ANALYTICAL METHOD FOR OBSERVED POWDER DIFFRACTION INTENSITY DATA BASED ON MAXIMUM LIKELIHOOD ESTIMATION

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ABSTRACT

A new methodology based on maximum likelihood estimation for structure refinement using powder diffraction data is proposed. The method can optimize not only the parameters adjusted in the Rietveld refinement, but also parameters to specify errors in a model for the statistical properties of the observed intensity. The results of the structure refinements about fluorapatite Ca₅(PO₄)₃F, anglesite PbSO₄ and barite BaSO₄ are demonstrated. The structure parameters of fluorapatite and barite optimized by the new method have become closer to single-crystal data than those optimized by the Rietveld method, while the structure parameters of anglesite, the values of which optimized by the Rietvled methods are already in good coincidence with the single-crystal data, are almost unchanged by application of the new method.

1. INTRODUCTION

The Rietveld refinement is an application of the weighted least-squares method to experimentally observed powder diffraction intensity data, based on the model for the crystal structure, peak profile and background intensities. In principle, the errors in optimized values of crystallographic parameters such as lattice constants, atomic positions, etc can be evaluated by the Rietveld method, if the experimental errors are known quantities. However, we often encounter too small statistical errors in the output of Rietveld programs, particularly in the cases: (i) strong X-ray source, (ii) long measurement time, (iii) high-resolution optics, (iv) high-sensitivity detectors, and (v) samples with high crystallinity and large scattering cross section. It means that the assumed experimental errors tend to be underestimated in those cases. Then the solution should simply be the use of appropriate values for the assumption about the experimental errors.

It has already been suggested that the statistical variance in observed powder diffraction intensities is dominantly caused by the finite number of particles that satisfy the diffraction condition, when the size of crystallites is not small enough (Alexander et al., 1948). This effect is referred as “particle statistics” (de Wolff, 1958), and it has experimentally been confirmed (Ida et al., 2009) that the observed statistical variance $\sigma^2$
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can be modeled as the sum of counting statistical variance \( (\sigma_c)_j^2 \) approximated by the expected value of the number of counts \( y(2\Theta_j) \) at the diffraction angle \( 2\Theta_j \), and particle statistical variance \( (\sigma_p)_j^2 \), that is,

\[
\sigma_j^2 \approx (\sigma_c)_j^2 + (\sigma_p)_j^2,
\]

\[(\sigma_c)_j^2 \approx y(2\Theta_j).\]  

The particle statistical variance \( (\sigma_p)_j^2 \) can be formulated by (Alexander et al., 1948; De Wolff, 1958; Ida et al., 2009)

\[
(\sigma_p)_j^2 \approx \frac{C_p [y(2\Theta_j) - b_j]^2 \sin \Theta_j}{(m_{\text{eff}})_j},
\]

where \( C_p \) is an unknown proportionality factor, \( b_j \) is the background intensity, and \( (m_{\text{eff}})_j \) is the effective multiplicity for reflection, defined by

\[
(m_{\text{eff}})_j = \frac{[y_1(2\Theta_j) + \cdots + y_m(2\Theta_j)]^2}{[y_1(2\Theta_j)]^2 + \cdots + [y_m(2\Theta_j)]^2},
\]

when \( m \) different reflections contribute to the observed intensity as follows,

\[
y(2\Theta_j) = b_j + y_1(2\Theta_j) + \cdots + y_m(2\Theta_j).
\]

It is quite likely that the statistical error proportional to the observed intensity also affect the statistical properties of the measured data, as has been suggested by Toraya (1998, 2000). Then we have assumed a three-term model for the statistical errors,

\[
\sigma_j^2 \approx (\sigma_c)_j^2 + (\sigma_p)_j^2 + (\sigma_r)_j^2,
\]

\[(\sigma_r)_j^2 = C_r [y(2\Theta_j)]^2,
\]

where \( C_r \) is another unknown proportionality factor in the statistical model for the observed powder diffraction intensity data.

The unknown parameters \( C_p \) and \( C_r \) in the statistical model cannot be optimized by the Rietveld method, but can be estimated from the experimental data by applying a
“maximum likelihood estimation” as an alternative to the least-squares method. In this article, the concept of the new methodology for analysis of powder diffraction data based on maximum likelihood estimation is described, and the results of analyses on fluorapatite Ca$_5$(PO$_4$)$_3$F, anglesite PbSO$_4$ and barite BaSO$_4$ are demonstrated.

2. MAXIMUM LIKELIHOOD ESTIMATION

Suppose that diffraction intensities \( \{Y_i, \cdots, Y_N\} \) observed at diffraction angles \( \{2\Theta_1, \cdots, 2\Theta_N\} \) are normally distributed around an appropriate model \( y(2\Theta_j) \) with a statistical error of \( \{\sigma_j\} \) at each data point. Then the probability \( P \) that this data set should be realized is given by

\[
P = \prod_{j=1}^{N} \frac{1}{(2\pi)^{1/2} \sigma_j} \exp \left(-\frac{\Delta_j^2}{2\sigma_j^2}\right),
\]

where \( \Delta_j \equiv Y_j - y(2\Theta_j) \) is the deviation of the observed intensity \( Y_j \) from the average intensity \( y(2\Theta_j) \). The maximum likelihood estimation means the optimization of the statistical model to maximize the probability \( P \), which is exactly equivalent to the minimization of the “unlikelihood estimator” \( U \) defined by

\[
U \equiv -2\ln P - N \ln(2\pi) = \sum_{j=1}^{N} \left(\frac{\Delta_j^2}{\sigma_j^2} + \ln \sigma_j^2\right).
\]

Note that the Rietveld method is nothing but the minimization of the weighted sum of the squared deviation \( S \), given by

\[
S = \sum_{j=1}^{N} \frac{\Delta_j^2}{\sigma_j^2},
\]

and the values of \( \{\sigma_j\} \) should always diverge to infinity, if they are allowed to be varied.

The plots shown in Fig. 1 schematically illustrate the capability of the maximum likelihood estimation to optimize the error model, simplifying the behavior of the unlikelihood estimator as a function of \( \sigma^2 \), \( U = \Delta^2 / \sigma^2 + \ln \sigma^2 \). It should be noted that the unlikelihood \( U \) has a minimum at a finite value of \( \sigma^2 \).
Fig. 1. Illustration to demonstrate the capability of the maximum likelihood estimation to optimize the statistical variance $\sigma^2$. The unlikelihood function $U = \Delta^2 / \sigma^2 + \ln \sigma^2$ always has a minimum at a finite value of $\sigma^2$.

3. ANALYTICAL PROCEDURES

The optimization of the overall statistical model by the maximum likelihood estimation can be divided into the following two steps (Ida and Izumi, 2011).

(i) Structure refinement by the Rietveld method with the user-defined errors $\{\sigma_j\}$, where $\sigma_j = Y_j^{1/2}$ is assumed at the initial stage.

(ii) Estimation of errors $\{\sigma_j\}$, determined by $C_p$ and $C_r$, by the minimization of the unlikelihood indicator $U(C_p, C_r)$, applying the deviations $\{\Delta_j\} = \{Y_j - y(2\Theta_j)\}$, individual model peak profile $\{y_i(2\Theta_j)\}$ and background intensities $\{b_j\}$, calculated by the former Rietveld refinement. The above steps (i) and (ii) are repeated until convergence, which typically needs 3–4 iterations.

