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Profile Analysis of Neutron Powder Diffraction Data at ISIS

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1. INTRODUCTION

The aim of this manual is to document the current suite of time-of-flight neutron powder diffraction profile refinement programs available to ISIS users. Aspects of data collation and normalisation specific to the individual diffraction instruments are dealt with elsewhere. It will be assumed the user has produced a suitable data file (.DAT file) containing the profile data consisting of point by point values of the corrected diffraction profile across the pattern.

The analysis of neutron powder diffraction data at ISIS by profile refinement utilises a suite of 'in-house' written and supported programs based on the Cambridge Crystallography Subroutine Library (CCSL). There is a technical manual[1] and companion appendices[2] for CCSL which gives full details of the general use of the library. A quick scan through the CCSL manual will give the user a general feel for the procedure to adopt in the use of the library and hence of the profile codes. The instructions documented in this handbook are complementary to those in the more specialist CCSL manual, and consequently go into no great detail regarding technical details of any of the CCSL routines.

The programs may be run from each individual user account, for example [USER01], once the appropriate login procedure has been set-up by the instrument scientists. The programs are mostly activated by one line commands and only a basic knowledge of a VAX editor should be required; details can be found in the 'VAX primer' available from Computer Support. Under no circumstances should it be necessary to copy command files or executable files into a local user account area. Should users wish to install the programs at their home institutes, a comprehensive export program package is also available.

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[1] Brown, P.J. & Matthewman, J.M., Rutherford Appleton Laboratory Report, RAL-87-010.

[2] Brown, P.J. & Matthewman, J.M., Rutherford Appleton Laboratory Report, RAL-90-021.

1.1 Refinement File Specifications

In the course of running the programs a number of input files are required and various output files may be generated. These files should all have the same name but different extensions, in order to facilitate automatic running of the programs. The name is usually a suitable mnemonic and may be up to a maximum length of six characters, for example SAMP01. The extensions and file types are summarised below:

.CCL	crystal data file, which contains structure and profile parameters and control cards to drive the refinement;
.CCN	updated crystal data file containing new values following a refinement;
.DAT	data file containing the observed diffraction profile for standard refinement programs;
.OUT	line printer file containing refinement output data;
.PRO	contains observed and calculated profiles for plotting using GENIE;
.HKL	reflection listing file which may contain intensity and peak shape information dependent on the program in use;
.FOU	contains observed and calculated structure factor for use with CCSL Fourier plotting routines;
.TOF	input data file for cell refinement program;
.CLP	output file for cell refinement program.

In addition two further GENIE intermediate format files may be produced:

.PIC	a converted .PRO file with observed, calculated and difference profiles for display in GENIE;
.TIC	which contains calculated peak positions that, in GENIE, may be plotted as markers;
.TAG	a lineprinter file giving a calculated reflection listing with (optional) peak intensity information.

2. SETTING-UP AND RUNNING A PROFILE REFINEMENT CALCULATION

2.1 Preparation of a data file

Full details of this are described elsewhere in the relevant instrument manuals. In essence a binary GENIE intermediate file is converted to ASCII format (x y esd) by means of a GENIE function:

>> FUNCTION Wn G:PROLSFILE Wn

Enter profile data filename : **SAMP01.DAT**

2.2 Preparation of a crystal data file

The crystal data file is the means by which the CCSL routines are informed of instrument and diffraction profile parameters and crystallographic information regarding the sample. In addition, this file contains the parameters controlling the course of the refinement as it proceeds and so is fundamental to the whole process. An example file is given at the end of this section. To prepare a crystal data file, EDIT a file with the name SAMP01.CCL, .CCL being the default extension for crystal data files in the CCSL system. Data input on the individual cards is essentially 'free-format' but upper case characters are required. Using the full screen editor described elsewhere, one should input the following lines of cards into the .CCL file.

2.2.1 Crystal Structure Cards

N or Title card

N Title, consisting of up to 79 characters of text

This card serving to identify the refinement is not actually compulsory for the successful running of the programs. For example:

N Al2O3 refinement as test example for handbook

C (Cell) card (compulsory) (in Å and °)

C a b c α β γ

If α. β or γ are omitted, it is assumed = 90°, except for hexagonal, trigonal cells, where $\gamma = 120°$ is deduced. The refinable parameters in reciprocal space are referred to as A*, B*, C*, D*, E* and F* in the refinement, where $A^*=a^{2*}$, $B^*=b^{*2}$, $C^*=c^{*2}$, $D^*=b^*c^*\cos\alpha^*$, $E^*=c^*a^*\cos^*\beta^*$ and $F^*=a^*b^*\cos\gamma^*$. Example:

C 4.75644 4.75644 12.98793 90 90 120

A (Atom) card (compulsory)

A name x y z B <label> s.o.f

This card includes atom name, fractional coordinates, isotropic temperature factor (Å^2), **optional** label and site occupancy factor). Example:

A Al 0.000 0.000 0.35203 0.6 1.0
A O1 0.69358 0.000 0.25000 0.8 1.0

An atom name has up to 4 characters, starting with a letter. The <label> is only needed if the required scattering factor is not given on an "F" card (see below) whose label is the starting letter of this "A" card. If s.o.f. is omitted, the occupancy is assumed equal to 1.

T (Temperature factor) card

T name type B_{11} B_{22} B_{33} B_{23} B_{13} B_{12}

(atom name, type of anisotropic temperature factor, Bij values (Å^2)) Example:

T Al 2 0.1027 0.1027 0.25794 0.00 0.00 0.05135
T O1 2 0.14677 0.18811 0.22677 0.03729 0.01866 0.09047

The type 0 creates an anisotropic temperature factor from an existing isotropic B, which is automatically set to zero (i.e. Bij=Biso (i=j), Bij=0 (i≠j), i,j=1,2,3). The temperature factor created is of the type 2:

$\exp(-1/4(B_{11}\, ha^*ha^* + \ldots + 2\, B_{23}\, kb^*lc^*\cos a^* + \ldots)$

Type 3 uses the expression: $\exp -2\pi^2(B_{11}\, ha^*ha^* + \ldots + 2\, B_{23}\, kb^*lc^*\cos a^* + \ldots)$

Type 4 uses the expression: $\exp -(B_{11}\, h\, h + \ldots +\ B23\, k\, l\ + \ldots)$

Type 5 uses the expression: $\exp -(B_{11}\, h\, h + \ldots +\ 2B_{23}\, k\, l\ + \ldots)$

F (Form factor) card (compulsory)

F name type b

(name, type of scattering factor or form factor, scattering length). Example:

```
F Al  1  0.3446
F O   1  0.5805
```

For neutron data, type 1 is for a neutron scattering length. This factor is applied first to all "A" card atoms with the same <label> and then to any remaining "A" card atoms whose starting letters match the scattering factor.

