

Chapter 3.2.7

DIFRAC

Single-Crystal Diffractometer Output Conversion Software

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3.2.7.1 Introduction

Users of several models of 4-circle single-crystal diffractometers may well have been struck by the diversity of form and content of the data files generated by diffractometer-manufacturers software. The form of the file can create difficulties in its transfer to other computing equipment and further renders the corresponding computer programs specific to a certain type or types of diffractometer. The difficulties in the content of the files manifest themselves principally by the paucity of the available information necessitating additional input to the data treatment software (e.g. type of radiation, wavelength of radiation, scan width, sense of rotation of angles on the single-crystal diffractometer, etc.). The problem has become aggravated in recent times by the rapid development in electronic data exchange. It is now frequent to exchange files by computer networking and electronic mail rather than by the standard means of the recent past, the 1/2in magnetic tape. The advent of machine-readable submission for publication, data-base and supplementary-material deposition further highlights the problem of missing data.

The motivation for producing this software arose from the work of the IUCr Subcommittee on Statistical Descriptors (Schwarzenbach, Abrahams et al., 1989). We wished to be able to perform structure refinements on the directly-observed quantities such as peak and background intensities (Schwarzenbach and Flack, 1991), crystal dimensions (Schwarzenbach, 1991; Blanc, Schwarzenbach and Flack, 1991) etc. which should not be corrected for any systematic effects. In this project we also had to face the problem of producing refinement and data-treatment software which would function smoothly on data produced by three different types of single-crystal diffractometer. Further it became clear that with the advent of machine-readable submission of structural papers to journals and data bases it would be highly advantageous to obtain a clear, complete, instrument-independent record of the diffractometer measurements and conditions in the form of a data file at the earliest possible opportunity i.e. while the crystal was still mounted on the instrument.

3.2.7.2 DIFRAC in WinGX

The implementation of DIFRAC in WINGX allows a choice of five serial diffractometer types:

1. CAD4
2. Siemens P21
3. Phillips PW1100
4. Stoe Stadi 4
5. Rigaku-Denki RD5

Only the CAD4 version has been tested (this is the only serial diffractometer type I *had* access to), the other four version are completely untested but come as is from the DIFRAC web-site. The output file is DIFRAC.CIF

3.2.7.3 DIFRAC System design

Table 1 presents the list of items that we considered essential to include in the converted single-crystal diffractometer output file. This information is intended to be complete and independent of the particular instrument used. It serves for the calculations of structure determination and refinement and contains the items considered necessary for machine submission of documents for publication or data bases. Some of the items we have chosen to include or exclude from our output list require special comment:

1. The chemical formula has been included in the converted output file although in some cases this might have to be revised as a result of the crystal structure analysis. The formula is useful in identifying the compound, and the element names and composition are necessary for running structure-solution and refinement software. Moreover, the subroutine (see below) which undertakes the interpretation of the chemical formula was already available to us.
2. On the other hand, the space group of the crystal has not been included. For a crystal of unknown structure, the exact space group will not be determined reliably until after structure refinement. Further it was thought that flexible software to test the integrity of the input of space group information in any form (e.g. a symbol, generators, or individual symmetry operations) would have greatly lengthened the time necessary to produce this version of DIFRAC.
3. The crystal orientation matrix (or matrices in the case of resetting) for the diffractometer (often called the UB matrix) and the diffractometer setting angles (omega, two-theta, chi, phi or kappa) for each reflection have not been included in the converted output file. All orientation information has been condensed into a crystal-based azimuthal angle psi for each reflection measurement. This psi is independent of the instrument geometry and axial definitions of the instrument. Full details are to be found in Schwarzenbach and Flack, (1989, 1992).
4. An index or code is included to identify the reference reflections. In our view it is not possible to correctly identify a reference reflection from its Miller indices alone. The inclusion of an index eases the work and programming of data-treatment and refinement software analysing the variations in the reference reflections.
5. The file includes a fairly detailed description of the incident-beam characteristics. This has been done to allow the calculation of polarization and beam-inhomogeneity corrections (Harkema, Dam, Van Hummel and Reuvers, 1980; Markov, Fetisov and Zhukov, 1990).

A choice had to be made concerning the format of the converted output file. The

necessity of being able to transmit the file over networks or by electronic mail imposes a clear-text (ASCII) form with no more than 80 characters per line. Additionally we required that the content and format of the file be clearly defined and relatively compact. The CIF - Crystallographic Information File (Hall, Allen and Brown, 1991) is available for just this purpose and we have it.

The information to be included in the converted output file is obtained from the following sources:

1. fixed geometrical details of the single-crystal diffractometer,
2. information in the diffractometer parameter file,
3. information in the diffractometer data file and
4. interactive questions and answers.

