



Chemical Crystallography using X-ray Detector Software [1]

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August 31, 2018

Abstract

In crystallography different data analysis softwares are required and used for efficient data review. These programs often require a conversion into their specific parameters, which is the function of the programs written and discussed in this paper. Two programs have been written and will be described herewithin for the appropriate file reading and matrix-multiplication operations that XDS [1] and spec [3] require. The first reads and copies the layout of the XDS template files, while making the required matrix transformation to the rotation axis and detector parameters, so that XDS can correctly read the file for each scan. The second program converts the orientation matrix XDS outputs from the coordinate system of the laboratory to that of the sample, which prepares the data for implementation into spec.

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1 Introduction

In chemical crystallography, different data processing programs are used, which offer users a variety of advantages and disadvantages. Users choose between different varieties of scans, primarily used are phi and omega scans at the P24 beamline of Petra III, which allow the detectors to measure the scattering produced from the X-ray diffraction of the sample. The data measurement is saved in scans, a single-degree-step rotation around one axis at a time for however many degrees the user chooses, where the starting and ending positions of the motors are recorded in junction with the diffraction points.

At the P24 beamline, X-ray Detector Software (XDS) [1] is primarily used in combination with the program spec [3], which takes the orientation matrix and lattice parameters that XDS produces and creates 3D-imaging of the chemical that was scanned, to analyze the detector output. XDS reads a template file that includes information about what rotation matrix and which scans are being used to produce a file containing the orientation matrix of the sample within the laboratory coordinate system, unless the rotation matrix has previously been converted into the sample coordinate system, as well as lattice parameters and other data that will not be further discussed.

To use XDS correctly, users are required to transform both the detector matrix, comprised of the directions of the x and y detectors and incident beam direction, and the rotation axis to reflect the initial orientation of the crystal, i.e. applying the beginning omega, chi, and phi rotations to the rotation axis as well as the theta rotation to the detector coordinates. After having applied these rotations, users are able to run XDS to receive unit cell constants and an orientation matrix in the lab coordinate system. Before running spec, users have to convert the given coordinates from the lab system to the sample system, which requires the inverse matrix operation of the matrix that was multiplied by the initial rotation axis.

Currently, users are expected to make the initial and detector-to-sample transformations manually, but the implementation of two programs written to automatically perform the aforementioned processes will eliminate that. These new programs will save the beamline and users time and manual labor.

2 Theory

2.1 Instrument

As chemical crystallography is P24's primary function, the theories and laws of crystallography are crucial for users and beamline management success in experiments. In the second experimental hutch, a four circle diffractometer with Eulerian cradle is installed for sample configuration and orientation. With this machine, see Figure 1, users can perform omega and phi scans as well as altering chi, omega, and phi initial positions. These rotations are crucial to achieve a full understanding the crystalline structures of samples tested. Knowing which rotations are possible and likely to be

applied determines how the resulting programs will be and have been written.

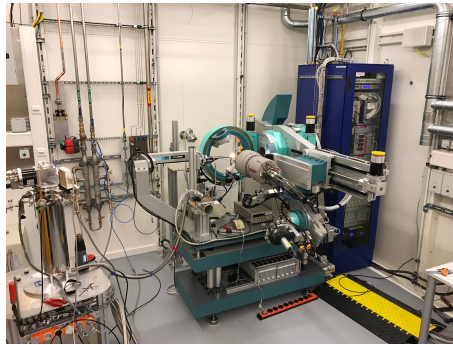


Figure 1: Huber 4 circle diffractometer [4]

2.2 Crystallography

In order to perform scans, x-ray beams are shot at the sample, then photons are diffracted by the crystalline structure. To understand the process that is taking place, an understanding and the use of Miller indices, see Figure 2, is needed. These indices will be used to represent all of the planes of the crystal that intersect with at least one of edge of the unit cell.

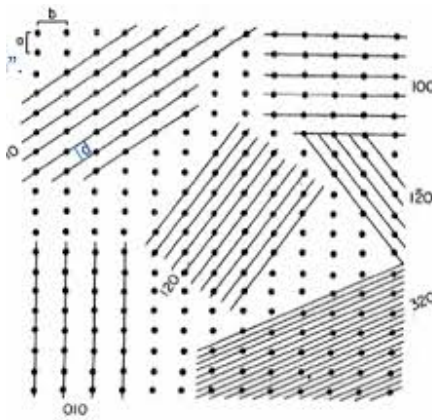


Figure 2: Miller Indices in 2-Dimensions [5]

Within these structures, the x-ray beam will interact with each plane according to Bragg's Law, see Figure 3. This interaction basis creates a relation between the wavelength, interplanar spacing, order of diffraction, and the angle of intersection between the incident x-ray wave and the planes of the crystal(theta). During experiments the wavelength will be constant as well as the order of diffraction staying within the first

order, so only theta and the interplanar spacing need to be calculated by programs, such as XDS.

