PROFIL Version 5.17

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Historical Note

PROFIL is an entirely new Rietveld program. Many other versions of the Rietveld program are simply modifications to earlier versions of the original code. This version, written in a simple subset of the Fortran-77 language, is not based on any of the earlier codes. The original version (1.0) was scratch written in order to refine parameters not available in the then current Rietveld programs. The early algorithms closely followed the traditional Rietveld approach of a data preparation (PREPRO) followed by a data refinement (PROFIL) stage.

Subsequent developments reduced the data preparation stage to zero calculation leaving the calculation of the peak positions and widths to the main refinement program. With the introduction of multiphase refinement in version 4.0, important modifications to the basic algorithms were made. In particular, the principle of dynamic peak-width allocation was introduced which allows intense or broad peaks with d-spacings at higher 2θ angles to be calculated ahead of those weaker peaks at lower 2θ.

With the introduction of this version, several important changes have been made. The most important change has been the revision of the code to produce a machine independent version. Currently, the program works on computers running either the VMS or Unix operating systems. As a result, the keyworded input, first introduced in version 3.0, has been extended. In addition, the introduction of refinable parameters has been easier with the automatic generation of refinement codewords. Further, the program now allows for the simultaneous refinement of both X-ray and neutron radiation data sets. The suite of programs based around PROFIL 5.0 now use a new standard format for the powder data files.

Another changes include further checks concerning symmetry and the option of LeBail style pattern decomposition. The earlier version already deduced the space group and its number from the symmetry operators (irrespective of setting). This version also checks that the codewords for the atomic coordinates and anistropic temperature factors are compatible with the site symmetry of the atoms. (Also, it does not rely on the atom being placed on the first special positions listed in the International Tables since the method used is deductive.) This should result in fewer singular matrices due to incorrect codewords.

Introduction

This manual is divided into four parts: The first part contains general information on the suite of programs available. The second part contains a description of the parameter file used by PROFIL. The third part outlines how to set up the files and carry out a Rietveld refinement. The fourth part contains technical information concerning PROFIL. The final part contains information on how to use PROFIL for pattern decomposition.

The PROFIL suite of programs comprises the following programs and are available for computers operating under VMS or Unix.

Data conversion programs:

SUMSPF Converts ILL D1A/D2B data to .SPF files.

PDSSPF Converts Daresbury PDS data to .SPF files.
RAWSPF Converts Siemens D500 data to .SPF files.
F1BSPF Converts ILL D1B data to .SPF files.
OUTFIT Converts PROFIL.OUT files to .FIT files.
SPFSUM Converts .SPF files to ILL D1A/D2B data files.
FITOUT Converts .FIT files to PROFIL.OUT files.

Data manipulation programs:
DIRSPF Lists the header block of multidata set .SPF files.
EDISPF Cuts large multidata set into smaller multidata set.
SPFADD Adds multiple data set together to give single data set.

Data plotting programs:
PLOT86 Interactive XY plotting program (N.B. by Andy Murray).
XYPLOT Produces PostScript plots of .SPF, .PRE, and .FIT files.
XYZPLT Produces 3-D pictures from multidata set files.

Data preparation and fitting programs:
PREPAR Prepares .PRE files from .SPF files.
PREPRO Generates binary data file.
PROFIL Main Rietveld program.

Other useful programs:
REFCEL Refines wavelength or unit cell parameters.
DRAGON Generates $h\ k\ l$ from space group and cell parameters.
BONDLA Standalone program to calculate bond lengths and angles.
JACKAL Ball $ stick / Space filling structure plotting program.

The general use of the programs is outlined below. The four latter programs have their own manuals and their use is only mentioned briefly in this one. Many of the programs are simple interactive programs with little need for documentation other than that described below.

Data conversion programs

SUMSPF, PDSSPF, RAWSPF, and F1BSPF

These programs convert diffractometer data from various sources to the standard powder format (.SPF) adopted by the PROFIL suite of programs. OUTFIT converts the old style observed and calculated data files .OUT to the new format files. An example of the format of the .SPF files is as follows:

```
CFCl3 ground in liquid N2 and run in 16mm vanadium sample can
     1       1       1
  3020       1    5.0000  155.9500    0.0500  2.990000  0.000000
   500.0      10.0      20:59:58 20-JUN-89  23266  23302 NEUTRON      D1A
   1.500     1.520     1.570     0.000     0.000     0.000     0.000     0.000
  5.000     24     26     27     28     32     35     40     48     53     61
          1.26   1.32   1.34   1.37   1.46   1.53   1.63   1.79   1.88   2.02
  5.500     70     77     88     97    103    115    124    134    144    147
          2.16   2.27   2.42   2.54   2.62   2.77   2.88   2.99   3.10   3.13
  6.000    156    158    170    180    181    188    195    198    207    209
          3.22   3.25   3.37   3.46   3.47   3.54   3.61   3.63   3.71   3.73
  6.500    213    215    219    223    228    234    230    232    232    226
```

```
        3.77   3.79   3.82   3.86   3.90   3.95   3.92   3.93   3.93   3.88
.......
```

The first line contains the title (A80). The second line contains the total number of data sets in the file, the format version (currently 1), and the individual data set number (3I8).

