



Indexing a Powder Pattern

- ◆ **Manual Indexing of Cubic Compounds**
 - Primitive Cubic Systems
 - Cubic Cells with Systematic Absences
 - Zero Point/Sample Displacement Errors
- ◆ **Autoindexing (indexing with a computer)**
 - Data input
 - Obstacles to Successful Autoindexing
 - Available Software Algorithms



Indexing Considerations

For a cubic system the expected lines in a powder pattern can be generated from the following relationships

- The relationship between the Miller indices of a peak (hkl) and the interplanar d-spacing

$$\mathbf{1/d^2 = (1/a^2)[h^2+k^2+l^2]}$$

- Bragg's Law

$$\mathbf{d = \lambda/(2\sin\theta)}$$

- Systematic Absences

Reflection Generation

Consider the following example of peak position generation.

Space group = Pm3m, $a = 4.0 \text{ \AA}$, $\lambda = 1.5406 \text{ \AA}$.

<u>h</u>	<u>k</u>	<u>l</u>	$h^2+k^2+l^2$	<u>d (Å)</u>	<u>2θ</u>
1	0	0	1	4.000	22.21
1	1	0	2	2.828	31.61
1	1	1	3	2.309	38.97
2	0	0	4	2.000	45.31
2	1	0	5	1.789	51.01
2	1	1	6	1.633	56.29
2	2	0	8	1.414	66.00
3	0	0	9	1.333	70.58
2	2	1	9	1.333	70.58
3	1	0	10	1.265	75.03



Manual Indexing

- ◆ Indexing a powder pattern is the reverse of peak generation. Namely we are given the peak positions and we use that information to determine:
 - The hkl index of each peak
 - The unit cell dimensions
 - The systematic absences, which gives information about the space group
- ◆ Manual indexing consists of the following steps
 - Determine d-spacing of each peak from its 2θ value (using Bragg's Law)
 - Create a table of $1/d^2$ values for each peak
 - Look for a common factor ($1/a^2$) that can be divided into each of the $1/d^2$ values



Indexing Example

Lets begin by working the previous example backwards.
Starting with the peak positions (recall $\lambda = 1.5406 \text{ \AA}$).

<u>2-theta</u>	<u>d</u>	<u>1000/d²</u>
22.21	4.000	62.5
31.61	2.828	125.0
38.97	2.309	187.6
45.31	2.000	250.0
51.01	1.789	312.4
56.29	1.633	375.0
66.00	1.414	500.2
70.58	1.333	562.8
75.03	1.265	624.9

Indexing Example (Continued)

With a little inspection (in this case) we see that all of the $1000/d^2$ values can be divided by 62.5

<u>2-theta</u>	<u>d</u>	<u>1000/d²</u>		<u>hkl</u>
22.21	4.000	62.5	62.5/62.5=1	100
31.61	2.828	125.0	125.0/62.5=2	110
38.97	2.309	187.6	187.6/62.5=3	111
45.31	2.000	250.0	250.0/62.5=4	200
51.01	1.789	312.4	312.4/62.5=5	210
56.29	1.633	375.0	375.0/62.5=6	211
66.00	1.414	500.2	500.2/62.5=8	220
70.58	1.333	562.8	562.8/62.5=9	221
75.03	1.265	624.9	624.9/62.5=10	310

The cubic unit cell parameter can then be calculated,
 $a = [1000/62.5]^{1/2} = 4.00$ Angstroms.

Indexing & Systematic Absences

The last problem was a particularly easy one because there were no missing peaks. Typically there will be some systematic absences. Consider the following example. Once again $\lambda = 1.5406 \text{ \AA}$.

<u>2-theta</u>	<u>d</u>	<u>1000/d²</u>
28.077	3.175	99.2
32.533	2.750	132.2
46.672	1.945	264.3
55.355	1.658	363.8
58.045	1.588	396.6
68.140	1.375	528.9
75.247	1.262	627.9
77.559	1.230	661.0

Indexing & Systematic Absences

It's immediately clear that 99.2 is not a common factor here. Though we can see that $132.2 - 99.2 = 33$ might be a common factor. So we'll give it a try.

