

# Chapter 3.2.4

## DREAR (Ver. Nov 2005)

### Data Reduction & Error Analysis Routines

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## 1.0 Introductory Notes on the DREAR Suite of Programs

The DREAR suite of programs provides data reduction for point detector data, from a Nonius CAD4 (*only with profiles*) or from Siemens P3/P4. The SORTAV program is part of the DREAR suite, but is described in its own manual. SORTAV & BAYES may be used for diffraction data from *any type* of diffractometer.

### 1.1 Brief program descriptions

Detailed program descriptions are provided in the Sections 2-6 below. Line printer output from each program is written to the file *DREAR.LST*, which can be examined using a text-editor before printing. The order in which the programs are normally run for serial detector data ( e.g. from a CAD4 or Siemens P4 diffractometer) is :

- Convert CAD4/P4 - reformats diffractometer files to binary *RAW.DATA* file.
- REFPK - reflection profile peak analysis.
- BGLP - background subtraction, based on the peak profile analysis & Lorentz and polarization corrections.
- TSCALE - time-dependent scaling with (up to) cubic (3rd degree) polynomials.
- *TDSCOR* - *empirical correction for thermal diffuse scattering (TDS). Not recommended for normal use*
- ABSORB - absorption corrections from indexed crystal faces and lengths of face normals by Gaussian numerical integration over crystal volume.
- SORTAV - sorting, inter-subset scaling, empirical absorption correction based on multiple symmetry-equivalent and/or azimuth rotation-equivalent measurements, averaging of replicate and equivalent measurements, and analysis of variance.
- BAYES - Bayesian probability expectation values of  $F^2$ ,  $\sigma(F^2)$  given the set of unique  $F^2_{meas}$  and  $\sigma(F^2_{meas})$ .

Some support is also offered for data collected on a KappaCCD diffractometer. These options are available from the **Data-Area Detector** menu item in WinGX.

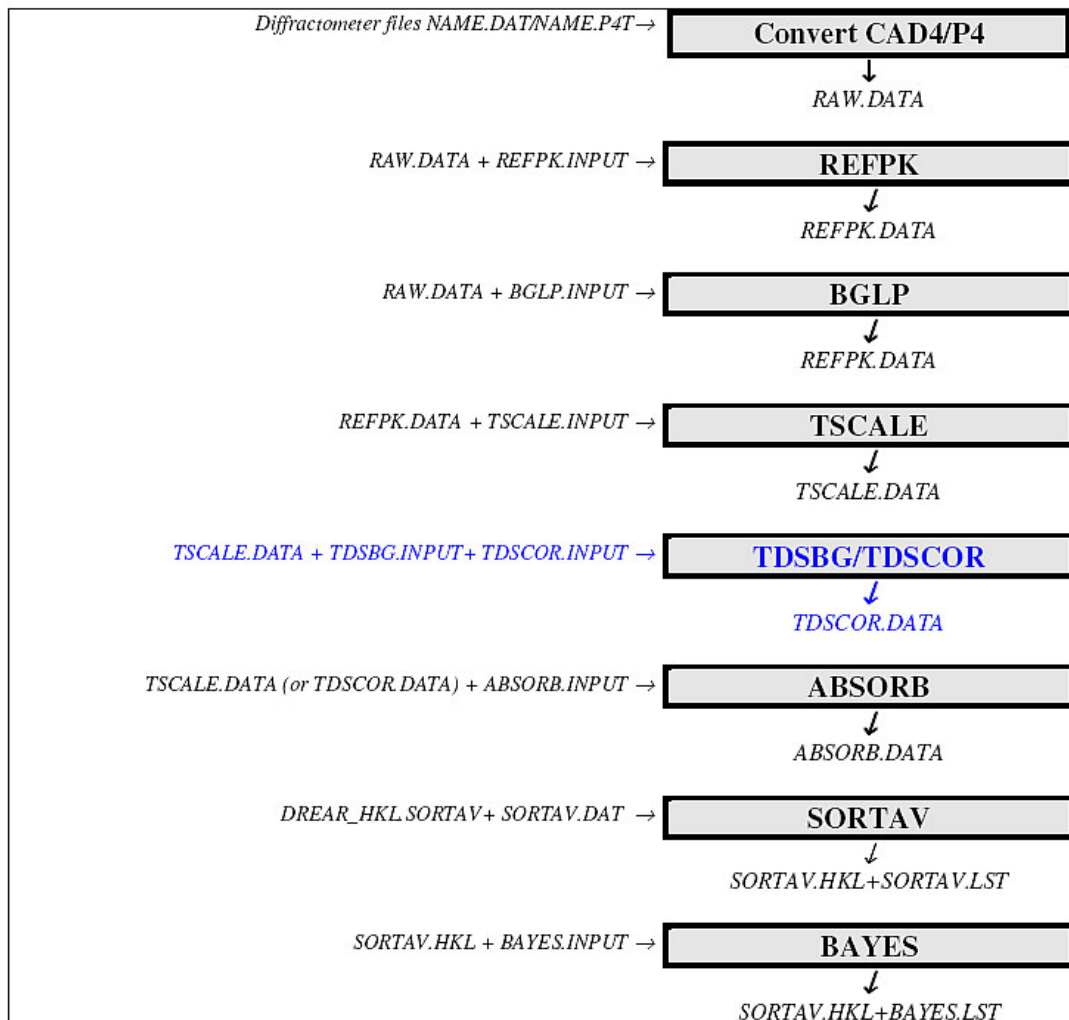
- DENZOX - read and interpret a set of *Denzo* .x files. This has been heavily modified, in a KappaCCD specific version, to write direction cosines to reflections files which serve as further input to SORTAV & BAYES.

The instructions for SORTAV, BAYES and DENZOX are given in separate manuals. Other programs in the DREAR suite, mainly used for processing oscillation-method area-detector data, are not considered further here .

- ROGERS/LEVY - absolute scale factor and overall anisotropic mean-square atomic displacement parameters by either the method of Donald Rogers or the method of Henri Levy and William Thiessen. Program LEVY is generally preferable.
- EVAL - normalized structure factor amplitudes  $E = k \times F / \sqrt{\epsilon \times \sum F_a^{*2} \times \langle \exp(-2 \times h_j \times b_{ij} \times h_i) \rangle}$ , where E is normalized by the Wilson expectation value of the intensity.
- LOCSSL - evaluate and apply anisotropically variable local scale factors for SIR or SAS pairs of data sets.
- DIFFE - evaluate renormalized SIR or SAS difference E-magnitudes.

## 1.2 Data reduction flow chart

Program names are indicated in upper case as PROGRAM, and file names in *UPPER CASE italics* as FILENAME.TYPE. Files {program}.DATA are reflection data files, and files named {program}.INPUT are parameter and program control data files. All these instruction files are generated by the DREAR GUI, but the programs may also be run directly using these files. The general recommend flow chart for running these programs is.



The program TDSBG/TDSCOR is optional, and is probably not necessary for normal use. All text output from programs (apart from SORTAV & BAYES) is directed to the file *DREAR.LST*.

### 1.3 Required program input files

The essential input files are diffractometer data files from Bruker/Siemens/Syntex P3 or P4 serial detector machines (\*.P4T) or from Enraf-Nonius CAD4 diffractometers (\*.DAT) in which profiles have been stored. CAD4 files without profiles *cannot be processed by the DREAR suite*.

If the user wishes to process other diffractometer data files, these must be converted to a binary file *RAW.DATA* which has the format given below. In addition, a file *DREAR.OMX* must also be supplied, which contains the following records, in free format.

Line 1	Unit cell parameters a, b, c (in Angstroms), alpha, beta, gamma (in degrees)
Line 2	UB(1,1), UB(1,2), UB(1,3)
Line 3	UB(2,1), UB(2,2), UB(2,3)
Line 4	UB(3,1), UB(3,2), UB(3,3)
Line 5	wavelength (alpha-1) , wavelength (alpha-2), attenuation factor, dead-time
Line 6	Goniometer type (1=Hamilton, 2=Busing-Levy, 3=Siemens P3, 4=CAD4)

UB is the diffractometer orientation matrix. If the attenuation factor and dead-time are not known, then zero's must be given. The goniometer type must be a number between 1 and 4.

### 1.4 Record structure in the binary reflection data output files

Most output reflection data files are unformatted, binary files - see individual programs for more detailed descriptions. The **Convert CAD4/P4** programs produce a file called *RAW.DATA* which contains up to 96 profile steps for use by the programs REFPAK and BGLP. The format for each record of the output file is :

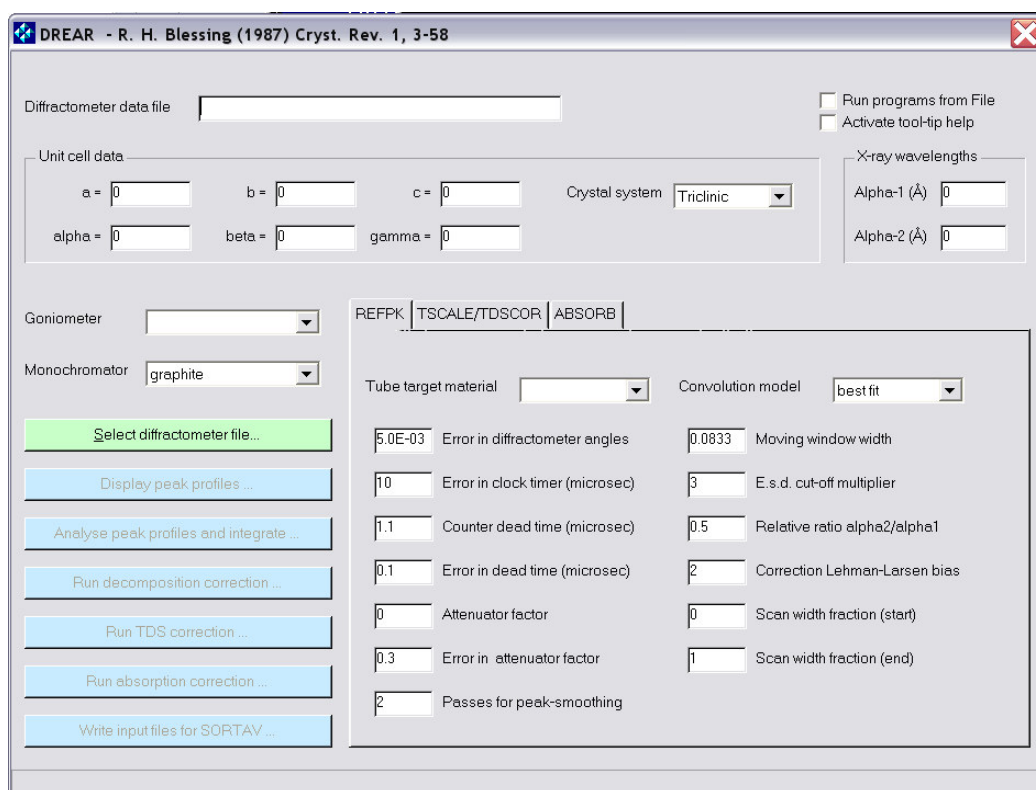
II, IH, IK, IL, A1, A2, A3, A4, WIDTH, SPEED, A1, A2, A3, A4, A5, XTIME, IY(96)

II	measurement serial number
IH, IK, IL	Miller indices
A1, A2, A3, A4	diffractometer setting angles:
	Int.Tab. two-theta omega chi phi
	Bus.Lev. two-theta omega chi phi
	P3/P4 two-theta omega phi chi
	CAD4 theta phi omega kappa
WIDTH	scan width (degrees $\theta$ )
SPEED	scan speed (degrees $\theta$ per minute)
A1, A2, A3, A4, A5	left background count, peak count, right background count, net intensity, sigma intensity (not used)
XTIME	radiation exposure time (hours)
IY(96)	step-scan counts

II is negative for standard reference reflection measurements. WIDTH is negative for measurements made using a beam attenuator. Single precision , integer\*4, real\*4 variables.