S (Symmetry) cards

S s_1, s_2, s_3

(symmetry operators defining the space group). Example:

```
S 1/3+X, 2/3+Y, 2/3+Z
S -X, -Y, -Z
S Y, X, 1/2-Z
S -Y, X-Y, Z
```

Only the space group generators (for example those defined in the International Tables for Crystallography Vol. A) are required plus any one of the lattice operators for face or body centring or one trigonal translation operator. For groups with a centre of symmetry, this must be at the origin. If no S cards are given space group P1 is assumed. The above cards have defined the crystal cell, symmetry and contents. In this sense the "crystal data" file is complete. However, for profile refinement this file contains further cards which guide the course of the refinement procedure.

2.2.2 Information (I) card(s)

This card controls the program output and refinement via a list of codewords and numerical values as shown below. Example:

```
I  NCYC 5  MCOR 0  PRIN 0  PRFO 0  PRPR 2  PRFC 0
```

The following provide an interpretation of the most common I card instructions:

NCYC	n	carry out n cycles of refinement (n=0 for simulated pattern)
CYC1	m	label the first cycle m
MCOR	k	print correlations above k% to the .OUT file
	k=0	print the entire correlation matrix
	k < 0	do not print any correlations
FRIE	1	1 imposes Friedels Law.

The following codewords have numerical values 0, 1, 2, 3 or 4:

PRIN	j	frequency at which output lists are printed
PRPR	j	create a formatted plot file (.PRO)
PRFO	j	create an hkl file for Fouriers
PRFC	j	list structure factors to the lineprinter file
PRSK	j	list slack constraint information to the lineprinter file

The value of j determines when these are carried out:

j = 0	omit
j = 1	first cycle of refinement
j = 2	last cycle of refinement
j = 3	first and last cycle of refinement
j = 4	every cycle of refinement

For use with CAILS:

PRCV	m	list the first m off-diagonal terms of the variance-covariance matrix for intensities in the .hkl file.

2.2.3 Compulsory Instruction/Parameter (L) Cards

These cards are used both to provide parameter information to the refinement and also to control the variation of parameters.

L REFI - this card defines the type of profile refinement performed. Currently allowed are:

11	neutron t-o-f full profile refinement with type 1 peak function (Gaussian convolved with double exponential decay and switch function)
12	neutron t-o-f full profile refinement with type 2 peak function (Voigt convolved with double exponential decay and switch function)
14	neutron t-o-f full profile refinement with type 2 peak function (Voigt convolved with double exponential decay and switch function) modified for use with POLARIS data
21	neutron constant wavelength full profile refinement with Gaussian peak function
31	x-ray constant wavelength full profile refinement with Gaussian peak
32	synchrotron x-ray constant wavelength full profile refinement with Voigt peak function

For each refinement type the appropriate peak function (PKFN) cards are required as outlined later. A positive number includes the data points which do not contribute to Bragg peaks ('background points') in the refinement and in working out agreement factors and is usually used with a background fitting option (see L BACK instructions). A negative prefix, for example L REFI -12, excludes data points which do not contribute to a reflection in the refinement. This provides a method of reducing problems with data corrupted by impurity, since only the regions where sample peaks are expected are fitted. Prefixes of 100 and 200 are also allowed to perform a Pawley refinement using CAILS (Cell And integrated Intensity Least Squares) and for the program SAPS (Structure And Peak Shape) respectively For example L REFI 112. The negative prefix is still applicable.

L SCAL - this card relates observed and calculated profiles such that Yobs = Yback + (SCAL * Ycalc) for each profile point. At present the card contains only one scale factor referred to as SCAL 1 in the refinement. Example:

L SCAL 0.1254

L ZERO - this card relates the observed and calculated profiles such that $T_{obs} = T_{calc} + ZERO$. The card contains the electronic detector delay zeropoint correction in microseconds and is referred to as ZERO in refinement. This is a known value and should be fixed at 8µs. Example:

L ZERO 8.0000

L PKFN - these are peak function cards for parameterising the variation of peak width with incident neutron wavelength. The individual cards required depend on which refinement type (L REFI) is being run. Usually there are two PKFN cards associated with Gaussian and Lorentzian components of the Voigt (convolution of Gaussian and Lorentzian) function. In general the format of an L PKFN card is:

L PKFN <name> <tolerance> <several reals>

The name corresponds to one of the variables describing the peak shape. This variable has a functional form determined by the "reals". The tolerance factor (with the exception of the 'SWCH' and 'POWR' cards) determine the range in the diffraction pattern over which a peak is to be calculated. It is intended to replace this format with an L PKFN TOLR card. The tolerance in the SWCH card determines the precision of the fit that may be achieved using the discrete Fast Fourier Transform algorithm used in the calculation of the peak shapes. Values of 1, 2 and 3 are allowed; 3 represents the highest precision and is recommended particulary when there is a large Lorentzian contribution. However there is a substantial time penalty (of the order of a factor of 10) between options 1 and 3. (The tolerance in the L PKFN POWR card has no significance.)

L PKFN TAUS - *tolerance taus1 taus2*, describe the 'thermal neutron' exponential decay. This is predicted to be a constant value, independent of neutron wavelength, i.e. taus2 = 2.8644.

L PKFN TAUF - *tolerance tauf1 tauf2*, describe the 'fast neutron' exponential decay. This is predicted to be proportional to wavelength, i.e. tauf1 = 0.

L PKFN SWCH - *tolerance swch1 swch2*, describe the 'switch function' linking TAUF and TAUS with wavelength.

The TAUS, TAUF, and SWCH cards characterise the moderator contribution to the peak shape and are normally not refined.

L PKFN SIGM - *tolerance sigm1 sigm2 sigm3*, describe the Gaussian component of the Voigt function. The tolerance determines how many Gaussian standard deviations within which a significant contribution to the profile is made. For time-of-flight refinements sigm1, sigm2 and sigm3 are parameterised according to:

$$\sigma^2 = \text{sigm1} + \text{sigm2} *\lambda + \text{sigm3} *\lambda^4$$

where λ is the neutron wavelength corresponding to the time of flight and is σ^2 the second moment of the Gaussian. The 3 parameters are measured in microseconds and are referred to as **SIGM 1, SIGM 2** and **SIGM 3** in the refinement.

