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A Rietveld-Analysis Program RIETAN-98 and its Applications to Zeolites

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Abstract

The latest version of a Rietveld-analysis program, RIETAN-98, for angle-dispersive diffraction has an advanced feature called partial profile relaxation, which means that primary profile parameters of (nearly) isolated reflections can be locally refined independently of secondary profile parameters. This technique was combined with split-type pseudo-Voigt and Pearson VII profile functions to get better fits between observed and calculated patterns. Furthermore, RIETAN-98 has been substantially integrated with a MEED program for a maximum-entropy method (MEM). Visualization of diffraction data by the MEM is very useful for modifying structural models imperfect with respect to positional disorder and various defects. We have been successfully applying RIETAN-98 to various zeolites with guest materials; three representative results of structure refinements will be demonstrated.

A Rietveld-analysis program, RIETAN [1], has been widely utilized, particularly in Japan and Asia, contributing to a large number of structural studies. RIETAN has a couple of versions for angle-dispersive diffraction and TOF neutron diffraction [2,3]. This article deals with some recent progress in RIETAN for angle-dispersive diffraction with emphasis on our original technology., *i.e.*, partial profile relaxation [3] and integration with a MEED program [4] for a maximum-entropy method (MEM) [5]. Partial profile relaxation, which was first implemented in the TOF neutron diffraction version [3], has been successfully applied to intensity data measured on the Vega diffractometer at the KENS pulsed neutron source. We have recently confirmed that this technology is very effective in the analysis of angle-dispersive diffraction data. MEM analysis of observed structure factors resulting from Rietveld refinement also proved to be helpful in modifying structural models. We have been fully utilizing new features of the latest version, RIETAN-98, to X-ray and neutron diffraction data of zeolites; its excellent ability of structure refinement will be manifested in some examples.

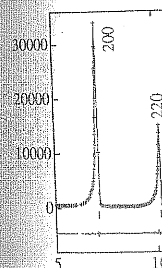
1. Principle of partial profile relaxation

The profile function in Rietveld analysis generally contains two types of profile parameters: primary profile parameter (PPP) and secondary profile parameter (SPP). We shall hereinafter confine our attention to angle-dispersive diffraction. The dependence of PPP's on θ is represented with physical foundations or in empirical ways to give equations including SPP's. For example, in the equation

$$H = (U \tan^2 \theta_k + V \tan \theta_k + W)^{1/2} \tag{1}$$

representing the full-width-at-half-maximum (FWHM), H_k, as a function of the Bragg angle, θ_k, H_k is a PPP specific for reflection k while U, V, and W are SPP's common to the whole 2θ range. We refine not PPP's but SPP's in Rietveld analysis. Such equations impose a kind of equality constraints on PPP's, sometimes failing to express relations between PPP's and θ_k satisfactorily. As a PPP deviates from an equation relating it to θ_k, the fit between observed and calculated profiles gets worse and worse. The resulting misfit gives rise to serial correlation committing a prerequisite of Gaussian distribution of residuals in least-squares methods.

We have devised a new technique called partial profile relaxation [3], where the PPP's of isolated reflections specified by the user are locally refined independently of SPP's. We may also 'relax' the



PPP's of reflections overlapped with other reflections to such an extent that each group of reflections can be readily resolved into the components. In Rietveld refinement with partial profile relaxation, PPP's of these reflections are all or partially freed from equations relating PPP's to θ_k and diffraction indices, *hkl*. 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. Part of PPP's may be constrained by the equations applied to reflections not to be relaxed. Though the profiles of only low-2θ reflections can be substantially relaxed except for relatively simple structures, better fits in this region lead to improvements in fits in a high-2θ region.

Partial profile relaxation is especially suitable for samples showing anisotropic profile broadening and/or highly asymmetric reflections in regions of 2θ less than 20°. This technique is sound and powerful in the point that neither assumption nor approximation is required in regard to the dependence of PPP's on θ_k. We can apply any flexible profile functions to relaxed reflections to improve the agreement between observed and calculated patterns. In principle, the profile relaxation technology can be introduced not only into Rietveld refinement but into Pawley refinement [6].

