Lesson 16

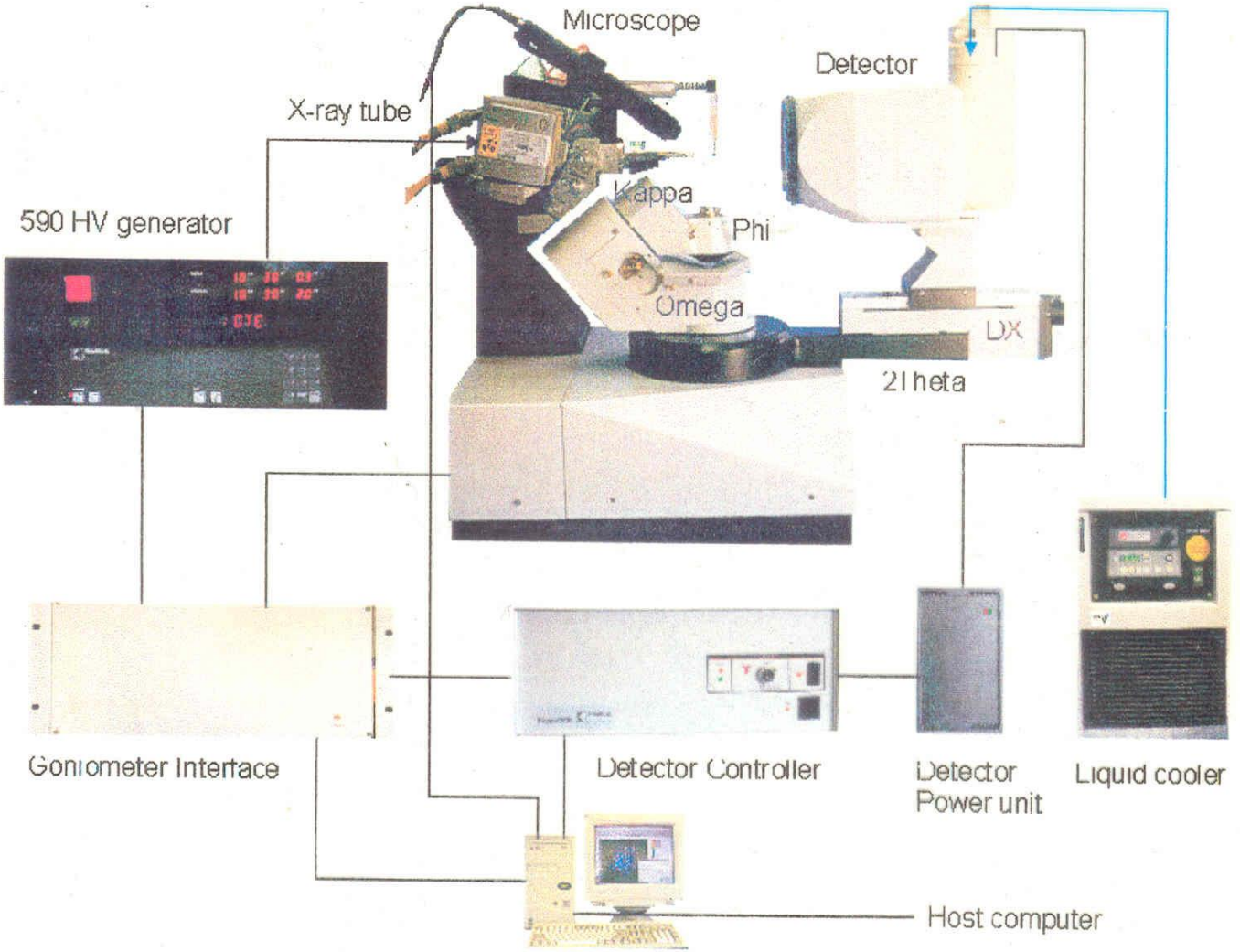
- Preliminary Steps to Data Collection
- While there are many types of equipment out there our discussions will be directed at area detectors and the equipment in the Purdue Lab

