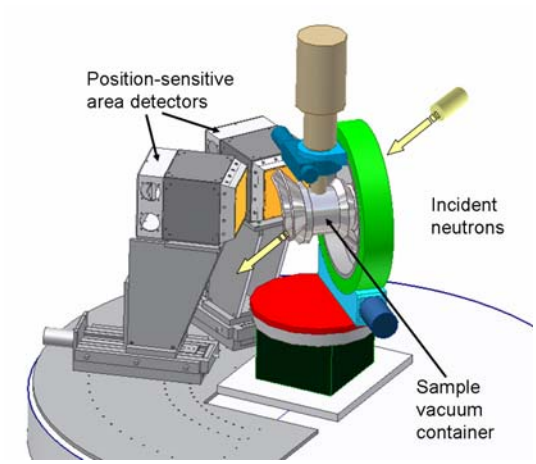
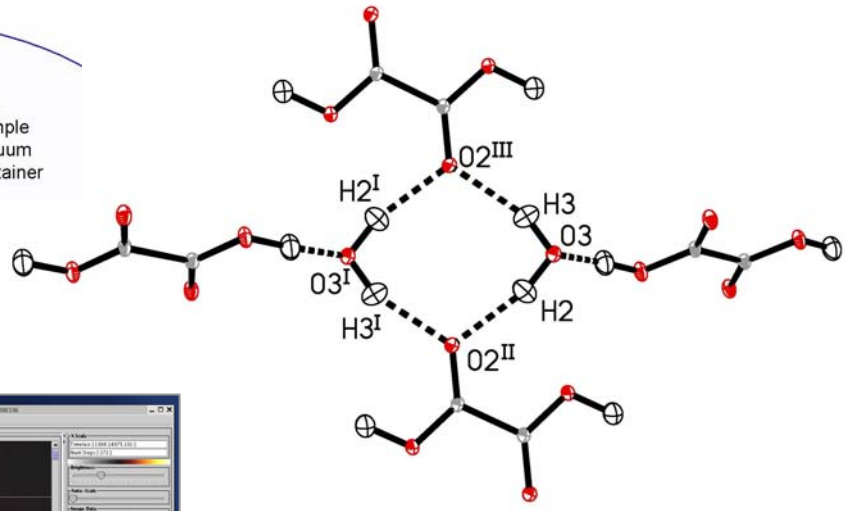
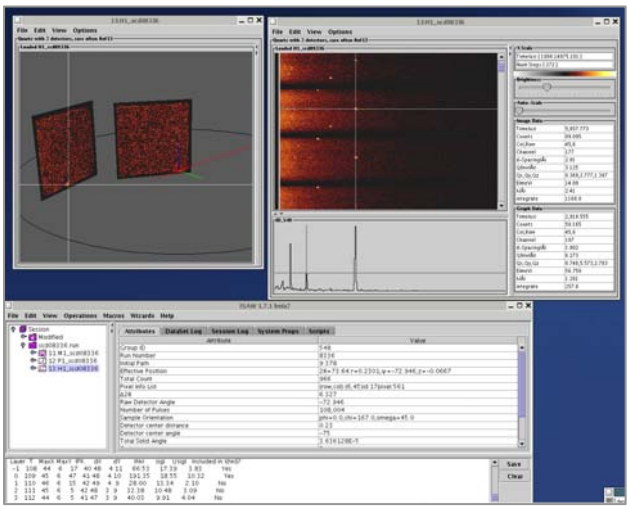
SCD User's Manual
Version 1.8
Oxalic Acid Tutorial

Paula M. B. Piccoli
IPNS
Argonne National Laboratory







SCD User's Manual

Version 1.8
Oxalic Acid Tutorial

About this Tutorial 3
What You Will Need 3
About Oxalic Acid 6
Data Visualization 7
Getting Started 7
Launching ISAW 7
Viewing the Data 8
Initial Peaks Wizard 11
Form 1: FindMultiplePeaks 11
Form 2: JBlind 14
Form 3: JIndex 16
Form 4: JScalar 18
Form 5: JLsqrs 20
Daily Peaks Wizard – integrating the data 24
Form 1: FindMultiplePeaksForm 24
Form 2: IndexJForm 25
Form 3: LsqrsJForm 27
Form 4: IntegrateMultiRunsForm 29
Calculating the Absorption Correction 31
Correcting the Data for Absorption - Anvred 32
Writing Files for Structure Refinement – anv2gsas 36
Structure Refinement – ox80 38
Graphical Representation of the Structure 39
Writing the Structural Report 39
Glossary 40
Appendix 1 – Using refedt 41
Appendix 2 – Integrating and Processing Portions of Data. 42

About this Tutorial

This tutorial is designed as a learning exercise, stepping the user through the data analysis and structure refinement procedures used for the Single Crystal Diffractometer (SCD) at IPNS. Using ISAW, the user will visually inspect sample data, determine an orientation matrix and integrate resulting peaks. Using IPNS helper programs, data will be corrected and processed for structure refinement. The structure can then be refined using an available refinement program such as GSAS or SHELX. The goal of the tutorial is provide you, the user, with knowledge of the software so that you can analyze your data.

This version of the tutorial is based on the ISAW 1.8 release. This new release has some improvements over the 1.7 series of releases. If you are running a version of ISAW in the 1.7 series, it is recommended that you upgrade to a 1.8 release.

This general tutorial may not answer all of the questions a user may have, nor will it address special circumstances. IPNS personnel are always on hand to answer questions that may arise.

This is also a work in progress. Suggestions are welcome to help this become a better learning tool for our users. Suggestions and comments can be addressed to ppiccoli@anl.gov.

What You Will Need

Start by visiting the SCD webpage located at:

http://www.pns.anl.gov/instruments/scd/ and
http://www.pns.anl.gov/instruments/scd/subscd/scd.shtml.

Download ISAW, GSAS, and the Oxalic Acid Tutorial from the Useful Links and Downloads. Install ISAW into a C:\isaw directory, and GSAS into C:\gsas. Open the file isaw_exec.bat with a text editor and replace ”256” in the line “java –mx256m -cp” with a larger value if your computer has more than 256MB of memory. ISAW version 1.8 requires the Java runtime environment (JRE) 1.5 or higher to work on the PC. (Previous versions of ISAW require a JRE of 1.4.2 or higher.) You can download this from the ISAW page.

Make a directory C:\scd directory, and unzip the tutorial programs here. The result should give C:\scd\exe, as well as the files C:\scd\Absorption.xls, C:\scd\spec_coeff.dat and C:\scd\instprm.dat. Because some of the helper programs are hardwired to look for certain files in certain places, make sure that these folders and files are in the correct places. The anvred.log file is from a 80 K data collection on oxalic acid, and contains the correct absorption correction values that are also listed within this tutorial.

GSAS is the standard program for refining data at IPNS due to the fact that it handles multiple histograms and extinction from neutrons very well. SHELX may also be used, for which we usually supply a scaled and extinction corrected hkl file from initial GSAS refinement.

ORTEP will directly read GSAS or SHELX files for graphical representations of the final structure. It is also compatible with the WinGX package, which offers other programs for plotting the structure.

To run these helper programs as well as GSAS *directly* from a DOS window prompt, set the PC system **path variable** to include C:\scd\exe;C:\GSAS\exe and add a new **system variable** GSAS to be C:\GSAS\ (assuming this is where the downloaded GSAS is located).

WinGX and ORTEP also require information to be placed in the path, and are specified at their websites.

The following page illustrates the data collection and analysis process for the SCD at IPNS, and outlines the programs used for each step. The Glossary at the end of this tutorial gives a brief description of programs or terms used throughout.

Happy refinements!

Steps in Single Crystal Diffraction at IPNS

Sample – single crystal at least $2mm^3$ in volume

Data Collection

Data visualization	ISAW
Find orientation matrix	newrun, ISAW (initial wizard)
Set up data collection	setang, newrun

Data analysis

Integration	ISAW (daily wizard)
Data corrections	absorption.xls, anvred
Write files for refinement	anv2gsas

Structure Refinement

GSAS/ SHELX	(structure refinement program)
refedt	(edits GSAS reflection files)

Graphical Representations of the Structure

ORTEP
WinGX

Special Tools

GSAS, ORFFE, other helper programs

About Oxalic Acid

The bundle containing this tutorial also contains two papers from the literature about oxalic acid (PDF formatted). Unit cell information needed to work on this tutorial can be found in the paper. A file named *atoms.txt* is also included in the tutorial bundle. This file contains the atoms and their positional parameters from structure refinements over several temperatures at IPNS. This information is necessary to enter the atoms and their fractional coordinates into GSAS during the refinement stages.

The experimental data was collected at 80 K on SCD at IPNS. The run files are compiled in a zip file and when extracted should end up in a "working directory" separate from the rest of the information downloaded from the website.

The goal in an experiment such as oxalic acid is to locate the nuclear positions of the hydrogen atoms – try leaving out one or two of the hydrogen atoms and find them in a difference Fourier map during refinement of the structure.

Data Visualization

Getting Started

ISAW is a data visualization program used to view, analyze and integrate raw data from SCD (as well as other instruments at IPNS). Information about computing practices at IPNS can be found at:

http://www.pns.anl.gov/computing/

You may run ISAW from your PC desktop or remotely on the SCD front end computer helios.pns.anl.gov. Data run files can also be downloaded to your PC via the SSH file transfer window, and these same operations can be run locally on your PC (useful if your computer connection is slow or you take your data with you – xterm windows have a tendency to time out if the connection is too slow). The above link provides information on downloading the latest version of ISAW and the java run time environment (JRE). Java **must** be installed on the computer intended to run ISAW. These are provided free to the user.

Launching ISAW

Launch ISAW by double-clicking on the ISAW icon or by typing ISAW from a DOS command window prompt. The initial ISAW screen should become visible at this point:

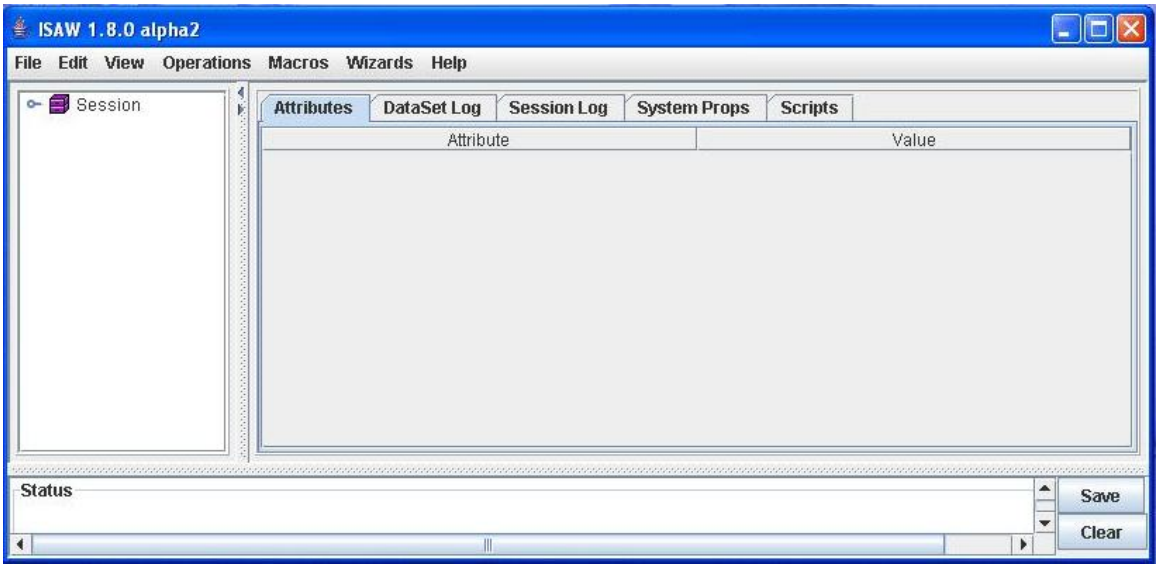


Figure 1

Entries under the Help item on the menu bar offer some introduction and online documentation.

The status bar at the bottom of the ISAW screen is an output screen. As operations are conducted in ISAW, this screen will provide information about what ISAW is doing and some brief results. Check the Status bar if something goes wrong in an operation; ISAW is quick to tell you if the input is incorrect.

Viewing the Data

Raw data may be viewed in ISAW by using the **File > Load Data > Local** menu options to load specific run files into ISAW:

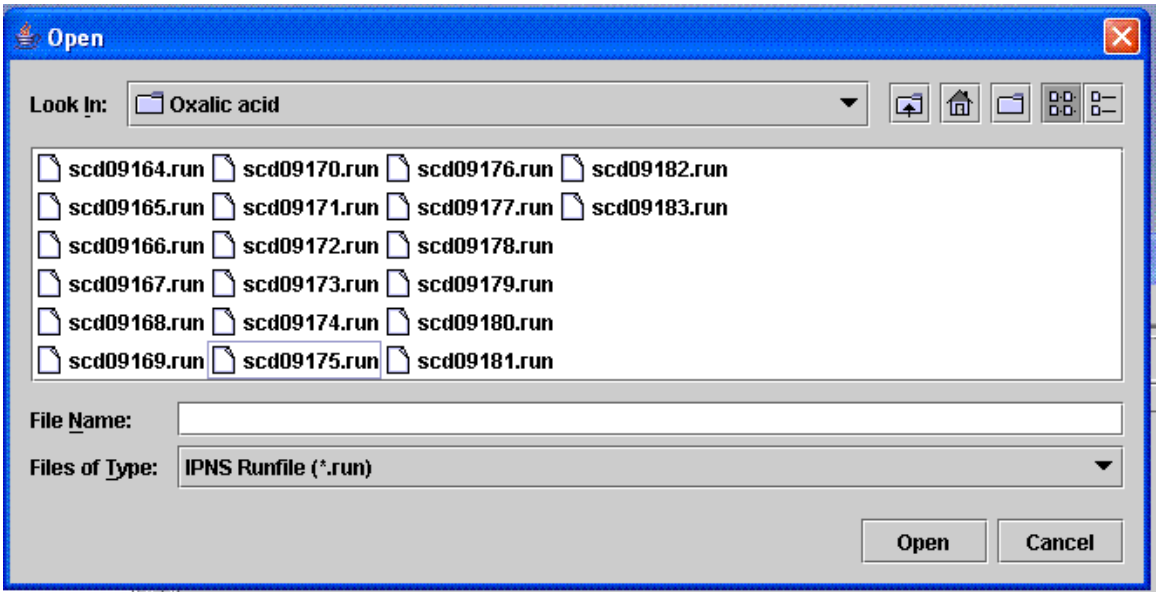


Figure 2

SCD run files have the extension *.run*. Raw data files stored on the scd computer will be found in the **scd/data** folder. Files in the example here are from a local folder on the PC's hard drive. Run files may be selected by selecting them and then selecting the Open button. This will then load the run file into ISAW for viewing purposes.

