

Analytical Application Note

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Quantitative X-Ray Fluorescence Analysis by Use of Fundamental Influence Coefficients

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The rigorous relationship existing between effective fundamental coefficients, as expressed by Tertian's identities, and Sherman's basic equations for x-ray fluorescence intensities is recalled. The properties of these coefficients in the case of binary systems are described, for usual as well as for some anomalous situations, and a general, accurate hyperbolic equation is suggested to account for coefficient variation with composition. The properties of effective coefficients in the general case of multicomponent systems (alloys, etc.) are then examined, and illustrated on the typical Fe—Ni—Cr ternary system, confirming the essential exactness of this approach. As a consequence, the authors propose to make use of calculated effective coefficients to apply mathematical matrix corrections, and give a first outline of the analytical procedure.

INTRODUCTION

To apply accurate matrix corrections in x-ray fluorescence analysis, two methods of theoretical calculation are today available: (1) the fundamental parameter approach as developed since 1968 by Criss and co-workers¹⁻³ and, (2) an approach based on the notion of fundamental coefficients, as described in a recent book by Tertian and Claisse.⁴ The object of this paper is to emphasize some aspects of these theoretical coefficients, and then discuss their mode of application to analysis. The symbols used in Ref. 4 will be retained.

1. FUNDAMENTAL COEFFICIENTS VERSUS FUNDAMENTAL PARAMETERS

Since both approaches rely on the calculation of theoretical fluorescence intensities after Sherman's equations, some basic relationship must exist between them. This correlation was established in 1977 by Tertian,⁵ using this simple demonstration. Consider a fluorescent element i in a multicomponent system (i, j, k, \dots) with C_i, C_j, C_k, \dots as the relative concentrations, R'_i as the relative intensity (with respect to the pure element) concerning primary fluorescence, and R_i as the total relative intensity. We can write by definition

$$R_i = R'_i(1 + h_{ij}C_j + h_{ik}C_k + \dots) \quad (1)$$

where $h_{ij}C_j, h_{ik}C_k, \dots$ account for the increments of relative intensity due to the selective excitation (i.e. secondary, possibly tertiary, etc. fluorescence), if present, of element i by elements j, k, \dots . Postulating the existence (to be confirmed below) of *effective* influence coefficients $\alpha'_{ij}, \alpha'_{ik}, \dots$ for primary fluorescence entails, after the classical Lachance-Trail equation,

$$C_i = R'_i(1 + \alpha'_{ij}C_j + \alpha'_{ik}C_k + \dots) \quad (2)$$

Finally, effective influence coefficients $\bar{\alpha}_{ij}, \bar{\alpha}_{ik}, \dots$ for the total fluorescence are defined by

$$C_i = R_i(1 + \bar{\alpha}_{ij}C_j + \bar{\alpha}_{ik}C_k + \dots) \quad (3)$$

Combining (see Appendix 1) Eqns (1) to (3) then results in the essential identities

$$\bar{\alpha}_{ij} = \alpha'_{ij} - h_{ij} \frac{C_j}{R_i} \quad (4)$$

$$\bar{\alpha}_{ik} = \alpha'_{ik} - h_{ik} \frac{C_k}{R_i}$$

etc., which show the structure and properties of effective coefficients:

(1) Any resultant coefficient such as $\bar{\alpha}_{ij}$ is the difference of two terms: α'_{ij} which accounts for primary fluorescence and can be, according to the case, positive or negative; and $h_{ij}(C_j/R_i)$, always positive, which accounts for selective excitation if present. From the foregoing derivation, both terms include third element effects. Coefficient $\bar{\alpha}_{ij}$ of course reduces to α'_{ij} when enhancement is absent.

(2) The coefficients are calculable from fundamental parameters. Given, typically for a reference composi-

tion, the C_i, C_j, C_k, \dots concentrations, the h_{ij} and R_i values are the normal output of the total intensity calculations. As to the α'_{ij} values, they result from a special calculation (see Appendix 2) which at the same time warrants their existence as effective influence coefficients for primary fluorescence.

(3) Eqns (4) show the essential variability of effective coefficients. They are fixed for a given composition and of practical value at or near this composition; otherwise they are more or less composition-dependent and, in particular, different according to whether binary or multicomponent systems are considered. All of these aspects are better illustrated on specific examples, as in the following sections.

2. ANALYSIS OF BINARY SYSTEMS

2.1 Monochromatic excitation

This is the simplest assumption, and the advantage is that it allows fast calculations. We call (i, j) the binary ($C_i + C_j = 1$) and consider i as the fluorescent element. Then, Eqn (3) reduces to

$$C_i = R_i(1 + \alpha_{ij}C_j) \quad (5)$$

where α_{ij} is the 'binary' coefficient, and Eqn (4) is written

$$\alpha_{ij} = \alpha'_{ij} - e_{ij} \frac{C_j}{R_i} \quad (6)$$

where $\alpha'_{ij} = (\mu_j^*/\mu_i^*) - 1$ (see Appendix 2) is a constant, and e_{ij} is the particular value of h_{ij} ; for the sake of clarity, we think it advantageous to use different symbols for the case of a binary (e_{ij}) and that of a multicomponent system (h_{ij}). Thus, if j actually excites secondary fluorescence from i and if we consider *one* reinforcing line (λ_j), e_{ij} , as a consequence of Sherman's equations, is

$$e_{ij} = \frac{1}{2} E_j \frac{\mu_{j,\lambda}}{\mu_{i,\lambda}} \times \frac{\mu_{i,\lambda_j}}{\mu_{s,\lambda_j}} L_0 \quad (7)$$

with

$$L_0 = \frac{\ln \left(1 + \frac{\mu_{s,\lambda}/\sin \psi_1}{\mu_{s,\lambda_j}} \right)}{\mu_{s,\lambda_j}} + \frac{\ln \left(1 + \frac{\mu_{s,\lambda_i}/\sin \psi_2}{\mu_{s,\lambda_j}} \right)}{\mu_{s,\lambda_j}} \quad (8)$$

where s stands for the binary specimen (for other definitions, see Ref. 4, section 5.3). If there are more than one reinforcing line, e_{ij} will be a summation of such terms. Finally, eliminating R_i between Eqns (5) and (6) results in

$$\alpha_{ij} = \frac{\alpha'_{ij}}{1 + e_{ij}C_j} \quad (9)$$

which can be considered as the fundamental equation for binary coefficient variation. This expression was first derived by Tertian and Vié le Sage,⁶ in terms of K coefficients ($K_{ij} = \alpha_{ij} + 1$), in which case the relation is

$$K_{ij} = \frac{K'_{ij} - e_{ij}C_j}{1 + e_{ij}C_j} \quad (9a)$$

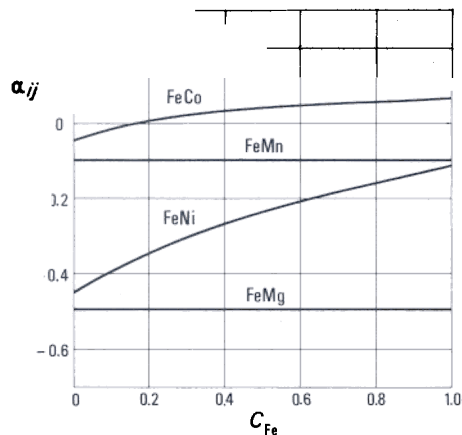


Figure 1. Binary coefficients for Fe fluorescence. Monochromatic excitation at $\lambda = 1.02 \text{ \AA}$.

When there is no enhancement from j , the coefficient naturally reduces to α_{ij}' (or K_{ij}'), i.e. a constant. By use of these formulas, any binary system can be readily investigated and Fig. 1 shows some typical examples referring to Fe fluorescence with an excitation line at $\lambda = 1.02 \text{ \AA}$.

2.2 Special situations

By still referring to monochromatic excitation, special or 'anomalous' situations are apt to show when there is some lack of balance between the selected excitation line and the elements i, j . Three examples will be given.

Figure 2 refers to the FeMo system with $\text{SnK}\alpha$ ($\lambda = 0.492 \text{ \AA}$) excitation. Though Mo is an enhancer for Fe, absorption predominates ($\alpha_{\text{FeMo}} > 0$) and a considerable variation of the coefficient with composition is observed.

A similar situation (Fig. 3) exists for the MgSi system when using $\text{NiK}\alpha$ ($\lambda = 1.66 \text{ \AA}$) excitation, with the difference that the curve is now convex towards the top of the diagram.

Finally, an anomalous situation is shown on Fig. 4 referring to the SiRb system when using $\text{SnK}\alpha$ excitation. Enhancement is considerable, since secondary fluorescence exceeds the primary component in the

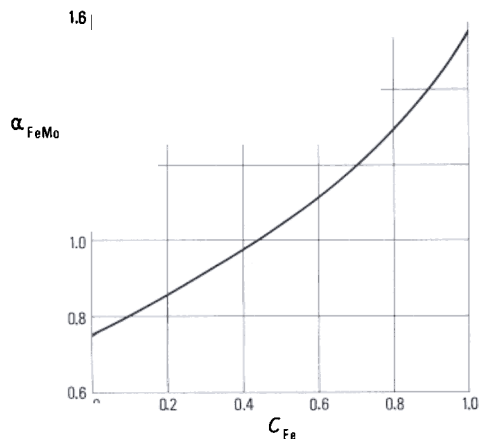


Figure 2. FeMo system. Monochromatic excitation at $\lambda = 0.492 \text{ \AA}$ ($\text{SnK}\alpha$).

