



AUSTRALIAN NUCLEAR SCIENCE AND TECHNOLOGY ORGANIZATION

LUCAS HEIGHTS RESEARCH LABORATORIES

LHPM

A COMPUTER PROGRAM FOR RIETVELD ANALYSIS
OF X-RAY AND NEUTRON
POWDER DIFFRACTION PATTERNS

by

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ABSTRACT

This manual gives detailed instructions for the Rietveld analysis computer program LHPM. The program is based on a program from Wiles and Young* but incorporates improvements which make it significantly different. Extensions to the program allow refinements of multiple x-ray and/or neutron datasets. A brief account of the Rietveld method and its implementation, and a program description are included.

*Program DBW3.2 of D.B. Wiles and R.A. Young, School of Physics and Engineering Experimental Station, Atlanta, Georgia 30332, USA.

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1. INTRODUCTION

The Rietveld method [Rietveld,1969, Rietveld,1967] for the analysis of X-ray and neutron powder diffraction patterns is now well established. (See, for example, reviews by [Cheetham and Taylor,1977], [Albinati and Willis,1982] and [Taylor,1985]) This is a method for crystal structure refinement that does not use integrated powder diffraction intensities, but employs directly the profile intensities obtained from step-scanning measurements of the powder diagram. The Rietveld method can also be used in conjunction with Fourier techniques to assist in the *ab initio* solution of crystal structures from powder diffraction data.

The first computer program for the implementation of the Rietveld method was described by Rietveld [1969]. This program was written specifically for the analysis of neutron diffraction data from fixed-wavelength diffractometers. The program had two steps: a data preparation step, and a refinement step. The program was developed further by [Hewat,1973] and applied by a number of other workers with great success. [Von Dreele, et al.,1982] extended the program to the refinement of neutron patterns recorded with time-of-flight diffractometers. Meanwhile, the first applications of the Rietveld method to the analysis of X-ray data were reported [Malmros and Thomas,1977] and [Khattak and Cox,1977]. Additional programs for Rietveld refinement have been described, including those by [Pawley, et al.,1977] and [Baerlocher,1993] which allow the refinement of crystal structures subject to quite sophisticated constraints, and The Generalised Structure Analysis System (GSAS) by [Larson and Von Dreele,1986] includes some of these features in a menu driven system.

[Wiles and Young,1981] described a program for the Rietveld analysis of either X-ray or neutron diffraction patterns recorded with conventional (fixed wavelength) diffractometers. This program incorporated certain important advances in that it allowed the refinement of the structures of two phases simultaneously, it accommodated data recorded at either one or two wavelengths (the two-wavelength option could be used for data obtained with the X-ray doublet), and it offered the choice of four peak shape functions. The background could be prescribed or refined as required. The program was relatively easy to use, with single-step operation (in contrast with earlier programs), a built-in table of X-ray scattering factors and neutron nuclear scattering lengths, and calculation of symmetry operators from a standard space-group symbol. [Wiles and Young,1981] referred to version DBW2.9 of their program, written in Fortran IV. Later, a version DBW3.2, written in Fortran 77, was distributed. This version benefited from the experience with DBW2.9 of a number of users, including ourselves. We made extensive use of version DBW3.2, then developed from it a new program called LHPM5, which is described below. The new program retains all the desirable features of the Wiles and Young program DBW3.2, and in addition incorporates the following changes:

- A rearrangement of the peak shape options, which also provides for the possible variation of peak shape across the pattern [Hill and Howard,1985, Hill,1984] and the application of different peak shapes for the different phases.
- Inclusion of a pure Voigt peak shape function, intended mainly for use in the analysis of neutron data. This is coded with a Gaussian component, the width of which varies according to the formula given by [Caglioti, et al.,1958], and a Lorentzian component with width varying as for particle-size broadening.
- An option to model peak asymmetry using either the asymmetric multiplying factor suggested by [Rietveld,1969] or the sum of (five) symmetric functions developed by [Howard,1982].
- Inclusion of a term of the form $(2\theta)^{-1}$ in the background function to account for the observed variation of background in the low angle region.
- A modification of the weighting scheme to provide for appropriate weighting of data from multicounter diffractometers. Weights may be based on either observed or calculated intensities as required.
- Calculation and output of coefficients for use in subsequent Fourier analyses.
- Extensive modification of the derivative calculations, to improve program structure and efficiency, and several other more technical program amendments.

The increasing use of synchrotron powder diffraction, time-of-flight neutron diffraction and simultaneous x-ray/neutron refinements has made it desirable to add several new capabilities to LHPM. These include:

- Ability to read new data formats, including higher precision 2θ values in the input and data files, and a listed format datafile consisting of rows of 2θ , Intensity (and optionally weight(Intensity)).
- Multiple x-ray and/or neutron histograms (datasets) allowing different scales, zeros, peak profile types and values, backgrounds, wavelengths, preferred orientations for each histogram - all of which are refinable.

- Ability to calculate and refine neutron time-of-flight data.
- Each histogram can have it's own scattering form factors/lengths, so can be used in anomalous scattering experiments. The ability to refine f' and f'' now allows extra flexibility with synchrotron diffraction data.
- Can interpolate x-ray form factors from a series of $(\sin(\theta)/\lambda, f)$ values, so that any form factor profile can be used. The old scheme of fitting the values to a form factor equation has been removed.
- An anisotropic gaussian peak broadening for all peak shape types.
- Ability to refine wavelength(s).
- A new absorption correction formula allowing $\mu_R > 1.0$, based on [Sabine, et al.,1997] for cylindrical geometry and a flat plate absorption correction based surface roughness by [Hermann and Ermrich,1987]
- New background functions to deal with amorphous background contributions
- Several technical amendments including: calculation of contributions from peaks at low 2θ (in addition to the high 2θ) beyond the observed data limits and improvements in the U, V, W calculations
- Ability to stop calculation of weak peaks, such as for large monoclinic cells in multiphase systems.
- Addition of a new peak shape specifically for TOF based on the convolution of a pair of split exponentials with a pseudo-Voigt function.
- Allows a phase to be calculated from atomic site information (normal method) or the intensities can be extracted using the Le Bail extraction method.
- Calculates bond distances and angles (with cross-correlation errors), and metal – oxygen/chlorine/fluorine bond valences.
- Addition of the Finger, Cox and Jephcoat asymmetry correction for the Pseudo-Voigt peak shape. [Finger et al, 1997].
- Has the option to use the Marquardt algorithm for least squares refinement. This dramatically increases the chances of convergence in an unstable refinement.

The LHPM program has been run successfully on the following computers: IBM-PC compatible's, Silicon Graphics, VAX-VMS, DEC-Station and DEC-Alpha's.

This manual documents version 6.6 of our computer program for the Rietveld analysis of X-ray and neutron powder diffraction patterns.

2. THE METHOD AND ITS IMPLEMENTATION

The basis of the Rietveld method [Rietveld,1969, Rietveld,1967] is the equation

$$y_{ic} = y_{ib} + \sum_p \sum_{k=k_1}^{k_2} G_{ik}^p I_k \quad (1)$$

where y_{ic} the net intensity calculated at point i in the pattern, y_{ib} is the background intensity, G_{ik} is a normalised peak profile function, I_k is the intensity of the k^{th} Bragg reflection, $k_1 \dots k_2$ are the reflections contributing intensity to point i , and the superscript p corresponds to the possible phases present in the sample.

The intensity I_k is given by the expression

$$I_k = S M_k L_k |F_k|^2 P_k A_k E_k \quad (2)$$

where S is the scale factor, M_k is the multiplicity, L_k is the Lorentz-polarisation factor, and F_k is the structure factor,

$$F_k = \sum_{j=1}^n f_j \exp[2\pi i(\mathbf{h}_k^t \mathbf{r}_j - \mathbf{h}_k^t \mathbf{B}_j \mathbf{h}_k)] \quad (3)$$

where f_j the scattering factor or scattering length of atom j , and \mathbf{h}_k , \mathbf{r}_j and \mathbf{B}_j are matrices representing the Miller indices, atomic coordinates and anisotropic thermal vibration parameters, respectively, and the superscript t indicates matrix transposition. The factor P_k is intended to describe the effects of preferred orientation: for powders unaffected by preferred orientation $P_k = 1$. The factor A_k is the absorption correction and E_k an extinction correction.

The positions of the Bragg peaks from each phase are determined by their respective set of cell dimensions, in conjunction with a zero parameter and the wavelength (or diffractometer constants) provided. All of these parameters may be refined simultaneously with the profile (see below) and crystal structural parameters. For TOF the position of the Bragg peak is calculated using

$$\text{TOF}_k = \text{DIFC} \cdot d_k + \text{DIFA} \cdot d_k^2 + \text{ZERO} \quad (4)$$

where d_k is the d spacing of the k^{th} reflection, DIFC is the diffractometer constant and is dependent on the path length of the instrument, DIFA is a variable correction factor and ZERO is the zero point value.

