BACKGROUND SUBTRACTION FOR TRACE-ELEMENT ANALYSIS –
ANALYTICAL COMPARISON OF METHODS

Rex Couture
Dept. of Earth and Planetary Sciences
Washington University
St. Louis, Missouri 93130

ABSTRACT
For wavelength-dispersive fluorescence analysis, the background is a nonlinear function of $2\theta$, and a linear interpolation between two background angles gives an erroneously high estimate. This discussion systematically develops and compares interpolation methods analytically, to demonstrate their strengths, weaknesses, and correct use. The background can be estimated from measurement at a single angle, or it can be interpolated as a function of $2\theta$, using coefficients determined empirically or by using Lagrange polynomials. Three or more background angles can be used to compensate for curvature. However, it is preferable to linearize the background by transforming either $2\theta$ or intensity. Most background subtraction methods, including measurement of a single background, and the commonly used two-background “shape-factor” method, implicitly transform $2\theta$. Background interpolated by using a $2\theta$ transform is not affected by a change in tube intensity or by a constant change in background, but requires a reference blank sample that may not be universally applicable. Interpolation of log intensity values is not affected by changes in tube intensity, and does not require a reference blank. Measured background normalized to the background estimated from sample composition is not affected by tube intensity or by a constant change in background.

INTRODUCTION
The problem of background subtraction in wavelength-dispersive analysis is well known. Since the continuum background is a nonlinear function of $2\theta$ (or energy), linear interpolation generally leads to erroneously high background estimates. Using closely spaced background angles reduces the errors, but does not eliminate the curvature. Improving the accuracy of interpolation is crucial for improving the analytical accuracy and for minimizing the number of background angles required.

The background is complex, with multiple components due to scattering from the sample and instrument parts. As shown in Fig. 1 and reference [1], diffraction by the sample in particular adds a component that is difficult to estimate a priori. Therefore, background subtraction must remain largely an empirical art.
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

Sponsored by the International Centre for Diffraction Data (ICDD).

This document is provided by ICDD in cooperation with the authors and presenters of the DXC for the express purpose of educating the scientific community.

All copyrights for the document are retained by ICDD.

Usage is restricted for the purposes of education and scientific research.

DXC Website  ICDD Website
Fig. 1. Estimated and measured backgrounds for SiO$_2$ and Fe$_2$O$_3$, and measured background for Fe foil. Log intensity was interpolated through points shown. Two separate curves are shown for each sample: from 20° to 23°, on the shoulder of the Rh Compton peak; and from 22° to 40°. Fe foil shows prominent, broad diffraction peaks that defy estimation of background intensity from composition.

Samples: polished, ultrapure SiO$_2$ glass (Suprasil, Heraeus-Amersil, Duluth, GA), 0.66 g/cm$^2$; Fe$_2$O$_3$, Johnson Matthey #10716, lot S20169A, 0.5 g/cm$^2$ pressed to 17 Mpa; Puratronic Fe foil, Johnson Matthey #11381, lot NM01756, 0.1 mm thick; Blank was determined with no sample or backing. Siemens SRS 300, Rh tube, 55 kV, 40 mA, 1° 2θ/min., LiF (200), fine collimator, 23-mm aperture, scintillation detector. Pulse-height settings: 0.5, 1.5.

Polynomial interpolation, using three or more background angles, can be used to compensate for curvature. Because the estimate consists of a linear combination of measured backgrounds, spectral interference corrections and calculation of total counting statistical errors are straightforward, and the method is well suited for background estimation [1]. This method is used by some commercial software packages. However, a polynomial is not necessarily the most accurate possible representation of the background. It might be better to interpolate a linear function or nearly linear function. In principle, polynomial interpolation of that linear function could still be used to compensate for any slight, residual nonlinearity.