Diffractometer Computer Interactions

- The actual control of the diffractometer is done by a computer.
- There are 2 approaches to this
  - Control the diffractometer by a dedicated computer which is on the internet and interacts with other computers (client-server model).
  - Directly hardwire the diffractometer to a computer

KappaCCD

Introduction



The KappaCCD consists of a X-ray source, 3-axes goniometer (Omega, Kappa, Phi) to position the crystal and a Theta-axis and DX to position the detector. The two-dimensional detector measures the X-ray, which is reflected in

Some KappaCCD Basics

- The computer that runs the ccd is called the server. It runs Windows98 and the monitor and keyboard are located next to the diffractometer.
- It can perform basic operations and is used in aligning the crystal in the beam and checking crystal quality.
- To keep other users out there is the concept of MASTERSHIP. When the server has MASTERSHIP no other computer can operate the ccd.

Client Computers

- These are LINUX computers that connect to the server over the internet. (Note LINUX is case sensitive).
- They run programs that do higher level calculations and then instruct the server to carry them out.
- Contain the Nonius software COLLECT package
- Client computers must have MASTERSHIP before they can control the unit.

The Rigaku Rapid II

- The diffactometer is hardwired to a computer.
- This computer provides both the simple server functions and also the higher level functions.
- The computer operates under Windows XP and is located on a desk nearest the instrument.
- The CrystalClear software has several methods of operation.
- Since only one computer can interact there is no MASTERSHIP issue.

Preliminaries

- Make sure x-rays are on and at proper intensity
- Make sure there is helium flow on the RAPID
- If running at low temperature make sure Oxford 700 is running and at the correct temperature.
- Ensure there is an xyz head on the instrument
- Check other unique instrument requirements to make sure it is running properly.
- Make sure you are set up to collect the data in the proper directory

Positioning the Crystal

- First, the crystal must be mounted on a fiber/loop on a magnetic base and placed on the xyz head.
- Care should be taken not to break the fiber during these processes.
- The goniometer must be positioned so it is perpendicular to the microscope/camera. Obviously, in this case z and either x or y will form a visible plane. To adjust the other axis a rotation of 90° is required.

Centering on the KappaCCD

- Use the server computer next to the instrument
- Gain MASTERSHIP
- Select mount
- Position perpendicular to the microscope.
- Adjust postion
- Rotate 90° by pressing button
- Adjust again
- Continue around until crystal is centered

Centering on the Rapid

- Using the manual control at the computer to set the diffractometer to omega=70, chi=0, phi=0
- Lossen the phi allen screw
- Adjust the crystal position
- Manually rotate the sample 90° in phi
- Adjust again
- Complete alignment.
- Tighten the phi allen screw.

Approaches to Data Collection

- Michael Rossman suggested the “Amercian Method”--shoot first ask questions later
  - Cannot use Laue group to shorten data collection
  - Do not know anything about the crystal until after all the data is collected
- Take some images for indexing
  - Can evaluate crystal quality
  - Check unit cell for correct size and if it is known
  - Calculate most complete and quickest data collection.

INDEXING on the KappaCCD

- There are two approaches to indexing crystals
- One is HKL2000 (denzo) a standard package used for macromolecular crystals.
- The other is DIRAX or CELL_NOW
- They require different input frames.

INDEXING WITH HKL2000

- Need to collect 10 frames each of 1° rotation.
- HKL2000 then indexes the frames.
- It uses partial spots—spots that appear on more than one frame.
- Can be run automatically or under user control
- Very robust
- Cannot index twined crystals—produces only one orientation matrix
- HKL2000 is started with the command kc.

Dirax -- cell_now

- These need the pixel location on the frame and also the rotation angle value which cannot be directly determined.
- Collect one 5° frame.
- Then collect the same frame while moving chi by 10° while doing the omega rotation. The change in the location of the spot between the two frames can be used to determine the rotation angle
- Collect 4 sets of these pairs of frames.

DIRAX

- Requires more user interaction.
- Can index twins or determine multiple orientation matrices.
- Should always be run even if cell_now is used.
- Called by the command “ndirax gui”

cellnow

- Cellnow is a local program that runs cell_now and creates the proper orientation matrices.
- Cell_now is a George Sheldrick program
- Very automatic but uses a good deal of time
- Can determine multiple orientation matrices but only if one unit cell is present (one compound).
- Sometimes obtains cells that are a multiple of that found in dirax. These are incorrect.

supergui

- This is the program that guides you through the entire indexing, data collect, and integration process.
- You use it by pushing buttons.
- It is fairly foolproof.
- Supergui in the Purdue lab also posts the structure name on the web site. To not post the name use superguinl.

Indexing on the Rapid

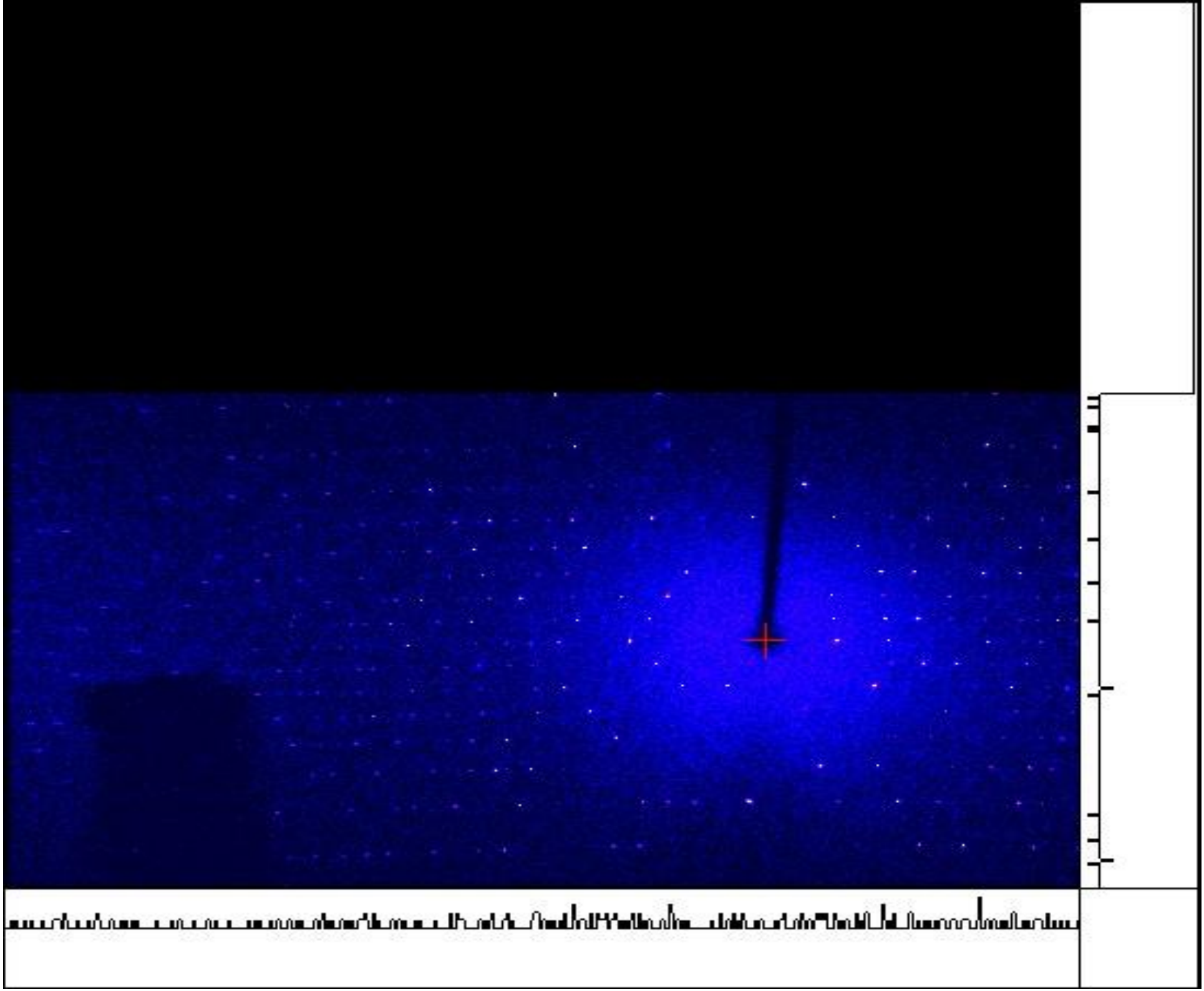
- Generally the routine d*trek in CrystalClear is used
  - This is the default and is represented by the American flag.
  - Requires 4 images of 5° at 70° intervals
  - Cannot index twins, etc. Twin indexing is done on the entire data set after collection.