The wavelength (or diffractometer constant) is refinable, but some or all of the cell dimensions must be fixed to avoid divergences in the least squares procedure. When more than one wavelength is used in a histogram, such as $K\alpha^1$ and $K\alpha^2$, the second wavelength is automatically tied to the first so that λ_1/λ_2 is constant. The ratio of the intensities for two possible wavelengths is absorbed in the calculation of $|F_k|^2$, so that only a single scale factor for each phase is required. This ratio is not a refinable parameter.

2.1 Peak Shape Functions

The peak profile function G_{jk} can be chosen from the following options:

(a) Pseudo-Voigt

$$G_{ik} = \gamma \frac{C_0^{1/2}}{H_k \pi} \left[1 + C_0 X_{ik}^2\right]^{-1} + (1-\gamma) \frac{C_1^{1/2}}{H_k \pi^{1/2}} \exp\left[-C_1 X_{ik}^2\right] \quad (5)$$

where $C_0 = 4$, $C_1 = 4\ln 2$, H_k is the full-width at half-maximum (FWHM) of the k^{th} Bragg reflection, $X_{jk} = (2\theta_i - 2\theta_k)/H_k$ and γ is a refinable 'mixing' parameter.

(b) Pearson VII

$$G_{ik} = \frac{\Gamma(\gamma)}{\Gamma(\gamma - 1/2)} \frac{C_2^{1/2}}{H_k \pi^{1/2}} \left[1 + 4C_2 X_{ik}^2\right]^{-\gamma} \quad (6)$$

where $C_2 = 2^{1/\gamma} - 1$ and Γ denotes the gamma function.

(c) **Voigt**

$$G_{ik} = \frac{C_1^{1/2}}{H_{Gk} \pi^{1/2}} \operatorname{Re} \left[\omega \left(C_1^{1/2} X_{ik} + i C_3 \frac{H_{Lk}}{H_{Gk}} \right) \right] \quad (7)$$

where $C_1 = 2 \ln 2$, $C_3 = (\ln 2)^{1/2}$, H_{Gk} is the FWHM of the contributing Gaussian, H_{Lk} is the FWHM of the contributing Lorentzian, ω is the complex error function, $\omega(z) = \exp(z^2) \operatorname{erfc}(z)$, and Re denotes its real part.

(d) **TOF Exponential \otimes Pseudo-Voigt**

$$G_{ik} = \frac{\alpha\beta}{2(\alpha+\beta)} \left[(1-\eta) (e^u \operatorname{Erfc}(y) + e^v \operatorname{Erfc}(z)) - \frac{2\eta}{\pi} \operatorname{Im} (e^p E_1(p) + e^q E_1(q)) \right] \quad (8)$$

where α and β are exponential decay terms defined to vary with d-spacing, d, as $\alpha = \alpha_0 + \alpha_1/d$ and $\beta = \beta_0 + \beta_1/d^4$ respectively. The functions Erfc and E_1 are the complex error function and complex exponential integral function respectively. The other terms are defined as $u = 0.5\alpha(\alpha\sigma^2 + 2X_{ik})$, $v = 0.5\beta(\beta\sigma^2 - 2X_{ik})$, $y = (\alpha\sigma^2 + X_{ik})/(\sqrt{2}\sigma)$, $z = (\beta\sigma^2 - X_{ik})/(\sqrt{2}\sigma)$, $p = -\alpha X_{ik} + i\alpha\gamma/2$, $q = -\beta X_{ik} + i\beta\gamma/2$ and $X_{ik} = (TOF_i - TOF_k)/H_k$, where H_k is the FWHM. The value σ is related to the FWHM of the contributing Gaussian by $H_G = \sigma (8 \ln 2)$, and γ is related to the Lorentzian FWHM by $H_L = \gamma$. The total FWHM is determined by the expression,

$$H_k = (H_G^5 + 2.69269H_G^4H_L + 2.42843H_G^3H_L^2 + 4.47163H_G^2H_L^3 + 0.07842H_GH_L^4 + H_L^5)^{0.2} \quad (9)$$

and the value η is determined by

$$\eta = 1.36603(H_L/H_k) - 0.47719(H_L/H_k)^2 + 0.11116(H_L/H_k)^3 \quad (10)$$

as given by Thompson et al.

The pseudo-Voigt and Pearson VII profile functions can be assigned a fixed shape of any type between their limiting Gaussian and Lorentzian forms ($\gamma = 0$ and 1 , respectively, for the pseudo-Voigt and $\gamma = \infty$ and 1 , respectively, for the Pearson VII). Alternatively, the peak shape can be varied across the pattern by application of the function

$$\gamma = \gamma_1 + \gamma_2 2\theta + \gamma_3 (2\theta)^2 \quad (11)$$

where γ_1 , γ_2 and γ_3 are refinable parameters (γ_3 is not operational for the Pearson VII function).

For both of these profile types, the variation of the peak FWHM is defined by the function described by [Caglioti, et al., 1958]:

$$H_k = (U \tan^2\theta + V \tan\theta + W)^{1/2} \quad (12)$$

where U , V and W are refinable parameters. The U parameter can have an additional (hkl) dependent term, U_{anis} , defined as $U_{anis} = U_a \cos^2\phi$, where ϕ is the angle between the (hkl) reflection and the direction of anisotropic broadening. The parameter U_a is refinable. The U value is typically associated with strain broadening. A particle size parameter, typically having a $\sec(\theta)$ dependence, can be calculated from U and W , via $\sec^2(\theta) = 1 + \tan^2(\theta)$.

In the case of the Voigt profile function, the widths of the Gaussian and Lorentzian components of the peaks are coded to vary in separate ways with 2θ . The Gaussian component width varies in accordance with equation (12), but the width of the Lorentzian component varies with $\sec\theta$ and $\tan\theta$:

$$H_{Lk} = \frac{180}{\pi} \frac{\lambda}{D} \sec(\theta) + \frac{180}{\pi} S \tan(\theta) = K_s \sec(\theta) + K_t \tan(\theta) \quad (13)$$

The Scherrer equation, the $\sec(\theta)$ dependent term, is an attempt to describe particle-size effects. We note that a physical interpretation of the resultant 'size' parameter, D , is likely to have meaning only in the case of neutron diffraction data for which the instrumental component of the peak shapes is Gaussian in form. The $\tan(\theta)$ term, is a strain dependent term, similar to that in equation (12).

For the TOF profile function, the widths are governed by a Gaussian component of the form:

$$H_{Gk} = \sqrt{\sigma_0^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4 + \sigma_3 d^2 \cos^2(\phi)} \sqrt{8 \ln(2)} \quad (14)$$

where d is the d -spacing (Å). The σ_1 term is related to strain broadening, the σ_2 term to particle size broadening and σ_3 is an anisotropic strain term. The Lorentzian component, H_{Lk} has the form,

$$H_{Lk} = (\gamma_0 + \gamma_1 d + \gamma_2 d^2) \quad (15)$$

Following [Rietveld,1969] three of the CW profile functions can be corrected for peak asymmetry using the semi-empirical function

$$A_{ik} = 1 - AS [\text{sign}(2\theta_i - 2\theta_k)] (2\theta_i - 2\theta_k)^2 \cot(\theta_k) \quad (16)$$

where AS is a parameter to be determined.

In the cases of the pseudo-Voigt and Voigt profile functions, an asymmetry correction may also be applied in the form of a sum of five pseudo-Voigt or five Voigt peaks. [Howard,1982] has demonstrated that this procedure provides a more physically appropriate correction for peak asymmetry in the case of neutron fixed wavelength powder diffraction data.

The asymmetry of Finger, Cox and Jephcoat can also be used in the case of the pseudo-voigt peak shape. It gives excellent results where instrumental asymmetry causes problems and the Howard asymmetry is inadequate. The asymmetry is defined by two parameters, S/L and D/L, where S/L is the source size to sample-detector distance ratio and D/L is the detector size to sample-detector distance ratio. It is best to fix these if known, as the refinements can sometimes be unstable with both parameters refined simultaneously. Use of the Marquardt algorithm can help in the stability.

2.2 Preferred Orientation

The intensity I_k of the Bragg peaks can be modified during structure refinement to allow for preferred orientation due to the presence of platy crystallites in the sample by use of the function ([Dollase,1986])

$$P_k = [P_1^2 \cos^2 \alpha_k + P_1^{-1} \sin^2 \alpha_k]^{-3/2} \quad (17)$$

where P_1 is a refinable parameter, and α_k is the acute angle between the scattering vector and the normal to the crystallites (calculated internally from the Miller Index of the crystal platelet face). Typically, for high symmetry space groups, P_k is calculated as a sum over all equivalent reflections since the angle α_k can be different for each equivalent reflection. For symmetries lower than tetragonal it is not required. This ability can be turned on and off using a flag (IPREF).

2.3 Absorption Correction

The value of I_k , may also be corrected for the effects of sample absorption by applying a transmission factor. For CW X-ray and neutron data the correction of [Sabine, et al.,1997] is used:

$$A_k = A_B(\mu R) \cos^2 \theta_k + A_L(\mu R) \sin^2 \theta_k \quad (18)$$

where μR is the product of the radius of the cylindrical sample and its linear absorption coefficient. The functions A_B and A_L are the Bragg and Laue absorption terms as calculated analytically by [Dwiggins,1973].