The startup ISAW screen will come back into the foreground with the run file appearing below the **Session** box in the left hand window. Clicking on the circle just to the left of the run file folder in this window will expand the folder to show the contents M1, P1 and H1. H1 contains the histogram information (raw data) to use for viewing the data. Click once on H1:

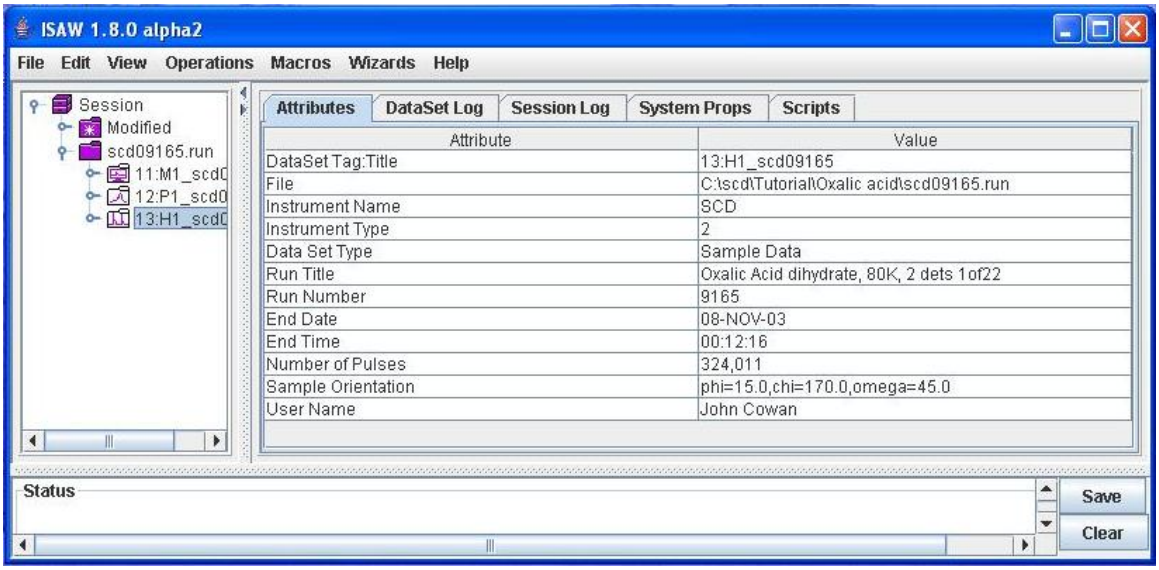


Figure 3

Information about the run file now appears in the Attributes box. The scroll bar on the right hand side will also give information about what time the run finished, how many pulses were collected, the sample orientation and the user name.

From the menu bar, select **View > Image View** to see time-of-flight spectra of each pixel on the area detectors.

Selecting **View > 3D View** will bring up the view of both detectors. The two views are linked in that clicking on a spot in the Image View will show you the corresponding reflection collected on each detector. The user can scroll through the data in time-of-flight by using the right hand scroll bar in Image View or the left and right arrow buttons in the 3D view.

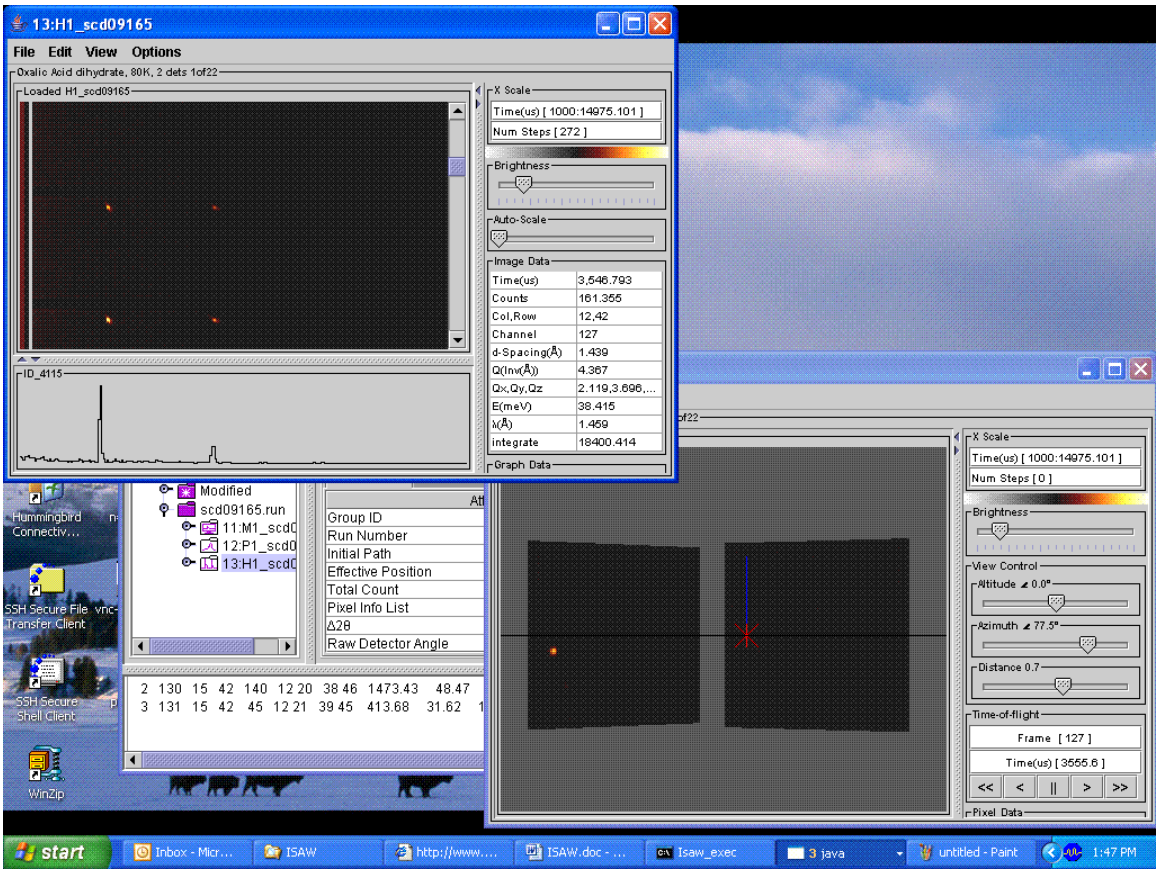


Figure 4

In this way the raw data may be viewed. It is a good way to examine the overall quality of the crystal and subsequent data.

Initial Peaks Wizard

The purpose of this wizard is to find and autoindex peaks to obtain the unit cell and the orientation matrix.

Form 1: FindMultiplePeaks

Data do not need to be loaded initially into ISAW in order to run the Initial Peaks Wizard.

1. From the initial ISAW screen, go to **Wizards > SCD > Initial Peaks Wizard**

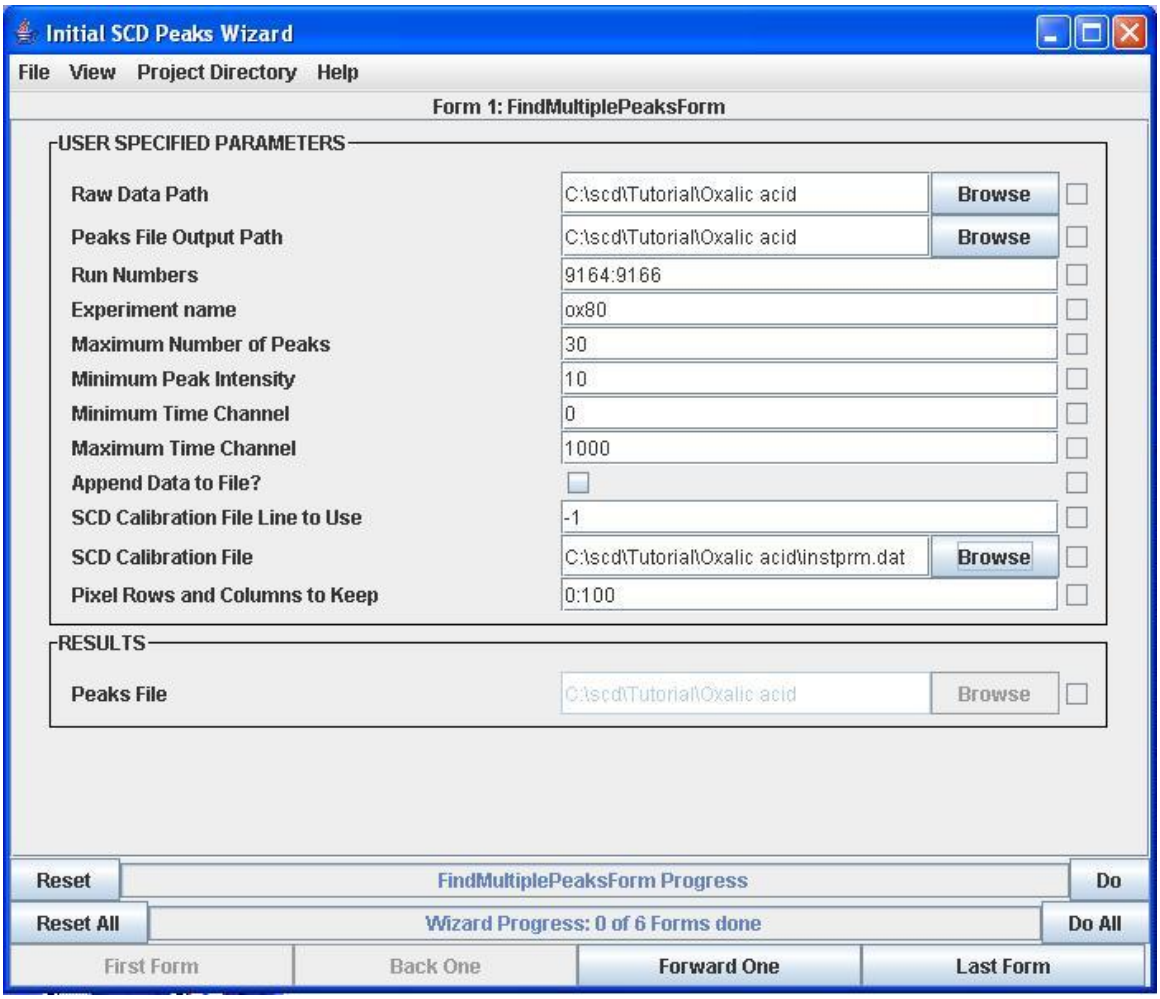


Figure 5

2. Set the **Project Directory** to **C:\scd\Tutorial\Oxalic acid**. The instrument calibration file *instparm.dat* (see step 7) has also been copied to this directory.

3. Set the Run Numbers to **9164:9166**. The colon indicates that all numbers in the series are included.
4. Choose an **Experiment name** that will identify it easily. Choose **ox80**.
5. Default values for Form 1 will locate up to 30 peaks from each detector in each run file with a **minimum peak intensity** of 10, with a **maximum time channel** of 1000 (this should cover all of the SCD run file data).
6. Initially there is no data file to append to, so leave this box unchecked.
7. Make sure the correct calibration file is used! The most recent instrument parameter files (**SCD Calibration File**) are located in the scd home directory on helios and has the file name *instprm_Jun04.dat* or something similar. These files are always dated with the month and year, and it is important to use the most recent file *for when the data was collected*. (This may not always be the "most recent" calibration file). For this example, the file *instparm.dat* has been provided. Please remember that this file will *not* be the one used for your data collection.
8. **Pixel Rows and Columns to Keep** allows the user to reject some detector pixels; this does not need to be adjusted to find the orientation matrix.
9. When input is complete, click on the **Do** box to find the peaks from the specified run files. When the **FindMultiplePeaksForm** has completed, the top progress bar will change color as shown below. The bottom bar shows that you have complete 1 of the 6 Forms in the wizard.

Figure 6

Also, in the message pane of the ISAW window, there will be a message "--- Done finding peaks. ---Peaks are listed in C:/scd/Tutorial/Oxalic acid/ox80.peaks."

Files written: *filename.peaks (ox80.peaks)* which may be viewed by selecting **View > Peaks File** from the menu bar.

