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An Improved Interference Correction for Trace Element Analysis

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ABSTRACT

Spectral interferences in quantitative electron beam microanalysis occur whenever a matrix element has an X-ray line that overlaps with that of an analyzed element. We report a more refined method of accounting for such interferences and show by the analyses of standard reference materials that its use allows accurate quantitative analysis of trace elements even when severe spectral interferences occur. Further, we show that this method can account for interferences in which the interfering and interfered elements mutually fluoresce and absorb one another. The technique is rapid, is easily incorporated into existing analytical software, and is calibrated on the instrument of interest at run time.

KEY WORDS: Microanalysis, spectral interferences, trace element analysis, peak overlaps, quantitative microanalysis.

1. INTRODUCTION

Spectral interferences (also called peak overlaps) occur whenever the wavelength of the characteristic X-ray used for analysis is near to or coincides with the characteristic X-ray line of one or more matrix elements and can be a serious source of error in quantitative microanalysis. For energy-dispersive spectrometry, the relatively poor resolution of Si(Li) detectors can induce large spectral interferences and, consequently, considerable effort has been expended in addressing this problem (*e.g.*, Fiori *et al.*, 1981, and Myklebust *et al.*, 1981). On the other hand, little attention has been paid to interferences in wavelength-dispersive spectrometry (WDS), possibly because of the inherently higher resolution of the technique. Nevertheless, there are many analytical situations in which an inaccurate interference correction can create large analytical errors, even for WDS analysis. In this article, we present an improved algorithm for the quantitative treatment of interference corrections in WDS X-ray microanalysis. We then show cases of trace element analysis where errors, due to spectral interferences, occur and demonstrate through analyses of standards that, even in these worst cases, the correction recommended in this study successfully accounts for the spectral interference(s).

The technique that we developed is an empirical one in which the interfering counts are estimated at the desired peak intensity wavelength and does not involve estimation of the entire background due to interferences.

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Such spectral processing techniques have been proposed and have been calibrated for specific instruments (*e.g.*, Roeder, 1985). Although these techniques can provide adequate corrections, they are, in general, time-consuming to calibrate and are sensitive to details of machine configuration. We present an easily implemented, flexible correction scheme that is not sensitive to various machine configurations.

2. EMPIRICAL ESTIMATION OF SPECTRAL INTERFERENCES

A quantitative interference correction requires an accurate estimate of the intensity of the interfering element. This intensity can be calculated from the ZAF corrected concentration of the interfering element in the unknown, the measured interference in a standard used for the interference correction, and the ZAF correction factors for the matrices of both the unknown and the interference standard.

In general, the concentration of an element A can be determined from its characteristic X-ray emission at wavelength λ_A according to Philibert (1968):

$$C_A^u = \frac{C_A^s}{[ZAF]_{\lambda_A}^s} [ZAF]_{\lambda_A}^u \frac{I_A^u(\lambda_A)}{I_A^s(\lambda_A)} \tag{1}$$

where the following notation has been adopted: C_i^j is the concentration of element i in matrix j; $[ZAF]_{\lambda_i}^j$ is the ZAF (atomic number, absorption, and fluorescence) correction term for matrix j (Z and A are for wavelength λ_i, and F is for the characteristic line at λ_i for element i); and $I_i^j(\lambda_i)$ is the measured X-ray intensity excited by element i in matrix j at wavelength λ_i.

In the case in which element A is interfered by another element, B (Figure 1), the measured X-ray counts at λ_A are the sum of those excited from elements A and B so that

$$I_A^u(\lambda_A) = I^u(\lambda_A) - I_B^u(\lambda_A) \tag{2}$$

where $I^u(\lambda_A)$ are the total measured counts at λ_A and $I_A^u(\lambda_A)$ are the uninterfered counts from element A. To estimate $I_A^u(\lambda_A)$, we can write, motivated by Equation 1:

$$C_B^u = \frac{C_B^s}{[ZAF]_{\lambda_A}^s} [ZAF]_{\lambda_A}^u \frac{I_B^u(\lambda_A)}{I_B^s(\lambda_A)} \tag{3}$$