For flat plate geometry, where absorption from weak surface roughness is a significant factor, the expressions of [Hermann and Ermrich,1987] are used:

$$A_k = (1 - P_0 - P_s(\theta)) = 1 - P_0 (1 + \alpha_0 (\tau/\sin(\theta)) (1 - \tau/\sin(\theta)) - 1) \quad (19)$$

where P_0 is the bulk term, while P_s is a θ dependent term and is a function of the packing density, α_0 , and the degree of roughness, τ . The parameters P_0 , α_0 and τ are refinable, although P_0 can be highly correlated to the scale factor.

For TOF neutron data, the absorption is corrected using,

$$A_k = \exp[-\mu R d] \quad (20)$$

where μR is refinable.

2.4 Extinction Correction

Extinction for constant wavelength is corrected using the [Sabine,1988] extinction correction,

$$E_k = E_B \cos^2\theta_k + E_L \sin^2\theta_k \quad (21)$$

where k is the reflection and E_B and E_L are the extinction at the Bragg ($\theta=90$) and the Laue ($\theta=0$) conditions respectively. These are given by,

$$E_B = \frac{1}{\sqrt{1+x}} \quad (22)$$

and

$$E_L = \begin{cases} 1 - \frac{x}{2} + \frac{x^2}{4} - \frac{5x^3}{48} + \dots & x < 1 \\ \sqrt{\frac{2}{\pi x}} \left[1 - \frac{1}{8x} - \frac{3}{128x^2} - \frac{15}{1024x^3} + \dots \right] & x > 1 \end{cases} \quad (23)$$

where $x = D \cdot (\lambda \cdot F_k / V)^2$, D = mosaic block size, λ = wavelength, F_k = structure factor of reflection k and V = volume of unit cell.

No extinction correction is used for neutron time-of-flight as yet.

2.5 Lorentz-Polarization Factor

The Lorentz-Polarization factor consists of two factors: a polarization correction and a powder specific correction. For x-ray diffraction, the incident x-ray beam can be polarized or non-polarized. If the incident beam is unpolarised then the scattered intensity (single crystal or powder) is modified by,

$$P = (1 + \cos^2(2\theta)) / 2 \quad (24)$$

For neutrons there is no polarization factor. Equation (24) is modified to become, for single crystal diffraction, the Lorentz-polarization factor,

$$LP = (1 + \cos^2(2\theta)) / (2 \sin(2\theta)) \quad (25)$$

This is the correction needed for a single crystal in an unpolarised beam. For a powder there is an additional term of $1/\sin(\theta)$.

2.6 Background

The background y_{ib} may be obtained in one of five ways:

- (i) by measurement in an independent data collection run without the sample in place (data on input unit 2),
- (ii) by estimation at several positions where no peaks appear to contribute and by linear interpolation for the points in between,
- (iii) by refinement of the polynomial function

$$y_{ib} = \sum_{m=-1}^n B_m (2\theta)^m \quad (26)$$

where B_m is one of six refinable parameters,

- (iv) by refinement using a type I or II Chebyshev polynomial function (shifted or non-shifted)

$$y_{ib} = \sum_{m=0}^n B_m T_m(2\theta) \quad (27)$$

where B_m are refinable parameters and T_m is the Chebyshev function (defined by $T_{n+1}(x) - 2xT_n(x) + T_{n-1}(x) = 0$, where $T_0 = 1$ and $T_1 = x$), or

- (v) by refinement of the function

$$y_{ib} = B_0 + B_1 Q + \sum_{m=1}^n B_{2m} \frac{\sin(QB_{2m+1})}{QB_{2m+1}} \quad (28)$$

where B_m are refinable parameters and $Q = 4\pi \sin(\theta)/\lambda = 2\pi/d$. This function is typically used when there is an amorphous component. The values B_{2m+1} are nearest neighbour distances r_{nn} and B_{2m} are the amplitudes. The B_1 term is either $B_1 Q$ or $B_1 \theta$ for TOF or CW respectively.

The number of background terms, n , used in the series calculations can be increased to accommodate complex backgrounds such as when a significant number of nearest neighbour distances are needed to describe the amorphous contribution to the background.

2.7 Quantitative Phase Analysis

Quantitative phase analysis can be performed on multi-phase samples using the formalism described by [Hill and Howard,1987]. The general scattering cross-section for Bragg scattering is proportional to N/V , where N is the number of unit cells contributing to the scattering and V is the unit cell volume. The scale factor, S , in equation (1) is then proportional to N/V .

The weight fraction of phase p can then be derived as

$$W_p = \frac{(SZMV)_p}{\sum_i (SZMV)_i} \quad (29)$$

where S is the scale factor, Z is the number of formula units per unit cell, M is the molecular weight of the formula unit, V is the unit cell volume and i is an index running over all phases. It is worth noting that $S.V$ is proportional to the number of unit cells diffracting (N) and $Z.M$ is just the molecular weight of the unit cell, hence $S.V.Z.M$ is proportional to the weight of the diffracting sample. Other fractions, such as volume fraction are also easily calculated, eg. $\text{VolumeFraction}_p = (S V^2)_p / \sum_i (S V^2)_i$

2.8 Thermal Parameters

The thermal parameter in equation (3) for atom j is given by,

$$\exp[-(\beta_{11} h^2 + \beta_{22} k^2 + \beta_{33} l^2 + 2\beta_{12} hk + 2\beta_{13} hl + 2\beta_{23} kl)] \quad (30)$$

where h,k,l are the Miller indices and $\beta_{11} \dots \beta_{23}$ are the anisotropic thermal parameters for atom j . If the IOTHER parameter is set then equation (30) takes the form

$$\exp[-2\pi^2 (a^* \langle u_{11} \rangle h^2 + b^* \langle u_{22} \rangle k^2 + c^* \langle u_{33} \rangle l^2 + a^* b^* \langle u_{12} \rangle hk + a^* c^* \langle u_{13} \rangle hl + b^* c^* \langle u_{23} \rangle kl)] \quad (31)$$

where $\langle u \rangle$ are the square of the thermal displacements (\AA^2), and a^* , b^* , c^* are the reciprocal lattice constants.

Similarly for isotropic thermal parameters we have,

$$\exp(-B_{iso} (Q/4\pi)^2) \quad (32)$$

and for IOTHER = 1,

$$\exp(-\frac{1}{2} \langle U_{iso} \rangle Q^2) \quad (33)$$

where $Q = 4\pi \sin(\theta)/\lambda$. The values in the input file must be given as B_{iso} and/or β 's, but when IOTHER=1 then the U 's are also printed. This is because the U 's do not obey the simple symmetry constraints.

2.9 Least Squares

The least-squares procedure uses the Newton-Raphson algorithm to minimise the quantity

$$R = \sum_i w_i (y_{io} - y_{ic})^2 \quad (34)$$

where y_{io} is the set of observed diffraction intensities collected at each step across the pattern (in the case of a detector array, y_{io} is the average from n contributing detectors), y_{ic} is the set of corresponding calculated values obtained from equation (1), and w_i is the weight assigned to each observation (see below).

The minimisation of R is undertaken over all data points contributing to the peaks and (when refined) the background.

Note that the contribution of each reflection to the calculated pattern is considered only over the range of 2θ within $\pm n.H_k$ of the centre of the Bragg peak position $2\theta_k$, where n is usually a number between 2 (for Gaussian peaks) and 7 (for Lorentzian peaks). Similarly, the contributions from peaks whose centres lie within nH_k of the end of the pattern or the upper or lower limits of user-defined 'excluded regions' in the main body of the pattern, are also included in the calculation of the intensity at a particular step. The excluded regions are normally invoked to remove from consideration any peaks from an impurity phase not able to be accounted for as second-phase. For TOF the same calculations are used except that the TOF value (in microseconds) is used instead of 2θ , and that a typical value used is 5. This is larger than a Gaussian due to the tailing exponentials in the TOF peakshape.

If x_m are the adjustable parameters in the model, then the normal equations matrix has elements given by

$$M_{mn} = - \sum w_i \left[(y_{io} - y_{ic}) \frac{\partial^2 y_{ic}}{\partial x_m \partial x_n} - \frac{\partial y_{ic}}{\partial x_m} \frac{\partial y_{ic}}{\partial x_n} \right] \quad (35)$$

In practice, the first term is omitted to simplify the calculations (ie. the second derivatives are ignored). The shifts, Δx_m , which will best reduce the residual are then given by

$$\Delta x_m = - \frac{1}{2} \sum_n M_{mn}^{-1} \frac{\partial R}{\partial x_n} \quad (36)$$

where \mathbf{M}^{-1} is the inverse of the matrix \mathbf{M} .

The calculated shifts are then applied to the adjustable parameters x_m and a new set of y_{ic} (ie. a new calculated pattern) is produced. The whole procedure is repeated iteratively until a criterion of completion is met say, that $\Delta x_m < 0.1 \sigma_m$ (σ_m defined below) or the number of cycles has exceeded a certain limit. Since the process is non linear, approximate starting values for all parameters are required for the first refinement cycle.