C:\scd\Tutorial\Oxalic acid\ox80.peaks

File Edit

0	NRUN	DETNUM		DETA	DETA2	DETD	CHI	PHI	OMEGA	MONCNT						
1	9164	17		-75.00	0.00	23.00	170.00	345.00	45.00	1078270						
2	SEQN	H	K	L	X	Y	Z	XCM	YCM	WL	IPK	INTI	SIGI	RFLG	NRUN	DN
3	1	0	0	0	27.09	13.16	52.44	-2.61	-6.67	0.6953	71	0.00	0.00	11	9164	17
3	2	0	0	0	26.24	94.30	53.20	-2.74	5.71	0.7007	164	0.00	0.00	11	9164	17
3	3	0	0	0	48.00	54.92	53.22	0.57	-0.30	0.7014	70	0.00	0.00	11	9164	17
3	4	0	0	0	23.89	46.83	61.93	-3.10	-1.53	0.7640	84	0.00	0.00	11	9164	17
3	5	0	0	0	6.76	84.77	61.96	-5.70	4.26	0.7635	65	0.00	0.00	11	9164	17
3	6	0	0	0	12.03	75.66	63.01	-4.90	2.87	0.7718	99	0.00	0.00	11	9164	17
3	7	0	0	0	21.02	56.07	62.97	-3.54	-0.12	0.7718	93	0.00	0.00	11	9164	17
3	8	0	0	0	8.10	41.89	64.19	-5.50	-2.28	0.7807	84	0.00	0.00	11	9164	17
3	9	0	0	0	92.08	16.32	75.19	7.28	-6.18	0.8690	78	0.00	0.00	11	9164	17
3	10	0	0	0	84.85	42.93	93.05	6.18	-2.13	1.0374	132	0.00	0.00	11	9164	17
3	11	0	0	0	80.37	69.19	97.27	5.50	1.88	1.0817	78	0.00	0.00	11	9164	17
3	12	0	0	0	71.91	94.01	98.93	4.21	5.67	1.0992	372	0.00	0.00	11	9164	17
3	13	0	0	0	59.11	5.71	101.18	2.26	-7.80	1.1236	94	0.00	0.00	11	9164	17
3	14	0	0	0	75.18	35.89	102.10	4.71	-3.20	1.1346	177	0.00	0.00	11	9164	17
3	15	0	0	0	74.11	49.84	105.18	4.55	-1.07	1.1699	138	0.00	0.00	11	9164	17

Figure 7

The file shows the peaks found in the search. Note that they are not indexed – there is no orientation matrix yet. The first two lines contain information about the run number, detector identification and parameters, and the diffractometer setting used for that run file. SEQN is the sequence number of the reflections searched for by ISAW. X, Y and Z refer to detector horizontal and vertical channels X and Y (0:100), and Z, the time channel of the neutron collected by the detector. These channels are listed as nonintegers due to a peak centroid analysis of the peak maximum channel and the 26 nearest neighbors. XCM and YCM refer to the position of the peak in units of cm from the center of the detector. WL is the wavelength of the reflection in Angstroms. IPK is the neutron counts in the XYZ channel at the peak maximum, INTI will be the integrated intensity and SIGI is the standard deviation after integration of the reflection.

10. Choose five to fifteen peaks of medium to high intensity by sequence number for unit cell determination to enter into Form 2. Select the **Forward One** button at the bottom of the Form 1 page to advance to Form 2.

Form 2: JBlind

JBlind is a program that attempts to find an orientation matrix from a sequence of peaks.

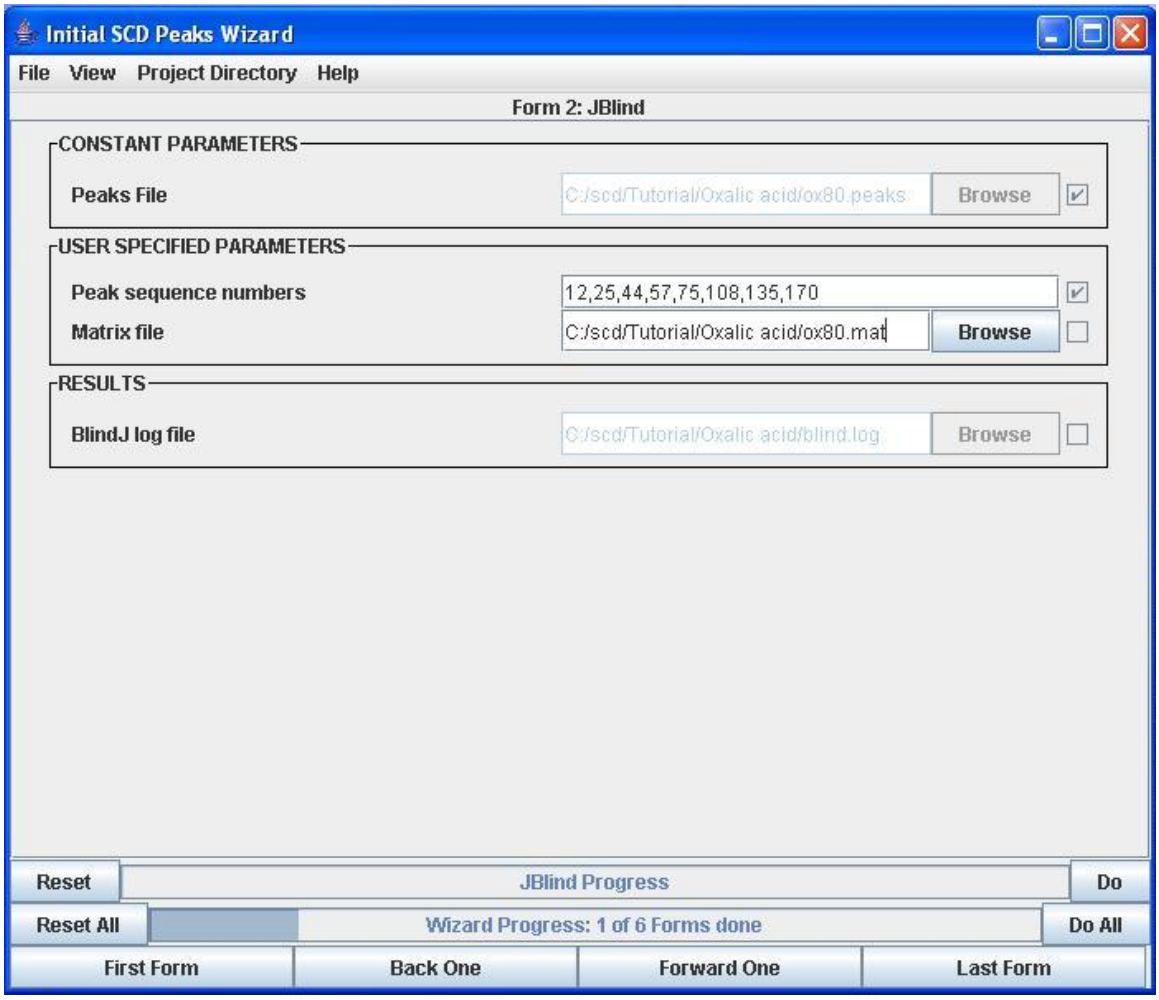


Figure 8

11. Input the peaks, separated by commas, in the **Peak sequence numbers** window. (You can use the peaks here in the example, or experiment with your own!)
12. A **Matrix file** name will need to be provided with the ***.mat*** extension. Choose **ox80.mat**.
13. Click **Do**.

Files written: *blind.log* and *filename.mat* (specified above). View either file using the **View** item on the menu bar.

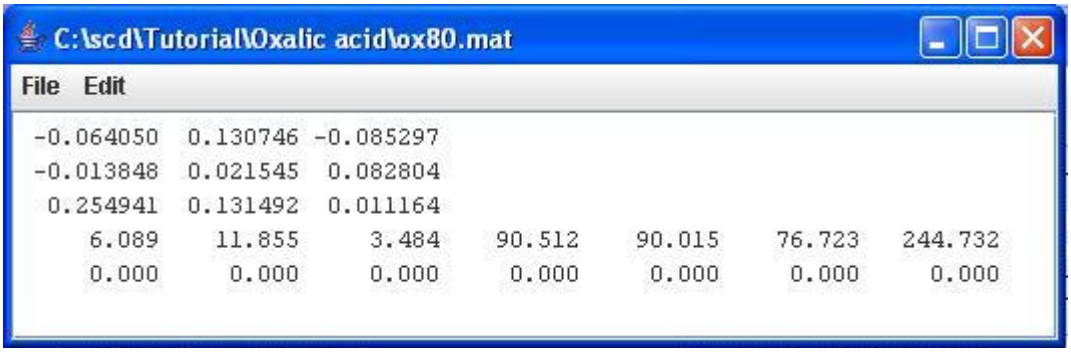


Figure 9

It can be seen that the axes are of the correct length but not in the correct order, which can be changed in a later form. Note that if Blind does not find the correct cell (conventional or reduced) the peak sequence numbers can be changed and the form run again. Occasionally Blind works better with fewer peaks. Form 2 will write over the log and matrix files, so remember to copy them to different files if saving them is important. Once a satisfactory matrix has been determined, click **Forward One** to move to the next form.

Form 3: JIndex

JIndex will index the peaks located in the peaks file (but not all of the peaks in the data). It is a good measure of how well the orientation matrix fits the data.

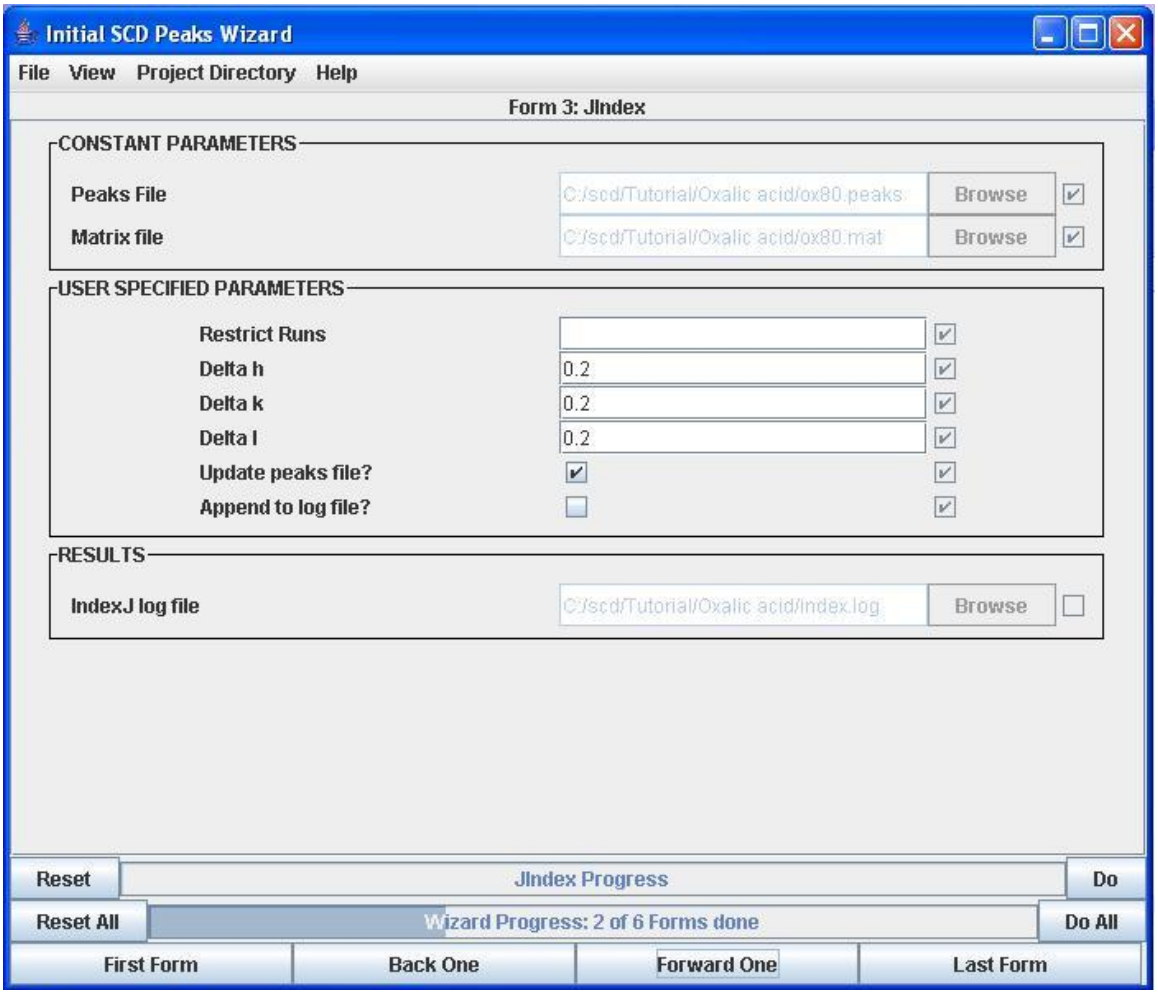


Figure 10

14. Use the **Restrict Runs** option if only a few runs (in the peaks file) are of interest; otherwise leave it blank.
15. **Delta h, k,** and **l** specify the tolerance of when to consider a peak properly indexed. The tolerance can be changed depending on the quality of the crystal, the accuracy of the initial orientation matrix, and the size of the unit cell. For small unit cells, 0.1 may be suitable, whereas for large unit cells, 0.3 may be necessary. A value of 0.2 is the default number which is suitable to start with.
16. Check the box to **Update the peaks file** – when you view the peaks file after Form 3 it will have the indexed hkl values of each peak.

Files written: the updated *filename.peaks* file and *index.log*. View these as before from the menu bar. The Status bar from the main ISAW window will inform you of the success rate of indexing (in this case, 170 of 180 peaks were indexed).