From images to indexing.

- No mater what software or diffractometer is used all indexing consists of several steps.
- These may occur in one program or many depending on the software.
- Idea is to find the most orthogonal unit cell with the shortest axes.
- Will index to a primitive cell and then can transform to centered if required.

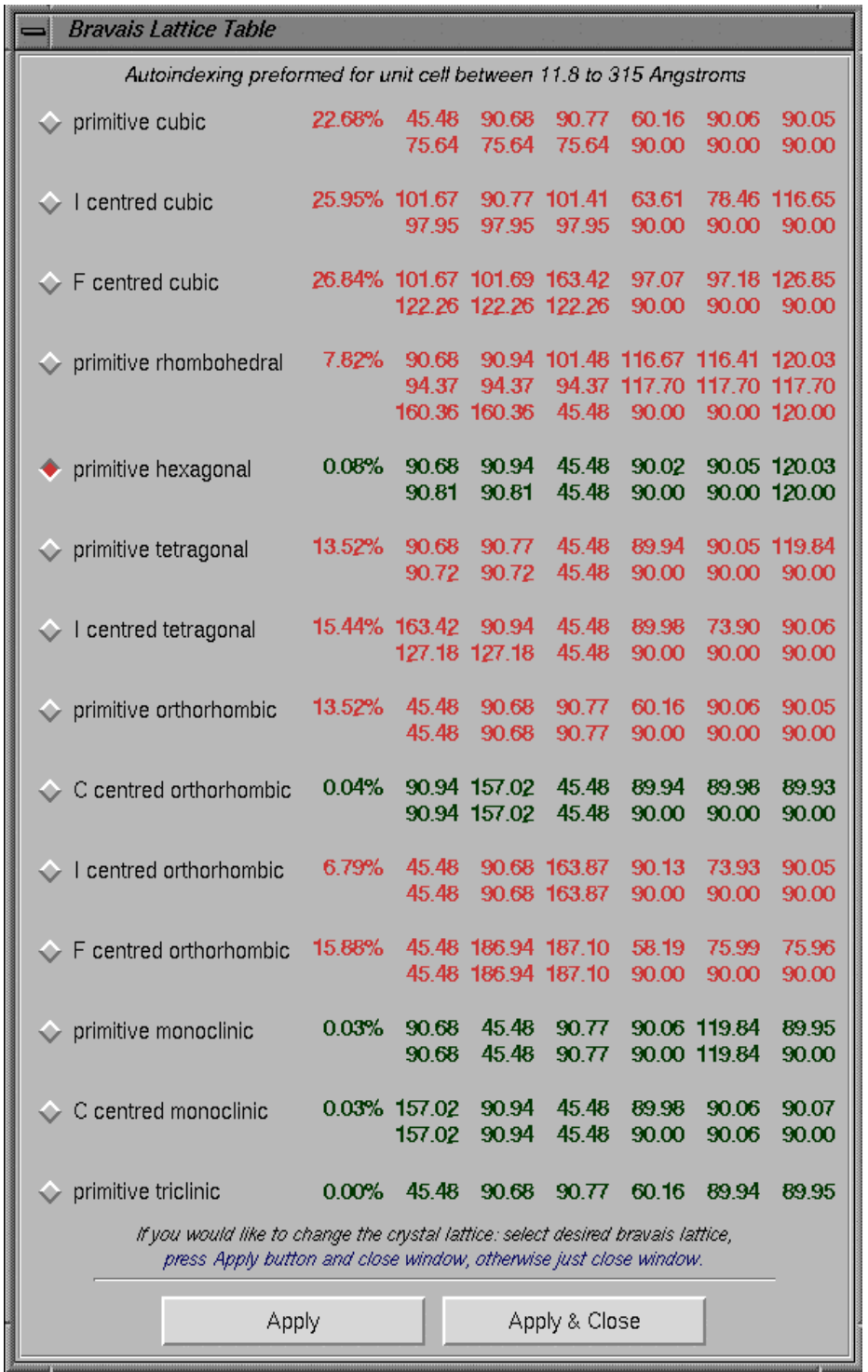