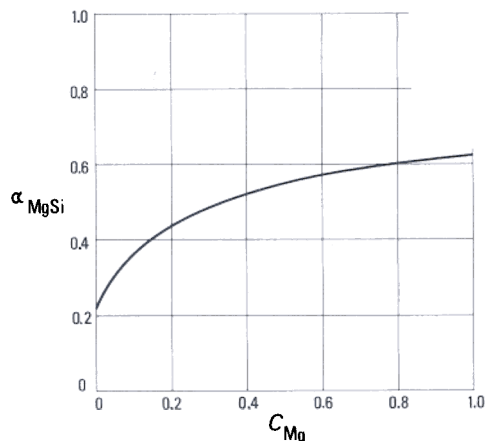


Figure 3. MgSi system. Monochromatic excitation at $\lambda = 1.66 \text{ \AA}$ ($\text{NiK}\alpha$).

interval $C_{\text{Si}} = 0-0.6$, and we see the curve go down to very low α values, α_{SiRb} becoming < -1.0 at $C_{\text{Si}} = 0.825$. Equation (5) implies that R_{Si} then exceeds unity, which means an unusual situation (Fig. 5). A similar case ($\text{SiO}_2\text{-ZrO}_2$) was studied by Criss⁷ in terms of fundamental parameters and involved the selective excitation of Si by both the K and L spectrum lines of Zr. In the present case, only the K lines of Rb are active.

2.3 Polychromatic excitation

Eqns (9) or (9a) apply as well for polychromatic excitation, provided that α_{ij}' and e_{ij} then represent values integrated over the incident spectral distribution, I_λ . Primary coefficient α_{ij}' , no longer a constant, can be calculated after Eqn (3B), Appendix 2, or

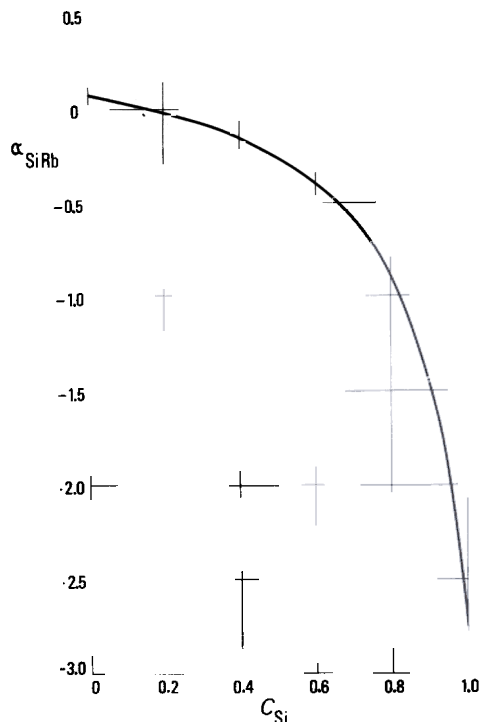


Figure 4. SiRb system. Monochromatic excitation at $\lambda = 0.492 \text{ \AA}$ ($\text{SnK}\alpha$).

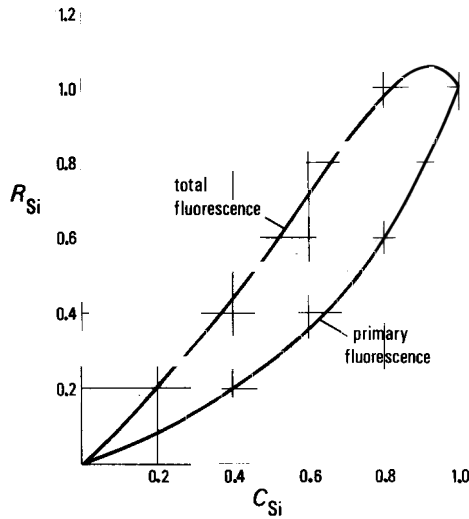


Figure 5. SiRb system. Illustrating the unusual situation for the relative intensity of Si.

alternatively after

$$\alpha_{ij}' = \frac{1}{C_i} \left(\frac{C_i}{R_i'} - 1 \right) \quad (10)$$

where R_i' is the calculated relative intensity for primary fluorescence. As to e_{ij} , it is deduced from Eqn (1), which for a binary simplifies into

$$R_i = R_i'(1 + e_{ij}C_j) \quad (11)$$

hence

$$e_{ij} = \frac{1}{C_i} \left(\frac{R_i}{R_i'} - 1 \right) \quad (12)$$

Typical examples of coefficient variation curves can be found in Reference 4, Chapters 7 and 10, and six of them will be again represented in section 3.3 (see Figs. 6–8). Let us emphasize that in the case of polychromatic excitation, binary coefficients concerning pure absorption (no enhancement present) are no longer constants but increasing functions of fluorescent element concentration; the variation is then governed by the theory of equivalent wavelength (Ref. 4, section 7.2).

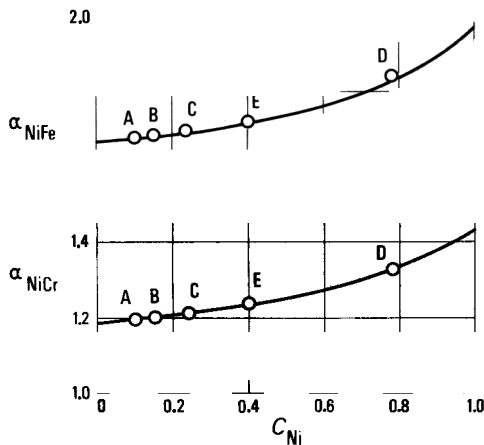


Figure 6. Ni fluorescence in the Fe—Ni—Cr system. Polychromatic excitation by a Cr-target tube. The curves refer to binary coefficients and the circles to multicomponent coefficients for the A, B, C, D, E compositions.