17. Go **Forward One** to reach Form 4.

Form 4: JScalar

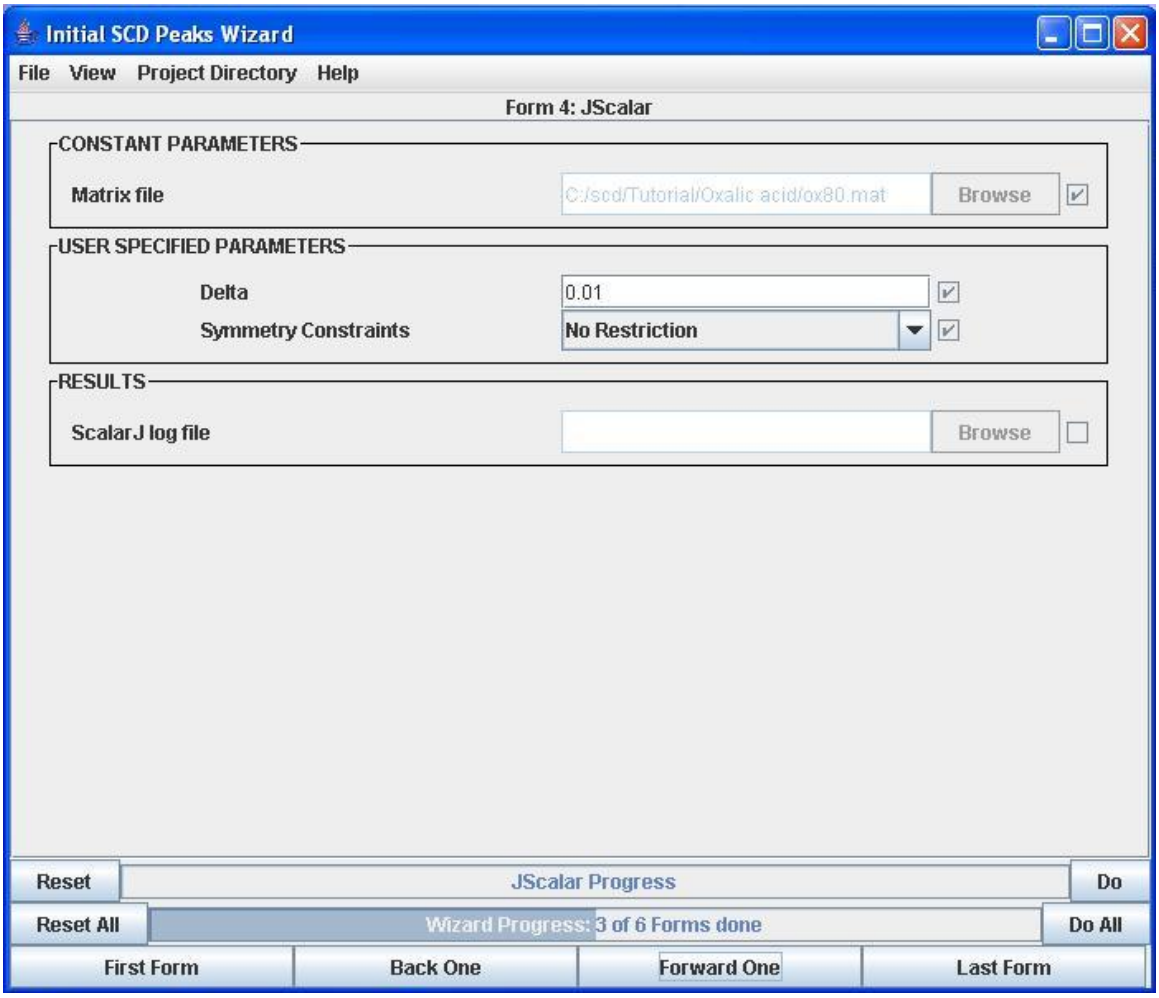


Figure 11

JScalar will assist in finding the correct transformation matrix for the initial orientation matrix if this is necessary by examining relationships of the elements of the metric tensor, but note that it is not foolproof if the initial matrix is not very precise! While JScalar works quite well most of the time, there are times when the user needs to intercede. The default is for No Restriction in terms of **Symmetry Constraints**. The figure above shows the drop menu in which the user can specify symmetry constraints. It is always worthwhile to run JScalar with no restrictions on symmetry to determine if the program can get the transformation matrix right on the first try. If it can't then imposing a symmetry constraint can help, especially in the case of a reduced cell.

Files written: *scalar.log*, which lists various transformation matrices (if it found any) and the resulting unit cells. In this case, the second transformation matrix (cell choice 2) to a primitive, monoclinic cell is the correct one for oxalic acid.

Go **Forward One** to reach Form 5 and perform the transformation.

C:\scd\Tutorial\Oxalic acid\scalar.log

File Edit

```
   16.579      1.217

CELL 1  TYPE IS

C, ORTHORHOMBIC

TRANSFORMATION MATRIX 1  IS

  1    0    0          -0.064050   0.130746  -0.085297
 -1    2    0  x UB =   0.036354  -0.087656   0.250905
  0    0    1           0.254941   0.131492   0.011164

     a          b          c        alpha       beta      gamma     cellvol
    9.423      5.927      3.484     90.512     90.332     38.972    122.367

CELL 2  TYPE IS

P, MONOCLINIC

TRANSFORMATION MATRIX 2  IS

 -1    0    0           0.064050  -0.130746   0.085297
  0    0    1  x UB =   0.254941   0.131492   0.011164
  0    1    0          -0.013848   0.021545   0.082804

     a          b          c        alpha       beta      gamma     cellvol
    6.089      3.484     11.855     90.512    103.277     89.985    244.733

CELL 3  TYPE IS

C, MONOCLINIC

TRANSFORMATION MATRIX 3  IS

  2    0    1           0.126841   0.392984  -0.159430
```

Figure 12

Form 5: JLsqrs

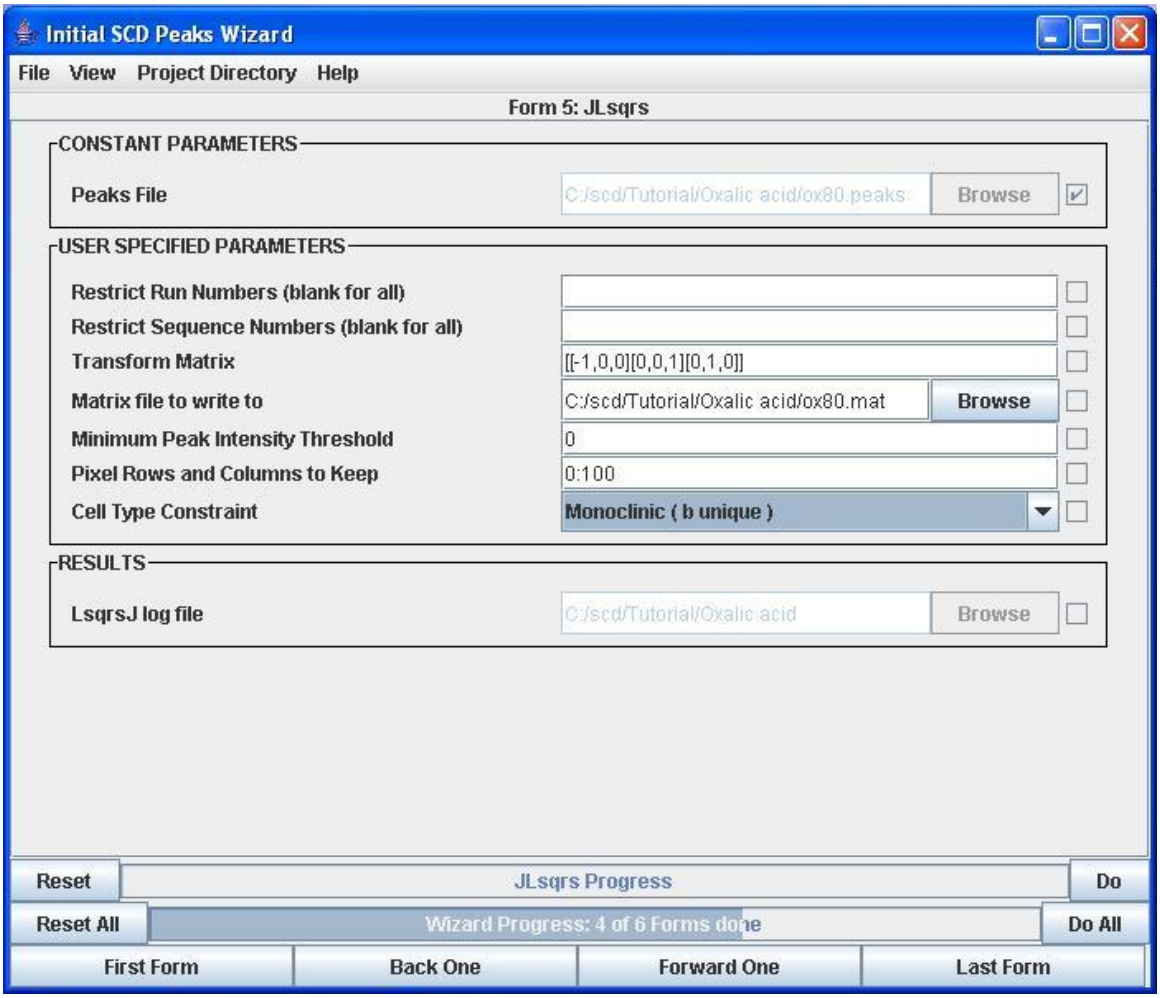


Figure 13

18. The **Matrix file to write to** must be specified. A new name may be chosen if the initial orientation matrix needs to be preserved; otherwise that initial file may be chosen and subsequently overwritten.
19. The **Transform Matrix** is written across rows and not down columns, therefore the matrix from JScalar:

```
 P, MONOCLINIC

TRANSFORMATION MATRIX 2  IS

-1    0    0            0.064050  -0.130746   0.085297
 0    0    1  x UB =    0.254941   0.131492   0.011164
 0    1    0           -0.013848   0.021545   0.082804
```

Will be written as **[[-1, 0, 0][0, 0, 1][0, 1, 0]]** in Form 5 above.

20. Version 1.8 of ISAW includes a **Cell Type Constraint** pull-down menu. This feature will fix those cell parameters imposed by Bravais lattice symmetry and refine the cell against these parameters. In this case, we know that oxalic acid is a monoclinic cell with a unique *b*-axis, and so the resulting α and γ angles should be exactly 90° with no errors. The resulting matrix may be viewed to confirm the transformation. Compare this with the original orientation matrix. This appears to be the correct unit cell for oxalic acid. You will notice that the output below has errors associated with it for both α and γ, however these would *not* be reported in subsequent crystallographic reports. Currently, ISAW is being improved to not report these errors.

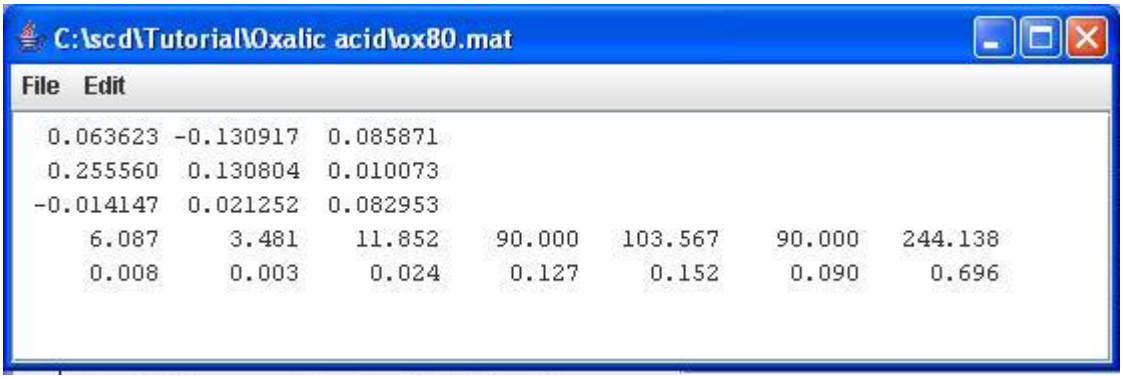


Figure 14

Files written: the new *filename.mat* file as specified above. In this case, we have chosen to overwrite the ox80.mat file.

21. Click **Do** to move to the next form.

Form 6 is another iteration of JIndex.

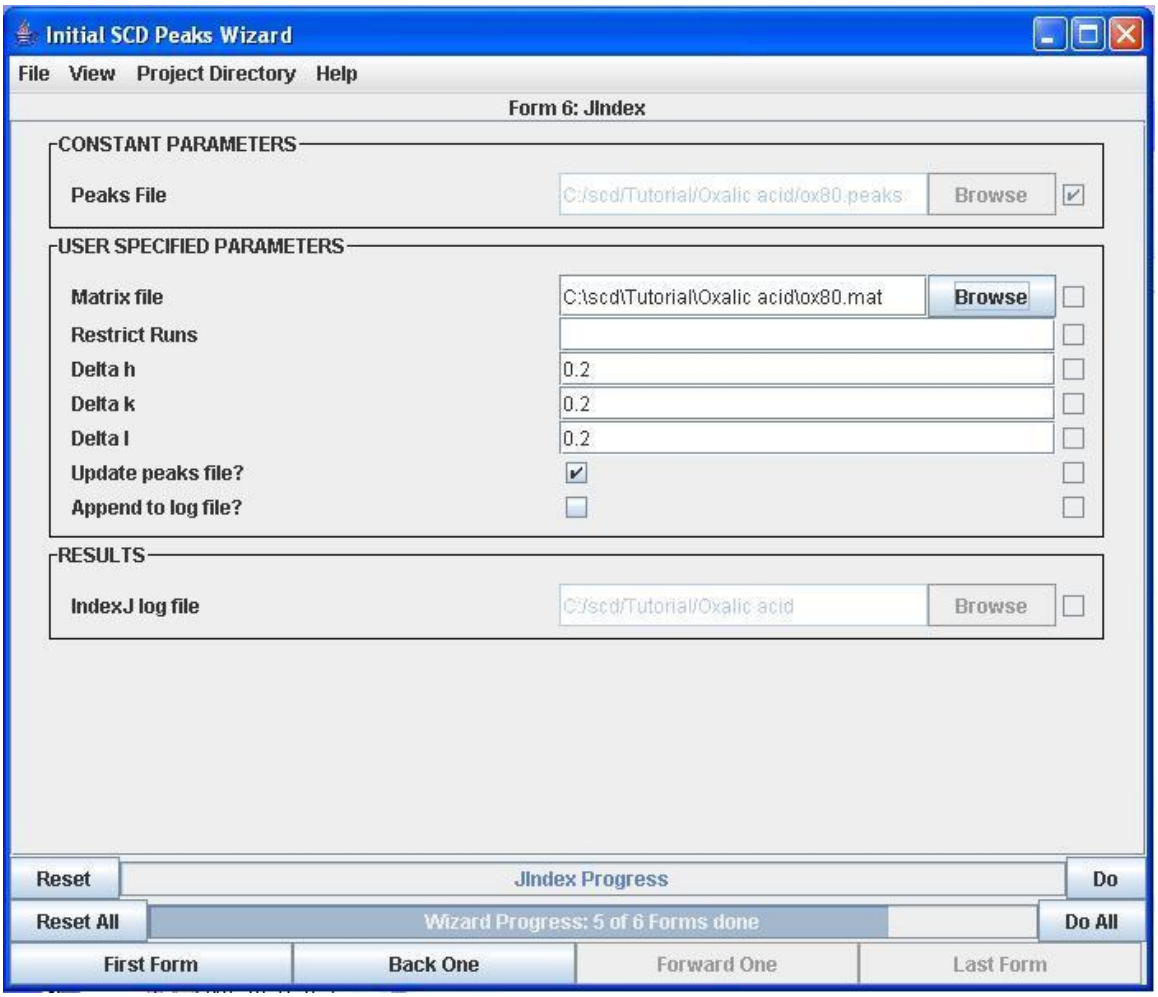
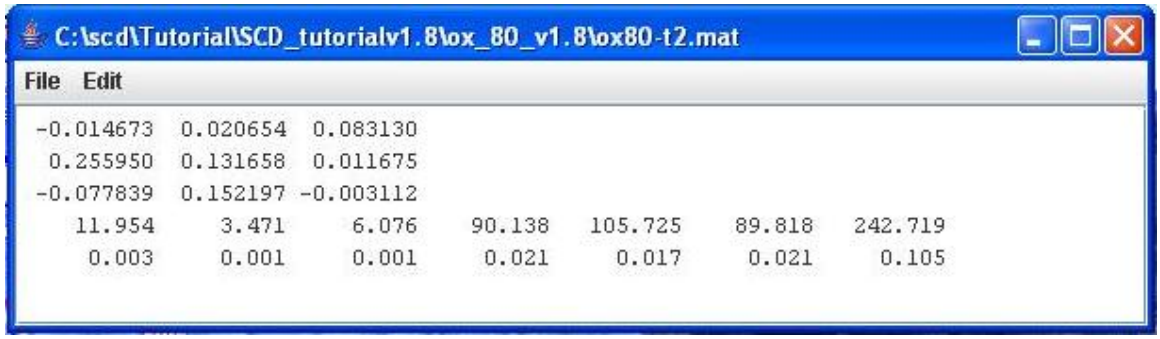


