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# FOURIER-FILTERING TECHNIQUES FOR THE ANALYSIS OF HIGH-RESOLUTION PULSED NEUTRON POWDER DIFFRACTION DATA

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## ABSTRACT

Rietveld profile refinements using high-resolution pulsed neutron powder diffraction data, collected at IPNS, often reveal broad intensity contributions from sources other than the crystalline materials being studied. Such non-crystalline intensity hampers standard Rietveld refinement, and its removal and/or identification is imperative for successful refinement of the crystalline structure. A Fourier-filtering technique allows removal of the non-crystalline scattering contributions to the overall scattering pattern and yields information about the non-crystalline material. In particular, Fourier transformation of residual intensities not accounted for by the Rietveld procedure results in a real-space correlation function similar to a radial distribution function (RDF). From the inverse Fourier transform of the correlation function a Fourier-filtered fit to the diffuse scattering is obtained. This mathematical technique was applied to data for crystalline quartz, amorphous silica, and to a simulated diffraction pattern for a mixture of the two phases.

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## INTRODUCTION

The development of Rietveld profile analysis[1,2,3] has revolutionized structure determination using neutron powder diffraction. High intensity, high resolution neutron diffraction data, as collected at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory[4], for

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example, are of sufficient quality to allow complete, detailed refinement of moderately complex structures, often in the presence of impurity crystalline phases. In addition, we have observed for a number of materials, particularly molecular-sieves[5], diffuse non-crystalline scattering components which actually begin to dominate the crystalline pattern at intermediate d-spacings. To facilitate complete and accurate refinement of the crystalline component(s) in such cases, it is necessary to devise a scheme for removing the diffuse components.

Possible sources of non-crystalline scattering include: (1) incompletely crystallized gels used in preparation of synthetic silicates and molecular sieves, (2) sample containers (glass or ceramic, for instance), (3) short-range ordering due to non-stoichiometry, etc., (4) thermal diffuse scattering (TDS) and (5) separate amorphous phase(s). Each of these scattering phenomena can be characterized as interference functions developed from short-range interaction of atoms in the sample. This scattering produces broad oscillations (relative to the Bragg scattering) superimposed on the crystalline pattern. The slowly oscillating nature of this scattering can be expressed in a physically meaningful way as the Fourier transform of a real-space correlation function, which in the case of scattering from an amorphous material, would be related to the atomic radial distribution function (RDF) for that amorphous component.

We report here a Fourier-filtering procedure whereby the anticipated form of the diffuse scattering is used to subtract previously unidentified non-crystalline contributions from the overall diffraction pattern, thus allowing completion of the crystalline refinement, while providing useful real-space information about the non-crystalline component(s), in the form of the calculated correlation function. The development of this procedure was motivated not only by the recognized need with molecular-sieve materials, but also by the recent success of other workers[6] in removing these non-crystalline contributions by fitting them with empirical functions.

**Theoretical Considerations**

Experimentally observed Rietveld intensities can be expressed, in reciprocal space, in the form:

$$Y_{obs}(Q) = [Y_C^X(Q) + Y_B(Q)] + Y_C^A(Q) \qquad (1)$$

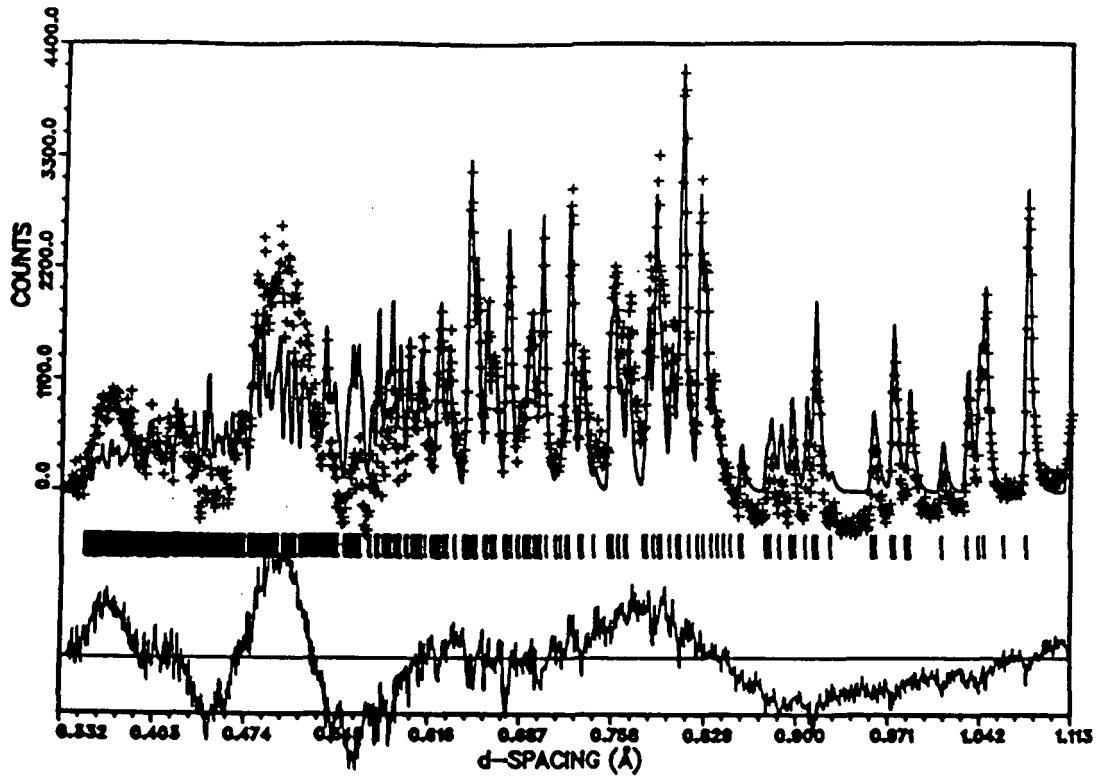


Figure 1. Rietveld profile fit for simulated quartz-silica mixture, from the backscattering (±150°) data banks on the SEPD time-of-flight powder diffractometer, before Fourier-filtering. The plus signs (+) are the observed, background subtracted intensities, $Y_{obs}(Q)-Y_B(Q)$. The solid line represents the calculated crystalline intensities, $Y_C^X(Q)$. The residual intensities, to be fit, are shown at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections. Note the poor fit due to the considerable non-crystalline scattering component.

where $Y_C^X(Q)$ are the calculated crystalline (Bragg scattering) intensities, $Y_B(Q)$ are calculated background intensities, $Y_C^A(Q)$ are the non-crystalline (distinct scattering) intensity contributions to be calculated and $Q = 4\pi\sin\theta/\lambda$ is the scattering vector. In a time-of-flight experiment data are collected in data banks centered about a number of fixed angles $2\theta=\pm150°$, $\pm90°$, $\pm60°$, $+30°$ and $-20°$, and the neutron wavelength is variable. Each data bank has its characteristic range of reciprocal space as determined by Bragg's equation. A typical Rietveld profile fit for a sample containing considerable non-crystalline scattering (a simulated quartz-silica mixture to be described below), before Fourier-filtering, is shown in Figure 1.

The objective of our Fourier-filtering procedure is to obtain values for $Y_C^A(Q)$ which are independent of the crystalline refinement, i.e., to

"filter" out sharp features (see Figure 1) in the Rietveld difference function, and remove these contributions from the Rietveld analysis. This necessitates representing the Rietveld difference intensities as the function Qi(Q) (shown in Figure 2 for the quartz-silica mixture) which in this case is related to (S(Q)-1), the distinct scattering part of the amorphous structure factor commonly used in glass diffraction analyses.