L PKFN GAMM - *tolerance gamm1 gamm2 gamm3* describe the Lorentzian component of the Voigt function. The 3 parameters are measured in microseconds and are referred to as **GAMM 1, GAMM 2** and **GAMM 3** in the refinement.

Example 1 (HRPD):

L PKFN TAUF 8.0000 0.0000 3.6451
L PKFN TAUS 8.0000 29.4747 2.8644
L PKFN SWCH 1.0000 4.6516 0.6920
L PKFN SIGM 5.0000 0.0000 200.000 0.0100
L PKFN GAMM 8.0000 0.0000 0.0100 0.0100

Example 2 (POLARIS):

L PKFN TAUF 10.0000 0.0000 0.5313
L PKFN TAUS 10.0000 10.5541 1.8339
L PKFN SWCH 2.0000 0.2995
L POWR 1.0 1.8000 (see below)

The instrumental peak shape parameters are listed above. Typical starting parameters for sample dependent and therefore refinable variables are shown underlined. The formulation of both Gaussian and Lorentzian peak shape components are correctly considered to cope with the effects of isotropic strain and isotropic particle size line-broadening effects. SIGM 2 can vary between 10 for a highly crystalline phase to 10^3 for a material displaying extreme line broadening due to strain in the sample. GAMM 2 also models strain broadening but is usually of order 10. SIGM 3 and GAMM 3 are sensitive to sample particle size effects and should be of order 10.

L POWR - This card is for specific use with the modified Ikeda-Carpenter peak shape function and is currently used only for POLARIS in conjunction with program TF14LS. For example:

L POWR 1.0 1.8000

L RTYP - is the card which defines the overall limits of the reflection data to be considered. The format is L RTYP *ntyp Tmin Tmax* with the times measured in microseconds. No step size appears when running a normal time-of-flight refinement; the logarithmically varying time-channel width is handled internally by the program . For example:

L RTYP 2 35000.00 120000

The format changes slightly with constant wavelength data where the format becomes
L RTYP *ntyp* $2\theta_{min}$ $2\theta_{max}$ step. For example:

L RTYP 3 7.076 29.996 0.010

A step size is also included when a simulated time-of-flight pattern is required. In this later case a typical 'step' size is 0.0004.

If ntyp = 1 then the reflection indices hkl are read from the file SAMP01.HKL. If ntyp = 2 then reflections will be generated by the program and written out to a file SAMP01.HKL. Having created a .HKL file following ntyp = 2 the program automatically writes a new L RTYP card with ntyp = 1 into the new crystal data file, thus the reflection listing only need be generated once. If ntyp = 3 then the reflection listing will be generated internally every time a refinement job is run: hkl indices are not written to file. The sign of ntyp determines whether space-group absences are included (positive) or excluded (negative) from the refinement.

L PKCN - this card gives the total instrument flight path in metres with an optional apparent variation of the flight path with (incident wavelength) in millimetres. The second term empirically accounts for the peak shift due to wavelength dependent sample absorption. In the refinement the terms are referred to as PKCN 1 and PKCN 2. The values are normally not refined but taken from a standard calibration. Example:

L PKCN 97.9890 -0.064

L THE2 - gives the fixed detector scattering angle for the experiment in degrees. Both the PKCN and THE2 cards are required to relate times of flight and d-spacings by the relation

$t = 505.55568 \times (\text{Total flightpath}) \times d\sin\theta$.

The THE2 parameter is not refineable. Example:

L THE2 174.000

The PKCN and THE2 values for ISIS diffraction data are tabulated below[3]:

HRPD

	Backscattering		90°	Low Angle
	1m	2m	Bank	Bank
PKCN 1	95.9647	97.9890	96.5780	98.7804
PKCN 2	0.00000	0.00000	0.00000	0.00000
THE2	168.329	174.000	90.000	28.0000

POLARIS

	A bank	B bank	C bank	D bank
PKCN 1	13.7038	14.0017	12.7981	12.4857
PKCN 2	-1.2334	-1.1533	-0.9507	-1.1441
THE2	20.0000	90.0000	145.0000	90.0000

L WVLN - when applicable this card gives the wavelength(s) of the radiation used. For example, station 9.1 at Daresbury may typically be:

L WVLN 1.4963

---

[3] Instrument calibrations may change following upgrades and reconfiguration.

whereas unmonochromated laboratory CuK_{α} will have two wavelengths:

L WVLN 1.540562 1.544390

L TTHM - gives the monochromator angle. This can effect the Lp correction. Example (lab X-ray):

L TTHM 26.57

L BACK - these cards parameterize the neutron background variation with time of flight and are of general format L BACK *ntyp (several reals)* for the first line and L BACK *(several reals)* for any subsequent lines. Up to twenty background parameters are permitted. The integer ntyp determines whether the background is evaluated by linear interpolation, spline fitted to a series of given points or arbitarly fitted by a polynomial function. In general, if ntyp is negative, the background is interpolated; if ntyp is positive the background is fitted. A combination of least-squares-fitted and interpolated background regions is not permitted. Current possible values of ntyp are the following:

ntyp = -2	the background is fitted by cubic splines (under development)
ntyp = -1	the background is subtracted by linear interpolation and each card should be of format: L BACK -1 Tof Yback: these cards must follow each other in strictly ascending order of time of flight.
ntyp = 1	the background is fitted by a polynomial function with up to 10 terms. The first back card should read L BACK 1 back1 back2 ... back5 with the optional second card reading L BACK back6 back7 ... back10, where backn is the numerical value of the polynomial coefficient. The backn coefficients may be spread over more cards if required.
ntyp = 2	Chebychev polynomial of the first kind is fitted: card format is identical to ntyp = 1.
ntyp = 3	Chebychev polynomial of the second kind is fitted: card format is identical to ntyp = 1
ntyp = 3	Fourier cosine series is fitted using the same card format as ntyp = 1.

For ntyp = 1, 2, 3 or 4, the program determines how many coefficients are to be used from the number of terms supplied on the BACK card(s): these are referred to as BACK 1 ... BACK n in refinement.