## 1.5 DREAR GUI

The use of the DREAR suite of programs in WinGX is simplified by using the DREAR GUI. This interface controls the running of all the programs and also writes out the *{program}.INPUT* files. If the user wishes to use less common features of the programs, it is possible to edit these input files and run the programs directly. The SORTAV program has its own GUI. The first action required of the user is to select a diffractometer data file. This is loaded and then converted to the DREAR binary format file *RAW.DATA*, and some data collection parameters are also written to the file *DREAR.OMX* (alternatively a pre-existing file *RAW.DATA* may also be selected). The available options are shown by the buttons on the left hand side of the GUI. These are greyed out if unavailable, green if active. If there are several possibilities, then the suggested one is shown in bright, green.



After selecting the data file, some parameters are loaded into the GUI, and the suggested option is highlighted in bright green.

DREAR - R. H. Blessing (1987) Cryst. Rev. 1, 3-58

Diffractometer data file   Run programs from File  
 Activate tool-tip help

Unit cell data

a =  b =  c =  Crystal system

alpha =  beta =  gamma =

X-ray wavelengths

Alpha-1 (Å)

Alpha-2 (Å)

Goniometer  REFPK | TSCALE/TDSCOR | ABSORB |

Monochromator

Tube target material  Convolution model

5.0E-03 Error in diffractometer angles  Moving window width

10 Error in clock timer (microsec)  E.s.d. cut-off multiplier

1.1 Counter dead time (microsec)  Relative ratio alpha2/alpha1

0.1 Error in dead time (microsec)  Correction Lehman-Larsen bias

13.780 Attenuator factor  Scan width fraction (start)

0.3 Error in attenuator factor  Scan width fraction (end)

2 Passes for peak-smoothing

Number of reflections successfully read from CAD4 file = 1846

DREAR - R. H. Blessing (1987) Cryst. Rev. 1, 3-58

Diffractometer data file   Run programs from File  
 Activate tool-tip help

Unit cell data

a =  b =  c =  Crystal system

alpha =  beta =  gamma =

X-ray wavelengths

Alpha-1 (Å)

Alpha-2 (Å)

Goniometer  REFPK | TSCALE/TDSCOR | ABSORB |

Monochromator

Tube target material  Convolution model

5.0E-03 Error in diffractometer angles  Moving window width

10 Error in clock timer (microsec)  E.s.d. cut-off multiplier

1.1 Counter dead time (microsec)  Relative ratio alpha2/alpha1

0.1 Error in dead time (microsec)  Correction Lehman-Larsen bias

13.780 Attenuator factor  Scan width fraction (start)

0.3 Error in attenuator factor  Scan width fraction (end)

2 Passes for peak-smoothing

BGLP finishes OK

Once the raw data have been processed and integrated by REFPK/BGLP, all options are available. They may be run in any order, but the suggested option is highlighted. When finished, the final binary data file should be converted into an



ASCII file suitable for input to SORTAV. A preliminary SORTAV input file SORTAV.INPUT is also written.

## 1.6 References

1. Blessing, R.H. (1987). Data reduction and error analysis for accurate single crystal diffraction intensities. *Cryst. Rev.*, **1**, 3-58.
2. Blessing, R.H. (1986). DREADD - Data reduction and error analysis routines for accurate single-crystal diffraction intensity measurements. *J. Appl. Cryst.* **19**, 412.
3. Blessing, R.H., and Langs, D.A. (1987). Data averaging with normal down-weighting of outliers. *J. Appl. Cryst.* **20**, 427-428.
4. Blessing, R.H., and Langs, D.A. (1988). A priori estimation of scale and overall anisotropic temperature factors from the Patterson origin peak. *Acta Cryst.* **A44**, 729-735.
5. Blessing, R.H. (1989). DREADD - Data reduction and error analysis for single crystal diffractometer data. *J. Appl. Cryst.* **22**, 396-397.
6. Blessing, R.H. (1995). An empirical correction for absorption anisotropy. *Acta Cryst.* **A51**, 33-38.
7. Blessing, R.H., Guo, D.Y., and Langs, D.A. (1996). Statistical expectation value of the Debye-Waller factor and  $|E(hkl)|$  values for macromolecular crystals. *Acta Cryst.* **D52**, 257-266.
8. Blessing, R.H. (1997). Outlier treatment in data merging. *J. Appl. Cryst.* **30**, 421-426.
9. Blessing, R.H. (1997). LOCSC: A program to statistically optimize local scaling of single-isomorphous-replacement and single-wavelength-anomalous-scattering data. *J. Appl. Cryst.* **30**, 176-177.
10. Blessing, R.H., Guo, D.Y., and Langs, D.A. (1998). Intensity statistics and normalization. in direct methods for solving macromolecular structures, NATO ASI Series volume, Series C: Mathematical and Physical Sciences, Vol. 507, Edited by S. Fortier, pp. 47-71. Dordrecht, The Netherlands: Kluwer Academic Publishers.
11. Blessing, R.H., and Smith, G.D. (1999). Difference structure factor normalization for determining heavy-atom or anomalous scattering substructures. *J. Appl. Cryst.*, (1999). **32**, 664-670

## 2.0 User's Instructions for the Programs REFPK and BGLP

### 2.1 Synopsis

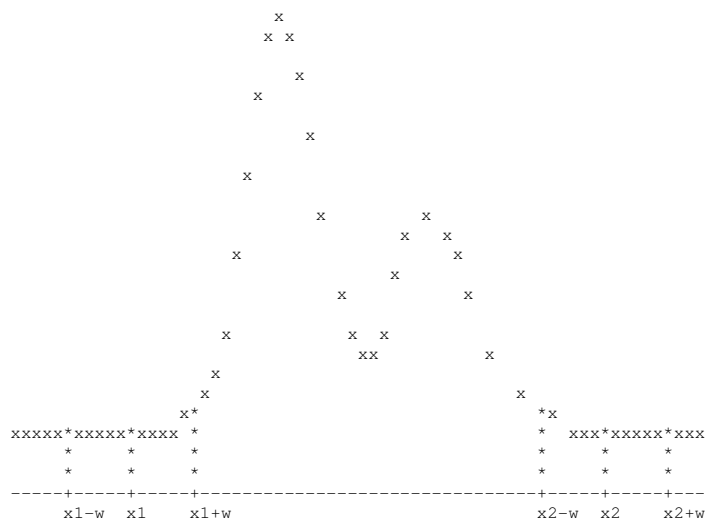
Program REFPK examines and analyzes  $\omega$  or  $\theta/2\theta$  scanned Bragg reflection profiles. Peak positions and peak widths are found for the reflections that pass several signal-to-noise tests. The displacements of these peaks from the midpoints of their scans and the base widths of these peaks are used as observations for least-squares calculations of parameters that allow peak positions and peak widths, which are scattering angle dependent and anisotropically variable, to be calculated for all reflections, including those with small signal-to-noise ratios.

The program BGLP applies :

- corrections for coincidence counting losses
- calculates the peak limits for each reflection using the parameters from program REFPK
- fits a least-squares straight line to the background outside the peak limits
- subtracts the background, divides out the Lorentz and polarization factors, and integrates the net reflection intensity between the peak limits
- calculates the estimated standard deviation of the net intensity.

### 2.2 Location of intensity-weighted peak centroids

In order to locate the intensity-weighted peak centroid, initial peak limits are obtained using a relatively narrow moving window of width  $w$  to find the smallest  $x$  for which the count rate integrated from  $x$  to  $x + w$  significantly exceeds that from  $x - w$  to  $x$ , and the largest  $x$  for which the count rate from  $x$  to  $x - w$  exceeds that from  $x$  to  $x + w$ .



The background is estimated by fitting a least-squares straight line to the count rate profile outside the initial peak limits, and the peak centroid weighted by the intensity above the estimated linear background is taken to correspond to the Bragg angle,  $\theta$ , for the intensity-weighted average wavelength,  $\lambda(K\alpha\text{-bar})$ . The

positions of  $\theta(K\alpha-1)$  and  $\theta(K\alpha-2)$  are calculated from the position of the peak centroid.

### 2.3 Location of peak limits

The peak limits are located by the method of Lehmann and Larsen, which seeks the two points in the scan profile between which integration of the net intensity gives minimum  $\sigma(I)/I$ . In practice, the routine actually seeks to maximize the inverse ratio  $I/\sigma(I)$  in order to avoid the problem of division by a zero value of  $I$ . See M. S. Lehmann and F. K. Larsen, *Acta Cryst.*, **A30**, 580 (1974) and R. H. Blessing, P. Coppens, and P. Becker, *J. Appl. Cryst.*, **7**, 448 (1974).

The minimum  $\sigma(I)/I$  criterion is inherently biased. It finds peak limits that are slightly within the peaks and thus slightly underestimates the area under the peaks. Lehmann and Larsen have shown that the bias of the peak limits is proportional to  $1/(2 + r)$ , where  $r$  is the integrated peak-to-background ratio. The peak limits found by the algorithm are corrected accordingly in program REFPAK, before the least-squares calculations of the peak width parameters.

### 2.4 Signal-to-noise tests

All reflections are screened in order to select observations for the least-squares calculations of the peak position and peak width parameters. Reflections for the least-squares calculations are selected on the basis of the following tests:

1. The routine for calculating the intensity-weighted peak centroid must find a significantly positive peak above the estimated linear background, i.e.,  $I > cutoff \times \sigma(I)$ , where typically  $cutoff = 3$ .
2. The routine for locating the peak limits must find true minima,  $\sigma(I)/I$ , at each side of the peak.

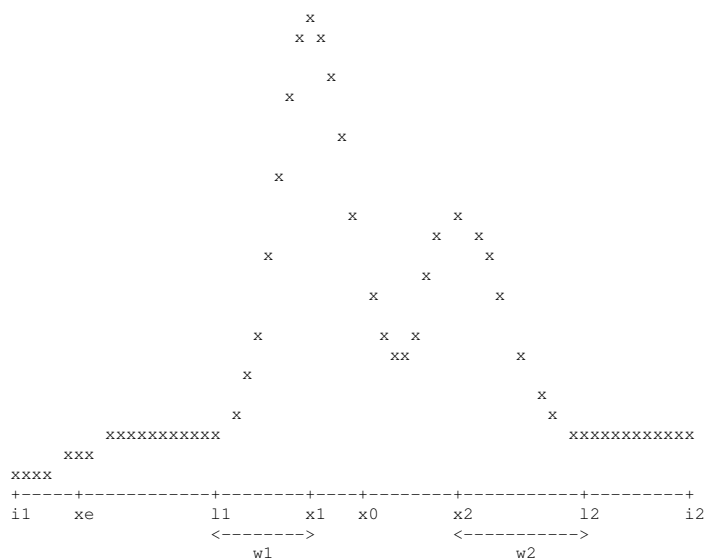
### 2.5 Calculation of peak positions

The least-squares fit of peak positions by program REFPAK is simply a recalculation of the diffractometer orientation matrix using as orientation angle observations the  $\omega$  values of the intensity-weighted peak centroids along with the diffractometer values of  $\chi$  and  $\phi$ . This gives an orientation matrix adjusted for the  $\omega$  peak displacements and averaged over the  $\chi$  and  $\phi$  settings used over the whole course of the data set measurement. Experience has shown that the recalculated orientation matrix is useful only when displacements of the peak centroids from the midpoints of the scans are small and only, or mainly, orientation dependent (i.e., due to fixed, small translational or rotational misorientation of the specimen crystal), and not significantly time dependent as well (i.e., not due to changes in orientation caused by crystal slippage). If there were manual or automatic reorientations of the crystal during the intensity measurements, the recalculated orientation matrix will be a kind of average over the several orientations. If there were large changes in orientation, more than a few degrees, then the data set should be subdivided into batches of approximately constant orientation, and the batches processed separately, because the peak width anisotropy parameters are orientation dependent.