Several methods have been used to express the functional form of the background as a linear function. For example, it is common practice to use SiO$_2$ glass or another pure material as a reference blank, and to calculate shape factors for each combination of background and peak angles [2, 3]. This method has the disadvantage that no single material is necessarily representative of all samples that might be encountered [1]. As an alternative, the logarithm of intensity is approximately linear in 2θ, as shown in Fig. 2. Interpolation of log intensity is demonstrated successfully for SiO$_2$ and Fe$_2$O$_3$, as shown in Fig 1. This method has the advantage that it does not require the use of any reference blank. For Fe$_2$O$_3$, the method was found to be superior to using SiO$_2$ as a reference [1].
The mathematical foundations of these methods have not been discussed very clearly in the literature, and in some cases the principles remain vague. In this paper, the methods are briefly developed and compared analytically. The objectives are to show how they are used, and to discern their advantages and disadvantages, without attempting to settle the question of accuracy. It will be shown that many commonly used methods implicitly transform either $2\theta$ or intensity to obtain a linear function. These functions are discussed in the following sections.

The methods are also considered for insensitivity to change in certain variables such as tube intensity, counter gas composition, and crystal fluorescence from sample radiation. Table 1 shows some of the variables that affect background. With an ideal method, any changes would not introduce significant errors in the estimated background. A change in tube intensity would affect background at all peaks and background angles proportionately. Other changes might introduce a constant component, with a constant added to background at all angles. A method is considered to be robust if it is invariant with respect to both intensity (multiplicative) changes and additive changes.

### Table 1. Changes in analytical conditions that affect background intensity

| Change in counter gas density or composition | Fluorescence of crystals or other spectrometer parts | Changes in crystal reflectivity (radiation damage, contamination) | Changes in sample mask-aperture combinations | Tube intensity changes | Tube aging, affecting tube lines and continuum background |

### ESTIMATION FROM A SINGLE BACKGROUND ANGLE

The essential assumption is that the ratio of backgrounds at any two angles is the same for all samples. This is equivalent to the assumption that background $B$ for sample $s$ at any angle $\theta$ is the product of functions $f(\theta)$ and $g(s)$:

$$B(\theta, s) = f(\theta)g(s).$$

Then

$$B(\theta, s) = \frac{f(\theta)}{f(\theta_i)}B(\theta_1, s),$$

where $\theta_1$ is the reference angle.
and

\[ \frac{B(\theta_1, s_1)}{B(\theta_1, s_2)} = \frac{g(s_1)}{g(s_2)} \]. \tag{3} \]

Equation 2 expresses the assumed proportionality of backgrounds at any two angles. The background at peak angle \( \theta \) is estimated from equation 2, with constant factor \( \frac{f(\theta)}{f(\theta_1)} \) determined from measurements on one or more reference blanks.

Unfortunately, the assumption (equation 1) is not universally valid. For example, the ratio of Fe\(_2\)O\(_3\) and SiO\(_2\) backgrounds varies by more than three-fold from 20° to 45° (LiF 200) [1]. This method should be restricted to a short interval between the peak and background angle, or to a narrow range of compositions.

**ESTIMATION FROM TWO BACKGROUND ANGLES, WITH REFERENCE BLANK**

This is the commonly used “shape-factor” method mentioned above [2, 3]. Assuming that equation 1 is valid, the background at peak angle \( \theta \) can be calculated from measurements at background angles \( \theta_1 \) and \( \theta_2 \), according to

\[ B(\theta, s) - B(\theta_2, s) = A(\theta)(B(\theta_1, s) - B(\theta_2, s)), \tag{4} \]

where

\[ A(\theta) = \frac{f(\theta) - f(\theta_2)}{f(\theta_1) - f(\theta_2)}. \tag{5} \]

This can be verified by substituting equation 1 into equation 4, and verifying that both sides of the equation are equal. Factor \( A(\theta) \) is determined empirically from one or more blank reference samples, using measurements at background and peak angles. If \( B(\theta, s) - B(\theta_2, s) \) is plotted against \( B(\theta_1, s) - B(\theta_2, s) \), \( A(\theta) \) is the slope. Some readers will recognize \( A(\theta) \) as a Lagrange interpolation polynomial [4], which is evaluated empirically in this case, if \( f(\theta) \) is not known.