The third line contains contains the number of data points in the powder pattern, the data file type, the 2θ angles of the first and last points and the step size in degrees, followed by the nominal wavelength(s), $\lambda_{(1)}$ (and λ_2) (2I8, 3F10.4, 2F10.6). The data file type has the value 1, 2, or 3 to indicate that the file is observed data only (`.SPF` file), observed and calculated data from `PROFIL` (`.FIT` file), or Rietveld input data (`.PRE file`), respectively.

The fourth line of the data file contains a monitor count value, a time count value, the time and date of the data set (or when the file was created), run identification numbers, data type, and instrument (2F10.1, 5X, A8, 1X, A9, 2I7, 1X, A12, 1X, A6). The data type *must* be one of `NEUTRON`, `SYNCHROTRON`, or `XRAY`. This information is used by the program `PROFIL`. The fifth line has 10 values and typically contains additional information on the sample such as temperature and position (e.g. χ, ω) values (8F10.3).

The input data files for Rietveld (`.PRE` files) contain extra lines before the powder diffraction data. Firstly, they contain the background as an array of (x,y) points, (2θ, intensity) in order of ascending 2θ value. The data is input one point per line (F8.3, I8) and the list is terminated with a negative 2θ value, e.g. -1.0 0.

There may be certain regions of the data that the user wishes to exclude from the refinement process. These follow the background information in the form of lower and upper 2θ values to indicate the range to be excluded. The list must terminate with a negative angle. Finally, the `.PRE` files may contain an h k l input list (usually generated from the program `DRAGON`), the first line of which is the number of reflections in the list (I8). Normally reflections are generated internally by `PROFIL` and this value will be zero.

The next lines contain the data. Each line starts with the 2θ angle of the first data point on the line, followed by the values of the next 10 data points in intervals determined by the step size of the data set (F8.3,10I7). Each data file contains a second line containing either the error on each data point (`.SPF` and `.PRE` files) (8X, 10F7.2) or the calculated value of the data point (`.FIT` files) (8X, 10I7), again with 10 values per line.

Following the powder diffraction data, the data files may also contain output reflection and excluded region information, in a similar format to that used by the `.PRE` files as input values.

Multidata set files are simply single data sets appended together, each starting with a title and with the data set number systematically incremented throughout the whole data file.

Data plotting programs

PLOT86, XYPLOT, XYZPLT

These programs are for plotting the observed (and calculated) data. PLOT86 is an older program that is used for interactive plotting on Tektronix compatible terminals. It has the option of a cursor allowing values to be picked directly off the screen and stored in a file. This program is mainly used to obtain the background of the data by graphical methods and to monitor the fit by the Rietveld method. XYPLOT, by contrast, is non-interactive and is written to produce high-quality XY plots for publication purposes. It outputs standard PostScript files that can be sent to most laser printers.

XYPLOT has been rewritten to work with the new standard format files used by the PROFIL suite of programs. PLOT86 currently reads the old files format only. Until it is revised, two data conversion programs, SPFSUM and FITOUT, are available that convert the .SPF and .FIT files to .SUM and .OUT files, respectively.

Data preparation and fitting programs

PREPAR

This program is used to create the Rietveld input data file from the .SPF files and background data point files. The default file extension of the latter is .BGR. the program requests the number of data sets to be fitted simultaneously (usually only 1), the data file name(s), and the background file name(s). The range of data to be fitted is specified interactively, as are any regions that are to be excluded from the fitting process.

PREPRO

This program reads in the data file (with default extension .PRE) and generates the binary data file PROFIL.BIN used by the Rietveld program PROFIL. The data file is normally created with the program PREPAR since most of the powder diffraction data is fixed format. PostScript plot files may be generated of the *.PRE files using the program XYPLOT. The program basically performs syntax checks only the crystallographic data.

PROFIL

This is the main Rietveld program. It uses two files for input, namely, the binary data file PROFIL.BIN and the crystal refinement file. The default file name for the latter is PROFIL.PAR, but the default file extension is .PRO, e.g. the file name SF6 will be interpreted as SF6.PRO. Output file generation is requested via the parameters specified in the crystal refinement file. The format of the file is described later.