where s refers to an interference standard that contains

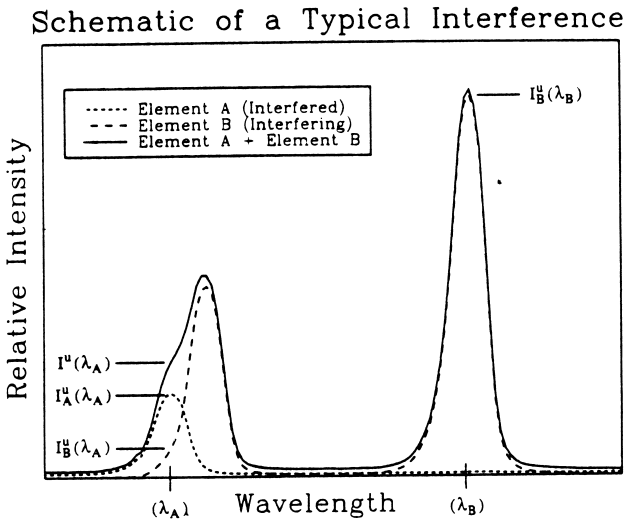

FIGURE 1. Schematic diagram showing a hypothetical spectral interference.

a known quantity of the interfering element B but none of the interfered element A. In rearranging Equation 3,

$$I_B^u(\lambda_A) = \frac{[ZAF]_{\lambda_A}^s}{C_B^s} \frac{C_B^u}{[ZAF]_{\lambda_A}^u} I_B^s(\lambda_A). \tag{4}$$

Since C_B^u is determined independently from

$$C_B^u = \frac{C_B^s}{[ZAF]_{\lambda_B}^s} [ZAF]_{\lambda_B}^u \frac{I_B^u(\lambda_B)}{I_B^s(\lambda_B)} \tag{5}$$

all of the necessary terms are known and Equations 2 and 4 can be combined with Equation 1 to yield:

$$= \frac{C_A^s}{[ZAF]_{\lambda_A}^s} [ZAF]_{\lambda_A}^u \frac{I^u(\lambda_A) - \dfrac{[ZAF]_{\lambda_A}^s}{C_B^s} \dfrac{C_B^u}{[ZAF]_{\lambda_A}^u} I_B^s(\lambda_A)}{I_A^s(\lambda_A)}. \tag{6}$$

It is difficult to estimate the F terms in Equation 4, because knowledge of all the excited lines would be required. Fortunately, except in some unusual cases, these F terms are generally near unity (most of the corrections tend to be in the Z and A components) and can be neglected. Consequently, we have approximated Equation 6 with

$$C_A^u \approx \frac{C_A^s}{[ZAF]_{\lambda_A}^s} [ZAF]_{\lambda_A}^u \frac{I^u(\lambda_A) - \dfrac{[ZA]_{\lambda_A}^s}{C_B^s} \dfrac{C_B^u}{[ZA]_{\lambda_A}^u} I_B^s(\lambda_A)}{I_A^s(\lambda_A)} \tag{7}$$

and it is this expression that we use in our following data reductions.

Similar approaches have been taken previously for WDS interference corrections but have adopted far more approximations. For example, a commonly used scheme (*e.g.*, Gilfrich *et al.*, 1978) is to take

$$I^{u}_{B}(\lambda_A) \approx \frac{I^{s}_{B}(\lambda_A)}{C^{s}_{B}} \frac{I^{u}_{B}(\lambda_B)}{I^{s}_{B}(\lambda_B)} C^{s}_{B} \qquad (8)$$

In contrast to Equation 4, this expression neglects the matrix effects of the unknown, analytical standard, and interference standard at (λ_A and λ_B) on the observed counts excited from element B. Hence, any differences in the ZAF corrections between the unknown and standards will create a systematic analytical error. Further, if A is a trace constituent in a matrix containing abundant B, these correction errors are greatly magnified. In the following sections, we use actual analyses on well-characterized standards to explore the ramifications of these assumptions and to test the validity of our correction scheme.