2. Partial profile relaxation in combination with split-type profile functions

In RIETAN-98, we have combined the technique of partial profile relaxation with the two split-type pseudo-Voigt and Pearson VII profile functions formulated by Toraya [7]. We further implemented a modified split-type pseudo-Voigt function

$$f(x) = \frac{(1+A)\left[\eta_{\mathrm{H}} + \sqrt{\pi \ln 2}\,(1-\eta_{\mathrm{H}})\right]}{\eta_{\mathrm{L}} + \sqrt{\pi \ln 2}\,(1-\eta_{\mathrm{L}}) + A\left[\eta_{\mathrm{H}} + \sqrt{\pi \ln 2}\,(1-\eta_{\mathrm{H}})\right]} \times$$

$$\left\{\eta_{\mathrm{L}} \frac{2}{\pi H_1}\left[1 + \left(\frac{1+A}{A}\right)^2 \left(\frac{x}{H_1}\right)^2\right]^{-1} + (1-\eta_{\mathrm{L}})\left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{2}{H_2} \exp\left[-\ln 2 \left(\frac{1+A}{A}\right)^2 \left(\frac{x}{H_2}\right)^2\right]\right\} \quad (2)$$

where $x = 2\theta_i - 2\theta_k$, $2\theta_i$ is the diffraction angle at the ith step, A is the asymmetry parameter, η is the fraction of the Lorentzian component, H_1 is the FWHM of the Lorentzian component, H_2 is the FWHM of the Gaussian components, and subscripts L and H are the regions of 2θ lower and higher than the peak position, respectively. Equation 2 is effective in the region $x < 0$. For $x > 0$, subscripts L and H should be replaced with each other, and A with $1/A$. The split-type pseudo-Voigt function of Toraya [7] corresponds to a special case of Eq. 2: $H = H_1 = H_2$. Equation 2 may be fit to observed profiles of only relaxed reflections; in this case, Toraya's pseudo-Voigt function is applied to all the other reflections. With partial profile relaxation and the combination of these two pseudo-Voigt functions, we have been successfully analyzing the crystal structures of various zeolites exhibiting reflections in 2θ regions lower than 20°, as illustrated in what follows.

Figure 1 exemplifies low-2θ parts of Rietveld-refinement patterns for a zeolite, hydrated Na-LTA (Linde Type A), with a lattice parameter a as large as 2.461 nm [8]. Its X-ray powder diffraction data were measured with CuKα radiation on (a) a conventional diffractometer and (b) a θ:θ scanning

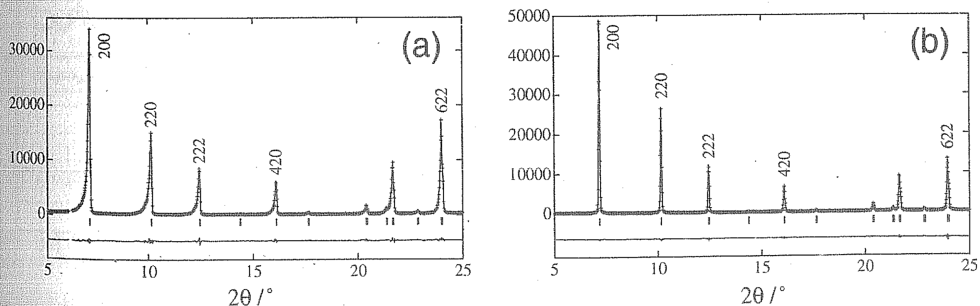


Fig. 1 Observed (plus marks), calculated (solid line), and difference (bottom) patterns of hydrated Na-LTA below 25°. Angular apertures of Soller slits: (a) 5° and (b) 1°.

