
CONTRIBUTED PAPERS

CONCEPT OF THE INFLUENCE COEFFICIENT

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This paper presents the basic concept of influence coefficients, which are used in XRF analysis to correct for matrix effects. Nowadays, influence coefficients can be classified into two categories depending on their method of calculation: empirical or theoretical. Furthermore, each category can be calculated from binary or multi-element standards. It will be shown how to calculate the four different types of influence coefficients in association with their respective algorithm. This paper will also show the true theoretical and fundamental nature of influence coefficients, supply an accurate and unique mathematical definition of these coefficients and promote their use to correct for matrix effects.

1. Introduction

When I started my career as XRF analyst, I was confronted with the problem of selecting the most appropriate method for calculating the composition of the samples to be analyzed. In order to use the most appropriate method in a given analytical context, I made an exhaustive study of the most popular methods [1] published between 1950 and 1980. From that study, I learnt which methods were appropriate, what specific conditions they must be applied, which features [2] would contribute to improve the quality of results and how to apply all this knowledge in practice. I have attempted to regroup all these effective features in new methods in order to improve analytical results. This paper summarizes the main conclusions of this study by presenting the three resulting optimized methods that cover the complete analytical range.

In quantitative X-ray fluorescence (XRF) analysis, one of the major problems is the correction for matrix effects (absorption and enhancement). Since the early fifties, many solutions have been proposed to solve this problem, but two methods in particular have stood out. The first one is the use of *influence coefficients*, which are numerical coefficients that correct for the effect of each matrix element on the element to be determined (or *analyte*) in a given specimen. For many years, these coefficients were determined experimentally by regression analysis using reference materials, and for this reason are typically referred to as empirical influence coefficients. They were considered as an empirical ap-

proach having little connection with X-ray fluorescence theory. They were considered useful only when no other alternative was available to solve the problem of the correction for matrix effects.

The second important method to correct for matrix effects was proposed, in 1968, by Criss and Birks [3]. They proposed the Fundamental-Parameters (FP) method, a fully theoretical approach, based on the Sherman equation [4]. This equation allows one to calculate theoretical net X-ray intensities emitted by each element from a specimen of known composition when it is irradiated by a polychromatic X-ray beam. At that time, the FP method was considered as the state-of-the-art method to correct for matrix effects. However, the FP method was not without a few weaknesses of its own, namely: how to calculate a better first estimate of the sample composition, how to eliminate the constraint of normalizing the concentrations to 100%, use of an unclear calibration procedure, how to match theory with each spectrometer, how to reduce the calculation time of each sample composition, etc.

In order to eliminate the respective disadvantages of the above two methods, Rousseau [5-7] proposed a new approach in 1982 that combines the practical flexibility of the influence coefficient concept and the theoretical exactness of the Fundamental-Parameters method. This new approach allows one to calculate theoretical influence coefficients within a new algorithm called the *Fundamental Algorithm*. These coefficients are called multielement influence

coefficients because they depend on the full composition of the matrix.

The Fundamental Algorithm, like the FP method, is also based on the Sherman equation making it a fully theoretical approach. The difference is that it manages to reconcile the concept of the influence coefficient with theory and eliminates all the weaknesses of the FP method mentioned above.

The goal of this paper is to show the true theoretical and fundamental nature of influence coefficients, to supply an accurate and unique mathematical definition of these coefficients and to promote their use for the correction of matrix effects. Nowadays, there is no reason to continue using empirical coefficients, which can be strong potential sources of errors and can thereby lead to inaccurate results.

2. Nature of Interelement (or Matrix) Effects

Quantitative XRF analysis is based on the principle that a correlation exists between the fluorescent X-ray intensities emitted by elements in a specimen irradiated by a sufficiently energetic X-ray beam and their concentrations. Generally, the relationship between intensities and concentrations for a specific analyte is not linear because of the various elements or matrix surrounding each atom of the analyte. The effects of the elements of the matrix on the analyte intensity are called interelement effects or matrix effects. The magnitude of these matrix effects depends on the original matrix composition of the sample and the technique employed to prepare the specimen. Several sample preparation techniques exist to reduce matrix effects. A powder sample can for instance be diluted with a binding material to prepare a pressed powder pellet, or fused with a flux to prepare a fused disc.

When a specimen is bombarded by X-rays, the matrix absorbs the incident X-ray beam and the X-ray fluorescence radiation is emitted by the elements of the specimen. This phenomenon is called *absorption effect*. The general rule about absorption effects is the following: when the wavelength of an analyte line A is just less than that of the absorption edge of a particular matrix element B, the A line is highly absorbed by the element B, and the A line intensity is reduced in a proportion equivalent to the B concentration.

Moreover, the correlation between intensity and concentration is further complicated when the X-ray fluorescence radiation from matrix elements has an energy high enough to excite the analytes present in

the specimen. This effect, called the *enhancement effect*, is due to the energy of characteristic X-ray lines of matrix elements sufficiently high to excite the characteristic X-ray lines of analytes having a lower energy. The general rule about enhancement effects is the following: when the wavelength of the analyte absorption edge (A) is just greater than that of the line of a particular matrix element B, the B line is absorbed by A, and the A line intensity is enhanced (or increased) in a proportion equivalent to the B concentration. This increase of intensities of the X-ray lines of analytes due to the matrix elements may be highly significant.

In conclusion, it can be said that, closer an analyte line A is relative to the absorption edge of a matrix element B, greater is the absorption of the analyte line A by the element B, and greater is the enhancement of the matrix element line B by analyte A. It is the combination of both these effects, absorption and enhancement, that is called matrix effects. The most significant matrix effects occur for the $K\alpha$ lines of the mid-range elements of the periodic table and when the atomic number difference of the two considered elements is 2.

3. What are Influence Coefficients?

In 1955, Sherman [4] prophetically proposed a mathematical expression to calculate net X-ray intensities emitted by each element in a specimen of known composition when it is irradiated by a polychromatic X-ray beam. However at that time, this equation did not become widely used because XRF analysts do not need to calculate intensities, which can be measured, but do want to calculate the composition of unknown samples. Furthermore, in order to calculate these intensities, the composition of the sample to be analyzed must be known when in practice it is of course unknown prior to the analysis. In the end, Sherman himself concluded that the proposed **theoretical** equation was too complex to be used in practice. He stated in a previous paper [8]:

"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."

