INTELLIGENT INTERPOLATION FOR BACKGROUND SUBTRACTION
– A HYBRID APPROACH FOR TRACE-ELEMENT ANALYSIS

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ABSTRACT
For wavelength-dispersive analysis of trace elements at near-background concentrations, background subtraction poses special problems because the background is complex and difficult to measure or predict with certainty. Several sources contribute. These include Compton- and Rayleigh-scattered tube continuum radiation, nondiscriminated higher-order radiation, fluorescence of instrument parts, Compton- and Rayleigh-scattered tube lines, unresolved spectral interferences, and electronic noise. Other complications include sample, source, and detector absorption edges, diffraction by the sample, limited sample thickness, and a complicated and variable geometry of the analyzed sample volume. This paper describes a Lagrange interpolation method, in which any suitable theoretical or empirical background estimate can be used to “linearize” the data and to improve the accuracy of interpolation. The method combines the advantages of prior methods. In particular, it easily allows spectral interference corrections and calculation of total counting statistical errors, and it does not require background positions free from spectral interference. In principle, it also allows placing upper limits on total background-subtraction errors. In a test on SiO2 and Fe2O3 backgrounds, the method estimated background intensities accurately and outperformed a method based on empirical shape factors.

INTRODUCTION
Previously used background-correction methods include: (1) estimation from the sample composition [1]; (2) the use of empirical shape factors that represent the background at discrete positions [2] [3]; and (3) estimation from tube lines [4] [5].

Estimation from tube lines requires certain assumptions about X-ray scattering [4] [5]. Estimation from the sample composition does not require these assumptions, but like all methods, it suffers from sample-related uncertainties discussed below.

The empirical shape factor method is often used when the highest accuracy is needed. It is based on the assumption that the ratio of background intensities at two background angles is independent of the sample composition. If this is true, then the ratio between two samples must also be independent of the angle. Fig. 1 shows ratios of background intensities for SiO2, Fe2O3, and Fe foil. (Materials and experimental conditions are described in Table 1, footnote.) Evidently, the accuracy of the assumption is highly questionable for some samples.
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The assumption can be expressed as

$$k_1 B(\theta_1) - B(\theta_p) - k_2 B(\theta_2) = 0,$$

(1)

where $B(\theta)$ is the background at angle $\theta$; $\theta_1$ and $\theta_2$ are background angles; $\theta_p$ is the peak angle; $k_1$ and $k_2$ are constants that are independent of the sample composition. Then, it is easily shown that the background at the peak is given by

$$B(\theta_p) - B(\theta_2) = F[B(\theta_1) - B(\theta_2)],$$

(2)

where shape factor $F = \frac{1}{1/k_1 - 1/k_2}$ can be determined from independently analyzed blanks.

In addition to possible difficulties caused by inaccuracy of the approximation and by absorption edges, this method may be limited by the accuracy, compositional range, and availability of standards, and may introduce systematic errors due to counting statistical errors in determination of the factors.

Sample transparency and diffraction by the sample add to the complexity of predicting the background. For samples that are not completely opaque to X-rays, the background may be reduced by an unknown extent, or scattering from material behind the sample may contribute. For pressed powder pellets, the effective source-sample distance, and therefore the background intensity, depend partly on the sample bulk density. For light-element samples, such as coal, the irradiated volume depends in a complicated way on the sample thickness, composition, density, and the irradiated area.

A large fraction of the background is due to coherent scattering of tube continuum radiation, which is subject to diffraction by the sample. Fig. 1 shows ratios of background intensities between SiO$_2$ glass, a pressed powder pellet of Fe$_2$O$_3$, and Fe foil. The foil shows relatively strong, diffuse diffraction peaks, which are probably due to preferred crystal orientation. In randomly oriented powdered samples, with divergent incident radiation, diffraction peaks are very diffuse and difficult to detect, but may be present nonetheless. The existence of even weak diffraction peaks demonstrates that there are inherent limitations to a-priori background estimates, and to any method that assumes a constant, simple dependence of background intensity on $2\theta$. The Fe foil presents a severe test for any background estimation method, and would require measurements at closely spaced angles.

In view of possible limitations of existing models, a more general method is needed. The purpose of this paper is to demonstrate the use of Lagrange interpolation formula, and to show how it can be combined with other models. Because Lagrange interpolation reduces the dependence on background standards, it has the potential for improving reliability, accuracy, and
detection limits, and for extending the range of sample types and compositions that can be analyzed with confidence.

