Development and Applications of the Pioneering Technology of Structure Refinement from Powder Diffraction Data

Fujio IZUMI
Advanced Materials Laboratory, National Institute for Materials Science, 1-1, Namiki, Tsukuba-shi, Ibaraki 305–0044

A couple of Rietveld-analysis programs, RITAN, for angle-dispersive diffraction and time-of-flight neutron diffraction have been extensively used for structural studies of many compounds. The history of their developments is briefly reviewed. The latest versions, RITAN–2000 for angle-dispersive diffraction and RITAN–2001T for the Vega and Sirius diffractometers at KENS have a practical feature of partial profile relaxation. In this technique, primary profile parameters of (nearly) isolated reflections can be individually refined independent of secondary profile parameters. It was combined with split-ratio functions to improve fits between observed and calculated patterns, particularly in samples exhibiting anisotropic profile broadening and reflections with very large lattice-plane spacings. RITAN–2000 and our own program for the maximum-entropy method (MEM), REMEDY, were virtually integrated into a structure-refinement system, PRIMA, whereby the pattern calculated from structure factors obtained by MEM fits to the whole observed pattern. ‘Observed’ structure factors estimated at the end of the whole-pattern fitting are analyzed again by MEM. Whole-pattern fitting and MEM analysis are alternately repeated until R factors in the former no longer decrease. Applications of this technology to three inorganic compounds having highly disordered structures are demonstrated, showing its excellent performance and effectiveness.

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1. Brief history of RITAN
1.1 Programs for conventional Rietveld analysis

The Rietveld method has been extensively utilized for structure refinement from X-ray and neutron powder diffraction data. In Japan, RITAN has contributed to a vast majority of structural studies using the Rietveld method. At the beginning of the ’80s, I was ambitious to build my own Rietveld-analysis program independent of any other preceding programs. At first, a simple Fortran program, XPD, was coded for only angle-dispersive X-ray diffraction. It was renamed RITAN after several functions including Rietveld analysis from neutron diffraction data had been implemented in it. RITAN was later modified to work with time-of-flight (TOF) neutron powder diffraction data measured on the diffractometer, HRP, installed at the KENS spallation neutron source (KEK). Since 1983, structures of many compounds, mainly superconducting copper oxides, were analyzed routinely with the dedicated program for HRP. RITAN used in the ’80s is outlined in Ref. 5.

In the next major release, RITAN–94, for angle-dispersive diffraction, the pseudo-Voigt function of Thompson, Cox, and Hastings made asymmetric by Howard’s procedure was added together with representation of anisotropic profile broadening. It was widely used for Rietveld refinements from X-ray powder diffraction data with Cu Kα radiation and neutron powder diffraction data taken on the powder diffractometer HRPD at the JRR–3M reactor (JAERI). For all the important functions included in RITAN–94 and the corresponding program for TOF neutron powder diffraction, refer to Ref. 9.

Several advanced techniques were introduced into the above two versions of RITAN:

1) Fletcher’s modified Marquardt method as one of non-linear least-squares methods using partial derivatives.
2) The conjugate-direction method as a nonlinear least-squares methods adopting direct search.
3) Incremental refinement where parameters refined in each cycle are specified or automatically determined by the program.
4) Imposing nonlinear restraints on interatomic distances and bond angles by an exterior penalty function method.
5) A convenient and user-friendly character user interface called Tink.

The combination of the modified Marquardt method and incremental refinement serves to expand the narrow range within which convergence is attained. The conjugate direction method often makes it possible to escape from local minima or stabilize convergence to the solution. Accordingly, we have been always using it in the intermediate and final stages of Rietveld refinement. The exterior penalty function method is effective in overcoming difficulties arising from small observation/variable ratios in powder diffraction data. Tink was devised as antithesis to the graphical user interface that is even slower and more unwieldy to use for power users. It is a preprocessor to convert a standard input file into a scratch file that contains only integer-, real-, and character-type variables input and dealt with actually by RITAN.

1.2 New-generation programs for structure refinement

After publishing many papers on Rietveld refinements of inorganic materials, we made a breakthrough in Rietveld refinement: partial profile relaxation. This technique, first accommodated in RITAN–96T for TOF neutron diffraction, enables us to improve the fit between observed and calculated patterns, particularly in diffraction...
data including reflections with profiles broadened anisotropically or large lattice-plane spacings, d. With partial profile relaxation, R factors often drop dramatically, which greatly enhances the precision and accuracy of the resultant structure parameters. The current version, RIETAN–2001T, incorporating this feature has been applied to most of TOF neutron powder diffraction data collected on the Vega and Sirius diffractometers installed at KENS in place of HRP.

In 1997, we started to extend the angle-dispersive version of RIETAN to a great extent11–16 and completed a multi-purpose pattern-fitting system, RIETAN–2000, in three years’ time (Fig. 1). RIETAN–2000 shares several useful and convenient features with RIETAN–2001T. We at first incorporated partial profile relaxation into the angle-dispersive version and confirmed its effectiveness.11–14 Then, we invented our original methodology of whole-pattern fitting based on the maximum-entropy method (MEM).15,16 which will be abbreviated as MPF (MEM-based Pattern Fitting) here. MPF offers a state-of-the-art structure-refinement technique alternative to the Rietveld method.1 Structural details that are hard to go into with the classical method of structure refinement, i.e., Rietveld analysis, can be clarified by MPF. It also serves to modify imperfect structural models in Rietveld refinement. As depicted in Fig. 1, RIETAN–2000 can be also used for Le Bail analysis17 and individual profile fitting. The Le Bail method derives ‘observed’ integrated intensities, |Fo|2, for ab initio structure analysis from powder diffraction data.18 In RIETAN–2000, it is modified so as to input initial integrated intensities estimated by Wilson’s statistics and calculated on the basis of partial structures.

In what follows, partial profile relaxation and MPF, which are now being utilized more and more, will be brought into focus. Applications of these two sophisticated techniques to structure refinements of five inorganic materials will be also demonstrated. Both of them must be useful for those who wish to take advantage of the advanced methods of structure refinement.

2. Partial profile relaxation

2.1 Principle

Profile functions for use in the Rietveld,11 Le Bail,17 and Pawley19 methods generally contain two levels of profile parameters: Primary Profile Parameter (PPP) and, in its turn, Secondary Profile Parameter (SPP). The dependence of PPP’s on θ (angle-dispersive diffraction) or d (TOF neutron diffraction) is represented empirically or with physical foundations to afford equations including SPP’s. For example, in the equation of Caglioti et al.,

\[ H_b = (U \tan^2 \theta_b + V \tan \theta_b + W)^{1/2}, \]

the full-width-at-half-maximum (FWHM), \( H_b \), is a PPP specific for reflection \( b \) with a Bragg angle of \( \theta_b \), \( U \), \( V \), and \( W \) are SPP’s common to the whole 2θ (d) range. We refine not PPP’s but SPP’s in the least-squares fitting of whole powder patterns. Such equations impose a kind of equality constraints on PPP’s, often failing to express relations between PPP’s and \( \theta_b \) (\( d_b \)) satisfactorily. As a PPP deviates from an equation relating it to \( \theta_b \) (\( d_b \)), the fit between observed and calculated profiles gets worse and worse.

We have devised a unique approach to pattern fitting, viz., partial profile relaxation where PPP’s of part of (nearly) isolated reflections are locally refined independent of global SPP’s.10–14 In Rietveld analysis under partial profile relaxation, PPP’s of these reflections are all or partially freed from equations relating PPP’s to \( \theta_b \) (\( d_b \)). On the other hand, peak positions and integrated intensities for the relaxed reflections are, respectively, calculated from lattice and structure parameters in the same fashion as those for the other reflections. PPP’s of only low-Q reflections (\( Q = 2\pi/d \)) can be substantially relaxed except for very simple structures. Nevertheless, better fits in this region lead to improvements in fits in the high-Q region.

Partial profile relaxation stemmed from a simple idea but lowers R factors more or less, and often dramatically. This technology can be also used in pattern decomposition and MPF described in Sect. 3.

2.2 Structural properties of a superconducting perovskite \((K_2,Ag)_{0.3}Bi_0.73\)BiO

Khasanova et al.20 discovered a new superconductor
$K_{1-x}Bi_{1+x}O_3$ with the highest $T_c$ of 10.2 K. This oxide proved to be a cubic perovskite $ABO_3$ with space group $Pm\bar{3}m$ and a lattice parameter, $a \approx 4.23 \ \text{Å}$. Its crystal data are indispensable for understanding how carriers are doped in the above solid solution. Hence, we measured TOP neutron powder diffraction data of a sample (ca. 50 mg) with a nominal composition of $K_{0.5}Bi_{0.5}O_3$ on Vega for ca. 70 h.

Multi-phase Rietveld analysis where partial profile relaxation was applied to five reflections gave a very good fit between observed and calculated patterns (Fig. 2). Refinement of occupation factors, $g$, for the A, B, and O sites revealed (a) substitution of 13% of Bi$^{3+}$ ions for K$^+$ ions at the A site, (b) exclusive occupation of the B site by Bi, and (c) the absence of oxygen vacancies ($\delta = 0$), which yield a chemical formula of $(K_{0.85}Bi_{0.15})BiO_3$. The oxidation state of Bi at the B site is estimated at +4.74 from this composition provided that the oxidation state of Bi at the A site is +3. These findings present unambiguous evidence for electron doping into the conduction band $\sigma^*$ derived from an antibonding mixture of Bi(6s)-O(2p) states. Apparently marked thermal motion for the A ($U_a = 0.050 \ \text{Å}^2$) and O ($U_{oo} = 0.038 \ \text{Å}^2$) sites must reflect marked positional disorder arising from a large difference in ionic radius between the K$^+$ and Bi$^{3+}$ ions.

2.3 Ultimate goodness-of-fit in Rietveld analysis of a zeolite

Partial profile relaxation generally gives better fits in Rietveld analysis and pattern decomposition of a compound exhibiting large $d$ reflections, whose calculated profiles are often difficult to fit to observed ones. Figure 3 illustrates observed, calculated, and difference patterns for X-ray Rietveld refinement of hydrated faujasite (Na-FAU, space

![Fig. 2. Rietveld-refinement patterns of $K_{0.5}Bi_{0.5}O_3$ plotted against $d$. Tick marks below the profiles indicate the peak positions of allowed Bragg reflections for $K_{0.5}Bi_{0.15}BiO_3$ (top),Cd (middle) used as a shield, and KOH–H$_2$O (bottom).](image)

![Fig. 3. Observed, calculated, and difference patterns for hydrated Na-FAU. X-Ray diffraction patterns between 90° and 35° are magnified in the inset.](image)
3. Beyond the ability of Rietveld analysis: MEM-based pattern fitting

3.1 Problem of the bias toward the structural model
MEM is a versatile approach to the estimation of a model from a limited amount of information by maximizing information entropy under constraints consistent with observed physical quantities. In recent years, Takata et al.\textsuperscript{21} have applied it actively to the determination of electron/nuclear densities from X-ray/neutron powder diffraction data. MEM infers electron/nuclear densities in such a way that they provide the maximum variance of structure factors, $F_c$ (MEM), within errors in observed structure factors, $F_o$. Detailed structural information can effectively be extracted from the diffraction data and reflected on the resulting electron/nuclear densities by MEM if the data have been appropriately measured. Because MEM can estimate non-zero structure factors of high-$Q$ reflections excluded in the analysis of 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 density maps than Fourier synthesis.\textsuperscript{22}

Takata et al.\textsuperscript{21} have estimated ‘observed’ structure factors, $F_o$(Rietveld), on the basis of the result of Rietveld analysis when dealing with overlapping reflections, as shown inside the upper box exhibited by broken lines in Fig. 4. 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. This expedient technique is also utilized to evaluate $R_B$ and $R_p$ in Rietveld analysis,\textsuperscript{11} integrated intensities in the Le Bail method,\textsuperscript{17} and electron/nuclear densities in Fourier synthesis. However, the $F_c$(Rietveld) data estimated in such a manner are doubly biased towards a structural model in the Rietveld analysis because both phases and calculated profiles used for the intensity partitioning are derived from the model.\textsuperscript{22} This approximate nature of the procedure for extracting integrated intensities lowers the accuracy of electron/nuclear densities determined by MEM analysis of $F_o$(Rietveld)’s.

The undesirable bias imposed by the structural model enlarges with increasing degree of overlap of reflections and lowering resolution in a powder pattern. MEM analysis of $F_o$(Rietveld)’s is certainly effective in modifying imperfect structural models in Rietveld analysis, as can be appreciated from location of residual water molecules in $\beta$ cages of a dehydrated zeolite Na-LTA\textsuperscript{23,23} and water molecules between two CoO$_2$ layers in a novel superconductor Na$_{0.985}$CoO$_{1.37}$H$_2$O (Fig. 5).\textsuperscript{24} Though this simple method is far from perfect for determining accurate electron/nuclear densities, MEM allows us to extract structural details from the $F_o$(Rietveld) data containing contributions neglected in the structural model. In addition, structure factors, $F_o$, observed actually can be evaluated for isolated reflections without any approximation.

3.2 Procedure of structure refinement by MPF
We have virtually integrated Rietveld-2000 and VENUS\textsuperscript{16} into a system named REMEDY\textsuperscript{11–16} to overcome the serious flaws in the oversimplified procedure of Takata et al.\textsuperscript{21} VENUS is a three-dimensional (3D) visualization system comprising three independent programs:
1) VEND: Visualization of Electron/Nuclear Densities,
2) VICS: Visualization of Crystal Structures,
3) PRIMA: PRactice Iterative MEM Analyses.

That is, VEND and VICS, respectively, visualize electron/nuclear densities and crystal structures, taking full advantage of the OpenGL technology. The super-fast MEM analysis program, PRIMA, was designed with MPF in mind, as can be inferred from its name.

As Fig. 4 represents schematically, MPF (lower box) follows Rietveld–MEM analyses (upper box). $F_o$(Rietveld) data estimated at the end of the final Rietveld analysis\textsuperscript{1} are analyzed by MEM with PRIMA to yield electron/nuclear densities, which are then visualized with VEND in three dimensions. A close inspection of the resultant density distribution may urge us to modify the structural model. Rietveld and MEM analyses are alternately carried out until a reasonable structural model is reached (the so-called MEM/Rietveld method).\textsuperscript{21}

$F_c$(MEM)’s can be calculated by the Fourier transform of electron/nuclear densities resulting from MEM analysis. It is these $F_c$(MEM) data that are used in MPF to minimize the bias towards the structural model. In each whole-pattern fitting (w.p.f.), we fit the calculated pattern to the observed one in the whole 2θ range by fixing structure factors at values of $F_o$(MEM) obtained by the previous MEM analysis and refining only parameters irrelevant to the structure, e.g., scale factor, and background, profile, and lattice parameters. $F_o$(w.p.f.) data estimated after the w.p.f. according to Rietveld’s procedure\textsuperscript{1} are analyzed again by MEM. In this way, w.p.f. and MEM analysis are alternately...
Fig. 5. Isosurfaces for number densities of electrons in Na$_{0.25}$CoO$_2$. Equidensity level: 1.3/Å$^3$. The densities were approximately determined by MEM from $F_o$ data estimated on the basis of an X-ray Rietveld refinement where H$_2$O molecules were neglected.

Fig. 6. Electron-density distribution determined by MPF for K$_x$Ti$_{12-2x}$Li$_{10-x}$O$_4$ ($x=0.8$). Isosurfaces in three unit cells were drawn with an equidensity level of 1.2/Å$^3$.

repeated until $R$ factors (usually $R_{exp}$) in the former no longer decrease. Such an iterative procedure is referred to as REMEDY cycles, as noted in Fig. 4. REMEDY cycles weaken the influence of the structural model on $F_o$(w.p.f.)’s. In other words, intensity reparation for overlapping reflections becomes more accurate with increasing number of cycles owing to extraction of additional structural information from observed intensities of Bragg reflections.

Fig. 7. (a) Isosurfaces of nuclear (coherent-scattering length) densities at a 0.6 fm/Å$^3$ level and (b) a bird’s eye view of nuclear densities up to 8% of the maximum (663.9 fm/Å$^3$) on the $z=1/2$ plane in Ba$_4$CaCu$_2$O$_6$CO$_3$.

The above sophisticated methodology achieves a significant breakthrough in better representation of static and dynamic disorder, chemical bonding, nonlocalized electrons, and anharmonic thermal motion. Crystal structures are expressed not by structure parameters but in practice by electron/nuclear densities at grid points in the unit cell. MPF is therefore flexible enough to attain the above purposes better than the classical approach to structure refinement, i.e., Rietveld analysis. The establishment of the MPF method leads to the availability of ultra-high-resolution X-ray/neutron microscopes that allow us to visualize powder diffraction data as 3D density images. X-Ray and neutron diffraction can be complementarily utilized for (a) more adequate expression of chemical bonding and (b) analysis of positional and orientational disorder, and anharmonic thermal vibration, respectively. Three representative structure refinements of compounds with highly disordered structures will be described here.

3.3 Positional disorder of K$^+$ ions interlayered in K$_x$Ti$_{12-2x}$Li$_{10-x}$O$_4$
A layered compound, K$_x$Ti$_{12-2x}$Li$_{10-x}$O$_4$ (space group
Comprises (a) lepidocrocite-like Ti_{2-x}Li_{x}O layer consisting of edge-sharing (Ti, Li)\textsubscript{6} octahedra and (b) charge-balancing K\textsuperscript{+} ions in the interlayer domain.\textsuperscript{20} Rietveld analysis from neutron diffraction data suggested that K\textsuperscript{+} ions are highly disordered between two layers. With a split-atom model, the positional disorder of K\textsuperscript{+} ions could not adequately be expressed in view of an extraordinarily large isotropic atomic displacement parameter, U, of about 0.13 Å\textsuperscript{2} for K.

We determined electron densities in K\textsubscript{4}Ti_{2-x}Li_{x}O\textsubscript{4} (x = 0.8) to visualize how K\textsuperscript{+} ions are distributed in between Ti_{2-x}Li_{x}O\textsubscript{4} layers.\textsuperscript{26} Its X-ray powder diffraction data was measured on the diffractometer described in Sect. 2.3. The diffraction data were analyzed by the Rietveld method on the assumption that the same octahedral site (4c) is occupied by Ti\textsuperscript{4+} and Li\textsuperscript{+} ions.\textsuperscript{20} Final R factors were R_{wp} = 11.51\% (S = 1.08) and R_{B} = 5.75\%. Subsequent three REMEDY cycles lowered R_{wp} to 10.59\% (S = 1.00) and R_{B} to 1.91\%. The dramatic decrease in R_{wp} is ascribable to the better representation of the static disorder of K\textsuperscript{+} ions by calculating structure factors from electron densities than from structure parameters in Rietveld analysis.

Figure 6 illustrates isosurfaces of electron densities (number densities of electrons) in K\textsubscript{4}Ti_{2-x}Li_{x}O\textsubscript{4} (x = 0.8). Neither negative densities nor distinct ripples appeared at all, which is a great advantage of MEM over Fourier synthesis. A winding stream of K\textsuperscript{+} ions along the [001] direction and (Ti, Li)–O bonds were clearly visualized by virtue of MEM. The positional disorder of K\textsuperscript{+} ions is partly attributed to large differences in the oxidation states and ionic radii between Ti\textsuperscript{4+} (0.605 Å) and Li\textsuperscript{+} (0.76 Å) ions sharing the same octahedral site. Thus, our first challenge to the determination of spatial distribution for highly disordered species was quite successful.

MPF is suited to structure refinements of intercalation and clathrate compounds where guests have often disordered configurations. In these compounds, split-atom models may fail in providing reasonable atomic displacement parameters or sufficiently low R factors.

### 3.4 Orientational disorder of CO\textsubscript{3}\textsuperscript{2–} ions in Ba\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{4}\textsubscript{δ}

The tetragonal structure of Ba\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{4}\textsubscript{δ} (space group P4\textsubscript{1}2\textsubscript{1}2\textsubscript{1}m) can be related to the perovskite-type compound ABO\textsubscript{3} by locating larger Ba atoms at an A site and smaller Ca, Cu, and O atoms at B sites. Ca atoms and CuO\textsubscript{4} squares lie on the z = 0 plane, Ba and O\textsubscript{2} atoms on the z = 1/4 plane, and Cu\textsubscript{2} (1b; 0, 0, 1/2) and C (1d; 1/2, 1/2, 1/2) atoms on the z = 1/2 plane. Of course, three O atoms form a triangular CO\textsubscript{3}\textsuperscript{2–} ion with the C atom at its center.

Rietveld analysis from neutron powder diffraction data showed that one O\textsubscript{3} atom is split into four pieces to occupy a 4b site on a line connecting C and Cu\textsubscript{2} atoms.\textsuperscript{27} However, the static orientational disorder of CO\textsubscript{3}\textsuperscript{2–} ions is so pronounced that positions of remaining two O\textsubscript{4} atoms could not be determined unambiguously.

We have recently reanalyzed neutron powder diffraction data measured on the BT–1 diffractometer at NIST by MPF and successfully visualized what was overlooked in the previous Rietveld analysis (Fig. 7).

### 4. Closing remarks

I take pride in significant contributions of RIETAN to a great number of X-ray and neutron powder diffraction studies in Japan. Our investigations into superconducting copper oxides\textsuperscript{14} are particularly outstanding. For example, we first analyzed the crystal structures of superconductors incorporating novel structural units: (Nd\textsubscript{2}–Sr\textsubscript{1}) (Nd\textsubscript{2}–Ce\textsubscript{1}) CuO\textsubscript{1–x} with fluoride-like blocks\textsuperscript{28} and (Ba\textsubscript{1}–Sr\textsubscript{1})\textsubscript{2}CuO\textsubscript{3−x} with carbonate-like charge reservoirs.\textsuperscript{25} These studies urged exhaustive searches for new superconductors bearing fluoride-type units and oxoanions. Having a wealth of knowledge about the crystal chemistry of high-T\textsubscript{c}...
superconductors, we put forward a rational method of describing their structures on ground of their structural features.\(^1\),\(^3\)

The techniques of partial profile relaxation and MPF were both devised to overcome limitations of conventional Rietveld analysis. RIETAN-2000 is distinguished from other programs for Rietveld analysis by these elegant methodologies. Furthermore, the VENUS system enhances the worth of RIETAN-2000, helping us understand crystal structures and electron/nuclear-density distribution three-dimensionally. Pair distribution function (PDF) analysis of neutron or X-ray powder diffraction data is a powerful method to obtain local nonrandom atomic displacements in both amorphous and crystalline materials.\(^2\),\(^3\) On the other hand, the MPF method is suitable for the analysis of average structures for crystalline materials whose structures are partly in static and dynamic disorder.

We have been pushing into developing software for ab initio structure analysis, expecting that RIETAN-2000, VENUS, and the forthcoming program will encourage the creativity of researchers in various fields. We sincerely hope that those who are impressed with the capabilities of our programs challenge to build excellent software for powder diffraction.

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References

Fuji Izumi got a master’s degree in applied chemistry at the graduate school of Gunma University in 1974. In the same year, he started to work at National Institute for Research in Inorganic Materials and earned a Ph.D. degree at the University of Tsukuba in 1980. Now, he is a senior researcher at Advanced Materials Laboratory, National Institute for Materials Science. His current research interests are neutron and X-ray powder diffraction, in particular, development of software for powder diffraction.