The recalculated orientation matrix will not, in general, give accurate lattice parameters. It is used only to estimate an  $\omega$  offset peak position for scans of weak reflections with no significant peak above background, and it is used for this purpose only when it is well-determined, *i.e.* only when the crystal misorientation is small. Otherwise, the scan midpoint is assumed to be the best estimate of the peak position in the weak reflection scans.

## 2.6 Calculation of peak widths

The least-squares fit of peak widths by program REFPK assumes that the reflection peaks result from a convolution of instrumental and spectral distribution functions with an anisotropic crystal size and mosaicity distribution function.



w1 and w2 are base widths of the half-peaks below  $\theta(\alpha-1)$  and above  $\theta(\alpha-2)$ , respectively. they are each assumed to be representable as either

$$w = [z(k) \times q(j, k) \times z(j)]^{1/2} + t \times \tan \theta \quad (1)$$

or

$$w = [z(k) \times q(j, k) \times z(j) + (t \times \tan \theta^2)]^{1/2} \quad (2)$$

or

$$w = [z(k) \times q(j, k) \times z(j) - 2 \times f \times t \times \tan \theta / \tan(\theta(m)) + t \times (\tan \theta / \tan(\theta(m)))^2]^{1/2} \quad (3)$$

The two half-peaks are treated separately, because the reflection peaks are not, in general, symmetric and the spectral lines do not have the same width. Equations (1) and (2) apply in the case of a  $\beta$ -filtered x-ray beam or a beam from a perpendicular geometry mono-chromator; equation (3) applies in the case of a parallel geometry monochromator.

In all three equations, index repetition implies summation.

- w1 and w2 have units of degrees of crystal rotation,  $\theta$ .

- are components of a unit vector perpendicular to the incident and diffracted beam directions.
- are elements of symmetric tensors that are related to the anisotropy of the size and of the mosaicity (fault structure) of the specimen crystal. See R. J. Nelmes, *Acta Cryst.*, **A36**, 641-653 (1980).
- t are (scalar) coefficients related to the spectral width of the characteristic  $\alpha$ -1 and  $\alpha$ -2 lines. Values of the full-width at half-height of the spectral lines are given by H. C. Compton and S. K. Allison, *X-rays in Theory and Experiment*, van Nostrand, NY 1935, pp. 744-745.)

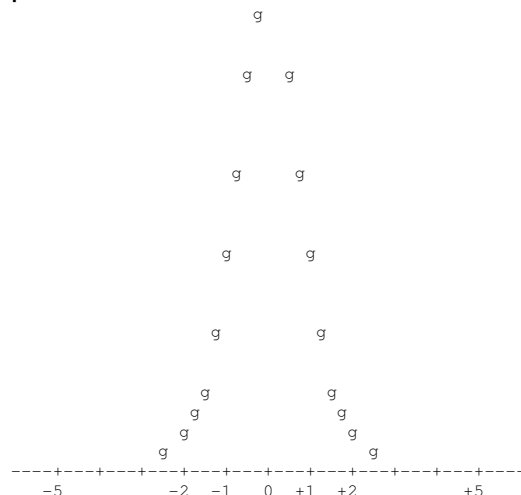
In equation (3),  $\theta(m)$  is the monochromator Bragg angle and  $f$  is a numerical constant with a value in the range  $1 \leq f \leq 2$ . See H. Dachs, 1978, *Neutron Diffraction*, pp. 25 ff. G. Bacon, 1975, *Neutron Diffraction*, pp. 101 ff..

All the various fixed, instrumental contributions to the reflection width, such as the finite size and the spatial intensity distribution of the x-ray source, are assumed to be implicit in the  $q$  tensors. All the various scattering angle dependent contributions, such as beam divergence, spectral broadening, and mosaic broadening, are assumed to be implicit in the  $t$  coefficients.

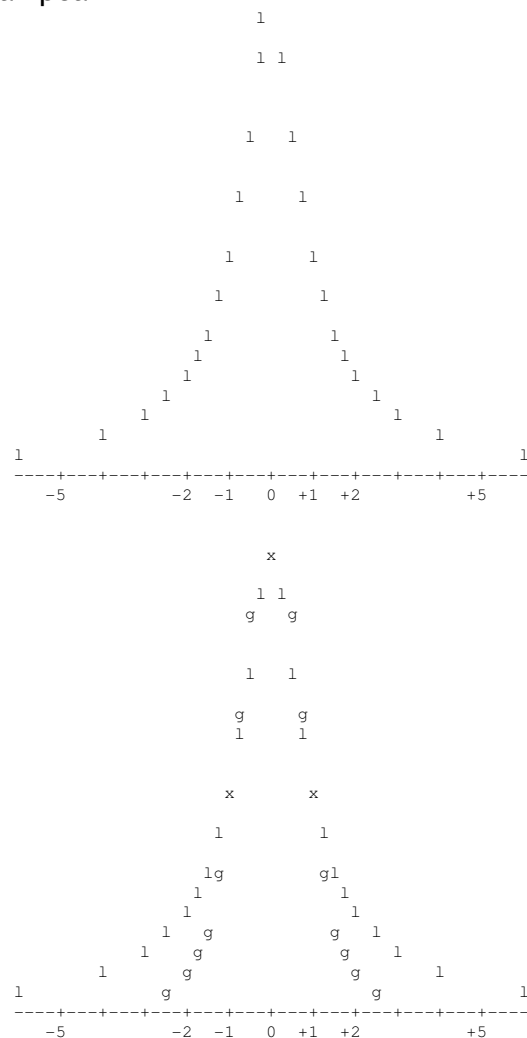
The vector components  $z(3)$  and the tensor components  $q(3,3)$  are referred to a Cartesian axial system fixed in the crystal. This axial system is the same as the system, labeled as, defined by Walter Hamilton in *International Tables for X-ray crystallography*, 1974, Vol. IV, pp. 273-284.

Equation (1) implies that the crystal anisotropy distribution, of width  $[z(k) \times q(j,k) \times z(j)]^{1/2}$ , and the spectral distribution, of width  $t \times \tan\theta$ , convolute as would two Lorentzian (or Cauchy) functions, and equation (2) implies that the two distributions convolute as would two Gaussian functions. Equation (3) implies convolution of Gaussian distribution functions for the specimen and monochromator crystal mosaicities and for the beam divergence. In the following sketches of Lorentzian and Gaussian peaks, the abscissae units are  $(x - x_0)/(w/2)$ , where  $w$  is the full width at half height, and the ordinate units are relative and normalized to a maximum height equal to ten half-widths at half-height.

Gaussian peak



Lorentzian peak



Note that a Lorentzian peak is somewhat narrower at the top and substantially wider at the bottom than a Gaussian peak with the same height and the same width at half height.

For  $\beta$  filtered or perpendicular geometry monochromator data, program REFPK tries both eq. (1) and eq. (2) as models for the base widths of the half-peaks. For each set of half-peak base widths, and for each of the two models, eq. (1) and eq. (2), the program fits by least-squares scalar spectral coefficients,  $t$ , and anisotropy tensor coefficients,  $q(3,3)$ . The model that gives the smaller root-mean-square error-of-fit,

$$\text{rmsd} = \sqrt{\frac{\sum[(w_{\text{obs}} - w_{\text{calc}})^2]}{[n_{\text{obs}} - n_{\text{par}}]}}$$

is chosen to calculate the base widths for each half-peak.

The least-squares fitting is done in two stages. First, the  $t$ -coefficients and isotropic  $q$ -values are fitted, and the type of convolution model is chosen. Then, using the fitted  $t$ -values, the anisotropic  $q$ -coefficients are fitted. This two-stage fitting is a variant on the procedure described by Blessing [*Cryst. Rev.* 1, 3-58

(1987)], which was a one-stage procedure that assumed fixed, precalculated  $t$ -values for eqs. (1) and (2), and fitted the  $t$ -coefficients along with the  $q$ -coefficients for eq. (3).

Note that the program is designed to fit *only the base widths* of the reflection peaks. It does *not fit Lorentzian or Gaussian functions to the profiles* of the peaks, although it does assume that either Lorentzian or Gaussian convolution properties are adequate approximations to calculate the width of the convolution product of the crystal anisotropy distribution and the spectral dispersion distribution.

## 2.7 Background subtraction

The program BGLP repeats the search for the intensity-weighted peak centroid for each reflection. For the very weakest reflections that do not have a significant peak above background for which an intensity-weighted centroid can be reliably located, BGLP resorts to the peak position estimated from the recalculated orientation matrix or to the scan midpoint.

Given the peak position for a reflection, BGLP uses the peak width parameters from REFPK to calculate the peak limits. It fits a least-squares straight line to the background outside the peak limits, and integrates the peak above background between the peak limits. For scans for which the absorption edge of a  $\beta$ -filter falls within the scan range, a structured background made-up of three straight-line pieces is fitted (see R. J. Nelmes, *Acta Cryst.* **A31**, 273-279 (1975)).

The structured background correction is found to be suitable for the low angle reflections from crystals with unit cells of small to moderate size. For the numerous very low angle reflections from macromolecular crystals, a simple straight-line background is, generally, a better approximation than the modeling of the structured background. This is because the shape of the background is often determined more by the scattering from the specimen capillary, mother liquor, *etc.* than by the spectral structure due to the white radiation and the  $\beta$ -filter absorption edge, which is often very close to the  $\alpha$ -reflection peak.

## 2.8 Input files

The following input files are required:

1. the raw reflection profile data file *RAW.DATA* is used by both programs REFPK and BGLP.
2. control data file REFPK.INPUT is described below.
3. an optional control data file HKLCOND.DAT, which gives the conditions limiting possible reflections, is also described below in Section 6.12.
4. control data file BGLP.INPUT is created by program REFPK.

Program BGLP does not require any additional input and is automatically run immediately following a satisfactory run of program REFPK.

### 2.81 Raw reflection profile data file *RAW.DATA*

The record structure of this unformatted, binary file is given in Section 1.4

## 2.82 Control data file REFPK.INPUT

Users must supply the data of records 1-8. Records 9-20 may be blank records, and the program will supply default data.