The correlation function D(r) is calculated as the 1-dimensional Fourier transform of Qi(Q):

$$D(r) = \frac{2}{\pi} \sum_{Q_{min}}^{Q_{max}} Q\, M(Q)\, i(Q)\, \sin(Qr)\, \Delta Q, \qquad (2)$$

where $i(Q)=[Y_{obs}(Q)-Y_C^X(Q)-Y_B(Q)]/Y_S(Q)$. M(Q) is a modification function which has the form $M(Q)=\sin(\pi Q/Q_{max})/(\pi Q/Q_{max})$. This function serves to ensure proper behavior at high Q values by converging to zero at $Q=Q_{max}$. $Y_S(Q)$ represents the incident white beam spectrum. D(r) contains maxima

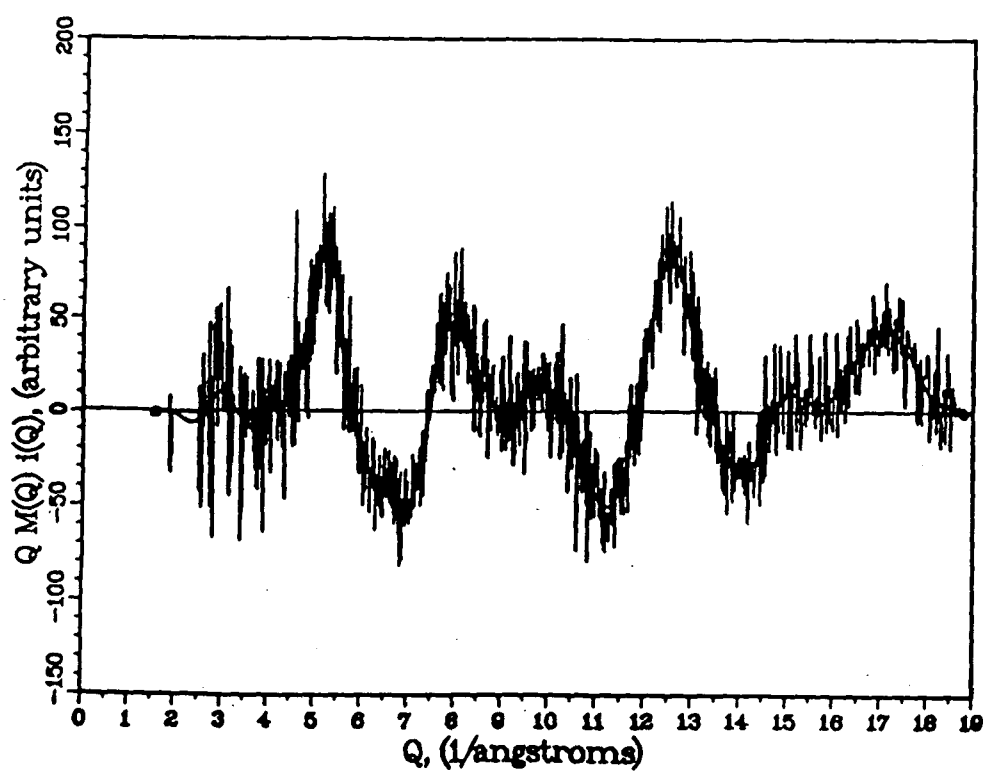


Figure 2. Residual intensities, QM(Q)i(Q), for simulated quartz-silica mixture, from the ±150° data banks, with an effective Q range of ~1.6-19.0 $Å^{-1}$. The jagged curve represents the raw data, while the smooth curve is the Fourier-filtered fit. A correlation limit ($r_{max}$) of 6.5 Å was used.

at interatomic spacings characteristic of the short-range interations giving rise to the non-crystalline scattering. D(r), derived from the quartz-silica mixture to be described below, for amorphous $SiO_2$ from the ±150° data banks is plotted in Figure 3. Comparable results are found from calculations using ±90° and ±60° scattering angle data.

From the inverse Fourier transformation of D(r), a smooth function $Y_C^A(Q)$ is calculated as:

$$Y_C^A(Q) = Y_S(Q) \sum_{r_{min}}^{r_{max}} D(r) \frac{\sin(Qr)}{(Qr)} \Delta r \qquad (3)$$

Filtering is accomplished by setting $r_{max}$ at some appropriate value, normally around 5-15 Å, depending on the range of significant correlation in the non-crystalline component. The smooth Fourier-filtered function is plotted along with the original Rietveld residual intensities in

