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Original Article

High Speed Matrix Corrections for Quantitative X-ray Microanalysis Based on Monte Carlo Simulated K-Ratio Intensities

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Abstract

Due to recent advances in modeling the production of characteristic X-rays, Monte Carlo simulation of electron–solid interactions can provide improved quantitative estimates of X-ray intensities for both homogeneous and heterogeneous interaction volumes. In the case of homogeneous materials, these modeled X-ray intensities can predict with excellent accuracy, matrix corrections for arbitrary compositions, arbitrary emission lines, and electron energies. By pre-calculating these Monte Carlo X-ray intensities for pure element standards and a range of compositions of binary systems, we can derive matrix corrections for complex compositions in real-time by parameterizing these k-ratios as the so-called alpha factors. This method allows one to perform Monte Carlo-based bulk matrix corrections in seconds for arbitrary and complex compositions (with two or more elements), by combining these binary alpha factors using the so-called beta expression. We are systematically calculating X-ray intensities for 11 compositions from 1 to 99 wt% for binary pairs of all emitters and absorbers in the periodic table, for the main emission lines (Kα, Kβ, Lα, Lβ, Mα, and Mβ) at beam energies from 5 to 50 keV, using Monte Carlo calculations based on a modified PENELOPE electron-photon transport code, although any other Monte Carlo software could also be utilized. Comparison of k-ratios calculated with the proposed method and experimental k-ratios from the Pouchou and Pichoir database suggest improvements over typical $\varphi(\rho z)$ methods. Additional comparisons with k-ratio measurements from more complex compositions would be ideal, but our testing of the additivity of the beta equation suggests that arbitrary compositions can be handled as well, except in cases of extreme fluorescence or absorption.

Key words: EPMA, matrix corrections, Monte Carlo, Penepma

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Introduction

The alpha/beta factor method was originally described by Ziebold & Ogilvie (1964), and utilized by Bence & Albee (1968) for matrix corrections based on a combination of analytical models and empirical measurements of simple oxides and silicates. For a binary compound Ziebold-Ogilvie made the empirical observation that the element concentration has a hyperbolic relationship with its measured X-ray intensity, or rearranging the terms, that the ratio between the element concentration and its k-ratio is approximately linear to the element concentration:

$$\frac{C_{ij}^{i}}{k_{ij}^{i}} = \alpha_{ij}^{i} + (1 - \alpha_{ij}^{i})C_{ij}^{i} \quad (1)$$

where C_{ij}^{i} is the concentration of element i in the binary compound ij; k_{ij}^{i} is the k-ratio defined as the ratio between the characteristic X-ray intensity of element i measured from the binary compound ij and the intensity of the same characteristic X-ray line measured from a pure standard of element i; and α_{ij}^{i} is the alpha factor, the correction factor for fluorescence, absorption, and atomic number effects.

The calculation of alpha/beta factors has evolved since the paper of Bence & Albee (1968) where α_{ij}^{i} was simply estimated as the C_{ij}^{i}/k_{ij}^{i} ratio as C_{ij}^{i} goes to zero. Albee and Ray (1970) showed improved results in binary compounds with strong fluorescence by calculating α_{ij}^{i} at the 50:50 composition ($C_{ij}^{i} = 0.5$). Since most silicate and oxide minerals are composed of major element concentrations in an oxygen matrix, this was a reasonable approximation for the use of slide rules at the time. In the late 1970s, Shaw and Albee (1979) proposed to parameterize alpha factors as a linear function of the element concentration to solve deviations from equation 1 of some binary compounds with large absorption and fluorescence correction. However, they pointed out that such parameterization only provided a small improvement to the quantification results. Later, Armstrong (1988*a*, 1988*b*) showed larger improvements by using a quadratic fit. As he summarized, constant alpha factors are applicable for binary compounds with small absorption and fluorescence correction; linear alpha factors fit binary compounds well where both elements have a similar atomic number but one is largely absorbed by the other; and quadratic alpha factors better describe binary compounds with dissimilar elements and large absorption corrections. Perhaps the two important points are that alpha factors must be parameterized as a function of the

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element concentration to properly fit all possible binary compounds, and that essentially any regression expression can be utilized, as long as it provides a good fit to the alpha factors obtained from k-ratios derived from empirical measurements, analytical calculations, or simulations.

From equation 1, the alpha factor of the emitting element i in a binary compound ij (α_{ij}^{i}) for a concentration C_{ij}^{i} and a k-ratio k_{ij}^{i} is equal to the following expression, as proposed by Rivers (1980, personal communication)

$$\alpha_{ij}^{i} = \frac{(C_{ij}^{i}/k_{ij}^{i}) - C_{ij}^{i}}{1 - C_{ij}^{i}} \tag{2}$$

Once binary alpha factors are obtained using k-ratios from measurements, analytical calculations or Monte Carlo simulations, we then combine them into beta factors in order to quantify systems with two or more elements, which is essentially the matrix correction term. Specifically, for a compound with N elements, where N is 2 or more, the beta factor is the weighted sum of the binary alpha factors, Bence & Albee, (1968), expressed as β:

$$c^{i} = \beta^{i} k^{i} \tag{3a}$$

$$c^{i} = \left[\frac{\sum_{j=1}^{N} C^{j}\alpha_{ij}^{i}}{\sum_{j=1}^{N} C^{j}}\right] k^{i} \tag{3b}$$

where c^{i} is the concentration of each element in the compound, i.e., $\{c^{1}, \ldots, c^{N}\}$. Note that we need to include not only the binary effect of element i by elements j, but also the weighted effect of element i by itself (for which the alpha factor is always 1.0). As shown in equation 3b, the β factor is analogous to the ZAF or $\phi(\rho z)$ matrix correction term when the standard is a pure element. As with all matrix correction procedures, the quantification using beta factors involves an iterative process, since the β factor is a function of the unknown concentrations.

