Calculation of Theoretical Alpha Coefficients for XRF Analysis of Major and Minor Elements in Iron-rich Geological Samples

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This paper introduces a method of calculating theorectical alpha coefficients for the X-ray fluorescence analysis of major and minor components in iron-rich samples. We choose a group of hypothetical standard samples whose average concentrations are those of the actual samples. The theoretical X-ray fluorescence relative intensities of the given components are calculated using the fundamental parameter NRLXRF program. We derived formulas from the Lachance-Traill equation and used these to calculate the basic, hybrid and modified alpha coefficients which are used respectively for the analysis of elements in compact specimens, oxides in compact specimens and oxides in diluted specimens. In order to use the theoretical alpha coefficients on-line, we also discuss the calculation of the alpha coefficients used in the D.J model.

Introduction

Recent systematic geochemical studies [1–5] of banded-iron formations and other iron-rich geological samples are of interest because such samples are associated with gold, silver and base-metal mineralization. This paper is a theoretical study of a versatile and accurate method for determining the major and minor elements in iron-rich and other geological samples using X-ray fluorescence analysis. The fusion method has been used for sample preparation. The 12–22 flux (12 $LiB_4O_7 + 22$ $LiBO_2$) recommended by Norrish and Thompson [6] has been used. Our experimental results showed that, although the matrix effects in the glass samples decreased largely, such inter-element effects were still serious, especially for the major component Fe_2O_3, resulting in errors [7] as high as 7% (absolute). Therefore, matrix effects must be accurately corrected.

For this reason, we propose a method of calculating the theoretical alpha coefficients which combines the best features of the fundamental parameters and the influence coefficients, known as the Combined Approach. After correcting the matrix effects using the theoretical alpha coefficients, more accurate data for the major and minor elements were obtained, and this would reduce the errors in our case to less than 0.7% (absolute) for the major component Fe_2O_3 [7].

The Mathematical Correction Models for Matrix Effects

In XRF quantitative analysis technique, it is well-known that there are many quantitative techniques available, starting from the sophisticated full-fundamental parameter method to different semi-empirical methods. In order to obtain accurate elemental concentrations from the corresponding X-ray intensities, scientists have proposed many mathematical methods and compensation methods. In this paper, we use the Combined Approach which has the best features of the fundamental parameters and the influence coefficients.

In XRF analysis, the three well-known influence coefficients correction algorithms for matrix effects are: Lachance-Traill (L-T) [8], Claisse-Quintin (C-Q) [9] and Rasberry-Heinrich (R-H) [10] models. Recently we have the Fundamental Algorithm proposed by Rousseau [11–12]. The above four algorithms for the correction of matrix effects are all concentration correction models in which mostly the L-T equation is used, especially in the analysis of fusion samples. The L-T equation reads

$$C_i = R_i\left(1 + \sum_{\substack{j=1 \\ j\neq i}}^{n} {}^{i}\alpha_{ij}^{x} C_j\right), \tag{1}$$

where C_i is the concentration of the analyte i, C_j the concentration of the matrix component j, R_i the relative intensity of analyte i, and ${}^{i}\alpha_{ij}^{x}$ the alpha coefficient (inter-element influence coefficient) of matrix compo-

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nent j on analyte i; the left-superscript i means that analyte i is the chosen as the eliminated component; the right-superscript x refers to the type of alpha coefficient, which can be B (basic), H (hybrid) or M (modified).

In this work, our experiment was carried out on a Philips PW1400 Automatic X-ray Fluorescence Spectrometer with data processing by the Philips XR14 (AN/UP) package [13]. Therefore the D.J model, a model similar to the L-T model, was employed, whose equation reads

$$C_i = (E_i R_i + D_i)\left(1 + \sum_{\substack{j=1 \\ j \neq e}}^{n} {}^{e}\alpha_{ij}^{x} C_j\right), \tag{2}$$

where C_i is the concentration of the analyte i, C_j the concentration of the matrix component j, E_i the inverse slope of the curve with R_i as y-axis and C_i as x-axis, D_i the intercept on the x-axis in concentration units, R_i the relative intensity of analyte i, and ${}^{e}\alpha_{ij}^{x}$ the alpha coefficient (inter-element influence coefficient) of matrix component j on analyte i; the left-superscript e is the eliminated component which can be any component in the specimen, the right-superscript x refers to the type of alpha coefficient which can be B (basic), H (hybrid) or M (modified).

Comparing (1) and (2), we observe that their difference is only in the eliminated component. In the L-T model, the analyte i itself is chosen as the eliminated component, whereas in the D.J model the analyte e is chosen as the eliminated component, which can be any component in the specimen. Since theoretical alpha coefficients whose eliminated component is different can be transformed from one into the other [7, 22], it follows that the D.J model is similar to the L-T model. Hence, in this paper, we first calculate the alpha coefficients in the L-T model whose eliminated component is the analyte i itself; then we calculate the alpha coefficients in the D.J model whose eliminated component is arbitrary.

Calculation of the Theoretical Alpha Coefficients in the L-T Model

For the calculation of theoretical alpha coefficients we took a set of hypothetical multi-element standard samples which are assumed to be similar to the unknown samples. Their theoretical X-ray fluorescence relative intensities were then calculated using the NRLXRF program. Thereafter, the theoretical alpha coefficients (basic, hybrid and modified) were calculated using the formulas derived from the Lachance-Traill equation for the analysis of the major and minor elements in iron-rich samples and other geological samples.