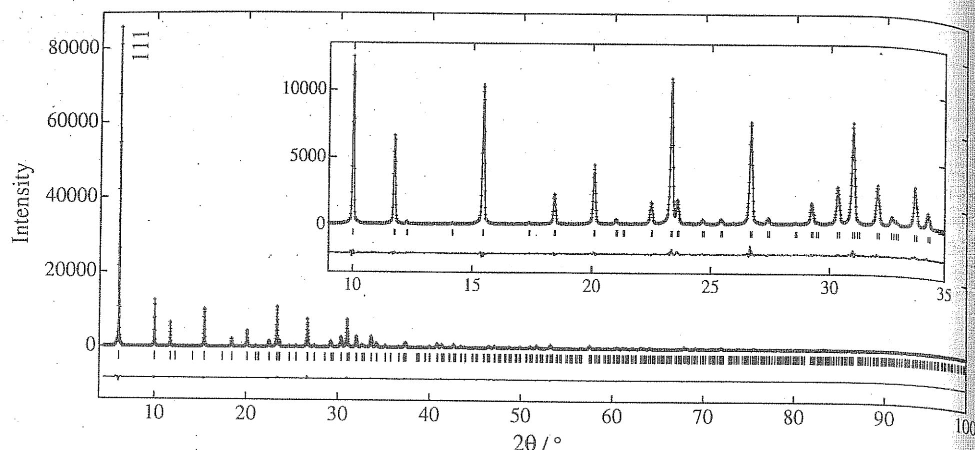


Fig. 2 Rietveld-refinement patterns for hydrated Na-X. X-Ray diffraction patterns between 9° and 35° are magnified in the inset.

diffractometer equipped with a pair of long horizontal Soller slits so as to suppress the axial-divergence error. PPP's of reflections with their indices attached were relaxed in this 2θ region. On combination with the technique of partial profile relaxation, Eq. 2 proved to be satisfactorily fit to the extremely asymmetric profiles in Fig. 1a and fairly symmetric ones in Fig. 1b. Unless otherwise stated, refinements with intensity data taken on the latter diffractometer will be described below.

Figure 2 displays observed, calculated and difference patterns for X-ray Rietveld refinement of hydrated Na-X (faujasite) with a lattice parameter of $a = 2.4988$ nm and 23 sites at general positions. PPP's were independently refined for 17 reflections to afford very low R factors: $R_{\mathrm{wp}} = 7.60\%$ ($R_{\mathrm{e}} = 5.23\%$), $R_{\mathrm{p}} = 5.11\%$, $R_{\mathrm{B}} = 1.75\%$, and $R_F = 1.19\%$. Na^+ ions are situated on framework planes. A large amount of water is included in supercages that consist of 12-membered rings and have a size of 1.3 nm. Each cage was found to be distorted because of the deviation of an Si:Al ratio from unity.

Figure 3 shows the result of neutron Rietveld refinement for $AlPO_4$-5 prepared by microwave heating and incorporating triethylamine as template molecules [9]. The intensity data were measured

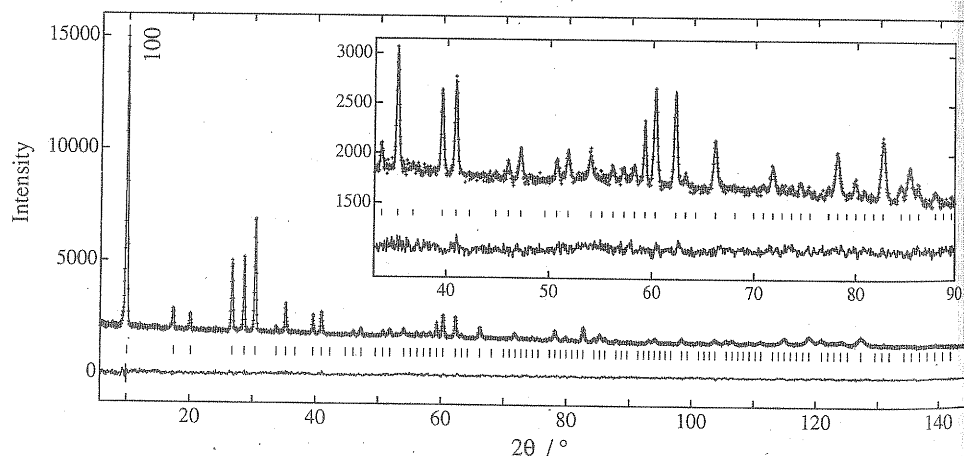


Fig. 3 Rietveld-refinement patterns for $AlPO_4$-5 containing triethylamine. Neutron diffraction patterns between 33° and 90° are magnified in the inset.

on the BT-1 diffractometer at NIST with a neutron wavelength of 0.20785 nm. Marked incoherent scattering from hydrogen atoms in triethylamine is responsible for the fairly high background. In Rietveld refinement based on space group P6cc, we relaxed the PPP's of ten reflections including the highly asymmetric 100 reflection near 10°. Each template molecule with roughly the symmetry of point group C_{3v} proved to be oriented in a so-called head-to-tail manner along the [001] direction. R factors were $R_{\mathrm{wp}} = 1.83\%$ ($R_{\mathrm{e}} = 1.90\%$), $R_{\mathrm{p}} = 1.56\%$, $R_{\mathrm{B}} = 4.25\%$, and $R_F = 3.28\%$. It should be pointed out that equations representing the dependence of the PPP's in the pseudo-Voigt function of Toraya [7] on θ_k could be applied to the neutron diffraction data without any modifications though they were originally optimized for the analysis of X-ray diffraction data.