Card	Parameter(s)	Description	Format
1	TITLE	Job title	(A)
2	FILE1	Name of raw reflection profile data file	(A)
3	FILE2	Name to be given to reduced data output file from program BGLP	(A)
4	CELL(6)	Lattice constants a,b,c(Å), $\alpha,\beta,\gamma$ (degrees)	(6F10.0)
5	DIFF	Diffractometer type (H, BL, P3, or CAD4) H Hamilton's diffractometer axes, W. Hamilton, International Tables for Xray Crystallography, Vol. IV, 1974, pp. 273-284 . BL Busing's and Levy's diffractometer axes, W. R. Busing and H. A. Levy, Acta Cryst., 22, 457-464 (1967). P3/P4 Bruker (nee Siemens, nee Nicolet, nee Syntex) P3/P4 diffractometer CAD4 Enraf-Nonius CAD4 diffractometer Otherwise, diffraction geometry is assumed to be for a diffractometer as defined by Hamilton	(A4)
6	TARGET	Chemical symbol for x-ray tube target (CU, MO, AG, or OTHER). For neutron data, enter NEUTRON.	(A2)
7	FILTER	Chemical symbol for $\beta$ filter (if any) NI, ZR, NB, PD, RH, or OTHER) Leave blank, or enter none, for data from large unit cell, macromolecular crystals, for which a simple straight-line background is, generally, a better approximation than modeling the background structure due to the white radiation and the $\beta$ -filter.	(A2)
8	MONOCR	Monochromator crystal (if any) (GRaphite, QUartz, or OTHER)	(A2)
9	THM, RHOM, FRACTD, SIGFD	Monochromator variables THM = monochromator Bragg angle $\theta$ RHOM = monochromator-diffractometer geometry angle $\rho$ . $\rho = 0.0^\circ$ for parallel geometry, $\rho = 90^\circ$ for perpendicular geometry FRACTD = monochromator dynamic diffraction (perfect crystal) fraction SIGFD = $\sigma(\text{FRACTD})$ , estimated standard deviation of FRACTD	(4F10.0)



### 3.2.4 DREAR - Data Menu

## WinGX - v 1.80

		<p>Default values of THM are stored in the program for graphite (0 0 0 2 reflection) and quartz (1 0-1 1 reflection) monochromator crystals for Cu, Mo, and Ag X-rays. Default values of <math>\rho</math> are stored for the Nicolet (Syntex) P3 (<math>\rho = 0.0^\circ</math>) and the Enraf-Nonius CAD4 (<math>\rho = 90^\circ</math>) diffractometers.</p> <p>The default value of FRACTD is zero, and a default value <math>SIGFD = 0.05 \times FRACTD</math> will be used unless the user supplies a non-zero value for SIGFD.</p>	
10	WLA1, WLA2, DWLA1, DWLA2, EDGE	<p>Wavelength values  WLA1 = <math>\alpha</math>-1 wavelength (Å)  WLA2 = <math>\alpha</math>-2 wavelength  DWLA1 = spectral line width (fwhh Å)  DWLA2 = spectral line width  EDGE = wavelength of K-absorption edge of <math>\beta</math>-filter</p> <p>Default data for wavelengths and spectral line widths are stored in the program for Cu, Co, and Ag K-<math>\alpha</math> X-radiation. Default data for K-absorption edge wavelengths are stored for Ni, Zr, Nb, Pd, and Rh <math>\beta</math>-filters. For neutron data, enter WLA1 = WLA2 and DWLA1 = DWLA2.</p>	(5F10.0)
11	SIGTHE, SIGTIM	<p>Estimated errors for the diffractometer scan angle and clock timer.</p> <p>SIGTHE (degrees <math>\theta</math>)  SIGTIM (microseconds)</p>	(2F10.0)
12	TAU, SIGTAU, ATT, SIGATT	<p>Counting constants for coincidence corrections</p> <p>TAU = dead time of quantum counting chain (microseconds)  ATT = correction factor for beam attenuator.</p>	(4F10.0)
13	IIMIN, IIMAX, XTMIN, XTMAX	<p>Beginning and ending reflection serial numbers or X-ray exposure times</p> <p>IIMIN, IIMAX = serial number limits  XTMIN, XTMAX = exposure time limits (hours)</p> <p>These limits can be used to process data in batches. Only reflections within given limits will be processed. The default procedure is to process all reflections. Default values: IIMIN = -100000, IIMAX = 100000; XTMIN = <math>-1.0 \times 10^5</math>, XTMAX = <math>+1.0 \times 10^5</math></p>	(2I10, 2F10.0)
14	SC1, SC2	<p>Scan limits in decimal fractions of scan width. Default values: SC1 = 0.0, SC2 = 1.0, but values of SC1 &gt; 0 or SC2 &lt; 1 can be used to allow for scans that were so wide as to overlap neighboring reflections.</p>	(4F10.0)

15	WINDOW	Width of the moving window (decimal fraction of scan width) used to find initial peak limits. Default value: WINDOW = 0.0833 = 1/12 = 8/96.	(F10.0)
16	CUTOFF	ESD multiplier for the various statistical significance tests. Default value: CUTOFF = 3.	(F10.0)
17	FL1	Multiplier for the correction for the Lehmann-Larsen bias. The peak limits are shifted to $l1' = l1 - f \times (x1 - l1)$ and $l2' = l2 + f \times (l2 - x2)$ , where $f = FL1 / (2 + (pk - bg) / bg)$ . Default value: FL1 = 2.	(F10.0)
18	WT2	Intensity of the $\alpha$ -2 wavelength relative to $\alpha$ -1. Default value: WT2 = 0.5, but a crystal monochromator, depending on how it is adjusted, can change the $\alpha$ -2/ $\alpha$ -1 intensity ratio and the intensity-weighted average wavelength, $wl0 = (wl1 + wl2 \times wt2) / (1 + wt2)$ .	(F10.0)
19	NSMOOTH	Number of passes of data-smoothing for peak location. Default value: NSMOOTH = 2. SET NSMOOTH = -1 to by-pass the smoothing of the scan profiles, which is normally done for the peak location parts of the analysis. Intensity integration is always done with the unsmoothed data.	(I10)
20	JMODEL	Allows the user to impose a choice between the Lorentzian (JMODEL = 1) and Gaussian (JMODEL = 2) convolution models. Default: JMODEL = 0.	(I10)

### 2.83 Control data file HKLCOND.DAT

This file, which is optional, gives the conditions limiting possible reflections so that any systematically absent reflections that were included in the intensity measurements will not be used to fit the peak position and peak width parameters in program REFPK. If the HKLCOND.DAT file is present when program BGLP is run, the absent reflections will not be included in the output reflection data file from program BGLP. The conditions MUST be entered in the form indicated in Section 6.12.

## 2.9 Description of program output

The printed output from programs REFPK and BGLP includes tables that list reflections with extreme values of several characteristic properties. The tables are presented in pairs in which the first table lists the reflections with the smallest values of a given property and the second those with the largest values. The property on which the table is based is stated in the heading above the table column headings, and the entries in the table are sorted in order of increasing value of the property in the tables of smallest values, and decreasing value in the tables of largest values.

These tables are prepared in order to provide the user with a guide for visual inspection of unusual reflection profiles using program VIEW. Program VIEW is run interactively. It plots the reflection intensity profiles stored on the raw reflection data file, DATA.RAW. The profile plots are displayed on the video terminal screen, and may also be printed on the line printer. The user should examine a fair sample of profile plots to check that the programs are setting the peak limits satisfactorily. The properties tabulated by program REFPK are:

- DX00, displacement of observed peak centroid from midpoint of scan (degrees  $\theta$ )
- D0=X00-X0C, difference between observed and calculated centroids (degrees  $\theta$ )
- WC=L2C-L1C, calculated base width (degrees  $\theta$ )
- WO-WC=(L2O-L1O)-(L2C-L1C), difference between observed and calculated full-peak base width (degrees  $\theta$ )

The properties tabulated by program BGLP are:

- $S = \sin\theta/\lambda$
- $Y = I/LP$ , Lorentz and polarization corrected net intensity
- X0, intensity-weighted peak centroid (step number)
- $W = L2 - L1$ , base width of reflection (degrees  $\theta$ )

Preceding the tables of reflections with extreme characteristics, the printed output from both programs REFPK and BGLP also includes a table that lists the special reflections of the types H00, 0K0, 00L, HH0, 0KK, H0H, AND HHH.

## 2.10 The output parameters from program REFPK

This is written by default to the file *BGLP.INPUT* file. The following code is used to write this file:

```
write (io2,600) atime
```

```

write (io2,600) adate
write (io2,600) title
write (io2,600) file1
write (io2,600) file2
write (io2,601) (a(i),i=1,6)
write (io2,602) idiff,ineutron
write (io2,601) thm,rhom,fractd,sigfd
write (io2,601) edge,wla1,wla0,wla2
write (io2,601) sigthe,sigtim
write (io2,601) tau,sigtau,att,sigatt
write (io2,601) window
write (io2,601) cutoff
write (io2,602) ismooth
write (io2,605) scl,sc2
write (io2,603) iimin,iimax,xtmin-0.005,xtmax+0.005
write (io2,604) ((u(i,j),j=1,3),i=1,3)
write (io2,604) ((sigu(i,j),j=1,3),i=1,3)
write (io2,600) model1
write (io2,604) ((q1(i,j),j=1,3),i=1,3)
write (io2,604) ((sigq1(i,j),j=1,3),i=1,3)
write (io2,604) t1
write (io2,604) sigt1
write (io2,600) model2
write (io2,604) ((q2(i,j),j=1,3),i=1,3)
write (io2,604) ((sigq2(i,j),j=1,3),i=1,3)
write (io2,604) t2
( write (io2,604) f )
( write (io2,605) xx0,xw1,xw2 )
600 format (1x,a)
601 format (1x,6f10.5)
602 format (1x,i10)
603 format (1x,2i10,2f10.3)
604 format (3(1x,3e15.8/))
605 format (1x,4f10.2)

```

### 2.11 The diffractometer orientation matrix written by the program

This is as defined by Walter Hamilton (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 273-284. It is equal to :

(a) the transpose of a Busing-Levy matrix pre-multiplied by the matrix

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(b) the transpose of an Enraf-Nonius CAD4 matrix

(c) the transpose of a Bruker (Siemens, Nicolet, Syntex) P3 matrix pre-multiplied by

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

### 2.12 Option to override use of calculated peak positions or widths

An optional last record written for BGLP by REFPK is the root-mean-square error-of-fit for the peak positions exceeds half the root-mean-square peak displacement. This record supplies a value :

$$XX0 = 0.5 \text{ (decimal fraction of the scan width)}$$

for the default peak position to be used if the peak centroid cannot be well determined. The user can supply or alter this value, or supply values

$$XX0 \ , \ XW1, \ XW2$$

for the default peak position and/or for the peak limits, and thus override the values calculated from the recalculated orientation matrix and the anisotropic peak width parameters from REFPK. The values must be supplied in units of decimal fraction of the scan width, e.g., peak position,  $XX0 = 0.6$ , and peak limits,  $XW1 = 0.25$  and  $XW2 = 0.95$ . The final peak limits will be repositioned about the intensity-weighted peak centroid, but the peak width will be kept fixed at  $(XW2 - XW1)$ .

### 2.13 The output reflection file *BGLP.DATA* from BGLP

This is an unformatted, binary file in which the record structure is:

II	Measurement serial number. -ve for standard reference reflections
IH	
IK	Miller indices
IL	
A1	
A2	diffractometer
7A3	setting angles
A4	
Y	$I/lp$
SIGY	$\sigma(I/lp)$
XTIME	x-ray exposure time (hours)

The diffractometer setting angles are as originally written by the diffractometer. Note that the order is important.

diff.type	a (1)	a (2)	a (3)	a (4)
INT.TAB.	two-theta	omega	chi	phi
BUSING-LEVY	two-theta	omega	chi	phi
P3	two-theta	omega	phi	chi
CAD4	theta	phi	omega	kappa

Angles transformed to conform to the conventions defined by Hamilton in *International Tables for X-ray Crystallography*, Vol. IV, 1974, pp. 273-284, are used within programs REFPK and BGLP, but the untransformed angles are written to the output file.

The value of  $Y = I/LP = F^2$  is given in units of counts per second per degree of crystal rotation. The estimated standard deviation  $\sigma(Y)$  results from a propagation-of-error analysis that allows for uncertainties due to Poisson counting statistics, scan angle setting errors, the counter dead time correction, and the beam attenuator factor.

### 3.0 User's Instructions for the Program TSCALE

Program TSCALE analyzes standard reference reflection intensities as functions of accumulated x-ray exposure time. It fits linear, quadratic, or cubic polynomials to the intensity vs. time data for each standard. The program chooses among the polynomial orders by means of the statistical f-test for the significance of an added term. If the behaviour of any standard is too complicated to be fitted by one of the polynomials, the user can, in a second run of the program, cut the data for that standard into time segments short enough to be adequately fitted by the low order polynomials. The user can also exclude any or all measurements of a given standard from the polynomial fitting, and eliminate from the data set any reflection measurements deemed unreliable. Results of the analysis are presented in tables and plots of the intensity vs. time data and the fitted polynomials. When the user is satisfied with the polynomial fitting, the polynomials are used to calculate scale factors to scale the intensity data either to the mid-time of the experiment or to some other reference time selected by the user.