Examples:

L BACK -1 53056.3 133.6
L BACK -1 67000.0 120.0

(part of a linear interpolation)

L BACK 2 112.573 4.096 -3.555 1.003
L BACK 0.566 -0.022

(1st type Chebychev polynomial fit using 6 terms: these would be referred to as BACK1 BACK 6 in refinement)

L SLIM - The parameters on this card determine which peaks CAILS and SAPS will actually fit. The first two parameters pertain to strict and slack constraints respectively and have been empirically determined. The third parameter determines a discrimination level for weak peaks used in SAPS but not CAILS. Example:

L SLIM 0.1 0.1 10

2.2.4 Optional Least Squares Instructions/Parameters (L) Cards

L ABSC - this card defines a two term absorption correction to be applied to the data. The format is L ABSC *ntyp abscl absc2* where abscl is a constant for the sample correcting for multiple scattering and absc2 is a wavelength dependent term correcting for sample attenuation. In the refinement these variables are referred to as ABSC 1 and ABSC 2 with default of no absorption correction. Since ABSC 1 is essentially a scaling term it is imperative that the overall scale factor SCAL 1 be fixed before refinement of the absorption. Example:

L ABSC 1 0.2140 1.5438

L EXCL - these cards define excluded regions in which neither Bragg peaks nor background are fitted and are ignored in the calculation of agreement factors. The format is L EXCL T_{min} T_{max} with T in microseconds. The cards should follow in strictly ascending order. The default is no excluded regions. Example:

L EXCL 70000.00 73000.00

L EXTN - this card defines the extinction correction to be applied to the data using the model of Sabine[4]. The card format is L EXTN ntyp size, where ntyp = 1 at present and size is the average crystallite size in microns. Default: no extinction correction. Example:

L EXTN 1 4.59

L PROR - this card defines the preferred orientation correction according to the March model after Dollase[5]. The format is L PROR *ntyp mcoef h k l*. Currently ntyp = 1, mcoef is the March coefficient and hkl is the direction of the preferred orientation. Default: no preferred orientation correction. Example:

L PROR 1 0.9 0 0 1

L TFAC - this card may be used to define the overall temperature factor for the profile. It is referred to as TFAC in the refinement: if omitted it is set to zero and fixed. Example:

L TFAC 1.2

L WGHT - this card defines the mode of weighting the observed data points. The format is L WGHT *nwt* with the integer nwt defining the weighting scheme: 1 = unit weights; 2 = use weight as read with reflections; 3 = calculate weight from data read in to account for number of counters (i.e. $1/\sigma^2$). The default is unit weights; however scheme 3 is recommended in most cases. Example:

L WGHT 3

2.2.5 Control L Cards

L VARY - During the course of a refinement the various parameters involved are refined by means of control L cards which take the form L VARY <param>. Typically these cards are appended sequentially as the refinement proceeds to the crystal data file. For example:

L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5

---

[4] Austr. J. Phys. **38** (1985), 507

[5] J. Appl. Cryst. **19** (1986), 267

Typically this card varying scale and background would be the first issued in a refinement procedure. (N.B. It is proposed to remove the serial number associated with SCAL i.e L VARY SCAL 1 will become L VARY SCAL.) Note also the inclusion of the keyword ONLY. If ONLY is omitted, a set of default parameters are refined, including atomic coordinates and unit cell. This card restricts the refinement to only those parameters quoted on this, and later L VARY cards, and is recommended. The keyword ALL is also permitted. For example

L VARY ALL XYZT

when refining all atomic coordinates and isotropic temperature factors. Individual parameters pertaining to specified atoms can also be refined. For example:

L VARY Al B11 O1 ITF

to refine B_{11} of atom Al and the isotropic temperature factor for atom O1.

L FIX - this card has exactly the same specification as an L VARY card except that it asks the specified parameter to be fixed not varied in the subsequent refinement. CCSL will fix automatically any parameters whose variation is prohibited by symmetry.

L RELA - this card contains relations between parameters which the user wishes to impose on the system over and above those symmetry constraints automatically produced. The format is L RELA 1 *a1 P1 a2 P2* which produces the constraint: a1*(shift in P1) = a2*(shift in P2). For example:

L RELA 1 1.0 Tl site -1.0 Pb site

L FUDG - this card allows the imposition of a damped shift on specified variables. The format is L FUDG *P fac* where P is the parameter and fac is the factor by which the calculated shift(s) will be multiplied by before being applied to the specified parameter P. Additionally the use of GE or LE restricts a parameter to be greater or less than a particular value. For example:

L FUDG ALL SITE 0.4
L FUDG SIGM 3 GE 0
L FUDG Al SITE LE 0.5

2.2.6 Y Cards

Any number of Y cards giving comments on the crystal data may be included. They are written to the updated parameter file (.CCN) and lineprinter file (.OUT).

2.2.7 Z cards

Any number of Z cards giving comments on the crystal data may be included. They are output to the updated parameter file (.CCN) but not to the lineprinter file (.OUT). They are normally use to 'comment out' any crystal data cards to be omitted for that run.

2.2.8 Example CCL file - Al_2O_3

```
N Al2O3 standard sample on HRPD - short d-spacings
I NCYC 5 MCOR 0 PRIN 0 PRFO 0 PRPR 2 PRFC 2 BMIN 0.0 BMAX 2.4
B BOND
C  4.75803  4.75803  12.99278   90.000   90.000   120.000
A Al    0.00000  0.00000  0.35218  0.00000
A Ox    0.69370  0.00000  0.25000  0.00000
T Al    2  0.32694  0.32694  0.38721  0.00000  0.00000  0.16346
T Ox    2  0.35999  0.36464  0.42713  0.03246  0.01624  0.18233
F Al    1  0.34460
F Ox    1  0.58050
S  1/3+X,2/3+Y,2/3+Z
S  -X,-Y,-Z
S  Y,X,1/2-Z
S  -Y,X-Y,Z
L REFI -12
L RTYP   2  16900  40000.00
L BACK   2      3.81293   2.49016   0.47858   0.04454   0.001580
L WGHT 3
L THE2 174.000
L SCAL   4.55283
L ZERO    8.0000
L EXTN   1    5.82498
L PKCN   97.9890    0.0000
L PKFN TAUF    8.0000    0.0000    3.6451
L PKFN TAUS    8.0000   29.4747    2.8644
L PKFN SIGM    5.0000    0.0000   29.3725
L PKFN GAMM   20.0000    0.0000    1.8917
L PKFN SWCH    1.0000    4.6516    0.6920
L VARY ONLY SCAL 1
L VARY BACK 1 BACK 2 BACK 3 BACK 4 BACK 5
L VARY A* C*
L VARY SIGM 2 GAMM 2
L VARY EXTN 1
ZL VARY ALL XYZ ALL BIJ
```

3. PERFORMING A PROFILE REFINEMENT

As mentioned earlier, from a correctly setup account all the refinement and utililty programs should be defined by one word commands. All least squares programs are cpu intensive and it is recommended therefore that the various 'batch' queues be used. Again the setup is already defined. Currently the full profile refinement programs are characterised by peak shape with types 1, 2 and 4 available as defined previously. These correspond to the former programs TF11LS, TF12LS and TF14LS respectively. CAILS (Cell and Intensities Least Squares), the Pawley type refinement, is a variant of the above programs and specific input details are described later. A unified system based around program REFINE is now operational. In this case the type of refinement performed will be determined from the L REFI card in the crystal data file.