(1) Hypothetical Multi-Element Standard Samples

We assume that the samples analysed consist of n components with average concentrations C_j where

$$\sum_{j=1}^{n} C_j = 1\,. \tag{3}$$

Suppose the concentration of one component changes by ΔC from C_j into $C_j + \Delta C$ with all other components unchanged except C_K changing into $C_K - \Delta C$ in order to satisfy (3). n is actually unknown. In this study, we have put $n = 14$ since we are interested in the following 14 elements: Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, and Ba. We have also taken $\Delta C = 0.01$ (1%). Using the average concentrations of iron-rich and other geological samples we have encountered, we set up the 14 hypothetical standard samples given in Table 1.

(2) Calculating the Theoretical X-ray Fluorescence Relative Intensities

The calculation of the theoretical X-ray fluorescence relative intensities was performed by the NRLXRF program [14–16]. The theoretical X-ray relative intensity can be calculated for any known composition and operating conditions. If we input the assumed compositions of the hypothetical standard samples given in Table 1, then the theoretical relative X-ray fluorescence intensities can be calculated using the fundamental parameter formulas modified by Criss and Birks [17]. Table 2 gives the theoretical X-ray fluorescence relative intensities for the assumed compositions given in Table 1, and also the operating conditions.

It is well-known that the loss-on-ignition (LOI) is also one analyte component when the fusion technique is employed for sample preparation. In order to calculate the alpha coefficients of LOI (see below), the theoretical X-ray fluorescence relative intensities of the elements Li, B, and O have to be calculated first. The theoretical X-ray fluorescence relative intensities of B and O were calculated using a modified

Table 1. The concentrations of 14 hypothetical standard samples for calculating the theoretical X-ray fluorescence relative intensities.

Sample	Na	Mg	Al	Si	P	S	K	Ca	Ti	V	Cr	Mn	Fe	Ba
HSS1	0.03	0.02	0.10	0.325	0.005	0.10	0.01	0.02	0.005	0.005	0.005	0.02	0.35	0.005
HSS2	0.02	0.03	0.10	0.325	0.005	0.10	0.01	0.02	0.005	0.005	0.005	0.02	0.35	0.005
HSS3	0.02	0.02	0.11	0.325	0.005	0.10	0.01	0.02	0.005	0.005	0.005	0.02	0.35	0.005
HSS4	0.02	0.02	0.10	0.335	0.005	0.10	0.01	0.02	0.005	0.005	0.005	0.02	0.35	0.005
HSS5	0.02	0.02	0.10	0.325	0.015	0.10	0.01	0.02	0.005	0.005	0.005	0.02	0.35	0.005
HSS6	0.02	0.02	0.10	0.325	0.005	0.11	0.01	0.02	0.005	0.005	0.005	0.02	0.35	0.005
HSS7	0.02	0.02	0.10	0.325	0.005	0.10	0.02	0.02	0.005	0.005	0.005	0.02	0.35	0.005
HSS8	0.02	0.02	0.10	0.325	0.005	0.10	0.01	0.03	0.005	0.005	0.005	0.02	0.35	0.005
HSS9	0.02	0.02	0.10	0.325	0.005	0.10	0.01	0.02	0.015	0.005	0.005	0.02	0.35	0.005
HSS10	0.02	0.02	0.10	0.325	0.005	0.10	0.01	0.02	0.005	0.015	0.005	0.02	0.35	0.005
HSS11	0.02	0.02	0.10	0.325	0.005	0.10	0.01	0.02	0.005	0.005	0.015	0.02	0.35	0.005
HSS12	0.02	0.02	0.10	0.325	0.005	0.10	0.01	0.02	0.005	0.005	0.005	0.03	0.35	0.005
HSS13	0.02	0.02	0.10	0.325	0.005	0.10	0.01	0.02	0.005	0.005	0.005	0.02	0.36	0.005
HSS14	0.02	0.03	0.10	0.325	0.005	0.10	0.01	0.02	0.005	0.005	0.005	0.02	0.35	0.015

Note: The concentration of one component in the diagonal line changes from C_j to $C_j+\Delta C$, where $\Delta C=1\%$.

Table 2. Theoretical X-Ray Fluorescence relative intensities R_i (%) calculated by using the NRLXRF program (Conditions: $\phi/\psi=64°/40°$; Rh, 50 kV, 18°, 0.3 mm).