The scale factor applied to a given reflection is a weighted average of the scale factors calculated from the several polynomials fitted to the several standards. The average can be weighted toward the standard whose reciprocal lattice vector direction is nearest that of the given reflection, so that the scaling is anisotropic. This can be useful when radiation damage has caused intensities to decay anisotropically. The average can also be weighted toward the standard that is nearest in intensity to the given reflection, so that strong data are scaled rather more by strong standards and weak data by weak standards. This can be helpful for subsequent refinement of extinction parameters with data sets with severe extinction. Finally, the average can also be weighted toward the standard that is nearest in  $\sin\theta/\lambda$  to the given reflection, so that high-angle data are scaled rather more by high-angle standards and low-angle data by low-angle standards. This can be helpful when changes in experimental temperature or crystal decay affect high-angle data more than low-angle data.

#### 3.1 The q-sum function

The program will prepares plots of intensity vs. time and q-sum vs. time for each segment of each standard. The q-sum function corresponding to a function  $y = y(x)$  given as data points  $[x(i), y(i)]$  is defined as

$$q[x(n)] = \text{sum } (i=1, n) [y(i) - y_0], \quad n=1, 2, \dots, n_{\text{max}},$$

where  $y_0$  is the mean value of  $y$ . If  $y(x)$  is linear, then

$$\begin{aligned} y &= a + b \times x \\ y_0 &= a + b \times x_0, \end{aligned}$$

and

$$\begin{aligned} q[x(n)] &= \text{sum } (i=1, n) b \times [x(i) - x_0] \\ q[x(n)] &= b \times \text{sum } (i=1, n) [x(i) - n \times b \times x_0]. \end{aligned}$$

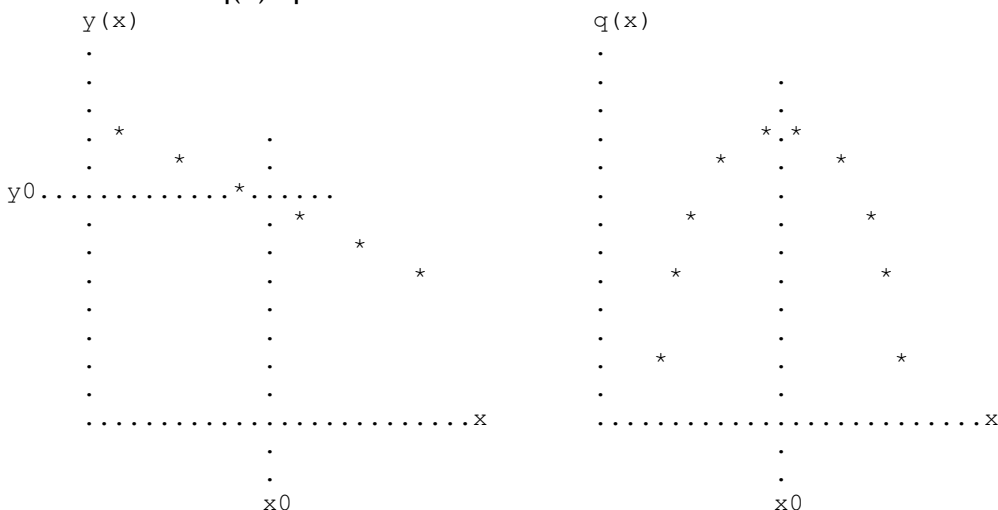
If the x-values are equally spaced at intervals of  $c$  units of  $x$ ,

$$\begin{aligned} \text{sum } (i=1,n) \ x(i) &= \text{sum } (i=1,n) \ (c \times i) \\ &= c \times \text{sum } (i=1,n) \ i \\ &= c \times n \times (n + 1)/2, \end{aligned}$$

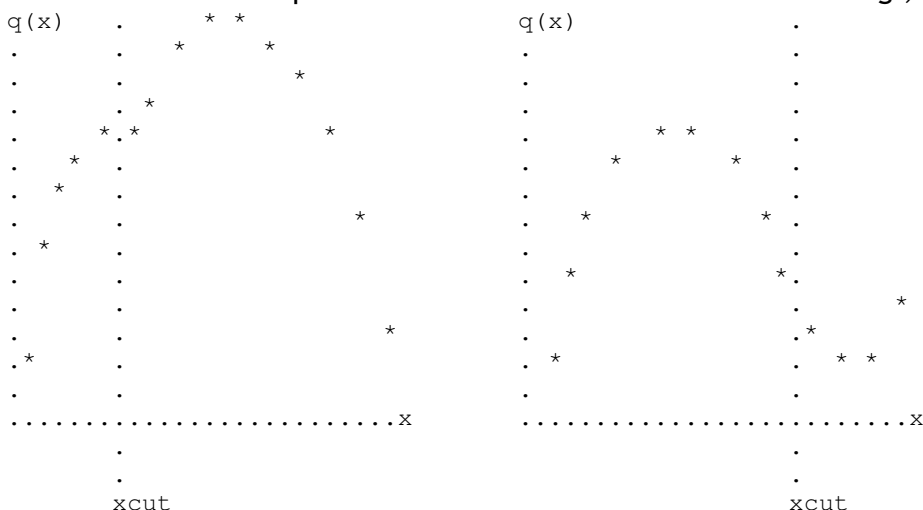
but, as the x values are equally spaced,  $n = x(n)/c$ , and

$$\begin{aligned} \text{sum } (i=1,n) \ x(i) &= x(n) \times [x(n)/c + 1]/2 \\ \text{sum } (i=1,n) \ (xi) &= [x(n)^2 + c \times x(n)]/(2 \times c) \end{aligned}$$

thus, if  $y(x)$  is linear, then  $q(x)$  is quadratic and if the line  $y(x)$  has negative slope, then the curve  $q(x)$  opens down.



To decide whether and where to cut the data into time segments, the user should examine the intensity vs. time and q-sum vs. time plots together. Points of discontinuity that seem to be intersections between both-up or both-down parabolic segments of the q-sum function, and points of inflection that seem to be intersections between one-up and one-down parabolic segments of the q-sum function should be considered as possible times at which to cut the data. e.g.,



In general, not all the time cuts suggested by the q-sum plots will be needed, because the  $q(x)$  discontinuities and inflections indicate linear segments of  $y(x)$ , but the program will also fit quadratic or cubic  $y(x)$  if they are statistically appropriate. Moreover, not all possible cuts are experimentally significant, and

the user should examine the intensity vs. time plots and the experimental records to decide which, if any, cuts to make.

### 3.2 Anisotropic, intensity and $\sin\theta/\lambda$ dependent scaling

The scale factor applied to a given reflection measurement is a weighted average of the scale factors calculated for the time of the given measurement from the several scaling polynomials. The weight for the  $i$ -th scale factor in this averaging is

$$w_i = w_0 \times w_1 \times w_2 \times w_3,$$

where the four weighting factors are defined as follows:

$$w_0 = 1/\sigma(i)^2$$

where  $\sigma(i)^2$  is the variance of the  $i$ -th scale factor as calculated from the variance-covariance matrix from the least-squares fit of the coefficients of the  $i$ -th scaling polynomial.

**IANISO** allows the scaling to be weighted toward the standard reflection with reciprocal lattice vector direction nearest that of the given reflection.

- if IANISO = 0,  $w_1 = 1$
- if IANISO  $\neq$  0,  $w_1 = 1/(1 + c_1^2 \times (1 - \cos^2\phi))$

where  $\cos\phi = (h \times h_i)/(h \times h_i)$ ,  $h$  and  $h_i$  are the reciprocal lattice vectors for the given reflection and the  $i$ -th standard reflection, respectively, and  $\phi$  is the angle between the two vectors.  $(h \times h_i)$  represents the dot product of the vectors, and  $(h \times h_i)$  represents the product of the vector magnitudes.

**IYDIFF** allows the scaling to be weighted toward the standard reflection that is nearest in intensity to the given reflection.

- if IYDIFF = 0,  $w_2 = 1$
- if IYDIFF  $\neq$  0,  $w_2 = 1/(1 + c_2 \times (y - Y_i)^2)$

where  $y$  is the unscaled intensity of the given reflection and  $Y_i$  is the intensity calculated from the  $i$ -th scaling polynomial at the time the given reflection was measured.

**ISDIFF** allows the scaling to be weighted toward the standard reflection that is nearest in  $\sin\theta/\lambda$  to the given reflection.

- if ISDIFF = 0,  $w_3 = 1$
- if ISDIFF  $\neq$  0,  $w_3 = 1/(1 + c_3 \times (h - h_i)^2)$

where, as above,  $h$  and  $h_i$  are the reciprocal lattice vector magnitudes ( $h = d^* = 2 \times \sin(\theta)/\lambda$ ) for the given reflection and the  $i$ -th standard reflection, respectively.

Reasonable orders of magnitude for the weighting coefficients are

$$c_1 = 10, \quad c_2 = 1, \quad \text{and} \quad c_3 = 10.$$

The user should consider setting IANISO or IYDIFF or ISDIFF  $\neq$  0 only if the standard reflections provide a good sampling of reciprocal lattice directions and the intensity range of the data. This normally requires nine or more different



standard reference reflections : three strong (one very strong), three medium, and three weak - all well-distributed over reciprocal space.

### 3.3 Modified values of the estimated standard deviations

Each reflection is scaled according to

$$y_{\text{corr}} = y/f,$$

where  $f$  is the weighted average inverse scaling factor

$$f = \text{sum}(w_i \times f_i) / \text{sum}(w_i)$$

and  $w_i = w_0 \times w_1 \times w_2 \times w_3$  as described above. The variance of the averaged  $f$  is taken to be

$$\sigma(f)^2 = \text{sum}(w_i^2 \times \sigma(f_i)^2) / (\text{sum}(w_i))^2$$

or

$$\sigma(f)^2 = (1/(n - 1)) \times \text{sum}(w_i \times (f_i - f)^2) / \text{sum}(w_i),$$

whichever is larger. The scaled variance for the reflection is then given by

$$\sigma(y_{\text{corr}})^2 = (\sigma(y)^2 + p^2 \times y^2) / f^2 + (y^2 / f^2) \times \sigma(f)^2,$$

where  $p$ , the proportionality constant for instrumental instabilities (see McCandlish, Stout, and Andrews, (1975). *Acta Cryst.* **A31**, 245.), is a measure of the excess scatter of the standard reference reflections, over and above their statistical scatter, about the smooth trend of their time dependence. i.e.,

$$p^2 = (\text{sum}((Y_{\text{meas}} - Y_{\text{calc}}(t))^2) - \text{sum}(\sigma(y_{\text{meas}})^2) / \text{sum}(Y_{\text{meas}}^2).$$

### 3.4 Program limits

- 20 standard reflections
- 10 segments for each standard
- 500 measurements in each segment
- 20 (ranges of) serial numbers and
- 20 (ranges of) exposure times for standard measurements to be omitted from the analysis
- 50 (ranges of) serial numbers and
- 50 (ranges of) exposure times for (non-standard) measurements to be rejected from the data set

### 3.5 Input files required:

#### 3.5.1 Reflection data file

*BGLP.DATA* from BGLP. This is an unformatted file described in Section 2.13. The diffractometer angles are not used by the program, but they are transferred to the output file for possible later use in absorption and extinction correction calculations.

### 3.2.4 DREAR - Data Menu

## WinGX - v 1.80

#### 3.5.2 Control data file TSCALE.INPUT

The user must supply at least records 1 - 4 followed by six blank records.

