Recommendations for Calculated Reference Powder Diffraction Patterns

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Abstract

The use of calculated powder patterns within the materials diffraction community has been described and referenced many times in the past. However, with the availability of increasing amounts of single-crystal-derived structural information, calculating powder patterns for identification and comparison may be easier, in some circumstances, than generating experimental reference patterns from well-characterized materials. For this reason, a task group of members of the International Centre for Diffraction Data, was formed "to make recommendations on the calculation of powder diffraction patterns and the use of these data for the characterization of crystalline materials."

Introduction

The use of calculated powder diffraction patterns can range from substituting calculated d-1 values for unavailable experimental reference patterns to that of modeling complex structural features of materials. [McCarthy, Martin, Holzer, Grier (1992)] Issues surrounding the parameters and methodologies for calculating diffraction patterns have been discussed for many years at the International Centre for Diffraction Data (ICDD), as well as within the broader powder diffraction community. In October 1992 a task group was formed to develop a set of recommendations for calculated patterns that were to be incorporated in the Powder Diffraction File.

Calculated diffraction patterns can be used for calculating reference intensity ratios [Hubbard, Evans, Smith (1976)], simulating ill-ordered materials [Reynolds (1989); Martorana, Deganello, Duca (1994)], validating experimentally observed intensities [Lowe-Ma (1991)], confirming structure type and phase purity [Cantrell, Beiter, Sullenger (1988); Blanchard (1986); Steele & Biederman (1994)], and for quantitative analyses [Smith, Johnson, Wims (1988); Sny-

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der & Bish (1989)]. In developing its recommendations, the task group specifically targeted the use of calculated patterns in phase identification. For that reason, the task group consciously limited the scope of its recommendations while recognizing that simulated patterns, which could include a variety of geometric configurations and optical conditions, would probably more accurately reflect observed diffraction data.

**Recommendations**

The recommendations below have been approved by the Board of Directors of the International Centre for Diffraction Data and are consistent with ICDD's current editorial guidelines for calculated patterns submitted to the Powder Diffraction File.

I. **Source of coordinate data.**

   *Only diffractometer- or synchrotron-derived single-crystal structure results are to be used as a source for the coordinate data.*

II. **Calculational parameters.**

   A. *Anisotropic thermal parameters are to be used if available. If anisotropic thermal parameters are not available, individual isotropic thermal parameters can be used.* (The use of an overall thermal parameter is unacceptable.)

   B. *Neutral atom scattering factors are to be used, but should include anomalous scattering.*

   C. *Intensities are to be calculated using copper Kα1 X-radiation only.*

   D. *If optical effects due to Bragg-Brentano geometry are included, current experimental conditions representative of data already in the Powder Diffraction File should be matched.* For example, intensities should be calculated for fixed slits with no incident or diffracted-beam monochromator and for a thick (flat) sample.

   E. *Crystallite-size broadening effects on profiles and intensities are not to be included.*

   F. *Pseudo-Voigt profiles with narrow full-width-at-half-maximum values representative of modern higher-resolution diffractometer data are to be used for convolution with the intensity delta functions.*

   G. *Reasonably complete 2θ ranges are to be reported.* Clearly, the lowest 2θ angle of the calculated pattern should be below the position of the first calculated peak position. The highest 2θ angle should represent some reasonable compromise between completeness and practicality. For small unit cells (and copper Kα X-radiation) a reasonable 2θ range might be 10° - 120°; for moderate unit cells the range might be 5° - 100°. For
large unit cells a reasonable 2θ range might be 1° - 80°. (Note that these suggested ranges are those of most value for general phase identification work but would usually be considered inadequate for powder-based crystal structure refinements.) *The profile should be calculated with a step size 0.02° (2θ).*

III. Additional information needed for inclusion of the calculated pattern in the Powder Diffraction File.

Complete, calculated profiles will contribute to next-generation databases consisting of full digital patterns. To facilitate evaluating the veracity of the calculated pattern, the following information is to be included with submission of a calculated pattern.