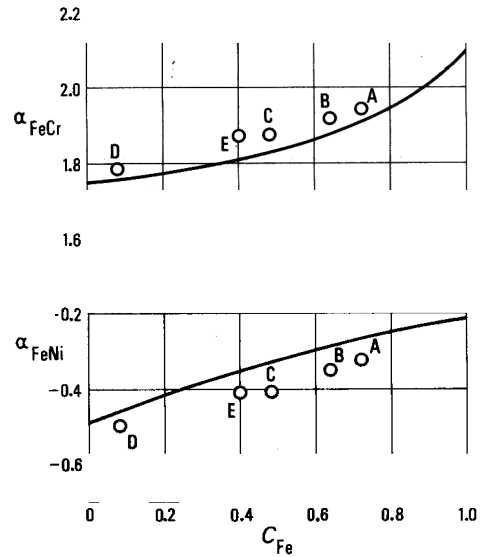


Figure 7. Fe fluorescence in the Fe—Ni—Cr system. Same remarks as for Figure 6.

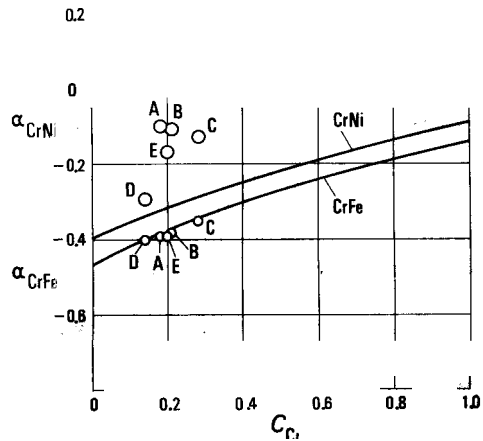


Figure 8. Cr fluorescence in the Fe—Ni—Cr system. Same remarks as for Figure 6. Larger circles belong to CrNi, smaller circles to CrFe.

2.4 Practical representation of binary coefficient variation

As was suggested in Ref. 4 (section 10.3) a hyperbolic function proves the best fit to represent the variation of binary coefficients with composition. In terms of α values, the equation amounts to

$$\alpha = \alpha_0 + \frac{\beta C_i}{C_i + \eta(1 - C_i)} \quad (13)$$

where

$$\beta = \alpha_1 - \alpha_0 \quad (14)$$

and α_0 and α_1 are the limiting values at $C_i = 0$ and $C_i = 1$, respectively. As for η , it was observed⁴ that

$$\eta = \frac{K_0 + K_1}{\alpha} = 1 + \frac{\alpha_0 + \alpha_1}{\alpha}$$

was a correct value (especially when considering polychromatic excitation) in many usual cases where

Table 1. Verification of Eqn(13) on six binary systems

FeNi (Fig. 1)			FeCo (Fig. 1)		
$\alpha_0 = -0.450$	$\alpha_1 = -0.115$		$\alpha_0 = -0.046$	$\alpha_1 = 0.064$	
$\beta = 0.335$	$\eta = 0.57$		$\beta = 0.110$	$\eta = 0.28$	
α_{FeNi} values			α_{FeCo} values		
C_{Fe}	Theory	Eqn(13)	C_{Fe}	Theory	Eqn(13)
0	-0.450	-0.450	0	-0.046	-0.046
0.2	-0.345	-0.348	0.2	0.007	0.006
0.4	-0.268	-0.269	0.4	0.032	0.032
0.6	-0.207	-0.207	0.6	0.047	0.047
0.8	-0.157	-0.156	0.8	0.057	0.057
1.0	-0.115	-0.115	1.0	0.064	0.064
FeMo (Fig. 2)			MgSi (Fig. 3)		
$\alpha_0 = 0.756$	$\alpha_1 = 1.555$		$\alpha_0 = 0.217$	$\alpha_1 = 0.624$	
$\beta = 0.799$	$\eta = 1.80$		$\beta = 0.407$	$\eta = 0.22$	
α_{FeMo} values			α_{MgSi} values		
C_{Fe}	Theory	Eqn(13)	C_{Mg}	Theory	Eqn(13)
0	0.756	0.756	0	0.217	0.217
0.2	0.860	0.854	0.2	0.436	0.434
0.4	0.977	0.972	0.4	0.523	0.523
0.6	1.117	1.119	0.6	0.571	0.572
0.8	1.297	1.307	0.8	0.602	0.603
1.0	1.555	1.555	1.0	0.624	0.624
SiRb (Fig. 4)			NiFe ^a (Fig. 6)		
$\alpha_0 = 0.067$	$\alpha_1 = -2.727$		$\alpha_0 = 1.660$	$\alpha_1 = 1.960$	
$\beta = -2.794$	$\eta = 7.55$		$\beta = 0.300$	$\eta = 2.81$	
α_{SiRb} values			α_{NiFe} values		
C_{Si}	Theory	Eqn(13)	C_{Ni}	Theory	Eqn(13)
0	0.067	0.067	0	1.660	1.660
0.2	-0.023	-0.023	0.2	1.688	1.685
0.4	-0.160	-0.160	0.4	1.719	1.718
0.6	-0.396	-0.396	0.6	1.763	1.764
0.8	-0.900	-0.901	0.8	1.835	1.836
0.9	-1.450	-1.453	0.9	1.890	1.889
0.95	-1.931	-1.933	1.0	1.960	1.960
0.975	-2.274	-2.274			
1.0	-2.727	-2.727			

^a Polychromatic excitation by Cr-target.