Find Spots

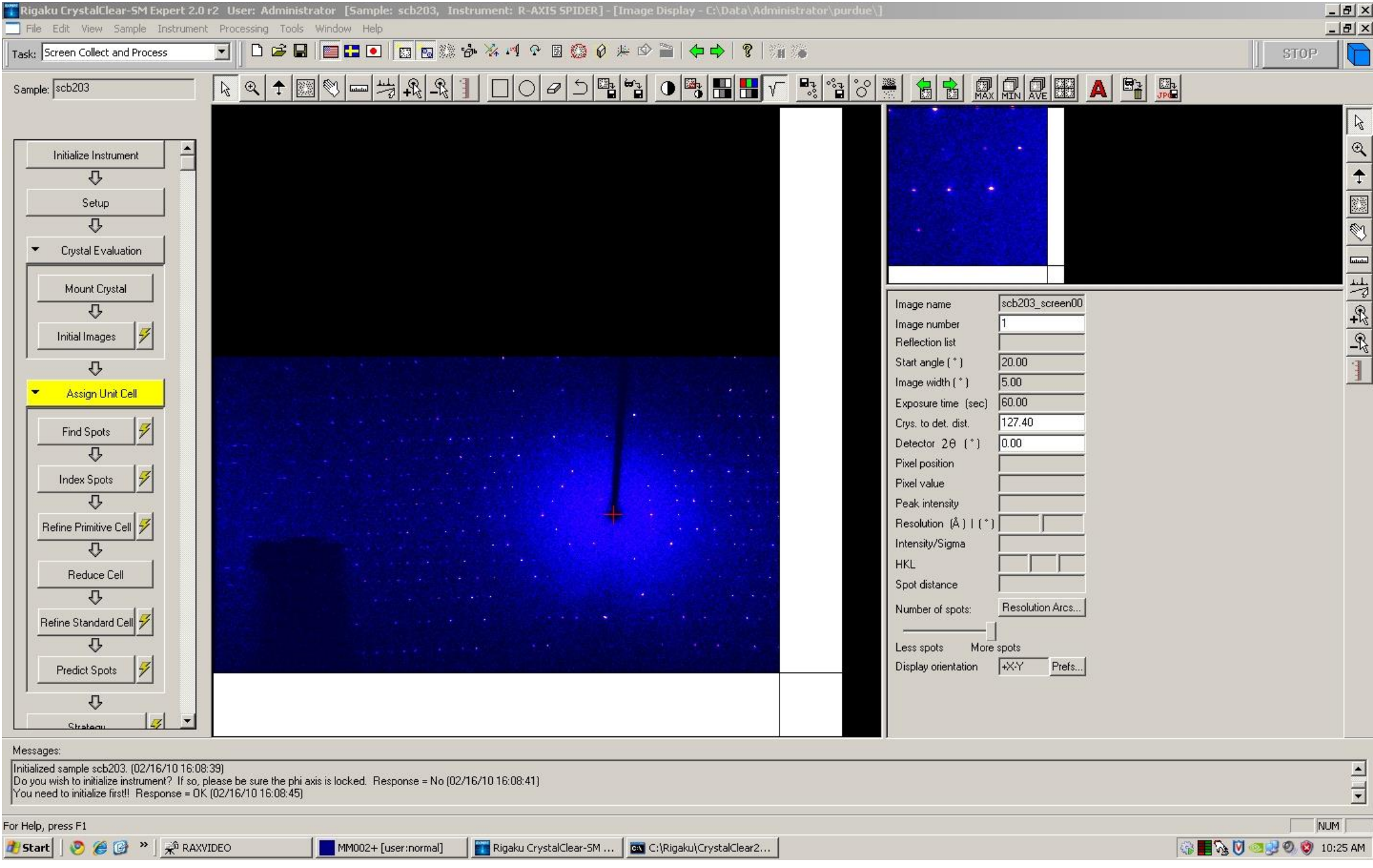
- The first step is to find the diffraction spots on the images.
- Usually there is some control over the size and shape of the spots and how intense they must be.
- In HKL2000 can control how many spots to accept.
- Ideally there is only one crystal so only one orientation matrix needs to be determined.



