

CCD Instructions

These instructions provide a short guide for a quick start with the Siemens SMART PLATFORM with CCD detector. The program package consists of **SMART** (for data collection), **SAINT** (for integration) and **ASTRO** (for detailed preplanning of the measuring strategy. It does not have to be used for standard measurements, but provides a nice tool to visualize what happens in reciprocal space during the data collection.). Furthermore structure solution (**XS**) and refinement (**XL**) programs are installed. Graphics can be done with **XP**.

Data Collection

1. Verify, that the Cooling device (small box to the left of the diffractometer) is switched on (green light) and check the temperature in the LCD display (on the right side of the diffractometer). It should be at about -55°C .

Create and move to a **new** subdirectory under the **c:\frames** (or **d:\frames**, **e:\frames**, **f:\frames**; at least 400 Mbyte should be free for a standard hemisphere run) directory with *mkdir yourname* generate your personal a subdirectory and *cd yourname* change to this directory. With *mkdir newdir* and *cd newdir* generate a directory for the measurement and change into it. *Newdir* is the ID-code of your substance and should not exceed eight characters.

2. Start the SMART program with *smart*. Compare the instruments θ , ω and ϕ angles with the values displayed in the window and update them when necessary using the **GONIOMETER/Update** option.

Only required if Instrument was switched off and/or Angles did not match (see 2.) :

Then drive all circles to zero with the **GONIOMETER/Zero** option.

With **GONIOMETER/Home axis** the θ and ω circle (1 and 2) have to be driven to their reference marks.

Verify the sample-detector distance under **CONFIGURE/Edit** (important) and fill in your username.

Be very careful, when changing of detector distance and collimator/beamstop. Any damage on this sensitive parts is very expensive and the instrument can be deadjusted very easily.

3. Optically align the sample as good as possible with the crosshair using the **GONIOMETER/Optical** option and the buttons for ϕ , κ , ω and *axis print*. Note the size and shape of the crystal (one unit in the microscope corresponds to 0.02mm)! Drive all axes to zero when done using **GONIOMETER/Zero**.

Adjust with **GONIOMETER/Generator** the values to 45 kV and 35 mA.

OPTIONAL (not recommended, better proceed to 4.):

Load the dark frame *c:\frames\dark\d60l16._dk* under **Detector/Load Dark**

Take a 60 sec. rotation frame image of the crystal using the **SCAN/Rotation** option. If there are no spots or if there are powder diffraction rings, restart with another crystal.

If the crystal diffracts well you should see spots up to the edges and the expected exposure time will be around 5 to 10 sec. per frame.

4. It is better to generate new darkframes for each measurement:

Generate under **Detector/NewDark** the corresponding dark frame for the desired exposure time

(for example *c:\frames\yourname\newdir\d10l16._dk* for 10 sec. and 16 frames or *c:\frames\yourname\newdir\d20l8._dk* for 20 sec. and 8 frames).

5. Determine initial cell parameters with the following series of commands.

o **SCAN/Matrix** with default parameters (15 frames, -0.3 deg. frame width) will record 3 series of frames (~ 25 minutes) and will automatically threshold the frames, pick spots, index spots, test for possible higher metric symmetry, and refine the cell parameters. You should see one or more lines of "1"s in the indexing step. Also, note the program's choice for Bravais lattice type.

The reliability of the indexing can be checked with the histogram: most reflections should be on the left side at small values. If there are lots of reflections on the right side of the histogram the automatic indexing has failed possibly due to twinning, too little frames, weak data or other problems like wrong sample-detector distance (check values in **CONFIGURE/Edit**). Ask the system manager for help if the problem persists.

6. In the CONFIGURE/Crystal menu type the proper values for the empirical formula, crystal habit, crystal color, crystal dimensions, and temperature of data collection (convenient, but not necessary).

7. In order to optimize the scans (frame width) and the subsequent integration the size of the reflections has to be determined. With DISPLAY/New Frame a frame of the previous matrix run should be loaded and under **GRAPH/Rocking** the size of a relatively strong reflection sufficiently away from the beamstop should be checked. The reflection should appear on 3 to 8 frames. Under **CURSORS/Vector** the diameter of a reflection (D-Deg.) should be determined. **In almost every case the standard frame width of 0.3 deg. is suitable.**

8. For a standard run change under SCAN/Edithemis the value for your desired exposure time. If you want to change the frame width then you have to change the number of frames accordingly (the product of frame width and frames should be constant and should not exceed

180 deg., e.g. change the no. of frames to 909 when your frame width is reduced to -0.15deg.). For weakly diffracting samples, increase the count times up to a maximum of 60 sec/frame.