The Marquardt algorithm can also be used. This adjusts the diagonal matrix elements of \mathbf{M} to

$$\mathbf{M}_{ij} = \mathbf{M}_{ij} (1 + \varepsilon) \quad (37)$$

where ε is the Marquardt parameter, and typically has values between 1.0 and 0.0001. The Marquardt value can be either fixed (IMQT = 1) or allowed to automatically vary depending on the quality of the fit (IMQT = 2). Once near convergence has been reached the value should be set to 0.0 (the automatic mode automatically does this), which is the normal Newton-Raphson mode of least-squares ($\varepsilon = 0$). A fixed non-zero value or the automatic mode is highly recommended for unstable refinements, but not recommend when convergence has been reached.

The values of the parameter esd's, σ_m , are calculated from the expression:

$$\sigma_m = \left[M_{mm}^{-1} \frac{\sum_{i=1}^N w_i (y_{io} - y_{ic})^2}{N - P} \right]^{1/2} \quad (38)$$

where M_{mm}^{-1} is the diagonal element of the inverse matrix, N is the number of observations (i.e. the total number of y_{io} 's when the background is refined), and P is the number of adjusted parameters.

The weight w_i assigned to the individual step intensity is the reciprocal of the variance σ_i^2 at the i th step and is usually based on counting statistics. For the cases in which the y_{io} include the background contribution, either as a refinable function or for subtraction by interpolation between user-selected points,

$$w_i = \frac{1}{\sigma_i^2} = \frac{n}{y_{ic}} \approx \frac{n}{y_{io}} \quad (\text{either weighting scheme may be selected}) \quad (39)$$

where n is the number of detectors contributing to the step intensity average. However, for the situation in which the background Y_{ib} is measured independently in a 'no-sample' experiment:

$$w_i = \frac{1}{\sigma_i^2} = \frac{n}{y_{io} + y_{ib}} \quad (40)$$

The quantities used to estimate the agreement between the observations and the model during the course of the refinement are as follows:

$$(i) \text{ The profile } R_p = \frac{\sum |y_{io} - y_{ic}|}{\sum y_{io}} \quad (41)$$

$$(ii) \text{ The weighted profile } R_{wp} = \left[\frac{\sum w_i (y_{io} - y_{ic})^2}{\sum w_i y_{io}^2} \right]^{1/2} \quad (42)$$

$$(iii) \text{ The Bragg } R_B = \frac{\sum |I_{kc} - I_{ko}|}{\sum I_{ko}} \quad (43)$$

where I_{ko} is the 'observed' integrated intensity of reflection k calculated at the end of the refinement after apportioning each y_{io} between the contributing peaks (and background when that is refined) according to the calculated intensities I_{kc} .

$$(iv) \text{ The expected } R_{exp} = \left[\frac{N-P}{\sum w_i y_{io}^2} \right]^{1/2} \quad (44)$$

$$(v) \text{ The goodness of fit, } \chi^2 = \frac{\sum w_i (y_{io} - y_{ic})^2}{N-P} = \left[\frac{R_{wp}}{R_{exp}} \right]^2 \quad (45)$$

(vi) The (unweighted) Durbin-Watson d-statistic [Flack, Vincent and Vincent 1980; Hill and Madsen 1986] for the analysis of serial correlation in the profile

$$d = \frac{\sum_{i=2}^N (\Delta y_i - \Delta y_{i-1})^2}{\sum_{i=1}^N \Delta y_i^2} \quad (46)$$

where N is the number of observations and Δy_i is the difference between the observed and calculated intensity at a given step i. Serial correlation is indicated (at the 99.9 per cent confidence level) unless $Q < d < 4-Q$ where

$$Q = 2 \left[\frac{N-1}{N-P} - \frac{3.0902}{(N+2)^{1/2}} \right] \quad (47)$$

and P is the number of least-squares parameters being estimated.

3. THE PROGRAM

3.1 Availability

The program (executable's, source, manual and sample files) can be obtained free of charge from the Neutron Scattering Group, ANSTO, Building 58, PMB 1, Menai, NSW, 2234, Australia. Please specify computer, media required (3½, 5¼' or CD) and return address. Alternatively, the program can be obtained from the anonymous ftp site:

ftp.ansto.gov.au /pub/physics/neutron/rietveld

Program users are requested to report to the authors any errors they may find in either the manual or the program. Changes to the code made at the local institutes are also welcome and will be incorporated into new versions for general redistribution.

3.2 Description

The program is written in FORTRAN 77/90. A brief description of the various subroutines and functions follows.

MAIN	Main program, which calls in succession the subroutines INPTR, ASSIGN, ITER and EXPUT.
INPTR	<p>Reads the control input (from unit 5), the data (from unit 4), and (if required) the separate file of background (from unit 2). Interprets codewords. If required, it interpolates background. Calls subroutines: SPGP, CELL2, LOOKUP, REFGEN and RTMT.</p> <p>SPGP - Interprets the space group symbol, and generates operators which SYMOPR uses to generate the full set of equivalent positions, and OP1 and SMTRY2 use to generate the full set of equivalent indices.</p> <p>CELL2 - Converts from unit cell parameters $a, b, c, \alpha, \beta, \gamma$ to the cell constants A,B,C,D,E,F used in the refinement</p> <p>LOOKUP - Searches BLOCK DATA to find the relevant X-ray scattering factors or neutron scattering lengths.</p> <p>REFGEN - With calls to GENLIM, OP1, SORT then SMTRY2 generates indices, sorts, and checks for symmetry related equivalents. References MULT to determine reflection multiplicities. Stores phase number and reflection indices in IREFS(n), multiplicity in MLT(n), width, position, Lorentz polarisation factor, and (if applicable) shape parameter in REFS(n,1)...REFS(n,4), respectively.</p> <p>RTMT - This subroutine works out and stores the operations of the space group. The operations are packed into IVEC. The subroutine calls SYMOPR, which in turn calls CEL000 and OPERTR.</p>
ASSIGN	Examines the pattern point by point, and determines which are the contributing reflections at each point. The serial numbers of the first and last reflections contributing at the i^{th} point are stored in KR(i). Note that the program calls ASSIGN only once, so the identification of contributing reflections is only as good as the input values of zero, lattice parameters, line widths, etc. will allow. Calls SORT in the two phase case.
ITER	<p>This subroutine controls the iterative solution of the least squares equations, and the cycle by cycle output of results. Calls subroutines CALCUL, SUMMAT, DPINV, CHISQ and OUTPTR.</p> <p>CALCUL - Calculates, for each reflection, the square of the structure factor, and the derivatives of this quantity with respect to the parameters on which it depends. Also calculates elements of derivatives with respect to profile parameters. The derivatives are stored in DERSTO.</p> <p>SUMMAT - This performs a calculation of intensity at each point in the pattern. It makes use of squared structure factors from CALCUL and peak shape information through a call to function PROFIL. Calculates derivatives using information passed from CALCUL in DERSTO, and PROFIL. Adds contribution from each point to the vector VX (cf dR/dx of equation (36)) and the matrix RJAC (M of equation (35))</p> <p>PROFIL - Calculates normalised peak shape functions and returns these with relevant derivatives to SUMMAT. Calls PVOIT in the evaluation of pseudo-Voigts, and WERF1 (which in turn calls the Harwell subroutine FC01A) in the evaluation of Voigt functions. Ancillary functions are called for determination of the gaussian and Lorentzian widths.</p> <p>DPINV - Inverts matrix RJAC, and returns shifts (cf Δx_m equation (36)) in VX.</p> <p>CHISQ - Evaluates residual (equation (34)) and other measures of fit (equations (41) - (45)).</p>

OUTPTR - Applies shifts to obtain new parameters after each cycle. and their standard deviations. Provides output after each cycle of refinement Calls DIRECT which calls ESD which calls ERROR.

EXPUT	This subroutine completes calculations and controls output after the final cycle of refinement It evaluates the 'observed' integrated intensities, and the Bragg R_B , as defined in equation (43). This subroutine provides output as requested, which may include a new input file and plots. Calls REWRIT and CALPLT. REWRIT - This operates (if requested) to provide a new input file incorporating the final parameter.
BLOCK DATA	This is a tabulation of scattering lengths and scattering factors, including anomalous dispersion coefficients (for X-rays). The neutron scattering lengths and X-ray scattering factors are from the <i>International Tables for X-ray Crystallography</i> [1995], Vol.C, p384-391 and 500-502, respectively and for O^{2-} from Hovestreydt [1983].

3.3 Parameters and Codewords

Parameters are stored internally in arrays XL(I,J), GLB(I), and PAR(I,J). XL contains the data for the atoms. The first index scans the atoms; the second, scans the parameters for the atom. GLB contains those parameters that apply to all phases, i.e. zero-point, background and wavelength (or diffractometer constant). PAR contains such parameters as scale factor, lattice constants, peak width/shape parameters, and preferred orientation parameters, which are phase dependent. The first index (I) scans the phases, the second (J) scans the parameter number.

