degree of success by stating the standard deviation of the difference between "true" and "found" for each analyte.

Paths to Achieving Linearity

In fact, one has to look somewhat deeper if one is to give due credit to Sherman and a host of analysts who followed the underlying goal Sherman set for himself. If it is accepted that the goal is to linearize, the literature also shows that analysts chose different paths to achieve linearity. One such choice is between the **theoretical** and the **empirical** approaches. It is evident that Sherman chose the former. Sherman went one step further, which may be expressed as, not only must the approach be **theoretical** but it also must be **explicit**. Given the quotations from Sherman cited previously, one can visualize that Sherman certainly

knew what the goal was, but pointed out a number of impediments for which a solution was not then available. Not mentioned, but very much an impediment, was the lack of powerful and indispensable mini computers, presently widely available. Sherman [2], like many others who followed in his footsteps, suggested a practical approach for dealing with "The problem for the analysis involving a polychromatic incident beam...".

Thus Sherman states: "The problem for the analysis involving a polychromatic incident beam of an arbitrary spectrum is to derive good linear approximations, similar to formula (6), which will present Q , the ratio of the intensity of the spectrum of Z_3 in a mixture to the intensity of the spectrum from free Z_3 , which will be explicitly independent of the spectrum of the incident beam." A "free" element is the description used by Sherman when referring to what is now called the "pure" element. (It should be noted that formula (6) is the number in the original text and does not refer to equation (6) in this paper.) Sherman also indicated that: "For a specific representation one may regard Z_1 , Z_2 and Z_3 as 24, 26, and 28, i.e. Cr, Fe, and Ni".

Sherman realized that he had treated XRF emissions only for monochromatic excitation with correction for absorption but no correction for enhancement. Knowing that analysis usually involves polychromatic excitation and corrections for both absorption and enhancement, he suggested a possible way out of the problem. Some of the reasons that led to his choosing an empirical approach, probably against his better judgement (authors' opinion), at that stage of the development of analytical methods are very well expressed by Criss [18]:

"Over the years, analysts have tried many different calculation approaches to account for inter-element X-ray absorption and fluorescence effects (matrix effects) in X-ray fluorescence analysis."

"Although the earlier influence-factor methods ... had a basis in physical theory,...those approaches got to be called 'empirical' since the factors themselves usually were calculated empirically, from measured standards. For many years that was the best way to proceed, because X-ray tube spectra were not accurately...".

"Moreover, most analysts used graphical methods ... did not have ready access to computers until the 1960's or later."

Visualized in this perspective, one can certainly conclude that Shiraiwa and Fujino [10], Criss and Birks [5], Claisse and Quintin [19], de Jongh [12],

Tertian [20, 21], Broll and Tertian [11], Broll [22], Rousseau [13], and hopefully one of the present authors (to name only some contributors listed in [7]) have, each in their own way, advanced knowledge of XRF analysis while remaining respectful and faithful to the spirit of Sherman.

Attempting to interpret the "spirit" of anyone's work is bound to be a very subjective exercise. It is like "beauty", purely in the eye of the beholder, and different, and therefore subjective, for each person. What good scientific debate requires is objectivity. The debate on the validity or otherwise of different influence coefficient algorithms is in great need of objectivity from all concerned.

CONCLUSION

As stated by Rousseau in [8]: "*The aim of this paper is to show that the Fundamental Algorithm is a powerful tool for checking the validity of any new expression relating the measured net intensity I_i to the concentration C_i of the analyte in a given specimen*".

Why the "Fundamental Algorithm is a powerful tool" is expounded in [7]: "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 numbers in <> relate to the reference numbers in [7]).

Faced with expressions such as the Claisse-Quintin algorithm, Tertian identity and equation (2), which by his own admission are: "*theoretically valid*" and hence "*equivalent*" to the Sherman equation, Rousseau then states: "*Three expressions are studied. For each expression, the main contributions and errors are explained,...*"

Given that these expressions are studied from the standpoint of assigning a special/primordial status to

"THE Fundamental Algorithm", "the final answer", it is therefore not surprising that all three expressions are found wanting, i.e. as "*superfluous*", "*of no interest*", "*in error*" and "*should not exist!*"

Do Rousseau's [7, 8] conclusions imply that for the past fourteen years:

- authors who have submitted papers on the correlation of intensity and concentration were wasting their time?

- reviewers and editors of journals who have accepted these for publication were remiss in their duty?

-course directors and instrument manufacturers who have used these materials have led students and customers astray?

If this really is so, then XRF spectrometry is in a sad state indeed. The present authors do not think that this is the case, believe that the discredited expressions **are** viable, consider that the door is still open to valid criticism, and are convinced that the topic of mathematical expressions relating intensity to concentration in X-ray fluorescence spectrometry should remain open to further development.

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