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Notes on the Rietveld-refinement program RIETAN-2001T for the TOF neutron powder diffractometers Vega and Sirius

Fujio IZUMI

This document has been written to help users of RIETAN-2001T analyze TOF neutron powder diffraction data measured on the Vega and Sirius diffractometers at the KENS pulsed neutron source. Though it is far from perfect, many comment lines sprinkled in the template file makes it easy to create input files.

There are three banks of one-dimensional position-sensitive detectors (PSD) in Vega and Sirius: backward, 90° (average 2θ), and forward banks. In future, we like to carry out simultaneous Rietveld refinements where three intensity datasets measured with the detector banks are combined together. For this purpose, many parameters are added, including dummy parameters for future use.

A function to model the calculated intensity, $f_i(\mathbf{x})$, is required in Rietveld analysis. It contains conversion, background, profile, preferred-orientation, lattice, and crystal-structure, and magnetic-structure parameters, \mathbf{x} , which are fixed (ID(I) = 0), refined (ID(I) = 1), or constrained (ID(I) = 2; calculated from other refinable parameters using a linear equality constraint) in Rietveld analysis.

All the parameters, \mathbf{x} , contained in the model function are stored in array A. They fall into two different types: (1) global parameters, (2) primary profile parameters for relaxed reflections, and (3) phase-dependent parameters.

1. Global parameters

Table 1 lists global parameters independent of constituent phases. Conversion parameters are used to convert the lattice-plane spacing, d , into TOF, t . Background parameters are used to calculate the background intensity with a Legendre polynomial.

In Table 1, I is the absolute parameter number for array A. For example, A(10) is c_4 for the 90° bank.

Table 1. Global parameters

I	Parameters	
1	Conversion parameter, c_0	(Backward)
2	Conversion parameter, c_1	(Backward)
3	Conversion parameter, c_2	(Backward)
4	Conversion parameter, c_3	(Backward)
5	Conversion parameter, c_4	(Backward)
6	Conversion parameter, c_0	(90°)
7	Conversion parameter, c_1	(90°)
8	Conversion parameter, c_2	(90°)
9	Conversion parameter, c_3	(90°)
10	Conversion parameter, c_4	(90°)
11	Conversion parameter, c_0	(Forward)
12	Conversion parameter, c_1	(Forward)
13	Conversion parameter, c_2	(Forward)
14	Conversion parameter, c_3	(Forward)
15	Conversion parameter, c_4	(Forward)
16	Background parameter, b_0	(Backward)
17	Background parameter, b_1	(Backward)
18	Background parameter, b_2	(Backward)
19	Background parameter, b_3	(Backward)
20	Background parameter, b_4	(Backward)
21	Background parameter, b_5	(Backward)

22 Background parameter, b_6 (Backward)
23 Background parameter, b_7 (Backward)
24 Background parameter, b_8 (Backward)
25 Background parameter, b_9 (Backward)
26 Background parameter, b_{10} (Backward)
27 Background parameter, b_{11} (Backward)
28 Background parameter, b_{12} (Backward)
29 Background parameter, b_{13} (Backward)
30 Background parameter, b_{14} (Backward)

31 Background parameter, b_0 (90°)
32 Background parameter, b_1 (90°)
33 Background parameter, b_2 (90°)
34 Background parameter, b_3 (90°)
35 Background parameter, b_4 (90°)
36 Background parameter, b_5 (90°)
37 Background parameter, b_6 (90°)
38 Background parameter, b_7 (90°)
39 Background parameter, b_8 (90°)
40 Background parameter, b_9 (90°)
41 Background parameter, b_{10} (90°)
42 Background parameter, b_{11} (90°)
43 Background parameter, b_{12} (90°)
44 Background parameter, b_{13} (90°)
45 Background parameter, b_{14} (90°)

46 Background parameter, b_0 (Forward)
47 Background parameter, b_1 (Forward)
48 Background parameter, b_2 (Forward)
49 Background parameter, b_3 (Forward)
50 Background parameter, b_4 (Forward)
51 Background parameter, b_5 (Forward)
52 Background parameter, b_6 (Forward)
53 Background parameter, b_7 (Forward)
54 Background parameter, b_8 (Forward)
55 Background parameter, b_9 (Forward)
56 Background parameter, b_{10} (Forward)
57 Background parameter, b_{11} (Forward)

58	Background parameter, b_{12}	(Forward)
59	Background parameter, b_{13}	(Forward)
60	Background parameter, b_{14}	(Forward)

2. Primary profile parameters for relaxed reflections

RIETAN-2001T has an original feature called partial profile relaxation, where primary profile parameters for isolated reflections in a low- Q region are refined without any constraints.