α is found to be an approximately linear function of R_i . In other cases, experience shows that it is just sufficient to ascertain (by trial and error) a suitable value of η to verify the hyperbolic relation. This is entirely supported by all the examples in this paper, as shown by the data in Table 1.

This is a remarkable generalization and Eqn (13), being unique and accurate in every situation (enhancement and/or absorption, monochromatic or polychromatic excitation), is thus apt to supersede previous empirical or semi-theoretical representations, namely of the Raspberry-Heinrich type⁸⁻¹⁰ and the Claisse-Quintin type.^{11,12}

2.5 Analytical applications

Binary alloy or compound (e.g. oxides, etc.) compositions can be determined over the whole range of concentrations by using the algorithm

$$\begin{aligned} C_i &= R_i(1 + \alpha_{ij}C_j) \\ C_j &= R_j(1 + \alpha_{ji}C_i) \end{aligned} \quad (15)$$

and introducing for α_{ij} and α_{ji} the theoretical coefficients just discussed.

Monochromatic excitation. The calculation is based on a few fundamental parameters and is comparatively straightforward (section 2.1). It provides the concerned $\alpha_{ij} = F(C_i)$ and $\alpha_{ji} = F(C_j)$ curves, and each of them can then be allotted a hyperbolic equation after Eqn (13). Substituting these functions in Eqns (15) allows C_i and C_j to be determined after the usual iterative procedure. In practice, it is more convenient and advantageous (see Ref. 4, section 10.2) to compare the unknown with a standard, instead of the pure elements.

Polychromatic excitation. The principle is quite the same (section 2.3) though calculations are obviously more time-consuming. Moreover, the obtained theoretical coefficients can prove less well-fitting in this case on account of the uncertainties affecting the actual incident spectral distribution. This difficulty, inherent to the use of fundamental parameters, will be again discussed in section 4. In practice, it can be assuaged by resorting to the 'comparison standard' procedure (see Ref. 4, sections 10.2 and 10.21).

3. ANALYSIS OF MULTICOMPONENT SYSTEMS

3.1 Multicomponent versus binary coefficients

It has been a permanent statement¹³⁻¹⁵ by one of us (R.T.) that on a general basis 'binary' coefficients, even if accurate, are not fit for analysing multicomponent specimens. Hence the necessity of imagining 'multicomponent' coefficients. The difference between the two categories (see Ref. 4, section 5.4) lies in the fact that third element effects can alter fluorescence intensities in multicomponent systems, while they are obviously absent in binary systems. Eqns (4) by including *all* effects allow the differences to be interpreted. Considering a given concentration level C_i and comparing Eqn (4), for the (i, j, k , etc.) specimen, with Eqn (6) for the binary (i, j) shows that $\bar{\alpha}_{ij}$ and α_{ij} as a rule are different because h_{ij} is different from e_{ij} , the R_i values are different, and even the α_{ij}' values (except when monochromatic excitation is used) are liable to be different in both cases. This will be largely illustrated in section 3.3.

Another important observation is that coefficient variation curves, so characteristic (Figs. 1-4) of binary associations, no longer exist, *basically*, for multicomponent systems where any zigzagged representation can show (Figs. 7 and 8), depending on the compositions. As a consequence, the intensity-concentration relationship is also subject to be 'zigzagged', which means that the very notion of calibration curve vanishes, on an absolute basis, when multicomponent specimens are investigated. This is particularly true when severe inter-element effects occur.

3.2 Calculation of multicomponent coefficients

The calculation assumes a given composition (namely that of a reference standard) and relies on Eqns (4). It is similar to that for binary systems but naturally more

time-consuming, on account of the number ($n \geq 3$) of elements and the combination of the various absorption-enhancement effects. By considering the general case of polychromatic excitation (I_λ), the course of operations is as follows:

(1) Theoretical relative intensities R_i' and R_i are calculated after Sherman's equations, i.e. by using some fundamental parameter program. Terms such as $h_{ij}C_j$, $h_{ik}C_k$, etc. form necessarily a part of the output, which provides the h_{ij} , h_{ik} , etc. values.

(2) The elements $dP_{i,\lambda}$ of primary fluorescence are associated (see Appendix 2) with the monochromatic $\alpha_{ij,\lambda}$, $\alpha_{ik,\lambda}$ etc. values to calculate the effective 'primary' coefficients α_{ij}' , α_{ik}' , etc. after Eqn (3B).