**THE LAGRANGE INTERPOLATION FORMULA**

The Lagrange interpolation formula [6] expresses the lowest-order polynomial that passes through all measured points. The interpolated background at \( \theta_p \) calculated from \( n \) background points \( \theta_1 \ldots \theta_n \) can be expressed as

\[
B(\theta_p) = I_1(\theta_p)B(\theta_1) + I_2(\theta_p)B(\theta_2) + \ldots + I_n(\theta_p)B(\theta_n),
\]

where

\[
L_1(\theta_p) = \frac{(\theta_p - \theta_2)(\theta_p - \theta_3)\ldots}{(\theta_1 - \theta_2)(\theta_1 - \theta_3)\ldots}
\]

and

\[
L_2(\theta_p) = \frac{(\theta_p - \theta_1)(\theta_p - \theta_3)\ldots}{(\theta_2 - \theta_1)(\theta_2 - \theta_3)\ldots}.
\]

Although equation 4 is an \( n-1 \)th-order polynomial in \( \theta_p \), the estimated background is a linear combination of measured background values in the unknown sample, and all coefficients are simple functions of peak and background angles. This means that the background can be estimated without reference to any analyzed background standard. It also means that counting statistical errors can easily be estimated and spectral interference corrections can easily be made.

If \( \Delta B(\theta_i) \) is the counting statistical error at background angle \( \theta_i \), the estimated counting statistical error at the peak angle is

\[
[\Delta B(\theta_p)]^2 = [L_1(\theta_p)\Delta B(\theta_i)]^2 + [L_2(\theta_p)\Delta B(\theta_i)]^2 + \ldots.
\]

It is relatively easy to correct for spectral interference at a background angle. In the presence of a spectral interference \( \Delta(\theta_i) \) at angle \( \theta_i \), the uncorrected background intensity is given by

\[
B'(\theta_p) = L_1(\theta_p)B(\theta_1) + L_2(\theta_p)[B(\theta_2) + \Delta(\theta_2)] + L_3(\theta_p)B(\theta_3),
\]

and the correction \( \Delta(\theta_p) \) at the peak angle is given by

\[
\Delta(\theta_p) = L_1(\theta_p)\Delta(\theta_i).
\]

Even though spectral interference at a background angle distorts the background shape, the background correction at the peak angle is nevertheless proportional to the height of the interfering peak.

**COMBINED METHODS**

A polynomial in \( \theta \) is not necessarily the most accurate representation of the background intensity at interpolated points. It may be possible to improve the interpolation by using a physical or empirical model that closely represents the "background shape" (dependence on \( \theta \)).

The background model is used to transform either \( \theta \) or the background intensity, resulting in an approximately linear function that can be interpolated accurately. Then the interpolation formula expresses either: (1) the background intensity as a polynomial of a function of \( \theta \) (instead of a polynomial in \( \theta \)); or (2) a function of the background intensity as a polynomial in \( \theta \).
suitable model can be used, including the shape factor model or estimation from the sample composition. In a sense, the model defines the shape, and the polynomial interpolation refines the curve and reduces the residuals.

Two examples illustrate interpolation of a function of $\theta$. First, as shown in Fig. 2, the logarithm of the background is approximately linear in $\theta$ above 22°. (The deviation below 22° is due to the Rh Compton peak.) Consequently, the expression

$$\ln B(\theta_P) = L_1(\theta_P)\ln B(\theta_1) + L_2(\theta_P)\ln B(\theta_2) \ldots$$  (9)

should approximate the background accurately above 22°. Since the $\theta$ dependence is not exactly logarithmic, three background points may give a more accurate interpolation than two points.

For the second example, it is assumed that the background can be predicted as a function $f(\theta)$ from the major-element composition. Then $\frac{B(\theta)}{f(\theta)}$ should be essentially independent of $\theta$, and interpolated values of this ratio should be accurate.

ESTIMATING INTERPOLATION ERRORS

The Lagrange interpolation formula offers one other powerful feature that is worth mentioning. With adequate knowledge of the spectrum, it is also possible to calculate an upper limit on the possible error due to interpolation [6]. If $n$ background angles are used, and $\max(B^{(n)})$ is the maximum value of the $n^{th}$ derivative with respect to $\theta$ within the range of background angles, then the maximum interpolation error is given by

$$-\frac{(\theta - \theta_1)(\theta - \theta_2)\ldots(\theta - \theta_n)}{n!} \max(B^{(n)}).$$  (10)

Although it may not be easy to specify the $n^{th}$ derivative, it does offer a formal method for evaluating systematic background errors. As an example, three background angles give a quadratic function of $\theta$ that passes exactly through the measured backgrounds. The error is a third-order polynomial that is 0 at the background angles.