Table 2 gives primary profile parameters for relaxed reflections (total number: NRELAX, number of profile parameters per reflection: NPRIM = 7). I is the absolute parameter number for array A.

Table 1. Primary profile parameters

Const.	I	Parameters
NPPPX	61	σ_0
	62	σ_1
	63	η
	64	σ_2
	65	γ_1
	66	γ_2
	67	R
68–	Seven ppp's are input repeatedly in the same order as parameters No. 61–67	

3. Phase-dependent parameters

Table 3 lists parameters related to constituent phases. In samples containing two or more phases, these parameters are input repeatedly. ‘ppp’ denotes primary profile parameter.

Table 3. Phase-dependent parameters

CONST	K	Parameters
NPPX1	0	Secondary profile parameter, σ_{01} (Backward)
	1	Secondary profile parameter, σ_{02} (Backward)
	2	Secondary profile parameter, σ_{03} (Backward)
	3	Secondary profile parameter, σ_{11} (Backward)
	4	Secondary profile parameter, σ_{12} (Backward)
	5	Secondary profile parameter, σ_{13} (Backward)
	6	Secondary profile parameter, η_1 (Backward)
	7	Secondary profile parameter, η_2 (Backward)
	8	Vacant
	9	Secondary profile parameter, σ_{21} (Backward)
	10	Secondary profile parameter, σ_{22} (Backward)
	11	Vacant
	12	Secondary profile parameter, γ_{11} (Backward)
	13	Secondary profile parameter, γ_{12} (Backward)
	14	Secondary profile parameter, γ_{13} (Backward)
	15	Secondary profile parameter, γ_{21} (Backward)
	16	Secondary profile parameter, γ_{22} (Backward)
	17	Secondary profile parameter, γ_{23} (Backward)
	18	Vacant
	19	Secondary profile parameter, R_1 (Backward)
	20	Secondary profile parameter, R_2 (Backward)
	21	Secondary profile parameter, R_3 (Backward)
	22	Secondary profile parameter, R_4 (Backward)
	23	Vacant
24	Vacant	
NPPX2	25	Secondary profile parameter, 0 (90°)

	26	Secondary profile parameter, 1	(90°)
	27	Secondary profile parameter, 2	(90°)
	28	Secondary profile parameter, 3	(90°)
	29	Secondary profile parameter, 4	(90°)
	30	Secondary profile parameter, 5	(90°)
	31	Secondary profile parameter, 6	(90°)
	32	Secondary profile parameter, 7	(90°)
	33	Secondary profile parameter, 8	(90°)
	34	Secondary profile parameter, 9	(90°)
	35	Secondary profile parameter, 10	(90°)
	36	Secondary profile parameter, 11	(90°)
	37	Secondary profile parameter, 12	(90°)
	38	Secondary profile parameter, 13	(90°)
	39	Secondary profile parameter, 14	(90°)
	40	Secondary profile parameter, 15	(90°)
	41	Secondary profile parameter, 16	(90°)
	42	Secondary profile parameter, 17	(90°)
	43	Secondary profile parameter, 18	(90°)
	44	Secondary profile parameter, 19	(90°)
	45	Secondary profile parameter, 20	(90°)
	46	Secondary profile parameter, 21	(90°)
	47	Secondary profile parameter, 22	(90°)
	48	Secondary profile parameter, 23	(90°)
	49	Secondary profile parameter, 24	(90°)
NPPX3	50	Secondary profile parameter, 0	(Forward)
	51	Secondary profile parameter, 1	(Forward)
	52	Secondary profile parameter, 2	(Forward)
	53	Secondary profile parameter, 3	(Forward)
	54	Secondary profile parameter, 4	(Forward)
	55	Secondary profile parameter, 5	(Forward)
	56	Secondary profile parameter, 6	(Forward)
	57	Secondary profile parameter, 7	(Forward)
	58	Secondary profile parameter, 8	(Forward)
	59	Secondary profile parameter, 9	(Forward)
	60	Secondary profile parameter, 10	(Forward)
	61	Secondary profile parameter, 11	(Forward)
	62	Secondary profile parameter, 12	(Forward)