The main difference between alpha factor and ZAF or $\phi(\rho z)$-based quantification is the computing power requirement. Alpha factors can be pre-calculated and tabulated for common compounds at typical acquisition conditions (accelerating voltage and takeoff angle). Solving for the unknown concentrations can easily be done by hand or with a simple spreadsheet (Bence & Albee, 1968). With the limited computing power at the time, this surely explains the popularity of alpha-factor-based quantification up to the 1990s for online quantification. The improvement in computer speed (and improved analytical models) effectively made the alpha-factor-based quantification obsolete. The calculation of matrix correction terms based on ZAF or $\phi(\rho z)$ is now trivial in comparison to image and video processing performed by modern-day computers.

Most of the $\phi(\rho z)$ matrix correction models use Monte Carlo simulations to get the value of some parameters, which cannot be obtained experimentally (Pouchou & Pichoir, 1991). There is however an interesting parallel to draw between how ZAF-based quantification was perceived in the 1970s and how Monte Carlo-based quantification is perceived today, i.e., ZAF calculations were too slow for online quantification, but were used for calculating the alpha factor parameters. While Monte Carlo simulations today could be used to quantify experimentally measured k-ratios within 3 min (Pinard et al., 2012; Mevenkamp et al., 2013), they are certainly still too slow for online quantification and especially for the quantification of large X-rays maps, where the matrix correction is solved for each pixel.

The f-ratio method (Horny, 2006; Horny et al., 2010) is one approach to solve this problem; Monte Carlo simulations are used with the f-ratio method to pre-calculate calibration curves and achieve fast quantification (Teng et al., 2018*a*, 2018*b*). In this work, we use alpha factors calculated from Monte Carlo simulations for fast quantification. Following early work by Armstrong (1988*a*, 1988*b*), we report accurate and precise quantification using alpha factors calculated from Monte Carlo for almost all possible binary combinations of elements in the periodic table at accelerating voltages of 5–50 kV.

Method

Beta factors were determined by fitting a quadratic equation to alpha factors based on k-ratios simulated with the PENFLUOR/FANAL programs (Llovet et al., 2012*b*), which uses Monte Carlo simulations for the primary and continuum intensity calculations (PENFLUOR), and an analytical model for fluorescence (FANAL). Although PENFLUOR/FANAL were originally developed to quickly calculate secondary fluorescence effects from boundary phases, if both the beam incident phase and the boundary phase are the same, the programs produce a homogeneous sample k-ratio which can be utilized to extract the matrix correction for bulk materials. PENFLUOR uses the general-purpose Monte Carlo PENELOPE (2012 version) to simulate the primary intensities at ten different beam energies (between 5 and 50 keV). From these PENFLUOR simulations, k-ratios at any beam energy and takeoff angle can be extracted using FANAL in a few seconds, which performs the necessary interpolation and fluorescence calculations. More details on PENFLUOR/FANAL, hereafter referred to as FANAL, can be found in Llovet et al. (2012*b*).

Using these programs, binary alpha factors were calculated for almost the entire periodic table at a nominal simulation time of 10 h (and again at 20 h), per binary composition using 1 h/beam energy (and again using 2 h/beam energy) with 11 compositions (from 1 to 99 wt%) for each element binary pair. This amounts to 110 h/binary and for all possible binary combinations of elements 45,375 days or 124 years of simulation time (and again double that simulation time for the 20 h/binary calculations). Fortunately, the calculations can be run in parallel on many workstations to reduce the real-time duration of these simulations and the simulations only have to be done once.

For comparison, k-ratio calculations were also performed using two analytical $\varphi(\rho z)$ models implemented in the open-source program CalcZAF, see Donovan (2015), specifically Armstrong (2012) and XPP, (Pouchou & Pichior, 1991). Simulations were also run using the Monte Carlo program PENEPMA (2011 version) (Llovet & Salvat, 2016), until a relative uncertainty of 1% on the calculated intensities was obtained for the X-ray line of interest (Pinard et al., 2007). The detector was centered on the specified takeoff angle and had an opening of ± 9°. For example, a hemispheric detector with an opening of 31°–49° was used in the simulations of a nominal take-off angle of 40°. For all simulations, elastic scattering parameters were set to 0.2, interaction forcing was activated with a forcing factor of −40 for the bremsstrahlung and inner-shell ionization collisions of electrons and the absorption energy threshold was set to be 100 eV below the energy of the X-ray line of interest. These

