MINIMIZATION OF MICROABSORPTION EFFECTS IN COMPLEX MIXTURES

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ABSTRACT

In using X-ray diffraction (XRD) and the Rietveld method there are many factors that affect the results and the interpretation of the data that are collected. One of these is microabsorption. Microabsorption has historically been ignored or accounted for using the Brindley correction. This correction has come under much debate in recent years. A recent Round Robin study on quantitative analysis included data that was less accurate overall when the correction was used. This study focuses on examining factors that will aid in minimizing microabsorption effects and assessing microabsorption effects under various conditions; including absorption characteristics of the sample, absorption characteristics of the internal standard and particle size of the internal standard. The data was examined using the Rietveld refinement method, and the results were then compared with and without the Brindley correction.

INTRODUCTION

The goal of any quantitative procedure is to obtain the most accurate results possible. Within XRD, there are a number of factors that influence the accuracy of the results. One of the more problematic factors, particularly when dealing with complex mixtures such as coal combustion by-products (CCBs), cements/concretes and geologic materials, is microabsorption. Microabsorption stems from differences in the interactions of each material with the X-ray radiation. Each material will absorb the X-ray radiation to a different extent depending on its linear absorption coefficient for the particular wavelength (energy) of radiation being used. In many complex mixtures the differences in linear absorption coefficients are typically large (for instance, CCBs have linear absorption coefficients ranging from 81 cm\(^{-1}\) for quartz to 1153 cm\(^{-1}\) for magnetite using copper radiation).

Microabsorption is not a new concept in XRD. G.W. Brindley described microabsorption and developed a method for correcting for its effect in quantitative XRD in the mid-1940’s [1]. His work derived a correction factor, \(\tau\), for microabsorption based on the difference in the linear absorption coefficient for a given analyte \(\mu_a\) and the mean linear absorption coefficient of a mixture \(\bar{\mu}\), and the average particle radius of that analyte, \(R\), by numerical integration of

\[
\tau = \frac{1}{V_a} \int_{0}^{\mu_a} e^{-(\mu_a - \bar{\mu})x} dV_a
\]  

(1)

where \(V_a\) is the volume of a particle of an analyte \(a\), \(\mu_a\) is the linear absorption coefficient for an analyte \(a\), and \(x\) is the length of the path of radiation in a particle of \(a\) with volume element \(dV_a\). The results of this numerical integration are tabulated as a function of \((\mu_a - \mu)*R\) in Brindley's paper [1].
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

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The quantitative analysis protocol used here utilizes a modified version of an equation used by Taylor [2], as given in Equation 2 [3]:

$$Wt. \, Frac. \, A = \frac{(Wt. \, Frac. \, A)}{\tau_A} \sum_{j=1}^{\infty} \frac{(Wt. \, Frac. \, j)}{\tau_j}$$

there $\tau_A$ and $\tau_j$ are the Brindley corrections for phases A and j, respectively. Using the weight fractions calculated in a Rietveld refinement, a spreadsheet corrects for microabsorption effects post-refinement.

The Brindley correction for microabsorption has since been used in quantitative studies using the Rietveld method [2-5]. Initial studies in XRD of CCB materials indicated that microabsorption would be a potential problem [3-4]. Further studies involving a sub-micron particle size rutile internal standard contradicted this study, giving results that were more accurate without the Brindley correction for microabsorption [3-4]. Additionally, preliminary indications from the Quantitative Analysis Round Robin show that the Brindley correction for microabsorption may indeed reduce the accuracy of results obtained using the Rietveld method [5]. Furthermore, a recent study on the National Institute of Standards and Technology (NIST) Fly Ash Standard Reference Materials (SRMs) [6] and complex mixtures of known composition [7] using different radiation sources indicates that microabsorption may indeed be a problem with CCB materials, even with the small particle size internal standard.

This study focuses on microabsorption effects in complex mixtures and their effect on the accuracy of the results obtained using the Rietveld method. Mixtures having a wide range of linear absorption coefficients (both the materials used to make the samples and the samples themselves) were examined in order to gain a better qualitative feel for the effects of microabsorption in complex mixtures.