3. MEM-based whole-pattern fitting and visualization of diffraction patterns

Application of D synthesis to powder data is hindered by the appearance of 'ripples' due to the termination effect even in D synthesis where Fourier coefficients with higher orders are regarded as negligible. This effect makes it difficult to extract physically meaningful residual distribution from D-synthesis maps. Recently, RIETAN-98 has been substantially integrated with the MEM program MEED [4] to form a joint software named REMEDY [10, 11]. In MEM analysis of relatively simple structures powder diffraction data, F_{o}'s were obtained by individual profile fitting [12], the Pawley method [6, 12], or the Le Bail method [13]. The combined use of whole-pattern fitting (including Rietveld analysis) and the MEM is effective for determination of electron/nuclear densities for compounds showing complex diffraction patterns from which F_{o}'s can be hardly derived by pattern decomposition without constructing any structural models.

Figure 4 gives the flow diagram illustrating the normal sequence of structure refinement with REMEDY and two related programs: Fousyn and Mevius developed by Kumazawa. Fousyn is used for Fourier/D synthesis, and Mevius for plotting contour maps and calculating fractional coordinates and atomic displacement parameters from three-dimensional electron/nuclear densities. 'Rietveld,' 'MEM,' and 'w.p.f.' (whole-pattern fitting), each in a pair of parentheses, denote analyses by which structure factors are derived.

After Rietveld analysis, 'observed' structure factors, F_{o}(Rietveld)'s, are evaluated by partitioning observed intensities among overlapping reflections in proportion to their profiles calculated from final parameters in Rietveld analysis [14]. The resulting F_{o}(Rietveld)'s are analyzed by the MEM to give three-dimensional electron or nuclear densities, which are more or less biased by a structural model in Rietveld analysis. Nevertheless, we can extract structural details from the F_{o}(Rietveld)'s by the model-free MEM because the F_{o}(Rietveld)'s contain contributions that have not been taken into account in the structural model. The visualization of diffraction data by the MEM is very useful for modifying

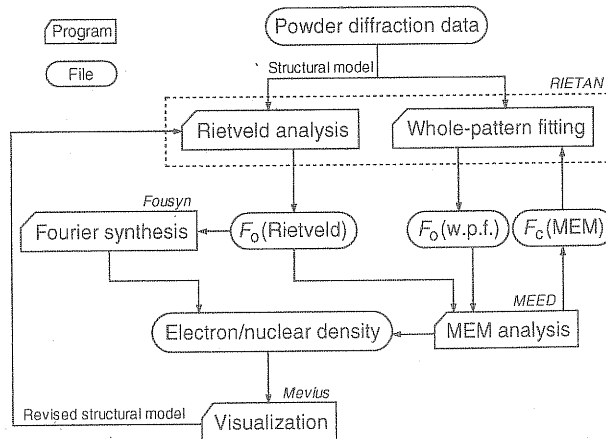


Fig. 4 Programs and files used in Rietveld analysis, MEM-based whole-pattern fitting, and Fourier synthesis.

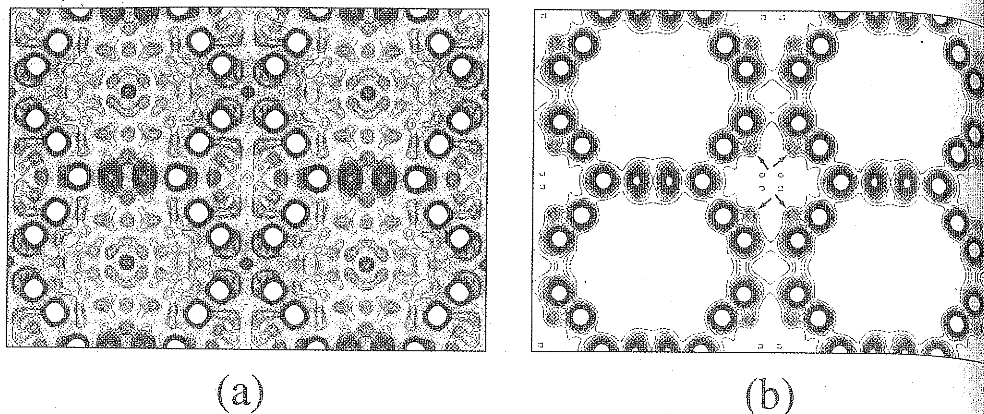


Fig. 5 Electron-density distribution on the (110) section determined for dehydrated Na-LTA by (a) Fourier synthesis and (b) MEM analysis.

structural models imperfect with respect to positional disorder, defects, and partially occupied sites.

Figure 5 shows electron-density maps on the (110) plane obtained by (a) Fourier synthesis and (b) MEM analysis for a sodium-type zeolite, Na-LTA, dehydrated by heating at 350 °C below 10^{-5} Torr for 72 h [8]. Both results were obtained by Rietveld analysis followed by Fourier/MEM analysis with the same number of F_o(Rietveld) data. The vertical axis is parallel to the c axis. Four low peaks pointed by arrows in (b) denote residual water in a β-cage. The termination effect makes it almost impossible to distinguish between residual water molecules and ripples in (a). By contrast, residual water can be clearly seen in (b) at four positions inside the β-cage despite an occupancy as low as 0.028.

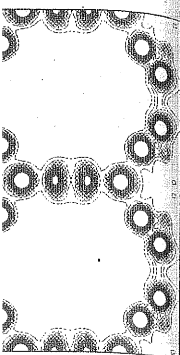
REMEDY is further capable of evaluating structure factors, F_c(MEM)'s, by Fourier synthesis of three-dimensional electron/nuclear densities. We can fit the powder pattern calculated from the F_c(MEM)'s to the whole observed one in order to refine parameters other than structure parameters. F_o(w.p.f.)'s obtained after the whole pattern fitting according to the procedure described above are analyzed again by the MEM. The pattern fitting and MEM analysis are alternately repeated in this manner until R factors in the pattern fitting no longer decrease. The effect of the initial structural model on F_c(MEM)'s diminishes with increasing number of iterations; thus, we can approach the final structure that reflects the observed intensity data more closely. Takata *et al.* [15] utilized a similar approach toward modeling disordered structures of metallofullerenes. REMEDY has the advantage of permitting partial profile relaxation, which makes it possible to obtain lower R factors and refine $|F_o|$'s of relaxed reflections when dealing with (a) neutron diffraction data and (b) X-ray diffraction data for centrosymmetric structures. This original feature will accelerate the convergence of MEM-based structure refinement provided that calculated profiles well agree with observed ones.

The above combined method is expected to model covalent bondings and disordered atomic arrangements more satisfactorily than the conventional Rietveld method. Work is now under way to improve the MEM part of REMEDY further and make integration of RIETAN and MEED more seamless. We will also apply REMEDY to a variety of compounds to demonstrate its great capability and versatility.

4. Other new capabilities

Other features implemented in RIETAN-98 are

1. two peak-shift functions with forms of Legendre polynomials for the split-type profile functions,
2. correction of surface roughness [16] on the basis of models of Sparks *et al.*, Suortti, Pitschke *et al.*, and combination of the Sparks *et al.* and Suortti models,
3. introduction of the anisotropic profile broadening effect into the split-type profile functions,



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4. imposing boundary restraints on interatomic distances and bond angles [1] using outputs from ORFFE,

5. analysis of intensity data measured with variable step widths and counting times,

6. a convenient and user-friendly character-based user interface using a preprocessor,

The first feature was designed to minimize correlations among peak-shift parameters. In the Bragg-Brentano geometry, surface roughness has a more serious effect on relative intensities than had been generally appreciated [16]. It should, however, be noted that the refinable parameters in the four models are highly correlated with each other and with the scale factor. Rietveld analysis under restraints is sometimes indispensable for dealing with zeolites with many atoms in their asymmetric units [17]. The fifth item is very useful for the structure refinement of zeolites because of the abrupt decrease in the diffraction intensity in the high-2θ region.

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