Other useful programs

REFCEL, DRAGON, BONDLA, and JACKAL

These programs supplement the PROFIL suite of programs and are standalone programs with their own manuals. Before fitting a powder diffraction pattern, it is often useful to be able to refine the lattice parameters from the peak positions alone. This can be performed with the program REFCEL. It is also useful to check the positions of the peaks against those calculated from known unit cell values (and space group). The program DRAGON generated lists of h k l values for this purpose. The main

Rietveld program can calculate bond lengths and angles at the end of each refinment, but is often useful to be able to calculate these values from coordinate values directly. This is done using the program `BONDLA`. Finally, having fitted the structure to the data, one needs a picture showing the arrangement of atoms or molecules within the unit cell. `JACKAL` is a non-interactive program that generates PostScript files of the crystal structure that are suitable for publication. The plot files are usually displayed first on workstations using PostScript previewers in order to obtain the best orientation, shading, light angles etc.

Contents of the `PROFIL.PAR` files

The files are free format within each line and case independent. Each line starts with a keyword and lines must be in the order given below. Variables are usually delimited by spaces, though commas and tabs may be used. Lines starting with the keyword `TEXT` are treated as comments lines. Variables are treated as either strings (A) or as integer/real numbers (I/F). The format type is indicated after each keyword. Reals with integer values may have the decimal point omitted, but integers are only accepted without it.

`TITLE` (A)
: This keyword is followed by a text string of up to 74 characters and is used to identify the parameter file.

`VERS` (F I)
: This keyword indicates the version of the refinement program and the number of refinements used. The values are *output* by `PROFIL`. Initial values can be set to zero or left blank.

`NPHASE` (I)
: This keyword specifies the number of phases (originally called patterns) that are to be fitted to the data.

`WGHT` (nF)
: This keyword allows the weights of different data sets to be varied. It has the value 1.0 for fits to single data set. For fits to multidata sets, the values of all the weights of the y_i points within the n^{th} data set are multiplied by the n^{th} specified value. If the value is zero, then the data set is ignored.

`OUTP` (n(A I))
: This keyword and its sub keywords and values indicate which output files are to be generated: The line may be left blank in which case `LIS 1 PAR 1` is assumed for a normal Rietveld refinement. Since a maximum of 10 sub keywords per line is allowed, the keyword `OUTP` may be repeated and further sub keywords given on a second line.

  `LIS` n : If $n = 1$ then the lineprinter listing `PROFIL.LIS` is generated (and in more detail if $n = -1$). By default, n is set to 1.

  `PAR` n : If $n = 1$ then a new parameter file `PROFIL.PAR` is generated at the end of the refinement (even if `NCYC 0` *v.i.*). If the input parameter file is `PROFIL.PAR`, then it will be renamed `PROFIL.V`*nn* where *nn* is a double digit integer number chosen sequentially.

FIT n : If $n = 1$ then the program generates the data file PROFIL.FIT that can be used to plot the observed, calculated, and difference powder diffraction patterns. The data file also contains information on the peak positions of each phase and excluded regions of the data. For the case of multidata set refinements, the file will contain all the information for each data set. The file has a standard format and may be converted to the old format using the program FITOUT (*v.s.*).

HKL n : If $n > 0$ then the data file PROFIL.HKL of $h\ k\ l$ and F_{hkl} that can be used for Fourier studies is generated. The integer n specifies that values for the n^{th} phase are to be output. Note that the structure factors refer to those used to fit the first data set only. If this is a neutron-radiation data set, then neutron-diffraction structure factors will be output. The file is keyworded starting with the title (TITLE), followed by cell parameter information (CELL), symmetry information (LATT and SYMM *v.i.*), and then the structure factors (HKLF). The latter lines consist of $h\ k\ l$, F_{hkl}(calc), ϕ_{hkl} (in rad.), and F_{hkl}(obs). Reflections incompletely calculated or totally excluded are indicated by a $\star$.

INT n : If $n > 0$ then the program generates the data file PROFIL.INT for the n^{th} data set containing $h\ k\ l$ and I_{hkl} for all phases. Reflections incompletely calculated or totally excluded are indicated by a $\star$ and comment.

COR n : If $n = 1$ then the data file PROFIL.COR is generated containing the full normalized variance-covariance matrix. All values are multiplied by 100%.

TAB n : If $n = 1$ then the program generates a table of refined parameters with esd values in () in a form suitable for publication. The table will contain information on each phase for multiphase refinements. For LeBail pattern decomposition, $n = 0$.