	63	Secondary profile parameter, 13	(Forward)
	64	Secondary profile parameter, 14	(Forward)
	65	Secondary profile parameter, 15	(Forward)
	66	Secondary profile parameter, 16	(Forward)
	67	Secondary profile parameter, 17	(Forward)
	68	Secondary profile parameter, 18	(Forward)
	69	Secondary profile parameter, 19	(Forward)
	70	Secondary profile parameter, 20	(Forward)
	71	Secondary profile parameter, 21	(Forward)
	72	Secondary profile parameter, 22	(Forward)
	73	Secondary profile parameter, 23	(Forward)
	74	Secondary profile parameter, 24	(Forward)
NPO1X	75	Preferred-orientation parameter, 1 r (March-Dollase function) or p_1 (Sasa-Uda function)	
NPO2X	76	Preferred-orientation parameter, 2 p_2 (Sasa-Uda function)	
NEXTX	77	Extinction parameter, E	
NSFX	78	Scale factor, s	
NAX	79	Lattice parameter, $a/\text{\AA}$	
NBX	80	Lattice parameter, $b/\text{\AA}$	
NCX	81	Lattice parameter, $c/\text{\AA}$	
NALPX	82	Lattice parameter, α/degree	
NBETX	83	Lattice parameter, β/degree	
NGAMX	84	Lattice parameter, γ/degree	
NOTX	85	Overall isotropic atomic displacement parameter, $Q/\text{\AA}^2$	
NG1X	86	Occupation factor, g_j	
	87	Fractional coordinate, x_j	
	88	Fractional coordinate, y_j	
	89	Fractional coordinate, z_j	
	90	Isotropic atomic displacement parameter, $B_j/\text{\AA}^2$, or anisotropic atomic displacement parameter, β_{11j}	
	91	Anisotropic atomic displacement parameter, β_{22j}	
	92	Anisotropic atomic displacement parameter, β_{33j}	
	93	Anisotropic atomic displacement parameter, β_{12j}	

- 94 Anisotropic atomic displacement parameter, β_{13j}
- 95 Anisotropic atomic displacement parameter, β_{23j}
- 96 Magnetic moment, μ_j/μ_B
- 97 Angle between the spin direction and a particular direction of the crystal (tetragonal, hexagonal, and rhombohedral), ϕ/degree
- 98 Angle between the spin direction and the a^* axis (orthorhombic, monoclinic, and triclinic), ϕ_a/degree
- 99 Angle between the spin direction and the b^* axis (orthorhombic, monoclinic, and triclinic), ϕ_b/degree
- 100 Angle between the spin direction and the c^* axis (orthorhombic, monoclinic, and triclinic), ϕ_c/degree
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4. Notes on parameters

For dummy parameters, refinement identifiers (ID) must be also input. A dummy parameter and a refinement identifier (ID) of zero must be input for p_2 in the case of the March-Dollase function.

Up to the first crystallographic site, an absolute parameter number, I, for array A is obtained by $KPHB(L) + K$, where L is the phase number, and $KPHB(L)$ is the number for the first parameter of phase L ($KPHB(1)$ depends on the number of relaxed reflections), and K is the relative parameter number for a phase-dependent parameter. For multiphase samples, phase-dependent parameters are repeatedly input in the order of increasing phase number, L. The values of the integer constants (NSFX, NPO1X, *etc.*) in the first column are given in SUBROUTINE SETNUM.

RIETAN-2001T has an original new feature called partial profile relaxation. Its development code is 'Margot' after a novel by Alexandre Dumas. For details in partial profile relaxation, please refer to my home page:

http://www.nirim.go.jp/~izumi/recent_research/Rigaku_J/Rigaku_J.html

In conventional Rietveld analysis, primary profile parameters are calculated from secondary ones, which are refined by a nonlinear least-squares method. In profile-relaxed Rietveld analysis, primary profile parameters (ppp's) are refined independently when part of reflections exhibit marked anisotropic profile broadening. No assumptions are required on the dependence of the ppp's on d . A label for a group of seven ppp's has a form 'PPP $n_{h.k.l}$ ', where n is the phase number, and h , k , and l are indices of a relaxed reflection broadened anisotropically. For example, if reflection 101 for phase No. 1 is broadened anisotropically, label 'PPP1_1.0.1' is input together with seven ppp's, which are refined quite independently of secondary profile parameters for the relevant phase. Integrated intensities and peak positions, t_0 , for the user-specified reflections are calculated in the same manner as those for the other reflections. An ID(I) value of 2 can be assigned to any ppp. If $A(I) = 0$ and $ID(I) = 0$ for a ppp of a relaxed reflection, it is calculated from secondary profile parameters.