Although the validity of equation 1, and therefore the validity of equation 4, have been questioned in the preceding section, it turns out that equation 1 is unnecessarily restrictive. Equation 4 has the form

\[ B(\theta, s) = f(\theta)g(s) + h(s). \tag{6} \]

Equation 4 can be derived from equation 6. That is, if equation 6 is true, then equation 4 is also true. Equation 6 is less restrictive than equation 1, and allows an additional degree of freedom in fitting empirical data. Unfortunately, it has no obvious physical basis, and the accuracy is untested.

**INTERPOLATION OF LOG INTENSITY DATA**

This method was discussed in reference 1. The background is estimated from

\[ \log B(\theta) = L_1(\theta) \log B(\theta_1) + L_2(\theta) \log B(\theta_2) \ldots, \tag{7} \]
where the coefficients $L_1(\theta)$ etc. are Lagrange polynomials, which are simple functions of $\theta$ that can be evaluated without empirical data. Fig. 2 shows the logarithmic relation.

**ESTIMATION FROM COMPOSITION**

One other untested idea is worth considering. As suggested previously, [1] the background can be estimated from the sample composition. This method is theoretically capable of compensating for absorption edges and other complex phenomena, but it is subject to experimental errors mentioned in Table 1. Background measurements could be used to compensate for these errors. Measured background divided by estimated background would be a nearly constant function of $\theta$ that could be interpolated.

**BACKGROUND INVARIANCE**

The functions previously discussed fall into two broad types. Type 1 functions, as defined here, express background as a function of a function of $\theta$. Type 2 functions express a function of intensity as a linear function of $\theta$.

If the background at $\theta$ can be determined from any background angle (from equation 1), so that

$$B[f(\theta)] = k_1 B[f(\theta_1)] = k_2 B[f(\theta_2)] \ldots ,$$  

then it can also be determined from a weighted average of values from multiple background angles, which is, of course, a linear combination of background measurements

$$B[f(\theta)] = a_1 B[f(\theta_1)] + a_2 B[f(\theta_2)] \ldots .$$  

Since it is a linear combination, an estimated background intensity interpolated as a function of any variable [e.g., $\theta, E, f(\theta)$, etc.] is not affected by a change in tube intensity. Additive invariance requires that the sum of coefficients

$$\sum a_i = 1.$$  

Proof: If

$$B'[f(\theta)] = B[f(\theta)] + \delta ,$$

then the estimated value of

$$B'[f(\theta)] = \sum a_i B'[f(\theta_i)] = \sum a_i B[f(\theta_i)] + \delta \sum a_i = B[f(\theta)] + \delta \sum a_i .$$

The estimated value $B'[f(\theta)] = B[f(\theta)] + \delta$ only if

$$\sum a_i = 1 .$$

The Lagrange interpolation formula meets this constraint. Consequently, interpolation of intensity is both additive-invariant and intensity-invariant; an average is intensity-invariant. It is recommended that the sum of coefficients be constrained by equation 13.
Type 2 functions may or may not be invariant, depending on the function. Log intensity interpolation is intensity-invariant. Estimation of background from composition is both intensity- and additive-invariant.

**DISCUSSION AND CONCLUSIONS**

Background can be measured at a single angle, but this method is not recommended except at angles near the peak. The estimate is intensity-invariant, and is additive-invariant if the coefficient is $\cong 1$.

Interpolation using three or more angles can be used to compensate for curvature without a reference blank. Curvature is compensated using Lagrange polynomial interpolation. Two or more angles are sufficient if reference standards are used (implicitly using a Type 1 function). The coefficients can be measured using at least n-1 blank reference standards, where n = the number of angles. The sum of coefficients should be constrained to 1. These methods are insensitive to changes in tube intensity and to constant added intensity. Both methods can be used with some, but not all, commercial software.

Two Type 2 transformations are suggested as alternatives, and can be used. Neither interpolation of log intensity, nor estimation from composition and measured values, require reference samples. Interpolation of log intensity is not additive-invariant.

In general, background methods have not been thoroughly studied. Some methods may not be very accurate over wide compositional ranges.

**ACKNOWLEDGEMENT**

I gratefully acknowledge discussions with Lars Couture, who provided the insight for equation 6.

---

**REFERENCES**