3.1 Running the Refinement Programs

The format to run the programs is:

```
$ PROGNAME <EXPERIMENT_NAME> <QUEUE_NAME>
```

For example:

```
$ REFINE SAMP01 BATCH
```

The optional parameter queue_name should be used to submit jobs to the batch queues (BATCH gives unlimited CPU). The program automatically assumes the correct default extensions .CCL, .CCN, .OUT and .PRO. In addition, when not running interactively, a log file <EXPERIMENT_NAME>.LOG will be produced in the current user directory, for example SAMP01.LOG. Before each set of refinement cycles the previous .CCN file should be edited for the next refinement and renamed to a .CCL extension. This is conveniently achieved by typing:

```
$ REVISE <EXPERIMENT_NAME>
```

or by explicitly typing:

```
$ ED/OUT=<EXPERIMENT_NAME>.CCL <EXPERIMENT_NAME>.CCN
```

whereby the .CCN is edited and, on exiting the editor, is automatically renamed CCL.

3.2 A Basic Profile Refinement Strategy

After creating the .DAT and .CCL files the user is ready to proceed with refinement. The first parameters refined, as discussed previously, should be the background and scale. Remember to include the keyword ONLY on the first L VARY card issued, otherwise the refinement will be overambitious in its early stages and may not converge. Since the refinement of scale and background involve only coefficients of ordinary or orthogonal polynomials, the problem is linear and should converge immediately (after 1 cycle) from whatever starting parameters. Only 3 cycles are required. The first L VARY card is thus

```
L VARY ONLY SCAL 1 BACK 1 BACK 2 BACK 3 BACK 4 BACK 5
```

The next step is to locate the Bragg peaks accurately by means of refining the cell dimensions; initially, reasonable estimates of cell dimensions are required for this stage in the refinement. If precise values of the lattice parameters are not available these should be obtained using program CELLSQ (see section 6). It may be also possible to begin refining the peak width at this stage of the refinement. If there is a large mis-match between the starting value and actual peak widths this can impair convergence of the cell dimensions. For an orthorhombic structure a further card may read:

```
L VARY A* B* C* SIGM 2
```

Atomic parameters may next be varied. Firstly, the positional parameters of all atoms are refined, which will alter the peak areas to improve the fit. Once these have stabilised, temperature factors are refined to account for atomic vibrations. If the data are of sufficient quality it may be possible to refine the thermal parameters anisotropically, but only if this leads to a reliable and significant improvement over an isotropic description of the harmonic displacements of the atoms. Suitable cards for an isotropic refinement may be:

```
L VARY ALL XYZ
L VARY ALL ITF
```

Assuming that the refinement to date has proceeded satisfactorily, one can vary all sample dependent peak shape parameters. Both Gaussian and Lorentzian components can be refined, and with high instrumental resolution these parameters are frequently significant factors in the profile. It should be remembered that REFI (+/-)12 must be used to refine Lorentzian components. These cards may be:

L VARY SIGM 2 SIGM 3
L VARY GAMM 2 GAMM 3

These stages represent the basic steps of refinement from where it may be necessary to continue with more parameters as discussed above.

3.3 R-factors

The progress of the refinement may be monitored via the lineprinter file to which R factors and chi squared values are written.

The goodness of fit using least-squares methods is naturally discussed using the χ^2 statistic:

$$\chi^2 = \frac{1}{N-P+C}\sum_i w_i\left[Y_i(\text{obs}) - Y_i(\text{calc})\right]^2$$

where N is the number of observations, P is the number of variables and C is the number of constraints. Traditionally, following Rietveld, the quality of fit may also be quoted with reference to the following four R factors:

i) Weighted Profile

$$R_{wP} = \left[\sum_i w_i\left|Y_i(\text{obs}) - Y_i(\text{calc})\right|^2 \Big/ \sum_i w_i Y_i^2(\text{obs})\right]^{1/2}$$

ii) Profile

$$R_P = \sum_i \left|Y_i(\text{obs}) - Y_i(\text{calc})\right| \Big/ \sum_i Y_i(\text{obs})$$

iii) 'Bragg' or Intensity

$$R_I = \sum_k \left| I_k(\text{obs}) - \tfrac{1}{c} I_k(\text{calc}) \right| \Big/ \sum_k I_k(\text{obs})$$

iv) Expected

$$R_E = \left[(N - P + C) \Big/ \sum w_i Y_i(\text{obs})^2 \right]^{1/2}$$

It should be noted that $\chi^2 = (R_{wP}/R_E)^2$ and therefore in a precise and accurate refinement the weighted profile R factor should be close to the expected R factor. The intensity R factor, R_I, is helpful in determining the quality of the structural fit since it relates to peak area and not peak shape. It is relatively insensitive to the peak shape description or incorrect lattice parameters and so is often a useful diagnostic tool.

However, it is of paramount importance to view observed and calculated profiles at each stage of refinement in order to assess the progress and correct strategy of refinement.

3.4 Examining the Profile Fit

Having performed the refinement the user is strongly recommended to study the profile fit using GENIE to examine the quality of the agreement. GENIE is used once the .PRO file has been converted to GENIE format using the program PICTIC. The screen output is also indicated:

```
$ PICTIC SAMP01

PICTIC Rutherford Version 1.0
PT> Assuming default extension of "CCL" Input profile file  (ASCII format)  :  SAMP01.PRO
Output file                        :  SAMP01.TAG
Input crystal data file            :  SAMP01.CCL
Output profile file (GENIE format):  SAMP01.PIC
Output tag file     (GENIE format) :  SAMP01.TIC
Program running -- please wait 7725 points have been read
Give name for Output file
Give name of Crystal data file
```

Next begin the GENIE session

```
$ GENIE
```

and once the GENIE prompt (>>) is obtained, issue the following command to begin a profile plot :

```
>> PLS
>>@G:PLS
>>
>>  *** Powder profile plotting routine ***
>>
>>T M
>> point plotting mode selected
>>  A M 1
>>  T H
>>   no graph header will be displayed
>>  Data file name (no extension) please? :  SAMP01
>>
```

```
>> RE W1 SAMP01.PIC 1
Reading block    1
>> RE W2 SAMP01.PIC 2
Reading block    2
>> RE W3 SAMP01.PIC 3
Reading block    3
>> RE W4 SAMP01.TIC 1
Reading block    1
>>
>>    Lower and upper limits? : 60000 80000
>>    Group into N bins. Give N : 2
```

At this point the plot of the difference divided by esd (W3) will appear at the bottom of the screen. <CR> should be hit once the plot has finished, to allow the observed profile (W1) to be plotted as points. Again hit <CR> for the overplot of the calculated profile (W2), a final <CR> ends the plotting. 'Tic' marks showing the peak positions (W4) can also be plotted simply by:

```
>> TIC ymin ymax
```

the ordinate values locating the tics on the graph. If one requires to look at a different range of the data in the profile file which has already been read into GENIE by use of PLS, one can use the procedure PLC (Plot Continue) which is less time consuming as it uses the already existing GENIE workspaces.

```
>> PLC
```

to which the command procedure responds

```
>> Lower and Upper limits? : 80000 120000
>> Group into N bins. Give N : 2
>>
```

Once again tic marks may be displayed.