Structure parameters (K = 86–96) are repeatedly entered as many times as the number of atoms in the asymmetric unit; subscript j denotes the site number. If an overall isotropic atomic displacement parameter (K = 85) is used to be given a non-zero value, isotropic/anisotropic atomic displacement parameters (K = 90–95) are skipped. On the other hand, *Q is not skipped but given a dummy zero value even if isotropic/anisotropic atomic displacement parameters are assigned for atoms in the asymmetric unit.* When

the isotropic atomic displacement parameter is assigned to the j th site, anisotropic atomic displacement parameters are skipped, and *vice versa*. The magnetic moment (K = 96) is input for only a magnetic atom in neutron diffraction.

The magnetic moment (K = 96) is input only for a magnetic atom in neutron diffraction (Shirane, 1959). Angles between the spin direction and the a, b, and c axes (K = 97–100) are necessary only for magnetic atoms when analyzing neutron diffraction data of non-cubic compounds showing magnetic scattering resulting from collinear spin arrangements (Shirane, 1959). Collinear magnetic structure factors for monoclinic and triclinic systems were derived by N. Yamada (1995) of the University of Electro-Communications independently of the famous work by Shirane (1959).

At present, the parameters for the BS bank are included in the model function, whereas those for the 90° and 30° banks are not used but reserved for future multi-bank Rietveld refinement.

5. Simulation

An incident spectrum corrected for absorption and multiple scattering is indispensable for simulation of a TOF neutron powder diffraction pattern. Then, *.int file must be included in the same directory (folder) as *.ins. The incident spectrum is input from this file.

6. Notes on the use of RIETAN-2001T on the Macintosh

RIETAN-2001T can be run on the Macintosh in a similar way as RIETAN-2000. Only the Power Macintosh version is supplied.

A preference file named 'Preferences,' which is self-evident, should be placed in the same directory as 'ran'. The content of this file must be edited to change creators of files input/output by RIETAN-2001T.

RIETAN-2001T can be run by double-clicking 'ran'. Specify an *.ins file in an open dialog-box.

7. Notes on the use of Igor Pro in combination with RIETAN-2001T

Igor Pro for the Macintosh is a graph-plotting program which is most powerful than SigmaPlot when drawing two-dimensional graphs. Igor text files output by RIETAN-2001T include not only refinement results but a series of commands to produce the patterns automatically. Igor Pro is, therefore, very rapid and convenient for plotting Rietveld-refinement/simulation patterns. Refer to the user manual of Igor Pro to learn details in Igor text files.

To plot Rietveld-refinement/simulation patterns, all what you must do is (i) to select 'Load Igor Text' in the 'Load Waves' submenu under the 'Data' menu and then specify a '*.pat' file to be read in, (ii) to double-click this file from the Finder, or (iii) to drag this file and drop onto an icon of Igor Pro. Smart operations like (ii) and (iii) are possible because Igor text files created by RIETAN-2001T hold information about the Type and Creator characteristics of Macintosh-format files.

Tick marks are plotted for up to three phases. Extra negative tick labels and corresponding ticks for the ordinate are erased using the feature of 'Enable ticks between' in the 'Tick Tweaks' sub-dialog under the 'Modifying Axes' item from the 'Graph' menu. Wave names for $y_i - f_i(x)$ and y coordinates of tick marks for the n th phase are 'delta' and 'yphasen' ('yphase1', 'yphase2', and 'yphase3'), respectively. A pattern of only one phase can be plotted in the case of simulation, as in SigmaPlot. Vertical positions of difference patterns and tick marks are adjusted by inputting commands in the command window in such a way as 'delta=delta+300' and 'yphase1=yphase1-120.'

With Igor Pro, we can also scale part of a graph manually. X and y coordinates of a point can be read in the following way:

- 1) Select the 'Show Info' item from the 'Graph' menu. The alternative to this operation is to press Command-I.
- 2) Click a cursor at home (two cursors, circle with + and square with \times , are available) and drag it to the desired point on the wave whose values you want to know.
- 3) X and y values appear in the readout area.
- 4) The cursor can be moved by (a) dragging the slide control right or left, (b) clicking on one side or the other of the slide control, (c) using arrow keys on your keyboard (particularly convenient when examining yphasen), or (d) dragging the cursor directly to the desired point. Note that the cursor can be moved to another wave.

- 5) If the cursor is no longer necessary, you can remove it from the graph by dragging it away from the plotting area.
- 6) Select the 'Hide Info' item from the 'Graph' menu. The alternative to this operation is to press Command-I.