Index the Spots

- Select the program and run.
- Output
  - CrystalClear gives the primitive cell
  - HKL2000 gives all the Laue groups and the fit.
  - Others give the best cell


Bravais Lattice Table
Autoindexing preformed for unit cell between 11.8 to 315 Angstroms
primitive cubic 22.68% 45.48 90.68 90.77 60.16 90.06 90.05
75.64 75.64 75.64 90.00 90.00 90.00
I centred cubic 25.95% 101.67 90.77 101.41 63.61 78.46 116.65
97.95 97.95 97.95 90.00 90.00 90.00
F centred cubic 26.84% 101.67 101.69 163.42 97.07 97.18 126.85
122.26 122.26 122.26 90.00 90.00 90.00
primitive rhombohedral 7.82% 90.68 90.94 101.48 116.67 116.41 120.03
94.37 94.37 94.37 117.70 117.70 117.70
160.36 160.36 45.48 90.00 90.00 120.00
primitive hexagonal 0.08% 90.68 90.94 45.48 90.02 90.05 120.03
90.81 90.81 45.48 90.00 90.00 120.00
primitive tetragonal 13.52% 90.68 90.77 45.48 89.94 90.05 119.84
90.72 90.72 45.48 90.00 90.00 90.00
I centred tetragonal 15.44% 163.42 90.94 45.48 89.98 73.90 90.06
127.18 127.18 45.48 90.00 90.00 90.00
primitive orthorhombic 13.52% 45.48 90.68 90.77 60.16 90.06 90.05
45.48 90.68 90.77 90.00 90.00 90.00
C centred orthorhombic 0.04% 90.94 157.02 45.48 89.94 89.98 89.93
90.94 157.02 45.48 90.00 90.00 90.00
I centred orthorhombic 6.79% 45.48 90.68 163.87 90.13 73.93 90.05
45.48 90.68 163.87 90.00 90.00 90.00
F centred orthorhombic 15.88% 45.48 186.94 187.10 58.19 75.99 75.96
45.48 186.94 187.10 90.00 90.00 90.00
primitive monoclinic 0.03% 90.68 45.48 90.77 90.06 119.84 89.95
90.68 45.48 90.77 90.00 119.84 90.00
C centred monoclinic 0.03% 157.02 90.94 45.48 89.98 90.06 90.07
157.02 90.94 45.48 90.00 90.06 90.00
primitive triclinic 0.00% 45.48 90.68 90.77 60.16 89.94 89.95
If you would like to change the crystal lattice: select desired bravais lattice,
press Apply button and close window, otherwise just close window.
Apply
Apply & Close