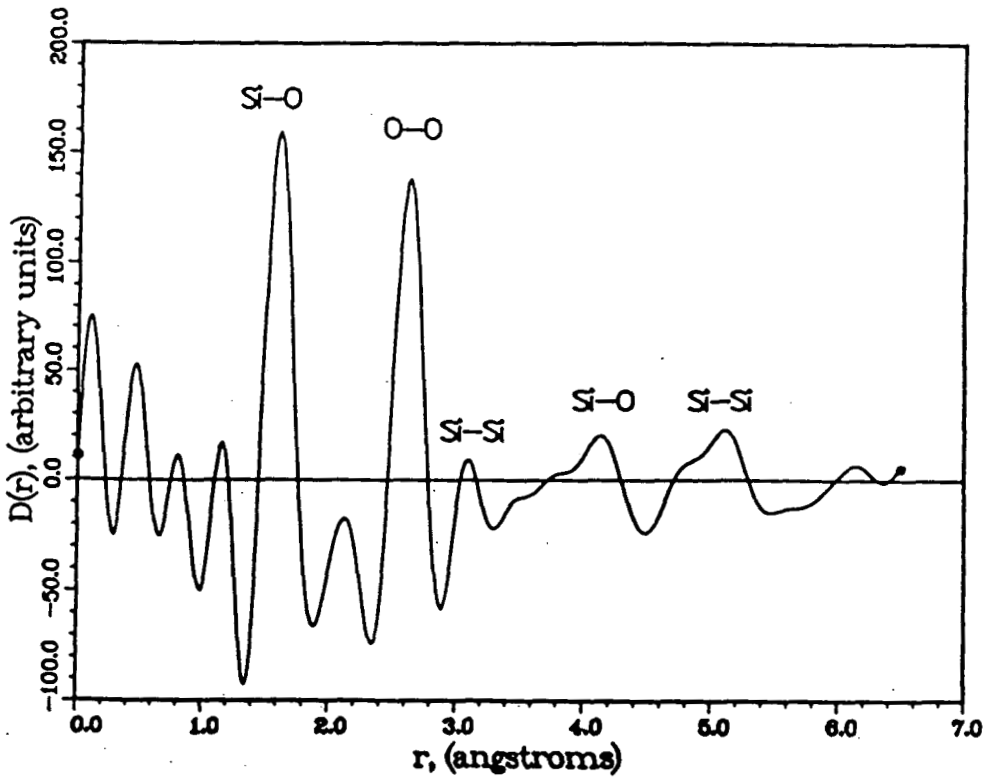


Figure 3. Correlation function, D(r), calculated from residual intensities, $[Y_{obs}(Q)-Y_C^X(Q)-Y_B(Q)]$, for simulated quartz-silica mixture, from ±150° data banks. Identifiable interatomic spacings are as follows: Si-O = 1.60, O-O = 2.63, Si-Si = 3.12, Si-O = 4.13, Si-Si = 5.11 Å. Additional unidentified features probably result from multiple scattering contributions, etc., which are currently ignored in this analysis.