Figure 15

22. Input the correct (most recent in this case) matrix file. JIndex will reindex the peaks in the peaks file to be consistent with the correct orientation matrix. Now you are almost finished with the Initial Wizard.

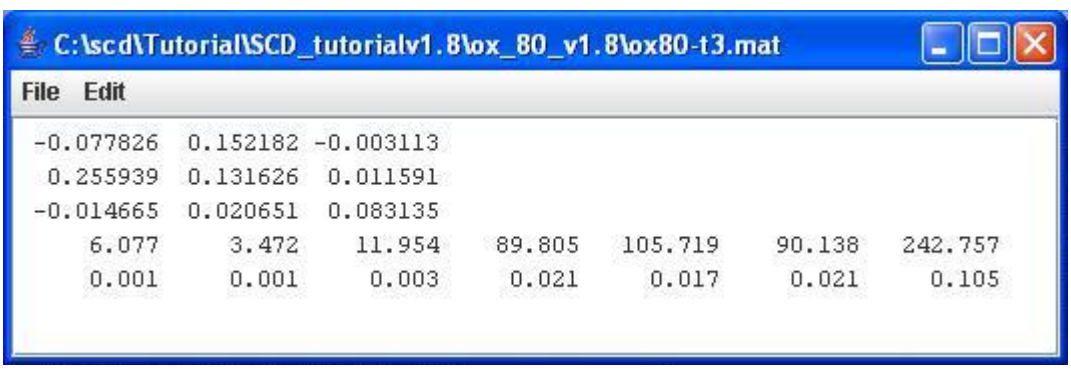
23. You might have noticed that the oxalic acid structure in the original literature has been solved in the space group $P2_1/n$. This space group is a nonstandard setting for $P2_1/c$. Although the unit cell you have just determined looks correct for oxalic acid, in fact what you have just found is the cell for the conventional setting. In order to refine oxalic acid data in $P2_1/n$, we will need to transform the cell from cell choice 1 ($P2_1/c$) to cell choice 2 ($P2_1/n$). The 3 x 3 transformation matrix can be found in Table 5.1 of the *International Tables for Crystallography, Volume A*. Return to Form 5 and enter **[[-1,0,-1][0,1,0][1,0,0]]** in the **Transform Matrix** box, remembering to write the matrix out to another file such as ox80-t2.mat. The following matrix file should be written:



Notice that the β angle value has changed slightly, and that *a* and *c* are in opposite positions. We will correct this momentarily.

24. Go forward to Form 6 and index the peaks again with the new matrix file.

25. To change *a* and *c* and obtain the correct matrix to match the literature values, return to Form 5 and enter **[[0,0,1][0,1,0][1,0,0]]** in the **Transform Matrix** box., saving the matrix file yet again to a new name such as ox80-t3.mat:



26. Again, return to Form 6 and index the peaks with the new, correct matrix file determined in step 25 above.

Files written: the Initial Wizard writes a file named *filename.x*, which is essential to move to the next step of the process, which is integration of all of the peaks in the run file. Make sure that this file exists before moving on to integration. The orientation matrix determined in the above steps may be used as a starting point for indexing and integrating the data set.

Daily Peaks Wizard – integrating the data

Integrating peaks in ISAW using the Daily Wizard is very similar to using the Initial Wizard – in fact, there are fewer steps to the procedure.

Form 1: FindMultiplePeaksForm

1. Launch the Daily Wizard using the **Wizards > SCD > Daily Peaks Wizard** routine:

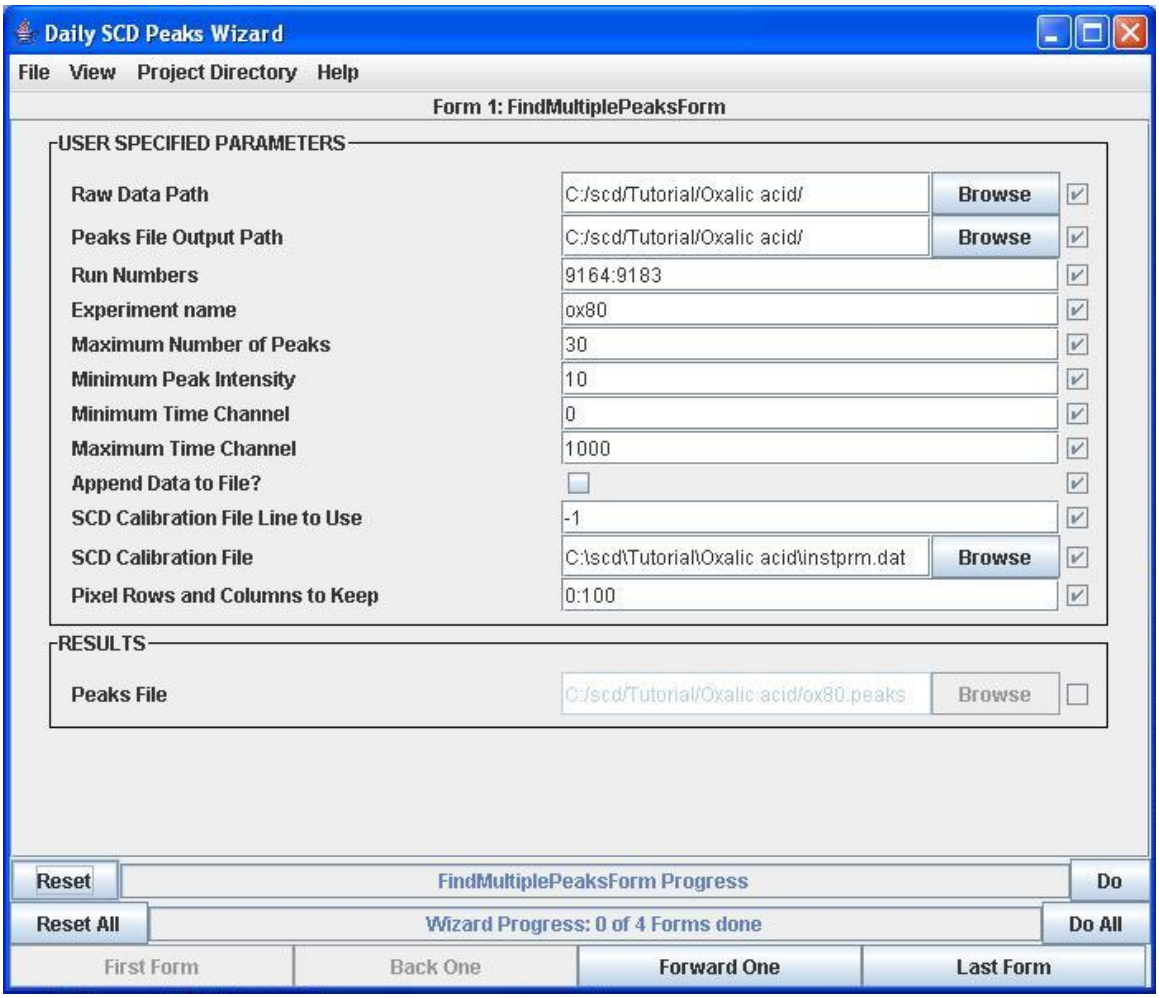


Figure 16

2. Input *all* of the **Run Numbers** for a complete integration of the data set (**9164:9183**).
3. Do not **Append Data to File** unless *only a portion* of the data had been integrated previously and the user intends to integrate additional run files from the same data set.

Occasionally, and especially for a long data collection, portions of the data may be integrated, reduced and put into GSAS for a quick check of the quality of the data. In this event, Daily Peaks can be executed for specific ranges of run files – for example, if there are a total of 18 runs in a data collection, the data might be integrated from runs 1:9. These data might be examined in refinements of the structure in GSAS. To integrate the remainder of the data, the user would then run Daily Peaks for runs 10:18. Details on incorporating this kind of "additional" data into GSAS after data reduction will be explained later.

4. Input the **SCD Calibration File**.
5. Click on **Do** to execute Form 1 and find peaks for *each* run file (even if some of these files were used to find the orientation matrix). Then move on to Form 2.

Form 2: IndexJForm

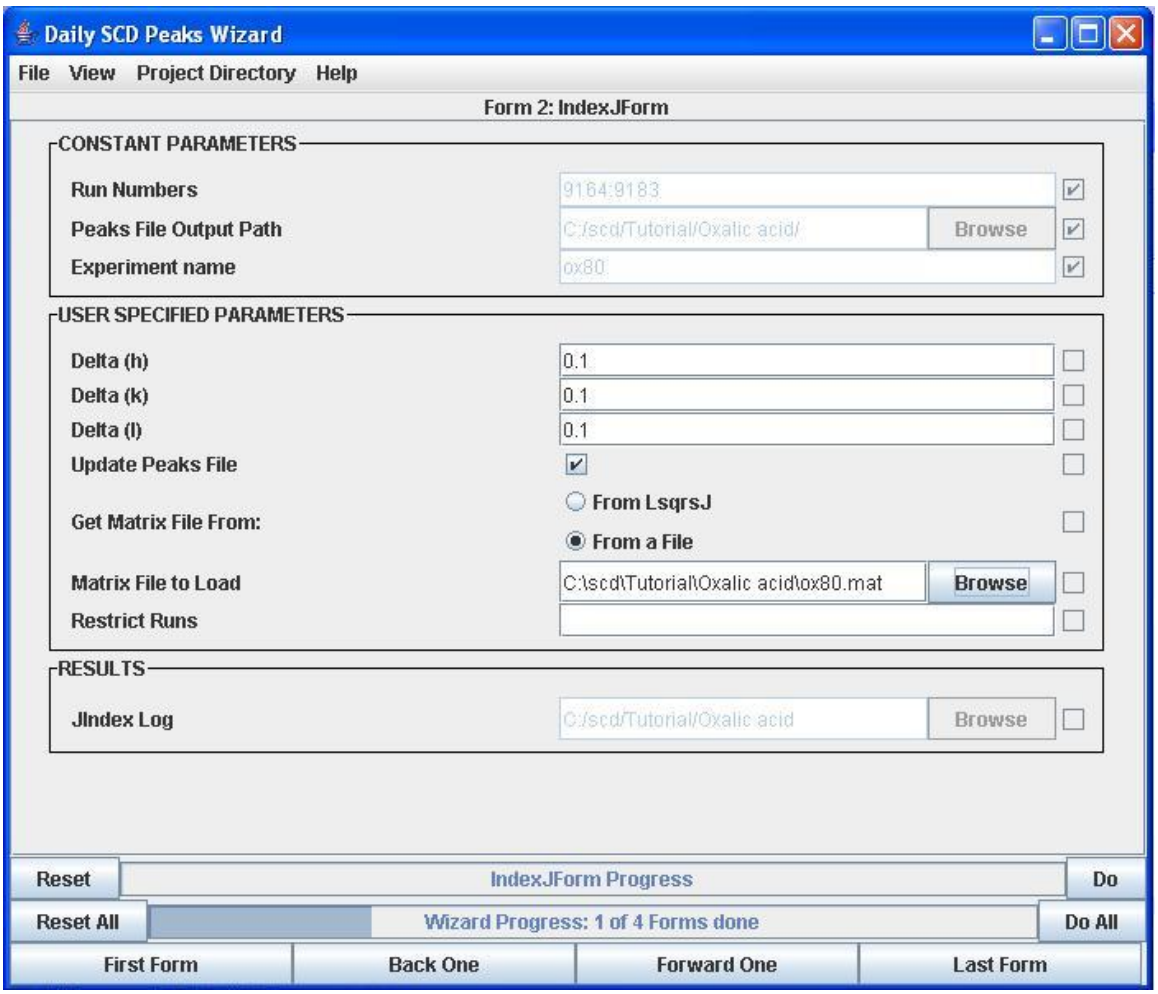


Figure 17

Here the peaks are indexed using the matrix determined previously. The orientation matrix determined prior to data collection may be used here or the orientation matrix can be redetermined from the actual data collection.

