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Abstract. The analysis of observed structure factors estimated after Rietveld analysis by the maximum-entropy method (MEM) gives electron or nuclear densities in the unit cell. The resultant densities are, more or less, biased toward a structural model in the Rietveld analysis. To overcome such a problem, we devised a sophisticated technique named MEM-based pattern fitting (MPF). For this purpose, a pattern-fitting system, RIETAN-FP, and a MEM analysis programs, PRIMA or its successor called Dysnomia, were virtually integrated into a structure-refinement system, whereby the pattern calculated from structure factors obtained by MEM is fit to the whole observed pattern. The resulting observed structure factors are analyzed again by MEM. In this way, whole-pattern fitting and MEM analysis are alternately repeated until $R$ factors in the former no longer decrease. MPF virtually represents the crystal structure by electron or nuclear densities. MPF is, therefore, very effective in visualizing positional, orientational disorder, chemical bonding, and anharmonic thermal motion. New programs, MPF_multi and VESTA 3, used in MPF are briefly introduced, and two representative applications of MPF to inorganic materials containing highly disordered chemical species are demonstrated.

1. Introduction
Since Collins [1] proposed an iterative procedure for reconstruction of electron-density images from imperfect single-crystal X-ray diffraction data, the maximum-entropy method (MEM) has been widely applied to various kinds of X-ray and neutron diffraction data. Later studies demonstrated that MEM makes it possible to extract maximum structural information from powder diffraction data, supplementing the classical methodology for structure refinement, i.e., the Rietveld method. MEM allows us to recover part of structural information lost in powder diffraction owing to the overlap of reflections and the absence of high-$Q$ reflections.

This paper, at first, reviews our original technique to determine electron and nuclear (coherent-scattering-length) densities from X-ray and neutron powder diffraction data, respectively. Next, new programs that have recently been developed for our technique are introduced. Structure refinements of two inorganic materials containing highly disordered chemical species are finally shown as examples.

2. The MEM/Rietveld method and its limitations
In recent years, Takata et al. [2] have applied MEM actively to the determination of three-dimensional (3D) electron/nuclear densities from X-ray/neutron powder-diffraction data. MEM derives the 3D den-
sities that maximize the information entropy, $S$, under some constraints [1]. With MEM, structural information can effectively be extracted from the diffraction data and reflected on 3D densities resulting from MEM analysis if the experimental data have been appropriately measured. Because MEM can estimate nonzero structure factors for high-$Q$ reflections excluded in the analysis of the powder diffraction data, the termination effect is less marked in MEM analysis than in Fourier synthesis. Thanks to these advantages, MEM provides us with less noisy 3D densities than Fourier synthesis.

Takata et al. [2] estimated ‘observed’ structure factors, $F_o(h_j) = F_o$\textsubscript{(Rietveld)}, for the $j$th reflection, $h_j$, on the basis of the result of Rietveld analysis [3] when dealing with overlapping reflections. That is, the observed net intensity at each point is apportioned in the ratio of profiles calculated from final structure and profile parameters and summed up for each reflection according to a procedure proposed by Rietveld [3]. This expedient technique is also utilized to evaluate $R_\theta$ and $R_F$ in Rietveld analysis, integrated intensities in the Le Bail method [4], and 3D densities by Fourier synthesis. After close checking of the resulting 3D densities, the structural model in Rietveld analysis is modified, if necessary. Rietveld and MEM analyses are alternately repeated until a reasonable structural model is reached, as shown in the upper box in figure 1. Such a procedure is referred to as the MEM/Rietveld method.

3. MEM-based pattern fitting
The $F_o$\textsubscript{(Rietveld)} data estimated from the refinable parameters are doubly biased toward the structural model in the Rietveld analysis because both phases and calculated profiles used for the intensity partitioning are derived from the model. To overcome such a grave failing of the oversimple MEM/Rietveld method, we devised a state-of-the-art technique of structure refinement called MEM-based pattern fitting (MPF) [5–7]. For MPF analysis, we have been using RIETAN-FP [8] for Rietveld analysis and whole-pattern fitting (w.p.f.), PRIMA [6] or Dysnomia (see section 4) for MEM analysis, and VESTA [9] for 3D visualization of crystal structures and electron- or nuclear-density distribution, as figure 1 illustrates.

MPF using the above programs comprises the following iterative procedures:
1) Intensity data in *.int are analyzed by the Rietveld method with RIETAN-FP on the basis of a structural model.
2) RIETAN-FP estimates observed structure factors, $F_o(h_j) = F_o$\textsuperscript{(Rietveld)}, and outputs their values to file *.fos together with observed integrated intensities, $I_o(h_j) = I_o$\textsuperscript{(Rietveld)}.
3) PRIMA or Dysnomia reads in *.fos, calculates the standard uncertainty (s.u.) of each $|F_o(h_j)|$ from $I_o$\textsuperscript{(Rietveld)}, and analyzes the data by MEM to yield 3D densities, $\rho(x,y,z)$, which are stored in file *.den (a text file) or *.pri (a binary file). Furthermore, structure factors, $F(h_j) = F$\textsuperscript{(MEM)}, are calculated by the Fourier transform of $\rho(x,y,z)$’s in the unit cell and output to file *.fba.

Figure 1. Structure refinement by MEM/Rietveld analysis followed by MPF.
4) The $\rho(x,y,z)$ data stored in *.den or *.pri are visualized as isosurfaces in three dimensions with VESTA.
5) After close examination of the density images, return to step 1 to modify the structural model if necessary.
6) With RIETAN-FP, the model function is fit to the whole observed diffraction pattern by refining parameters irrelevant to the crystal structure: scale factor, profile parameters, peak-shift parameters, and background parameters (w.p.f.). Each structure factor in the model function is not calculated from any structure parameters but fixed at the $F$(MEM) values recorded in *.fba.
7) RIETAN-FP estimates $F_o(hj) = F_o$(w.p.f.) and $I_o(hj) = I_o$(w.p.f.) and outputs them to file *.fos.
8) Terminate unless decreases in reliability indices, usually $R_{wp}$, in step 6 are significant compared with those in the final Rietveld analysis or the previous w.p.f.
9) PRIMA or Dysnomia reads in *.fos, calculates the s.u. of $|F_o(w.p.f.)|$ from $I_o(w.p.f.)$, and analyzes the data to give 3D densities, $\rho(x,y,z)$, from which $F$(MEM)’s are calculated by Fourier transform. The resulting densities and $F$(MEM)’s are output to *.den or *.pri, and *.fba, respectively.
10) Return to step 6.

MPF (a lower box drawn with broken lines in figure 1) follows the MEM/Rietveld analyses (an upper box drawn with broken lines in figure 1). Structural details are changed in steps 3 and 9 while the agreement between observed and calculated patterns is improved by fixing structure factors at $F$(MEM)’s in step 6. It is the $F$(MEM) data that minimize the bias toward the structural model. Steps 6–10, which are repeated until the convergence is attained, are referred to as REMEDY cycles, serving to minimize the bias imposed on density distribution by the structural model in Rietveld analysis.

The influence of the structural model in the Rietveld analysis on final 3D densities diminishes by repeating REMEDY cycles. In other words, intensity repartitioning for overlapping reflections becomes more accurate with increasing number of iterations owing to derivation of additional structural information by MEM. Such an iterative method is somewhat similar to the Le Bail method [4] but differs from it in the point that structure factors in w.p.f. are fixed at $F$(MEM)’s resulting from the previous MEM analysis.

The above sophisticated methodology achieves a significant breakthrough in better representation of static and dynamic disorder, chemical bonding, and anharmonic thermal motion. Crystal structures are expressed not by structure parameters but in practice by 3D densities in voxels in the unit cell. MPF is, therefore, flexible enough to attain the above purposes better than a traditional approach to structure refinement, i.e., Rietveld analysis.

4. A new MEM analysis program, Dysnomia

We have recently developed a new C++ program, Dysnomia, for MEM analysis. Dysnomia outperforms its predecessor, PRIMA, in computation speed, memory efficiency, scalability, and reliability. Dysnomia automatically switches between discrete Fourier transform (DFT) and fast Fourier transform (FFT) algorithms depending on the number of observed reflections, the number of voxels in the unit cell, and space-group symmetry. In both DFT and FFT routines, symmetry operations are fully utilized wherever possible to reduce computation time. The OpenMP technology is adopted for parallel processing on standard personal computers. Executable files of Dysnomia for Windows, Mac OS X, and Linux are currently available.

Two types of MEM algorithms are implemented in Dysnomia. One is 0th-order single pixel approximation (ZSPA) [10], and the other is a variant of the Cambridge algorithm [11]. In general, electron or nuclear densities calculated by the two algorithms are mostly consistent with each other. However, the normalized residuals of the structure factors, $\Delta F_j$ obtained by the ZSPA algorithm do not satisfy true maximum-entropy (MaxEnt) conditions whereas the Cambridge algorithm always affords solutions close to the true MaxEnt ones [12]. In both algorithms, the maximum of the information entropy, $S$, defined as

$$S = -\sum \rho_k \ln(\rho_k/\tau_k)$$  \hspace{1cm} (1)
is iteratively approached by the method of undetermined Lagrange multipliers:

\[ Q = S - \lambda C - \mu (\sum \rho_k - 1). \tag{2} \]

In equations (1) and (2), \( \rho_k \) is the normalized density at voxel (grid point) \( k \), \( \tau_k \) is the density derived from prior information, \( \lambda \) and \( \mu \) are Lagrange multipliers, and \( C \) is the constraint related to observed values. The so-called \( F \) constraint, \( C_F \), containing \( F_o(h) \)'s is usually used as \( C \).

Let \( N_F \) be the total number of observed reflections, and \( \sigma(h) \) the standard uncertainty of \( |F_o(h)| \), then \( C_F \) is formulated as

\[ C_F = \frac{1}{N_F} \sum_j \left[ \frac{|F_o(h)| - F(h)|}{\sigma(h)_j} \right]^2 - 1 = \frac{1}{N_F} \sum_j (\Delta F)^2 - 1 = 0. \tag{3} \]

The use of the \( F \) constraint is based on an assumption that the experimental errors in \( F_o(h) \) are random with a Gaussian distribution. However, in the case of MEM analysis from X-ray diffraction data, normalized residuals of the observed and calculated structure factors, \( \Delta F \), of some low-\( Q \) reflections tend to be overestimated. In order to reduce such a tendency, Dysnomia adopts a series of generalized \( F \) constraints [13]:

\[ C = \sum_n \lambda_n C_{jn} \tag{4} \]

with

\[ C_{jn} = \frac{1}{N_{jm_n}} \sum_j w_j (\Delta F)^2 - C_w = 0, \tag{5} \]

where \( \lambda_n \) is the relative weight for each of \( C_{jn} \), \( m_n \) is the even \( n \)-th order central moment of normal (Gaussian) distribution, \( w_j \) is the weighting factor, and \( C_w \) is the criterion for convergence. When \( w_j = 1 \), the ideal constraint is \( C_w = 1 \) for even numbers of \( n \) because \( \Delta F \) is expected to obey Gaussian distribution. Such a rigorous constraint seems to be hardly satisfied in actual problems. Therefore, Dysnomia always determines \( C_w \) automatically in such a way that equation (3) also holds. Each value of \( \lambda_n \) must be manually set. Default values of \( \lambda_n \) are 1 for \( \lambda_2 \) and 0 for \( \lambda_n \) \( (n > 2) \), which corresponds to the conventional \( F \) constraint.

The convergence of the Cambridge algorithm is judged by the gradient of equation (2):

\[ \frac{1}{N_s} \sum_s (\partial Q / \partial \rho_j)^2 < \varepsilon, \tag{6} \]

where \( N_s \) is the total number of voxels in the unit cell, and \( \varepsilon \) is a small threshold value; \( \varepsilon \) is usually set at about \( 10^{-6} \) and at \( 10^{-4} \) in analyses with very slow convergence.

For \( w_j \) in single-crystal X-ray diffraction, an empirical weighting on the basis of \( n \)-th power of the lattice-plane spacing, \( d \), has been proposed [14]. Dysnomia allows us to give arbitrary values of \( w_j \), instead of including \( w_j \) in \( \sigma(h) \), which makes it easier to separate the effect of weighting from differences in the overall scale of \( \sigma(h) \).

5. Automation of MPF analyses

MEM derives densities giving \( F_o(h) \)'s that agree with \( F_o(h) \)'s within \( \sigma(h) \)'s. With PRIMA or Dysnomia, \( \sigma(h) \) is estimated on the basis of the law of propagation of errors in combination with counting statistics:

\[ \sigma(h) = \frac{|F_o(h)|}{2} \left[ \frac{1}{EI_o(h)} + \left( \frac{\sigma(s)}{s} \right)^2 \right]^{1/2}, \tag{7} \]

where \( E \) is the factor to adjust \( \sigma(h) \), \( s \) is the scale factor, and \( \sigma(s) \) is the s.u. of \( s \). \( E \) is approximately equal to \( 1/\Delta 2\theta \) \((2\theta: \) step width). \( E \) is usually determined so as to give reasonable \( \sigma(h) \)'s and achieve convergence with a minimum number of MEM cycles. In addition, \( E \) must be adjusted in such a way
that the resulting density distribution is physically and chemically reasonable.

We have recently developed two scripts for automatic execution of MPF analyses: a batch file, MPF_multi.bat, for Windows and a shell script, MPF_multi.command, for Mac OS X. Figure 2 illustrates a flowchart of a series of MPF analyses where $E$ is changed as specified in an input file, *.prf, for MEM analysis. Input files for PRIMA/Dysnomia and RIETAN-FP are set up by MPF_multi.bat or MPF_multi.command. The optimum value of $E$ is determined by (a) checking a log file, *.log, containing reliability indices and other information about the Rietveld, MEM, and w.p.f. analyses during the REMEDY cycles and (b) visualizing 3D voxel data stored in *.den or *.pri.

6. A new version of the 3D visualization system, VESTA 3
We have been developing a next-generation 3D visualization system, VESTA 3, whose main new features are as follows:
1) drawing the external morphology (faces) of crystals,
2) superimposing displays of multiple structural models and isosurfaces with different levels,
3) extended bond-search algorithm to allow more sophisticated search for complex molecules, cage-like structures, etc.,
4) Significant performance improvements in rendering of isosurfaces and calculation of slices,
5) calculations of electron and nuclear densities from structure parameters,
6) support of undo and redo in GUI operations.

7. Applications of MPF to inorganic materials containing highly disordered chemical species
Two representative examples of applying MPF to inorganic materials showing static and dynamic disorder will be described in what follows. Their disordered structures cannot be represented adequately by conventional Rietveld refinements adopting split-atom models.

In a whitlockite-like phosphate, $\text{Sr}_{9.3}\text{Ni}_{1.2}(\text{PO}_{4})_7$, parts of $\text{Sr}^{2+}$, $\text{Ni}^{2+}$, and $\text{PO}_4^{3–}$ ions exhibit highly disordered arrangements [15]. We found positions of these atoms by MEM/Rietveld analysis from its synchrotron X-ray powder diffraction data measure on BL15XU at SPring-8 and built a split-atom model. Subsequent two REMEDY cycles decreased $R_{wp}$ ($S$), $R_{b}$, and $R_f$ a great deal from 5.39 % (2.30), 2.80 %, and 1.88 % in the final Rietveld refinement adopting the split-atom model to 5.18 % (2.20), 1.03 %, and 0.82 %, respectively. Figure 3 shows isosurfaces of electron densities determined by MPF for $\text{P}_1\text{O}_4$ tetrahedron. Evidently, such pronounced orientational disorder of the oxoacid anions can hardly be represented by the split-atom model, which is the main reason why MPF lowered $R_b$ and $R_f$ dramatically.

The conductivity of $\text{Rb}_4\text{Cu}_{6}^{+}\text{I}_{9}^{-}\text{Cl}_{13}$ at room temperature is 0.34 S/cm, which is the highest of all the superionic conductors [16]. Its structure gradually changes without any phase transitions from a low-temperature phase, where $\text{Cu}^+$ ions hardly migrate to the high ionic conductor because lattice
defects are generated by thermal excitation. Figure 4 illustrates results of MPF structure refinements for Rb$_4$Cu$_{16}$I$_{7.2}$Cl$_{12.8}$ at 280 K from neutron powder diffraction data measured on the HB-4 diffractometer at HFIR [17]. Rb$_4$Cu$_{16}$I$_{7.2}$Cl$_{12.8}$ contains three Cu sites in the asymmetric unit: Cu$^{1}$ and Cu$^{2}$ at $24e$ and Cu$^{3}$ at $8c$. From figure 4, we conclude that Cu$^{1}$ and Cu$^{2}$ atoms are delocalized spirally to form $[\text{Cu}^{1}-\text{Cu}^{2}-\cdots]$ chains, which are main conduction pathways in this material. On the other hand, MPF analysis from diffraction data measured at 11 K showed all the Cu atoms to be localized at the definite positions of $24e$ and $8c$.

References