

12.X-04 PROFILE FUNCTIONS IN RIETVELD ANALYSIS.

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Some structural results obtained in Rietveld analyses can depend significantly on the choice of reflection profile function used. Which profile function is the most appropriate depends on both the instrument and the specimen. While a Gaussian representation is quite suitable for energy-dispersive data taken with synchrotron radiation (Glazer, Hidaka & Bordas, 1978, *J. Appl. Cryst.*, **11**, 165-172) and reasonably though not entirely suitable for neutron angle-dispersive data (Suortti, 1980, NBS Special Publ. 567, 1-20), it is often distinctly not the best choice for use with Guinier camera data (Malmros & Thomas 1977, *J. Appl. Cryst.*, **10**, 7-11) nor with x-ray θ - 2θ diffractometer data, to which the remaining comments specifically apply. No known choice of profile function is ideal. The relative unsatisfactoriness of various functions can be assessed, in part, by comparisons both of various R values and of obs - calc pattern-difference plots for Rietveld refinements using the different profile functions with the same data.

R_{Bragg} is mainly sensitive to the fit of the crystal structural model; $R_{\text{weighted-profile}}$ and the difference plots are also sensitive to the disparities between the calculated and observed profile shapes and background functions. The profile functions most explored experimentally in Rietveld analysis are the Gaussian (G) for which $I(x) \propto \exp(-k^2x^2)$ and the Lorentzian-related functions, $I(x) \propto (1 + k^2x^2)^{-n}$, wherein the function is a Lorentzian (L) if $n=1$, a modified Lorentzian (ML) if $n=2$, and an "intermediate Lorentzian" (IL) if $n=1.5$. Also being explored are a pseudo-Voigt function (Wertheim, Butler, and Buchanan, 1974, *Rev. Sci. Instrum.*, **44**, 11, 1369-1371) used by Hindeleh and Johnson (1978, *Polymer*, **19**, 27-32) and the Pearson VII function used by Immirzi (1980, *Gazz. Chim Ital.*, **110**, 381-387). Tests were carried out with these six functions (including an asymmetry factor) and X-ray powder patterns having differing degrees of profile broadening. The isotropic temperature factors were especially strongly affected ($>5\sigma$) by the choice of profile function while background and site occupancy parameters were only marginally affected. Not significantly affected were positional and lattice parameters. The G function generally gave the distinctly poorest results of the six; which function was (often marginally) "best" depended on the reflection profile breadths and on which criterion (e.g., R_B or R_{WP}) was used.

Other profile functions which have been successfully used or suggested may yield better results when similar comparisons are made. These include a polynomial function used by Baerlocher & Hepp, (1980, NBS Special Publ. 567, 165), the Voigt function examined by Langford (1978, *J. Appl. Cryst.*, **11**, 10-14) and by Suortti, Ahtee & Unonius (1978, U. Helsinki Report Series in Physics HU-P, **63**, 16pp) and the Edgeworth series suggested by Wilson (1973, *J. Appl. Cryst.*, **6**, 230-237). The Edgeworth series is especially interesting because it has a physical rationale based on the central limit theorem and can accommodate skewness and kurtosis. Various investigators' current assessments of the usefulness of these functions for Rietveld analyses are reviewed.

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12.X-05 ESTIMATION OF UNCERTAINTY IN STRUCTURE

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The estimation of uncertainty requires consideration of the related, but nevertheless distinct, questions of statistical precision and of possible bias. Experimental observations may usually be assumed to be uncorrelated, because any one observation is not influenced by the fact that other observations have been made of the same or different quantities at the same or different times. This being the case, if the model is consistent with the data, each term consisting of the squared difference between observed and predicted values, expressed as a fraction of the variance of the observation, contributes, on the average, $(n-p)/n$ to the sum. Here n is the total number of data points, and p is the number of adjusted parameters in the model.

In the Rietveld [*J. Appl. Cryst.*, **2**, 65 (1969)] method of powder refinement the observations are the intensities at specific points in a powder pattern and are assumed to have the Poisson distribution characteristic of random events. The model is a set of peaks with an assumed shape, whose integrated areas are functions of the crystallographic parameters. Denoting the weighted sum of squared residuals by S^2 , $S^2 \approx (n-p)$ if the model fits the data, and, provided the numbers of counts in the individual data points are large enough, has the χ^2 distribution with $(n-p)$ degrees of freedom. Hypothesis tests based on the χ^2 distribution may be used to assess the adequacy of the model. If the tests show the model to fit the data, and the model has allowed all important parameters to vary, then the inverse of the Hessian matrix is the variance-covariance matrix for the parameters and the standard deviations of the individual parameters are the square roots of its diagonal elements.

The e. s. d. s are measures of precision, the minimum width of an interval within which the "true" value of the parameter may confidently be assumed to lie. For good precision to translate into corresponding accuracy it is required that the model be free of bias, which arises when the model implicitly assumes an incorrect value for some parameter that is correlated with the ones in which we are interested. For example, an incorrect wavelength will obviously bias the values of the cell constants, while neglect of the attenuation of the beam in the sample will bias all temperature factors. An incorrect peak-shape function also tends to bias temperature factors, as does an incorrect background level. Although the peak shapes in neutron diffraction are usually Gaussian, they are not always. Analyses should therefore include a study of the shapes of resolved peaks. If the peak shape function is satisfactory, background may be included as a refineable parameter and estimated even in the absence of points in a broad range that contain no contribution from a Bragg reflection.

Two or more models that appear to be within the range of adequate fit may be compared with one another by use of statistical tests, such as Hamilton's R-factor ratio test, based on the F distribution. If, however, statistical tests indicate that the model is not adequate, there must be at least one missing parameter, and both precision and bias depend on the unknown correlation between this parameter and the refined ones. Thus the confidence interval cannot be determined by means of statistical techniques.

If the powder pattern is well resolved, and if the criteria for adequate fit are satisfied, substantially identical results may be obtained by using integrated intensities, instead of the intensities at individual points, as the data. However if peaks are not resolved, their integrated intensities are correlated, and the weight matrix is not diagonal. The estimation of uncertainty in this case is hampered by a conceptual difficulty in defining the rank of a non-singular but possibly ill-conditioned matrix.