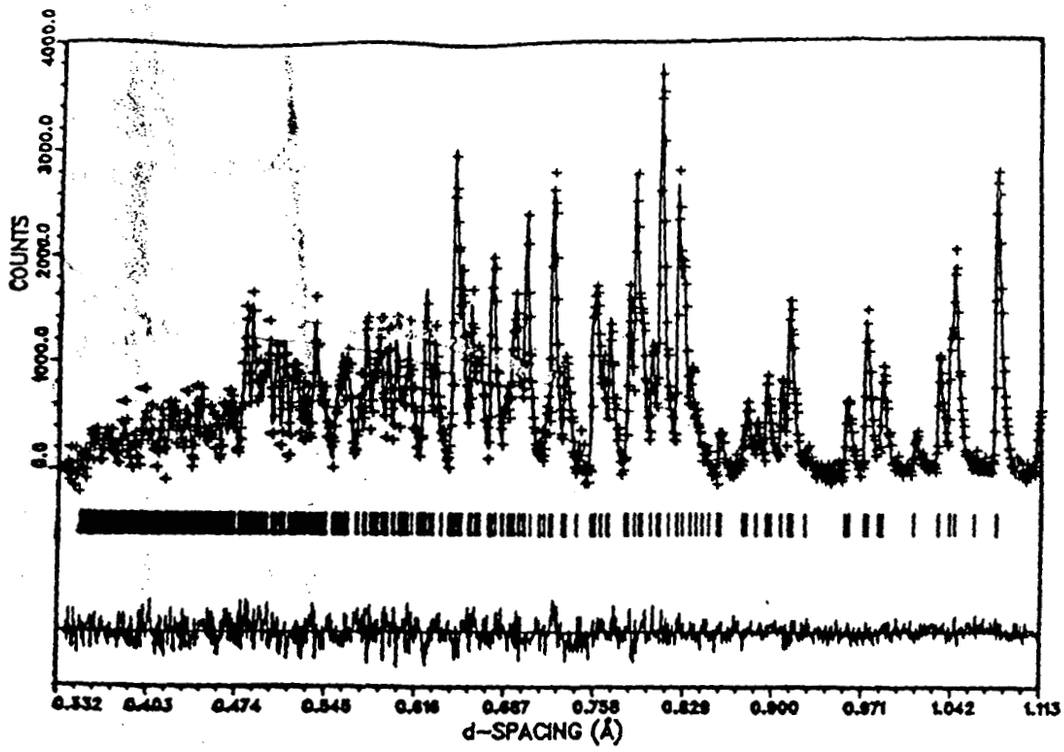


Figure 4. Final Rietveld profile fit for simulated quartz-silica mixture, after two iterations of Fourier-filtering. Note that the residual intensities have been reduced to zero, within the experimental error of the measurements, throughout the range of this plot. Symbol definitions are as described in Figure 1.

Figure 3. Figure 4 shows the final Rietveld profile fit for the simulated quartz-silica mixture after Fourier-filtering using a value of $r_{max}$=6.5 Å.

## ITERATIVE REFINEMENT PROCEDURE

Unfortunately, the crystalline and non-crystalline scattering are not completely decoupled. The overall reliability of the real-space non-crystalline information is strongly related to how well the crystalline model fits the Bragg scattering. Conversely, if there is a large contribution from non-crystalline scattering, refinement of the crystalline model will be effected. In particular, the Rietveld refinement will attempt to compensate for non-crystalline scattering by anomalously adjusting thermal parameters, etc. For these reasons it is important to devise an appropriate iterative procedure which will allow accurate refinement of the crystalline model, while simultaneously retaining information about the non-crystalline scattering.

The procedure used involves initial refinement of those structural parameters least effected by the non-crystalline scattering, using the original uncorrected data. This provides a reasonable starting point for the Fourier-filtering. As the analysis proceeds, crystalline refinements are done on corrected data only, and subsequent Fourier-filtering corrections are made based on intensity differences between the original uncorrected data and the improved crystalline model.

To illustrate the procedure and the accuracy of results, we have applied the Fourier-filtering procedure to data from a "purely crystalline" sample and from a mixed crystalline-amorphous sample, each with known composition. Neutron powder diffraction data were collected on the special environment time-of-flight powder diffractometer (SEPD) at IPNS for samples of crystalline α-quartz ($SiO_2$) and amorphous silica ($SiO_2$). A simulated pattern for a mixed sample was produced by summing together the data from these two samples. Conventional Rietveld refinement using the two data sets (α-quartz alone and α-quartz mixed with amorphous silica) revealed that both contained observable non-crystalline scattering components. These amorphous contributions were extracted by Fourier-filtering and the refinements were continued.

The iterative procedure followed in both cases was as follows: (1) refinement of structural parameters, including isotropic thermal parameters using the uncorrected data, (2) Fourier-filtering to produce the first corrected data sets, (3) continued refinement including anisotropic thermal parameters, using corrected data, (4) calculation of second corrected data sets by removal of first corrections and Fourier-filtering based on current crystalline structural models, (5) final refinements using second corrections.

## RESULTS

In this and other similar experiments it is important to determine how extensively the crystalline refinement is effected by such manipulation of the diffraction data and how meaningful the derived non-crystalline information is. Final crystalline structural parameters from the refinements of quartz and the quartz-silica mixture (after two iterations of Fourier-filtering) are tabulated along with results from a previous refinement of α-quartz[7] (also using IPNS data) in Table 1. The present refinements are in very good agreement with each other and, in fact, with the previous refinement.