Rigaku CrystalClear-SM Expert 2.0 r2 User: Administrator [Sample: scb203, Instrument: R-AXIS SPIDER] - [Image Display - C:\Data\Administrator\purdue\]
File Edit View Sample Instrument Processing Tools Window Help
Task: Screen Collect and Process
STOP
Sample: scb203
Initialize Instrument
Setup
Crystal Evaluation
Mount Crystal
Initial Images
Assign Unit Cell
Find Spots
Index Spots
Refine Primitive Cell
Reduce Cell
Refine Standard Cell
Predict Spots
Image name scb203_screen00
Image number 1
Reflection list
Start angle (°) 20.00
Image width (°) 5.00
Exposure time (sec) 60.00
Crys. to det. dist. 127.40
Detector 2θ (°) 0.00
Pixel position
Pixel value
Peak intensity
Resolution (Å) | (°)
Intensity/Sigma
HKL
Spot distance
Number of spots:
Resolution Arcs...
Less spots
More spots
Display orientation
+X-Y
Prefs...
Messages:
Initialized sample scb203. (02/16/10 16:08:39)
Do you wish to initialize instrument? If so, please be sure the phi axis is locked. Response = No (02/16/10 16:08:41)
You need to initialize first!! Response = OK (02/16/10 16:08:45)
For Help, press F1
NUM
Start
RAXVIDEO
MM002+ [user:normal]
Rigaku CrystalClear-SM ...
C:\Rigaku\CrystalClear2...
10:25 AM

Get the best cell paramters

- This is done by least squares on parameters to get the best fit to the observed peaks.
- This provides the errors for the cell.
- If need be the cell can be checked to ensure it is in the highest symmetry cell and then this cell refined using constraints (i.e. 90° angles at exactly 90.000)
- Also check that reflections are observed where expected

Is the cell worth collecting on

- Is the cell volume consistent for the molecule?
  - For organics the average non-hydrogen atom has a volume of 17Å^3
  - For inorganics the average volume per non-hydrogen atoms is 20Å^3
  - If the number of formula units in the cell is known then the approximate cell volume can be calculated