Matrix	Na Kα	Mg Kα	Al Kα	Si Kα	P Kα	S Kα	K Kα	Ca Kα	Ti Kα	V Kα	Cr Kα	Mn Kα	Fe Kα	Ba Kα
B	1.575335	2.628016	18.33188	59.73021	2.297267	40.37190	8.203518	18.87996	7.654289	9.004075	10.80929	35.83475	77.70496	15.40589
O	0.4459742	0.7028359	5.329829	27.13084	0.5295950	13.76552	1.796229	4.514054	1.581697	1.857851	2.239387	9.628720	39.94220	3.402876
Na	0.6756732	0.6044772	3.840445	14.84252	0.1885281	5.068215	0.5173368	1.260856	0.3922689	0.4502641	0.5058271	1.765761	32.94448	0.8704836
Mg	0.4502583	0.9186337	3.827574	14.79889	0.1881477	5.057833	0.5162876	1.258317	0.3915004	0.4493794	0.5048580	1.763009	32.89769	0.8687733
Al	0.4500772	0.6123629	4.271923	14.75620	0.1877970	5.048635	0.5154093	1.256203	0.3908596	0.4486379	0.5040401	1.760668	32.85745	0.8673473
Si	0.4497400	0.6119049	3.882813	15.41423	0.1873659	5.036325	0.5140417	1.252831	0.3898101	0.4474172	0.5026919	1.756811	32.79144	0.8650141
P	0.4492772	0.6113497	3.879447	14.95308	0.5675743	5.029202	0.5131473	1.250563	0.3890701	0.4465390	0.5017040	1.753940	32.74144	0.8633723
S	0.4487612	0.6105884	3.874561	14.93736	0.1891736	5.583790	0.5115306	1.246768	0.3879647	0.4452803	0.5003335	1.750048	32.67514	0.8609078
K	0.4478874	0.6098574	3.873187	14.94459	0.1893508	5.089170	1.034207	1.237433	0.3847847	0.4414466	0.4959628	1.737180	32.44842	0.8538637
Ca	0.4471333	0.6089261	3.867872	14.92879	0.1892285	5.086085	0.5178880	1.886949	0.3830633	0.4395143	0.4938827	1.731301	32.34888	0.8500197
Ti	0.4460265	0.6075321	3.859825	14.90468	0.1890399	5.081385	0.5178240	1.261330	1.170833	0.4476696	0.4917061	1.724738	32.23052	0.8665188
V	0.4455318	0.6068623	3.855726	14.89173	0.1889330	5.078609	0.5176810	1.261075	0.3903296	1.341261	0.5020521	1.719331	32.14056	0.8658909
Cr	0.4445571	0.6056553	3.848826	14.87100	0.1887690	5.074455	0.5174227	1.260553	0.3916524	0.4471740	1.503554	1.757076	32.02561	0.8671911
Mn	0.4440016	0.6049669	3.845004	14.86131	0.1887254	5.073693	0.5183281	1.263181	0.3928552	0.4508476	0.5038428	2.633222	32.79890	0.8711811
Fe	0.4433374	0.6039380	3.838126	14.83825	0.1885296	5.068421	0.5179945	1.262489	0.3927737	0.4508457	0.5064751	1.758985	33.69165	0.8717663
Ba	0.4408798	0.5979462	3.797270	14.70842	0.1874052	5.038038	0.5131428	1.249736	0.3864812	0.4426090	0.4887116	1.702577	31.69781	2.571785

Note: The values of the elements B and O were calculated by using the binary-sytem method, and those of the elements Na – Ba were calculated by using the multi-system method and the concentrations given in Table 1.

NRLXRF program, which was extended to handle longer X-ray wavelengths. These intensities are also given in Table 2. However, the intensity of Li could not be calculated by this modified program. Therefore, the alpha coefficients of Li were evaluated instead, using those of oxygen (see below).

(3) Calculation of the Inter-Element Influence Coefficients

In general, the measured characteristic intensity for polychromatic excitation is a function of the mass concentration of all the elements present; symbolically,

$$R_i = f(C_1, C_2, \ldots, C_n). \tag{4}$$

If A_{ij} is the influence coefficient of matrix element j on analyte i, perhaps the most common functional relationship [17–18] is

$$\frac{C_i}{R_i} = \sum_{j=1}^{n} A_{ij} C_j. \tag{5}$$

Using this equation in conjunction with the theoretical relative X-ray fluorescence intensities of Table 2 and the concentration values of Table 1, we can obtain the n^2 A_{ij} values for the elements Na–Ba. These A_{ij} values are given in Table 3, where we observe that A_{ii} ranges from 1.051 to 1.482, which is quite different from monochromatic excitation with $A_{ii} = 1$.

(4) Calculation of the Basic Alpha Coefficients

In the Lachance-Traill (L-T) equation, the analyte i itself is chosen as the eliminated component. From (3), we have

$$C_i = 1 - \sum_{\substack{j=1 \\ j \neq i}}^{n} C_j. \tag{6}$$

Substituting (6) into (5), we obtain the L-T equation for the analysis of elements:

$$C_i = R_i' \left(1 + \sum_{\substack{j=1 \\ j \neq i}}^{n} {}^{i}\alpha_{ij}^{\mathrm{B}} C_j \right). \tag{7}$$

where $R_i' = R_i A_{ii}$ and

$${}^{i}\alpha_{ij}^{\mathrm{B}} = \frac{A_{ij}}{A_{ii}} - 1. \tag{8}$$

Therefore, for polychromatic excitation, the basic alpha coefficients should be calculated using (8), where

Table 3. Influence coefficients A_{ij} calculated by using the equation: $C_i/R_i = \sum_{j=1}^{n} A_{ij} C_j$. (Conditions: $\phi/\psi = 64°/40°$; Rh, 50 kV, 18°, 0.3 mm).

Matrix	Na Kα	Mg Kα	Al Kα	Si Kα	P Kα	S Kα	K Kα	Ca Kα	Ti Kα	V Kα	Cr Kα	Mn Kα	Fe Kα	Ba Kα
Na	1.162	5.455	4.051	2.751	2.136	1.535	1.313	1.039	0.775	0.663	0.566	0.521	0.439	0.350
Mg	1.350	1.163	4.927	3.396	2.672	1.940	1.706	1.359	1.024	0.882	0.756	0.698	0.590	0.463
Al	1.529	1.194	1.160	4.032	3.169	2.300	2.036	1.626	1.233	1.066	0.916	0.849	0.720	0.558
Si	1.862	1.439	1.201	1.117	3.781	2.785	2.552	2.055	1.578	1.370	1.182	1.098	0.935	0.714
P	2.320	1.736	1.433	1.132	1.206	3.066	2.891	2.344	1.822	1.590	1.378	1.284	1.098	0.823
S	2.832	2.144	1.758	1.361	1.231	1.226	3.507	2.831	2.188	1.906	1.651	1.538	1.315	0.989
K	3.702	2.536	1.850	1.255	0.984	0.723	1.400	4.041	3.253	2.881	2.532	2.385	2.063	1.468
Ca	4.455	3.038	2.205	1.485	1.155	0.812	1.107	1.403	3.837	3.379	2.956	2.775	2.395	1.733
Ti	5.565	3.791	2.744	1.838	1.418	1.024	1.131	0.979	1.424	1.307	3.405	3.215	2.792	0.613
V	6.063	4.155	3.019	2.027	1.568	1.131	1.185	1.011	1.407	1.452	1.309	3.580	3.097	0.655
Cr	7.047	4.811	3.484	2.331	1.798	1.293	1.281	1.077	0.974	1.431	1.482	1.081	3.487	0.568
Mn	7.610	5.187	3.742	2.474	1.859	1.322	0.944	0.747	0.584	0.519	0.955	1.184	0.911	0.304
Fe	8.284	5.750	4.208	2.814	2.134	1.527	1.068	0.833	0.610	0.520	0.439	0.957	1.051	0.266
Ba	10.799	9.069	7.012	4.747	3.725	2.717	2.893	2.450	2.683	2.584	4.028	4.724	4.617	1.236