The complexity of theory has caused many difficulties for XRF analysts and is the reason why **approximate** methods proliferated between the years 1950 and 1980. Many models have been proposed (mostly the same algorithm expressed in different formalism or symbolism), among which similar models have been developed with identical symbols that refer to quite different entities, and vice versa. The result of such an explosion of algorithms is that it has contributed to create a great confusion regarding influence coefficients and to discredit their use.

Thus, because of the complexity of theory, analysts have sought to condense the total matrix effect of every matrix element j on the analyte i by a single entity, the *influence coefficient*. This coefficient is then a number that quantifies the total matrix effect of an element j on the analyte i in a given specimen. This correction increases with the concentration C_j of the element j in the sample. An influence coefficient is then always multiplied by a concentration term in models of the type:

$$(\dots + X_{ij}C_j + x_{ik}C_k + \dots) \quad (1)$$

where the symbols x_{ij} and x_{ik} are influence coefficients (x is used temporarily to designate any type of influence coefficients), and where, by convention, the subscripts "ij" identify the coefficient as relating to the effect of the matrix element j on analyte i .

In their paper of 1966, Lachance and Traill [9] were the first to emphasize the concept of the influence coefficient for the correction of matrix effects. They were also the first to propose an equation to calculate theoretical influence coefficients. They called them "alpha" coefficients. These alpha coefficients have very specific properties: they are calculated from theory (see Eqn 10 in Ref. 2) 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 ignored.

Nowadays, there are many different types of influence coefficients. Unfortunately, many XRF scientists or analysts continue to call all of them with the same designation: "alpha" coefficients. It makes little sense to do it because they all have different properties and it becomes impossible to distinguish between them. Furthermore the original alpha coefficients proposed by Lachance and Traill are no longer used in practice. To overcome this problem, Rousseau proposed in 1994 a new terminology and symbolism

Table 1. Classification, terminology and notation used by the modern concept of the influence coefficient.

Method of Calculation	Standards	
	Binary	Multi-Element
Empirical	b_{ij}	e_{ij}
Theoretical	a_{ij}	$\alpha_{ij}, \epsilon_{ij}$

[10] to identify each type of modern influence coefficients. Here the details.

Nowadays, influence coefficients can be classified into two categories depending on their method of calculation: empirical or theoretical. Furthermore, each category can be calculated from binary or multi-element standards as illustrated in Table 1. To represent each type of influence coefficients, the following symbolism has been proposed:

- b_{ij} designates empirical influence coefficients calculated from experimental data using binary standards (the letter "b" is for binary);
- e_{ij} designates empirical influence coefficients calculated from experimental data using multi-element standards (the letter "e" is for empirical);
- a_{ij} designates theoretical influence coefficients calculated from fundamental theory using binary standards (the letter "a" is a throw-back to "alpha" coefficients);
- α_{ij} and ϵ_{ij} designate theoretical influence coefficients (α_{ij} : for absorption, ϵ_{ij} : for enhancement) calculated from fundamental theory using multi-element standards.

The selected notation is based on the following convention: a Roman letter is used to represent **constant** coefficients valid for a given concentration range rather than for a given sample. Greek symbols are used to represent **variable** coefficients that depend on the whole matrix composition of each sample. Thus, their names indicate the method of calculation and their representative symbols indicate whether they remain constant or vary with each sample composition. Thus, with a simple name and a symbol one can easily identify the type of influence coefficients used and its properties.

We will study the four different types of influence coefficients that are used in XRF analysis to correct for matrix effects [11]:

- 1) The empirical coefficients calculated from regression analysis and valid for the set of reference materials on hand only. They can be calculated from binary or
- 2) Multi-element reference materials;
- 3) The *theoretical binary coefficients* that are essentially constant for a given concentration range;
- 4) The *theoretical multielement coefficients* calculated from one given specimen composition and valid for this specimen only.

Each of these coefficient types will be presented in association with an algorithm to explain how to use them in practice. We assume for all the methods presented hereafter that specimens are **homogeneous**, have a **flat and polished** surface and an **infinite thickness** with respect to the depth of penetration of the incident radiation. First, a procedure for evaluating each proposed analytical method will be defined.

4. Pseudo-Experimental Verification

To experimentally verify the accuracy of the different types of influence coefficients and their associated algorithms, a large number of reference materials must be available. However, this accuracy depends on many experimental factors such as the reliability of the calibration reference materials, surface effects, spectrometer stability, background subtraction, interference, etc. For all these reasons, the accuracy of results obtained from experimental measurements is insufficient for the intended refined verification of the accuracy of influence coefficients. Consequently, in the present paper, all the required relative intensities, R_i , are calculated (by the Sherman equation) rather than measured. It must be pointed out that such a pseudo-experimental verification does not detract from the general validity of the solution to the matrix effect problem, provided that the calculated relative intensities R_i represent reality, as shown by Rousseau [12]. Furthermore, this approach shows only the contribution of the algorithm to the improvement of the accuracy of results, without taking into account the errors introduced by the experimental measurements. However a valid comparison of algorithms and of their influence coefficients requires that the R_i values be the same for all of them. Then, from the same data it becomes easy to determine which algorithm yields the more accurate calculated concentrations. There is no doubt that the best one of these algorithms thus determined will also be the best one in practical situations.

The pseudo-experimental verification of all types of influence coefficients was made from three groups of 36 hypothetical standards [13] given in Table 2. The standard compositions of these three groups are the same except that each group of analyzed standards are composed of elements, oxides and oxides diluted in a flux (fused discs), respectively. The relative intensities of the 36 standards for each group have been calculated using the Modified Sherman Equation (16) in Ref. (2). The choice of compositions of these standards is not necessarily realistic, but they have been selected because their calculation requires strong matrix effect corrections.

Knowing the relative intensities for each of the three groups: elements, oxides and fused discs, the standard compositions have been recalculated by using different types of influence coefficients in different algorithms. For each of the groups, the criterion used to compare the accuracy of each algorithm was the mean relative error of the 36 totals of analyzes. The compilation of results is given in Table 3. Thus, these three groups of reference materials cover the full range of concentrations: wide (elements), medium (oxides) and limited (dilution in fused discs). In conclusion a recommendation of a specific algorithm for each range is given.