3. ANALYTICAL METHODS

For this study, all data were acquired with an ARL SEMQ eight spectrometer wavelength-dispersive microprobe at the University of California at Berkeley. Samples were run at an operating voltage of 15 kV using a sample current of 40 nanoamps as measured on synthetic MgO. Analyzing crystals were chosen to minimize the interferences in all cases by selecting the smallest 2d spacing crystal that could be used for the analytical line. Detector slit widths were normally 2–4 mm. All measurements were off-peak corrected after careful spectrometer scanning to ensure that both off-peak positions were free from any interfering lines. Pulse height analysis was used for all measurements. Typically, the on-peak counting time was 40 seconds, the off-peak counting time was 20 seconds on each off-peak position, and each result was calculated by averaging some 20–40 points. All analyses were calculated using the integrated CITZAF $\phi(\rho z)$ matrix correction routines (Armstrong, 1988) within the PRSUPR program (Donovan *et al.*, 1990 and 1992).

We tested each algorithm by incorporating both Equations 7 and 8 into the ZAF iteration loop of the PRSUPR electron microprobe data acquisition and data reduction program, shown schematically in Figure 2. Because interference corrections are most important in trace element analyses, we used this routine to analyze several well-characterized standard reference materials, which contain trace elements that experience several spectral interferences. After correcting the X-ray count data for dead time, background, beam, and standard drift, both expressions were evaluated and the errors calculated. The results appear in Table 1.

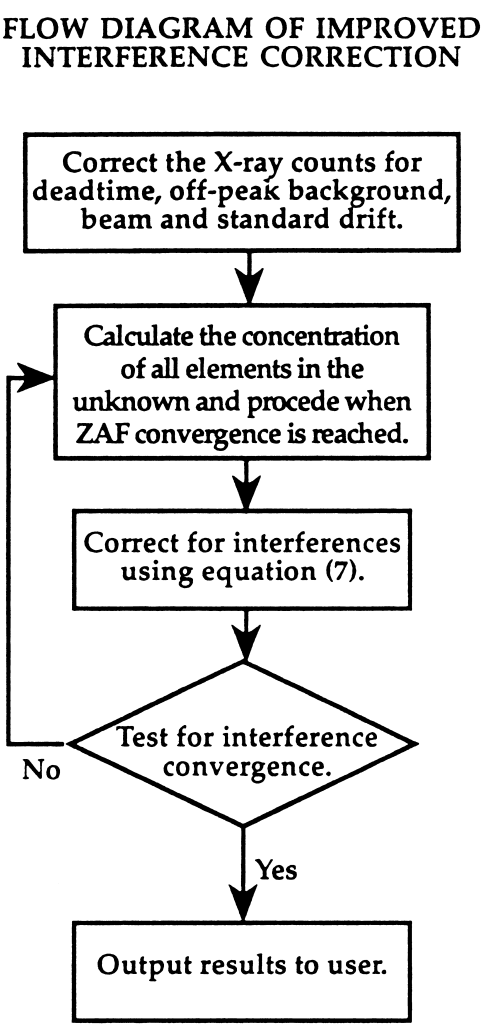

FIGURE 2. Flow diagram of the interference correction presented in this study.

In addition to using an accurate correction scheme, errors caused by spectral interferences in WDS analysis can be reduced by instrumental settings. For example, if the interfering line is a higher order reflection, the interference can be reduced or nearly eliminated by careful use of pulse height analysis or by judicious selection of an analyzing crystal, which naturally suppresses that high-order reflection. Interfering lines of the same energy can only be reduced by the use of higher resolution analyzing crystals (*i.e.*, smaller 2d spacing) or narrow detector slits. All of these methods, however, can reduce signal intensity and increase the sensitivity of the analysis to intensity, peak shift, and peak shape changes (Goldstein *et al.*, 1981).