(3) Finally, Eqns (4) are applied to reckon the effective $\bar{\alpha}_{ij}$, $\bar{\alpha}_{ik}$, etc. coefficient values. Similar calculations are made for the n fluorescent elements. The comparison between multicomponent and binary coefficients will now be exemplified on the typical case of Fe—Ni—Cr alloys.

3.3 Application to the Fe—Ni—Cr alloy system

Calculations were made for five different alloy compositions A, B, C, D, E by assuming a Cr-target tube excitation¹⁶ at 45 kV and a $\psi_1 = \psi_2 = 45^\circ$ geometry. As concerns selective excitation (FeNi, CrFe and CrNi) we supposed, for simplicity, that the $K\alpha$ and $K\beta$ lines of the enhancing element are concentrated on the $K\alpha$ line position, thus retaining *one* reinforcing line per element. Tertiary fluorescence of chromium was omitted.

Table 2 includes the compositions of the alloys and the calculated data, leading to the $\bar{\alpha}_{ij}$ effective coefficients. Note that the $\bar{\alpha}_{ij}$ values coincide with the α_{ij}' values for the FeCr, NiFe and NiCr interactions (pure absorption).

Binary coefficients were derived in a previous paper¹³ and the corresponding curves are reproduced in Figs 6–8 to be compared with the effective coefficients for A, B, C, D, E. We can see (Fig. 6) that there is no deviation as concerns Ni fluorescence which is simply governed by absorption (no third element-effect). On the contrary, Fig. 7 shows marked deviations for the FeNi (absorption-enhancement) and even the FeCr (absorption) interactions; for the latter, FeCr, crossed effects appear on account of the discontinuity introduced in the specimen absorption curve by the presence of nickel. Finally, deviations are most pronounced (Fig. 8) for the CrNi interaction while they happen to be negligible (but this is occasional) for CrFe. On the whole we verify that, of the three elements, chromium is the one most subject to third element effects, a fact to be corroborated at the analytical stage.

3.4 Analysis

Analysis is achieved by introducing the appropriate coefficients and the measured relative intensities in the Lachance–Traill type algorithm

$$\begin{aligned} C_{Fe} &= R_{Fe}(1 + \alpha_{FeCr}C_{Cr} + \alpha_{FeNi}C_{Ni}) \\ C_{Ni} &= R_{Ni}(1 + \alpha_{NiFe}C_{Fe} + \alpha_{NiCr}C_{Cr}) \end{aligned} \quad (16)$$

Table 2. Data concerning Fe—Ni—Cr alloys

Alloys		A	B	C	D	E
Compositions	C_{Fe}	0.72	0.64	0.48	0.08	0.40
	C_{Ni}	0.10	0.15	0.24	0.78	0.40
	C_{Cr}	0.18	0.21	0.28	0.14	0.20
Primary relative intensities	R_{Fe}'	0.5322	0.4551	0.3146	0.0669	0.2913
	R_{Ni}'	0.0413	0.0644	0.1116	0.5855	0.2067
	R_{Cr}'	0.1855	0.2136	0.2784	0.1446	0.2070
Total relative intensities	R_{Fe}	0.5470	0.4744	0.3369	0.0929	0.3306
	R_{Ni}	0.0413	0.0644	0.1116	0.5855	0.2067
	R_{Cr}	0.2535	0.2833	0.3501	0.1900	0.2577
h_{ij} factors	h_{FeNi}	0.2780	0.2840	0.2958	0.4986	0.3378
	h_{CrFe}	0.4820	0.4613	0.4216	0.5019	0.4596
	h_{CrNi}	0.1950	0.2058	0.2290	0.3508	0.2453
α_{ij}' coefficients (primary)	α'_{FeCr}	1.939	1.914	1.867	1.778	1.868
	α'_{FeNi}	0.039	0.030	0.013	-0.067	-0.001
	α'_{NiFe}	1.677	1.684	1.697	1.837	1.723
	α'_{NiCr}	1.195	1.200	1.211	1.325	1.232
	α'_{CrFe}	-0.047	-0.036	-0.015	-0.030	-0.032
	α'_{CrNi}	0.037	0.043	0.054	-0.038	0.019
$\bar{\alpha}_{ij}$ coefficients (effective)	$\bar{\alpha}_{FeCr}$	1.939	1.914	1.867	1.778	1.868
	$\bar{\alpha}_{FeNi}$	-0.327	-0.353	-0.409	-0.497	-0.410
	$\bar{\alpha}_{NiFe}$	1.677	1.684	1.697	1.837	1.723
	$\bar{\alpha}_{NiCr}$	1.195	1.200	1.211	1.325	1.232
	$\bar{\alpha}_{CrFe}$	-0.389	-0.378	-0.352	-0.400	-0.389
	$\bar{\alpha}_{CrNi}$	-0.101	-0.110	-0.129	-0.296	-0.171