Card	Parameter(s)	Description	Format
1	TITLE	job title	A
2	FILE1	name of input reflection data file	A
3	FILE2	name for output file of scaled data	A
4	ITABL, IPLOT, IQSUM, IGRAPH, IAPPLY, IANISO, IYDIFF, ISDIFF	Control variables. ITABL If non=zero print tables of intensity vs. time data for (each segment of) each standard. IPLOT If non-zero gives line printer plots of intensity vs. time for (each segment of) each standard. IQSUM If non-zero gives line printer plots of Q-sum vs. time for (each segment of) each standard. IGRAPH If non-zero graph the inverse scaling functions for the several standards. IAPPLY If non-zero apply scaling factors and write the output file of scaled data. IANISO If non-zero apply scaling factors with anisotropic weighting. C1 = IANISO IYDIFF If non-zero apply scaling factors with weighting by intensity difference. C2 = IYDIFF ISDIFF If non-zero apply scaling factors with weighting by $\sin(\theta)/\lambda$ difference. C3 = ISDIFF Recommended control variables for a first run are: 1, 1, 0, 1, 0, 0, 0, 0	8I10
5	CELL(6)	Lattice parameters a, b, c, alpha, beta, gamma	6F10.0
		For each of the five record types 6 to 10, supply at least the blank terminator record. Record types 6 to 8 control the calculation of the scaling functions, and record types 9 and 10 allow the user to edit the data set.	
6	IH, IK, IL, XTCUT	Exposure time cuts. One record per cut IH, IK, IL, XTCUT (maximum xtime for the segment) + BLANK TERMINATOR RECORD	3I4, F10.0
7	IH, IK, IL, I1	Serial numbers of standard measurements to be omitted from the calculation of scaling functions One record per measurement (or range of measurements) IH, IK, IL, I1 (or I1, I2 (inclusive)) + BLANK TERMINATOR RECORD	3I4, 2I10

### 3.2.4 DREAR - Data Menu

## WinGX - v 1.80

8	IH, IK, IL, X1	Exposure times of standard measurements to be omitted from the calculation of scaling functions. One record per measurement (or range of measurements) IH, IK, IL, X1 (or X1, X2 (inclusive)) + BLANK TERMINATOR RECORD.	3I4, 2F10.0
9	I1 (OR I1, I2)	Serial numbers of data to be rejected from the data set. One record per measurement (or range of measurements) I1 (or I1, I2 (inclusive)) + BLANK TERMINATOR RECORD.	2I10
10	X1 (OR X1, X2)	Exposure times of data to be rejected from the data set. One record per measurement (or range of measurements) X1 (or X1, X2 (inclusive)) + BLANK TERMINATOR RECORD.	2F10.0
11	REFT	Reference time for the scaling. If left blank or entered as zero, the program will default to the mid-time of the experiment.	F10.0

### 3.6 Description of the output

The output reflection data file produced if IAPPLY = 1 is an unformatted file with the same record structure as the input reflection data file. The output  $Y = I/LP$  value is the scaled value, and the output  $SIGY = SIGMA(I/LP)$  is scaled and includes contributions from the instrumental instability and from the estimated error in the scaling factor.

Reference reflections designated on records of type 7 or 8 for omission from the calculation of the scaling functions will not be omitted from the output reflection data file unless they have also been designated for omission from the data set by means of records of type 9 or 10. Also if IAPPLY = 1, the printed output includes a table of special reflections of the types H00, OK0, 00L, HH0, OKK, H0H, AND HHH. Following this table the program prints the minimum, maximum, and mean values of the weighted-average scaling factors applied to the reflections and the minimum, maximum, and mean values of the relative error in the scaling factors.

#### 4.0 User's Instructions for the Programs TDSBG/TDSCOR

An empirical thermal diffuse scattering (TDS) coefficient is evaluated according to

$$I_{\text{meas}} = I_{\text{Bragg}} \times (1 + \alpha),$$

where  $I_{\text{meas}}$  is the measured Bragg-plus-TDS (*i.e.*, elastic-plus-inelastic) intensity;  $I_{\text{Bragg}}$  is the pure Bragg (elastic) intensity; and the TDS coefficient,  $\alpha$ , is the ratio of the inelastic to the elastic scattering. *i.e.*,

$$\alpha = I_{\text{tds}} / I_{\text{Bragg}} = (I_{\text{meas}} - I_{\text{Bragg}}) / I_{\text{Bragg}}$$

Empirical estimates of  $\alpha$  values are obtained from  $\alpha_{\text{obs}} = (I_1/I_2) - 1$ , where  $I_1$  is the net intensity above a single least-squares straight line fitted to the two background samples at either side of the peak, and  $I_2$  is the net intensity above a model TDS background function. The peak limits for fitting these backgrounds are calculated using the peak width parameters in the file *BGLP.INPUT* from program REFPK. The program provides four simple models for the TDS background:

1. A pair of least-squares straight lines,  $y = a + b1 \times x$  and  $y = a + b2 \times x$ , the first fitted to the lower angle background sample and the second to the higher angle background sample, with the constraint that the two lines intersect at the abscissa of the intensity-weighted centroid of the peak.
2. A pair of exponential curves,  $y = a \times \exp(b1 \times x)$  and  $y = a \times \exp(b2 \times x)$ , which are fitted linearly as  $\ln(y) = \ln(a) + b1 \times x$  and  $\ln(y) = \ln(a) + b2 \times x$ , respectively. The first curve is fitted to the lower angle background sample, and the second to the higher angle background sample, again with the constraint that the two curves intersect at the abscissa of the intensity-weighted centroid of the peak.
3. A Lorentzian peak,  $y = 1/(a + b \times x^2)$ , which is fitted linearly as  $1/y = a + b \times x^2$  to the background outside the peak limits.
4. A Gaussian peak,  $y = a \times \exp(-b \times x^2)$ , which is fitted linearly as  $\ln(y) = \ln(a) + b \times x^2$  to the background outside the peak limits.

The coefficient  $\alpha$  is in general an anisotropic quantity, and it is known that the equivalent isotropic  $\alpha$  values vary proportionately as  $\sin^2\theta/\lambda$ . The program calculates least-squares parameters for both an isotropic and an anisotropic fit to the empirical  $\alpha$  values,  $\alpha$  (obs).

To calculate isotropic  $\alpha$  values, the program evaluates a coefficient  $\alpha$  (0), defined by

$$\alpha_{\text{calc}} = \alpha(0) \times \sin^2\theta/\lambda$$

by fitting a least-squares straight line with zero intercept ( $y = a \times x$ ) to  $\alpha$  (obs) versus  $\sin^2\theta/\lambda$ . To calculate anisotropic  $\alpha$  values, the program evaluates least-squares values of six coefficients  $\alpha_{ij}$  ( $i \leq j = 1,3$ ) of a symmetric second rank tensor, defined by

$$\alpha_{\text{calc}} = (1/4) \times h_j \times \alpha_{ij} \times h_i,$$

where index repetition implies summation. *i.e.*,

$$\alpha_{calc} = 1/4 \times \sum_{i=1,3} \sum_{j=1,3} h_i h_j \times \alpha_{ij}$$

where  $h_i = ih_i \times a_i^*$  ( $ih_i$  are the Miller indices of the reciprocal lattice point, and  $a_i^*$  are the lengths of the reciprocal lattice translation vectors). For the least-squares evaluation of both  $\alpha(0)$  and  $\alpha_{ij}$ , the quantity minimized is

$$\chi^2 = \sum wt \times (\alpha_{obs} - \alpha_{calc})^2$$

and the weights are given by a product of two weighting factors,  $wt = wt1 \times wt2$  where

$$wt1 = 1 / [\{\sigma(l_1) / l_2\}^2 + \{(\sigma(l_2) \times l_1) / l_2^2\}^2], \text{ and}$$

$$wt2 = 1 / [1 + a2 \times \sin^2\theta / \lambda].$$

The weighting factor  $wt1$  is the reciprocal of the variance of the ratio  $l_1 / l_2$ , and the weighting factor  $wt2$ , with variable coefficient  $a2$ , allows the user to emphasize the fit to the lower angle data, for which the cusp character of the TDS peak under the Bragg peak is not pronounced, and for which the simplest TDS background model, a pair of intersecting straight lines, might be expected to be an adequate model of the low, broad TDS peak - see, e.g., E. Barnighausen, *J. Appl. Cryst.*, **8**, 477 (1975); **11**, 221 (1978). The weighting by  $wt2$  is reinforced by the weighting by  $wt1$ , because of the generally smaller  $\sigma(l) / l$  ratios for the lower angle data. Only reflections that pass several quality tests are used as observations in the least-squares fit of the TDS coefficients, and the numbers of reflections that fail the several tests are tabulated:

- N1 rejected because the intensity-weighted peak centroid was poorly determined
- N2 rejected because one or the other background sample was too short
- N3 rejected because the background levels at the two ends of the scan were too unequal
- N4 rejected because  $l < \{cutoff2 \times \sigma(l)\}$  for one or the other estimate of  $l$
- N5 rejected because the fit of the model TDS background was not significantly better than the fit of the linear background

#### 4.1 Input files required for programs TDSBG/TDSCOR

1. *RAW.DATA* file of raw reflection profile data
2. *BGLP.INPUT* file from program REFPK
3. *HKLCDON.DAT* file from programs REFPK and BGLP (optional)
4. *TDSBG.INPUT* file written by the DREAR GUI

## 4.2 Control data files TDSBG.INPUT and TDSCOR.INPUT

Card	Parameter(s)	Description	Format
<b>file</b>	<b>TDSBG.INPUT</b>		
1	ISYSTEM	crystal system (1= triclinic, 2=monoclinic, 3=orthorhombic, 4=tetragonal, 5=trigonal, 6=hexagonal, or 7=cubic). Default ISYSTEM=1	I10
2	IMODEL	TDS background model (1=straight lines, 2=exponential curves, 3=Lorentzian peak, or 4=Gaussian peak). Default IMODEL=1	I10
3	FMIN, FMAX	Minimum and maximum width of background samples to be fitted. FMIN, FMAX are multiple or fraction of half-peak base-width. FMIN is used to select scans with sufficiently wide background samples at either side of the peak. FMAX limits the width of the background sample to which the TDS model will be fitted at each side of the peak. Default FMIN=FMAX=1.0	2F10.0
4	A2	Weighting coefficient for $\sin\theta/\lambda$ . weighting	F10.0
5	NEWCUT	Threshold for statistical significance tests. If NEWCUT $\neq$ 0, it replaces the value of cutoff from the <i>BGLP.INPUT</i> file from program REFPK Default NEWCUT=0.0	F10.0
6	SMIN, SMAX	$\sin\theta/\lambda$ .limits for reflections to be used in the analysis. Default SMIN=0.0, SMAX=9.0	2F10.0
<b>file</b>	<b>TDSCOR.INPUT</b>		
1	FILE1	name of input reflection data file	A
2	FILE2	name for output file of TDS corrected data	A
3	MODE, ICOR, ICON	MODE is data format (always 1). ICOR=1 for isotropic, ICOR=2 for anisotropic TDS model. ICON=0 do not apply, ICON=1 apply crystal symmetry constraints to anisotropic model.	3I5

## 5.0 User's Instructions for the Program ABSORB

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Absorption corrections from indexed crystal faces and lengths of face normals by Gaussian numerical integration over the crystal volume. If output of the absorption-weighted mean path length,  $t_{bar}$ , and the reverse-incident and diffracted beam direction cosines,  $S_0$  and  $S_1$ , is requested,  $S_0$  and  $S_1$  are given as components referred to the direct space crystal axes  $a$ ,  $b$ ,  $c$ . The IORIENT code for this format in SORTAV is -7 (NOTE : this is different to the standard SHELX convention !)

### 5.1 Purpose

Calculate and apply absorption corrections for crystals with natural faces, in or out of capillaries.

### 5.2 Introduction

This program calculates and applies Gaussian numerical integration absorption corrections to crystals with natural faces or crystals that can be approximated by natural faces, De Titta (1985). It will also calculate and correct for absorption by glass capillaries of various sorts and allows for a completely general orientation of the capillary with respect to the crystal and the goniometer head. The program has been tested against data supplied by Alcock (1974) and Flack, Vincent & Alcock (1980). Along with the transmission factors the programs produce a variety of geometrical calculations concerning the crystal shape.

