

Chapter 4.3

REFINED METHODS

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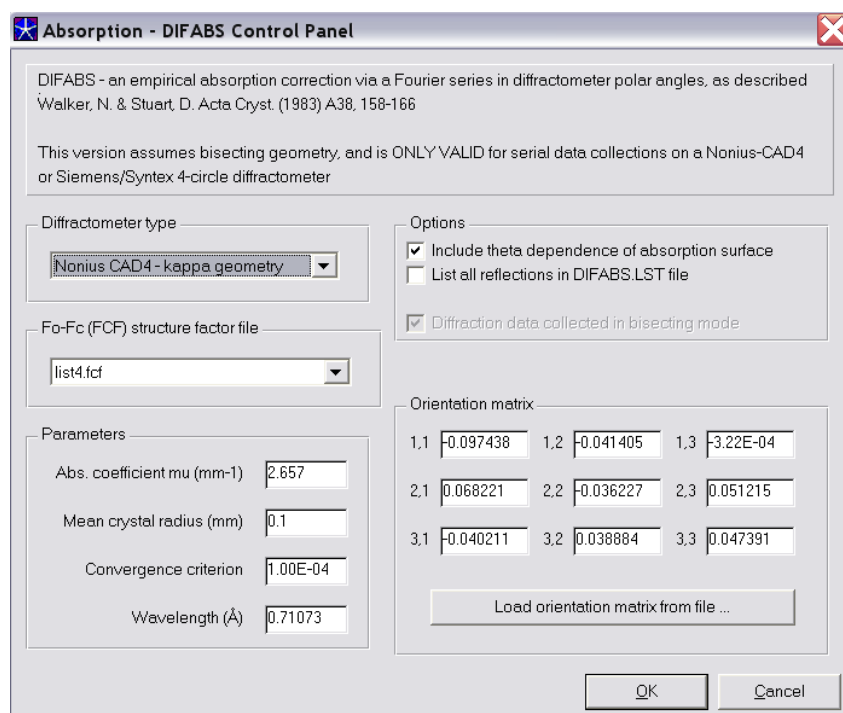
These methods are the least scientifically valid methods, in that they require a refined model, and provide a "correction" for the data based on the assumption that any consistent differences between the calculated and observed structure factors are due to absorption. The differences between the observed and calculated structure factors are modelled using a variety of mathematical formalisms, but all methods in this section suffer from the philosophical problem that the data is being modified according to the model.

All programs (except DELABS) read the structure factor file *name.FCF* written by the LIST 4 SHELXL command. This should be the result of refinement with the best model available and with the following caveats :

- all atoms are included in the model, including all H atoms
- all atoms are refined with *isotropic* thermal parameters (this is VERY important)
- an extinction correction is included (if necessary)
- the MERG 0 instruction is used, to suppress merging of the data and provide all equivalents in the *name.FCF* file.

These refined methods have fallen out of favour in the recent past, but if numerical corrections cannot be carried out, and if no extra intensities were measured, then these methods remain the only ones capable of providing some sort of correction for absorption. For most crystals containing elements heavier than the first row transition metals, it is likely that absorption is the single most important contributor to the systematic errors.

4.3.1 DIFABS

**Synopsis**

A low order term Fourier series is used to model an absorption surface for differences between the observed structure factors and those obtained from a structure factor calculation (after isotropic least squares refinement). Spherical polar angles are used to define the incident and diffracted beam path directions. This reduces the number of angles required to four - viz. PHI(p), MU(p), PHI(s) and MU(s). A theta-dependent correction is evaluated to allow for diffracted beams with different path lengths occurring at the same polar angles. Again, a low order term Fourier series is used; in Bragg angle, THETA.

DIFABS is written by Stuart and Walker (Acta Cryst (1983), A39, 158). This version is specific for CAD4 or P4- 4 circle geometry and usually provides a more satisfactory fit than the version DELABS implemented in PLATON.

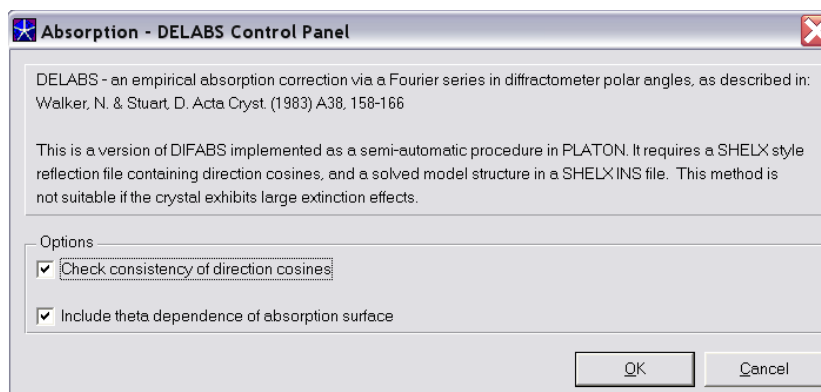
Files read

name.OMX - the orientation matrix (written by programs XCAD4 or PROFIT).
name.FCF - a structure factor file written by SHELXL using the LIST 4

Files written

DIFABS_CAD4.HKL - absorption corrected reflection file
DIFABS.LST - List file giving summary of the applied corrections
DIFABS.CIF - CIF containing relevant information

4.3.2 DELABS



The DELABS filter in PLATON for empirical absorption correction requires two inputfiles:

shelxl.hkl : (SHELX HKLF 4 + Direction Cosines) reflection file

shelxl.res : A file containing the current set of refined parameters.

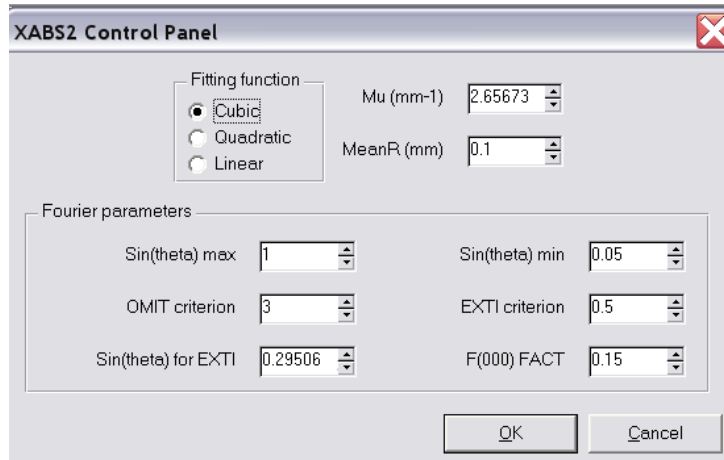
Notes:

The required direction cosines on **shelxl.hkl** should conform with the SHELX76 style. Such a file should be made available by the data reduction program used.

The optional **NOCHECK** sub-keyword overrules the checking of the direction cosines. This option should be used for good reasons and with great care.

- DELABS will calculate the structure factors needed for this procedure internally using the positional and displacement parameters given in the '.res' file. When applicable, all anisotropic displacement parameters are converted to U(eq)'s.
- DELABS can also handle (pseudo)-merohedral twins described with the SHELXL TWIN/BASF mechanism.
- A DELABS run may be done (when applicable) on the reflection file modified by SQUEEZE.
- Be aware of the fact that the use of DELABS/DIFABS as an Empirical Absorption correction technique is considered to be 'sloppy crystallography' by some crystallographers/referees/journals.
- DELABS/DIFABS will in general 'correct' for more than just absorption. It will take care of systematic errors related to data collection on crystals too large for the homogeneous part of the X-Ray beam.
- In general, anisotropic thermal parameters will be less meaningful because their average deviation from spherical tends to be 'absorbed' in the correction, making the heaviest atom in the structure look isotropic.
- This implementation attempts to avoid possible human errors due to (or related with) cell transformation matrices, scaling factors, anisotropic displacement parameter model etc.

4.3.3 XABS2

**Synopsis**

XABS2 is a program to calculate empirical absorption corrections from the calculated and observed structure factors. The original XABS (H. Hope and B. Moezzi, Jul83, Feb84, May85) obtained 12 coefficients from a linear least-squares fit in $\sin^2\theta$ to $(1/A \text{ vs } \sin^2\theta)$, by minimizing weighted differences between F^2_{obs} and F^2_{calc} . XABS2 calculates either 24, 18 or 12 coefficients from a least-squares fit of $(1/A \text{ vs } \sin^2\theta)$ to either a cubic, quadratic or linear equations in $\sin^2\theta$ by minimization of F^2_{obs} and F^2_{calc} differences. You can choose whether to do a linear, quadratic or cubic fit. A cubic fit is better for Cu Ka radiation with data to $2\theta > 90$ degrees. A linear fit is better for Mo Ka or Cu data that has a restricted resolution, such as in macromolecular crystallography.

The program XABS2 is written by Sean Parkin et al.

Files read

name.FCF - written by SHELXL (LIST 4, MERG 0 instructions, based on ISOTROPIC refinement).

name.INS - for unit cell information only.

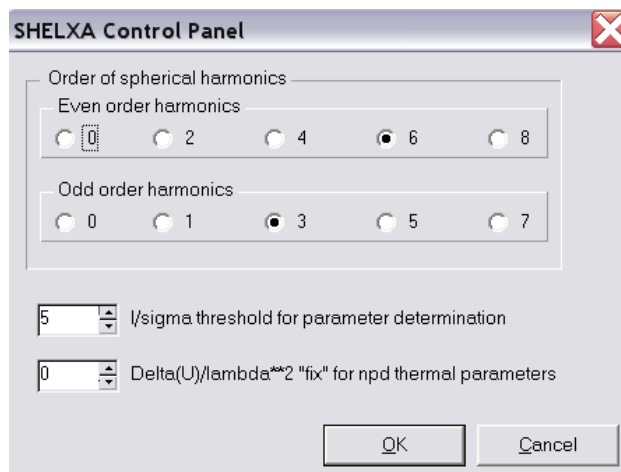
Files written

XABS2.HKL - absorption corrected reflection file

XABS2.LST - List file giving summary of the applied corrections

XABS2.CIF - CIF containing relevant information

4.3.4 SHELXA



The program **SHELXA** has been kindly donated to the system by an **anonymous user**. This applies "absorption corrections" by fitting the observed to the calculated intensities as in the program DIFABS. SHELXA is intended for **EMERGENCY USE ONLY**, eg. when the world's only crystal falls off the diffractometer before there is time to make proper absorption corrections by indexing crystal faces or by determining an absorption surface experimentally by measuring equivalent reflections at different azimuthal angles etc.

SHELXA reads an *name.FCF* file written by SHELXL (using LIST 4 or LIST 6 and any combination of MERG, OMIT etc.) or a .raw file in SHELX HKLF 4 format containing "direction cosines", and writes a new SHELX .hkl file in HKLF 4 format. **THIS WILL OVERWRITE AN EXISTING .hkl FILE !** The following restrictions apply to the use of SHELXA:

(a) The structure should not be twinned (racemic twinning is allowed), the data should have been collected from one crystal (inter-batch scale factors should not have been refined), and there may not be a re-orientation matrix on the HKLF instruction. Otherwise there are no restrictions on the type of structure (SHELXA is equally (un)suitable for proteins) or the instructions used in the SHELXL refinement.

(b) It is understood that any structure determined by means of this scientifically dubious procedure **WILL NEVER BE PUBLISHED !** The anonymous author of SHELXA has no intention of ever writing a paper about it that could be cited and thereby ruin his reputation.

The absorption is modeled by spherical harmonic functions using full-matrix least-squares more or less by the method of Blessing (1995). It is not this model that should be regarded as dubious, just the way SHELXA misuses it. Data are used for

parameter determination if the $I/\sigma(I)$ ratios for both the observed and calculated intensities exceed a given (by the `-t` switch) or assumed threshold (equal to 5.0). The `-u` switch specifies an artificial $\Delta U/\lambda^2$ value that is applied to the calculated intensities; this helps to prevent atoms going NPD, but the default value is zero. The `-e` and `-o` switches specify the highest even and odd order spherical harmonics to employ; the refinement could be unstable if these are too high, especially if only part of reciprocal space is sampled, eg. because only an asymmetric unit was collected for a high symmetry structure. Allowed values are (0,2,4,6,8) and (0,1,3,5,7) respectively. Thus:

```
shelxa -t3 -u0.002 -e4 -o1 baddata
```

would read `baddata.raw` and `baddata.fcf` and write `baddata.hkl`, with data with $I > 3\sigma(I)$ used to fit the absorption parameters, a $\Delta U/\lambda^2$ of 0.002 effectively added to all current isotropic displacement parameters, and highest even and odd harmonics 4 and 1 respectively. Such UNIX switches will also be recognized under MSDOS, VMS etc.; no spaces are allowed between the letter and value. The values employed for these switches are summarized by the program (on the standard output device). The filename stem (here `baddata`) must come last. Usually the default values should prove sensible, ie:

```
shelxa baddata
```

The data may be re-processed when, for example, extra atoms are added; however, as with DIFABS, best results are obtained if the procedure is last run with the final ISOTROPIC model; re-running it after anisotropic refinement will result in a deterioration of the structure and (most important) the R -factors. The ΔU fudge should not be used repetitively, because the effects will be cumulative !

Note that all esd 's estimated by SHELXL using data "corrected" in this way will be invalid unless the number of parameters used in the absorption model is input as the third L.S. parameter. This number depends on the settings of the `-e` and `-o` switches and is output by SHELXA.

The program can read either standard SHELX direction cosines (relative to the crystal reciprocal axes), or orthogonal direction cosines calculated by the method given in Blessing's paper. Siemens and Stoe write the SHELX .raw (HKL 4) format as standard, for CAD4 diffractometers XCAD4 is suitable. Users of other makes of diffractometer and area detectors will enjoy writing their own programs to generate direction cosines using Blessing's method; the anonymous author of SHELXA is of course not able to enter into any correspondence about this! For very large structures it may be necessary to change the number of reflections the program can handle by increasing the values of MR and MF in the PARAMETER statement at the start of the main program, and recompiling it.