XYZ n : If $n > 0$ then the data file PROFIL.XYZ is generated containing the coordinates and symmetry information of the n^{th} phase in a format suitable for the plotting program JACKAL. For LeBail pattern decomposition, $n = 0$.

ATM n : If $n > 0$ then the program generates the data file PROFIL.ATM containing the coordinates of *all* of the atoms in the unit cell of the n^{th} phase. For LeBail pattern decomposition, $n = 0$.

BON n : If $n > 0$ then the keyworded data file PROFIL.BON is generated which may be used as input to the bond length and angle calculation program BONDLA. For LeBail pattern decomposition, $n = 0$.

REF n : For normal Rietveld refinement, $n = 0$. For Lebail pattern decomposition set $n = 1$ to obtain a file containing $h\ k\ l$ and I_{hkl} that may be used for further cycles of refinement.

INS n : If $n = 1$ then the keyworded data file PROFIL.INS in SHELX format is produced. This is useful for direct method solutions using the SHELX program XS.

RES n : If $n > 0$ then the keyworded data file PROFIL.RES in SHELX format is produced. This is useful for plotting with the SHELX program XP, e.g. for ellipsoid plots. It may also be used as an input file to the Cerius program by Molecular Simulations. For LeBail pattern decomposition, $n = 0$.

SHFT (4F)

This keyword is followed by 4 real numbers that can be used to damp the refinement process. The 4 reals (which must be in the range $0 \leq x \leq 1$) are set normally to 1.0. They refer to atomic coordinate parameters, atomic thermal parameters, linear parameters (e.g. scale factor, site occupation numbers), and non-linear parameters (e.g. cell parameters, wavelength).

NCYC (I)

This keyword and value specifies the number of cycles of refinement which must be in the range $0 \leq n \leq 99$. It is recommended to set NCYC= 0 each time a new parameter file is created by hand using an editor as this allows syntax checks to be performed. In addition, the user can check that the contents of the lineprinter file are correct.

The next few lines starting with WAVE and ending with SCAT or ANOM must be repeated as a group for each data set that is being fitted.

WAVE (F A [F])

This keyword is followed by a value specifying the wavelength of the radiation that was used to collect the data. It is followed by the sub keyword FIX or VARY to indicate whether the wavelength is a fixed or refinable parameter. If VARY is specified, then it may be followed by an optional codeword indicating parameter number and multiplier (*v.i.* **Codewords**).

ZERO (F A [F])

This keyword and value specifies the zero-point error in the 2θ scale of the diffractometer. Its value is followed by the sub keyword FIX or VARY to indicate whether the 2θ zero-point error is a fixed or refinable parameter. If VARY is specified, then it may be followed by an optional codeword.

ABSC (3F)

This keyword has 3 arguments. The first specifies the absorption coefficient μr used to correct the absorption of a *cylindrical* sample. The second specifies the diameter $(2r)$ of the sample and is used only to calculate a theoretical value of the absorption coefficient (N.B. The second values is currently unused). The third value specifies the absorption coefficient, μd, when a thin film is used to cover a flate plate sample. (Only one of the corrections may be used with any one data set.)

SCAT (A F)

The line containing this keyword should be repeated for each chemical element in the sample. The first sub keyword is the chemical element symbol e.g. Pb for lead. If the value that follows is left unspecified, then the program substitutes *either* the value of the neutron scattering length b for neutron radiation data *or* the value of Z for X-ray radiation data. In addition, and for the latter case only, the program automatically supplies an X-ray form factor and anomalous dispersion terms f' and f'' set to zero. If Z is non-zero, then the additional lines starting with the keywords `FORM` and `ANOM` must be given.

`FORM` (2F)

This keyword applies only to X-ray data and when the value of Z in `SCAT` is non-zero. For each value of `SCAT`, 5 lines beginning `FORM` must be specified where the values a(i), b(i) on each line are used to specify the form factor according to the equation $f(0) = \sum a_i \exp\{b_i(\sin\theta/\lambda)^2\}$.

`ANOM` (2F A [2F])

This keyword applies only to X-ray data and when the value of Z in `SCAT` is non-zero. After the X-ray form factor specified by `FORM`, a single line is required to specify the anomalous dispersion terms f' and f''. Their values are followed by the sub keyword `FIX` or `VARY` to indicate whether the dispersion terms are fixed or refinable parameters. If `VARY` is specified, then 2 optional codewords may follow. (N.B. Currently only the `FIX` option is available).

The next lines starting with `LATT` and ending with `PEAK` (if single phase) or `BOND` should be given as a group for each diffracting phase in the sample.

Space group symmetry information should be given either using `SPGP` or `LATT` combined with `SYMM`. (Non-standard settings are encouraged where appropriate but should be specified using `LATT` and `SYMM` information.)