A. *The computer program should be specified, and, to verify its computational "correctness" and accuracy, a "standard" pattern is to be calculated and submitted; peak positions and integrated intensities along with a complete step-by-step profile are to be included for the "standard" pattern.*

B. *Complete reference documentation of the single-crystal structure determination used as the basis of the calculation and the source of unit cell parameters, coordinates, and thermal parameters for the calculated pattern must be specified and included. In addition, the density, the formula, and bond distances are to be calculated from the coordinates and site occupancies actually used in generating the calculated pattern.*

C. *All calculational parameters (as per Section II above) must be described.*

D. *The data for a calculated pattern when submitted will include: (1) a list of peak positions and integrated intensities for peaks with \( I_{\text{calc}} > 0.1\% \) (overlapped peaks with multiple indexing can be so indicated with one or two of the most significant \( hkl \)'s followed by an "M"); and (2) a full, 0.02° step-by-step, digital pattern.*

The task group recognizes and *emphasizes* that optical and instrument-specific effects, as well as specimen effects, beyond those considered in Section II (above) will affect experimental intensities. Calculated and experimental intensities will differ to the extent that these effects are not included.

**Further Recommendations - the FWHM Function**

The recommendation for the profile function, as originally approved and endorsed (II.F. above), was too ambiguous to provide adequate guidelines for modifying existing computer
code. The following recommendation, which contains a more specific guideline for the full-width-at-half-maximum profile function for a calculated powder pattern, has also been approved by the ICDD.

IV. Clarification of Recommendation II.F.

*Reference calculated patterns should represent narrow divergence and higher-resolution diffraction conditions.* A Cagliotti function is often used to describe the variation of peak profile width with angle:

$$FWHM^2 = U \tan^2 \theta + V \tan \theta + W.$$  

However, the task group recognizes that the Cagliotti function does not adequately model experimental data under all optical conditions, especially at low angles, and therefore, *recommends for calculating powder patterns the use of the function*

$$FWHM^2 = A \tan^2 \theta + B \tan \theta + C + D \cot^2 \theta$$  

with $A = 0.002717$, $B = -0.00076$, $C = 0.003638$, and $D = 0.0000649$. See Cheary & Cline (1994) for additional discussion of this function. *Corresponding values to be used in the Cagliotti function (if the recommended four-parameter $FWHM^2$ function is not available) are $U = 0.003092$, $V = -0.00219$, and $W = 0.00476$.*

The data from which these coefficients are derived were obtained from a pressed specimen of NIST Standard Reference Material, SRM 660 (LaB$_6$), which is certified for use as a line profile standard [Rasberry (1989)] and introduces a minimum of specimen-induced profile broadening to the observed profiles.  

Powder diffraction data obtained from NIST SRM 1976 and submitted to the ICDD for a variety of diffractometers under various conditions have recently been studied. SRM 1976 is a sintered alumina plate certified for measurement of instrument sensitivity [Reed (1991)], and, although not certified as a profile-shape standard, this SRM also exhibits a minimum of sample-induced profile broadening. The profile widths calculated from the submitted data yield average values of $U = 0.0065$, $V = -0.0040$, $W = 0.0070$ as coefficients in the Cagliotti function. These values should not be assumed to represent high resolution conditions and are not part of the recommendation. They do, however, represent an estimate of the magnitude of the $U$, $V$, $W$ values that

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*Data were collected on a Siemens D5000 diffractometer using theta-theta geometry and a long fine-focus Cu tube operating at 45kV and 40mA. The optical conditions consisted of: a 0.40 degree divergence slit, a 0.053 degree receiving slit, a goniometer radius of 216mm, a graphite post monochromator, and incident Soller slits with an aperture of ~2 degrees. The sample was spun while the data were collected. FWHM values were obtained from a least-squares refinement of a split-Pearson VII function against the observed profiles using Siemens Diffrac AT software. The coefficients were obtained by curve fitting the observed FWHM values against the FWHM functions. Commercial equipment and manufacturers have been identified in order to adequately specify the experimental procedure and do not imply a recommendation or endorsement by the ICDD, the National Institute of Standards and Technology, nor the authors.*

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might be expected for a Cagliotti FWHM function from a diffractometer under somewhat lower resolution conditions.

Acknowledgments

Discussion of calculated powder patterns within the materials diffraction community has occurred many times and programs for such calculations have existed for a number of years [Smith (1963); Jietschko & Parthe (1965); Jahanbagloo & Zoltai (1966); Smith (1989)]. In addition to the task group members, a number of specialists in the field contributed many substantive comments and suggestions while consensus on the recommendations was being reached. Although the following list is certainly not complete, the task group does wish to recognize the helpful contributions made by L. A. Andrews, J. Dann, C. R. Hubbard, R. Jenkins, D. Louër, R. L. Snyder, and J. Visser.

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