5. Empirical Binary Influence Coefficients

As already shown in a previous paper [2], *multi-element influence coefficients* can be calculated from theory. However, these coefficients depend on the full sample composition to be analyzed (see Eqns 28 and 29), which in practice is unknown prior to analysis and they must be calculated for each sample. A set of theoretical influence coefficients calculated from a sample composition is "unique" because each sample composition is "unique". Any other samples containing the same elements but in different proportions will generate a different set of influence coefficients. The problem is that sample compositions are unknown prior to the analysis.

This last property of influence coefficients has caused many problems to the XRF analysts and is the reason why empirical and approximate methods have proliferated between the years 1950 and 1980. By empirical method we mean a method based only on observation and experimentation. Another concept that appeared at the same time as the empirical influence coefficients was the concept of binary coefficients. They are based on the hypothesis that the total matrix effect on the analyte i is equal to the sum

Table 2. Compositions (in %) of the 36 hypothetical standards.

Standard	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Cr ₂ O ₃	MnO	Fe ₂ O ₃	LOI	Total
1	0.10	4.00	10.00	60.00	0.10	1.00	1.00	10.00	2.50	0.50	0.40	10.00	0.00	100.00
2	3.00	1.00	15.00	60.00	0.10	0.10	5.00	5.00	3.00	0.70	0.10	5.00	0.00	100.00
3	10.00	0.50	20.00	65.00	0.50	0.50	0.50	0.50	0.50	0.50	0.50	1.00	0.00	100.00
4	0.50	0.10	5.00	80.00	0.10	0.10	1.00	2.00	1.00	0.10	0.10	10.00	0.00	100.00
5	2.00	25.00	0.10	60.00	0.50	0.10	3.00	3.00	0.50	0.30	0.50	5.00	0.00	100.00
6	1.00	50.00	1.00	40.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00	100.00
7	2.00	1.00	0.10	35.00	0.30	0.10	0.10	40.00	0.50	0.10	1.00	20.00	0.00	100.00
8	0.50	2.00	15.00	75.00	1.00	0.10	1.30	2.00	0.50	0.50	0.10	2.00	0.00	100.00
9	2.00	20.00	30.00	40.00	0.10	1.00	0.10	0.50	5.00	0.20	0.50	0.60	0.00	100.00
10	2.00	30.00	0.10	0.10	0.20	0.10	0.50	50.00	0.80	0.20	1.00	15.00	0.00	100.00
11	0.50	20.00	0.50	50.00	0.10	0.50	0.90	0.50	4.00	1.00	2.00	20.00	0.00	100.00
12	0.40	0.40	1.00	95.00	1.70	0.30	0.20	0.20	0.20	0.10	0.10	0.40	0.00	100.00
13	4.00	25.00	10.00	40.00	0.10	0.40	4.00	0.10	0.20	0.20	1.00	15.00	0.00	100.00
14	0.10	2.00	1.00	50.00	1.00	0.10	0.10	45.00	0.10	0.20	0.10	0.30	0.00	100.00
15	5.00	10.00	5.00	70.00	2.00	0.10	0.30	0.50	3.00	1.00	0.10	3.00	0.00	100.00
16	7.00	5.00	25.00	45.00	0.10	0.10	5.00	8.00	0.20	0.10	0.50	4.00	0.00	100.00
17	3.00	15.00	10.00	65.00	0.40	1.00	1.50	0.50	0.10	1.00	0.50	2.00	0.00	100.00
18	0.50	5.00	20.00	50.00	0.20	2.00	0.10	9.00	1.00	0.10	0.10	12.00	0.00	100.00
19	1.00	20.00	0.10	50.00	0.10	0.10	0.10	25.00	2.00	0.10	0.50	1.00	0.00	100.00
20	1.50	0.50	15.00	70.00	1.50	0.20	7.50	0.80	0.50	1.00	1.00	0.50	0.00	100.00
21	0.20	0.20	18.20	65.00	0.20	0.20	15.00	0.20	0.20	0.20	0.20	0.20	0.00	100.00
22	4.00	12.00	10.00	70.00	0.30	0.10	0.10	0.10	0.40	0.50	2.00	0.50	0.00	100.00
23	0.10	1.00	1.00	70.00	0.10	0.10	0.10	25.00	0.10	0.10	2.00	0.40	0.00	100.00
24	2.00	10.00	5.00	5.00	2.00	1.00	2.00	50.00	1.00	1.00	1.00	20.00	0.00	100.00
25	0.20	2.00	15.00	60.00	0.20	0.50	0.40	20.00	0.10	1.00	0.10	0.50	0.00	100.00
26	8.00	1.00	10.00	70.00	0.50	0.10	2.00	0.40	2.50	0.50	0.50	4.50	0.00	100.00
27	1.00	1.00	15.00	50.00	1.00	0.10	1.00	5.00	5.00	0.80	0.10	20.00	0.00	100.00
28	3.00	2.00	20.00	70.00	0.40	1.00	0.50	0.50	0.40	0.10	0.10	2.00	0.00	100.00
29	0.10	30.00	20.00	45.00	0.10	0.10	0.10	2.00	0.10	1.00	0.50	3.00	0.00	100.00
30	0.50	30.00	3.00	65.00	0.30	0.10	0.10	0.20	0.20	2.00	0.10	0.50	0.00	100.00
31	0.50	2.50	5.00	60.00	0.10	0.20	0.30	15.00	1.00	0.30	0.10	15.00	0.00	100.00
32	1.00	6.00	1.00	75.00	0.20	0.10	0.70	10.00	4.00	0.20	1.00	0.80	0.00	100.00
33	0.50	40.00	1.00	40.00	0.50	0.20	0.30	3.00	0.20	0.30	2.00	12.00	0.00	100.00
34	5.00	20.00	0.10	65.00	0.40	0.30	0.20	5.00	3.00	0.40	0.50	0.10	0.00	100.00
35	0.20	20.00	0.50	35.00	0.10	0.10	1.00	30.00	1.00	0.10	2.00	10.00	0.00	100.00
36	3.00	0.50	10.00	60.00	0.20	0.10	0.50	5.00	0.10	0.50	0.10	20.00	0.00	100.00

Table 3. Mean relative error (%) obtained by recalculating the composition of the 36 hypothetical standards of each group for every given algorithm.