The parameters are mapped to the elements of the normal matrix by user codewords entered for each parameter. A zero codeword means that the parameter is not being refined. For each refined parameter, the codeword is formed as:

$$\text{sign}(A) (10P + |A|)$$

where P is the parameter position in the matrix and A is the factor by which the computed shift will be multiplied before use. As an example, assume that there is a wish to vary the x,y,z coordinates of an atom yet keep $y = x/2$. The codewords may be set as x: 31.00, y: 30.50, z: 41.00; then x and y will be assigned to the third normal matrix element and z to the fourth. Also, 1.00 times the shift in the third parameter will be applied to x, and 0.50 times this shift to y. The full shift in the fourth parameter will be applied to z. Parameter positions for the three types of parameters are stored in the arrays LP(I,J), LGLB(I), LPAR(I,J), and the required shifts stored in A(I,J), AGLB(I) and APAR(I,J). The shifts are also multiplied by a relaxation factor before being applied to the parameters. The user may supply four different relaxation factors which apply to four different classes of parameters.

3.4 Distribution Tape

The distribution tape contains a minimum of 9 files, although the precise number of may vary depending on the version. All these files are written in ASCII code. The files are as follows:

File	Name	Contents
1	LNEW12CON.FOR	Program
2	LNEW13.FOR	Core subroutines and functions
3	DISTANG.FOR	Subroutine for angle/distance calculations
4	NSYMSUB.FOR	Subroutines SPGP, RTMT, SYMOPR, OPERTR, OP1, SMTRY2, CELL000
5	BLOKDATA.FOR	BLOCK DATA
6	PROFILE.FOR	Subroutines PROFIL, VHALF (+ others)
7	PROFASYM.FOR	Subroutines PROFVAL for the Finger, Cox, Jephcoat asymmetry
8	DATAREAD.FOR	Subroutines DATAREAD, READFORM, READFREE
9	CORRECT.FOR	Subroutines ABSCAT, ALSCAT, EXTCW, EXTTOF (+others)
10	BACKGND.FOR	Subroutines BACFN, BACKDER, READBCK
11	BONDGEN.FOR	Subroutines for bonds and bond valences
12	MISC.FOR	Subroutines ESD, ERROR, DPINV

3.5 Notes on Compilation

The program was compiled at the Lucas Heights Research Laboratories with MS-Powerstation Fortran v4.0 or Digital Fortran 6.0. The following remarks may be of assistance:

- (a) The source code is divided into several files. These may be merged at the beginning or compiled separately for subsequent combination at the link-edit step.
- (b) The bit manipulation routines IAND, IOR, IEOR which are invoked by subroutines in the INPTR group are FORTRAN 77 extensions which may not be recognised by every compiler (eg early versions). If these are unrecognised, the relevant bit manipulation functions will have to be added locally.
- (c) The function NARG (gets number of command line arguments) and the subroutine GETARG (returns the argument value) may not be implemented on all machines. These can be removed with little effort and no loss in functionality. The Unix code needs this feature removed.
- (d) The memory allocation routines may need to be changed depending on the compiler, as these are FORTRAN 90 operations.

4. OPERATION OF THE PROGRAM

The program applies to either X-ray or neutron diffraction patterns. It allows the refinement of the structures of multiple phases simultaneously, and it accommodates data recorded at one or two wavelengths. Multiple x-ray and/or neutron histograms (datasets) can be used in the refinement. Currently it is not applicable in the case of magnetic neutron scattering.

Refinement of the structure can proceed if the following input information is supplied:

- (i) a set of step scan data in equal 2θ or time increments,
- (ii) 2θ /TOF limits and step width,
- (iii) values for the radiation wavelengths (or diffractometer constants) and their intensity ratio (if required),
- (iv) initial values for structural and profile parameters,
- (v) 2θ /TOF zero and type of background (measured, interpolated, or refined),
- (vi) space group symbol of each phase,
- (vii) chemical symbol (and valence state in the case of X-ray data) of each atom, if accessing the set of stored scattering factors or scattering lengths,
- (viii) profile shape function, anisotropic vector, and distance from peak centre for intensity cut-off in units of H_k ,
- (ix) preferred orientation vector and asymmetry parameter for each phase,
- (x) refinement termination control (either number of cycles or parameter shift test),
- (xi) damping (relaxation) factors for the shifts applied to four different types of parameters, and
- (xii) output controls (the full output can be lengthy).

The space group symbol input under (vi) above takes a form identical to that used in the International Tables for X-ray Crystallography: no symmetry cards are required. Note, however, that since every atom is permuted through all of the symmetry operations of the general position, the site occupancy input to the program for each atom must be reduced by an appropriate factor if the atom occupies a special position in the unit cell.

Neutron scattering lengths and X-ray scattering factors can be accessed from the program's data blocks by the use of a standard chemical symbol (see note (vii) above). For non-standard X-ray values the program permits the scattering data to be input with the usual 9-parameter function, or as pairs of scattering factor and $\sin 2\theta$ values. For neutrons, the scattering length can also be input separately.

Parameters that can be adjusted simultaneously in the least-squares refinement include the following:

- (i) zero parameter
- (ii) background function (up to 6 parameters),
- (iii) unit cell dimensions (up to 6 parameters for each phase),
- (iv) overall scale and overall isotropic thermal vibration parameters for each phase,

- (v) atomic coordinates, thermal vibration (isotropic or anisotropic) and site occupancy parameters for each phase,
- (vi) preferred orientation parameter,
- (vii) profile shape parameters for each phase (up to 4 for the 2θ -variable pseudo-Voigt option, and up to 3 for the Pearson VII option; in the case of the Voigt function, the peak shape is determined by the width parameters),
- (viii) peak half-width parameters for each phase (up to 4 for the pseudo-Voigt and Pearson VII functions, and up to 5 for the Voigt function), and
- (ix) anisotropic peak shape (gaussian contribution only)
- (x) wavelength or diffractometer constant
- (xi) histogram scale factors (except for the first histogram)
- (xii) peak asymmetry parameter for each phase.

Note that only the 2θ and background parameters apply 'globally' to the entire pattern.

5. MAXIMUM PARAMETER VALUES

A typical set of parameter values is given below. Depending on the problem these can be changed and the program recompiled.

Histograms	5	MAXDS
Phases	8	NUPH
Wavelengths	2	
Observations (steps)	16000	IDSZ
Atoms (total from all phases)	200	NATS
Reflections (total from both wavelengths)	4000	IRS
Allowed parameters in least-squares	250	MSZ
Reflections contributing to a given step intensity	500	NIPOI
Excluded regions	30	MAXEXCL
Scattering sets	30	MAXFF
Background points for interpolation	30	MAXBK
Scattering factor pairs: $\sin\theta/\lambda$, f	50	MFCO

The number of observations, reflections, atoms, refinable parameters and contributing reflections to a given step can be changed globally by changing the following lines in PARAM.INC:

```
PARAMETER (IDSZ=16000,IRS=4000)
PARAMETER (NATS=200,NIPOI=500,NUPH=8)
PARAMETER (MAXIPAR = 26, MAXIGL = 16, MAXEXCL = 30, MAXBK = 30)
PARAMETER (MAXDS=5, MAXGP = MAXIGL*MAXDS, MAXAP = MAXIPAR*MAXDS)
PARAMETER (MSZ=100,MSZM = MAXAP)
PARAMETER (MAXFF = 16, MFCO = 50)
```

The number of data points and the number of reflections per phase can also be changed via environment variables. This is particularly useful if you want to perform refinements with multiple histograms, but still conserve computer memory. For DOS/Windows systems these can be set on the command line using:

“set IDSZ=30000”, and “set IRS=500”

6. INPUT AND OUTPUT FILES - OVERVIEW

- Unit 2: Contains the background profile data obtained in a 'no sample' experiment - otherwise unused. Data in format 10(12,16), 10(11,17), 1018 or other. The experimental conditions used to collect the background pattern are assumed to be identical to those used for the sample
- Unit 4: Contains the observed step-scan data for refinement of the structure and profile (see below). Also used when calculating powder patterns – although the filename is changed automatically so that any real data is not overwritten.

- Unit 5: Contains the control variables and the crystal structural and profile parameters (see below). If requested, the information is updated to unit 8 at the end of a refinement.
- Unit 6: This is the main output unit. It contains all the control variables and starting parameters for the unambiguous reconstruction of a run, together with the results of each cycle of refinement and various other optional details (see below).
- Unit 7: Contains a summary of the agreement indices at the completion of each cycle. Normally assigned to the terminal when the program is run interactively.
- Unit 8: Contains the input control variables and the updated crystal structure and profile parameters from a completed refinement run.
- Unit 9: Contains the plot information for plotting, including the observed and calculated patterns, zero, positions and (hkl) for each peak and wavelength.
- Unit 10: Contains the generated bonds and valences if requested
- Unit 11: Contains the generated distances and angles (with errors) if requested
- Unit 20: Contains the 'observed' and calculated structure factors and other information necessary for Fourier analysis or Shelx input.

7. INPUT AND OUTPUT FILES - DETAIL

7.1 Unit 4: Observed Stepscan Data

There are currently several different types of data formats that can be read. Each type have several options that allow some flexibility in the reading of the file. They are:

1) data file consisting of:

Line 1: contains the variables THMIN, STEP and THMAX in (3F8) or (*) format:

THMIN -	starting angle for pattern }	
STEP -	step size	} in degrees 2θ or TOF (μs)
THMAX -	finishing angle	}

The remaining space on this line may be used for sample identification.

