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 diff-
raction patterns have developed along two branches: off-
line application of numerical procedures to the collected
digital pattern, and on-line use of an intelligent algo-
rithm 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 di-
rections. One is the Parrish technique of profile fit-
ting, 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 fit-
ting is a substantially improved method for precisely
locating the peak centroid, or 'best position' for diff-
ractometer 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 diff-
erences 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 func-
tion 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 deriv-
ative 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 lo-
cate individual peak positions with a precision, $\Delta d/d$,
of 5 to 10 x 10^{-4}; for broad peaks, resulting from
crystallite size of ~ 100 Å, $\Delta d/d$ can be as high as 3 x
10^{-3}. With profile fitting, however, $\Delta d/d$ is usually
5 to 10 x 10^{-5} and may be as low as 5 x 10^{-6}. A prem-
ium 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 dis-
cussed 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, Depar-
tment 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 re-
finement using the crystal structure itself to fit the
diffraction pattern can be regarded as three complemen-
tary 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 geo-
metry 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 tech-
nique is not necessarily the lack of an accurate profile
function. Impurities, line broadening and preferred
orientation are often more cumbersome problems to over-
come. Although parameters may be derived with limited
precision, the Rietveld technique appears to be a power-
ful tool for structural studies; recent structure deter-
minations of unstable $CaCl_2(NH_3)_n$ (n = 2-8) phases and
the hydrogen storage compound $NiMg_2H_4$ 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.