3.5 Bond Length and Bond Angle Calculations

Bond length calculations may be simply performed on a .CCL or .CCN file by the use of program BONDS:

```
$ BONDS SAMP01
```

which assumes a default of .CCL. The program creates a file SAMP01.BON containing bond lengths and angles for the structure. The minimum and maximum bond lengths calculated are defined on the crystal data file "I" card by means of BMIN and BMAX instructions. B cards can also be used to specify whether either bond length or bond angle values or both are to be calculated, for example: "BOTH"; "BOND" or "ANGL". The cards may further be qualified with atom names. For example:

```
I NCYC 5 MCOR 0 PRIN 0 PRFO 0 PRPR 0 BMIN 0.8 BMAX 2.4
B BOTH
```

will calculate bond lengths and angles for atoms separated by between 0.8 and 2.4Å. CCSL does not take into account Van de Waals or covalent radii to explicitly define the bonding limits.

4. FOURIER CALCULATIONS

Fourier calculations may be performed using the program FOULAS. Data input is from a file SAMP01.FOU containing I_{hkl}(calc) and I_{hkl}(obs) values. The map drawing information cards (M cards) are read from a crystal data file. Graphical output is to a Tektronics screen (default) or automatically sent to a laser printer (option L), for example:

```
$ FOULAS SAMP01 L
```

The .FOU file is an optional output file created during the course of a normal refinement (see 3.2.2). The individual M cards controlling the Fourier plot should be appended appropriately in the .CCL file before each plot. Given below are a sample of the minimum M cards required for Fourier calculations; the user is referred to the CCSL manual for full details.

4.1 M Cards

M AXES - three sets of three numbers are given which relate crystallographic directions to the axes of the computed map. A default of a unit matrix is assumed. For example:

```
M AXES 0,0,1, 1,0,0, 0,1,0
```

specifies the crystallographic z,x,y directions along computed x,y,z axes.

M CONT - may be followed by a list of contours. Inclusion of the word STEP should be followed by a contour range and step size. Format: *cmin cmax stp* which are start value, end value and step size respectively. The word STEP and value for stp should be omitted for NDIM=2 (see below) for projections using 2-D data.

```
M CONT STEP -95, 95, 10
```

M DELT - delta is the resolution length for the Fourier calculation. The scattering density is averaged over a cube of side two delta.

```
M DELT 0.5
```

M DTYP - this determines the type of data input and is fixed at type 1.

M DTYP 1

M FTYP - determines the type of Fourier: FTYP=1 F_{calc} Fourier; FTYP=3 F_{obs} Fourier; FTYP=5 difference Fourier. For example:

M FTYP 5

M MESH - defines the map grid with respect to details from the M AXES card. The format is initial value, final value and step for map x and then map y in fractional coordinates.

M MESH -0.5 0.5 0.025 0.25 1.25 0.025

M NDIM - is the number of dimensions of the Fourier: 2;3 or 4. Option 2 produces a section using 2-D data, 3 produces sections of a 3-D Fourier map and 4 produces integrated projections of a 3-D Fourier map. The default value is 3.

M NDIM 3

M PLOT - this card gives the height of the plot. No value is given for NDIM=2, for NDIM=3 one or more values are given on one or more cards and for NDIM=4 two values are given to define the limits of the integration.

M PLOT 0.125

M SMAX - defines the maximum value for $\sin\theta/\lambda$; data input which exceed this limit are not used in the Fourier calculation.

M SMAX 1.0

5. GEOMETRIC SLACK CONSTRAINTS

The initial implementation of geometric slack constraints was simply the ability to use a bond length as an "observation", giving its esd to be used in weighting. The format of the L BOND card has been:

L BOND <observed value> <esd> <first atom spec> TO <second atom spec>

where an <atom spec> defined particular site coordinates in the structure, related to one on an "A" card, but not necessarily identical to it. The current programs have been updated so that both bond lengths and bond angles are available as "observations". Capacity also exists for future extension to allow "one bond=another bond", "one angle=another angle" and "the angle at this bond is 180°". Constraints on angles between bonds which do not intersect, will also be implemented.

5.1 L Cards

L SLAK - this card indicates constraints are wanted and gives details of weighting. The format is L SLAK *styp swght*. *styp* has a units digit d1 and a tens digit d2 such that:

d1=1 means refine using only the slack constraints;
d1=2 means refine using both slack constraints and conventional least squares observations;
d2=1 means use unit weights;
d2=2 means use weight as read with the observation;
d2=3 means read sigma with the observation, weight by $1/(\sigma^2)$ and if d1=2, each slack constraint is given the additional weight swght.

For example:

L SLAK 32

I PRSK 4 - in order to print all slack constraint information to the .OUT file this (optional) card should be inserted with the existing instruction parameters.

L ATOM - all atoms involved in bonds, "target atoms", must be related to the original set of "A" cards. It is often possible to use the original atom as a target atom; however it is sometimes necessary to give a transformation from an original atom to give the target atom in which case an L ATOM card is required.