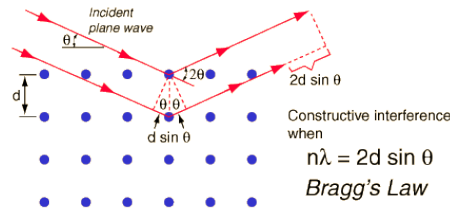


Figure 3: Bragg's Law [2]

The detector shows the diffraction points, following Bragg's Law, allowing conclusions to be made about the interplanar spacing when the detector distance is also being taken into account, which is achieved by considering Laue conditions. With Laue conditions being met, the difference between the reflected wave vector and the primary one will be inversely proportional to the interplanar spacing of the crystal for first-order diffraction. Miller indices can be multiplied by reciprocal lattice coordinates to find the distance between planes in the reciprocal system. This distance is then inversely proportional to the real-space distance between the planes. The distance from the sample to the detectors has to be taken into account through these equations and then can be used to calculate the interplanar distances. All of these processes fore-described are carried out by XDS, using the rotation axis that is supplied to calculate the smallest possible distance between planes and subsequently the angles between planes. Using spec and the data from XDS with appropriate transformations applied, users receive a 3D-representation of the crystalline structure. This data can be important to determine the value of a crystal for different uses.

3 Program

3.1 XDS Conversion Program

3.1.1 Mathematics

Within the program written to aid users in using XDS and later spec, matrixes are essential to the functions performed. Hereforth is described the mathematical processes that are involved in the first program.

For the initial rotation of the rotation axis given by the XDS template, three vector rotations are performed, in the order of phi, then chi, then omega rotations, if the scan is of the phi type. Both the phi and omega rotations are rotations around the Y-axis, using a rotation matrix of the given theta angle that the user manually inputs in the

command line.

$$\begin{bmatrix} \cos(\theta) & 0 & \sin(\theta) \\ 0 & 1 & 0 \\ -\sin(\theta) & 0 & -\cos(\theta) \end{bmatrix}$$

Similarly, for the chi rotation, an X-axis rotation matrix is used with a different theta angle, also found in the command line.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta) & -\sin(\theta) \\ 0 & \sin(\theta) & \cos(\theta) \end{bmatrix}$$

These rotational matrixes are then multiplied by the rotation axis vector that the program reads from the template file, performing the following mathematical procedure.

$$\begin{bmatrix} R_x \\ R_y \\ R_z \end{bmatrix} = \begin{bmatrix} \cos(-\omega) & 0 & \sin(-\omega) \\ 0 & 1 & 0 \\ -\sin(-\omega) & 0 & -\cos(-\omega) \end{bmatrix} * \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\chi) & -\sin(\chi) \\ 0 & \sin(\chi) & \cos(\chi) \end{bmatrix} * \begin{bmatrix} \cos(-\phi) & 0 & \sin(-\phi) \\ 0 & 1 & 0 \\ -\sin(-\phi) & 0 & -\cos(-\phi) \end{bmatrix} * \begin{bmatrix} R_ix \\ R_iy \\ R_iz \end{bmatrix} \quad (1)$$

For the detector matrix, a similar rotation is performed with only a theta rotation as given by the command line.

$$\begin{bmatrix} D_x \\ D_y \\ D_z \end{bmatrix} = \begin{bmatrix} \cos(-\theta) & 0 & \sin(-\theta) \\ 0 & 1 & 0 \\ -\sin(-\theta) & 0 & -\cos(-\theta) \end{bmatrix} * \begin{bmatrix} D_Xx & D_Xy & D_Xz \\ D_Yx & D_Yy & D_Yz \\ B_x & B_y & B_z \end{bmatrix}$$

These functions are used in the first program to convert the template coordinates into those of each phi scan, so that XDS can run properly. If the given scan is an omega scan, the program performs an identity matrix, with all omega, chi, and phi angles converted to zero. The orientational matrix that XDS outputs is in the coordinate system of the laboratory, so it is necessary to convert the matrix into that of the sample coordinate system, which the second program will do.

3.1.2 File Reading

In order to make implementation into XDS quicker, the first program also reads the template for XDS forms and replaces the sections specified. These sections are all declared in the command line and include the file being read, all rotations, data frame names, and the upper limit for data frames and the spot range. In order to perform the math aforementioned, the program reads the detector x and y axis and the incident beam direction, being the z coordinates, and places the coordinates into a matrix for the detector, which will have the specified theta rotation performed on it. The rotation axis

is also read from the template and used as the initial vector in the rotation axis that XDS will read after having a phi, chi, then omega rotation applied. To aid users in using this new program, the program also reiterates what each argument in the command line is being used as within the program, e.g. "Argument 3 : -9 is the omega rotation".