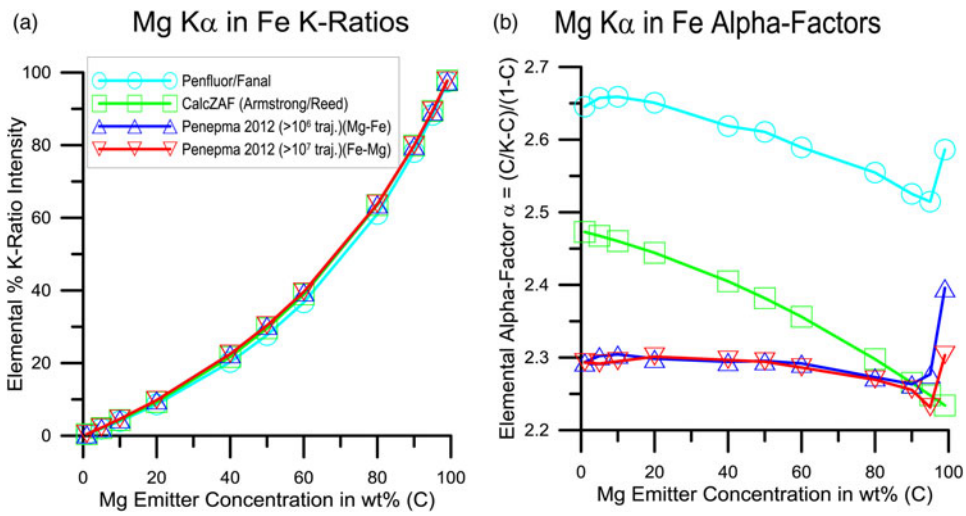

Fig. 1. (**a**) Plot of Mg Kα k-ratios versus the weight fraction of Mg at an accelerating voltage of 15 kV and a takeoff angle of 40°. (**b**) Plot of Mg Kα alpha factors versus weight fraction as calculated by equation 3 of the same emitter-absorber system k-ratios. It is clear that the concentration versus k-ratio plot (**a**), is difficult to evaluate, while the concentration versus alpha factor plot (**b**) is an improvement for comparing analytical models.

simulation parameters were optimized before running all the simulations (Pinard et al., 2009), to achieve the best simulation efficiency, (Llovet & Salvat, 2017), without influencing the accuracy of the results.

PENEPMA and FANAL are two programs based on the same general purpose Monte Carlo code, PENELOPE. PENEPMA however, makes no simplifying assumptions regarding the geometry for the fluorescence calculations. Every electron and X-ray trajectory is simulated in detail. While it would be unrealistic to calculate all alpha factors with PENEPMA because each beam energy and take-off angle would require a separate simulation, it nonetheless offers a good comparison for some cases. By contrast, FANAL speeds up the calculations by only simulating electron trajectories and analytically calculating the emission, absorption and fluorescence of X-rays. In addition, FANAL calculates intensities for a range of beam energies and take-off angles for each compositional simulation.

For some ternary compounds, the assumption of additivity of alpha factors in the beta equation was tested and the magnitude of the matrix correction factor was compared between the different models. For a sample of known concentration, and assuming a pure element standard, the matrix correction factor for element i ($[M]^i_U$) can be calculated from the k-ratio (Philibert & Tixier, 1968):

$$[M]^i_U = \frac{c^i_U}{k^i} \tag{4}$$

where c^i_U and k^i are, respectively, the weight fraction and k-ratio of element i in the sample. This equation equivalently applies to k-ratios calculated from analytical models, empirical measurements or Monte Carlo simulations.

The accuracy and precision of the Monte Carlo-based alpha factors were also tested using the k-ratio database of Pouchou & Pichoir (1991). It consists of experimental k-ratios for binary compounds measured at different beam energies and takeoff angles. Out of the 826 k-ratios reported in the database, 777 were considered in this work, excluding cases where the emitted line is either B Kα or Cu Lα since they could be subject to significant state peak shift and shape effects (Bastin & Heijligers, 2013; Gopon et al., 2013). In total, 103 unique element pairs were evaluated. Calculated and experimental k-ratios are compared by looking at the distribution of ratios of the calculated versus experimental k-ratios, i.e., k_{calc}/k_{exp}. A value close to unity indicates that the calculated k-ratios match the experimental ones. The mean of this distribution is an indicator of the accuracy of the calculated k-ratios, while the standard deviation is an indicator of the precision.

Results and Discussion

Figure 1a shows a typical plot of k-ratios versus concentration for the Mg Kα in the Fe-Mg binary (takeoff angle of 40° and an accelerating voltage of 15 kV) calculated from Armstrong's analytical $\varphi(\rho z)$ model (Armstrong et al., 2013), Monte Carlo simulations using PENEPMA (Llovet & Salvat, 2016) and hybrid simulation and analytical calculations of FANAL (Llovet et al., 2012b). Mg Kα is highly absorbed by Fe, which results in the negative curvature. However, the differences in absorption between the models are not easily visible in this plot.

Figure 1b shows the same Mg Kα k-ratios but instead plotted as alpha factors as a function of the Mg concentration (equation 2). The hyperbolic relationship accentuates the significant differences in the matrix corrections for the methods shown. The magnitude of the absorption effect decreases with decreasing Fe concentration, as expected.