Table 3. Analysis of Fe—Ni—Cr alloys

Alloy	Element	True	Concentrations (%)		
			Binary coefficients (Ref. 13, 14)	Effective coefficients (Table 2)	Gliding coefficients Eqns(17)
A	Fe	72.00	71.61	72.00	72.09
	Ni	10.00	9.95	10.00	10.04
	Cr	18.00	17.61	18.00	18.01
B	Fe	64.00	63.53	64.00	64.07
	Ni	15.00	14.89	15.00	15.05
	Cr	21.00	20.36	21.00	20.98
C	Fe	48.00	47.63	48.00	48.00
	Ni	24.00	23.78	24.00	24.07
	Cr	28.00	26.91	28.00	27.91
D	Fe	8.00	8.15	8.00	
	Ni	78.00	77.74	78.00	
	Cr	14.00	13.47	14.00	
E	Fe	40.00	39.67	40.00	
	Ni	40.00	39.56	40.00	
	Cr	20.00	18.76	20.00	

$$C_{Cr} = R_{Cr}(1 + \alpha_{CrNi}C_{Ni} + \alpha_{CrFe}C_{Fe})$$

and then proceeding to the usual iterative calculation of concentrations. Table 3 allows to compare: (a) the results (column 4) obtained with binary coefficients taken at the exact level of fluorescent element concentration; as expected, they let subsist distinct dis-

crepancies, especially for chromium; (b) the results (column 5) obtained with effective coefficients; these restore by definition, so to speak, the true concentrations; (c) as an indication (column 6) some results obtained with gliding coefficients. These were determined by drawing a straight line across the A, B, C figurative points (Figs 6–8) and giving this line a suitable equation. In the present case, these linear approximations amount to

$$\begin{aligned}\alpha_{\text{FeCr}} &= 1.73 + 0.29C_{\text{Fe}} \\ \alpha_{\text{FeNi}} &= -0.58 + 0.36C_{\text{Fe}} \\ \alpha_{\text{NiFe}} &= 1.67 + 0.15C_{\text{Ni}} \\ \alpha_{\text{NiCr}} &= 1.18 + 0.14C_{\text{Ni}} \\ \alpha_{\text{CrNi}} &= -(0.06 + 0.24C_{\text{Cr}}) \\ \alpha_{\text{CrFe}} &= -0.44 + 0.29C_{\text{Cr}}\end{aligned}\quad (17)$$

which define the gliding coefficients. We can see (column 6) that they provide results nearly as good as the exact coefficients, but only for a certain type of compositions. Coefficients in Eqns (17) would not do for the other alloys, especially for D.

4. MATHEMATICAL MATRIX CORRECTION METHODS: A DISCUSSION

From the foregoing, the existence, coherence and capabilities of effective multicomponent coefficients are confirmed. By suitable adaptation these factors apply to every kind of analysis, that is alloys or compound mixtures, in compact as well as in diluted specimens, and they can be considered as infallible, provided they are correctly adjusted. This adjustment is the crucial problem, to be here briefly discussed with special reference to alloy analysis.

For such compact specimens, subject to severe inter-element effects, full experimental calibration is not only much difficult and time-consuming, but most often out of reach on account of the practical impossibility to prepare all the necessary reference compositions. Theoretical correction factors are then favoured, but they meet with a new difficulty, to wit the presumable differences between the actual and the supposed working conditions, regarding both the fundamental and the instrumental parameters. This is inevitable, and analytical inaccuracies from this source can only be remedied: (a) by an improved knowledge of the theoretical and practical conditions, (b) concurrently and necessarily by some *compensation* procedure, generally based on the measurement and/or evaluation of one or several standard specimens.

From this viewpoint the original¹ fundamental parameter approach failed, on a practical basis, because it aimed at dispensing with standards and, in this way, suffered wholly from the uncertainties concerning the parameters. As to its novel forms,^{2,3} they revert resolutely to the use of standards but after adaptive regression techniques¹⁷ which, by combining fundamental parameters with empirical or semi-empirical coefficients, are not only composite but necessarily complicated.

In contrast to this, the method we develop can be considered as all fundamental. As was indicated (section 3.2) the modified program directly supplies theoretical values of effective coefficients for as many compositions as are of interest for the problem on hand. Depending on the range of compositions, these coefficients will be used either as practical constants, for a limited range, or possibly as gliding coefficients for larger ranges. So far, no actual measurements have been made. The analysis will consist in measuring the fluorescence intensities, e.g. I_i for the unknown and I_i^* for an appropriate standard, and using the 'comparison standard' algorithm (see Ref. 4, section 10.2) based on

$$C_i = C_i^* \frac{I_i}{I_i^*} \times \frac{1 + \sum_{j \neq i} \alpha_{ij} C_j}{1 + \sum_{j \neq i} \alpha_{ij} C_j^*} \quad (18)$$

where the α_{ij} values are the effective coefficients calculated for the standard. Then, two situations may occur:

(1) The compositions of unknown and standard are comparatively close to each other. In this case, the uncertainties concerning the true coefficients will be more or less absolved as to the effect on the quotient $(1 + \sum_j \alpha_{ij} C_j) / (1 + \sum_j \alpha_{ij} C_j^*)$ and the analysis will prove correct, to all practical ends. This is comparable to the operation of de Jongh's ALPHAS programs.¹⁸

(2) The compositions are fairly different. In this case, either gliding α_{ij} values have to be substituted in the numerator or, *better*, the output of algorithm (18) for C_i, C_j, C_k , etc. is considered as an approximation of the unknown composition and new α_{ij} values are requested from the calculation program, to be substituted in the numerator. One step should be sufficient to reach the correct composition unless the unknown and the standard are too dissimilar. If so, one should preferably change the standard.