An underlying design principle in this arrangement is that information from the diffractometer files should be used, if available, otherwise a question will be asked just once only. This is most important to avoid confusion and frustration on the part of the user. It further explains our preference for installing the executable programs on the computer controlling the diffractometer so that each installation may be customized for its instrument and have access to those files which are not specific to the user.

3.2.7.4 DIFRAC Saved Answers

A system of saving the answers given to the questions asked by DIFRAC has been installed. This makes it possible to vastly speed up the use of DIFRAC if one has to rerun the program. Expert users might like to use this system to reduce the time necessary to run the question-and-answer session even in the case of a single run of DIFRAC. In every run of DIFRAC during the question-and-answer session, answers to questions are written to a file <compid>.qan , where <compid> is the compound identification of the compound studied. On each line of this file is an integer code of 6 digits identifying the question, followed by up to 80 characters as typed in reply to the question. The table below gives the correspondence between the integer code and the question asked.

At the beginning of a run, DIFRAC looks to see if a file called <compid>.qan is present:

- If <compid>.qan is present, the contents of this file are copied to a file <compid>.qao
- If <compid>.qan is not present, DIFRAC looks to see if a file answer.sty is present. If answer.sty is present, its contents are copied to <compid>.qao . During the question-and-answer session, saved answers are retrieved from the newly created <compid>.qao file and displayed to the user with a message ****Saved answer - Return to accept.* It is thus only necessary to type a *"Return"* to reply to the question with the saved answer.

For expert users wishing to create a-priori or edit existing <compid>.qan files, it is essential that the answers in this file appear in ascending order of their integer code. The integer code must occupy columns 1 to 6 of the file and the answer commences directly in column 7.

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000020 Give a title - max 66 characters:
000040 Do you wish to display the contents of this file (Y,N)?
000060 Do you wish to display the contents of this file (Y,N)? <compid>
000080 Do you wish to display the contents of this file (Y,N)? <compid>
010020 Do you have refined cell dimension data (Y,N)?
010040 Enter a, b, c, alpha, beta, gamma in Angstroms and degrees:
010060 Enter s.u.s in a, b, c, alpha, beta, gamma:
010080 Enter cell volume and s.u. in cubic Angstroms:
010100 How were these cell dimensions measured? enter wavelength,
temperature(k), 2theta-min, 2theta-max, number of reflections:
010120 Cell dimension data OK (Y,N)?
050020 Have you measured the density (Y/N)?
050040 Enter density, s.u. and temperature(K) of measurement:
050060 Density data OK (Y,N)?
100020 Make a choice for the shape of the crystal:
100040 Give sphere radius and s.u. in mm:
100055 How many indexed faces does the crystal have?
100060 Input one face per line: h,k,l,d, su(d).d and su(d) in mm. Finish with CTRL Z:
100080 Crystal shape OK (Y,N)?
150020 Enter Z, the number of formula units per cell:
150040 Enter chemical formula
150060 <chemical formula second line>
150080 Do you have a chemical analysis (Y/N)?
150100 Wt % and su of element:
150120 Do you have an observed value of the formula weight (Y/N)?
150140 Enter observed formula weight and s.u.(Daltons):
150160 Chemical formula data OK (Y,N)?
200020 Enter the melting-point temperature of the compound in K:
200040 Enter a description of the source of the chemical compound under study. If not known
leave blank:
200060 Enter the trivial name of the compound. If not known leave blank:
200080 Enter the mineral name of the compound
200100 Chemical compound data OK (Y,N)?
250020 Enter the colour of the crystal:
250040 Enter a description of the crystal quality and habit
250060 Enter special details concerning the preparation or mounting of the crystal otherwise
blank:
250080 Crystal data OK (Y,N)?
300020 Filter index xxx:
300040 Diffractometer attenuator data OK (Y,N)?
350020 Did you use a beta-filter(b) or a monochromator(m) (B,M)?
350040 Have you a measured value of the monochromator polarization ratio (Y,N)?
350060 Give polarization ratio and s.u.:
350080 Give monochromator 2-theta angle in degrees:
350100 Have you a measured value of the monochromator inhomogeneity half-width (Y,N)?
350120 Give inhomogeneity half-width(mm):
350140 Give beta-filter absorption edge wavelength(a):
350160 Diffractometer monochromator data OK (Y,N)?
400020 Have you a measured value of the counter dead time (Y,N)?
400040 Give measured dead-time and s.u. in microseconds:
400060 Counter dead time data OK (Y,N)?
450020 Enter temperature (k) and pressure during intensity measurement:
450040 Environmental conditions data OK (Y,N)?
500020 Enter the number of your name in the list:
500040 Enter your name as: family name(s) first name(s) or initials:
500060 Enter your address (5 lines):
500080 Enter your e-mail address:
500100 Enter your telefax number:
500120 Enter your telephone number:
500140 Name address data OK (Y,N)?

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3.2.7.5 Storing Raw Intensities

Raw observed intensity data are output to the converted file. In the current version of the program we have dealt only with low-angle background - integrated peak - high-angle background counts, thus leaving the problem of the transfer of profile data to a later date. Conversion of raw counts to net intensities P_{obs} (i.e. with background subtracted and allowing for differences in effective scan speed) or to $|F_{obs}|^2$ values (i.e. applying a Lorentz- polarization correction to the net intensity) is not undertaken by this software. As the raw data are conserved in the converted file, a more detailed modelling and refinement of background than that normally undertaken at present will be feasible, whilst retaining the possibility of a classic data reduction. As manufacturers' diffractometer-control software specifies and records its scan conditions (i.e. scan time, scan width, scan speed and number of scans) in many different forms, we have chosen to standardize this information into four intensity-measurement coefficients cp , cb , cl , and ch most convenient for least-squares calculations.

Let Q_{obs} be the observed integrated-intensity count measured by scanning over the reflection profile, and L_{obs} and H_{obs} the observed low- and high-angle background counts respectively. The model relating the raw observations of a diffraction experiment to derived parameters may be written as $Q_{calc} = cp P_{calc} (vm) + cb B_{calc} - Q_{obs}$, $L_{calc} = cl B_{calc} - L_{obs}$ and $H_{calc} = ch B_{calc} - H_{obs}$. P_{calc} is the calculated net integrated intensity per unit inverse scan speed and is a function of vm adjustable parameters describing the crystal structure, the scale factor, secondary extinction and possibly other physical quantities. B_{calc} is the calculated count rate per unit time of the mean background and is itself an adjustable parameter. One can see that in general, cp is equal to the time to count the peak divided by the scan width i.e. the effective scan speed allowing for multiple scans over the same peak, cb to the time to count the peak, cl to the time to count the low-angle background and ch to the time to count the high-angle background.

It follows that the scan width is equal to cb / cp . For a classical treatment, the net intensity P_{obs} may be calculated from the raw counts by using:

$$P_{obs} = [Q_{obs} - 0.5 cb (L_{obs} / cl + H_{obs} / ch)] / cp.$$

3.2.7.6 Content of the converted output file

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Compound, measurement and experimenter identification
  General descriptive title
  Compound/measurement identification code
  Date and method of creation of the converted output file
  General experimental technique and special details
  Name and postal, e-mail, telephone and telefax addresses of the experimenter

Instrument specification
  Type of single-crystal diffractometer
  Specification of software used to control the instrument
  Detector dead time and s.u.
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Radiation description
 Type of radiation (i.e. neutrons, electrons, X-rays)
 Mean wavelength
 Wavelengths and intensity weights of radiation components
 Polarization fraction of incident beam and s.u.
 Incident beam spatial half-width at the crystal

Filter and attenuator information
 Wavelength of beta filter absorption edge
 For each attenuator filter: its reciprocal transmission factor with s.u. and index

Environmental conditions
 Temperature with s.u.
 Pressure with s.u.

Compound and crystal specification
 Measured density with s.u. and temperature
 Melting point
 Colour and description of the crystal
 Source
 Common chemical and mineral names
 Measured formula mass with s.u.
 Chemical formula
 Chemical analysis in mass%
 Number of formula units per cell

Cell dimension and its determination
 Cell dimensions with s.u.s
 Cell volume with s.u.
 Temperature
 Specification of radiation used
 Minimum and maximum two-theta of reflections
 Number of reflections
 h, k, l, two-theta and wavelength code of each reflection

Crystal-shape description: either (a), (b) or (c)
 (a) h, k and l of each face and its distance with s.u. from centre
 (b) Radius with s.u. of a spherical crystal
 (c) Radius and length with s.u.s of a cylindrical crystal

Intensity measurement procedure
 Minimum and maximum $\sin(\theta)/\lambda$
 Total number of reflections measured
 Minimum and maximum values of h, k and l

Reference-reflection description
 Time interval between measurement of reference reflections
 Number of reference reflections measured
 For each reference reflection: its h, k and l Miller indices and reference code

Reflection-specific information
 Miller indices h, k and l
 Counts: peak, low- and high-angle background counts (Qobs, Lobs and Hobs)
 Intensity-measurement coefficients: cp, cb, cl and ch (defined in text)
 Crystal-based azimuthal angle
 Elapsed time of measurement
 Attenuator-filter index
 Scale-factor index
 Reference-reflection index
 Background scanning mode
 Scan type
 Total horizontal and vertical detector aperture

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