Then start the measurement under **SCAN/Hemisphere** where only jobname and title have to be changed. If you choose as jobname 'a', then the standard files in SAINT (integration program) fit already and no changes have to be made.

(If greater redundancy is needed, use **SCAN/Editruns** and adjust here the desired values for exposure time and frame width. If the crystal diffracts to very high angles, then 2-THETA and OMEGA can be changed to -35 for all runs to acquire data above 70 deg. in 2-Theta. Data collection is started with **SCAN/Multirun.**)

A data collection interrupted with the **esc** button can continued with **SCAN/ResumeRuns.**

9. Determine the orientation matrix from the measured frames:
Under **ReflectionArray/Threshold** search for reflections on 20 to 50 frames. Use the sequence *newfile1.001, newfile2.001, newfile3.001, newfile1.300*.
Then **index** the reflections, choose the **Bravais** lattice and perform a **LeastSquares** refinement of the orientation matrix. When the least squares fit of the matrix is performed a file *newfile1.p4p* is written.
10. Under **Goniometer/Generator** please set kV to 20 and mA to 5 (standby of the generator) to protect the xray tube.
11. Leave SMART and copy *newfile1.p4p* to *newfile2.p4p*, *newfile3.p4p* and *newfile.p4p*

INTEGRATION

1. Copy the data via ftp to Manet:

leave SMART with **COMMANDS/Exit** and type *ftp manet*.
Give your login name and your password and change the working directory to */usr/ccd/username*. Then type:

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prompt  
bin  
mput *.*
```

When the data transfer is complete leave ftp with *quit* and type *del *.** (cleans the directory)

Alternatively the same procedure can be done for the machine Manray and the directory */usr/home/xray/username*

Attention: There is no backup from the complete xray harddisk!

Important data like *.raw, *.p4p, *.abs have to be copied to your home directory

2. Login at MANET, change working directory to */usr/ccd/integ* and start the saint program by typing:

saint /k2:n

where n = 1 triclinic, 2 monoclinic a-unique, 3 monoclinic b-unique, 4 monoclinic c-unique, 5 orthorhombic, 6 tetragonal, 7 hexagonal, 8 rhombohedral, 9 cubic.

3. In the **INTEGRATE** menu of saint, change the following items to correspond to the values for the current sample. The following examples presume that the base file name is "newfile", that there are two scan runs being performed numbered 1, 2 and 3 and that the cell is primitive monoclinic.

Option

[I]: *newfile1.001,newfile2,newfile3*

[M]: *newfile1.p4p newfile2,newfile3*

[R]: *newfile1.raw,newfile2,newfile3*

[Z]: *dt*

[S]: XY-size determined from **CURSORS/Vector**, Z-size det. from **Graph/Rocking**.

(values are not critical since defaults are often o.k., but better choose too large than too small!).

Suppress size refinement: *N*

Set the Resolution [U] to a reasonable value (determined from a couple of frames with **CURSOR/Pixel**).

4. Start the integration with the "!" command.
Check the output on the screen from time to time. The values for **%2sig** should frequently be smaller than 50 and **CORR** should be in the range 0.25 to 0.8.
If the value for **%2sig** are always around 100 and the values for **CORR** very often smaller than 0.25 than something might be wrong with the orientation matrix.
5. When the data collection is finished delete all frames since the used disc space is huge.
Edit the *newfilem._ls* file to record the refined cell parameters and the number data used to refine the cell. The *newfilem._ls* contains the number of data used in the time decay, scaling, and the actual decay of the data (when integrated with the parameter [Z]=d).
6. Log onto one of the other SGI computers in your own account and copy the */usr/ccd/integ/newfile*.** files to your directory.

The *newfile*.raw* files contain the data including direction cosinus for later absorption corrections, the *newfile*.p4p* files contain the information for the orientation matrix and cell parameter.

Important:

Since a normal hemisphere generates already 360 Mbyte of data, the frames should be deleted as soon as possible! In the case of difficult problems (superstructures, twins, uncertain cell determination) where new integrations might be necessary, please save your data as soon as possible to a CD. Follow the procedure, given in our internal homepage.

Absorption Correction

1. Perform the empirical absorption correction with Sheldrick's SADABS program by typing *sadabs*. Read in the *newfilem.raw* file and answer all the questions (use the default values recommended by the program whenever possible) and let the program write a *newfilem.hkl* file.
2. Type *xprep* and read in the *newfilem.hkl* file. The lattice constants are automatically read in from the file *newfilem.p4p*. Determine the space group and let the program write an *.ins* file with a new name.

It is advisable to merge the data with **XPREP (Options [M] and [A])** after noting the R_{int} . (Options [D] and [S]) and limiting the dataset to a reasonable resolution (Option [H], cut the dataset at that value where R_{sigma} exceeds 0.25). Write the actual dataset to file with [W]. All steps are written to a *filename.prp* file.

Solution, Refinement, Graphics

1. Start the structure solution with *xs filename* and check the result in the *filename.lst* file or with the graphic program **XP**. Copy the *filename.res* file to *filename.ins* and start the refinements with *xl filename*. The programs **XS** and **XL** correspond to **SHELXS96** and **SHELXL96** with minor changes. For twins **SHELXL96** should be used (bug in **XL**!).
2. Here is a standard sequence of commands for the graphic program **XP** to produce plots of small molecule structures:
xp
read filename (reads filename.res file)
fmol (sets up connectivity list)
grow atomname (atomname could be for example the metalatom in the molecule)
proj (structure can be rotated with the buttons)
telp 0 -50 (plots ellipsoids with 50% probability), typing B leaves the naming routine writes plotfile.)
draw filename (choose option A for files which can be sent to a postscript queue with *qprt*)

additional useful commands:

- pick* (allows to select and name atoms)
- file filename* (writes files for further refinement with **XL**)
- undo atomnames* (deletes bonds between named atoms)

kill atomnames (deletes atoms)
link or *join* (draws bond between named atoms)

Please read the manuals for more details! Its easy to understand and contains lots of examples!

Structure Checklist.

Completed crystal structures must pass the following tests.

1. The model must be chemically reasonable. Similar bonds should have similar geometries.
2. The structure should be refined to convergence, that is the maximum shift/error ratio should be < 0.1 . All non-hydrogen atoms should be refined with anisotropic displacement parameters provided that there are at least 10 data per parameter. Lower data-to-parameter ratios indicate that either the data were not collected to a high enough scattering angle, or that Friedel-related (or equivalent) data were not collected for a noncentrosymmetric space group.
3. There should be no atoms with displacement parameters which are "non-positive definite". The displacement parameters should be checked for signs of systematic error. For example, ellipsoids of heavy atoms aligned in one direction may indicate a need for an absorption correction.
4. Non-centrosymmetric space groups should be refined with the correct absolute structure.
5. The weighting scheme should be adjusted so as to produce nearly constant values for the variances as functions of intensity and resolution as well as a goodness of fit with a value around 1.0.
6. There should be no obvious outliers in a list of "worst-fitting data."
7. The final difference map should have no abnormally high peaks or low valleys.

Report Crystal Structure.

Most journals which accept crystal structures require the following information in the crystal structure report.

* Data collection

Source of sample and conditions of crystallization.

Habit, color, and dimensions of the crystal.

Formula, formula weight.

Unit cell parameters and volume with esds. The number of data theta range of data used to determine cell.

Crystal type and space group.

Z, density, and absorption coefficient.

Instrument and temperature.

- * Structure solution
 - no. of data collected, no. unique[R(int)].
 - Method and programs for structure solution.
 - Absorption correction details, if applied.
- * Structure refinement
 - Method and programs for refinement.
 - no. of data refined, no. restraints, no. parameters.
 - Weighting scheme.
 - R1, wR2, S values.
 - Maximum shift/error.
 - Maximum and minimum of difference map.
- * Tables and figures
 - Positional parameters and isotropic or equivalent displacement parameters.
 - Bond distances, angles, and torsion angles.
 - Anisotropic displacement parameters.
 - Structure factor tables (often required for review but discarded by the journal).
 - A labelled figure showing the displacement ellipsoids.
 - A packing diagram.