MATERIALS AND METHODS

Materials used for this study include CeO$_2$ (ceria, fluorite structure, Cerac, Inc.), Cr$_2$O$_3$ (Eskolaite, corundum structure, Cerac, Inc.), Al$_6$Si$_2$O$_{13}$ (mullite, Kyoritsu Ceramic Materials CO), SiO$_2$ (quartz, US Silica, Inc.), Fe$_2$O$_3$ (hematite, Aldrich), Fe$_3$O$_4$ (magnetite, Aldrich), silica gel (amorphous, EM Reagents), TiO$_2$ (rutile, DuPont, R900 grade), TiO$_2$ (rutile, Alpha Aesar), and ZnO (zincite, wurtzite structure, Alpha Aesar). The particle size and amorphous content of each material was determined, as shown in Table 1. The amorphous content was either determined using SRM 676, which is undergoing certification for amorphous content [8], or using the R900 grade rutile from DuPont. The amorphous content of the rutile was determined using SRM 676. The particle sizes of the materials were determined using either X-ray disc centrifuge particle size analysis or by point counting using a scanning electron microscope (SEM). Determination of the amorphous content allows for a greater confidence in the accuracies reported as the composition of the mixtures will be better defined, while the particle sizes are required for the Brindley correction for microabsorption.

Data were collected in Bragg-Brentano geometry, from 20-80° 2θ, with a step size of 0.03° and a counting time of 2 seconds per step. The data were analyzed using the Rietveld method [9] as...
implemented in the General Structure Analysis System (GSAS) [10]. The refinement protocol has been outlined previously [3,4].

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle Size</th>
<th>Amorphous</th>
<th>Material</th>
<th>Particle Size</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ (R900)</td>
<td>0.35</td>
<td>11.6</td>
<td>TiO₂</td>
<td>0.9</td>
<td>6.7</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.6</td>
<td>0.1</td>
<td>CeO₂</td>
<td>1.1</td>
<td>4.8</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.6</td>
<td>0.7</td>
<td>Al₆Si₂O₁₃</td>
<td>2.1</td>
<td>11.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.4</td>
<td>5.0</td>
<td>Fe₃O₄</td>
<td>3.5</td>
<td>26</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>1.7</td>
<td>6.0</td>
<td>CaSO₄·2H₂O</td>
<td>10</td>
<td>7.7</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1</td>
<td>5.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Particle Size and Linear Absorption Coefficient of Internal Standards

Two different rutile materials were chosen for this study. The first is a small particle size material used in coatings; the second is a “larger” particle size material. There are conflicting properties within the smaller particle size material; the smaller particle size should minimize microabsorption effects, while it has a larger surface area resulting in a higher amorphous content. A comparison of the weighted relative error for three mixtures using both rutile materials (Figure 1) indicates the two rutile internal standards show the same trends; however, the smaller particle size internal standard shows a lower weighted relative error for the uncorrected data than the larger particle size material. Focusing on the larger particle size rutile and the alumina, these internal standards have approximately the same particle size, while having different absorption qualities (alumina = 124cm⁻¹, rutile = 579cm⁻¹). Examining the results of three mixtures using these two internal standards indicates the rutile yields lower weighted relative errors for mixtures with linear absorption coefficients near that of the rutile (Figure 1). However, the errors associated with the alumina internal standard appear to decrease (relative to the rutile) in mixtures with larger linear absorption coefficients. This trend is unexpected, especially given the rutile results indicate the errors increase as the linear absorption coefficient of the mixture becomes further removed from that of the internal standard. For the alumina, the error appears not to follow this trend.

Figure 1. Comparison of relative errors when using different internal standards (smaller particle size rutile (R900), alumina, and larger particle size rutile).
**Trends in Errors for Individual Phases**

The typical description of microabsorption suggests that for a phase with a linear absorption coefficient less than that of the mixture, the intensity of the diffracted peaks for that material will be “increased” relative to a situation without microabsorption. The increased intensity would yield a positive relative percent error. The same logic indicates that when the linear absorption coefficient of the phase is more than that of the mixture, the diffracted intensity for that material will be “decreased” relative to a situation without microabsorption. This decrease in intensity will cause the weight fraction of the material to be underestimated, resulting in a negative relative percent error. This would in theory, in a simplistic view, yield a linear relationship between the error in a phase due to microabsorption and the linear absorption coefficient of the mixture, with a zero error at the point at which the linear absorption coefficient of the phase equals that of the mixture. Unfortunately, in realistic situations, there are other phases in the material, each adding a microabsorption effect. However, theory still predicts a linear relationship between error due to microabsorption and the linear absorption coefficient of the mixture (Figure 2). The results here tend to indicate that this is not the case. It appears that the errors for an individual phase are not as sensitive to the difference between the linear absorption coefficient of the phase and the average for the mixture, but rather on the difference between the linear absorption coefficient of the internal standard and the average for the mixture. The errors for an individual phase appear to fit a 2nd order polynomial whose minimum/maximum is located near the linear absorption coefficient of the internal standard when plotted versus the linear absorption coefficient of the mixture (Figure 2). The minimum/maximum of the curve appears to be shifted slightly from the linear absorption coefficient of the internal standard towards the linear absorption coefficient of the individual phase as noted in Figure 2 by the shifts of the minimum when quartz in the phase being examined and the shift of the maximum when Cr₂O₃ is the phase being examined.