TABLE 1 Comparison of Analyzed Trace Elements in Samples Using Both the Traditional Count Ratio Interference Correction (Equation 8) and the Method Presented in This Study (Equation 7)

Matrix	Element	No Correction		Equation 8		Equation 7	
	Wt %	Wt %	% Dev	Wt %	% Dev	Wt %	% Dev
SRM K-497	Zr 0.32[a]	0.702	+119.%	0.364	+13.7%	0.364	+13.7%
SRM K-963	Ti 0.290[b]	0.377	+30.1%	0.274	−5.52%	0.292	+0.7%
Amph-357	F 0.26	0.355	+36.4%	0.225	−13.6%	0.271	+4.1%
SRM 1159	Co 0.022	0.145	+560%	0.010	−55.3%	0.024	+8.9%
SRM 654b	Cr 0.025	0.268	+971%	−0.020	−184.2%	0.021	−16.6%

[a]Value not certified.
[b]Value determined by atomic absorption.

SRM K-497 includes: P 31.59, Mg 6.49, Al 5.97, O 52.46, Pb 0.86, Ce 0.94, Ta 0.71, Ti 0.22, Fe 0.26, Si 0.13.

SRM K-963 includes: Ba 39.53, Si 22.23, Zn 2.93, Pb 1.32, O 31.70, Al 0.11, Zr 0.40, Ti 0.27, Ce 0.80, Ta 0.95, Fe 0.35.

Amph-357 includes: SiO2 39.31, Al2O3 15.37, MgO 13.89, K2O 1.36, TiO2 4.14, Na2O 2.36, O 0.47, CaO 12.54, FeO 8.90, MnO 0.10.

SRM 1159 includes: Ni 48.2, Fe 51.0, C 0.007, Mn 0.30, P 0.003, S 0.003, Si 0.32, Cu 0.038, Cr 0.06, Mo 0.01.

SRM 654b includes: Ti 88.974, Al 6.34, V 4.31, Fe 0.23, Si 0.045, Ni 0.028, Sn 0.023, Cu 0.004, Mo 0.013, Zr 0.008.

4. RESULTS

We have analyzed five analytical standards to (1) illustrate that the method presented successfully corrects for interferences, even in extremely difficult cases, and (2) show when simpler methods do and do not fail.

In the first example, we demonstrate the equivalence of the two expressions by measuring the concentration of Zr in an aluminum-magnesium-phosphorus oxide glass sample (NIST SRM K-497) using an analytical standard and an interference standard, each (NIST SRM K-496) almost identical in composition to the sample. Consequently, even though the uncorrected overlap to the P Sk$\alpha_{5,6}$ line is almost 120%, the ZAF coefficients nearly cancel and the two expressions yield similar values (Table 1).

Such ideal standards are, unfortunately, rarely available. For example, when determining the concentration of a trace level of Ti in a silicon-barium-zinc oxide glass sample (NIST SRM K-963) that is significantly interfered by the Ba Lα_1 line, although the analytical standard used (NIST SRM K-489) to determine Ba is essentially identical to the sample, the barium fluoride (BaF) standard used for the interference measurement is not.

At the analytical wavelength for Ti, the differences between the ZA(F) correction for the sample (Z * A = 1.046) and the interference standard (Z * A = 0.914) were large enough to affect the calculation of the interfering counts (0.914/1.046 = 0.873); this causes Equation 8 to overcorrect the interfering intensity by some 13%.

A third example is of particular interest to geologists as determinations of trace F in the presence of an FeLα_1 spectral interference are quite common in silicate minerals, such as biotite (K_2(Mg, Fe^{+2})$_{6-4}$(Fe^{+3}, Al, Ti)$_{0-2}$[$Si_{6-5}Al_{2-3}O_{20}$](OH, F)$_4$) and amphibole (Ca_2(Na, K)(Mg, Fe^{+2}, Fe^{+3})$_4$Ti[$Si_6Al_2O_{22}$](O, OH, F)$_2$). Here, we examined an amphibole standard containing a known concentration of F and 8.90% FeO using a W/Si layered dispersive element (LDE) analyzer. Although the spectral overlap from FeLα_1 with an LDE analyzer is much greater than that seen with the traditional crystalline rubidium acid phthalate (RAP) and thallium acid phthalate (TAP) analyzers, the increased count rate from the LDE improves the detection limit of the light elements significantly. However, the interference correction also becomes more important due to the lower resolution of the LDE.