As the concentration of the emitting element approaches 100 wt%, the alpha factors calculated from FANAL and PENEPMA deviate from the smooth, monotonous decrease as a function of the Mg concentration. This is due to precision errors in the Monte Carlo simulations. Very small differences between the k-ratio and concentration have large effects in a hyperbolic relationship. As shown in Figure 1b, increasing the number of trajectories from 10^6 to 10^7 decreases the error near 100 wt%. However, the effect on the calculated beta factor (which includes the contribution from the element absorbed/fluoresced by other absorbing/fluorescing elements and also the contribution of the element absorbed by itself) for concentrations approaching the

Table 1. Matrix correction factors for the different analytical and Monte Carlo models both with and without alpha factor parameterization. To test the beta expression for additivity of binary alpha factors, matrix corrections at 15 keV for three ternary materials are compared for two analytical $\phi(\rho z)$ expressions and PENEPMA and PENFLUOR Monte Carlo calculations, and also fitted to binary alpha factors for each model: (1) Armstrong's $\phi(\rho z)$ model, (2) Armstrong $\phi(\rho z)$ model with alpha factors, (3) PAP $\phi(\rho z)$ model, (4) PAP $\phi(\rho z)$ model with alpha factors, (5) PENEPMA Monte Carlo simulations, (6) PENEPMA with alpha factors (7) PENFLUOR/FANAL semi-analytical Monte Carlo simulations, and (8) PENFLUOR/FANAL with alpha factors. The relative difference between the full model and the alpha factor parameterization is also shown for each model.

	Comparison of Matrix Correction Factors								
	Fe_2SiO_4			Alloy 18/8 (Fe74Cr18Ni8)			Alloy TiAlV (Ti90Al6V4)		
	Fe Kα	Si Kα	O Kα	Fe Kα	Cr Kα	Ni Kα	Ti Kα	Al Kα	V Kα
PAP $\phi(\rho z)$ model	1.1160	1.3394	1.5263	1.0080	0.8367	1.0506	1.0091	1.3755	1.0294
PAP $\phi(\rho z)$ model (alpha factors)	1.1178	1.3307	1.6021	0.9981	0.8935	1.0494	1.0090	1.3830	1.0298
Relative difference %	0.2	−0.6	5.0	−1.0	6.8	−0.1	0.0	0.5	0.0
Armstrong $\phi(\rho z)$ model	1.0953	1.3395	1.5987	1.0069	0.8386	1.0445	1.0078	1.4113	1.0267
Armstrong $\phi(\rho z)$ model (alpha factors)	1.0965	1.3278	1.6387	0.9968	0.8957	1.0435	1.0076	1.3904	1.0271
Relative difference %	0.1	−0.9	2.5	−1.0	6.8	−0.1	0.0	−1.5	0.0
PENEPMA	1.1095	1.3405	1.4395	1.0169	0.8621	1.0712	1.0062	1.3841	1.0285
PENEPMA (alpha factors)	1.0923	1.3369	1.4961	1.0023	0.7387	1.0842	1.0053	1.3935	1.0344
Relative difference %	−1.6	−0.3	3.9	−1.4	−14.3	1.2	−0.1	0.7	0.6
PENFLUOR/FANAL	1.0952	1.3395	1.5987	1.0069	.8386	1.0445	1.0078	1.4113	1.0267
PENFLUOR/FANAL (alpha factors)	1.0896	1.4275	1.5919	1.0069	.9326	1.0820	1.0054	1.4968	1.0213
Relative difference %	−0.5	6.6	−0.4	0.0	11.2	3.6	−0.2	6.1	−0.5

pure element (equation 3b) are dominated by the pure element alpha factor, which is defined as 1.0 at 100 wt%. Therefore, these high concentration element factors, which are subject to random statistics in Monte Carlo simulations, can safely be ignored in the alpha/beta factor regressions. In other words, the effect on the element by other elements decreases as the concentration of said element approaches the pure element, where C/K = 1 when C = 1 (see equation 1). This strategy is used for all subsequent alpha/beta factor calculations.

Table 1 compares the matrix correction factors for a ternary compound (Fe_2SiO_4) and alloys (Fe74Cr18Ni8 and Ti90Al6V4) for four different matrix correction methods (two analytical models and two Monte Carlo programs), by comparing the calculated matrix correction terms from each of the four methods to beta factors derived by fitting these k-ratios to calculated binary alpha factors. The results show larger differences between the different matrix correction methods and the beta factors derived from them, for the cases of strong absorption (O Kα in Fe_2SiO_4) and strong fluorescence effects (Cr Kα in Fe74Cr18Ni8). The remaining results suggest that the assumption of additivity in the beta factor expression (equation 3b) for these compositions, is at least approximately correct.

The small differences between analytical and Monte Carlo-based matrix correction factors in Table 1 are both encouraging and surprising since the Monte Carlo simulations of FANAL are based on first principle calculations of electron scattering and X-ray emission, without any special modification to match experimental X-ray microanalysis data.

To assess the accuracy and precision of Monte Carlo-based alpha factor quantification, calculated k-ratios were compared to 777 experimental k-ratios of the Pouchou and Pichoir database (Pouchouand Pichoir (1991). Figure 2 shows the comparison for k-ratios calculated by four methods: (1) Armstrong's analytical $\phi(\rho z)$ model, (2) Monte Carlo simulations with PENEPMA, (3) FANAL simulations and (4) alpha factors derived from FANAL simulations using 10 h of simulation per binary composition. Table 2 summarizes the average and standard deviation calculated from the distributions, as well as the total time to calculate the 777 k-ratios for the calculations shown in Figure 2.

With a relative error of 3.1%, the results of Armstrong's analytical $\varphi(\rho z)$ model is essentially what we can expect from a typical analytical model currently used for quantitative analysis. By comparison, using the XPP $\phi(\rho z)$ method, which was originally "tuned" to the Pouchou and Pichoir k-ratio database, yields an error of 1.0015 ± 0.0234 (2.3%). The results of PENEPMA (1.00645 ± 0.02173, 2.2%) demonstrate that the same level of accuracy and precision as analytical models can be achieved using first principle calculations and without any adjustment to its physical models and quantities. This level of accuracy and precision is what we are striving for with the Monte Carlo-based alpha factor method described in this paper, without the approximately 300 days (single CPU time) that were required to obtain the results in Figure 2b.

For this comparison, each specific composition from the Pouchou and Pichoir database was calculated using FANAL. The results show the same level of accuracy as for PENEPMA and Armstrong's analytical $\varphi(\rho z)$ model and a precision that roughly falls in between those obtained from these two methods. This increase of the standard deviation may potentially be attributed to the simplified model for secondary fluorescence in

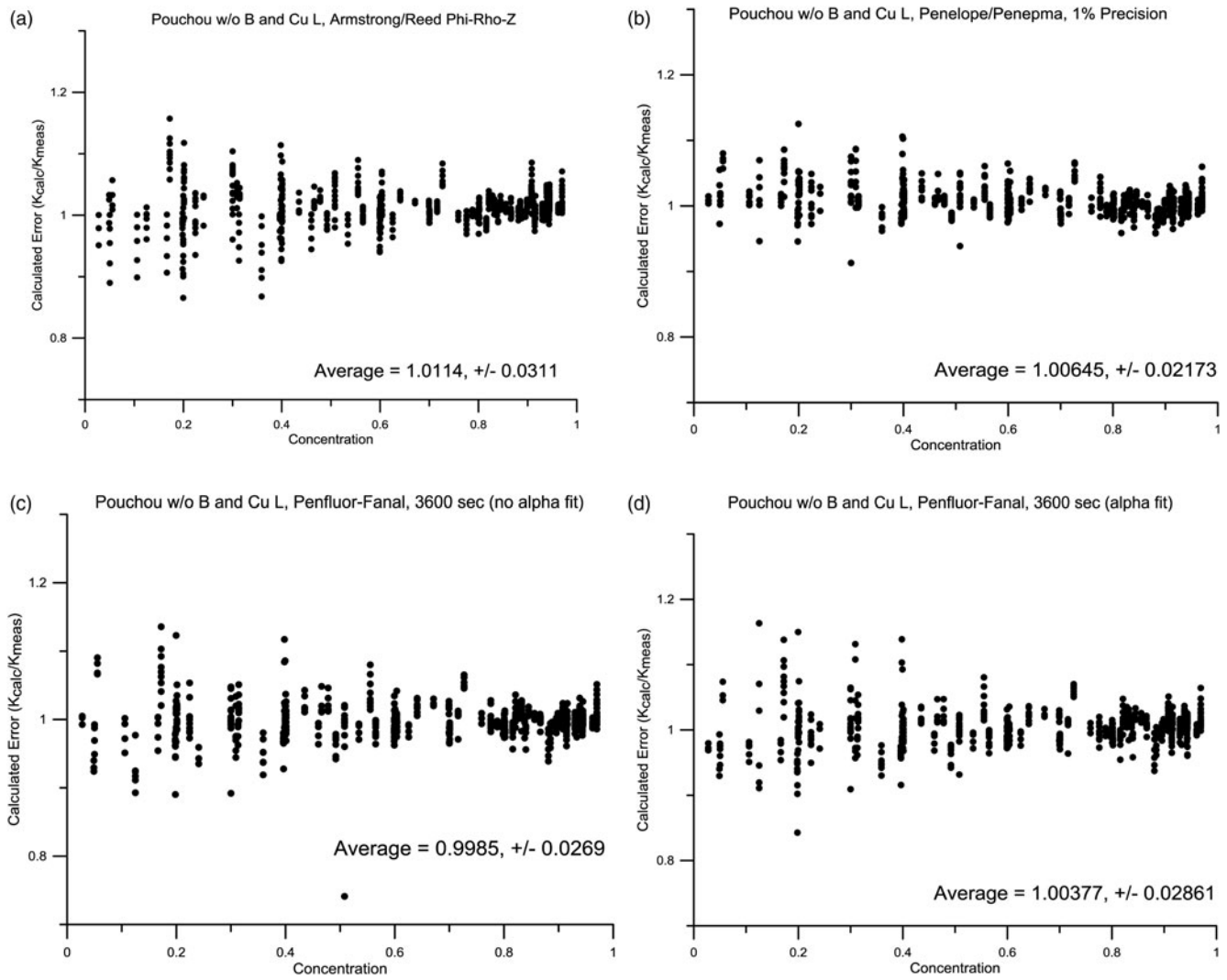

Fig. 2. Ratio of calculated and experimental k-ratios as a function of the emitter concentration. Experimental k-ratios from 777 binary compounds from the Pouchou and Pichoir database [pouchou1991] (excluding k-ratio from B Kα and Cu Lα X-ray lines). Calculated k-ratios from (**a**) Armstrong's analytical $\varphi(\rho z)$ model, (**b**) Monte Carlo simulations with PENEPMA, (**c**) PENFLUOR/FANAL simulations and (**d**) alpha factors derived from a quadratic fit of k-ratios from PENFLUOR/FANAL simulations using 10 h/binary composition (11 compositional binaries from 1 to 99 wt%).