ALGORITHM	ELEMENTS	OXIDES	FUSED DISCS
Lachance-Trail	0.92	0.19	0.02
Claisse-Quintin	0.29	0.04	
COLA	0.28	0.06	
Fundamental	0.05		

of the effects of each element j of the matrix, each of these effects being calculated independently of each other. In other words, from a practical point of view, it is easier to consider a sample as a sum of binary mixtures rather than as a multi-element mixture. Of course, this approach is an approximation because one cannot isolate the matrix effect of each element j on the analyte i from the effect of the rest of the matrix. The physical properties of each element j are affected by the rest of the matrix and if the same element j is present with the same concentration C_j in different matrix, it will affect the analyte i differently. But this approach allows one to correct for matrix effects with accuracy as long as the composition range of samples to analyze is fairly limited. With this approach it was then possible to calculate a set of binary influence coefficients valid for a given composition range rather than for a given sample. In other words, with binary coefficients it is assumed that the coefficient b_{ij} is a constant for a given range of C_i and C_j rather than

being a variable dependent on the whole matrix composition of each sample.

The binary influence coefficients can be calculated empirically from experimental data (intensities and concentrations) obtained from binary reference materials. In this case, they are called *empirical binary influence coefficients* and represented by the symbol b_{ij} (the letter "b" is for **binary**). They are often used in algorithms similar to the one proposed by Lachance and Traill [9]. They can also be calculated from theory as it will be demonstrated in Section 7.

Table 4. Net intensities measured from binary mixtures of SiO₂ and Al₂O₃, as fused disc, where Si is the analyte i . Relative intensities R_i , and also the values of the expression (C_i/R_i-1) , have been calculated. The fused disc composition is: 1 g sple+5 g Li₂B₄O₇+0.3 g LiF. X-ray tube was operated at 60 kV, 45 mA.

SAMPLE		I _i	R _i	(C _i /R _i -1)	C _j
SiO ₂	Al ₂ O ₃	cps			
0.2	0.8	2419	0.1605	0.2464	0.8
0.25	0.75	2998	0.1989	0.2573	0.75
0.4	0.6	5043	0.3345	0.1957	0.6
0.5	0.5	6450	0.4279	0.1686	0.5
0.6	0.4	7952	0.5275	0.1375	0.4
0.75	0.25	10,398	0.6898	0.0873	0.25
0.8	0.2	11,172	0.7411	0.0795	0.2
1.0	0.0	15,075	1.0	0.0	0.0

The empirical binary influence coefficients can be determined from the Lachance-Traill algorithm [9] (LT):

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

which becomes for a binary compound

$$C_i = R_i(1 + b_{ij} C_j) \quad (3)$$

or

$$(C_i/R_i - 1) = b_{ij} C_j \quad (4)$$

Equation (4) has the general form of a straight-line equation, i.e.

$$Y = m_i X \quad (5)$$

where the slope m_i is equal to the coefficient b_{ij} . This method will be used to determine the value of empirical binary coefficients b_{ij} . On paper, this method is very simple. It essentially consists to:

1. Prepare a set of binary specimens, for example, fused discs, containing the analyte i and the matrix element j , in different proportions covering all the concentration range met in practice; prepare also a fused disc of the pure analyte.

2. Measure all the intensities I_i (corrected for dead time, background and any interference) of each binary specimen, also the intensity $I(i)$ of the pure analyte and calculate the relative intensities R_i knowing that

$$R_i = I_i / I(i) \quad (6)$$

3. Plot the curve of the expression $(C_i/R_i - 1)$ as a function of the concentration C_j . The average value of the slope of this curve, for the selected concentration range, will give the researched coefficient b_{ij}

4. Repeat steps 1, 2 and 3 for every analyte. As an example for this procedure, the value of the coefficient $b_{SiO_2-Al_2O_3}$, which corrects for the overall of matrix effects of alumina on silica, has been determined. The measured intensities are given in Table 4 and the curve drawn from these data is given in Fig. 1. The obtained experimental value for the coefficient b_{ij} for this binary mixture is 0.344. The theoretical value is 0.3482.

Although the determination of the coefficients b_{ij} seems relatively easy on paper, it is in fact far from being so simple in practice. The main difficulties to overcome are the following:

1. The preparation of fused discs is a long and laborious work, requesting the services of a competent and meticulous technician. The number of fused discs necessary can become very large. Indeed, a minimum of 300 discs would be required to determine the 132 coefficients b_{ij} needed for the analysis of the samples containing the 12 analytes in Table 2. And in order to enhance accuracy, it is preferable to prepare every disc in duplicate, or even in triplicate!
2. It might be very difficult, often impossible, to prepare all the fused discs required in the determination of b_{ij} coefficients in the desired proportions of i and j . It is doubtful, for example, that we can succeed in preparing homogenous discs having a flat and smooth surface for the following binaries: Mg-Fe, P-Si, P-Fe, Mn-Ti, etc; and for the discs containing the following pure analytes: Mg, P, Ti, Cr, Mn.
3. All the possible experimental errors, particularly those mentioned at the previous section, can be present in the final value of b_{ij} so that the true value of b_{ij} especially if it is small, can be completely hidden and wrong.
4. It might be difficult to find all the chemical products in the desired form that are required in the preparation of the fused discs.
5. It is obvious that the poor homogeneity of fused discs, the spectrometer instability and the weighting errors will affect the accuracy of the measured intensities. These error sources are probably the cause of the misalignment of the intensity $I_i(0.2, 0.8)$ in Fig. 1.
6. If the coefficients b_{ij} are not constant for a given range of C_j , it becomes difficult to select the average value.
7. To make valid the dead time correction, it is necessary not to exceed the linearity region of detectors. It might be difficult to cover all the concentration range and stay within this upper limit at the same time, especially for the fused discs of the pure analytes.

In the face of all these difficulties, it is simply impossible to empirically determine **all** the coefficients b_{ij} necessary for the analysis of samples in Table 2. Only a few of them can be determined satisfactorily and the rest with a varying success. On the other hand, with some valid empirical values of b_{ij} the analyst can possibly complete the series of

required coefficients by using, with some reserve and caution, the calculation methods as proposed by G.R. Lachance [14, 15].

For all these reasons and those mentioned at the next section, we cannot recommend this method, but without advising to discard it completely.