For this measurement, we used a natural magnetite (approximately FeO · Fe_2O_3) as the interference standard and a biotite standard as the analytical standard for Fe. The effect on the analytical intensity of the F Kα (and the interfering Fe Lα_1) line by these various matrices is considerable, ranging from 200–350%. In Table 1, we can see that the difference between the two values from each expression is about 500 ppm for this sample. Samples containing less F and more Fe will produce even more divergent results.

Several analytical difficulties arise in situations where large fluorescence effects are present. The most serious of these are when either the matrix absorption or the fluorescing X-ray within a sample affect the fluoresced analytical or the interfering lines in different ways. For example, in K-band fluorescence, both the Kα and the Kβ are equally fluoresced by characteristic lines of other matrix elements. However, if a major element absorp-

tion edge lies between the two fluoresced K lines, they will suffer unequal degrees of absorption. This would be the case, for example, in Ni-Fe alloys with significant concentrations of Mn, since the Mn absorption edge lies between the Fe $K\beta_{1,3}$ and the Fe $K\alpha$ lines, both of which are fluoresced by the Ni $K\alpha$ line.

L-line fluorescences are more complicated, primarily because situations exist in which not all L lines are fluoresced equally by a characteristic X-ray. This is due to the fact that several absorption edges exist for the L band. Examples can be found where the primary analytical L line is fluoresced by a characteristic X-ray, but the secondary L line of the same element, which is causing an interference with another element, is not. In both of the above K- and L-band fluorescence scenarios, the use of Equation 8 will cause errors to be introduced in the interference correction calculation.

But what of K-band fluorescences where no major element absorption edges lie between the fluoresced analytical line and a secondary line causing an interference? In such cases, the fluorescence effects on the interfering element cancel. Therefore, because Equation 8 completely neglects the matrix correction of the interfering line, only the absence of the absorption and atomic number corrections are of concern, whereas Equation 7 can slightly underestimate the fluorescence contribution to the interference correction because of the dropped F term in our approximation of the matrix correction of the interfering X-ray. In fact, with K-band fluorescences, it might be desirable to retain the F terms for the correction of the interfering line by using the value calculated for the primary analytical line of the interfering element and using the full expression of the interference correction, as shown in Equation 6. However, we can see from the Fe-Ni alloy in the fourth example (SRM 1159) that the effect of the missing F term is small. Here, the Co $K\alpha$ line is interfered by the $K\beta_{1,3}$ line of Fe, which is, in turn, significantly fluoresced by the presence of Ni in the sample. Even though the matrix correction for the interfering line in Equation 7 only corrects for the absorption and atomic number effects, the difference between the two expressions is only about 140 ppm and our model still yields the better analysis.

In a final example, we have analyzed trace Cr in a titanium-aluminum-vanadium alloy (NIST SRM 654b) where a major concentration of Ti causes an interference on V, which, in turn, strongly interferes with the Cr analytical line. Because Equation 7 is incorporated into the ZAF iteration loop of our quantitative analysis program, the concentrations of each element are correctly determined after several iterations. Equation 8, on the other hand, dramatically overcorrects the V interference on Cr resulting in a negative weight percent.

5. CONCLUSIONS

We have reported a more refined technique for the accounting of spectral interferences in WDS analyses. Accurate interference corrections are most important for trace element analyses. We have shown that, whereas approximate techniques based on raw X-ray counts can yield adequate results in some circumstances, they will fail for trace element analyses in which there are mutual fluorescences and absorptions between the interfering and interfered elements or when the standards and unknown samples have different matrices. The method presented here overcomes these obstacles and is recommended for general use in the correction of X-ray peak intensities for spectral interferences.

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