Table 2. Summary of error distributions of various methods presented in this paper on the Pouchou and Pichoir k-ratio database, Pouchou & Pichoir (1991), (excluding B Kα and Cu Lα emissions which could be subject to chemical state peak shift or shape effects) for the 777 binary measurements. The calculation time corresponds to the time for a single processing unit to calculate or simulate the 777 k-ratios from the database.

Matrix Correction Method	Calc. Time	Average	Std. Dev.
PAP $\phi(\rho z)$ model	~30 min	1.0150	0.0234
Armstrong's $\phi(\rho z)$ model	~30 min	1.0115	0.0311
PENEPMA Monte Carlo (alpha factors not calculated)	~300 days	1.0065	0.0217
PENFLUOR/FANAL	~32 days	0.9985	0.0269
PENFLUOR/FANAL (alpha factors, quadratic fit) (using 10 h/alpha binary)	~30 min	1.00377	0.02861
PENFLUOR/FANAL (alpha factors, four-coefficient fit) (using 20 h/alpha binary)	~30 min	1.00363	0.02899

FANAL in comparison to the detailed, stochastic strategy of PENEPMA. Another potential source of error is that k-ratio measurements in the Pouchou and Pichoir database at an accelerating voltage of 4 kV were extrapolated in FANAL since the simulations only covered a range of beam energies from 5 to 50 keV. In terms of calculation time, k-ratio calculations using FANAL are faster than Monte Carlo simulations using PENEPMA (approximately 32 versus 300 days), but still too slow for online quantification.

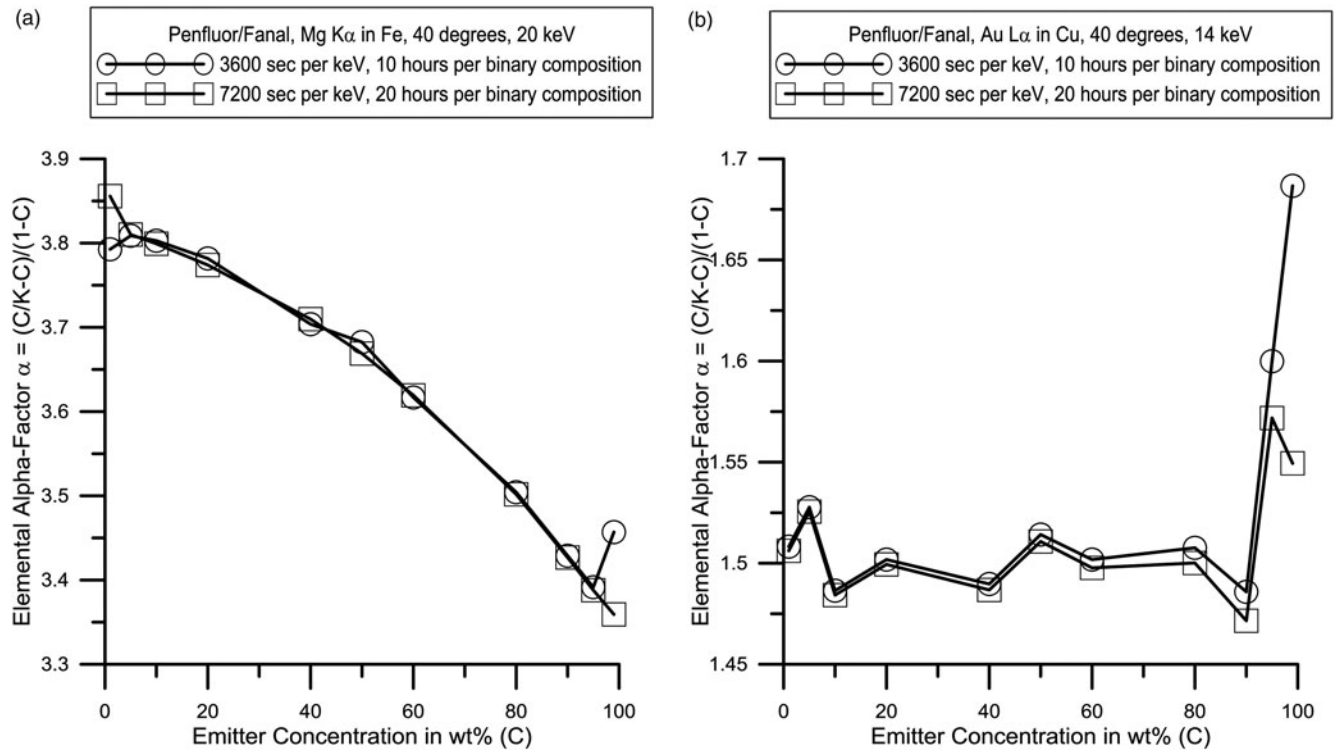

Fig. 3. Comparison of alpha factors derived from PENFLUOR/FANAL calculations at 1 and 2 h/energy for (**a**) Mg Kα in Fe at an accelerating voltage of 20 kV and (**b**) Au Lα in Cu at an accelerating voltage of 14 kV (takeoff angle of 40°).