6. Empirical Multi-Element Influence Coefficients

One of the first types of influence coefficients to be used was the *empirical multi-element influence coefficients*. They are based on the experimental observation that the magnitude of the total matrix effect (absorption and enhancement) of any matrix element j on analyte i , in a given specimen, can be quantified by an influence coefficient e_{ij} (the letter "e" is for empirical). Lachance and Traill [9] were among the first to apply these coefficients to practical analytical applications by proposing an equation of the following form:

$$C_i = R_i (1 + \sum_j e_{ij} C_j) \quad (7)$$

where R_i is the ratio of the intensity of analyte i in the specimen (I_i) relative to the intensity of the pure analyte i ($I_{(i)}$); C_i and C_j are respectively concentrations of analyte i and of matrix element j . The Lucas-Tooth and Pyne model [16] and the Raspberry-Heinrich model [17] are other good examples of the empirical approach.

The empirical coefficients (e_{ij}) used for matrix effect corrections can be obtained by *linear multiple regression analysis* using measured intensities and compositions of multi-element reference materials that cover the concentration ranges of elements of interest. These coefficients are calculated during the calibration in the following way. The relative intensity R_i is defined as equal to

$$R_i = I_i / I_{(i)} = 1 / I_{(i)} A_i = k_i A_i \quad (8)$$

where k_i is the calibration factor [18]. Combining this last equation with the equation (7) leads to

$$1/k_i A_i C_i = I_i + \sum_j e_{ij} A_j C_j$$

or

$$I_i = 1/k_i A_i C_i - \sum_j e_{ij} A_j C_j \quad (9)$$

This is a multiple variable linear equation of the following form:

$$Y = a_1 X_1 + a_2 X_2 + a_3 X_3 + \dots + a_N X_N \quad (10)$$

where $a_1, a_2, a_3, \dots, a_N$ are the unknown coefficients to be determined by the method of *least squares*, using the measured intensities and the concentrations of an appropriate set of multi-element reference materials. The success of this method depends on the availability of reference material compositions that closely match the compositions of the unknown samples. As the number of analytes increases, so must the number of reference materials required. In fact, to avoid any divergent solution of the respective simultaneous equations, it is recommended to use at least $2(N+1)$ reference materials, where N is the number of analytes to be determined.

It should be noted that empirical coefficients obtained by regression analysis of multi-element reference materials do not generally have the same values as those determined from theory. This does not present a problem for the results of analysis provided that the reference materials cover the concentration range of each analyte in the samples. Best results are obtained only when the samples and reference materials are of the same type and prepared in the same way.

The great advantage of empirical coefficients is that they have only to be calculated once for a given set of reference materials, and without the need to resort to complex theory. Their use is quite simple and practical. It is the best approach to use when one has to analyze non-homogeneous specimens or when it is not possible to eliminate problems such as the variations of particle size or mineralogical effects. Empirical coefficients can tolerate a less meticulous preparation of specimens. There is also no need for reference materials that the concentration total I closes to 100%.

On the other hand, the preparation and measurement of an adequate number of reliable reference materials could be long and tedious and can easily yield empirical coefficients that are often not very accurate and have no physical meaning. Furthermore, this statistical approach is sensitive to experimental errors in the data and the calculated coefficients can **only** be applied to unknowns of compositions similar to those of the reference materials used. In other words, empirical coefficients are liable to be inaccurate, depend on the composition of reference materials used and consequently their range of application is limited. The use of empirical coefficients, with all their potential problems, must then be limited as much as possible.

Furthermore, the analyst must be extremely cautious when using empirical coefficients calculated by multiple regression analysis because such an approach contains many potential pitfalls. Empirical coefficients can not only correct for matrix effects but can also conceal the correction of other effects present, such as errors of measured intensities, poor reference material chemical data, poor sample preparation, variations of particle size effects, mineralogical effects, surface effects, and so on. Unfortunately all these effects have a tendency to fluctuate from specimen to specimen, so that unknown specimens analyzed using empirical coefficients give results depending on these fluctuating factors and then can be more or less reliable. The analyst must be aware that empirical coefficients, derived from multiple regression calculations, can be so badly out in terms of magnitude, and sometimes even have the incorrect sign, that any intensity correction by using them is likely to be pure guesswork.

An easier and much more practical solution to these problems is to compute theoretical coefficients. They have many advantages over empirical coefficients. Such advantages include the use of only a few reference materials for setting up the calibration lines, the possibility of application to wider concentration ranges, and they can be calculated for any combination of elements and experimental conditions within a few seconds! Furthermore, theoretical influence coefficients allow any potential error source to be detected, isolated, and estimated, thereby giving greater confidence in the reliability of results.

7. Theoretical Binary Influence Coefficients

As already shown in Section 5, binary coefficients can be calculated empirically. They can also be calculated from theory, i.e., from the equation proposed by Sherman. With this equation, the intensities emitted by representative binary standards are calculated rather than being measured. With this approach, one assumes that the composition of a complex sample is made up of a series of binary elements or compounds where one considers the effect of one matrix element at a time on each analyte, independently of the rest of the matrix composition. Thus, a series of influence coefficients is calculated from hypothetical compositions for the binary series of elements or compounds that comprise the samples. In such a case, the coefficients are called *theoretical binary influence coefficients* and represented by the symbol a_{ij} .

With theoretical influence coefficients, relative intensities are used in most correction models for purposes of convenience. As the relative intensity R_i is defined as the ratio of the measured net intensity of the analyte in the specimen relative to the intensity of the pure analyte, this does not mean that the measurement of the pure analyte is required in practice unless it is the only reference material available. If influence coefficients are obtained from theory, then the intensity $I_{(i)}$ of the pure analyte i can be determined from a set of multi-component reference materials as follows:

$$C_i = R_i \cdot [1 + \dots] = I_i / I_{(i)} \cdot [1 + \dots] \quad (11)$$

where

C_i concentration of the analyte i

R_i relative intensity of the analyte i in the specimen

I_i measured net intensity of analyte i

$I_{(i)}$ intensity of the pure analyte i

$[1 + \dots]$ any valid mathematical model correcting for matrix effects

The last equation can be rewritten in the form:

$$I_i = I_{(i)} \cdot C_i / [1 + \dots] \quad (12)$$

This equation has the general form of a straight-line equation, i.e.

$$Y_i = m_i X_i \quad (13)$$

where m_i is the slope of the line. Thus, using a series of multi-element reference materials, you can plot a calibration line where the slope is nothing else than the calculated net intensity of the pure analyte [6].