4. APPLICATIONS TO X-RAY POWDER DIFFRACTION DATA

In this section, the applications of the new structure refinement method based on the maximum likelihood estimation to fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, anglesite $\text{PbSO}_4$ and barite $\text{BaSO}_4$ are demonstrated. Further details about the analytical results have been described elsewhere (Ida and Izumi, 2011).
4.1. Fluorapatite, Ca$_5$(PO$_4$)$_3$F

Cu $K\alpha$ X-ray powder diffraction data of fluorapatite, Ca$_5$(PO$_4$)$_3$F, were originally attached to the DBWS Rietveld program package developed by Young et al. (1995), and are currently available as an example data set in the RIETAN-FP package (Izumi and Momma, 2007). The space group of fluorapatite is $P6_3/m$ (No. 176).

The differences in atomic coordinates between the structure refined from the powder and single-crystal diffraction data (Sudarsanan et al., 1972) are plotted in Fig. 2. All the atomic fractional coordinates optimized by our new method have become closer to the single-crystal data than those obtained by the Rietveld method.

![Fluorapatite, difference from single-crystal data](image)

**Fig. 2:** Deviations of the fractional coordinates of fluorapatite optimized by the Rietveld (triangles) and new (circles) methods from those obtained by the X-ray analysis of a synthetic single crystal by Sudarnan et al. (1972).

4.2. Anglesite, PbSO$_4$

Cu $K\alpha$ X-ray powder diffraction data of anglesite, PbSO$_4$, supplied for a Rietveld refinement round robin (Hill, 1992), were reanalyzed. The data are available as an example file in the FullProf package (Rodríguez-Carvajal, 1993). The space group of anglesite is $Pnma$ (No. 62).

The differences in atomic coordinates between the structure refinements from the powder and synthetic single-crystal diffraction data (Miyake et al., 1978) are plotted in Fig. 3.
The atomic coordinates optimized by the new analytical method are almost unchanged from the results obtained by the Rietveld method. It should be noted that the results of the Rietveld method have already been in good agreement with the single-crystal data within the experimental errors. It is suggested that the powder diffraction data were collected almost under an idealistic condition for the Rietveld structure refinement. This example shows rather favorable behavior of the new analytical method, on the point that it does not cause unwanted modification to the satisfactory results of the Rietveld method.

![Graph showing deviations in coordinates](image)

Fig. 3: Deviations of the fractional coordinates of anglesite optimized by the Rietveld (triangles) and new (circles) methods from those obtained by the single-crystal X-ray structure analysis by Miyake et al. (1978).

### 4.3. Barite, BaSO₄

Cu Kα₁ X-ray powder diffraction data of barite, BaSO₄ are available as an example file in the RIETAN-FP package (Izumi and Momma, 2007). The space group of barite is Pnma (No. 62), and isostructural to anglesite.

The differences in atomic coordinates between the structure refinements from the powder and synthetic single-crystal diffraction data (Miyake et al., 1978) are plotted in Fig. 4. This example shows significant improvements in the coincidence with the single-crystal data by applying the new analytical method. It should be emphasized that the results of the new analytical method are closer to the single-crystal data than those obtained by the Rietveld method, even though the Rietveld and new analytical methods are applied to the exactly same powder diffraction data, while the sample for the single-crystal analysis is different from what used in the powder diffraction experiment. The improved
coincidence with the single-crystal data may be ascribed to the lower probability to satisfy the diffraction condition due to the use of monochromated X-ray source on collection of the powder diffraction intensity data of BaSO₄.

Fig. 4: Deviations of the fractional coordinates of barite optimized by the Rietveld (triangles) and new (circles) methods from those obtained by the single-crystal X-ray structure analysis by Miyake et al. (1978).

5. CONCLUSIONS

A new method based on the maximum likelihood estimation for structure refinement from powder diffraction data has been developed. A model for statistical errors affected by particle statistics in experimental data can be optimized by the method. The method has been applied to the powder diffraction data of fluorapatite, anglesite and barite. The structures refined by the new method show improved agreement with the single crystal data, as compared with those obtained by conventional Rietveld refinements. The new method can be used as an alternative to the Rietveld method for structure refinement.

REFERENCES