3.2 Coordinate Transformation

In the second program, the XDS output file is being read and the orientation matrix contained in that file will be transformed back into sample coordinates, instead of being in the laboratory coordinate system. In order to perform the previously mentioned task, it is necessary to reverse the rotation that was applied in the first program. Since the orientation matrix that was given by XDS is being used, vector multiplication is no longer included, only matrix rotations and multiplication. To reverse the previous rotations, the opposite of the initial angles have to be used as well as the rotations being performed in the opposite direction, i.e. omega, chi, then phi rotations.

$$\begin{bmatrix} S_1 & S_2 & S_3 \\ S_4 & S_5 & S_6 \\ S_7 & S_8 & S_9 \end{bmatrix} = \begin{bmatrix} \cos(\phi) & 0 & \sin(\phi) \\ 0 & 1 & 0 \\ -\sin(\phi) & 0 & -\cos(\phi) \end{bmatrix} * \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(-\chi) & -\sin(-\chi) \\ 0 & \sin(-\chi) & \cos(-\chi) \end{bmatrix} * A$$

$$A = \begin{bmatrix} \cos(\omega) & 0 & \sin(\omega) \\ 0 & 1 & 0 \\ -\sin(\omega) & 0 & -\cos(\omega) \end{bmatrix} * \begin{bmatrix} R_{Xx} & R_{Xy} & R_{Xz} \\ R_{Yx} & R_{Yy} & R_{Yz} \\ R_{Zx} & R_{Zy} & R_{Zz} \end{bmatrix}$$

Once these rotations have been applied, all orientation matrixes for scans of the same sample should match and are ready to be read by spec.

4 Implementation

4.1 Experiment

To test out the functionality of the programs, a sample of aluminum oxide, with known parameters at room temperature, was scanned from different initial positions in a phi scan in the P24 beamline of Petra III at DESY. The following data was collected by using the first new program, "xds_program.C", then XDS [1], then the second new program, "matrix_transformation_program.C".

4.1.1 Data

Table 1 gives an overview on which scans were performed. Because there were difficulties with identifying the accuracy of the wavelength of the beam and some general alignment, only one successful scan was able to be used of the aluminum oxide sample, although data from previous experiments was also tested to demonstrate the functionality of the program.

Table 1: Initial Rotations in Degrees

Run Number	Type	Theta	Omega	Chi	Phi
1	phi	0	-5	-60	0

Table 2: Unit Cell Parameters

Run Number	X	Y	Z	Angle (1)	Angle (2)	Angle (3)
1	4.7600	4.7600	12.9930	90.000	90.000	120.000
Accepted Value [8]	4.759020	4.759020	12.991024	90.000	90.000	120.000

$$Key = \begin{bmatrix} X_x & Y_x & Z_x \\ X_y & Y_y & Z_y \\ X_z & Y_z & Z_z \end{bmatrix}$$

Table 3: Sample Orientation Matrix

Scan	X_x	X_y	X_z	Y_x	Y_y	Y_z	Z_x	Z_y	Z_z
1	-1.26709	-3.27499	-3.21355	4.48372	1.59253	0.13445	3.09700	-9.42797	8.38701

This data offers a quick comparison between the different scans and the accuracy of the programs in combination with one another in a more qualitative aspect. A further analysis of the accuracy of these programs is required with a quantitative method as to show definitely how well these programs can work with one another.

4.1.2 Analysis of Accuracy

With the following tables, a quantitative comparison between the accepted and experimental value of the sample is done to evaluate the accuracy of the entire experimental setup, with the two new programs being included in the process. The percentages of errors that were recorded in comparison to previous studies' expected values are minimal enough to show the accuracy of the programs.

Table 4: Data Comparison - Unit Cell

Parameter	Deviation	% Error
X	0.00098	0.0206
Y	0.00098	0.0206
Z	0.001976	0.0152

4.2 Future

These programs can be implemented into the P24 beamline to improve downtime in analyzing data, since previously users had to manually transform each matrix to manually change the XDS template provided for the beamline. With all these small tasks eliminated, processing user's data should be significantly hastened, so that users will be able to perform more scans on samples and potentially bring more samples, making the P24 beamline more attractive to new and returning scientists. Given that the programs allow for descriptors, i.e. "-o" or "-p", to be given, it can be quickly adjusted either within the command line or by adding new descriptors into the program if they are not already defined. This allows the programs to progress with the beamline and new potentials, such as different equipment with more parameters that can be changed, quickly.

5 Conclusion

The new programs have demonstrated their effectivity in efficiency and accuracy, with the first experiment acting as a test for the program. Given that the lattice parameters were within 0.0206% of the accepted value [8], the program proved its accuracy. Given its continued performance, it will be implemented into the P24 beamline to assist future users. Since it has the capabilities to work with both phi and omega scans as it is in its current state, it should prove useful in all experiments. This will save time during data processing and allow for less potential human error, since all mathematics needed will be carried out by the program.

6 Acknowledgements

I would like to thank the Petra III - Ada Yolath extension team for their support and coffee, especially to my supervisor, Martin Tolkiehn, for explaining every detail of photon science and crystallography to me. I would also like to acknowledge and praise the DESY Summie program organizers and lecturers for all their hard work and patience with all of the students.

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