$A_{ii} \neq 1$, and this is different from the algorithms of other workers [19]. It should be observed that for ${}^{i}\alpha^{B}_{ij}$ the eliminated component i in the left superscript is the analyte i itself, and the B in the right superscript denotes basic alpha coefficients which can be used for correcting matrix effects in the system.

Table 4 gives the basic alpha coefficients in which the coefficients for the elements Na–Ba were calculated using the values of A_{ij} in Table 3 and (8), while the coefficients of O and B were calculated using the theoretical X-ray fluorescence relative intensities of Table 2 together with the binary system formula of the L-T equation

$${}^{i}\alpha^{B}_{ij} = \left(\frac{C_i}{R_i} - 1\right)\bigg/ C_j . \tag{9}$$

For the element Li, its basic alpha coefficients cannot be calculated by using (9) since its theoretical relative X-ray fluorescence intensity cannot be obtained by using the NRLXRF program. We therefore evaluated the basic alpha coefficients of the element Li using the following formula [20]

$${}^{i}\alpha^{B}_{ik} = ({}^{i}\alpha^{B}_{ij} + 1)\left(\frac{Z_k}{Z_j}\right)^{n} - 1 . \tag{10}$$

Let $k = \mathrm{Li}\,(Z_{\mathrm{Li}} = 3$, $j = \mathrm{O}$ $(Z_{\mathrm{O}} = 8)$ and $n = 3.20$, then

$${}^{i}\alpha^{B}_{i,\,\mathrm{Li}} = ({}^{i}\alpha^{B}_{i,\,\mathrm{O}} + 1)\left(\frac{3}{8}\right)^{3.20} - 1 , \tag{11}$$

The basic alpha coefficients of the elements Li, B, and O are given in Table 4.

(5) Calculation of the Hybrid Alpha Coefficients

When two or more basic alphas are combined as one coefficient, we refer to this as hybrid alpha coefficient. In the analysis of oxides [19] in powder rocks or cement samples, both the basic alpha coefficients and the concentration of oxygen must be considered; hence, hybrid alpha coefficients should be used. For the case of oxides, we can derive the following formula from (7):

$$C_{i(0)} = R_{i(0)}\left[1 + \sum_{\substack{j=1\\ j\neq i}}^{n} \left({}^{i(0)}\alpha^{\mathrm{H}}_{i(0),\,j(0)}\, C_{j(0)}\right)\right] \tag{12}$$

with

$${}^{i(0)}\alpha^{\mathrm{H}}_{i(0),j(0)} = \frac{W^{j(0)}_{j}\,{}^{i}\alpha^{\mathrm{B}}_{ij} + (W^{j(0)}_{\mathrm{O}} - W^{i(0)}_{\mathrm{O}})\,{}^{i}\alpha^{\mathrm{B}}_{i,\mathrm{O}}}{1 + W^{i(0)}_{\mathrm{O}}\,{}^{i}\alpha^{\mathrm{B}}_{i,\mathrm{O}}} \tag{13}$$

where $W^{j(0)}_{j}$ is the weight fraction of element j in oxide $j(0)$, $W^{j(0)}_{\mathrm{O}}$ and $W^{i(0)}_{\mathrm{O}}$ are the weight fractions of oxygen in oxide $j(0)$ and oxide $i(0)$, respectively, ${}^{i}\alpha^{\mathrm{B}}_{i,\mathrm{O}}$ is the basic alpha coefficient of oxygen on analyte i, ${}^{i}\alpha^{\mathrm{B}}_{ij}$ the basic alpha coefficient of the matrix element j on analyte i and ${}^{i(0)}\alpha^{\mathrm{H}}_{i(0)\,j(0)}$ the hybrid alpha coefficient of the matrix oxide $j(0)$ on analyte oxide $i(0)$; the left superscript $i(0)$ means that the eliminated component is oxide $i(0)$ and the right superscript H denotes hybrid.

In this work, we have used 12–22 flux (12 $\mathrm{Li_2O_4O_7}$ + 22 $\mathrm{LiBO_2}$). Since such a flux contains more than two elements, its hybrid alpha coefficients cannot be calculated by using (13) and should be calculated by using

$${}^{i(0)}\alpha^{\mathrm{H}}_{i(0),\mathrm{f}} = \frac{W^{f}_{\mathrm{Li}}\,{}^{i}\alpha^{\mathrm{B}}_{i,\mathrm{Li}} + W^{f}_{\mathrm{B}}\,{}^{i}\alpha^{\mathrm{B}}_{i,\mathrm{B}} + (W^{f}_{\mathrm{O}} - W^{i(0)}_{\mathrm{O}})\,{}^{i}\alpha^{\mathrm{B}}_{i,\mathrm{O}}}{1 + W^{i(0)}_{\mathrm{O}}\,{}^{i}\alpha^{\mathrm{B}}_{i,\mathrm{O}}} , \tag{14}$$

where f is the 12–22 flux and $W^{\mathrm{f}}_{\mathrm{Li}}$, $W^{\mathrm{f}}_{\mathrm{B}}$, and $W^{\mathrm{f}}_{\mathrm{O}}$ are the weight fractions of the elements Li, B, and O in the 12–22 flux, respectively.