METHODS AND RESULTS

As a test, a background model was constructed for Fe$_2$O$_3$, using logarithmic interpolation (equation 9). Five background angles between 22° and 37° were used to construct a 4th-order polynomial. The results are shown in Fig. 3. There is virtually no apparent systematic interpolation error, except for possible small errors at about 22° and 35°. Extrapolation beyond 37°, however, produces large errors.
Fig. 3. Results of a logarithmic fit for $\text{Fe}_2\text{O}_3$, with 5 background angles (shown by dots). Lines show $2\sigma$ counting statistical errors.

Table 1 shows the results of a comparison with the shape-factor method (equation 2), for $\text{SiO}_2$ and $\text{Fe}_2\text{O}_3$. Background intensities were measured at 23°, 26°, and 29°. Interpolated log values were calculated from equation 9, using either all three angles, or alternatively, adjacent pairs. For the shape factor method, the coefficients were calculated for adjacent pairs, using $\text{SiO}_2$ as a reference. The interpolated and extrapolated values were compared with measured values.

Overall, Lagrange interpolation clearly performed much better than the shape-factor method. For Lagrange interpolation, the errors were only slightly higher than expected from counting statistical errors. With three backgrounds, all errors for $\text{SiO}_2$ were $<2.5\times$ total counting statistical errors, and for $\text{Fe}_2\text{O}_3$, $<3.7\times$. With two backgrounds, all errors for $\text{SiO}_2$ were $<1.8\times$ total counting statistical errors; and for $\text{Fe}_2\text{O}_3$, $<5.0\times$.

**DISCUSSION**

It is significant that Lagrange interpolation outperformed the shape-factor method without using a reference blank. The main reason is that the $\text{SiO}_2$ background, which was used as a reference for the shape-factor method, does not approximate the $\text{Fe}_2\text{O}_3$ background shape as well as the logarithmic approximation (equation 9).

As discussed above, one very promising possibility is to combine Lagrange interpolation with estimation from the sample composition. The potential advantage is that the calculated background is supposed to represent the background shape accurately, including absorption edges. As an example of calculated backgrounds, Yamada et al. [1] successfully used...
background intensities calculated from scattering cross sections and mass absorption
coefficients, for analysis of Fe ores for Pb, Zn, V, and K with a simultaneous spectrometer.
Since sequential spectrometers have generally higher background levels, calculated backgrounds
alone may not be adequate, and background measurements is advisable.

Table 1. Comparison of interpolation/extrapolation methods *

<table>
<thead>
<tr>
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<th>Fe$_2$O$_3$</th>
<th></th>
<th>SiO$_2$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Background (counts/s)</td>
<td>Error (counts/s) †</td>
<td>Background (counts/s)</td>
</tr>
<tr>
<td>22°</td>
<td>1336</td>
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<td>3.35</td>
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<td>24°</td>
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<tr>
<td>30°</td>
<td>777</td>
<td>5.59</td>
<td>12.34</td>
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</tbody>
</table>

* Samples: (1) polished, ultrapure SiO$_2$ glass (Suprasil, Heraeus-Amersil, Duluth, GA), 0.66
g/cm$^2$; (2) Fe$_2$O$_3$, Johnson Matthey #10716, lot S20169A, 0.5 g/cm$^2$ pressed to 17 MPa; (3)
Puratronic Fe foil, Johnson Matthey #11381, lot NM01756, 0.1 mm thick. Siemens SRS 300,
Rh tube, 55 kV, 40 mA, 180 s counting time, LiF (200), fine collimator, 23-mm aperture,
scintillation detector. Pulse-height settings: 0.5, 1.5.
† Interpolated (or extrapolated) value – measured value.
The total uncertainty (1σ) in the error ascribed to counting statistics ranges from 3 to 6 counts/s
for Fe$_2$O$_3$ and 4 to 9 counts/s for SiO$_2$.
‡ Logarithmic interpolation, 3 background points (equation 9). Background angles at 23°, 26°,
and 29°.
° Logarithmic interpolation, 2 background points (equation 9). Background-angle pairs 23°-26°;
26°-29°.
** Equation 2 (F determined from SiO$_2$). Background-angle pairs 23°-26°; 26°-29°.

REFERENCES
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