Line 2+: the remainder of the file consists of the step-scan profile data in (10(I2, I6)), (10(I1, I7)) or 10F8 format where the first field contains the number of detectors contributing to the mean count given in the second field; the first field may be left blank for single counter data.

2) The second data format is:

Line 1: a sample identification line

Line 2+: the following lines contain the data in the format (2θ/TOF, I_{obs}) or (2θ/TOF, I_{obs} , w_i). The data is read in free format. THMIN and THMAX are found from the first and last 2θ/TOF in the file, and STEP calculated assuming a constant step. If no w_i is read it is calculated assuming absolute I_i , i.e. $w_i = 1/I_i$.

3) The third data format is the GSAS format:

Line 1: a sample identification line

Line 2: specifies the start, step and number of steps in GSAS format: 'BANK 1.....ESD/STD'

Line 3+: the remainder of the file consists of the step-scan profile data. Depending on whether the file is a 'ESD' or 'STD' type GSAS file the program will read in either a 5(2F8) format where the first field contains the counts and the second field gives the standard deviation of the counts, or 10(I2,I6) as previously defined in 1), respectively.

The 'ESD' format can be useful for variable time counting if the counts are renormalised to a constant scale.

7.2 Unit 5: Control Variables and Structure and Profile Parameters

An asterisk (*) before a line number indicates that the line's existence depends on the value of a control variable. A hash (#) means this line is repeated for each histogram.

Line	Format	Description
1.	(A80)	TITLE - any 80 characters to be used to label the printout
2.		Histogram control line. There is a line for each histogram. The first line determines the number of histograms in JOBTYP.
2.1 #	(814)	<p>JOBTYP</p> <p>0 - X-ray data, CW</p> <p>1 - neutron data (nuclear scattering only), CW</p> <p>2 - pattern calculation, CW X-ray</p> <p>3 - pattern calculation, CW neutron</p> <p>4 - TOF neutron data</p> <p>5 - pattern calculation, TOF neutron</p> <p>+ (number of histograms - 1)*10 (first line only) (eg. 31 = 4 histograms, the first of which is neutron data)</p> <p>NPROF - profile shape function</p> <p>1 - pseudo-Voigt} modified by the [Rietveld,1969] asymmetry</p> <p>2 - Pearson VII }----- correction, if required</p> <p>3 - Voigt }</p> <p>4 - pseudo-Voigt]_____ modified by a sum of five peaks asymmetry</p> <p>5 - Voigt] correction if required</p> <p>6 - pseudo-Voigt)----- asymmetry of Finger, Cox and Jephcoat</p> <p>7 - Jorgensen TOF</p> <p>NPHASE - number of phases (not used in lines NDS > 1)</p> <p>NBCKGD - background correction</p> <p>-2 - -5 - background to be refined in the form</p> $\sum_{m=0}^5 B_m T_m(2\theta)$ <p>where T_m is a Type I Chebychev Polynomial, shifted Type I, Type II or shifted Type II for -2, -3, -4 and -5 respectively</p> <p>-1 - background to be refined in the form</p> $B_0 + B_1 Q(\text{or } \theta) + \sum_{m=1}^n B_{2m} \frac{\sin(QB_{2m+1})}{QB_{2m+1}}$ <p>0 - background to be refined in the form</p> $\sum_{m=-1}^n B_m (2\theta)^m$ <p>1 - background to be read from unit 2</p> <p>2 ...MAXBK - background to be determined by interpolation between this number of points (maximum = MAXBK)</p> <p>NEXCRG - number of excluded regions (maximum = MAXEXCL) in histogram</p> <p>NSCAT - number of scattering sets used in histogram (these scattering sets needed only for those scatterers not included in the scattering factor table) (max = MAXFF)</p> <p>IWT- weighting scheme of histogram</p> <p>0 - weight = 1/y(obs)</p> <p>1 - weight = 1/y(calc) (after first cycle)</p> <p>ABSTPYE - absorption correction type</p> <p>0 - Cylindrical geometry using Sabine correction.</p> <p>1 - Flat plate geometry using Hermann correction</p>

3.	1911,1X,3F8	<p>Output control flags - 0 = off, 1 = on:</p> <p>1 IOT- observed and calculated step intensities</p> <p>2 IPL - line printer plot</p> <p>3 IPC - integrated intensities and Bragg R</p> <p>4 MAT- correlation matrix</p> <p>5 NXT - generate new input file on unit 8</p> <p>6 LST1 - reflection list</p> <p>7 LST2 - input step intensity data list</p> <p>8 LST3 - merged reflection list for the two phases</p> <p>9 IPL1 - symmetry operators</p> <p>10 IPL2 - offline plot data on unit 9</p> <p>0 = No plot file</p> <p>1 = General File for Kaleidigraph, Origin, Axum, Excel etc.</p> <p>2 = ILL format output (JPLOT format)</p> <p>3 = Normalised (2θ, Y(meas), Y(calc), Y(diff)) (RPLOT format)</p> <p>4 = (2θ, Y(meas), Y(calc), Y(diff))</p> <p>11 IFOUR- Fourier coefficients on unit 20 (needs IPC = 1)</p> <p>0 = No file</p> <p>1 = symmetry op's, (3I4, 2F8) for hkl, F^2_{obs}, σF^2_{obs}</p> <p>2 = Shelx format (3I4, 2F8) of hkl, F^2_{obs}, $\sigma(F^2_{obs})$</p> <p>3 = Fourier format (3I4, 2F8) of hkl, F^2_{obs}, phase.</p> <p>4 = Fourier format (3I4, 2F15) of hkl, F^2_{calc}, phase.</p> <p>5 = Fourier format (3I4, 2F15) of hkl, F_{obs}, F_{calc}.</p> <p>6 = EXTRA/Sirpow format (3I4,2F15.4) of hkl, fwhw, F^2_{obs}</p> <p>12 NFMT - format of data file(s)</p> <p>0 = format option 10(12,16) (default)</p> <p>1 = format option 10(11,17)</p> <p>2 = format option 10F8</p> <p>3 = GSAS: format 5(I_{obs}, esd) if ESD, format 10(F2,F6) if STD</p> <p>4 = format (2θ, I_{obs}, W_{obs}) or (t, I_{obs}, W_{obs})</p> <p>5 = format (2θ, I_{obs}) or (t, I_{obs})</p> <p>13 LSYN - THMIN,STEP,THMAX read as F12 (default is F8)</p> <p>14 LMR - read histograms from separate data files (default is for the histograms to be read from one file)</p> <p>15 DSBB - not used currently</p> <p>16 IBCK - 0 = 6 Background terms read/used in series expressions (eq.s 17-19)</p> <p>1 = 12 background terms read/used in series expressions</p> <p>17 IPREF- 0 = Non-summed March/Dollase Preferred Orientation Function</p> <p>1 = Summed March/Dollase Preferred Orientation Function</p> <p>18 IOTHER- 0 = thermal parameters output as B's and β's</p> <p>1 = thermal parameters output as U^2's</p> <p>19 IMQT- 0 = Normal Newton-Raphson Least-squares</p> <p>1 = Marquardt algorithm, uses fixed value VMAQRT</p> <p>2 = Marquardt algorithm, automatically adjusts VMAQRT. If VMAQRT is 0.0 then it automatically selects its value, else it starts from the users input value.</p> <p>RMIN - minimum radius for bond/angle calculations and bond valence calc's</p> <p>RMAX - maximum radius for bond/angle calculations (if zero no bonds calculated)</p> <p>VMAQRT - set value or starting value for the Marquardt algorithm.</p>
4.1#	(9F8)	<p>LAMDA(1) } wavelengths in angstrom (smallest first)</p> <p>LAMDA(2) }</p> <p>or</p> <p>DIFC } TOF instrument constants TOF = DIFC*d + DIFA*d² + ZERO</p> <p>DIFA }</p> <p>RATIO - intensity ratio LAMDA(2) : LAMDA(1) (in TOF can put detector θ)</p> <p>WEIDS - histogram weighting factor (if 0.0 then automatically becomes 1.0)</p> <p>WDT - width (range) of calculated profile (in units of H_k) beyond which it is set to zero</p>