`SPGP` (A [A])

This keyword specifies the space group as given in the International Tables for Crystallography. An optional keyword value is the symmetry of the origin. (N.B. This keyword is currently unavailable until complete tests have been performed.) Internally, the program converts the information into `LATT` and `SYMM` type values.

`LATT` (2A)

This keyword has 2 string values giving (a) the centrosymmetricity of the *origin* (not the space group) as either `C` (centric) or `A` (acentric) and (b) the Bravais lattice centring as one of `P` (primitive), `A` (A-face centred), `B` (B-face centred), `C` (C-face centred), `F` (all-face centred), `I` (body centred), or `R` (rhombohedral obverse centring with hexagonal axes).

`SYMM` (A , A , A)

This keyword is given for each line of symmetry operators. The symmetry operator should be given in the form printed in the International Tables for Crystallography with the translational part of the operator in fractional form (e.g. 0.5 is written as `1/2`). All the translational parts must be an integer multiple of $\frac{1}{24}$. Note that it is *not* necessary to give *all* the symmetry operators of the space group. The program only requires sufficient operators that when multiplied together generate the complete space group. x, y, z

may be omitted. Ones containing lattice centrings are converted into `LATT` information.

`CELL` (6F)

This keyword specifies the values of the lattice parameters a, b, and c in Ångstroms and α, β, and γ in degrees.

Following the cell information, the contents of the asymmetric unit of the crystallographic cell are specified. This consists of lines starting with the keywords `ATOM`, then optionally `TLS` and `SHELL`. Anisotropic atoms may have the one of the optional keywords `BETA`, `BIJ`, or `UIJ` following the keyword `ATOM`.

`ATOM` (A 5F A)

Atom label:

The first sub keyword specifies an atom label. The atom label *must* follow certain conventions. It must start with the chemical symbol of the scattering element followed optionally by one or two digits. If a single digit is used, then a letter may be used in addition e.g. Na(2A). The use of brackets around the digit(s) (and letter) are optional and are added automatically by the program if omitted. The program must be able to match the chemical element to one of those specified in the list of scatterers. When the list of scatterers differs between two data sets (commonly H and D), the program will attempt to match the symbol to that used for the first data set only.

x y z:

The next 3 values specify the fractional x, y, z coordinates of the atom. The program will adjust the values, if necessary, so that they lie within the range $-0.5 \leq x \leq 1.5$, $-0.5 \leq y \leq 1.5$, and $-0.5 \leq z \leq 1.5$.

B(iso):

The next value gives the isotropic temperature factor, B, which is used in the form $\exp\{-B(\sin\theta/\lambda)^2\}$. When specified the final sub keyword of the line should be left blank or set to one of `ISO` or `I->A` (*v.i.*).

N:

This next value specifies the number of atoms of that type within the unit cell. In order to obtain site occupation factors it is necessary to divide each value by N_{xyz}, the number of positions in the unit cell corresponding to the general position x, y, z. N, rather than *s.o.f*, should be used so that the correct sample density is calculated.

B(type):

The final sub keyword of the line is used to specify whether an atom is to be treated as isotropic (`ISO`) or anisotropic (`ANISO`). If `ANISO` is given, then B(iso) is forced to be zero and a further line must follow starting with one of the keywords `BETA`, `BIJ`, or `UIJ` (*v.i.*). It may also be used to indicate whether an isotropic value is to be converted to anisotropic (`I->A`) or vice-versa (`A->I`).

`BETA` (6F)

This line specifies the anisotropic temperature factor in the form given by

$$\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{23}kl + 2\beta_{31}lh + 2\beta_{12}hk)\}.$$

The order of the terms β_{ij} follows the order in the above equation. This is the form used internally by the Rietveld program but for publication purposes either B_{ij} or U_{ij} are recommended. All forms are listed in the lineprinter file but B_{ij} only is used for the output files `PROFIL.PAR` and `PROFIL.TAB`.

`BIJ` (6F)

This line specifies the anisotropic temperature factor in the form given by

$$\exp\{-(B_{11}h^2a^{\star^2} + B_{22}k^2b^{\star^2} + B_{33}l^2c^{\star^2} +$$

$$2B_{23}klb^\star c^\star + 2B_{31}lhc^\star a^\star + 2B_{12}hka^\star b^\star)/4\}.$$

The order of the terms B_{ij} follows the order in the above equation.