Table 5 gives the hybrid alpha coefficients calculated by using (13) and (14).

(6) Calculation of the Modified Alpha Coefficients

For the analysis of oxides in the case where a powdered sample is fused in a fixed sample-to-flux ratio to produce a solid solution glass disc, or in the case where a powdered sample is mixed in a fixed sample-to-binder ratio and pressed into pellets we should use the modified alpha coefficients. For such cases, if we express the results as oxide concentrations in the original sample and consider the sample-to-flux ratio in the glass disc, we can derive from (12) the following formula:

$$C_{i(0)} = R'_{i(0)}\left[1 + \sum_{\substack{j=1\\ j\neq i}}^{n} {}^{i(0)}\alpha^{\mathrm{M}}_{i(0),j(0)}\, C_{j(0)}\right] \tag{15}$$

with

$${}^{i(0)}\alpha^{\mathrm{M}}_{i(0),j(0)} = \frac{{}^{i(0)}\alpha^{\mathrm{H}}_{i(0),j(0)}}{\left(\dfrac{g_{\mathrm{f}}}{g_{\mathrm{s}}}\right){}^{i(0)}\alpha^{\mathrm{H}}_{i(0),\mathrm{f}} + (g_{\mathrm{f}} + g_{\mathrm{s}})/g_{\mathrm{s}}} , \tag{16}$$

where ${}^{i(0)}\alpha^{\mathrm{H}}_{i(0),\mathrm{f}}$ is the hybrid alpha coefficient of the flux f on analyte oxide $i(0)$, ${}^{i(0)}\alpha^{\mathrm{H}}_{i(0),j(0)}$ the hybrid alpha coefficient of the matrix oxide $j(0)$ on analyte oxide $i(0)$, g_{f} and g_{s} are the weights of the flux and sample in the mixture, and ${}^{i(0)}\alpha^{\mathrm{M}}_{i(0),j(0)}$ is the modified alpha coef-

Table 4. Theoretical basic alpha coefficients ${}^{i}\alpha_{ij}^{B}$ used in the Lachance-Traill equation (Conditions: $\phi/\psi = 64°/40°$; Rh, 50 kV, 18°, 0.3 mm; Eliminated component: Analyte i).

Matrix	Na Kα	Mg Kα	Al Kα	Si Kα	P Kα	S Kα	K Kα	Ca Kα	Ti Kα	V Kα	Cr Kα	Mn Kα	Fe Kα	Ba Kα
Li	−0.803	−0.875	−0.915	−0.941	−0.959	−0.970	−0.976	−0.981	−0.986	−0.989	−0.991	−0.992	−0.993	−0.994
B	0.275	−0.244	−0.505	−0.660	−0.786	−0.836	−0.887	−0.912	−0.939	−0.949	−0.959	−0.963	−0.968	−0.972
O	0.556	1.883	0.974	0.353	−0.056	−0.304	−0.448	−0.568	−0.687	−0.735	−0.781	−0.808	−0.833	−0.857
Na	0.0	3.690	2.492	1.463	0.771	0.252	−0.063	−0.259	−0.456	−0.543	−0.618	−0.560	−0.582	−0.717
Mg	0.162	0.0	3.247	2.040	1.216	0.582	0.219	−0.031	−0.281	−0.393	−0.490	−0.410	−0.439	−0.625
Al	0.316	0.027	0.0	2.610	1.628	0.876	0.454	0.159	−0.134	−0.266	−0.382	−0.283	−0.315	−0.549
Si	0.602	0.237	0.043	0.0	2.135	1.272	0.823	0.465	0.108	−0.056	−0.202	−0.073	−0.110	−0.422
P	0.997	0.493	0.235	0.013	0.0	1.501	1.065	0.671	0.279	0.095	−0.070	0.084	0.045	−0.334
S	1.437	0.844	0.516	0.218	0.021	0.0	1.505	1.018	0.537	0.313	0.114	0.299	0.251	−0.200
K	2.186	1.181	0.595	0.124	−0.184	−0.410	0.0	1.880	1.284	0.984	0.709	1.014	0.963	0.188
Ca	2.834	1.612	0.901	0.329	−0.042	−0.338	−0.209	0.0	1.695	1.327	0.995	1.344	1.279	0.402
Ti	3.789	2.260	1.366	0.645	0.176	−0.165	−0.192	−0.302	0.0	−0.100	1.298	1.715	1.657	−0.504
V	4.218	2.573	1.603	0.815	0.300	−0.077	−0.154	−0.279	−0.012	0.0	−0.117	2.024	1.947	−0.470
Cr	5.065	3.137	2.003	1.087	0.491	0.055	−0.085	−0.232	−0.316	−0.014	0.0	−0.087	2.318	−0.540
Mn	5.549	3.460	2.226	1.215	0.541	0.078	−0.326	−0.468	−0.590	−0.643	−0.356	0.0	−0.133	−0.754
Fe	6.129	3.944	2.628	1.519	0.769	0.246	−0.237	−0.406	−0.572	−0.642	−0.704	−0.192	0.0	−0.785
Ba	8.293	6.798	5.045	3.250	2.089	1.216	1.066	0.746	0.884	0.780	1.718	2.990	3.393	0.0

Table 5. Theoretical hybrid alpha coefficients ${}^{i(0)}\alpha^{H}_{i(0),j(0)}$ used in the Lachance-Traill equation (Conditions: $\phi/\psi = 64°/40°$; Rh, 50 kV, 18°, 0.3 mm; Eliminated component: Analyte $i(0)$).