		<p>CTHM - coefficient in formula for polarisation correction when using a monochromator: $LP = LP*[CTHM*\cos^2 2\theta + 1]$ (ignored for neutron data)</p> <p>TMV- value of μ, where μ = linear absorption coefficient</p> <p>RLIM - peaks below this angle corrected for asymmetry using the [Rietveld,1969] model (ignored for NPROF = 4 and 5, which correct at all angles in the pattern) (the first RLIM is used for all histograms)</p> <p>FFMIN- peaks less than this value are not included in the fit (in terms of $F ^2$)</p>
4.2 * #	9F8	<p>If TOF data or calculation is selected these values are the incident spectrum values A0..A9 in the expression:</p> $\text{IncSpec} = A0 + A1\exp(-A2 / \text{TOF}^2) / \text{TOF}^5 + A3\exp(-A4 \text{TOF}^2) + A5\exp(-A6 \text{TOF}^3) + A7\exp(-A8 \text{TOF}^4)$ <p>If already incident spectrum corrected (e.g. ISIS data) then set A0 = 1.0, A1...A8=0.0</p>
5.	(I4,5F4,3F8)	<p>NCYCLE - number of least-squares cycles</p> <p>EPS - run terminates when all parameter shifts are less than EPS*esd</p> <p>RELAX(1) - relaxation factors for parameter shifts: coordinates, isotropic temperature factors, site occupancies</p> <p>RELAX(2) - anisotropic temperature factors</p> <p>RELAX(3) - scale factors, $2\theta/\text{TOF}$ zero point, background parameters, unit cell, preferred orientation, overall temperature factor</p> <p>RELAX(4) - peak FWHM, asymmetry, shape</p> <p>THMIN - starting angle for pattern }</p> <p>STEP - step size } in degrees 2θ or TOF (μs)</p> <p>THMAX - finishing angle }</p> <p>These angles are required only for pattern calculation modes(JOBTYP = 2,3,5), but if present for other modes, these values take priority over those present on unit 4, and may be used to consider subsets of points in the observed pattern.</p> <p>Note: if ISYN=1 then these values are read as F12</p> <p>CW – codeword for wavelength or DIFC (for histogram 1)</p> <p>CDIFA - codeword for DIFA (for histogram 1) (0.0 for CW)</p>
*5.1 #	6(free format)	<p>THMIN, STEP, THMAX - start, step and finishing angles/TOF of next histogram</p> <p>HSCAL, CHSCAL - histogram scaling factor and codeword. The histogram scaling factor is relative to histogram 1, i.e. histogram 1 has a scaling factor of 1.0 and other histograms are relative to this.</p> <p>CW – codeword for wavelength or DIFC of histogram</p> <p>CDIFA - codeword for DIFA of histogram (0.0 for CW)</p> <p>Note: Since this line is read as free format - EVERY number must be present.</p>
*6. (#)	2F8	<p>If NBCKGD > 2 for a histogram, then there are NBCKGD lines: (if more than one histogram then NBCKGD(NDS) lines follow one after another)</p> <p>POS – position in $2\theta/\text{TOF}$</p> <p>BCK – background intensity at this position</p>
*7. (#)	(2F8)	<p>If NEXCRG > 0 for a histogram, then there are NEXCRG lines:</p> <p>ALOW - low angle bound } in degrees 2θ or TOF</p> <p>AHIGH - high angle bound }</p>
*8. (#) *8.1	(A4,4F8)	<p>If NSCAT >0 for a histogram, then there are NSCAT sets of lines:</p> <p>NAM – symbol identifying this scattering set</p> <p>DFP - $\Delta f'$, or neutron scattering length</p> <p>DFPP - $\Delta f''$ (ignored in the neutron case)</p> <p>CDFP - codeword for $\Delta f'$</p> <p>CDFPP - codeword for $\Delta f''$</p>

*8.2	(F8,8F9)	In the X-ray case (only), either one line of the form A1 B1 A2 B2 A3 B3 A4 B4 C, the coefficients for the analytic approximation to f, or a set of lines of the form POSI, SCAT, where $\text{POSI} = \sin(\theta)/\lambda$ $\text{SCAT} = f$ max number of pairs = 28 (MAXCO-2) The set is terminated by a line with -100 in the first position. If the first form is desired, A2 must not be zero.
9.	I8	MAXS - number of parameters varied
10.		Global parameters:
10.1 #	5(2F8),/5(2F8)	ZER – zero point for 2θ (in degrees) or TOF (in μs) FLGZER - codeword for zero point If there is more than one histogram the zeros and codewords continue on the same line. When there is more than 5, 10,... histograms the values and codewords continue on the next line(s).
*10.2 (#)	(6F12) or (6F12,/,6F12)	If NBCKGD < 0, there is a line pair for each histogram: If IBCK = 1 then the following lines continue for another line i.e. (6F12,/,6F12) BACK – background coefficients B _m in the expression $y_{ib} = \sum_{m=-1}^n B_m (2\theta)^m$ m = 6 or 12 depending on the IBCK flag.
	(6F12) or (6F12,/,6F12)	FBACK - codewords for background parameters
11.		NPHASE sets of lines:
11.1	(A80)	PHSNM - name of phase
11.2 #	(I2,2X,I2,2X, 3F4,8X,3F4)	N – number of atoms (when N = 0 the phase will be refined using the Le Bail intensity extraction method) Z – number of formula units per unit cell (only required for Quantitative Analysis when molar percentages are needed) PREF- preferred orientation direction expressed as three decimal Miller Indices ANISO- anisotropic peak broadening direction expressed as three decimal Miller Indices (when all zero the anisotropic profile functions are not used and the values and codewords are not used)
11.3	(20A1)	SYMB - space group symbol in Hermann-Mauguin notation (International Tables for X-ray Crystallography) e.g. P ₂ ₁ 2 ₁ 2 ₁ = P 21 21 21 P3bar = P -3 P6 ₃ /m = P 63/M Short forms of the space group symbol and non-standard settings may be acceptable. It is advisable to print and check the symmetry operators, particularly for those space groups for which alternative origins are shown.
*11.4	(2A4,8X,5F8)	N line pairs: (not applicable for the Le Bail extraction,N=0) LABEL – identification characters for atom NTYP - link to scattering data for atom: either NAM from line 8.1, or chemical symbol and valence to access internal table of values x,y,z- fractional atomic coordinates B – isotropic temperature factor (or U depending on IOTHER flag) ON – site occupation fraction (related to site multiplicity)
	(6F8)	β ₁₁ , β ₂₂ , β ₃₃ , β ₁₂ , β ₁₃ , β ₂₃ - anisotropic temperature factors (or <U> ² 's depending on IOTHER flag)
11.5	(G12,4X,F8)	S – scale factor

		Q – overall isotropic temperature factor
11.6 (after # 1)	(4F8)	<p>U,V,W,U_a - coefficients in the expression for peak FWHM: $H_k^2 = (U + U_a \cos^2 \phi) \tan^2 \theta + V \tan \theta + W$ (this is the total peak FWHM for NPROF = 1, 2, 4 but only the Gaussian component width for NPROF = 3, 5), ϕ is the angle between reflection hkl and ANISO (U_a used only when the values of ANISO are non-zero)</p> <p>or</p> <p>$\sigma_0, \sigma_1, \sigma_2, \sigma_{anis}$ - coefficients in the expression for peak FWHM for NPROF = 7: $H_k^2 = (\sigma_0 + \sigma_1 d^2 + \sigma_2 d^4 + \sigma_{anis} d^2 \cos^2 \phi)$</p>
* 11.6.b	(4F8)	<p>For TOF peak shape NPROF = 7, the following line is read: ALPHA0 } used to calculate $\alpha = \alpha_0 + \alpha_1/d$ ALPHA1 } BETA0] used to calculate $\beta = \beta_0 + \beta_1/d^4$ BETA1]</p>
11.7	(6F8)	<p>a,b,c – cell dimensions in angstroms α, β, γ - cell interaxial angles in degrees</p>
11.8 (after # 1)	(4F8)	<p>P1- preferred orientation parameters in the expression: $I_{calc}^{corr} = I_{calc} [P1^2 \cos^2 \alpha_k + P1^{-1} \sin^2 \alpha_k]^{-3/2}$ where α_k is the acute angle between the scattering vector and the normal to the crystallites (platey habit)</p> <p>R – absorption R value used in calculating μR. For flat plate this is P₀. AS1 – asymmetry parameter (for either Rietveld or peak-sum model) (not used in TOF peak shapes). This is S/L in NPROF=6. AS2 – asymmetry parameter D/L in the Finger, Cox and Jephcoat method (NPROF = 6). Not used in other profile functions.</p> <p>Peak shape function parameters: either $\gamma_1, \gamma_2, \gamma_3$ in the expression $\gamma = \gamma_1 + \gamma_2 2\theta + \gamma_3 (2\theta)^2$ (NPROF = 1,2,4,6),</p> <p>or</p> <p>Ksec, the parameter related to particle size broadening in the Lorentzian component of the Voigt function (for NPROF = 3,5) (Lorentzian terms currently not used in NPROF = 7) Ktan, the Lorentzian strain broadening term (for NPROF = 3,5)</p> <p>EXT – extinction parameter</p>
* 11.10 (# after 1)	(2F8)	POR, ROU - if ABSTYPE=1, the flat plate absorption values, POR and ROU are read. They represent the porosity and roughness of the sample.
11.11		N line pairs (these, and lines 11.11 - 11.15 are not required for calculated patterns: JOBTYP=2,3,5):
	(5F8)	Cx Cy,Cz - codewords for fractional atomic coordinates
		CB – codeword for isotropic temperature factor
	(6F8)	CON – codeword for site occupation fraction
		C β_{11} , C β_{22} , C β_{33} , C β_{12} , C β_{13} , C β_{23} - codewords for anisotropic temperature factors
11.12	(F8,8X,F8)	CS – codeword for phase scale factor (not to be confused with histogram scale) CQ – codeword for overall isotropic temperature factor
11.13 (after # 1)	(4F8)	<p>CU,CV,CW, CU_a - codewords for peak FWHM parameters of each histogram Or Cσ_0, Cσ_1, Cσ_2, Cσ_{anis} - codewords for TOF peak FWHM</p>