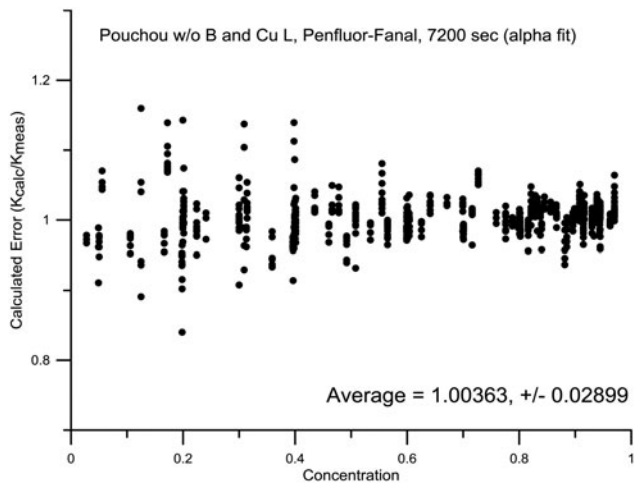

Fig. 4. Ratio of calculated and experimental k-ratios as a function of the emitter concentration. Experimental k-ratios from 777 binary compounds from the Pouchou and Pichoir database [pouchou1991] (excluding k-ratio from B Kα and Cu Lα X-ray lines). Calculated k-ratios from alpha factors derived from a quadratic fit of k-ratios from PENFLUOR/FANAL simulations with a simulation time of 2 h/beam energy, 20 h/binary composition (11 compositional binaries from 1 to 99 wt %).

The last comparison is with the proposed Monte Carlo-based alpha factor method where alpha factors are derived from FANAL simulations. With a relative standard deviation of 2.85%, this new method improves upon the precision of Armstrong's analytical $\varphi(\rho z)$ model, though is not quite as good as the results from PENEPMA simulations. The accuracy and precision are also approximately equal to the FANAL simulations without the use of alpha/beta factors. This proves the suitability of the alpha/beta factor-based quantification method by testing both the hyperbolic relationship between intensity and concentrations (alpha factors), and also the additivity of the alpha factors using the beta expression (see Tables 1 and 2). It is also worth considering that these beta factors were calculated using a generic database of coefficients fitting a quadratic equation to the pre-calculated binary alpha factors covering a range of binary compositions, which allows the calculation of beta factors for arbitrary compositions. In other words, the binary composition k-ratio database we calculated is not specific to the experimental measurements of Pouchou and Pichoir but covers almost all possible combinations of elements. It is, therefore, possible to obtain fast and accurate quantification of any sample.

We now look at two strategies to further improve the results of the Monte Carlo-based alpha factor method: longer simulation time for the FANAL simulations and high-order fit of the alpha factors versus concentration curves. The influence of the simulation time for the simulations is evaluated in Figure 3 where the simulation time was increased from 10 h/binary composition (1 h/beam energy) to 20 h (2 h/beam energy). Increasing the simulation time improves precision at high concentrations of the emitting element in the hyperbolic relationship, where we are basically subtracting two large numbers from each other. For example, the minor precision issues at high concentrations of Mg in the Mg-Fe binary compound observed in Figure 1b are eliminated with the longer simulation time, as shown in Figure 3a. Low overvoltage analytical situations, where photon simulation precision is limited due to poor ionization efficiency, are also improved. Figure 3b shows the example of Au Lα in Cu at an accelerating voltage of 14 kV, an overvoltage of 1.4. Increasing the simulation time however, only slightly improves