Matrix	Na Kα	Mg Kα	Al Kα	Si Kα	P Kα	S Kα	K Kα	Ca Kα	Ti Kα	V Kα	Cr Kα	Mn Kα	Fe Kα	Ba Kα
Flux (12-22)	0.729	0.194	−0.025	−0.179	−0.308	−0.390	−0.575	−0.635	−0.695	−0.723	−0.795	−0.834	−0.843	−0.889
Na_2O	0.0	1.417	1.126	0.832	0.609	0.356	−0.093	−0.211	−0.333	−0.398	−0.549	−0.540	−0.529	−0.729
MgO	0.309	0.0	1.293	0.995	0.767	0.505	0.033	−0.099	−0.231	−0.303	−0.476	−0.472	−0.460	−0.690
Al_2O_3	0.482	0.088	0.0	1.143	0.895	0.615	0.114	−0.026	−0.165	−0.242	−0.429	−0.425	−0.411	−0.664
SiO_2	0.657	0.210	0.055	0.0	1.032	0.751	0.240	0.091	−0.056	−0.140	−0.350	−0.345	−0.327	−0.620
P_2O_5	0.794	0.303	0.132	0.014	0.0	0.814	0.312	0.160	0.013	−0.074	−0.298	−0.289	−0.266	−0.593
SO_3	0.934	0.412	0.227	0.093	0.006	0.0	0.443	0.272	0.160	0.011	−0.234	−0.223	−0.198	−0.555
K_2O	0.783	0.316	0.138	−0.022	−0.135	−0.257	0.0	1.940	1.688	1.499	0.931	1.085	1.212	0.109
CaO	1.107	0.539	0.317	0.125	−0.015	−0.178	−0.218	0.0	1.780	1.570	0.976	1.117	1.238	0.146
TiO_2	1.449	0.779	0.514	0.286	0.118	−0.047	−0.236	−0.294	0.0	−0.045	0.946	1.087	1.216	−0.611
V_2O_5	1.569	0.871	0.595	0.356	0.181	0.006	−0.224	−0.292	−0.047	0.0	−0.215	1.176	1.301	−0.605
Cr_2O_3	1.914	1.140	0.836	0.561	0.361	0.151	−0.134	−0.211	−0.218	0.120	0.0	−0.162	2.100	−0.606
MnO	2.181	1.348	1.018	0.700	0.452	0.213	−0.300	−0.392	−0.465	−0.503	−0.272	0.0	−0.054	−0.756
Fe_2O_3	2.314	1.474	1.146	0.825	0.571	0.321	−0.243	−0.350	−0.457	−0.512	−0.638	−0.238	0.0	−0.788
BaO	3.589	3.169	2.853	2.323	1.959	1.516	1.066	0.920	1.372	1.396	2.261	3.397	4.275	0.0

Note: Flux (12–22) is the mixture of 12 $Li_2B_4O_7$ and 22 $LiBO_2$.

ficient of matrix oxide $i(0)$ on analyte oxide $i(0)$; the right superscript M denotes modified.

When a powdered rock sample and flux are fused to produce a solid solution glass disc, it is well-known that the volatile constituents (such as carbon dioxide and crystal water) volatilize. This loss of volatile constituents from the sample-flux mixture during fusion gives rise to higher apparent concentrations of the remaining constituents in the glass disc. Therefore, the matrix correction of the volatile constituents becomes very important in the analysis of the major and minor constituents in glass discs. This loss of the volatile constituents is often referred to as the loss-on-ignition (LOI) and in XRF as the "LOI problem" [19]. The "LOI problem" can be treated quantitatively using influence coefficients. According to de Jongh [21], we can assume the atomic number of LOI to be zero and then derive a formula for the modified alpha coefficients of LOI on analyte oxide $i(0)$:

$$ {}^{i(0)}\alpha^{\mathrm{M}}_{i(0),\mathrm{LOI}} = \frac{-1}{\left(\dfrac{g_{\mathrm{f}}}{g_{\mathrm{s}}}\right) {}^{i(0)}\alpha^{\mathrm{H}}_{i(0),\mathrm{f}} + (g_{\mathrm{f}} + g_{\mathrm{s}})/g_{\mathrm{s}}}, \qquad (17) $$

where ${}^{i(0)}\alpha^{\mathrm{M}}_{i(0),\mathrm{LOI}}$ is the modified alpha coefficient of the LOI on analyte $i(0)$ when the eliminated component is the analyte $i(0)$ itself and ${}^{i(0)}\alpha^{\mathrm{H}}_{i(0),\mathrm{f}}$ the hybrid alpha coefficient of the flux on analyte $i(0)$ when the eliminated component is the analyte $i(0)$ itself.

From (17), the modified alpha coefficients of the LOI on the analyte $i(0)$ are only related to the hybrid alpha coefficients of the flux on the analyte $i(0)$ and the weights of the flux and sample.

Table 6 gives the modified alpha coefficients of fused glass discs for iron-rich samples and other geological samples in which the dilution ratio $g_{\mathrm{f}}/g_{\mathrm{s}}$ is 5.

Calculation of the Theoretical Alpha Coefficients in the D.J Model

In the above we have calculated the theoretical alpha coefficients which are given in Table 4 for basic alphas, Table 5 for hybrid alphas and Table 6 for modified alphas, which can be used, respectively, for the analysis of elements in compact specimens, oxides in compact specimens and oxides in diluted specimens. However, these alpha coefficients cannot be used online directly in the D.J model. Since they were calculated using formulas derived from the L-T model in which analyte i (or oxide $i(0)$) is chosen as the eliminated component. In the D.J model, however, the eliminated component is arbitrary and can be SiO_2 (for silicate), CaO (for carbonate) or LOI, etc. Therefore, for on-line work we must calculate the Alpha coefficients which can be used in the D.J model.