The modern concept of theoretical binary coefficients can be used by three different algorithms. These three algorithms, among all the proposed ones, have been favored because of their accuracy and their sound theoretical basis. They are:

First, the Lachance-Trail [9] (LT) algorithm:

$$C_i = R_i (1 + \sum_j a_{ij} C_j) \quad (14)$$

where R_i is the ratio of the measured net intensity I_i to the measured net intensity of the pure analyte i . The binary coefficient a_{ij} is calculated using the following equation [2]:

$$a_{ij} = \frac{\alpha_{ij} - \epsilon_{ij}}{1 + \epsilon_{ij} C_{jm}}$$

where α_{ij} and ϵ_{ij} , defined by equations (28) and (29), are calculated for the special case of a binary standard having a composition (C_{im}, C_{jm}) , where C_{im} is the mid-value of the calibration range of the analyte i and where

$$C_{jm} = 1 - C_{im} \quad (16)$$

Nowadays, the alpha coefficients as proposed by Lachance and Traill [9] are no longer used in practice because of their lack of accuracy. They have been replaced by the *theoretical binary influence coefficients* a_{ij} , which, as opposed to the alpha coefficients, take into account the enhancement effect as well as the polychromaticity of the incident radiation [2].

This approach assumes that the coefficient a_{ij} is a **constant** (it is an approximation!) when it is applied to specimens with a limited concentration range (0-10%), such as, for example, oxides in rock samples diluted in fused discs. In this case, the calculation method by itself (Eqns 14 and 15) introduces a theoretical mean relative error of only 0.02% on the calculated concentrations. On the other hand, for concentration variations greater than 10%, the concentrations calculated by this algorithm associated to the a_{ij} coefficients are unacceptable (see Table 2).

In the case of diluted samples such as fused discs or pressed powder pellets, the theoretical binary influence coefficient (a_{ij}) defined above can be modified by incorporating a constant term. For example, when a sample is fused in a fixed sample/flux ratio to produce a fused disc, or when a pulverized sample is mixed in a fixed sample/binder ratio and pressed, the a_{ij} coefficient can be modified by including the weight fraction and the composition of the flux or the binder, which are essentially constant for every specimen. In this case, the a_{ij} coefficient is referred to as a *modified* coefficient. The coefficients a_{ij} can also be modified to express them in terms of oxides rather than elements themselves.

Two different a_{ij} coefficients, calculated for the correction of matrix effects of two different matrix elements on the analyte, can be combined to form only one coefficient. In this case, the new coefficient is referred to as a *hybrid* coefficient. It is an elegant way to eliminate the measurement of one analyte and to correct for its matrix effects even if it has not been measured or its concentration is not known. However, this approach introduces more approximations and must be used with caution and applied with great care. The terminology "modified" and "hybrid" influence coefficients has been proposed by Lachance [14] in

1979 but his methods of calculation have not been retained.

When samples are prepared as fused discs, volatile products (e.g. CO_2 , H_2O , SO_2 , Cl, F, etc.) can be lost during the fusion and/or it can be accompanied with a gain in weight due to oxidation (e.g. $\text{FeO} \rightarrow \text{Fe}_2\text{O}_3$). In this case, there are three different ways to calculate the sample composition:

- 1) A conventional Loss On Ignition (LOI) is done on the pulverized sample BEFORE the fusion and the ignited powder is used to prepare the fused disc. In this case, there is usually NO further loss of volatile or gain in weight during the fusion and all the calculated concentrations in the fused disc are adjusted to take into account the LOI and get the analyte concentrations in the sample [36]. This approach generates accurate results except it is time consuming.
- 2) A conventional LOI is done on the pulverized sample, but the original sample is used to prepare the fused disc. In this case, there is loss of volatile and/or gain in weight during the fusion. It changes the sample/flux ratio and may severely affect the accuracy of results. The method developed by us takes this phenomenon into account by using a theoretical approach based on the famous Sherman equation [36]. The coefficient thus calculated for the loss of volatile products and/or gain in weight is included in the term $[1+\dots]$ correcting for matrix effects, even if it is not an influence coefficient. This approach generates accurate results and it is less time consuming than the previous one because the LOI and the fused disc can be done at the same time.
- 3) No conventional LOI is done on the pulverized sample. In this case, there is loss of volatile and/or gain in weight during the fusion and the LOI value is unknown. The LOI value is calculated by difference between 100% and the sum of calculated concentrations in the sample [36]. This approach introduces more approximations in the calculation method and is sensitive to any experimental errors. Since the accuracy of this approach is more "unpredictable", it must be applied with caution and great care.

Second, the Claisse-Quintin algorithm [6, 19, 20, 21] (CQ):

The Claisse-Quintin algorithm (CQ) can be described as an extension of the Lachance-Traill

algorithm (LT) taking into account the fact that the LT coefficient, a_{ij}^{LT} , (Eqn 15) is not a constant but varies with the concentration of the matrix elements. According to Claisse and Quintin the LT coefficient a_{ij}^{LT} varies linearly with the concentration C_j , i.e.

$$a_{ij}^{LT} = a_{ij} + a_{ijj}C_j$$

Thus, the general form of the Claisse-Quintin algorithm for a multicomponent sample can be written as:

$$C_i = R_i \left[1 + \sum_j (a_{ij} + a_{ijj}C_M)C_j + \sum_j \sum_{k>j} a_{ijk}C_jC_k \right] \quad (17)$$

where the matrix concentration C_M is the sum of all elements in the sample except i, i.e.

$$C_M = 1 - C_i = C_j + C_k + \dots + C_N \quad (18)$$

and where the "crossed" ternary coefficient a_{ijk} has been added to compensate for the fact that the total matrix correction cannot be strictly represented by a weighted sum of binary corrections. The binary coefficients a_{ij} and a_{ijj} are calculated from theory at hypothetical binary compositions of $(C_i, C_j) = (0.2, 0.8)$ and $(0.8, 0.2)$, respectively. The cross-product coefficient, a_{ijk} , is calculated at the ternary composition of $(C_i, C_j, C_k) = (0.30, 0.35, 0.35)$. To be more explicit, if for a ternary system (C_i, C_j, C_k) , the variable $F_i(C_i, C_j, C_k)$ is defined by

$$F_i(C_i, C_j, C_k) = \frac{1}{C_j} \left(\frac{C_i}{R_i} - 1 \right) \quad (19)$$