**The Brindley Correction**

The two main concerns with microabsorption are (a) how to minimize microabsorption effects and (b) how to correct for its effect. We have already demonstrated that decreasing the particle size of the internal standard and choosing an internal standard with a linear absorption coefficient near that of the mixture (although the range of is fairly large) will lower the overall weighted relative error for a mixture. The second concern will be addressed here. Does the Brindley correction improve the accuracy of the data?

A comparison of corrected and uncorrected data can be seen in Figure 3. Examination of the data indicates that the corrected data shows less variability than the uncorrected data. In fact, the weighted relative percent errors for all three internal standards are all within the same range, contrary to the results for the uncorrected data.

**Effect of the Particle Size on the Brindley Correction**

The effect of the particle size used in the Brindley correction on the accuracy of the results has been examined previously [3,5]. This study seeks to verify the information provided by these studies. It appears that the Brindley correction tends to over-correct for phases with large
Figure 2. Graphical representation of (a) the theoretical relative percent errors for phases in mixtures with differing linear absorption coefficients for CeO$_2$, quartz, Cr$_2$O$_3$ and ZnO using small particle size rutile internal standard and (b) the relative error for quartz and Cr$_2$O$_3$ in mixtures with different linear absorption coefficients when the internal standard is rutile (small particle size) and alumina.

Figure 3. Comparison of the corrected and uncorrected weighted relative percent errors for small particle size rutile, large particle size rutile, and alumina internal standards for mixtures with varying average linear absorption coefficients.

particle sizes (>1-2 µm). This can be seen particularly when the mixtures from the Quantitative Phase Analysis Round Robin (QPARR) [5] are examined. The particles sizes for the materials used in the Round Robin study were reported as 28 µm for alumina, 1.4 µm for ZnO and 3.6 µm for CaF$_2$. Prior to evaluation of the data, the particle size of the alumina was confirmed by SEM analysis. The weighted relative error for the mixtures in the QPARR increase by approximately 500% when the Brindley correction is applied using the actual particle sizes of the materials mentioned above, as shown in Table 2. However, the weighted relative error decreases when a value of 2.8 µm is used for the particle size of the alumina.

CONCLUSIONS

The preliminary data indicates that when dealing with microabsorption there are a number of things to keep in mind when setting up your experiment. The internal standard appears to affect the accuracy of Rietveld results. Rutile, both particle sizes studied, is more accurate with mixtures having similar absorption coefficients. Alumina, however, seems to be less dependent
on the absorption coefficient of the mixture and gives results with lower errors in mixtures with high absorption coefficients (without using the Brindley correction).

Table 2. Examination of Particle Size on Average Weighted Relative Error and Maximum Relative Standard Deviation for All Phases in theQPARR (Participants is the Average Weighted Relative Error for the Average Reported Values for All Participants). Particle Size Used for Alumina is in Parentheses (in microns).

<table>
<thead>
<tr>
<th>Participants No Correction</th>
<th>Micro (2.8)</th>
<th>Micro (1)</th>
<th>Micro (28)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Weight. Err.</td>
<td>1.70</td>
<td>2.01</td>
<td>1.07</td>
</tr>
<tr>
<td>Max RSD</td>
<td>21.7</td>
<td>25.2</td>
<td>17.4</td>
</tr>
</tbody>
</table>

As Brindley indicated in his paper, microabsorption is particle size dependent. In particular for quantification, smaller particle size internal standards tend to give better overall results. However, Brindley predicts a linear relationship between the microabsorption error and the linear absorption coefficient, while these experiments appear to follow a 2nd order polynomial with an inflection point near the point at which the linear absorption coefficient of the mixture and internal standard are equivalent.

Use of the Brindley correction appears to stabilize the errors to approximately the same value, regardless of the linear absorption coefficient of the mixture or internal standard used. The correction is then useful for mixtures that have absorption coefficients significantly different than the internal standard. However, when a small particle size internal standard is used, the Brindley correction actually increases the error in the results. In addition, knowing the particle size of the materials is critical to employing the Brindley correction and the correction tends to fail when the particle sizes become larger than about 5 microns.

REFERENCES