6. Make sure to have the correct **Matrix File to Load**, especially if you have saved a transformed matrix to a different file name.
7. Click on Do.

Check the status bar to find out how many peaks have been indexed. If this number is not very large, try increasing the delta values from 0.1 to 0.2. The next form (JLsqrs) will fit each individual run file with its own orientation matrix. After this step you may return to Form 2 and re-index the peaks using the **Get Matrix File From: From LsqrsJ** option.

8. Move on to Form 3 when the peaks have been indexed.

Form 3: LsqrsJForm

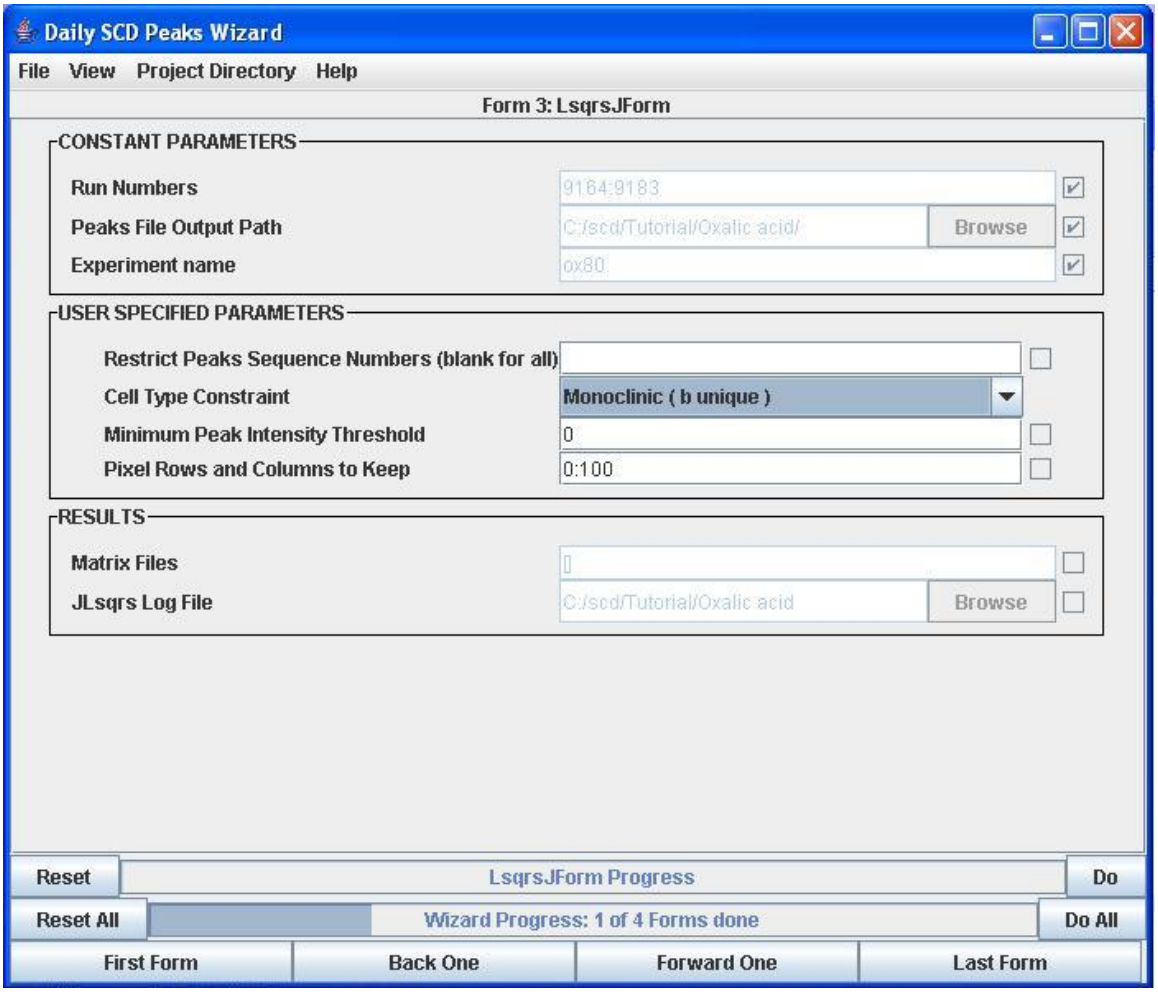


Figure 18

Default values may be used for Form 3, except for the **Cell Type Constraint** which is new with this release. It is suggested that you choose Triclinic (i.e., no constraints) at this stage in order to accurately calculated peak positions and integrated intensities. The LsqrsJForm will refine the loaded matrix file against each run file and write an individual orientation matrix for each run file to allow for small misalignments of the sample during data collection. Each of these matrices may be viewed after the procedure is complete. Matrices written will be labeled with the experiment name, run file number and the letters "ls" in front of it (for example, "*lsox809164.mat*"). Additionally, an overall ls matrix file ("*lsox80.mat*") is written for the overall data set. This matrix, is now correct by symmetry constraints (i.e. the 90° angles are constrained to be 90°), is the one used during data reduction and GSAS file creation. Do not report the errors given by ISAW in subsequent publications of the unit cell parameters.

9. Click on **Do** to write the least squares matrices and then, if you are satisfied, move on to the integration step. Least squares matrices can be used to re-index peaks in Form 2 in order to obtain more accurate least squares matrices.

Form 4: IntegrateMultiRunsForm

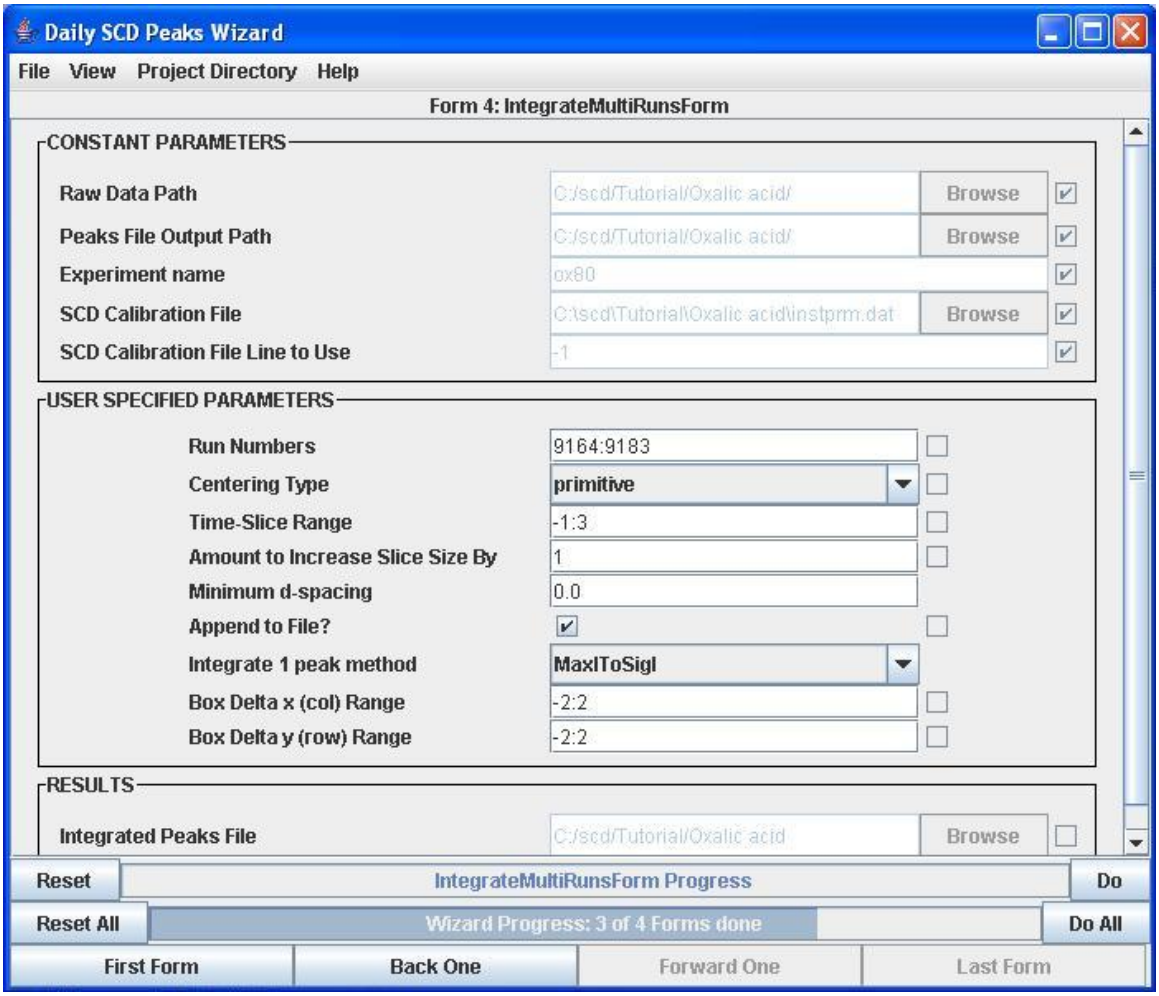


Figure 19

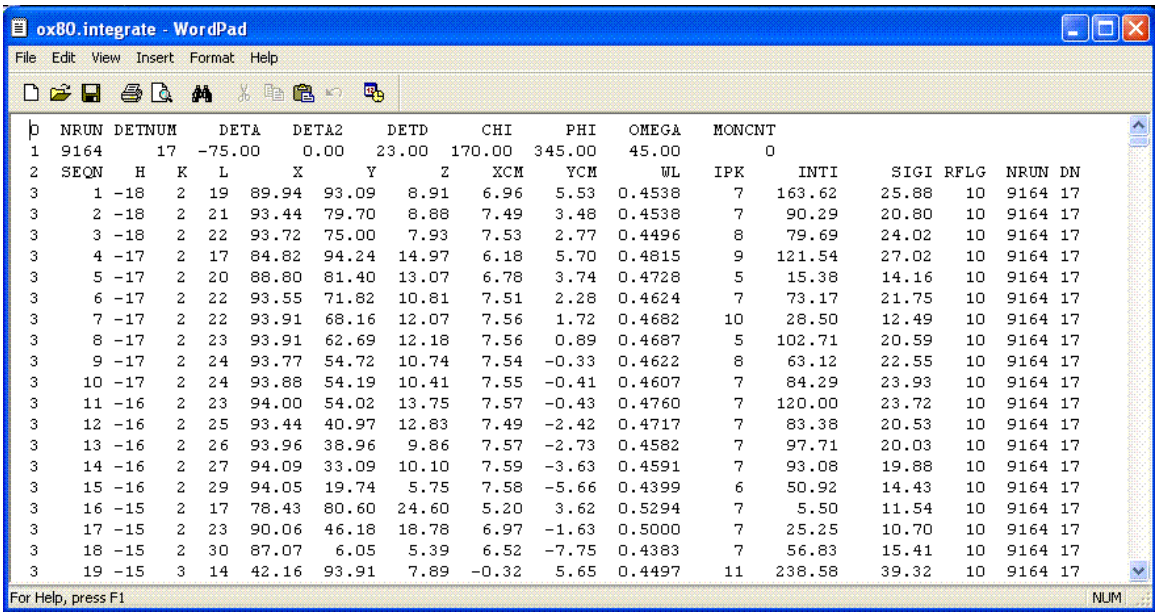
Form 4 is where integration takes place.

10. **Run Numbers** may be restricted to include all or part of the total data (depending on which section of the data is needed).
11. If Append to File is not checked, this information will be lost, however if portions of the data have already been integrated (example 1:9) then *do not* re-integrate this data and append it or there will be redundant data.
12. Make sure that the **Centering Type** information is correct.
13. Unless there is an unusual circumstance regarding the quality of the data, use the default values for the **Time-Slice Range** and **Amount to Increase Slice By**. The time-slice range values of -1:3 refer to the relative time channels about the peak center for a total of 5 channels. The value of 1 in the next box refers to the increase in the peak dimensions on each time-slice. This is a value added to the maximum $I/\sigma(I)$ (see next item) dimenstion in order to make sure that the entire peak is integrated.

14. A drop-down menu allows the method of integration can be specified; the standard method of **maxI/sigI** is useful for most applications. This is a three-dimensional Lehman-Larson integration for which the peak size is varied to maximize the $I/\sigma(I)$ ratio. **Note:** do *not* use the **maxI/sigI – old** integration routine!

Files written: *filename.integrate, integrate.log*. It may be viewed in ISAW (this could take some time to open) or opened with a text editor (faster). Compare the .integrate file with the .peaks file written in Form 1 of the Initial Wizard – it can be seen that the peaks are now integrated. The *integrate.log* file is useful in examining the peak dimensions and intensities on each time-slice for that peak.