From the above, we already know that in the D.J model the eliminated component is arbitrary. However, it is very important to choose appropriate eliminated components. Based on our experience, we find that it is more convenient to choose the LOI as the eliminated component. The main advantage is that the Alpha coefficients can be used on-line in the Philips X14 (AN/UP) software package. The other advantage is that it is unnecessary to determine the concentration of the LOI before XRF analysis. Hence, below we discuss methods of calculating theoretical alpha coefficients whose eliminated component is LOI.

(1) Calculation methods using the Transformation Model of the Theoretical Alpha Coefficients

We have already derived the transformation formula for different eliminated components, which is given by [22]

$$ {}^{\mathrm{A}}\alpha^{\mathrm{M}}_{i(0),j(0)} = \frac{{}^{\mathrm{B}}\alpha^{\mathrm{M}}_{i(0),j(0)} - {}^{\mathrm{B}}\alpha^{\mathrm{M}}_{i(0),\mathrm{A}}}{1 + {}^{\mathrm{B}}\alpha^{\mathrm{M}}_{i(0),\mathrm{A}}}, \qquad (18) $$

where ${}^{\mathrm{A}}\alpha^{\mathrm{M}}_{i(0),j(0)}$ is the theoretical modified alpha coefficients of matrix $j(0)$ on analyte $i(0)$ when the eliminated component is A, ${}^{\mathrm{B}}\alpha^{\mathrm{M}}_{i(0),j(0)}$ the theoretical modified alpha coefficients of matrix $j(0)$ on analyte $i(0)$, when the eliminated component is B, and ${}^{\mathrm{B}}\alpha^{\mathrm{M}}_{i(0),\mathrm{A}}$ the theoretical modified alpha coefficients of matrix A on analyte $i(0)$ when eliminated component is B. Since A and B are arbitrary, if we let A = LOI and B = $i(0)$, then we can get from (18)

$$ {}^{\mathrm{LOI}}\alpha^{\mathrm{M}}_{i(0),j(0)} = \frac{{}^{i(0)}\alpha^{\mathrm{M}}_{i(0),j(0)} - {}^{i(0)}\alpha^{\mathrm{M}}_{i(0),\mathrm{LOI}}}{1 + {}^{i(0)}\alpha^{\mathrm{H}}_{i(0),\mathrm{LOI}}}, \qquad (19) $$

where ${}^{\mathrm{LOI}}\alpha^{\mathrm{M}}_{i(0),j(0)}$ is the theoretical modified alpha coefficient of matrix $j(0)$ on analyte $i(0)$ when the eliminated component is LOI.

Equation (19) can be used to transform the theoretical alpha coefficients used in the L-T model whose eliminated component is analyte $i(0)$ into those used in the D.J model whose eliminated component is the LOI. Hence, we can get Table 7 from Table 6 using (19).

Table 6. Theoretical modified alpha coefficients ${}^{i(0)}\alpha^{M}_{i(0),j(0)}$ used in the Lachance-Traill equation (Conditions: $\phi/\psi = 64°/40°$; Rh, 50 kV, 18°, 0.3 mm; Eliminated component: Analyte $i(0)$, flux: $12\,Li_2B_4O_7 + 22\,LiBO_2$; dilution ratio: $g_f/g_s = 5.01/1.0$).

Matrix	Na Kα	Mg Kα	Al Kα	Si Kα	P Kα	S Kα	K Kα	Ca Kα	Ti Kα	V Kα	Cr Kα	Mn Kα	Fe Kα	Ba Kα
LOI	−0.104	−0.144	−0.170	−0.196	−0.233	−0.247	−0.320	−0.354	−0.396	−0.419	−0.493	−0.546	−0.559	−0.644
Na_2O	0.0	0.203	0.192	0.163	0.136	0.088	−0.030	−0.075	−0.132	−0.167	−0.217−	−0.295	−0.296	−0.469
MgO	0.033	0.0	0.220	0.195	0.171	0.125	0.010	−0.035	−0.091	−0.127	−0.235	−0.258	−0.257	−0.444
Al_2O_3	0.050	0.013	0.0	0.224	0.200	0.152	0.037	−0.009	−0.065	−0.101	−0.212	−0.232	−0.230	−0.427
SiO_2	0.068	0.030	0.009	0.0	0.230	0.185	0.077	0.032	−0.022	−0.059	−0.173	−0.189	−0.183	−0.399
P_2O_5	0.082	0.043	0.023	0.003	0.0	0.201	0.100	0.057	0.005	−0.031	−0.147	−0.158	−0.149	−0.381
SO_3	0.097	0.059	0.039	0.018	0.001	0.0	0.142	0.096	0.042	−0.005	−0.115	−0.122	−0.111	−0.357
K_2O	0.081	0.045	0.023	−0.004	−0.030	−0.063	0.0	0.686	0.669	0.629	0.459	0.593	0.678	0.070
CaO	0.115	0.077	0.054	0.024	−0.003	−0.044	−0.070	0.0	0.705	0.658	0.481	0.610	0.693	0.094
TiO_2	0.150	0.112	0.088	0.056	0.026	−0.011	−0.076	−0.104	0.0	−0.019	0.467	0.594	0.681	−0.393
V_2O_5	0.163	0.125	0.101	0.070	0.040	0.002	−0.072	−0.103	−0.019	0.0	−0.106	0.642	0.728	−0.389
Cr_2O_3	0.189	0.164	0.142	0.110	0.081	0.037	−0.043	−0.074	−0.087	0.050	0.0	−0.088	1.175	−0.390
MnO	0.226	0.193	0.173	0.137	0.101	0.053	−0.096	−0.139	−0.184	−0.211	−0.134	0.0	−0.030	−0.486
Fe_2O_3	0.240	0.212	0.195	0.162	0.127	0.079	−0.078	−0.124	−0.181	−0.215	−0.314	−0.130	0.0	−0.507
BaO	0.372	0.455	0.486	0.455	0.437	0.374	0.341	0.325	0.544	0.585	1.115	1.856	2.391	0.0

Note: LOI is Loss-On-Ignition.

