What’s Still Missing with the Fluorescence Corrections and Should We Care?

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Of the corrections employed for quantitative electron microprobe analysis, the correction for effects of fluorescence by characteristic x-ray lines has changed the least since the early re-parameterization of Castaing’s original correction by S.J.B. Reed in 1965 [1], and formal correction for the effects of continuum fluorescence is still seldom applied with no consensus parameterization employed by the standard software provided for EDS and WDS analysis systems. With regard to the characteristic fluorescence correction, part of the reason for the lack of change is the brilliance of Reed’s formulation of a useful set of equations. However, although he noted in his original paper that a number of simplifications had been made due to lack of fundamental measurement data and to aid in calculation and he and others later proposed substitution of better data sets and equations [e.g., 2,3], most correction programs still retain the original simplified expressions. Alternate methods have been proposed based on use of parameterized expressions for the primary ϕ(ρz) distribution coupled with numerical integration of the fluorescing and fluoresced x-ray path lengths [e.g., 4-6] and from Monte Carlo calculations [e.g., 7-10]. These alternate expressions can be used or modified to calculate correction for fluorescence in thin films, layered specimens, particles, inclusions, and across phase boundaries. But none of these are yet in common use and most still involve assumptions or simplifications to avoid the very extensive set of calculations a truly rigorous fluorescence correction would require. Moreover there are virtually no sets of measurements of k-ratios in well characterized systems where fluorescence effects are important to determine if the various correction algorithms actually work [e.g. 11].

We are in the process of evaluating each of the components of the conventional fluorescence corrections, updating those portions for which there are improved data sets and/or algorithms, determining for which types of specimens and under which analytical conditions these changes would be significant. (A 10% error may sound significant; but if it is a 10% error of a 5% correction, it only has a 0.5% effect on the answer.) These changes are being incorporated in the CALCZAF, CITZAF and TRYZAF correction programs [e.g., 12]. We also are using numerical integration and Monte Carlo calculations to find when the more rigorous expressions produce significantly different results for bulk specimens and to see whether their calculations for more complicated geometries can be parameterized into simpler expressions. Finally we are evaluating test specimens that can be used to evaluate the accuracy of the various corrections.

Updated compilations of fluorescence yields and mass absorption coefficients have only percent-level effects on the magnitude of characteristic fluorescence in most cases where it is a significant correction. The mass absorption coefficients used in the continuum fluorescence correction, particularly around absorption edges, can have a larger effect. Of much greater significance is the correction for the absorption ‘jump ratio’ (the ratio of the mass absorption coefficients just above and below the absorption edge of the fluorescing line). This is a multiplying factor in the fluorescence correction, i.e., a 10% error in the value results in a 10% error in the calculated ratio of fluorescence to primary emitted radiation. Reed, in his original correction [1], used constant values of 0.88 for K-lines, 0.75 for L lines and did not recommend a value for M lines. A subsequent replacement of simple functions of atomic
number [2] used values available at the time that differ considerably from current data. We have calculated the jump ratios for all K, L and M edges using the NIST XCOM data base [13]. They indicate variation in K lines for \( Z = 11 \) to \( 35 \) from 0.92 to 0.86 which can be expressed by a simple polynomial expression of \( Z \). The L-III jump factors have significantly greater variation, ranging from 0.65 to 0.80, and requiring a series of fitted curves for its various segments. Similar relations hold for the L-II and L-I jump ratios. The M-V jump ratios vary in an extreme fashion, ranging from \(<0.05\) to 0.7 and showing a complicated relation with shell occupancy. Tabulated values need to be used for them as is also the case for the M-I through M-IV shells.

Another multiplicative factor in the fluorescence correction that needs to be updated is the ratio of the primary electron-generated intensities of the fluorescing and fluoresced x-ray lines which Reed expressed as a simple function of overvoltage. The original expression results in errors or 20% or more for cases with very low and very high overvoltages [3]. Reed [2] proposed an alternate expression which shows better agreement with calculated intensities from Monte Carlo calculations and numerical integration of \( \phi(\rho z) \) expressions. But differences at high and low overvoltages for K-K, L-L, and M-M fluorescence and even larger differences for K-L, L-K, L-M, M-L, K-M and M-K fluorescence exist among the Reed formula, Monte Carlo and \( \phi(\rho z) \) calculations, and experimental measurements of x-ray intensity at multiple beam energies.

An example of typical differences in the fluorescence correction in the most basic cases of K-K fluorescence can be seen for the fluorescence of Fe K\( \alpha \) by Ni K\( \alpha \) in FeNi\(_3\) for a beam energy of 15 keV and a spectrometer take-off angle of 40°. The ratio of emitted Fe K\( \alpha \) produced by characteristic fluorescence to that emitted from primary electron excitation is calculated to be 16.7% using numerical integration of a \( \phi(\rho z) \) distribution [4], 15.3% using Monte Carlo calculations [9], and from \( 15.1\% \) to \( 19.7\% \) using different parameterizations of the Reed equation [12]. The calculated characteristic fluorescence contribution using these expressions ranges from 22% to 32% at 30 keV and from 6.5% to 8.6% at 10 keV. High precision measurements of Fe K\( \alpha \) as a function of beam energy in Ni-rich alloys vs. Fe metal can be used to evaluate which of the expressions provides the best correction.

References: