Notes on RIETAN-2000

1. Profile functions

For details in the split pseudo-Voigt function (NPRFN = 1) and split Pearson VII function (NPRFN = 3), refer to Toraya (1990) and Izumi (2000a).

The above split profile functions for reflection K consist of full-width at half maximum (FWHM) H_K, asymmetry parameter A, Lorentzian fraction η (pseudo-Voigt) and decay parameter m (Pearson VII), whose dependence on the Bragg angle θ_K is represented as

$$H_K(\theta_K) = \left[(U+U_e\cos^2\varphi_K)\tan^2\theta_K + V\tan\theta_K + W_K + P_e(\cos\varphi_K\sec\theta_K)^2\right]^{1/2}$$

$$A(\theta_K) = a_0 + a_1(2^{1/2} - \operatorname{cosec}\theta_K) + a_2(2 - \operatorname{cosec}^2\theta_K)$$

$$\eta(2\theta_K) = \eta_0 + \eta_1(2\theta_K)$$

$$m(2\theta_K) = -1.517 + 0.980[m_0 + m_1(2\theta_K)] + 1.578[m_0 + m_1(2\theta_K)]^{-1}$$

φ_K is the acute angle between the reciprocal-lattice vector of reflection K and an anisotropic-broadening axis, $h_a\boldsymbol{a}^* + k_a\boldsymbol{b}^* + l_a\boldsymbol{c}^*$. U_e and P_e were introduced to represent anisotropic broadening due to lattice-distortion and crystallite-size effects, respectively. Two pairs of η and m are assigned to regions of 2θ lower and higher than the peak position.

In the modified split pseudo-Voigt function, the FWHMs of the Lorentzian and Gaussian components may be different from each other (Izumi, Kumazawa, Ikeda & Ida, 1998; Izumi & Ikeda, 2000; Izumi, 2000a). This flexible profile function can be applied to reflections whose primary profile parameters (PPPs) are relaxed when NPRFN = 2; all the other reflections are fit with the split pseudo-Voigt function of Toraya (1990). That is, the modified split pseudo-Voigt function cannot be applied to reflections in the whole 2θ region.

PPPs, which are of course optional, should be placed after the background parameters.

The profile function is selected from the following four options according to the value of NPRFN:

0) NPRFN = 0

The pseudo-Voigt function of Thompson, Cox & Hastings (1987). It was modified in such a way that anisotropic profile asymmetry can be corrected for.

NASYM = 0: Made asymmetric according to a procedure proposed by Finger, Cox, and Jephcoat (1994).

NASYM = 1: Made asymmetric according to a procedure proposed by Howard (1982).

The feature of partial profile relaxation (Izumi & Ikeda, 1999) is not applicable to this profile function. Bear in mind that refinement with NPARN = 0 and NASYM = 0 is very time-consuming.

1) NPRFN = 1

The split pseudo-Voigt function of Toraya (1990). Partial profile relaxation (Izumi & Ikeda, 1999) is also carried out with the same function.

2) NPRFN = 2

The split pseudo-Voigt function of Toraya (1990) is applied to reflection not to be relaxed, in the same manner as in NPRFN = 1. On the other hand, the modified split pseudo-Voigt function is applied to relaxed reflections. ID(I) is the same as in the case of NPRFN = 1. The FWHMs of Lorentzian and Gaussian components are set equal to each other when ID(I) = 3.

3) NPRFN = 3

The split Pearson VII function of Toraya (1990) is used as a profile function, regardless of the use of partial profile relaxation. ID(I) is the same as in 1).

If NCUT is 1, the user can specify the 2θ region where the profile of each relaxed reflection is calculated. Set NCUT at 1 if NPRFN is 2; Otherwise, RIETAN will stop, issuing an error message.

Equations of the three split profile functions are explicitly represented in Izumi (2000a), which can be browsed and printed out as a PDF document at the following URLs:

http://homepage.mac.com/fujioizumi/recent_research/Rigaku_J/Rigaku_J.html

for a manuscript form and

for a reprint form.

2. Peak-shift functions

The peak-shift function is selected from the following five cases:

NSHIFT = 0: t_0.

= 1: $t_0 + t_1\cos2\theta_K + t_2\sin2\theta_K + t_3\tan\theta_K$.

= 2: $t_0 + t_1(2\theta_K) + t_2(2\theta_K)^2 + t_3(2\theta_K)^3$.

= 3: $t_0 + t_1\tan\theta_K + t_2\tan^2\theta_K + t_3\tan^3\theta_K$.

= 4: Legendre polynomials where $2\theta_K$'s are normalized between 0 and 1.

= 5: Legendre polynomials where $\tan2\theta_K$'s are normalized between 0 and 1.

Here, t_0–t_3 are peak-shift parameters.

Options 0–3 are just the same as those described in the user's manual of the program for Pawley refinement by Toraya (1990). In NSHIFT = 4 and 5, Legendre polynomials are respectively used in which $2\theta_K$ (NSHIFT = 2) and $\tan\theta_K$ (NSHIFT = 3) are normalized between –1 and 1 to decrease correlations among t_0–t_3.

The lattice parameters of a standard sample (mixed as an internal standard or only itself) are fixed, and t_0–t_3 (or part of them) are refined in Rietveld analysis. The four peak-shift parameters, t_0–t_3, should be determined with a standard sample having a similar absorption coefficient, and only the zero-point shift, t_0, is refined in actual structure refinement. Ideally, two separate measurements with and without an internal standard are preferable, which is, however, impossible in most cases.

3. Surface-roughness factor

Four different models for correction of surface roughness are available for the Bragg-Brentano geometry:

1) Model of Suortti (1972)

$$S_R(\theta_i) = 1 - p\exp(-q) + p\exp(-q/\sin\theta_i)$$

2) Model of Sparks et al. (1992)

$$S_R(\theta_i) = 1 - t(\theta_i - \pi/2)$$

3) Combination model

$$S_R(\theta_i) = r_s\left[1 - p\exp(-q) + p\exp(-q/\sin\theta_i)\right] + (1 - r_s)\left[1 - t(\theta_i - \pi/2)\right]$$

4) Model of Pitschke et al. (1993)

$$S_R(\theta_i) = 1 - pq(1 - q) - \frac{pq(1 - q/\sin\theta_i)}{\sin\theta_i}$$

where p, q, t, r_s are parameters to be refined in a least-squares method.

Needless to say, the surface-roughness factor is not required for neutron powder diffraction and synchrotron X-ray powder diffraction.

4. Le Bail Refinement

When NMODE is 4, conventional Le Bail refinement (Le Bail, Duroy & Fourquet, 1988) is applicable only to the first phase whereas conventional Rietveld refinement is applied to the other phases, if any. This means that *no structure parameters should be input for the first phases when NMODE = 4.*

In Le Bail refinement with a partial structure (NMODE = 5), structure parameters should be given for all the phases. Initial integrated intensities are calculated from these structure parameters.

A file named *.ffo is always created after Le Bail refinement. *If *.ffo is renamed *.ffi (o: output, i: input), integrated intensities in that file are input when NSFF = 1. Both *.ffo and *.ffi are compatible with the *.hkl file for SIRPOW (Altomare et al., 1994) for resolving the phase problem by the direct method.*

It is highly recommend that in the first Le Bail refinement, initial integrated intensities are estimated by means of Wilson's statistic (NSFF = 0). From the next Le Bail analysis on, integrated intensities are usually input from *.ffo by setting NSFF at 1.

Note that the profile cutoff (PC) should be large enough, *e.g*., 0.05–0.15 (the profile function is calculated down to peak intensity × PC), in an initial stage when the profile is calculated up to points where the peak intensity normalized to 1 drops to PC. PC must be decreased gradually during a series of Le Bail refinements where refinable parameters should be updated (NUPDT = 1).

To learn further details in Le Bail analysis in RIETAN-2000, refer to Izumi (2000b).

5. Features related to a maximum-entropy method (MEM)

Refer to Izumi, Kumazawa, Ikeda & Ida (1998), Izumi (2000a), Izumi, Kumazawa, Ikeda, Hu, Yamamoto & Oikawa (2001), and Izumi & Dilanian (2004) to obtain detailed information about these features.

If NMODE = 0 （Rietveld analysis） and NMEM = 1, F_o(Rietveld) data estimated on the basis of the result of Rietveld analysis (Rietveld, 1969) are output to a MEM data set binary file, *.fos. This file is read in by PRIMA (Izumi & Dilanian, 2004), which carries out MEM analysis to record a 3D densities files, *.pri and a feedback data file, *.fba, storing structure factors, F_c(MEM). These two are both binary files. VEND (Dilanian & Izumi, 2004) is used to input *.pri to visualize 3D electron/nuclear-density distribution. The structural model in the Rietveld analysis is rebuild after close checking of the density image, if necessary. These processes corresponds to the so-called MEM/Rietveld method (Takata, Nishibori & Sakata, 2001).

Further, MEM-based pattern fitting (MPF) must be used to determine more accurate electron/nuclear densities. When NMODE is 2 (MPF) and NMEM is 1 (first phase) in *.ins, F_c(MEM)'s are input from *.fba by RIETAN-2000, and whole-pattern fitting (w.p.f.), where parameters other than structure parameters are refined, is carried out (Izumi, Kumazawa, Ikeda & Ida, 1998; Izumi, 2000a) by a nonlinear least-squares method. The resulting F_o(w.p.f.) data is output to *.fos, which is analyzed by MEM to get *.fba again (Izumi, Kumazawa, Ikeda, Hu, Yamamoto & Oikawa, 2001). In this way, MEM analysis with PRIMA and whole-pattern fitting with RIETAN-2000 are alternately repeated until R factors in the latter no longer decrease.

In MPF (NMODE = 2, 3), all the structure parameters that have been refined in the final Rietveld analysis must be input together with their ID(I)'s (dummies). They are used to

calculate anomalous scattering factors in X-ray diffraction whereas they are dummy data in neutron diffraction. Of course, we should never input 1 for the ID(I)'s of the structure parameters.

If NPRFN = 2, the integrated intensities of relaxed reflections are refined. In other words, the integrated intensities of relaxed reflections are calculated on the basis of the current structural model on the use of the split pseudo-Voigt and Pearson VII function of Toraya (1990).

6. Additional features in New Tink

Block If, else, end if, and else if similar to those in Fortran 77 can now be used. You will see many examples in template files. For example, in the following lines

```
If NBEAM = 1 and NTRAN = 1 then
   DSANG = 0.5: Angle/degree of the divergence slit at the minimum 2-theta.
   RGON = 185.0: Goniometer radius/mm.
SWIDTH = 20.0: Irradiation width/mm for the sample.
   else if NBEAM = 1 and NTRAN = 2 then
   PCOR1 = 0.5: Fraction of the perfect crystal contribution.
   SABS = 1.0: (Linear absorption coefficient)*(effective thickness).
else if NBEAM = 1 and NTRAN = 3 then
   XMUR1 = 0.0: (Linear absorption coefficient)*(radius).
end if
```

the three blocks are skipped unless NBEAM is 1. Otherwise, the first, second, and third blocks are input when NTRAN is 1, 2, and 3, respectively.

Suppose that `Destination` is a string in a pair of lines

```
Go to *Destination
.....
*Destination
```

An unconditional jump to the line of label '*Destination' is carried out when encountering the line of 'Go to *Destination'. An example is included in template files, where a jump to the end of each file is included if NMODE is 1.

7. Files input and output by RIETAN-2000

1) Input files

*.ins: Input data.

*.int: Step-scanned intensity data.

*.bkg: Background spectrum.

*.ffi: An input file storing integrated intensities for Le Bail analysis.

*.ffe: A file created by ORFFE for imposing nonlinear constraints.

Created only when *.ffe is absent and NDA > 0

*.fba: A binary data file created by PRIMA for whole-pattern fitting with RIETAN-2000.

2) Output files

*.itx: Results of Rietveld analysis or simulation.

Used to plot a Rietveld-refinement patterns or a simulated pattern.

*.hkl: Data for Fourier/D syntheses.

*.xyz: ORFFE data (sample.xyz)

*.fos: A binary data file for MEM analysis with PRIMA.

*.ffo: An output file storing integrated intensities for Sirpow and Le Bail analysis.

*.lst: Output file (corresponding to a printer output).

In the above list, '*' may be replaced with any other sample names.

RIETAN-2000 can read in intensity files, *.int, for angle-dispersive X-ray powder diffraction data taken with variable times per step to improve counting statistics in high-angle regions. An example of such files are shown below:

```
FVFM
  5.010  84.0  1.0
  5.020  90.0  1.0
  5.030  88.0  1.0
....
109.990 52.0  2.0
110.000 52.0  2.0
```

where a label 'FVFM' (Fully Variable Format) is located at the first line, which is followed by a series of 2θs, counts, and multiplicities for measurement times per step. All the counts must be divided by the multiplicities to achieve smooth connection of the intensities.

In a reflection list output in *.lst, columns for observed integrated intensities (Iobs) give the following data:

Iobs: Full observed (positive) and calculated profiles have been obtained.
'-': Part of the observed profile is lacking as a result of excluding a 2θ region.
'W': Full observed (negative) and calculated profiles have been obtained.
'H': Part of the profile exceeds $2\theta_{max}$.
'G' + Iobs: Group of reflections with nearly equal d spacings.

8. Modifications of ORFFE instructions

RIETAN-2000 should be used in combination with an extended version of ORFFE (Busing, Martin & Levy, 1964), which is included in the current distribution files. To increase the maximum number of symmetry operations, this version has been extended in such a way that five-columns are assigned to an atom designation, which led to changes in formats of two most important functions of ORFFE.

Function 201

All distances (less than l_{max}) between A_{max} atoms in the asymmetric unit and atoms in all asymmetric units, i.e., all combinations of C and S. For details in A, C, and S, refer to an output of ORFFE.

Columns
1–5   201
6–10 A_{max}, the number of atoms in the asymmetric unit.
26–30   The integer $10l_{max}$. If this is left blank, then $l_{max} = 4.0$ Å.

The format of this line is (2I5,15X,I5).

Function 2

Bond angle defined by three atoms.

Columns

1–5	2
6–15	Atom designation 1.
16–25	Atom designation 2 (vertex).
26–35	Atom designation 3.

The format of this line is (7I5). Each atom designation consists of A and 1000C+S (5 columns for each).

These two functions, if any, must be ordered as above.

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