Table 3.4 Equivalent data for diffraction groups

Diffraction group (with related chiral group)	Conditions as for	Additional conditions for $I(hkl) \equiv$	Additional conditions for $I(\bar{h}\bar{k}\bar{l}) \equiv$	Multiplicity of centrosymmetric general data
$\bar{1}$ (1)	–	–	–	2
2/*m* (2)	$\bar{1}$ (1)	$I(\bar{h}k\bar{l})$	$I(h\bar{k}l)$	4
mmm (222)	2/*m* (2)	$I(h\bar{k}\bar{l})$, $I(\bar{h}\bar{k}l)$	$I(\bar{h}kl)$, $I(hk\bar{l})$	8
4/*m* (4)	$\bar{1}$ (1)	$I(\bar{h}\bar{k}l)$, $I(\bar{k}hl)$, $I(k\bar{h}l)$	$I(hk\bar{l})$, $I(k\bar{h}\bar{l})$, $I(\bar{k}h\bar{l})$	8
4/*mmm* (422)	4/*m* (4)	$I(\bar{h}k\bar{l})$, $I(h\bar{k}\bar{l})$, $I(\bar{k}\bar{h}l)$, $I(kh\bar{l})$	$I(\bar{h}kl)$, $I(h\bar{k}l)$, $I(khl)$, $I(\bar{k}\bar{h}\bar{l})$	16
$\bar{3}$ (3)	$\bar{1}$ (1)	$I(kil)$, $I(ihl)$,	$I(\bar{k}\bar{i}\bar{l})$, $I(\bar{i}\bar{h}\bar{l})$*	6
$\bar{3}m1$ (321)	$\bar{3}$ (3)	$I(\bar{k}\bar{h}l)$, $I(\bar{h}\bar{i}l)$, $I(\bar{i}\bar{k}l)$	$I(hil)$, $I(khl)$, $I(ikl)$	12
$\bar{3}1m$ (312)	$\bar{3}$ (3)	$I(kh\bar{l})$, $I(hi\bar{l})$, $I(ik\bar{l})$	$I(\bar{k}\bar{h}l)$, $I(\bar{h}\bar{i}l)$, $I(\bar{i}\bar{k}l)$	12
6/*m* (6)	$\bar{3}$ (3)	$I(\bar{h}\bar{k}l)$, $I(\bar{k}\bar{i}l)$, $I(\bar{i}\bar{h}l)$	$I(hk\bar{l})$, $I(ih\bar{l})$, $I(ki\bar{l})$	12
6/*mmm* (622)	6/*m* (6)	$I(\bar{k}\bar{h}l)$, $I(\bar{h}\bar{i}l)$, $I(\bar{i}\bar{k}l)$	$I(hil)$, $I(khl)$, $I(ikl)$	
		$I(kh\bar{l})$, $I(hi\bar{l})$, $I(ik\bar{l})$	$I(\bar{k}\bar{h}l)$, $I(\bar{h}\bar{i}l)$, $I(\bar{i}\bar{k}l)$	24
$m\bar{3}$ (23)	*mmm* (222)	$I(klh)$, $I(k\bar{l}\bar{h})$, $I(\bar{k}l\bar{h})$, $I(\bar{k}\bar{l}h)$	$I(\bar{k}\bar{l}\bar{h})$, $I(k\bar{l}h)$, $I(\bar{k}lh)$, $I(kl\bar{h})$	
		$I(lhk)$, $I(\bar{l}h\bar{k})$, $I(l\bar{h}\bar{k})$, $I(\bar{l}\bar{h}k)$	$I(\bar{l}\bar{h}\bar{k})$, $I(\bar{l}hk)$, $I(l\bar{h}k)$, $I(lh\bar{k})$	24
$m\bar{3}m$ (432)	$m\bar{3}$ (23)	$I(l\bar{k}h)$, $I(lk\bar{h})$, $I(\bar{l}\bar{k}h)$, $I(\bar{l}kh)$	$I(lkh)$, $I(l\bar{k}\bar{h})$, $I(\bar{l}k\bar{h})$, $I(\bar{l}\bar{k}h)$	
		$I(\bar{k}\bar{h}l)$, $I(\bar{k}hl)$, $I(kh\bar{l})$, $I(k\bar{h}l)$	$I(khl)$, $I(\bar{k}\bar{h}l)$, $I(\bar{k}h\bar{l})$, $I(k\bar{h}\bar{l})$	
		$I(\bar{h}l\bar{k})$, $I(\bar{h}lk)$, $I(h\bar{l}k)$, $I(hl\bar{k})$	$I(hlk)$, $I(\bar{h}\bar{l}k)$, $I(\bar{h}l\bar{k})$, $I(h\bar{l}\bar{k})$	48

*In trigonal and hexagonal crystals, $i = -h - k$.

Other Considerations

- For an accentric cell divide Z by 2
- For A, B, C, and I centered cells multiply Z by 2
- For an F centered cell multiply Z by 4
- For an R centered cell Z by 3
- Remember there are other things that can effect Z
  - More than one in the asymmetric unit
  - Special Position
  - Solvent in the cell
  - Dimer or polymer

An example

- Formula C54 H50 N9 Ru2
- CELL 10.0003 20.0034 25.6160 74.969 81.982 79.121
- Cell Volume 4838
- Number on non-hydrogen atoms 65 V=65x20=1300
- Triclinic try Z=2 V=2600
- Suggest Z=4 or Z'=2. Cell is of right size.

Is it a known crystal structure?

- Check the Cambridge Structural Database (CSD)
  - Both the Rigaku and Nonius software have automatic links for doing this.
  - The Purdue Lab maintains its own small database of all structures done in the lab. This prevents collection on starting material, etc. This is used as part of the check
  - If no organic carbon is in the sample then must check the Inorganic Database at the Chemistry Library web site.

Set up and Collect Data

- The software will calculate the best data collection parameters.
- For the Rigaku must know if you want centric or accentric data collection
- Must determine the scan time for the images
  - Nonius will do this
  - Rigaku must guess though usually the default of 60s is good.
- When in doubt go with the defaults!!

Next Class

- Lets look at things in action in the Crystallography Lab
- Class will be held in WTHR 234 Friday and NOT in 214.