`UIJ` (6F)

This line specifies the anisotropic temperature factor in the form given by

$$\exp\{-2\pi^2(U_{11}h^2a^{\star^2} + U_{22}k^2b^{\star^2} + U_{33}l^2c^{\star^2} +$$

$$2U_{23}klb^\star c^\star + 2U_{31}lhc^\star a^\star + 2U_{12}hka^\star b^\star)\}.$$

The order of the terms U_{ij} follows the order in the above equation.

`TLS` ()

Optional keyword. For further information, please consult the author.

`SHELL` (A 6F or A 2I F)

Optional keyword. This keyword allows atoms that are dynamically disordered on the surface of a sphere to be described in terms of symmetry-adapted spherical harmonic functions. For further information, please consult the author.

The next pair of lines (`INST` and `PEAK`) should be repeated as a group for each data set that is being fitted simultaneously.

`INST` (4F)

This keyword has 4 real values starting with the scale factor and then the 3 resolution (or peak width) parameters U, V, and W. The full-width at half height (FWHH) of the peaks is given by the formula

$$Fw^2 = U\tan^2\theta + V\tan\theta + W.$$

`PEAK` (A 2F)

This keyword is followed by a sub keyword that describes the peak-shape function to be used in the refinement. Peak shape functions currently available are `GAUSS` (Gaussian) and `PVOIGT` (pseudo-Voigt). Following the sub keyword, the first real number is the value of the asymmetry parameter that is used when fitting neutron diffraction data to account for the low-angle peak asymmetry. For the pseudo-Voigt peak-shape function, the correction term applies only to the Gaussian part of the peak shape. The second real number applies only to the pseudo-Voigt peak-shape function and is the value of η as given by

$$pV(x,w) = (1-\eta)G(x,w) + \eta L(x,w)$$

When a data file is initially created for a single phase refinement, `PEAK` can be the last line of the file. The program will then generate the remainder of the file automatically in the output file `PROFIL.PAR`. It is easier for the user to edit the new output file than to create the rest of the file by hand.

Codewords

The first group of lines that follow start with one of the keywords `FIX` or `VARY` followed by a sub keyword indicating the parameter type. The keyword `FIX` indicate that all the parameters are fixed and all the codewords corresponding to those parameters are set to zero. If the keyword `VARY` is specified, then some or all of the parameters within the group specified by the sub keyword may be refined. If no codewords, are given then they are generated automatically starting with parameter number 1000.

A codeword, Cw, consists of two parts: A parameter number, Np, and a shift multiplier, Sm. The latter normally takes the value of 1.0, but may take other values when certain parameters are tied together. For example, refinement of the coordinates of an atom on the special position x, $2x$, z requires that the y coordinate shifts twice as much as the x coordinate during the refinement. The parameters are always renumbered starting at 1. The codeword is a composite number given by

$$\mathrm{Cw} = \mathrm{Np} * 10 + \mathrm{Sm}.$$

If the shift multiplier is negative, then the absolute value of it is added to 10$\times$ the parameter number and the whole codeword is then made negative.

`VARY CELL` (6F)

These keywords are followed by 6 optional reals for the cell codewords.

`VARY Atom-Label XYZBN` (5F)

For each line starting with the keyword `ATOM`, there must be an equivalent line starting with `FIX` or `VARY` followed by the atom name. This may be followed by one of the keywords `XYZ`, `XYZB`, `XYZBN`, `B`, `N`, `BN`, or `XYZN` to vary xyz, xyz & B(iso), etc.. The first option allows refinement of the atom coordinates only and leaves the site occupation number and isotropic temperature factor (if used) fixed. The third option allows all the parameters on the `ATOM` line to be refined, and so on. Codewords are generated automnatically for each parameter type unless given explicitly. The program will apply symmetry constraints to atoms on special positions automatically.

`VARY BIJ` (6F)

This optional line should follow each of the lines above for any atom with an anisotropic temperature factor. There are 6 optional codewords for each of the B_{ij} values. The program will apply symmetry constraints to the values automatically. This line must be present for all atoms where either β_{ij}, B_{ij}, or U_{ij} are input, even if there is an instruction to convert from an anisotropic to isotropic temperature factor (`A->I` *v.s.*). Conversely, it should be absent if there is an instruction to convert from an isotropic to an anisotropic temperature factor (`I->A` *v.s.*). In the latter case, 6 codewords will be generated automatically if the codeword for B(iso) is non-zero.

`VARY TLS` ()

Optional keyword. For further information, please consult the author.

`VARY Atom-Label XYZR` (6F)

These optional lines are for shell refinement. See note above on `SHELL`.

The next lines with sub keywords `SCALE` to `PEAK` should be specified as a group for each data set that is being fitted simultaneously.

`VARY SCALE` (F)

This keyword is followed by an optional codeword for refinement of the scale factor.