You have now integrated the data and are ready to move on to the data reduction stage.



ox80.integrate - WordPad

File Edit View Insert Format Help

0	NRUN	DETNUM	DETA	DETA2	DETD	CHI	PHI	OMEGA	MONCNT					
1	9164	17	-75.00	0.00	23.00	170.00	345.00	45.00	0					
2	SEQN	H	K	L	X	Y	Z	XCM	YCM	WL	IPK	INTI	SIGI	RFLG	NRUN	DN
3	1	-18	2	19	89.94	93.09	8.91	6.96	5.53	0.4538	7	163.62	25.88	10	9164	17
3	2	-18	2	21	93.44	79.70	8.88	7.49	3.48	0.4538	7	90.29	20.80	10	9164	17
3	3	-18	2	22	93.72	75.00	7.93	7.53	2.77	0.4496	8	79.69	24.02	10	9164	17
3	4	-17	2	17	84.82	94.24	14.97	6.18	5.70	0.4815	9	121.54	27.02	10	9164	17
3	5	-17	2	20	88.80	81.40	13.07	6.78	3.74	0.4728	5	15.38	14.16	10	9164	17
3	6	-17	2	22	93.55	71.82	10.81	7.51	2.28	0.4624	7	73.17	21.75	10	9164	17
3	7	-17	2	22	93.91	68.16	12.07	7.56	1.72	0.4682	10	28.50	12.49	10	9164	17
3	8	-17	2	23	93.91	62.69	12.18	7.56	0.89	0.4687	5	102.71	20.59	10	9164	17
3	9	-17	2	24	93.77	54.72	10.74	7.54	-0.33	0.4622	8	63.12	22.55	10	9164	17
3	10	-17	2	24	93.88	54.19	10.41	7.55	-0.41	0.4607	7	84.29	23.93	10	9164	17
3	11	-16	2	23	94.00	54.02	13.75	7.57	-0.43	0.4760	7	120.00	23.72	10	9164	17
3	12	-16	2	25	93.44	40.97	12.83	7.49	-2.42	0.4717	7	83.38	20.53	10	9164	17
3	13	-16	2	26	93.96	38.96	9.86	7.57	-2.73	0.4582	7	97.71	20.03	10	9164	17
3	14	-16	2	27	94.09	33.09	10.10	7.59	-3.63	0.4591	7	93.08	19.88	10	9164	17
3	15	-16	2	29	94.05	19.74	5.75	7.58	-5.66	0.4399	6	50.92	14.43	10	9164	17
3	16	-15	2	17	78.43	80.60	24.60	5.20	3.62	0.5294	7	5.50	11.54	10	9164	17
3	17	-15	2	23	90.06	46.18	18.78	6.97	-1.63	0.5000	7	25.25	10.70	10	9164	17
3	18	-15	2	30	87.07	6.05	5.39	6.52	-7.75	0.4383	7	56.83	15.41	10	9164	17
3	19	-15	3	14	42.16	93.91	7.89	-0.32	5.65	0.4497	11	238.58	39.32	10	9164	17

For Help, press F1 NUM

Figure 20

ISAW writes two files that are needed for the data reduction process:

filename.mat
filename.integrate

If any of these ISAW processes were conducted remotely on helios, the above two files need to be downloaded to the computer where refinements will be taking place. If ISAW was run on your local computer in your working directory, you already have them.

* For instructions on how to integrate portions of data and process them for refinement on a daily basis, see Appendix 2.

Calculating the Absorption Correction

The Excel spreadsheet *Absorption.xls* (found in the C:\scd directory) is designed to calculate the linear absorption coefficients for the sample, as well as the radius of the sample **in cm**. The program *anvred* will use these numbers as part of the data reduction. Input the numbers listed in red into the file: number of atoms in the formula unit, *Z*, cell volume and weight of the crystal (**in mg**).

The linear absorption coefficient is

$$\mu = \frac{Z}{V}\sum_i n_i \sigma_i$$

where *Z* is the number of formula units in the unit cell, *V* is the unit cell volume in Å^3, n_i is the number of atoms of a particular element or isotope in the formula unit, and σ_i is either the total cross section or the true absorption cross section for atom *i* in barns (10^{-24} cm^2).

The three numbers from this spreadsheet that you will need for *anvred* are:

μ_s: the total scattering linear absorption coefficient, including both coherent and incoherent scattering

μ_a: the linear absorption coefficient for true absorption

R (in cm)

For oxalic acid the numbers you will need are:

$\mu_s = 1.302$ cm^{-1}

$\mu_a = 1.686$ cm^{-1}

$R = 0.170$ cm

In the event that you have a sample that does not have an element listed in the spreadsheet, go to:

http://www.ncnr.nist.gov/resources/n-lengths/

and click on the element you wish to enter into the spreadsheet. You will want to enter the total scattering cross section into the σ-s column and the absorption cross section for 2200 m/s neutrons (Abs xs) into the σ-a column, as well as the atomic weight.

Correcting the Data for Absorption - Anvred

The Fortran program *anvred* will correct the data for sample absorption, the incident spectrum, and the efficiency of the ^{6}Li glass scintillation detector. From a DOS command window in your working directory, type

`>anvred`

to launch the program. The following screen should appear. If it does not, make sure the PC system path variable PATH= C:\scd\exe.

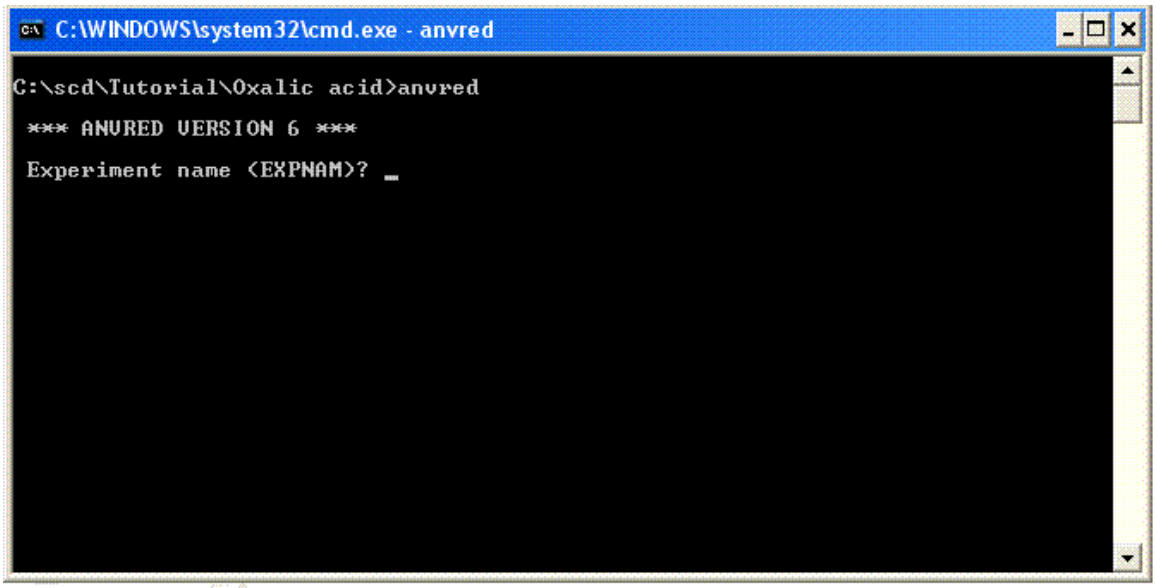


Figure 21

1. Enter the experiment name (**`ox80`**) without any file extension.
2. Assuming that the EXPNAM is the same as you have chosen from ISAW, the defaults can be taken for input and output reflection file.
3. Use the overall least squares matrix (**`lsox80.mat`**) as the matrix filename and type.
4. Enter the number that corresponds to the correct cell type (**`1`**).
5. Enter **`y`** to do the absorption correction.
6. Enter μ_s and μ_a from the Absorption.xls spreadsheet.

```
C:\WINDOWS\system32\cmd.exe - anvred

C:\scd\Tutorial\Oxalic acid>anvred

 *** ANVRED VERSION 6 ***

 Experiment name (EXPNAM)? ox80
 Input the name of the input reflection file (ox80.integrate):
 Input the name of the output reflection file (ox80.hkl):
  ***New output reflection file is being created.***
 Enter matrix file filename.filetype: lsox80.mat
 Cell type: (1)=P, 2=A, 3=B, 4=C, 5=F, 6=I, 7=R? 1


 Do you wish to do an absorption correction (Y,(N))? y

 Input linear absorption coefficients (mu) corresponding to:
   (a) Total scattering (wavelength independent); and
   (b) True absorption at (Lambda) = 1.8 Angstroms.
   (*) Use dimensions of reciprocal centimeters. (*)

(Free Format) (a)Mu(scattering); (b)Mu(absorption):  1.30157733  1.68592024_
```

Figure 22

7. Answer **y** if the numbers you entered are correct.
8. Type **2** to do a spherical (Gaussian) correction.
9. Enter the radius of the crystal (in cm) as calculated by Absorption.xls (**0.170**).

```
C:\WINDOWS\system32\cmd.exe - anvred
 Optionally, add the number of grid points
  on (x), (y), and (z) for types [2], [3] and [4].
        [ 1 ]  Spherical correction (original);
        [ 2 ]  Spherical correction (Gaussian);
        [ 3 ]  Numerical correction, crystal reference frame;
        [ 4 ]  Numerical correction, orthogonal ref. frame.
Type of absorption correction: 2
 Spherical Absorption Correction --
Enter radius of sphere, in cm.: 0.170

  Spherical absorption corrections will be
  calculated using numerical integration
  on a Gaussian grid.
 Number of points on Gaussian grid:        512
 Number of points on (x):   8;     on (y):   8;     on (z):   8

 Integrated crystal volume (cm**3):          0.20586E-01

               4/3(pi)r**3 (cm**3):          0.20580E-01

The incident spectrum is derived from vanadium data obtained on SEPD.
Select a detector efficiency of:
   (1) 0.79448 * WL
or (2) 1.00928 * WL
Input (1) or 2: _
```

Figure 23

10. Enter **1** to correct for the incident spectrum.
11. Enter **14** to select the correct incident spectrum coefficient. If this step results in the program quitting, make sure that the file *spec_coeff.dat* is located in the C:\scd directory. Option **14** is the most recent spectral coefficient correction (2005).

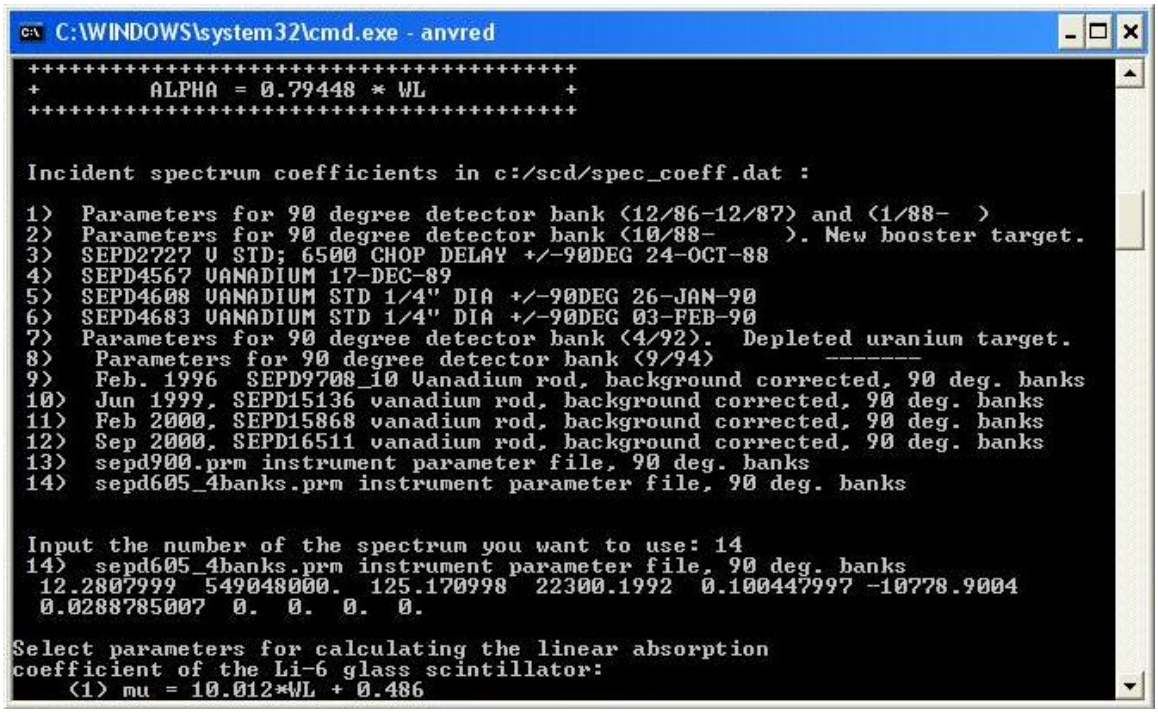


Figure 24

12. Input **2** select the parameters for calculating the linear absorption coefficient of the glass scintillator.
13. Use the default input for minimum I/sigI, and number of X and Y detector channels to include all of the data.
14. Set N = **5** to reject peaks within 5 channels of the border.
15. Type **y** to reject peaks for which the centroid calculation fails.
16. Use the default of **0** for minimum peak count.
17. Set a minimum *d*-spacing of **0.5**. (This is a general standard. If data are especially weak and noisy, this level can be changed here. GSAS also has a way to set a cutoff for *d*-spacing, so it can be changed to a higher number during refinement if necessary).
18. Use a scaling factor of **1.0** to apply to F^2 and σF^2.

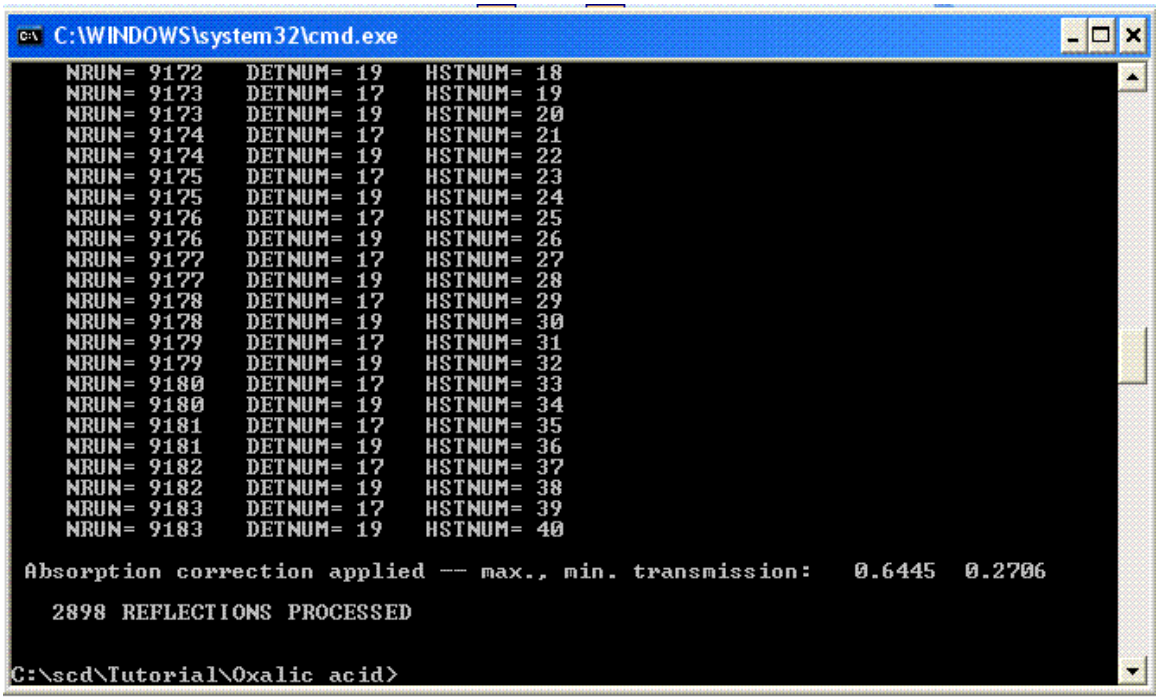


Figure 25

At this point anvred will process and correct the data. There should be twice as many histogram numbers as there are run files. Maximum and minimum transmission are reported for the sample (this information is contained in the log file).

