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A New Methodology for Structure Refinement from Powder Diffraction Data

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This document is intended to introduce the key concept about a new analytical method for structure refinement from powder diffraction data, which has been published as a research paper [Ida, T. & Izumi, F. "Application of a theory for particle statistics to structure refinement from powder diffraction data", *J. Appl. Cryst.* 44(5), 921-927 (2011)].
The method is based on "maximum likelihood estimation", but definitely different from the Rietveld method, because it is not a "least-squares method" in principle.

Suppose that diffraction intensities $\{Y_1, Y_2, \cdots, Y_N\}$ observed at diffraction angles $\{2\Theta_1, 2\Theta_2, \cdots, 2\Theta_N\}$ are normally distributed around the calculated mean values $y(2\Theta_j)$ with the standard deviation of σ_j, then the probability that the intensity Y_j is observed should be proportional to the value:

$$p_j(Y_j) = \frac{1}{\sqrt{2\pi}\sigma_j} \exp\left(-\frac{\Delta_j^2}{2\sigma_j^2}\right), \tag{1}$$

where Δ_j is the deviation defined by

$$\Delta_j = Y_j - y(2\Theta_j). \tag{2}$$

When independence of the deviation Δ_j can be assumed, the probability that the set of intensity data $\{Y_1, Y_2, \cdots, Y_N\}$ is realized should be proportional to the product:

$$P(Y_1, Y_2, \cdots, Y_N) = p_1(Y_1)\, p_2(Y_2) \cdots p_N(Y_N), \tag{3}$$

which we can consider as a "likelihood estimator". Maximum likelihood estimation is the maximization of $P(Y_1, Y_2, \cdots, Y_N)$, which is identical to the minimization of the value:

$$S \equiv -\ln P(Y_1, Y_2, \cdots, Y_N) - N \ln\sqrt{2\pi} = \sum_{j=1}^{N} \left(\ln\sigma_j + \frac{\Delta_j^2}{\sigma_j^2}\right) \tag{4}$$

It is known that statistical variance σ_j^2 can be approximated by the sum of two terms caused by counting statistics $(\sigma_{\text{count}})_j^2$ and particle statistics $(\sigma_{\text{particle}})_j^2$, that is,

$$\sigma_j^2 \approx (\sigma_{\text{count}})_j^2 + (\sigma_{\text{particle}})_j^2 \tag{5}$$

In a traditional measurement system, the counting statistical variance $(\sigma_{\text{count}})_j^2$ is approximated by

$$(\sigma_{\text{count}})_j^2 \approx y(2\Theta_j), \tag{6}$$

and particle statistical variance $(\sigma_{\text{particle}})_j^2$ can be modelled by

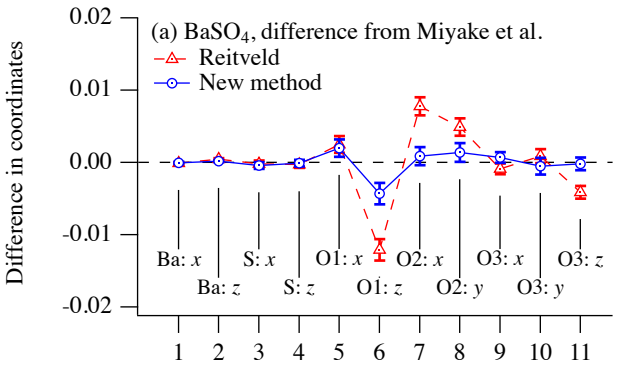
$$(\sigma_{\text{particle}})_j^2 \approx \frac{C_{\text{particle}}\left[y(2\Theta_j) - b(2\Theta_j)\right]^2 \sin\Theta_j}{m_j}, \tag{7}$$

where C_{particle} is an unknown proportionality factor, $b\left(2\Theta_j\right)$ the background intensity, and m_j the multiplicity of reflection.

We can uniquely determine the value of C_{particle} by minimizing $S = \sum_{j=1}^{N} \left(\ln \sigma_j + \frac{\Delta_j^2}{\sigma_j^2} \right)$, the value of which become infinite at both ends: $\sigma_j \to 0$ and $\sigma_j \to \infty$.

Note that it is impossible to estimate the statistical errors by the Rietveld method, because it only minimizes the sum of squared deviation: $S' = \sum_{j=1}^{N} \frac{\Delta_j^2}{\sigma_j^2}$.

Figure 1 compares the results of structure analysis from $BaSO_4$ powder diffraction data by the Rietveld and new methods. It is clearly seen that all the structure parameters optimized by the new method have become closer to the values determined from a single-crystal data (Miyake *et al.*, 1978).



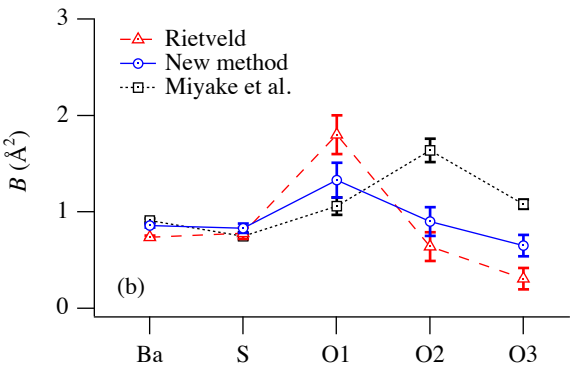


Fig. 1
(a) Deviations of the fractional coordinates optimized by the Rietveld and new methods, which are respectively marked by triangles and circles, from those optained by the single-crystal X-ray analysis by Miyake *et al.* (1978) for $BaSO_4$.
(b) Isotropic atomic displacement parameters optimized by the Rietveld and new methods (triangles and circles, respectively) and equivalent isotropic atomic displacement parameters calculated from the single-crystal data (Miyake *et al.*, 1978; Lee *et al.*, 2005).