Note that: if $C_j=0$, then

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

where the ratio C/R_i is calculated by the Fundamental Algorithm (Eqn 27) for a ternary system:

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

fC

$$a_{ij} = 1/3[-F_i(0.2, 0.8, 0) + 4F_i(0.8, 0.2, 0)] \quad (20)$$

$$a_{ijj} = 5/3[F_i(0.2, 0.8, 0) - F_i(0.8, 0.2, 0)] \quad (21)$$

$$a_{ijk} = 20/7[F_i(0.3, 0.35, 0.35) - F_i(0.3, 0.7, 0) - F_i(0.3, 0, 0.7)] \quad (22)$$

$$\hat{1} \ddagger +, a \quad f_i \quad f_j \quad fC \quad f_j \quad \ddagger +, a$$

As with the LT algorithm, when a pulverized sample is mixed in a fixed sample/binder ratio and pressed, the influence coefficients of the CQ algorithm can be modified by including the weight fraction and the composition of the binder, which are essentially constant for every specimen. The influence coefficients of this algorithm can also be modified to express them in terms of oxides rather than elements themselves. The hybrid coefficients are not calculated for the CQ algorithm because there is no LOI (or gain in weight) during the preparation of pressed pellets.

Third, the *Lachance* [22, 23] algorithm (or COLA):

$$C_i = R_i \left\{ 1 + \sum_j \left[a_1 + \frac{a_2 C_M}{1 + a_3 (1 - C_M)} \right] C_j + \sum_j \sum_k a_{ijk} C_j C_k \right\} \quad (23)$$

where the binary coefficients a_1 , a_2 and a_3 are defined by the following equations:

$$a_1 = F_i(0.999, 0.001, 0) \quad (24)$$

$$a_2 = F_i(0.001, 0.999, 0) - F_i(0.999, 0.001, 0) \quad (25)$$

$$a_3 = \frac{F_i(0.001, 0.999, 0) - F_i(0.5, 0.5, 0)}{F_i(0.5, 0.5, 0) - F_i(0.999, 0.001, 0)} - 1 \quad (26)$$

where the function F_i is given by the equation (19). The "crossed" coefficients a_{ijk} proposed by Claisse and Quintin (see Eqn 22) has been retained and included in equation (23). The Lachance algorithm can be used for a broad range of concentrations (0-100%), for example, alloys. In this case, the calculation method by itself introduces a theoretical mean relative error of 0.3% on the calculated concentrations (see Table 2).

The algorithm proposed by G. R. Lachance [22] in 1981 and called COLA is as accurate as the CQ algorithm (see Table 2), except that it is valid for a larger concentration range (0-100%). This algorithm has been proposed mainly as a substitute for the Fundamental-Parameters approach because of the lack of availability of powerful mini-computers in the early eighties. Today, with the recent generation of PCs, this is no longer a problem. The COLA method can therefore be replaced advantageously by the Fundamental Algorithm approach.

The experimental verification of these three algorithms done by Pella et al. [24], confirms the

expected theoretical accuracy. Consequently, XRF analysts should consider the theoretical binary coefficient approach within the LT and CQ algorithms as a valuable alternative to the Fundamental-Parameters approach, especially when the variations of matrix effects or composition of samples to analyze are small. The NIST [25] has also published (on paper only) a computer program, called NBSGSC, enabling one to use these three algorithms in combination with theoretical binary influence coefficients.

For the calibration and calculation of sample compositions using the two first presented algorithms with their associated theoretical influence coefficients, some commercial WINDOWS™ software packages, such as CiLT and CiROU, running only on PC, are also available [26].

8. Theoretical Multi-Element Influence Coefficients

A better approach to empirical coefficients or to theoretical binary coefficients is the Fundamental-Parameters method proposed by Criss and Birks [3] in 1968. With this method a first estimate of concentrations is evaluated from measured intensities. This estimate of composition is then used to calculate a new set of intensities from which a new revised estimate of composition is calculated. This process is iterated until the difference between compositions of two consecutive cycles becomes insignificant.

The great advantage of this method is its theoretical exactness. However, although this method has been improved by many researchers since its publication, the original proposed method suffered from the following weaknesses: to be able to use this method a first approximation of the sample composition is absolutely necessary. Frequently, however, a poor first approximation is generated from measured intensities because such intensities have been strongly modified by the matrix. To improve the first approximation, concentrations are normalized during the process of calculation. This normalization step must absolutely be avoided if accurate results are required, and its use is definitely not recommended. The proposed calibration procedure is also somewhat ambiguous and inefficient and its range of application is limited as well. Speed of calculation is very slow because the complex parts of the Sherman equation are calculated for each iteration and many such iterations are required since the first approximation of the composition is often very far from the final composition.

The Fundamental-Parameters approach proposed by Criss and Birks is an application of the equation derived by Sherman. By simply manipulating the Sherman equation and by doing absolutely no approximation at all during the process of derivation, Rousseau [2] deduced new theoretical expressions for multi-element influence coefficients in which the corrections for both absorption and enhancement effects are clearly and accurately defined. They are used in the Fundamental Algorithm

where

$$\varepsilon_{ij} = \frac{\sum_k W_{ij}(\lambda(k)) \delta_{ij} \lambda(k)}{\sum_j W_{ij} \lambda(k)} \quad (29)$$

where α_{ij} and ε_{ij} are the multi-element influence coefficients correcting for absorption and enhancement effects, respectively. The equations that define the symbols $W_{ij}(\lambda_k)$, $b_{ij}(\lambda_k)$ and $d_j(\lambda_k)$ are given in the Ref. (2).

Since the α_{ij} and ε_{ij} coefficients depend on the total matrix composition they must be calculated for each sample in the following way: a first estimate of the composition is calculated using the Claisse-Quintin algorithm

$$C_i = R_i [1 + \sum_j (a_{ij} + a_{ijj} C_M) C_j + \sum_j \sum_k a_{ijk} C_j C_k] \quad (30)$$

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

The Fundamental Algorithm (Eqn 27) can be applied to any type of samples of any composition. This calculation method by itself introduces a theoretical mean relative error of only 0.05% (see Table 2). An experimental verification of this method done by Rousseau and Bouchard [27] on different types of alloys confirmed the accuracy and versatility of the method.