Table 7. Theoretical modified alpha coefficients ${}^{LOI}\alpha^{M}_{i(0),j(0)}$ used in the D.J model (Conditions: $\phi/\psi = 64°/40°$; Rh, 50 kV, 18°, 0.3 mm; Eliminated component: LOI; flux: $12\,Li_2B_4O_7 + 22\,LiBO_2$; dilution ratio: $g_f/g_s = 5.0/1.0$).

Matrix	Na Kα	Mg Kα	Al Kα	Si Kα	P Kα	S Kα	K Kα	Ca Kα	Ti Kα	V Kα	Cr Kα	Mn Kα	Fe Kα	Ba Kα
LOI	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Na_2O	0.116	0.405	0.436	0.446	0.462	0.444	0.427	0.432	0.438	0.434	0.439	0.554	0.598	0.489
MgO	0.151	0.168	0.470	0.486	0.507	0.493	0.486	0.493	0.504	0.503	0.510	0.636	0.686	0.560
Al_2O_3	0.171	0.182	0.205	0.522	0.544	0.529	0.524	0.533	0.547	0.548	0.556	0.692	0.747	0.607
SiO_2	0.192	0.203	0.216	0.244	0.583	0.574	0.584	0.597	0.619	0.621	0.632	0.789	0.855	0.685
P_2O_5	0.207	0.218	0.232	0.247	0.287	0.594	0.617	0.635	0.664	0.669	0.683	0.857	0.932	0.735
SO_3	0.224	0.237	0.252	0.266	0.289	0.328	0.679	0.696	0.726	0.730	0.746	0.936	1.018	0.804
K_2O	0.206	0.221	0.233	0.238	0.248	0.244	0.471	1.609	1.763	1.805	1.880	2.512	2.809	2.002
CaO	0.244	0.258	0.270	0.274	0.283	0.269	0.368	0.547	1.823	1.855	1.923	2.551	2.842	2.068
TiO_2	0.283	0.298	0.311	0.313	0.321	0.321	0.359	0.386	0.656	0.689	1.894	2.515	2.815	0.703
V_2O_5	0.297	0.313	0.327	0.330	0.339	0.330	0.365	0.388	0.625	0.722	0.764	2.621	2.922	0.713
Cr_2O_3	0.337	0.359	0.377	0.380	0.391	0.377	0.408	0.432	0.513	0.809	0.973	1.010	3.937	0.712
MnO	0.368	0.393	0.414	0.414	0.417	0.397	0.329	0.333	0.351	0.359	0.708	1.205	1.201	0.441
Fe_2O_3	0.383	0.415	0.440	0.445	0.451	0.433	0.356	0.356	0.356	0.352	0.353	0.918	1.270	0.383
BaO	0.531	0.698	0.790	0.809	0.849	0.824	0.972	1.051	1.556	1.730	3.174	5.297	6.698	1.805

Note: LOI is Loss-On-Ignition.

(2) Calculation Method Using the Theoretical Hybrid Coefficients in the L-T Model

By substituting (16) and (17) into (19), we get the equation

$$ {}^{\mathrm{LOI}}\alpha^{\mathrm{M}}_{i(0),\,j(0)} = \frac{1 + {}^{i(0)}\alpha^{\mathrm{H}}_{i(0),\,j(0)}}{1 + {}^{i(0)}\alpha^{\mathrm{H}}_{i(0),\,\mathrm{f}}} \frac{g_{\mathrm{s}}}{g_{\mathrm{f}}} . \qquad (20) $$

Using (20) and the values of the hybrid alphas given in Table 5, we also can calculate the modified alphas given in Table 7, which can be used in the D.J model.

It is not only convenient to calculate the modified alphas whose eliminated component is the LOI using (20), but also the physical meaning is clearer. The reason is that from (20) we can see clearly that, as the ratio of flux-to-sample increases, the alpha coefficients decrease. This shows that the matrix effects have become smaller.

Discussion

In this paper, we propose a calculation method of the theoretical alpha coefficients comprising basic, hybrid and modified alpha coefficients. In general, basic, hybrid and modified alpha coefficients can be used, respectively, for the analysis of elements and oxides in compact specimens and oxides in diluted specimens.

In this paper we discuss in detail the calculation of the alpha coefficients in the L-T model and the D.J model. Our conclusion is that the D.J model is similar to the L-T model; the difference is only in the eliminated component, which is analyte *i* itself in the L-T model but arbitrary in the D.J model. The alpha coefficients used in these two models can be transformed into each other by using the transformation model of the theoretical alpha coefficients proposed by us [7, 22].

In this paper, we calculated the alpha coefficients whose eliminated component is the LOI. The main advantage is that this kind of alphas can be used on-line in the D.J model in the Philips PW1400 X-ray Spectrometer XR 14 (AN/UP) software package and it also can be used in the software package in the Rigaku 3080 X-ray Spectrometers and other models of the instrument. Our experimental results show that the matrix effects can be accurately corrected by using these alphas. For example, for the analysis of the major component Fe_2O_3 in iron-rich samples, errors can be as high as 7% (absolute) without using the alphas for the correction of matrix effects, while such errors could be reduced to less than 0.7% (absolute) for Fe_2O_3 determination when the alphas are used to correct matrix effects. The operating conditions and instrumental setting have been given in detail in [7].

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