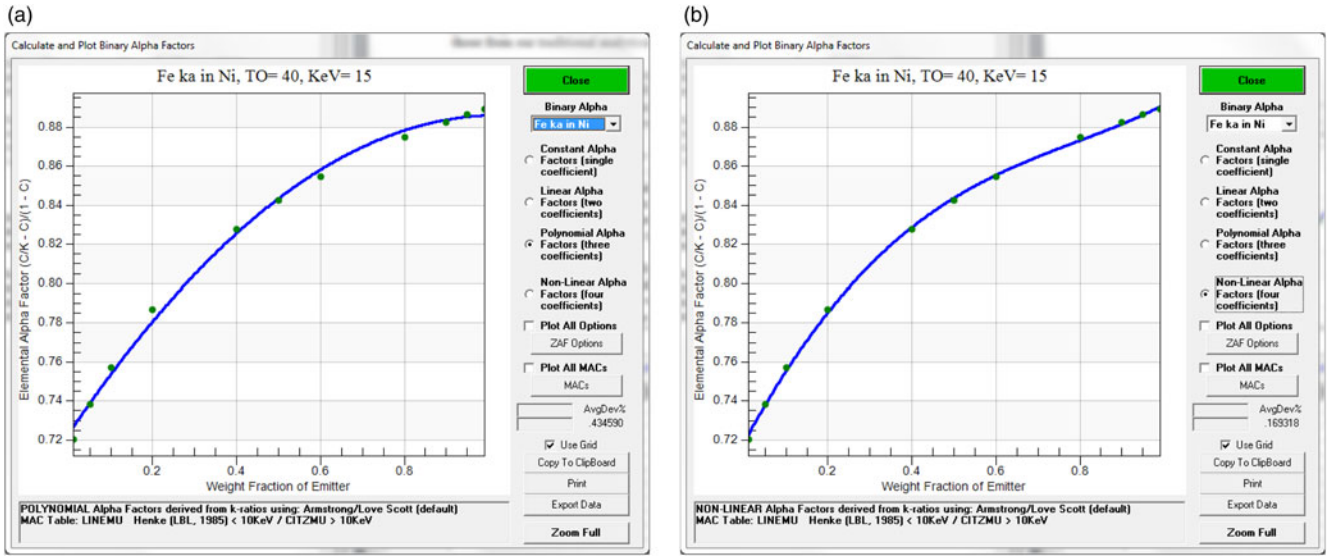

Fig. 5. Screenshots from the CalcZAF EPMA utility [donovan2015] comparing the polynomial (**a**) and non-linear (**b**) alpha fit methods in a highly fluorescing system of Fe Kα in Ni at 15 keV.

the level of accuracy, while slightly decreasing the precision based on the Pouchou and Pichoir database as seen in Figure 4. The improvement in the distribution of calculated versus experimental k-ratios, k_{calc}/k_{exp}, as a function of the element concentration is shown in Table 2 (average of 1.00363 ± 0.02899 for the 20 h simulations versus 1.00377 ± 0.02862 for the 10 h simulations). While we are re-calculating the entire periodic table with a simulation time of 20 h/binary composition, to improve precision at low overvoltage conditions as seen in Figure 3b, the initial simulation time of 10 h is sufficient for most analytical situations.

Besides the longer simulation time, it was found that a non-linear, four-coefficients-fit alpha method provides an additional small but significant improvement over a quadratic fit. We added an exponential term to the quadratic expression used so far, resulting in the following four-coefficient alpha factor expression:

$$\alpha_{ij}^{i}(C_{ij}^{i}) = a_{ij}^{i,1} + a_{ij}^{i,2}C_{ij}^{i} + a_{ij}^{i,3}(C_{ij}^{i})^2 + a_{ij}^{i,4}\exp(C_{ij}^{i}) \qquad (5)$$

where $a_{ij}^{i,1}$ to $a_{ij}^{i,4}$ are the fit coefficients. The additional exponential term allows a better fit, especially for elemental binaries with excessive absorption or fluorescence. Figure 5 compares the new and quadratic fit for the alpha factors of Fe Kα in Ni. This binary compound notably requires a large fluorescence correction. The four-coefficient alpha factor fit improves the average relative standard deviation from 0.434%, with the quadratic fit, to 0.169%. Applying the four-coefficient alpha factor fit to the FANAL k-ratios obtained with a simulation of 20 h yields an average of 1.0033 and a standard deviation of 0.0285 for the 777 k-ratios in the Pouchou and Pichoir database, (Pouchou & Pichoir, 1991), which shows a small improvement over the results using a quadratic alpha factor fit (1.00363 ± 0.02899).

Conclusions

By utilizing the hyperbolic relationship between intensity and concentration for binary element pairs we can pre-calculate k-ratios from Monte Carlo simulations for typical beam energies and takeoff angles to obtain polynomial or non-linear alpha factors. These alpha factor expressions can then be utilized in the beta expression to provide matrix corrections for arbitrary compositions in seconds.

From the comparison with the experimental k-ratios from the Pouchou and Pichoir database, the new alpha/beta factor matrix correction based on FANAL Monte Carlo simulations has a comparable accuracy to typical analytical/numerical expressions and methods commonly in use today. However, comparison of ternary compound and alloys show larger differences between the model and the alpha factors for strong absorption and fluorescence effects. Additional improvements in Monte Carlo modeling may further improve the accuracy of these Monte Carlo-based alpha fit matrix corrections over time, without the need for methods based on analytical expressions with their inherent approximations and "tuning" biases with respect to specific data sets.

The current database tabulation (matrix.mdb) of approximately 400,000 Monte Carlo simulated k-ratios for Kα, Kβ, Lα, Lβ, Mα, and Mβ emission lines from 5 to 50 keV and takeoff angles for 40°, 52.5°, and 75°, is available with the free CalcZAF EPMA utility[a]. We continue to perform additional simulations to fill in the remaining gaps in the periodic table coverage and to perform higher precision simulations for low overvoltage analytical situations and other low precision situations.

We finally note that for ultimate accuracy in these fast Monte Carlo alpha method matrix corrections, one could calculate k-ratios for typical beam energies and X-ray lines using the PENEPMA Monte Carlo code, however that will take considerably more initial modeling time because each beam energy (and takeoff angle) would need to be modeled individually for each binary (alpha) composition. The advantage of the FANAL method (using Monte Carlo modeling for the primary intensities and a simple geometric model for fluorescence), is that one Monte Carlo simulation per alpha composition includes all beam energies (from 5 to 50 keV) and even various takeoff angles. But with enough parallel processing capability, it might be worth modeling the most

[a]http://www.probesoftware.com/Technical.html and https://github.com/openmicroanalysis/calczaf

common binary (alpha) pairs at typical (say 15 and 20 keV) electron beam energies for best matrix correction accuracy.

In summary, this alpha factor matrix correction method will work with k-ratios derived from any source, be they empirical measurements, analytical expressions, and now, for any preferred Monte Carlo method.

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