### 5.3 Method

The application of Gaussian quadrature techniques for calculating transmission factors was described by Busing & Levy (1957). Poppens (1970) described the matrix algebra necessary for the calculations. A fuller description of the techniques is given in appendix A. The place in the scheme of things for absorption correction is after time-dependent scaling and before sorting-merging-averaging the data.

### 5.4 Program setup

A list of information should be assembled before running the program. Items necessary include:

1. name of the crystal
2. input reflection file name
3. output reflection file name to be used by ABSORB
4. unit cell dimensions

5. x-ray wavelength symbol (for Cu, Mo, or Ag  $K_\alpha$  or  $K_\beta$ ) or radiation wavelength and linear absorption coefficient (for other X-radiations or neutrons)
6. elemental composition of the crystal chemical unit and the number of crystal chemical units per unit cell
7. Miller indices of the crystal faces and their perpendicular distances from a common origin point in or on the crystal
8. desired reciprocal lattice directions for the axes of the Gaussian integration grid and desired number of grid divisions along each axis
9. Diffractometer type and diffractometer orientation matrix
10. If a capillary crystal enclosure was used, the type of glass and the capillary diameter and wall thickness
11. If a correction is needed for an inhomogeneous, quasiparallel beam from an incident-beam monochromator, the coefficients of a polynomial fitted to the profile of the beam.
12. The linear absorption coefficient must be in units of reciprocal millimeters (not centimeters), and the face normal lengths must be in units of millimeters (not centimeters).

### 5.5 Crystal faces

Each face of a crystal can be completely specified by its Miller indices and the distance to the face from a point within or on the surface of the crystal. This distance is measured along the line perpendicular to the face which passes through the point chosen as the absorption origin. It is particularly advantageous to select a vertex (corner) of the crystal as the absorption origin since the perpendicular distances of the three planes which form the vertex are uniquely zero.

### 5.6 Grid point data

The three directions along which the grid for Gaussian integration is laid out are specified by three reciprocal axial vectors. Generally the three principal directions are chosen ( $a^*$ ,  $b^*$ ,  $c^*$  corresponding to 1,0,0; 0,1,0; and 0,0,1) but for crystals of non-uniform dimensions (thin plates, long needles) it may be advantageous to specify one grid along a direction most rapidly varying in dimension. Gaussian grid weights and fractions are tabulated for the values 2-10 inclusive, 12, 16, 20, 24, 32, 40, 48, 64, 80 and 96. Current program dimensions restrict the total number of grid points to  $\leq 4096$ ; e.g.,  $16^3$ ,  $4 \times 10 \times 96$  are acceptable. Keep in mind that computer time goes up roughly linearly with the number of grid points sampled and that acceptable results for approximately equi-dimensional crystals with moderate absorption can be had with as few as  $2 \times 2 \times 2$  points.

### 5.7 Capillary data

If the crystal is encapsulated in a capillary tube and if you wish to make the capillary correction you must specify the type of glass (pyrex, fused quartz or Lindemann), the diameter and the thickness of the capillary. In addition you must specify the orientation of the capillary on the goniometer head and the displacement of the crystal from the capillary axis (see Section 4.10). It is worth noting that the capillary orientation is most easily specified if the capillary axis is parallel to the phi axis of the diffractometer, and that variations in absorption



due to the capillary are minimized when the crystal center of mass is along the capillary axis.

## 5.8 Units

All linear dimensions, such as the face-perpendicular distances, the radius and thickness of the capillary, the edges and diagonals of the crystal, etc. are in millimeters. The linear absorption coefficients  $\mu_x$  for the crystal and  $\mu_c$  for the capillary are in reciprocal millimeters.

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## 5.9. The Absorption Correction Technique

### 5.9.1 Vectors

The unit cell real and reciprocal vectors are the natural frames for the absorption correction. To review notation we state without further explanation

real basis vectors:  $a, b, c$

reciprocal basis vectors:  $a^*, b^*, c^*$

real metric tensor:  $g = \begin{pmatrix} a.a & a.b & a.c \\ b.a & b.b & b.c \\ c.a & c.b & c.c \end{pmatrix}$

reciprocal metric tensor:  $g^* = \begin{pmatrix} a^*.a^* & a^*.b^* & a^*.c^* \\ b^*.a^* & b^*.b^* & b^*.c^* \\ c^*.a^* & c^*.b^* & c^*.c^* \end{pmatrix}$

length of a real vector:  $d = xa + yb + zc$   
 $d = (d.d)^{1/2}$   
 $= [(xa + yb + zc).(xa + yb + zc)]^{1/2}$   
 $= [x^2 a.a + y^2 b.b + z^2 c.c + 2(xya.b + yzb.c + zxc.a)]^{1/2}$   
 $d = \begin{bmatrix} (x & y & z) \\ & g & \\ & & (x) \end{bmatrix}^{1/2} = \begin{bmatrix} (x) \\ (y) \\ (z) \end{bmatrix} = (x^t g x)^{1/2}$

length of a reciprocal vector:  $d^* = ha^* + kb^* + lc^*$

$$d^* = \begin{bmatrix} (h & k & l) \\ & g^* & \\ & & (h) \end{bmatrix}^{1/2} = \begin{bmatrix} (h) \\ (k) \\ (l) \end{bmatrix} = (h^t g^* h)^{1/2}$$

### 5.9.2 Conversion of bases:

The physical vector  $q$  can be expressed in either the real space basis,

$$q = xa + yb + zc = [x \ y \ z] \begin{pmatrix} a \\ b \\ c \end{pmatrix} = x^t a,$$

$$\begin{pmatrix} b \\ c \end{pmatrix}$$

or the reciprocal basis set basis,

$$q = ha^* + kb^* + lc^* = [h \ k \ l] \begin{pmatrix} a^* \\ b^* \\ c^* \end{pmatrix} = h^T a^* ,$$

where the real and reciprocal space components of  $q$  are related by

$$\begin{pmatrix} h \\ k \\ l \end{pmatrix} = \begin{pmatrix} x^* \\ y^* \\ z^* \end{pmatrix} = g \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

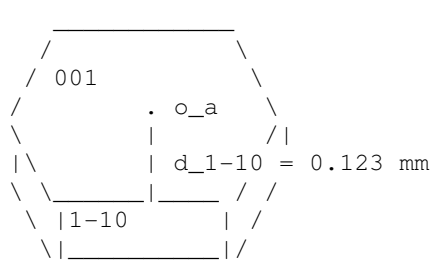
or

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} h^* \\ k^* \\ l^* \end{pmatrix} = g^* \begin{pmatrix} h \\ k \\ l \end{pmatrix} .$$

note, however, if xyz are unitless then  $x^* y^* z^*$  are in  $\text{\AA}^{-2}$ .

### 5.9.3 Face vectors

Let a crystal be bounded by natural faces. Then the complete description of the geometry of a crystal bounded by  $n$  faces is given by specifying the Miller indices  $hkl$  and perpendicular distances  $d_{hkl}$  of the  $n$  faces from an absorption origin  $o_a$  on or within the crystal



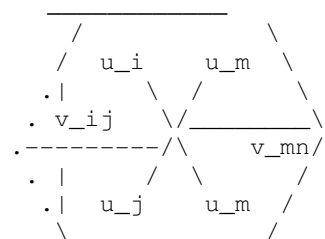
i	$h_i \ k_i \ l_i$	$d_i$ (mm)
1	0 0 1	$d_1 = 0$
2	1 -1 0	$d_2 = 0.123 \text{ mm}$
3	$h_3 \ k_3 \ l_3$	$d_3$
.	.	.
.	.	.
.	.	.
n	$h_n \ k_n \ l_n$	$d_n$

a face direction is defined by the unit vector

$$u_{hkl} = d_{hkl}^* / d_{hkl}^* .$$

### 5.9.4 Vertices of a crystal

The vertices (corners) of a crystal are where three faces meet at a point. Vertex vectors are constructed as follows. The point where three faces intersect must fulfill the three equalities



$$\begin{aligned} v_{ijk} \cdot u_i &= d_i \\ v_{ijk} \cdot u_j &= d_j \\ v_{ijk} \cdot u_k &= d_k \end{aligned}$$

here,  $v_{ij}$  is a virtual vertex,  
and  $v_{mm}$  is a physical vertex.

If we express  $v_{ijk}$  in terms of its real basis components

$$v_{ijk} = \begin{bmatrix} a & b & c \end{bmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}$$

and  $u^*_i, u^*_j, u^*_k$  in terms of their reciprocal space components

$$u^* = \begin{bmatrix} a^* & b^* & c^* \end{bmatrix} \begin{pmatrix} u_{i1} \\ u_{i2} \\ u_{i3} \end{pmatrix}, \text{ etc.,}$$

then

$$\begin{aligned} v_{_1} u_{_i1} + v_{_2} u_{_i2} + v_{_3} u_{_i3} &= d_{_i} \\ v_{_1} u_{_j1} + v_{_2} u_{_j2} + v_{_3} u_{_j3} &= d_{_j} \\ v_{_1} u_{_k1} + v_{_2} u_{_k2} + v_{_3} u_{_k3} &= d_{_k} \end{aligned}$$

in matrix notation

$$\begin{pmatrix} u_{_i1} & u_{_i2} & u_{_i3} \\ u_{_j1} & u_{_j2} & u_{_j3} \\ u_{_k1} & u_{_k2} & u_{_k3} \end{pmatrix} \begin{pmatrix} v_{_1} \\ v_{_2} \\ v_{_3} \end{pmatrix} = \begin{pmatrix} d_{_i} \\ d_{_j} \\ d_{_k} \end{pmatrix} \quad \text{or} \quad u v = d$$

so

$$\begin{pmatrix} v_{_1} \\ v_{_2} \\ v_{_3} \end{pmatrix} = u^{-1} \begin{pmatrix} d_{_i} \\ d_{_j} \\ d_{_k} \end{pmatrix}$$

where  $u^{-1}$  represents the matrix inverse to  $u$ .

Not all vertices generated in this manner are real, physical vertices. Consider the two-dimensional example of the virtual vertex vector  $v_{mn}$  formed by the virtual intersection of the  $m$ -th and  $n$ -th crystal planes. This vertex vector lies outside the physical boundaries of the crystal. So for a point to be a vertex it must also satisfy

$$\{ v_{ijk} \cdot u^*_l \leq d_l, \quad l = 1 \text{ to } n \text{ planes} \} .$$

### 5.9.5 The transmission factor $a$

For monochromatic radiation passing parallel through a block of material the transmission factor  $a$  is given by

$$a = i/i_0 = \exp(-\mu t)$$

where  $i_0$  is the intensity of the unattenuated beam,  $i$  the intensity of the attenuated beam,  $t$  the thickness of material, and  $\mu$  the linear absorption coefficient. In order to calculate the transmission factor we must know either  $i/i_0$  or  $\mu t$ . Generally it is easier to estimate  $\mu t$ .

### 5.9.6 The linear absorption coefficient $\mu$

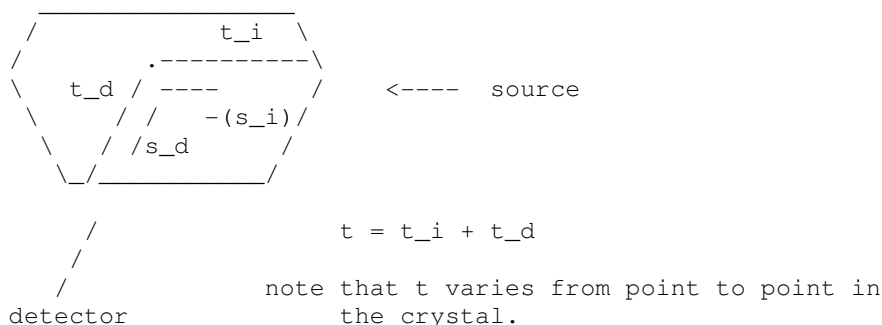
The value of  $\mu$  is calculated according to the mixing rules described in the International Tables for X-ray crystallography, Vol. II. briefly,

$$\mu = \rho \sum_i f_i (\mu/\rho)_i, \quad i = 1, 2, \dots, n,$$

where  $\rho$  is the mass density,  $f_i$  the mass fraction of the  $i$ -th element in the unit cell and  $(\mu/\rho)_i$  is the mass absorption coefficient of the  $i$ -th element. Values of  $(\mu/\rho)$  are taken from Vol. IV of *International Tables for X-Ray Crystallography*.