Every atomic position which is to be involved in a geometric constraint must given either on an "A" card for an original atom or on an L ATOM card in the format:

```
L ATOM <new name for target atom> <name of original atom> S L C1 C2 C3
```

or the format:

```
L ATOM <new name for target atom> <name of original atom> x y z
```

The program distinguishes between these formats by the presence of a decimal point in the "x". All atom names in any context should start with a letter and be up to four characters long. A general transformation will consist of: S, a symmetry operator, specified by its number as printed by the CCSL program in the .OUT file; L, a lattice translation, also specified by its number as printed; C1, C2, C3, three whole number cell shifts in the x,y,z, directions. Thus S=1, L=1 and C1=C2=C3=0 would specify the original atom. When xyz are given in the format the program produces its own S, L, C1, C2 and C3. For example, consider the following two "A" cards:

```
A P 0.4675 0      5/6    0.4
A O1 0.4220 0.2690 0.3965 0.8
```

In this case P specifies the original atom but the oxygen atom we wish to include in the constraint has the actual coordinates 0.704, 0.126, 0.7298, being related to the original O1 by a symmetry operator (-Y, X-Y, 1/3+Z) which is number 2 followed by a cell shift of 1 in the x direction. To define the bond ends, we know P, but the new atom related to O1 is given a new name O1S1, and defined on an atom card thus:

```
L ATOM O1S1 O1 2 1 1 0
```

or of course:

```
L ATOM O1S1 O1 .704 .126 .72986
```

L BOND - these cards specify the bond length "observation" and have the format:

L BOND <name of bond> <name of one atom> <name of other atom> obs esd

The <name of bond> allows reference to the bond for more complicated constraints and should be different from the names of any atoms. The names of the atoms at the bond ends must appear in either the original "A" card list or on an L ATOM card. The sequence in which the two atom names appear is immaterial, as is the sequence of any L BOND and L ATOM cards. Following the above example we may have:

L ATOM O1S1 O1 2 1 1 0 0
L BOND B1 P O1S1 1.53580 0.0020

L ANGL - to specify bond angle constraints this card is given in the format:

L ANGL <name of angle> <name of one bond> <name of other bond> obs esd

or the format:

L ANGL <name of angle> <atom name 1> <atom name 2> <atom name 3>

in which case the required angle is subtended at atom 2. Again the angle name must not clash with other names. The value of obs is given in degrees.

6. CELLSQ - LEAST-SQUARES REFINEMENT OF LATTICE PARAMETERS

The full profile fitting programs necessarily require initially reasonable estimates of the unit cell dimensions. If precise values of the lattice parameters are not available these can be obtained using program CELLSQ from manually measured and indexed Bragg reflections.

6.1 Generating the .TOF file

The program input requires a .CCL file which includes approximate starting values of the unit cell and appropriate symmetry cards in addition to the minimum control cards. (Additional cards not required by the program are ignored.) Data are read from a file SAMP01.TOF of the following (free) format:

```
h k l    time of flight (ms)          e.s.d (ms)
```

Reflection positions are measured in GENIE using the cursor command; hit 'C' to mark each peak. Once sufficient peaks have been located the values can be written to a file using the command

```
>> KEEP/C <filename>
```

Note, the KEEP/C command keeps ALL cursor positions marked throughout the GENIE session. Care must be taken to avoid duplication of Bragg peaks or the use of a single GENIE session to locate Bragg peaks in more than one material!

6.2 Performing the Cell Refinement

The program is run by typing

```
$ CELLSQ  SAMP01
```

Necessarily, only the cell parameters may be refined, i.e the card:

```
L VARY ONLY ALL CELL
```

should be used in the .CCL file. The refined values from the program are written to the .CCN file as with a full profile refinement, however the lineprinter file carries the extension .CLP.

6.3 Generating a reflection listing

A reflection listing in TOF and d-spacing may be generated from the .CCL file using program TIC:

```
$ TIC  SAMP01
```

The program produces a line printer file (.TAG) and also a GENIE format file (.TIC). The reflection positions contained in the .TIC file may be read into a GENIE work space and may be plotted as tick marks on a diffraction pattern by:

>> P/T Wn y_{min} y_{max}

7. CAILS - PAWLEY REFINEMENT

CAILS (Cell And Intensity Least Squares) is the CCSL Pawley type refinement program. It differs from the traditional Rietveld refinement technique in that only cell constants, peak width paramters and integrated intensities in the form of unnormalised $|F^2|$ are refined. The extraction of integrated intensities is an important step for the Direct Methods approach to structure solution, and routines to assist in space group determination are mentioned below. In cases where a structure is not well known CAILS may also be used as a preliminary stage to establish accurate cell and peak width parametres, prior to full profile refinement.

7.1 A Basic CAILS Refinement Strategy

CAILS is implemented by running REFINE with the appropriate L REFI card setting (see 2.2.3). Remember to include the card:

L SLIM 0.1 0.1 10

The refinement proceedes in the normal manner; however the overall scale factor must remain fixed; while intensities are varied instead. For example, the card for the initial 3 cycles of refinement may read:

L VARY ALL INTS ALL BACK

The refinement would then be completed by varying cell and peak width parameters as appropriate. The values for the refined intensities with esds are written to the .HKL file

7.2 Examining the .HKL file

The values for the refined intensities with esds are written to a .HKL file as illustrated in the table below. There are 12 columns in this data file. The first three are the three Miller indices; the refined values of $|F^2|$ along with estimated standard deviations follow. Column 6 contains the clump number associated with the reflection: reflections which are very close together may be clumped into a single observation. The remaining n columns (C1 - C5 in the current example) give the percentage correlations between the clumps. The mth entry for the kth clump indicates correlation between kth and (k+m)th clumps. Unsurprisingly, clumps that are very close together have intensities that are very highly (negatively) correlated. If there are a large number of such a correlations then the first two entries on the L SLIM card should be increased.

h	k	l	I	σI	N	C1	C2	C3	C4	C5
1	0	1	63.394	1.8925	1	-88	13	-4	4	2
0	1	1	38.807	1.8776	2	-9	10	2	0	0
2	0	0	63.697	1.3033	3	-5	6	3	0	2
0	2	0	81.671	1.4332	4	7	3	0	-2	4
1	1	1	15.052	0.3316	5	4	1	-1	4	2
2	1	0	7.977	0.5687	6	2	0	2	1	0
2	0	1	2.228	0.6469	7	1	1	1	1	0
2	1	1	3.569	0.5060	8	-41	1	1	0	0
1	2	1	18.033	0.6036	9	2	2	3	1	2
2	2	0	17.582	1.0095	10	3	3	2	2	2
0	0	2	45.230	2.3452	11	4	2	3	3	2
1	0	2	59.613	1.6251	12	3	4	4	2	1
2	2	1	1.091	0.5592	13	3	2	2	2	2
...										
0	4	0	69.552	4.2625	27	2	2	2	2	1
2	2	2	0.997	0.6055	28	2	2	1	2	2
4	1	0	0.997	0.6055	28	2	2	1	2	2
3	0	2	3.283	1.9082	29	2	2	2	2	2
...										
6	0	1	9.708	12.6604	88	-95	69	4	1	1
3	3	3	10.889	8.3152	89	-82	-3	-1	-1	-2
2	5	2	17.158	3.7331	90	5	2	2	3	3
...										
5	1	3	-1.473	1.8250	118	8	8	5	0	0
1	6	2	33.809	1.3860	119	8	7	0	0	0
1	5	3	33.809	1.3860	119	8	7	0	0	0
6	3	1	-0.458	1.9104	120	19	0	0	0	0
3	6	1	1.210	2.0540	121	0	0	0	0	0

7.3 Space Group Determination

The output from CAILS may be used to assist in the space group determination of an unknown structure. In this case the program should be run using the holosymmetric space group consistent with the crystal class; in other words the highest symmetry space group in that crystal class with no systematic absences (e.g. Pmmm, P4/mmm and Pm$\overline{3}$m in orthorhombic, tetragonal and cubic classes respectively. The space group determination program, DINOS, uses as input the .HKL file from the Pawley refinement.