`VARY UVW` (3F)

This keyword is followed by optional codewords for refinement of the peak width parameters U V W. It is frequently desired to vary only 1 or 2 of the UVW parameters. Under these circumstances, include only those required in the keyword, e.g. `VARY VW` to refine V and W only.

`VARY PEAK` (2F)

This keyword is followed by optional codewords for refinement of the peak asymmetry parameter and the Gaussian-Lorentzian ratio η when a pseudo-Voigt peak-shape function is used. Note that the codeword for peak asymmetry is only generated automatically for neutron data sets.

Following the codeword lines, additional optional information may be supplied. For example, restraints (or "slack constraints") are given using the keyword `CHEM`.

`CHEM` (A 2F or A [I 3F])

For each chemical restraint, a group of lines starting with the keyword `CHEM` is required. The first line has a sub keyword giving the restraint type which must be one of `DIST`, `ANGLE`, or `SAME` for distance, angle, or same distance restraints respectively. These are followed by two values giving the magnitude of the restraint (which is zero for the difference between two distances) and the error. Since the error is used to weight the restraint, its value must be non-zero. The smaller its value, the bigger the weight of the observation.

The number of lines that follow depend on the restraint type and is 2, 3, and 4 for distance, angle, and same distance, respectively. Each of the subsequent lines specifies an atom label. Since the atom in the list given by `ATOM` may have different coordinates to that required for the restraint, then optional symmetry information may be specified on the line. This comprises an integer which is the number of the symmetry operator (as given in the lineprinter listing) and a fractional translational x, y, z. If the structure is centrsymmetric and an inversion of the coordinates is needed, then the symmetry operator number is set negative. Note that the effect of inversion on the symmetry operator $\frac{1}{2}-x, \frac{1}{4}+y, \bar{z}$ results in $\frac{1}{2}+x, \frac{3}{4}-y, z$.

For three atoms given in an angle restraint, the angle refers to that subtended by the second atom with respect to the first and third in the list. In order to restrain two distances to be the same, then the observation is the the difference between them is zero. This allows the magnitude of the distance to refine whilst keeping both distances similar. One distance is between the first and second and the other is the third and fourth atoms in the list.

`BFAC` (A 2F or A [I 3F])
: (Restraints on the temperature factors for rigid bonds has not yet been reincorporated in version 1.0)

`OCCN` (A 2F or A [I 3F])
: (Restraints for site occupation numbers have not yet been introduced.)

`BOND` (3F)
: This keyword is followed by 3 values to specify the limits for bond length and angle calculations. The first 2 values specify a minimum and maximum distance in which bond lengths and angles will be calculated. The last value is used to specify a maximum contact distance below which only distance values are calculated.

An example of a typical parameter file created with a text editor is shown below.

```
TITLE D2S phase III run on D1A
VERS
NPAT 1
WGHT
OUTP
SHFT 1 1 1 1
NCYC 0
WAVE  1.9106
ZERO -0.2
ABSC 0
SCAT S
SCAT D
LATT C P
SYMM  -x,-y,1/2+z
SYMM  x,1/2-y,-z
SYMM  -x,1/2+y,1/2-z
CELL 4.076 13.380 6.721
ATOM S1 -0.042  0.144   0.25  0.3  4
ATOM S2  0.460  0.401   0.25  0.3  4
ATOM D1  0.172  0.216   0.25  1.0  4
ATOM D2  0.193  0.073   0.25  1.0  4
ATOM D3  0.672  0.379   0.105 1.0  8
INST   1.0 0.2 -0.5 0.5
PEAK
```

After running through PROFIL with zero cycles, the new parameter file has the appearance as shown below.

```
TITLE D2S phase III run on D1A
VERS     5.00       0
NPAT     1
WGHT    1.000
OUTP   LIS 1 PAR 1 FIT 0 HKL 0 INT 0 COR 0 TAB 0 XYZ 0 ATM 0 BON 0 REF 0
SHFT    1.000   1.000   1.000   1.000
NCYC     0
TEXT Parameters for data set number 1 (Wav., 2th. zero, abs., & b/f values)
WAVE  1.9106001   FIX
ZERO   -0.20000   FIX
ABSC      0.000       0.0       0.000
SCAT S         2.847000     Neutron b value
SCAT D         6.674000     Neutron b value
TEXT Diffracting material (or phase) 1
TEXT Space group  57 : Pbcm
LATT      C     P
SYMM        x,                 y,                 z
SYMM       -x,                -y,              1/2+z
SYMM        x,              1/2-y,               -z
SYMM       -x,              1/2+y,             1/2-z
CELL    4.076000  13.380001   6.721000    90.0000    90.0000    90.0000
ATOM S(1)    -0.042000  0.144000  0.250000    0.3000    4.00000  ISO
ATOM S(2)     0.460000  0.401000  0.250000    0.3000    4.00000  ISO
ATOM D(1)     0.172000  0.216000  0.250000    1.0000    4.00000  ISO
ATOM D(2)     0.193000  0.073000  0.250000    1.0000    4.00000  ISO
ATOM D(3)     0.672000  0.379000  0.105000    1.0000    8.00000  ISO
TEXT Instrumental parameters for material (or phase) 1 in data set 1
INST   0.1000000E+01    0.200000   -0.500000    0.500000
PEAK GAUSS      0.000000
TEXT R-factors:      Rwp =724.5%     Rexp =  5.9%     RI =737.4%
TEXT Refinement codewords for diffracting material (or phase) 1
FIX  CELL
FIX  S(1)   XYZ
FIX  S(2)   XYZ
FIX  D(1)   XYZ
FIX  D(2)   XYZ
FIX  D(3)   XYZ
FIX  SCALE
FIX  UVW
FIX  PEAK
BOND     0.0100    2.0000    3.5000
```