11.13.b (after # 1)	(4F8)	CA0, CA1, CB0, CB1 - codewords for alpha and beta terms in the TOF peak profile NPROF = 7
11.14	(6F8)	CA, CB, CC, CD, CE, CF - codewords for the coefficients defined by $1/d^2 = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk$ (these coefficients are related to the cell constants)
11.15 (after # 1)	(3F8)	CP1 – codeword for the preferred orientation parameters of each histogram CR – codeword for the absorption R value for each histogram CAS1 – codeword for the asymmetry parameter for each histogram (AS cannot be released for Rietveld asymmetry if RLIM is lower than the position of the first reflection). This is S/L for NPROF=6. CAS2 – codeword for asymmetry parameter D/L in NPROF=6.
11.16 (after # 1)	(4F8)	$C\gamma_1$, (or CKs), $C\gamma_2$, (or CKt) $C\gamma_3$ - codewords for the peak shape function parameters for each histogram (CKs, CKt are only necessary in the case of NPROF = 3,5; $C\gamma_3$ should not be released for NPROF=2) CEXT - Codeword for Extinction Parameter
11.17 (after # 1)	(2F8)	CPOR, CROU - codewords for the flat plate absorption correction, porosity and roughness (read only if ABSTYPE =1)

7.3 Unit 6: Main Output File

The output at the end of a run includes the following:

- (i) a complete identification of the refinement conditions, starting parameters and subject
- (ii) symmetry operators for the general position of the space group,
- (iii) a reflection list for each phase (separate and merged),
- (iv) the input and background-corrected profile data list with w_i values and range of contributing reflections to each step intensity
- (v) the final values, shifts and esd's of all parameters after each cycle of refinement
- (vi) a list of all agreement indices after each cycle, the R-factors being expressed as percentages
- (vii) the average intensity difference for the profile, taken in blocks of 20 steps
- (viii) the correlation matrix,
- (ix) the 'observed' and calculated integrated Bragg intensities together with their estimated standard deviations, and the derived Bragg R-factor expressed in per cent
- (x) the observed and calculated individual step intensities, and
- (xi) a line printer or off-line plot of the observed, calculated and difference profiles, together with reflection position markers.

All but (i) and (v)-(vii) of these output features are optional.

7.4 Unit 9: Plot File Output

Depending of the IPL1 value the following types of files are produced:

IPL1 = 0: No plot file

IPL1 = 1: Standard 10(I2,I6) or 10(I1,I7) file

IPL2 = 2: Plot File consisting of y_{obs} , y_{calc} , IREFS, and REFS. This format historically originated from the ILL (Grenoble) and is typically called the ILL plot file. The programs JPLOT and LHPMPlot plot this file. The source and executable of JPLOT are included with this package. Currently it only runs on the IBM-PC, Vax/VMS and Alpha/VMS computers, but is modular so that only one subroutine needs changing to adapt it to other computers. The program LHPMPlot runs under Windows 95.

IPL2 = 3: A file consisting of $2\theta/\text{TOF}$, normalised y_{obs} , y_{calc} , y_{diff} values and the $2\theta/\text{TOF}$ positions of the reflections. Typically this is used as input into a plotting package for publication plots. (eg. KalediaGraph™ and Origin™, Axum™, SigmaPlot™ or Excel™)

IPL2 = 4: A file consisting of $2\theta/\text{TOF}$, y_{obs} , y_{calc} , y_{diff} and the $2\theta/\text{TOF}$ positions of the reflections. Typically this is used as input into a plotting package for publication plots. (eg. KalediaGraph™ and Origin™, etc)

7.4 Unit 10: Bond Valence Output File

Bond and bond valence calculations are output in this file. A summary of each phase is also printed.

7.5 Unit 11: Distance and Angle Calculations

The distance and angle calculations are output in this file. The correlation matrix is used in these calculations.

7.6 Unit 20: Fourier Output File

The five printed options are:

I FOUR = 1: The observed Fourier file is written as $h, k, l, F^2_{\text{obs}}, \sigma F^2_{\text{obs}}$, and has the symmetry operators and cell dimensions printed at the beginning of the file.

I FOUR = 2: The file is written as $h, k, l, F^2_{\text{obs}}, \sigma(F^2_{\text{obs}})$ and can be used in Shelxs type programs.

I FOUR = 3: The Fourier file is written as $h, k, l, F^2_{\text{obs}}$, phase.

I FOUR = 4: The Fourier file is written as $h, k, l, F^2_{\text{calc}}$, phase.

I FOUR = 5: The Fourier file is written as $h, k, l, F_{\text{obs}}, F_{\text{calc}}$. (for pattersons)

I FOUR = 6: EXTRA/Sirpow format (3I4,2F15.4) of $hkl, \text{FWHM}, F^2_{\text{obs}}$. For Sirpow 92+.

8. HINTS

Due to the complexity of the Rietveld method, several helpful suggestions and cautionary notes are given to help the beginning/intermediate user.

8.1 The Data File

The program can read in 2 types of file: a fixed format and a free format. Problems typically arise when the data is read in the wrong format. Typically neutron data does not need the high angular positional option (LSYN=1) and so the header in the data file can be read easily using 3F8. Neutron data usually has many detectors contributing to each count, so data read as 10(I2,I6) is the most popular (NFMT = 0), or the GSAS format (NFMT=3) For synchrotron data the starting, step and finishing angles may need more significant figures than 3F8 allows. Using the LSYN=1 option these values are read in free format (hence a space must separate the values, unlike 3F8 where no space is required), but the input file must also be changed (line 5), so that the angles are read in correctly. The Data is typically read as 10I8 (NFMT = 2).

If in doubt then the program can read data using a free listed format, where each line consists of angle(or TOF), intensity and weighting (the weighting is optionally). This is the surest way of reading the data, but the files are somewhat larger. Remember to put a header line or the first line will not be read and or will not know the beginning of the next dataset in the file.

Several freeware packages are available for converting from one format to another. These are helpful when combining different datasets for a combined refinement.

Problems when reading free format occur when comma or tabs are used as separators; spaces are the only allowed form of separator.

Problems arise in fixed format when the number of points does not match the header line expectations. Make sure that the number of points is accurately input.

8.2 The Input File

Below is a list of the more common problems.

8.2.1 Multiple Histograms

The first JOBTYP line determines the number of histograms the program will process. For each *additional* histogram you want to refine you add 10 to the JOBTYP value of the first line (only). For example, if you want to refine 2 Histograms in total, then JOBTYP of the first line (second in the file) will be 10 (because there is 1 additional histogram to refine)+ whatever JOBTYP value the first histogram will be, say 0 for x-ray data refinement. The next JOBTYP line (the next line in the file) will only have the JOBTYP of the second histogram, say 1 for neutron data refinement.

When there is more than one histogram, parameter values for each histogram are read directly after one another before going onto new values. For example, the scattering set data for a second histogram is read directly after the first histogram scattering set, before it starts to read in any other variables.

8.2.2 Wavelength/DIFC

To refine the wavelength or DIFC, the peaks must generally be already very close to the Bragg markers. If not, it is likely that the values will not converge. A simple check calculation (say with just the background refining) is a simple way of telling.

8.2.3 Time-of-Flight

Time-of-flight data is given in microseconds, and so starting/ending values are typically in the range 5000 to 100000, depending on the instrument. It is not wise to refine the alpha, beta, DIFA and zero values in samples other than calibration samples, as these are instrumental. Some institutes, such as ISIS, correct data for the incident spectrum; in these cases set A0 =1.0 and A1..A9 = 0.0 on line 4.2.

8.2.4 Scattering Factors

For anomalous scattering experiments, $\Delta f'$ needs to be implicitly input. The values of f' and f'' can be obtained using a program such as FPRIME. It is not wise to refine the $\Delta f''$ in phases with centrosymmetric space groups.

8.2.5 Background

For normal backgrounds the simple polynomial, option 0, with two or three varying parameters is adequate. If the background tails upwards at low angles, then B₁ may be needed. For an amorphous background, the new function, option -1, may be useful. If the amorphous component is known, then fixed R values are best. It may be necessary to include more R values than the default (two) allows. This is achieved with the IBCK=1 option.

An amorphous x-ray background will not be described well by the amorphous function. This is due to the angular dependence of the x-ray form factors not being included in the calculations.

8.2.6 Preferred Orientation

The summation over equivalents, Flag IPREF=1 on line 3, is highly recommended for high symmetry space groups. For high symmetry space groups, such as cubic, this summation is essential to obtaining a good fit. For orthorhombic and lower symmetry it is not required, but it does not affect the result if it is on.

8.2.7 Peak Shape

The peak shape, apart from the structural values, are the most difficult parameters to refine. For lab x-rays, in particular, the peak shape is hard to model well.

If the FCJ asymmetry function is used (NPROF=6), then the two values should not be refined simultaneously, although by using the Marquardt algorithm a stable refinement is possible. A good approach is to initially have these two parameters at zero, and only when the refinement has somewhat converged, release them individually.

They can sometimes be constrained together, such as in neutron diffraction where these values are measurable, and have a fixed ratio.

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