Files written: *expnam.hkl, anvred.log*. This file is a text file that can be reviewed by opening it with a text editor.

Writing Files for Structure Refinement – anv2gsas

The Fortran program *anv2gsas* will write the single crystal reflection files used by GSAS to do refinements. It will write information to the GSAS experimental file *expnam.exp*; this must be created first. Typing **anv2gsas** at the DOS prompt will give you the information on setting up the EXP file:

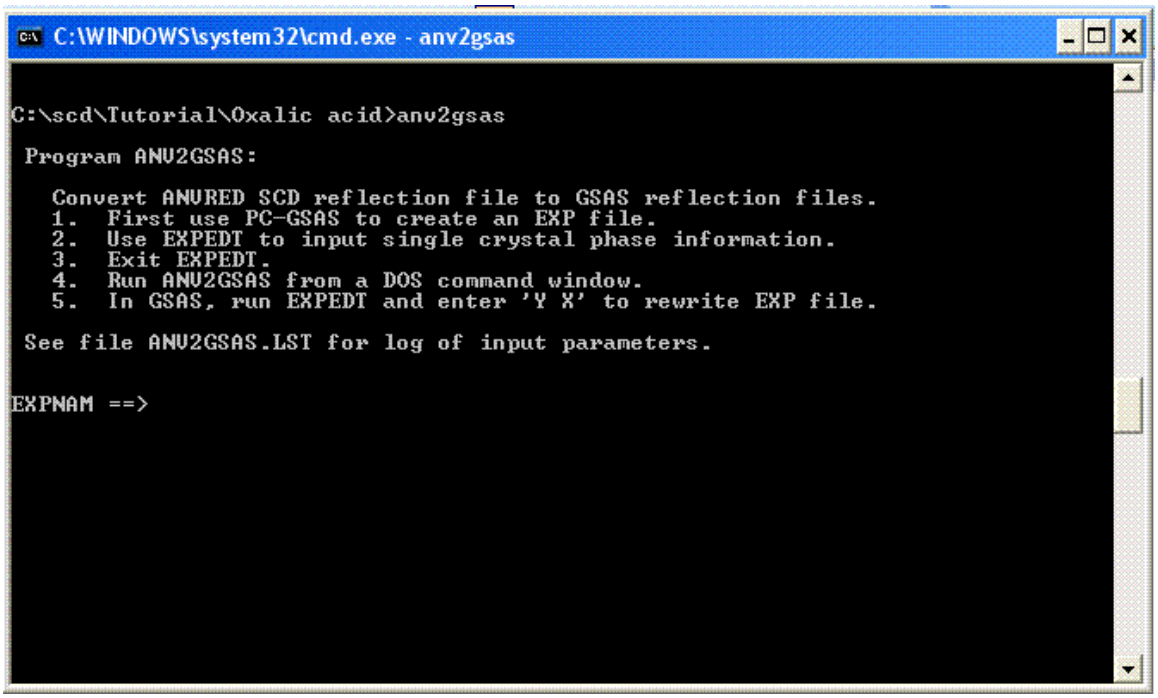


Figure 26

1. First, follow the anv2gsas instructions to set up the GSAS EXP file. Matrix information is obtained from the overall least squares matrix, and the space group should be known.
2. Type **ox80** for the EXPNAM.

```
C:\WINDOWS\system32\cmd.exe - anv2gsas

EXPNAM ==> ox80
ANVRED file name (name.hkl) ==> ox80.hkl

The first line of the ANVRED file is:
 -11   2  12   44.45   46.62   1  0.6370 0.2434   9164     65 0.2316 0.7265 0.63


 Type RETURN or ENTER to use default values in <...>


 Integrated intensities obtained with
      (1) PEAKINT
   or (2) INTSCD or INTEGRATE?
 Input 1 or <2> ==> 2

Run number of first histogram ==> <  91>9164

 GSAS histogram number of first histogram.
Enter a 1 if these are the first or only data.
Enter n+1 if there are already n histograms.
Input new histogram number < 1> ==> 1

 SIG(Fo**2) = sqrt( SIGFOSQ**2 + ( P * FOSQ)**2 + K )
Input P <0.04> ==> 0
Input K <0> ==> 0

 Lattice constants:
       6.077000  3.472000 11.850000   90.0000  103.8440   90.0000
```

Figure 27

3. Enter the name of the hkl file (**`ox80.hkl`**).
4. Enter **`2`**; the integrated intensities were obtained using INTEGRATE.
5. Enter the run number of the first histogram: **`9164`**.
6. There is no other data so type **`1`**. (See special instructions if portions of the data have already been integrated for preliminary refinements.)
7. Enter **`0`** or P and K. The P value may be changed in GSAS at a later time. If it is desirable to change P and K down the line, anv2gsas can be run again. The histograms will then be processed.
8. At the DOS prompt, type **`cnvfile`**. When prompted for a datafile to convert to GSAS format, type **`ox80.exp`**. Hit return again.
9. Type **`expedt ox80.exp`**.
10. Type **`y x`** to make sure the GSAS file is formatted correctly. You are now ready to input atoms and begin refining the structure!

Structure Refinement – ox80

GSAS is the standard method of refining single crystal neutron diffraction at IPNS. It is not a structure solution program – structures have usually been solved by x-rays prior to the neutron experiment. If you would like to use SHELX to refine the structure, we typically refine extinction in GSAS and then import the data into SHELX. Contact IPNS SCD personnel if you are interested in this – instructions are being formulated for this purpose.

GSAS can be downloaded from a link on the SCD webpage. It is *highly recommended* that the user go through the GSAS tutorial provided with the program to learn how to use GSAS; this tutorial will not address these issues as the GSAS tutorial is much more thorough. While PC-GSAS or Brian Toby's EXPGUI are common ways to use GSAS, if the path structure is set up as specified at the beginning of this tutorial the user can type the appropriate command (for example **`expedt, genles, fourier,`** etc.) at a DOS prompt in the working directory.

The initial EXP file (*expnam.exp* or *ox80.exp* for this example) was created in the anv2gsas step of preparing data for structure refinement, but no atoms were added to the file at that time. The atoms may either be input by hand or by reading in the *atoms.txt* file provided with this tutorial.

General steps in GSAS refinement would follow:

1. Convergence of the scale factors (no refinement on atom position).
2. Refine the atomic positions.
3. Refine the isotropic thermal parameters.
4. Refine the extinction. Data from SCD is best handled with a Type I Lorentzian correction.
5. Examine the Fourier difference maps for hydrogen atoms.
6. Refine the hydrogen atoms as above.
7. Once the atoms have been found, you can use the program **refedt** to reject disagreeable reflections based on several criteria. Be careful when using this option and ask questions if you need to! Outliers could result from incorrect integration, high extinction and absorption and resolution limitations. These should be checked as a justification for rejecting peaks. You can also use the robustness feature to modify weights of outliers in GSAS.
8. Refine the anisotropic displacement parameters for all atoms.
9. Examine Fourier difference maps again to check for other problems.
10. When the structure is complete, run **`disagl`** to obtain final bond distances and angles with esd's.
11. Weighting factors can be added to improve the goodness of fit, which can be calculated by taking the square root of CHI^2, found in the *expnam.lst* file.

Graphical Representation of the Structure

ORTEP 3 for windows (also part of the WinGX package) will read GSAS EXP files directly. This is the simplest method to produce a picture of the molecule as well as track your progress visually while using GSAS.

FOBS and DELF maps can be created in GSAS using the **`forplot`** routine.

Writing the Structural Report

This tutorial contains a template file named *reporttemplate.doc*. It is a general template complete with references to assist in preparation for publication. Any value that needs to be supplied by the user is in red text.

`Gsas2cif` is a program that will write a basic *cif* file for deposition of atomic coordinates to a database such as the Cambridge Structural Database. It will not appear exactly as a *cif* generated by SHELX.

Glossary

CHI	chi angle
DETNUM	detector number
DETA	detector angle in the horizontal plane
DETA2	detector angle out of the horizontal plane
DN	detector number again, same as DETNUM
H,K,L	h,k,l
IPK	neutron counts at peak maximum
INTI	integrated peak intensity
MONCNT	incident beam detector monitor counts
NRUN	run number
OMEGA	omega angle, fixed at 45 deg.
PHI	phi angle
RFLG	reflection flag, usually equal to the crystal number
SEQN	sequence number
SIGI	sigma for INTI based on counting statistics
WL	wavelength in Angstroms
X,Y,Z	histogram channels
XCM,YCM	distance from the detector center in centimeters

Appendix 1 – Using refedt

Refedt is a program used to edit the GSAS single crystal reflection files. It can be used to reject reflections in the refinement based on various criteria. Use this with care however – refedt should not be utilized until most (preferably all) of the atoms have been located from the Fourier maps and the refinement is stable near an $R(F^2)$ value of 20%. It is important that rejection of data is justifiable (see page 38, number 7). Ideally, rejecting a small number of outliers should not affect the model, but should reduce the R-factors.

Refedt is invoked by typing at the DOS prompt:

> **refedt**

Typical input follows, as well as a listing of the processed reflections. The file *refedt.lst* is written which contains a log of the input and output. Refedt can also be run again with all "0" values for input to return the data set to its original state, so nothing it truly lost. This example is not taken from oxalic acid data.

```
EXPNAM ==> bpme2

 Number of histograms ==>   34


Input minimum wavelength <0.0>:   0.5

Input maximum wavelength <99.0>:   99.

Input minimum extinction correction <0.0>:   0.

Input maximum FOSQ/FCSQ ratio <0 for no test>:   2.

Input maximum FCSQ/FOSQ ratio <0 for no test>:   2.

Input maximum ABS(FOSQ-FCSQ)/SIGFOSQ <0 for no test>:  0

Input maximum FOSQ/SIGFOSQ <0 for no test>:  0
```

```
 IHST   H    K    L       DSP       LAM      FOSQ   SIGFOSQ      FCSQ     FCTSQ    EXTCOR      TBAR

Processing histogram   1
    1  -5.   1. -22.     0.514     0.586    54.570    33.960     6.490     3.182     1.000     0.141
    1  -5.   2. -19.     0.582     0.598    41.120    18.070     3.970     1.947     1.000     0.141
    1  -4.   1. -22.     0.527     0.628    49.970    23.850     6.930     3.398     1.000     0.140
    1  -4.   1. -18.     0.630     0.711    69.410    22.520   143.254    70.305     0.999     0.140
    1  -4.   1. -17.     0.662     0.735    31.890    22.880   103.997    51.033     0.999     0.140
    1  -4.   2. -19.     0.599     0.655    19.190    16.090    64.285    31.532     1.000     0.141
    1  -4.   2. -17.     0.660     0.693    14.020    13.280     0.581     0.285     1.000     0.141
    1  -4.   2. -15.     0.734     0.734    92.440    19.110    28.968    14.208     1.000     0.141
    1  -4.   3. -22.     0.524     0.564    55.400    41.640     3.344     1.640     1.000     0.141
```

Appendix 2 – Integrating and Processing Portions of Data.

There are some instances where it may be valuable to integrate portions of data and process them to check for initial structure quality while the remainder of the data is being collected, instead of waiting until all of the data has been collected. In this case saving your wizard state at the end of the integration step is very valuable, as it allows you to reload the wizard state and change the run numbers for the next portion of data, appending it to the files you have already created. Note that if you reload a saved wizard state and reintegrate all of the data that was previously processed, ISAW simply add to the existing integrate file and you will have multiple histogram data. When following this procedure, you only need to integrate and process the data you haven't already integrated.

When using the Daily Wizard to integrate portions or remainders of data:

1. Check the **Append to File** box to make sure that subsequent portions of data are included in the *expnam.integrate* file.
2. Delete the *expnam.hkl* file.
3. Run anvred on the entire *expnam.integrate* file to generate the new *expnam.hkl* file.
4. When running anv2gsas on the new hkl file, enter the new "Run number of first histogram" from the data you have just processed (not the first histogram overall). You are also prompted to enter 1 if these are the only data or n+1 if there are already histograms present. Here you want to use the n+1 option; for example, if you have already processed 5 run files for a total of 10 single crystal reflection files, use 11 as your n+1 value.
5. A file named exp-file.inc should also be generated. Open this file with a text editor and copy the information inside of it.
6. Open the expnam.exp file with a text editor and replace the relevant information with that found in exp-file.inc. (If the information in exp-file.inc is only for the newly generated histograms, append these in the right places. I don't remember this being the case however.)
7. Run cnvfile on expnam.exp.
8. EXPEDT expnam.exp and enter Y X to write the file.
9. In GSAS, turn off all atom refinement parameters (and extinction) and refine the scale factors until they converge.
10. Turn refinement back on and continue.