Although the output is “fixed” format, there is no need to keep it this whilst editing it since the input file is read as free format. The program adds some text comments to help break the file into sections. This is particularly useful for large parameter files, especially when fitting either multidata set of multiphase data.

Setting up the files for Rietveld refinement

It must emphasised that the purpose of the Rietveld method is to refine structures and not to solve them. Hence before commencing a refinement, it is essential to have some knowledge of the unit cell, space group, and its contents, i.e. a structural model. The instrumental parameters are usually known approximately from studies of simple materials such as Ni or Si that are frequently used for instrument calibration.

Step 1. Some Rietveld programs use polynomial functions to fit the background scattering associated with every powder diffraction pattern. PROFIL requires that the background is estimated graphically as a series of points that are connected by straight lines. Intermediate points are obtained by linear interpolation. This step is readily carried out using the program PLOT86 with the cursor and the command B. PLOT86 generates a file called BACK.DAT containing the background points. However, the file *must* be edited since the 2θ values are still given in the old units of $\frac{1}{100}^\circ$, but it is a simple edit to convert these values to degrees.

Step 2. Generate the Rietveld data (.PRE) file. This can be done automatically using the program PREPAR. If the data file is not in the required format, first convert it to the standard format that is now used (*v.s.*). PREPAR also requires a file containing the background information. The file is free format with 2 values per line (2θ, intensity). A warning message will be given if the program detects that the 2θ values are in the old $\frac{1}{100}^\circ$ units. The 2θ values must be given in ascending order.

Step 3. Generate a binary data file from the .PRE file using the program PREPRO. This program performs a few syntax checks on the data file but does no calculations on the data.

Step 4. Create, using a text editor, a file containing the crystallographic model as described in the previous section, i.e. starting with TITLE and ending with PEAK. Set the number of cycles of refinement to zero and run the program PROFIL using this parameter file. Assuming that the option OUTP PAR 1 has been specified, the program will create a new parameter file with all the refinable parameters set to FIX. Edit the new parameter file, e.g. change FIX SCALE to VARY SCALE, reset the number of cycles of refinement to 3, and rerun the program. If the refinement does not converge in the given number of cycles, simply rerun without editing the new parameter file until convergence occurs.

Step 5. Check the results by typing (or printing) the lineprinter file PROFIL.LIS. Check that bond lengths and angles listed in the lineprinter file make sense. Regularly observe the progress of the fit in terms of the calculated data by using the output option OUTP FIT 1. The file can be plotted using the programs FITOUT (to convert the data file) and PLOT86. This is better check than simply looking at the R-factors.

Step 6. Once the structure has been refined successfully, it may be plotted using the program JACKAL. Also tables of the parameters with e.s.d.s are listed in file PROFIL.TAB. Automatic tables of bond lengths, etc. are not yet available.

Technical information on the program PROFIL

The program follows the basic procedure as outlined in the original paper by H. M. Rietveld (*J. Appl. Cryst.* (1969) **2**, 65–71) and only a brief résumé is given here.

(To be finished)

The thin-film absorption correction for flate plate sample geometry is given by the simple geometric expression:

$$A_{hkl} = \exp(-2\mu d/\sin\theta).$$

Since the correction is applied to the model, calculated intensities are multiplied by this factor.

R-factors.

Pattern decomposition PROFIL

A method of whole pattern decomposition was first described by G. S. Pawley in 1981. More recently, an alternative alorithm based on the Rietveld method of obtaining I(obs) has been suggested by LeBail. It is this latter method that has been implemented in this version of PROFIL.