### 5.9.7 The path length $t$

For a crystal mounted on a diffractometer the calculation of  $t$ , the total path length, is broken down into calculating  $t_i$  and  $t_d$ , the path lengths along the incident and diffracted beam directions, respectively.



Concentrating on one volume element at  $p$  we see that

$$t_{dj} = d_j - p \cdot u^*_j / (s_d \cdot u^*_j)$$

where the volume element of interest is specified by vector  $p$  relative to the absorption origin  $oa$ , the diffracted beam direction is specified by the vector  $s_d$ ,  $t_{dj}$  is the distance from the point  $p$  to the  $j$ -th crystal face,  $d_j$  is the perpendicular distance to the  $j$ -th crystal face, and  $u^*_j$  is the unit vector describing the direction of the perpendicular to the  $j$ -th face.

A similar expression exists for  $t_{ij}$ , the distance to the source

$$t_{ij} = d_j - p \cdot u^*_j / (s_i \cdot u^*_j)$$

where  $s_i$  is the unit vector in the direction of the reverse primary beam. Note that  $u^*_j$ 's are expressed in terms of their reciprocal basis components. It is advantageous to express  $p$ ,  $s_d$  and  $s_i$  in terms of their real basis components. Also note that, for every point  $p$  in the crystal, we must test each face (1 to  $n$ ) to calculate  $t_{ij}$  and  $t_{dj}$  ( $j = 1$  to  $n$ ). for a particular point  $p$  the face through which the beam penetrates is that one with  $t_i (> 0)$  a minimum and the face of beam exit is that with  $t_d (> 0)$  a minimum.

### 4.9.8 Getting $S_i$ and $S_d$ in terms of their real space components

A detailed description of the various coordinate frames of use on a diffractometer has been given by Busing and Levy (1967). To get the real space

components of the unit vectors defining the directions of the reverse primary and diffracted beams, respectively, we need to know the observed angles for a particular reflection  $\{2\theta, \omega, \phi, \chi\}$  or  $\{\theta, \kappa, \phi_\kappa, \chi_\kappa\}$  on the P3/F or CAD4, respectively, the orientation matrix UB, and the diffractometer conventions. For the P3/F a reflection measured on the positive side of  $2\theta$  has real space components, similarly here  $g^*$  has its usual meaning,  $UB^{-1}$  is the inverse of the orientation matrix printed by the P3/F, and  $R^{-1}$  is the inverse of the P3/F rotation matrix. For a reflection measured on the P3/F at angles  $\{2\theta, \omega, \phi, \chi\}$  we define R by its elements

$$\begin{aligned} R11 &= \cos(\omega-\theta)\cos(\phi) + \sin(\omega-\theta)\cos(\chi)\sin(\phi) \\ R12 &= \cos(\omega-\theta)\sin(\phi) - \sin(\omega-\theta)\cos(\chi)\cos(\phi) \\ R13 &= -\sin(\omega-\theta)\sin(\chi) \\ R21 &= \sin(\omega-\theta)\cos(\phi) - \cos(\omega-\theta)\cos(\chi)\sin(\phi) \\ R22 &= \sin(\omega-\theta)\sin(\phi) + \cos(\omega-\theta)\cos(\chi)\cos(\phi) \\ R31 &= \sin\chi(\chi)\sin(\phi) \\ R32 &= -\sin\chi(\chi)\cos(\phi) \\ R33 &= \cos(\chi) \end{aligned}$$

For the CAD4 a reflection measured on the positive side of  $2\theta$  has components for a reflection measured at  $\{\theta, \kappa, \phi_\kappa, \chi_\kappa\}$

$$R_{CAD} = \begin{matrix} A & B & C & D & E \end{matrix} \quad \text{where}$$

Note that both  $R_{P3}$  and  $R_{CAD}$  are rotation matrices with the property

$$R^{-1} = R^t \quad (\text{inverse equals transpose});$$

that is, R is unitary. For the CAD4  $a = 49.96681$  deg.

### 5.9.9 Specifying the sampling points

We have seen that the path lengths  $t_i$  and  $t_d$  depend not only on the particular reflection under consideration (that is to say that  $s_i$  and  $s_d$  change from reflection to reflection depending on the diffractometer angles) but also that for any particular reflection  $t_i$  and  $t_d$  vary within the crystal. If we had, for example, a rectangular crystal such as at the left we might look at 6 points in the crystal for a sampling of the absorption, and since the 6 points were representative of equal volumes of the crystal each would have an equal weight in an averaging procedure.

We would look at each point  $p_i$  in turn, calculate the vector  $p_i$  for the point, get  $t_d$  and  $t_i$ , and calculate the transmission factor for that point

$$a_i = \exp\{-\mu_x(t_d + t_i)_i\}$$

then the average transmission factor would be ? If, however, the six sampling points were not representative of equal crystal volumes, for various reasons, such as we see in this case below, then we would properly weight the absorption by the volume of the element ...

In the limit of sampling an infinite number of points, each with volume  $dv$  ....

Since we cannot hope to sample much more than 4K points in a crystal per reflection we retreat to... We now have to consider ways of sampling the crystal volume. The isometric grid, illustrated above, presents some difficulties. First, we can see that sometimes a grid point can lie just outside the crystal and therefore is not a valid sampling point. Second, it is difficult to design an isometric grid which samples close to, but always inside, the surface of the crystal. The Gaussian technique answers both objections. A full explanation of the layout of the Gaussian grid is beyond the scope of this technical report; a description of the one-dimensional Gaussian integration technique is given by Whittaker & Robinson (1967).

### 5.10 Capillary Correction

If the crystal is encapsulated in a thin-walled glass capillary severe, asymmetric absorption effects can be seen to arise from the capillary alone. In order to correct for the capillary absorption, its orientation relative to the phi axis and position relative to the crystal must be known. The program will, as an option, make corrections for three types of capillary glass (pyrex, fused quartz, lindemann) and three wavelengths (Ag, Mo, Cu). the values of mu\_cap used are given in the table.

	mu_cap (in mm <sup>-1</sup> )		
glass			
lindemann	0.094	0.161	1.483
pyrex-7740	0.368	0.717	7.105
fused quartz	0.411	0.807	8.021

Most capillaries have a nominal wall thickness of 0.01 mm and radii of 0.3, 0.4 and 0.5 mm are typical. The technique for the capillary correction has been briefly described by Wells (1960). In order to use it in complete generality we here define a coordinate frame fixed in the standard Huber goniometer head with arcs.

- Place the goniometer head on a table with a wall directly behind it. Rotate the goniometer head until the notch in the base faces to the right as you look towards the wall (i.e., if the direction of view towards the wall is north place the notch to the east). The top arc is now perpendicular to your point of view, and the scribe marks can be read. If the capillary is inclined with its top to the left and base to the right it is inclined with angle sigma positive.
- Turn the goniometer so that the notch faces you. The bottom arc can be read. If the capillary appears to be inclined top left/bottom right again it is inclined with angle tau positive.
- If the capillary is mounted rigidly in the brass pin with its axis parallel to the pin axis sigma and tau can be read directly from the arcs of the goniometer head. If the capillary is tilted with respect to the pin it is better to disregard the arc readings and determine sigma and tau by a simple experiment. Orient the notch to the right again. Shine a parallel source of
- light (ao microscope light) on to the capillary and observe the shadow of the capillary on the wall. put dots on the wall (pencil) to record the shadow. Place a t square on the table and draw a line vertical (perpendicular to the

table top) through the dots. The angle sigma can be read with a protractor. Similarly tau can be measured.

- The values of sigma and tau so obtained are usually +10 to -10 degrees and with care can be read to plus-or-minus 0.5 degrees. The positive directions for both angles holds for the use of the goniometer head on either the CAD-4 or P3/F.
- To determine the displacement of the crystal from the capillary axis we make the assumption that either the center-of-mass of the crystal is at the diffractometer center or is displaced a known amount. The former is obviously preferable and we treat it here. For the P3/F we assume the telescope has been aligned so that the cross-hairs point at the instrument center and the grid markings are horizontal in the field of view. Set chi = 335 degrees so that the phi axis is perpendicular to the telescope axis. We define the capillary displacement vector  $k$  by its components in the diffractometer phi coordinate frame. The sense of  $k$  is that it is from the diffractometer origin to the capillary axis. The phi base vectors are oriented as shown below at the 4 values of phi which bring the arcs parallel and perpendicular to the telescope axis.
- Each small hash mark on the P3/F telescope corresponds to 0.06 mm. An example of a capillary displaced +0.15 mm in  $x$  is shown below. This can be read by averaging the hash mark values of the outer diameter of the capillary intersecting the horizontal axis. better technique suggests averaging the results at phi = 25 and phi = 205; phi = 115 and phi = 295 deg.
- For the CAD-4 similar arguments hold. At kappa = 134.89 deg the phi\_kappa axis is perpendicular to the telescope axis. Each division on the telescope is 0.02 mm. The phi axial system corresponding to arcs parallel and perpendicular to the telescope axis is shown below

## 5.11 File Structures and Program Limitations

### 5.11.1 Data files

Input is normally the output of a scaling program such as TSCALE. The output file has the same form as the input file, with direction cosines and  $tbar$  values. Both files are unformatted binary.

### 5.11.2 Control file - ABSORB.INPUT

*ABSORB.INPUT* is a formatted file which is created and edited by the DREAR GUI

### 5.11.3 Limitations

number of crystal bounding faces: 50  
number of vertices: 150  
number of Gaussian grid points: 4096  
grid divisions permissible: 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 16, 20, 24, 32, 40, 48, 64, 80, 96

### 5.11.4 Constants

The molecular weight is calculated from atomic weights of the Sargent-Welch periodic table of the elements (1968) except for Li. The mass absorption

coefficients ( $\mu/\rho$ ) for six wavelengths (Ag, Mo, Cu)  $\times$  ( $\alpha$ -bar,  $\beta$ ) are from *International Tables* Vol. IV. The composition of glasses and densities are from Shand (1958). The Gaussian weights and fractions are from Abramowitz & Stegun (1972) and are those compiled by P.J. Davis and I. Polonsky. see page 887, eq. 25.4.29 and Table 25.4 (pgs. 916-919). The limits of the integration have been changed from  $\{-1$  to  $+1\}$  to  $\{0$  to  $1\}$ , see Whittaker & Robinson (1967).

## 5.12 References for ABSORB

1. Alcock, N. (1974). Absorption and extinction corrections: Calculation methods and standard tests, *Acta Cryst.* **A30**, 332-335.
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4. Coppens, P. (1970). in *Crystallographic Computing*, F.R. Ahmed, Ed., Munksgaard, Copenhagen.
5. Davis, P.J. and Polonsky, I. (1972) in *Handbook of mathematical functions*, M. Abramowitz and I.A. Stegun, Eds., Dover Press, NY.
6. Flack, H.D., Vincent, M.G. and Alcock, N.W. (1980). Absorption and extinction corrections: standard tests, *Acta Cryst.* **A36**, 682-686.
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8. Wells, M. (1960). *Computation of absorption corrections on EDSAC II*, *Acta Cryst.* **13**, 722-726.
9. Whittaker, E. and Robinson, G. (1967), *The Calculus of Observations*, Dover Publications, Inc., NY
10. DeTitta, G.T. (1985). ABSORB: An absorption correction program for crystals enclosed in capillaries with trapped mother liquor. *J. Appl. Cryst.* **18**, 75-79.