This accounts for the general principle. Concerning practical aspects, typical applications are under investigation and will be reported.

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APPENDIX 1. TERTIAN'S IDENTITIES

The original demonstration⁵ referred to K coefficients ($K_{ij} = \alpha_{ij} + 1$). A similar one can be made directly on the α values. Writing Eqn (2) as

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

and Eqn (3) as

$$\frac{C_i}{R_i} = 1 + \bar{\alpha}_{ij} C_j + \bar{\alpha}_{ik} C_k +$$

gives, by subtracting side to side,

$$\frac{C_i}{R_i'} - \frac{C_i}{R_i} = (\alpha_{ij}' - \bar{\alpha}_{ij}) C_j + (\alpha_{ik}' - \bar{\alpha}_{ik}) C_k + \quad (1A)$$

Similarly, Eqn (1) can be written

$$\frac{R_i}{R_i'} - 1 = h_{ij} C_j + h_{ik} C_k +$$

or, by multiplying both sides by C_i/R_i ,

$$\frac{C_i}{R_i'} - \frac{C_i}{R_i} = h_{ij} \frac{C_i}{R_i} C_j + h_{ik} \frac{C_i}{R_i} C_k +$$

Comparing Eqns (1A) and (2A) and identifying the terms in C_j , C_k , etc. results in Eqns (4):

$$\begin{aligned} \bar{\alpha}_{ij} &= \alpha_{ij}' - h_{ij} \frac{C_i}{R_i} \\ \bar{\alpha}_{ik} &= \alpha_{ik}' - h_{ik} \frac{C_i}{R_i} \text{ etc} \end{aligned}$$

APPENDIX 2. EFFECTIVE COEFFICIENTS FOR PRIMARY FLUORESCENCE

With monochromatic (λ) excitation, the coefficient is given by the well-known expression

$$\alpha_{ij,\lambda} = \frac{\mu_{i,\lambda}^*}{\mu_{i,\lambda}} - 1 = \frac{\mu_{i,\lambda} + A\mu_{i,\lambda}}{\mu_{i,\lambda} + A\mu_{i,\lambda}} - 1$$

When considering a polychromatic (I_λ) incident spectrum, we can divide it in a number N of monochromatic components λ to $\lambda + d\lambda$ and write for the contribution of each component to primary fluorescence P_i , in terms of relative intensity,

$$C_i = \frac{dP_{i,\lambda}}{dP_{i1,\lambda}} (1 + \alpha_{ij,\lambda} C_j + \alpha_{ik,\lambda} C_k + \dots) \quad (1B)$$

or

$$C_i = \frac{dP_{i,\lambda} + dP_{i,\lambda} \alpha_{ij,\lambda} C_j + dP_{i,\lambda} \alpha_{ik,\lambda} C_k + \dots}{dP_{i1,\lambda}}$$

where $dP_{i,\lambda}$ and $dP_{i1,\lambda}$ refer to the specimen and the pure element, respectively. There are N similar expressions where C_i , C_j , C_k , etc. are constants so that C_i is also the quotient of the sum of numerators over that of denominators, hence after rearrangement:

$$C_i = \frac{\sum_{\lambda} dP_{i,\lambda} \left(\sum_{\lambda} dP_{i,\lambda} \alpha_{ij,\lambda} \right) C_j \left(\sum_{\lambda} dP_{i,\lambda} \alpha_{ik,\lambda} \right) C_k}{\sum_{\lambda} dP_{i1,\lambda} \sum_{\lambda} dP_{i1,\lambda} \sum_{\lambda} dP_{i1,\lambda}} +$$

that is by putting the first term (which is none other than R_i') in factor,

$$C_i = R_i' \left(1 + \frac{\sum_{\lambda} dP_{i,\lambda} \alpha_{ij,\lambda}}{\sum_{\lambda} dP_{i,\lambda}} C_j + \frac{\sum_{\lambda} dP_{i,\lambda} \alpha_{ik,\lambda}}{\sum_{\lambda} dP_{i,\lambda}} C_k + \dots \right)$$

By identifying Eqn (2B) with Eqn (2) we derive the effective coefficients for primary fluorescence:

$$\alpha_{ij}' = \frac{\sum_{\lambda} dP_{i,\lambda} \alpha_{ij,\lambda}}{\sum_{\lambda} dP_{i,\lambda}} = \frac{\sum_{\lambda} dP_{i,\lambda} \alpha_{ij,\lambda}}{P_i} \quad (3B)$$

$$\alpha_{ik}' = \frac{\sum_{\lambda} dP_{i,\lambda} \alpha_{ik,\lambda}}{P_i} \text{ etc.}$$

This relation was worked out by R. Rousseau (Geological Survey of Canada, Ottawa, Internal Report) and given its present formulation through a correspondence (May 1981) between one of us (R. T.) and R. Rousseau.