

**12.X-09** CRITICAL REVIEW OF PEAK FINDING/REFINEMENT. R. L. Snyder, Alfred University, Alfred, New York, 14802, and J. W. Edmonds, Dow Chemical Company, Midland, Michigan, 48640.

Methods for locating peaks in digitized powder diffraction patterns have developed along two branches: off-line application of numerical procedures to the collected digital pattern, and on-line use of an intelligent algorithm to collect the data. The latter approach allows real time optimization of step width and count time and should produce the highest quality results. However, current algorithms are relatively simple and inferior to the off-line procedures.

Off-line methods have settled into two productive directions. One is the Parrish technique of profile fitting, which implicitly corrects for all instrumental aberrations and simultaneously produces refined peak positions and integrated areas. The other method is more widely used and involves algorithms with all or most of the following:

- 1) Background determination--normally a  $\pm n\sigma$  approach
- 2) Noise determination or elimination
- 3) Data smoothing--signal averaging, Fourier transform and digital filtering
- 4) Peak position determination--usually second derivative
- 5) Spectral stripping--usually a Rachinger correction
- 6) Peak refinement--profile refinement dominates

Current research indicates that future algorithms will be dominated by profile fitting methods. Profile fitting is a substantially improved method for precisely locating the peak centroid, or 'best position' for diffractometer and film work. This technique involves least square fitting of an analytically or experimentally optimized peak shape to data points across the entire observed peak profile. Since the minimization of differences can occur across the entire peak shape, the final position is less susceptible to spurious noise. This noise usually affects the peak shape adversely at data points near  $I_{\max}$  where the second derivative is most sensitive.

It is due to a low signal/noise ratio, even under the most favorable of x-ray diffraction conditions, that the operationally preferred second derivative function has limitations in the accuracy with which it can locate the best peak position. In addition to the discrepancy between 'observed' and 'true' peak position that results from overlapping peaks, the second derivative function with simultaneous smoothing will produce two different peak positions for broad peaks depending on the scanning or 'processing' direction (i.e., high to low angle, or vice versa). For reasonably sharp isolated peaks, the second derivative function can locate individual peak positions with a precision,  $\Delta d/d$ , of 5 to  $10 \times 10^{-4}$ ; for broad peaks, resulting from crystallite size of  $\sim 100 \text{ \AA}$ ,  $\Delta d/d$  can be as high as  $3 \times 10^{-3}$ . With profile fitting, however,  $\Delta d/d$  is usually 5 to  $10 \times 10^{-5}$  and may be as low as  $5 \times 10^{-6}$ . A premium is placed on data quality, not quantity, so fewer data points are required across a peak to accurately refine peak position.

Various approaches to profile fitting will be discussed and include:

Profile Type	User *	Application
Multiple Lorentzians	Parrish D	Peak location and refinement
Modified Lorentzian	Werner, D Cox, Young	Rietveld refinement
Voigt	Langford D	Crystallite size
Split Pearson Type VII (Variable shape)	Edmonds F/D	Peak location, refinement, and crystallite size

\*D = diffractometer, F = film

**12.X-10** PROFILE REFINEMENT. By P.-E. Werner, Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, Fack, S-106 91 Stockholm, Sweden.

Profile refinement of powder diffraction data as a tool for structure determination will be discussed in terms of 'real world problems'. Accurate data collection, profile analysis without structural information and refinement using the crystal structure itself to fit the diffraction pattern can be regarded as three complementary profile refinement steps. The possibilities to identify impurities and index an unknown phase are strongly related to the resolution and accuracy of the measuring system. By use of a microcomputer controlled film-scanner without any lenses, prisms or mirrors, high quality data can be extracted from photographs obtained in a well adjusted Guinier camera. Transmission geometry and internal standard technique also greatly reduce the problems of zero calibration and geometrical aberrations. Unfortunately, the ideal samples usually used to illustrate line profile analysis and Rietveld refinement procedures are rare. The weak link in a structure determination using a profile refinement technique is not necessarily the lack of an accurate profile function. Impurities, line broadening and preferred orientation are often more cumbersome problems to overcome. Although parameters may be derived with limited precision, the Rietveld technique appears to be a powerful tool for structural studies; recent structure determinations of unstable  $\text{CaC}_2(\text{NH}_3)_n$  ( $n = 2-8$ ) phases and the hydrogen storage compound  $\text{NiMg}_2\text{H}_4$  will serve to illustrate this.

**12.X-11** POWDER DATA COLLECTION AND ANALYSIS MINI COMPUTERS AND SEARCHING. By Gerald G. Johnson Jr., Associate Professor of Computer Science, The Pennsylvania State University, University Park, Pennsylvania.

The remarkable advances of the past decade in automated single crystal diffractometry are now being paralleled in automated powder diffractometry. This breakthrough has been developed along with more and more powerful (in terms of both CPU capability and on-line storage) mini computers. These advances have thus allowed the introduction of powerful algorithm techniques for processing of experimental data in powder diffractometry (as discussed in the first five papers).

It is the purpose of this paper to discuss the advances in the identification of crystalline phases from a set of standards. The author of this paper and others (notably Frevel and Nichols, independently) developed publicly available search and match methods over fifteen years ago, but these initial approaches were on large-scale batch-oriented mode computer hardware (main frames). Since that time, many others have made use of the increased power of today's computers to perform the same task, by now in interaction mode. A review of the present state of the art of known computer/diffractometer systems will be compared, and certain guidelines will be established. Illustration of algorithm approaches, along with the use of the JCPDS File, will be pointed out in this talk.