7.3.1 Filtering of overlapped reflections

The program DINOS is in principle easy to run, however, care must be taken with the .HKL file and a filtering procedure is recommended. Accidental overlapping reflections may lead to apportioning of intensity to reflections that are in fact systematically absent. Completely overlapping reflections and reflections with a high degree of correlation should thus be filtered out of the .HKL file. The computer program HKL_FILTER has been written to perform such a filtering. It may be executed by typing:

```
$ HKL_FILTER
```

The user is requested to give the maximum permitted correlation between Bragg peaks. Above this limit the Bragg peaks are deemed to be too close together. 80% is the recommended value, but inspection of the .HKL file may suggest a different value. (N.B. In the .CCL file the I card must contain a PRCV <n> entry where n≈5.) The output file from HKL_FILTER is assigned the extension .HKF. This file should be inspected before using DINOS. With high symmetry systems in particular, the number of reflections may be small. Manual modification of the .HKL file is sometimes more appropriate.

The filtering process may have left a large number of small d spacing reflections. These should be treated with some suspicion and it may be necessary to remove them to ensure a successful run of DINOS. It is important to recognise during the filtering exercise that some flexibility in the input to DINOS may be necessary to ensure successful space group determination.

7.3.2 Space group determination by examination of systematic absences

DINOS determines space groups, or more particularly the extinction symbol, by assessing the hkl pattern of reflections that are sytematically present. Reflections are deemed to be present if their intensity exceeds the standard deviation of the intensity by a given amount, i.e.:

$$|F|^2/\sigma\left(|F|^2\right) > R$$

Ideally, R should be in the range 3-5. Different values should be chosen to see whether consistency of space group determination is achieved. In general, the higher R is, the more systematic absences will be permitted and the greater the number of glide planes and screw axes will be predicted. Consistency of space group determination for different R is reassuring, but does not guarantee correct space space group assignment. If discrepancies do occur then the fewest assumptions should be made. However, if, for example, a c glide perpendicular to the b axis is predicted for an orhtorhombic unit cell, then the user should return to CAILS and adopt the space group Pmcm rather than Pmmm for the refinement. This iterative process is repeated until the user is content that a space group consistent with the data has been obtained.

To run DINOS type

```
$ DINOS
```

The program prompts for the name of the Miller index file.

```
Enter input filename:
```

The filtered .HKF file is preferred over the .HKL file although both may be used. After entering the input filename the following option is displayed:

```
(1)    Monoclinic        (2)    Hexagonal
(3)    Trigonal          (4)    Orthorhombic
(5)    Tetragonal        (6)    Cubic
```

Enter the appropriate choice. The cutoff value for $|F|^2/\sigma(|F|^2)$ is then requested.

Enter threshold intensity/esd:

A values of between 3 and 5 is recommended. The extinction symbol consistent with the systematic presences and absences will be presented at the end of the screen output. It must be emphasised that the possible space group(s) consistent with the extinction symbol generated by DINOS may not necessarily be correct. Bragg peaks from impurity phases may for example suggest systematic presences that are absent and thus lead to incorrect space group assignment; an accidental monoclinic β angle of 90.00° may lead to the incorrect crystal class. There are no guarantees!

8. DEVELOPMENTAL REFINEMENT PROGRAMS

8.1 SAPS - hkl dependent line broadening analysis

High resolution diffraction data is particularly sensitive to line broadening effects not usually revealed in diffraction patterns of more modest resolution. Physical effects in the sample may lead to anisotropic line broadening with an (hkl) dependence across the pattern. Under such circumstances the existing peak shape parameterization of Gaussian and Lorentzian terms which vary simply as a function of the time-of-flight of the reflection may prove an inadequate model. A general procedure to allow for such peak shape variation must therefore include (hkl) dependency and in a general form would involve the capability for "learning" the shape of each individual peak. This procedure is implemented by SAPS (Structure And Peak Shape).

This program, under current development, permits the profile to be refined using the known structure in the standard manner. Additionally each peak is assigned an individual Gaussian and Lorentzian peak width to permit a complete line-broadening analysis to be performed in a model-independent manner.

SAPS is run using program REFINE with the L REFI card code number 212. In a similar manner to running CAILS, an L SLIM card must be included in the .CCL file. During the refinement the individual Gaussian and Lorentzian peak widths are referred to as SIGS n and GAMS n. Thus the control card

L VARY ALL SIGS ALL GAMS

may be employed.

The individually refined peak width parameters are written to the output file, .HKL, as illustrated below. Note, in the example shown, only the Lorentzian peak widths have been refined. Results from the normal structural refinement appear in the .OUT file in the usual way.

h	k	l	I	σI	σ	$\sigma\sigma$	Γ	$\sigma\Gamma$
1	1	2	124.483	0.4704	58.281	0.0000	204.421	1.8283
1	2	1	5.341	0.2336	60.660	0.0000	163.753	12.6649
1	2	1	70.897	0.3886	66.912	0.0000	203.692	2.9354

1	0	2	43.947	0.2913	67.525	0.0000	252.323	5.1653
-2	1	1	41.827	0.2981	68.763	0.0000	271.398	5.2674
-1	1	2	4.959	0.1426	71.052	0.0000	193.868	19.9442
-2	1	0	95.259	0.4724	72.783	0.0000	149.412	2.0380
-1	2	0	7.240	0.1904	74.870	0.0000	139.006	12.5021
0	2	1	1.561	0.1054	75.768	0.0000	156.305	54.0505
0	1	2	13.272	0.3135	76.291	0.0000	247.126	12.52316

The columns in the file, from left to right, are: the miller indices h, k and l; peak intesity I and e.s.d σI, Gaussian peak width σ and e.s.d σσ; Lorentzian peak width Γ and e.s.d σΓ.