Figure 3 shows that the interatomic spacings derived from the Fourier-filtering are as expected for an amorphous $SiO_2$ material. The precise structure of amorphous silica is obviously not known, but the first and second neighbor distances 1.60 and 2.63 Å are representative of approximately tetrahedral coordination of oxygen atoms around silicon. Similarly the third neighbor distance of 3.12 Å is consistent with inter-tetrahedral (Si-O-Si) angles of slightly less than 180°. Additional identifications at 4.13 and 5.11 Å are made based on packing of tetrahedra defined by the first, second and third neighbor coordination. From Fourier transform theory the reliability of these data will decrease with increasing correlation distance, so data beyond ~3.0 Å are only approximate. Unlabelled maxima in the correlation function are probably due to multiple scattering and absorption in the amorphous component which are partially compensated by the Rietveld background calculations but otherwise ignored at this point.

Table 1. Comparative refinements of quartz with and without amorphous silica component added (150° data bank, space group $P3_121$, with two independent atoms, Si and O). Two iterations of Fourier-filtering.

| Parameter | Quartz | Quartz-Silica Mixture | Reference[6] |
|---|---|---|---|
| Si, x | .4700(3) | .4696(4) | .4700(2) |
| y | .0000 | .0000 | .0000 |
| z | .3333 | .3333 | .3333 |
| $\beta_{11}$ | .0096(5) | .0095(8) | .0068(3) |
| $\beta_{22}$ | .0039(6) | .0053(10) | .0054(6) |
| $\beta_{33}$ | .0027(3) | .0025(5) | .0044(6) |
| $\beta_{13}$ | -.0018(7) | -.0029(12) | .0006(2) |
| O, x | .4131(2) | .4133(3) | .4131(2) |
| y | .2675(2) | .2672(3) | .2677(2) |
| z | .2151(1) | .2146(2) | .2144(1) |
| $\beta_{11}$ | .0148(4) | .0166(7) | .0195(4) |
| $\beta_{22}$ | .0130(4) | .0124(6) | .0120(3) |
| $\beta_{33}$ | .0070(2) | .0072(3) | .0072(1) |
| $\beta_{12}$ | .0097(4) | .0097(6) | .0104(3) |
| $\beta_{13}$ | .0016(2) | .0012(4) | .0023(2) |
| $\beta_{23}$ | .0026(2) | .0025(3) | .0045(2) |
| $a_0$, $b_0$ | 4.9137(1) | 4.9136(1) | 4.9141(1) |
| $c_0$ | 5.4053(1) | 5.4054(1) | 5.4060(1) |
| $R_{wp}$, % | 4.41 | 2.26 | 3.11 |
| $R_{exp}$ | 3.43 | 1.88 | |

For this relatively simple crystalline material, two iterations of Fourier-filtering were needed. More than two iterations might be expected for more complex structures, depending on the correctness of the crystalline model in the initial stages of the analysis.

This Fourier-filtering technique is currently being applied in the analysis of $AlPO_4$ and $AlSiO_4$ molecular-sieves. Preliminary results[5] show that Fourier-filtering does facilitate completion of the crystalline refinement of these materials. Is is not known whether the non-crystalline scattering observed in these data is due to short range ordering in the sample or from a separate amorphous phase. The calculated correlation functions are, however, consistent with those expected for amorphous materials having chemical compositions $AlPO_4$ and $AlSiO_4$, respectively.

## CONCLUSION

Fundamental to the Fourier-filtering technique is the use of only low order harmonics in the Fourier summation. With this we fit only slowly oscillating features in the residual intensity function which are not due to errors in the crystalline model, thus minimizing correlations between the crystalline and non-crystalline scattering components and allowing us to treat them simultaneously as separate phases. The Fourier-filtering is done on the entire diffraction pattern, providing us with useful structural information about both the crystalline and non-crystalline components.

Results presented here - using data prepared from the summing of separately measured crystalline and amorphous $SiO_2$ diffraction data - demonstrate the effectiveness of the Fourier-filtering technique. Additional experiments with truly mixed crystalline and amorphous samples will be performed to more thoroughly determine the role of multiple scattering and absorption in these multi-phase samples and to further assess the accuracy of derived non-crystalline correlation data.

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