However, this theoretical approach needs to be adapted to the experimental data of each spectrometer, since theory cannot account for all the instrumental parameters. This is done through a smart calibration procedure that compares the measured intensities to the calculated intensities [6,11,18].

Furthermore, if the mathematical expressions used to calculate influence coefficients are exact, that does not imply that all physical parameters used in these expressions, such as mass absorption coefficients [28, 29], fluorescence yields [30, 31], transition probabilities [32], calculated incident spectra [33], etc., are themselves exact or without errors. To this day, there is some uncertainty in the values of fundamental parameters. Fortunately the calibration procedure [18] allows one to adapt the Fundamental Algorithm to experimental data by reducing the effect of these errors to a level less than 0.1 %.

As with the LT and CQ algorithms, when a pulverized sample is mixed in a fixed sample/ binder ratio and pressed, the influence coefficients of the Fundamental Algorithm can be modified by including the weight fraction and the composition of the binder, which are essentially constant for every specimen. The influence coefficients of the Fundamental Algorithm can also be modified to express them in terms of oxides rather than elements themselves. The hybrid coefficients are not calculated for the Fundamental Algorithm because there is no LOI (or gain in weight) determination during the preparation of pressed pellets or alloys.

The calibration and calculation of sample compositions using the Fundamental Algorithm and its associated theoretical influence coefficients cannot be done without computer programs. A commercial WINDOWS™ version of the software package called CiROU [34], running only on PCs, is available [26].

Lachance and Claisse [35] have recently introduced another type of influence coefficients. They are still called *theoretical multi-element influence coefficients* but are defined by:

$$\alpha_{ij}^* = \frac{\alpha_{ij} - \varepsilon_{ij}}{1 + \sum_j \varepsilon_{ij} C_j} \quad (31)$$

which are used in association with the LT algorithm:

$$C_i = R_i (1 + \sum_j \alpha_{ij}^* C_j) \quad (32)$$

The α_{ij}^* coefficient regroups in one entity the α_{ij} and ε_{ij} coefficients of the Fundamental Algorithm

rather than to keep them separated. Note that this coefficient is not new. Indeed, Rousseau [5] introduced it many years ago before Lachance and Claisse. They use a different symbolism, but the meaning of each symbol is the same.

In practice, there is no benefit in using the LT algorithm rather than the Fundamental Algorithm. In fact, not only is there no benefit but one also loses something. By using equation (32) rather than equation (27) we lose the *mathematical robustness*, i.e. equation (32) requires more iterations before to get the final result (the convergence process is slower) and this equation is also more sensitive to any error in measured intensities [36].

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 of this approach are presented in Ref. (37).

To conclude this Section, we have presented three different algorithms to cover the complete analytical range. First, to calculate limited concentration ranges (0-10%), we have proposed the Lachance-Traill algorithm in combination with theoretical binary influence coefficients as calculated by Rousseau. Second, to calculate medium concentration ranges (0-40%), we have proposed the Claisse-Quintin algorithm in combination with theoretical binary influence coefficients as calculated by Rousseau. Finally, The Fundamental Algorithm has been proposed to calculate wide concentration ranges (0-100%). Thus, we offer accurate analytical methods able to work effectively in any analytical context: diluted samples, pressed pellets and alloys.

9. Conclusion

As already stated in Ref. (1): "To obtain satisfactory results when using empirical correction methods, an appropriate number of reference materials must be available for covering the analyte concentration ranges of interest. As the analyte concentration ranges of the samples to be analyzed increase and the elemental composition varies considerably, then it becomes less likely that a large number of appropriate reference materials will be available. In such situations, theoretical correction methods are more attractive and efficient to use, because these methods are applicable to wide concentration ranges and only a limited number of reference materials are required for good accuracy of results."

At the current state of our knowledge, theoretical influence coefficients calculated from fundamental parameters give sufficient accuracy in many instances to suit most of the requirements of the analyst. Although they do not yet represent a universally applicable calculation method, they are getting very close to such an ideal, and a substantial proportion of current research in XRF analysis is directed towards improving fundamental techniques even more.

When theoretical influence coefficients are used for the correction of matrix effects, only a limited number of reference materials are required for the calibration procedure [18] and obtain good accuracy of results. For best accuracy, reference materials of the same type as the unknown samples should be used. This will compensate considerably for uncertainties in the fundamental parameters (for example, fluorescence yields, mass absorption coefficients, etc.). Also, the preparation of samples and reference materials should be identical, otherwise differences between the two types of specimens can lead to inaccuracy.

No method for matrix effect corrections, including that using theoretical influence coefficients, cannot correct for physical effects, i.e. for particle size, mineralogical or surface effects, but only for elemental interactions, i.e. for variations in chemical composition of the samples or reference materials.

It is possible to determine trace elements using the Compton scatter peak for the correction of the absorption effects without knowing the composition of major elements [38]. However, the variation of the sample compositions must be limited. By using theoretical influence coefficients for the correction of both matrix effects, absorption and enhancement, it is possible to determine trace elements, as well as major elements, even in the case of a broad variation of sample compositions. Their use for the determination of trace elements will increase rapidly over the next few years. The only drawback with theoretical influence coefficients is that the major element composition of the sample must be known in advance, although it is less and less an obstacle with the increasing automation of XRF spectrometers and of their control software.

Since there is no longer any need for using empirical coefficients to correct for matrix effects, only two types of influence coefficients remain usable. Firstly the theoretical binary influence coefficients that are constant in a given concentration range of C_i and are independent of the matrix compo-

sition. They are used in theoretically valid algorithms, such as the Lachance-Trail or Claisse-Quintin. Secondly, the theoretical multi-element influence coefficients calculated from an estimate of the composition of each sample and then used in the Fundamental Algorithm to obtain a more accurate composition of the sample. This last method offers the maximum of accuracy in XRF analysis, this accuracy being limited only by the quality of sample preparation and the quality of reference materials, but so are all other methods of matrix effect correction.

Because of their accuracy, theoretical influence coefficients must be used as often as possible but they are particularly useful in the following three cases:

1. To supplement empirical influence coefficients;
2. To predict potential matrix effect problems;
3. To be used exclusively in those cases where a few reference materials only are available.

Finally, today there are some high quality commercial computer programs to perform quantitative XRF analysis that incorporate the most modern correction methods, as well as all the tools necessary for the XRF analyst to obtain reliable results.

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