<u>2-theta</u>	<u>d</u>	<u>1000/d²</u>		<u>hkl</u>
28.077	3.175	99.2	$99.2/33=3$	111
32.533	2.750	132.2	$132.2/33=4$	200
46.672	1.945	264.3	$264.3/33=8$	220
55.355	1.658	363.8	$363.8/33=11$	311
58.045	1.588	396.6	$396.6/33=12$	222
68.140	1.375	528.9	$528.9/33=16$	400
75.247	1.262	627.9	$627.9/33=19$	331
77.559	1.230	661.0	$661.0/33=20$	420

From the absences we see that the compound is F-centered,
 $a = [1000/33]^{1/2} = 5.50$ Angstroms



Zero Point/Sample Displacement

- ◆ One thing that complicates indexing efforts is inaccuracy in determination of the peak positions. Generally it is best to fit the entire peak profile, using a program such as X-fit.
- ◆ Even then we can still have errors in the peak positions due to

- Misalignment of the diffractometer leading to a constant zero point shift (Z) of the 2θ positions

$$2\theta(\text{Accurate}) - 2\theta(\text{obs}) = \Delta 2\theta = Z$$

- The sample height is too high or too shallow (by an amount s), due to irreproducibility in loading a sample holder.

$$2\theta(\text{Accurate}) - 2\theta(\text{obs}) = \Delta 2\theta = 2s \cos\theta/R$$

where R is the radius of the diffractometer circle.



Zero Point/Sample Displacement

- ◆ At low angles the zero point error and the sample height displacement error are difficult to distinguish ($\cos\theta$ is close to 1 at low angles). Therefore,
 - It is not generally possible to determine the two errors independently.
 - Normally it is sufficient to consider only the sample height displacement, and neglect the zero point error (or vice versa)
- ◆ Systematic inaccuracies in the peak positions can sabotage the whole indexing process for lower symmetry systems. Therefore it is important to keep the diffractometer well calibrated, and strive to minimize errors in the sample height.
- ◆ To eliminate these systematic 2-theta errors use an internal standard.



Autoindexing

- ◆ Manual indexing of cubic unit cells is a reasonably straightforward process.
- ◆ Tetragonal, trigonal and hexagonal cells can also be indexed manually with some experience, but it is not a trivial exercise.
- ◆ Generally indexing is done using a computer program. This process is called autoindexing.
- ◆ The input for an autoindexing program is typically:
 - The peak positions (ideally 20-30 lines)
 - The wavelength
 - The uncertainty in the peak positions
 - The maximum allowable unit cell volume



Autoindexing Obstacles

- ◆ **Impurities** - Peaks which don't belong to the main phase seriously hamper the autoindexing algorithms.
- ◆ **Zero point/Sample Height Error** - This can be avoided by using care in the data collection, or by using an internal standard.
- ◆ **Degrees of Freedom** - In practice there are often 9-10 degrees of freedom in an autoindexing problem and only 20-30 observations. So the problem is not as over-determined as we would like.
- ◆ **Peak overlap** - As the size of the unit cell increases, the symmetry is lowered, the instrumental resolution decreases, or the d-spacing increases peak overlap makes it difficult to accurately determine individual peak positions.



Autoindexing Software

- ◆ A number of the most useful autoindexing programs have been gathered together by Robin Shirley into a single package called **Crysfire**. You can download Crysfire from the web and find tutorials on its use at **<http://www.ccp14.ac.uk/tutorial/crys/index.html>**
- ◆ To go from an observed diffraction pattern to the unit cell dimensions and space group try the following steps:
 - Fit the peaks using a program such as X-Fit (<http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm>)
 - Take the X-fit output file and convert to a Crysfire input file, as described on the web
 - Run Crysfire to look for the best solutions
 - Use the program Chekcell to evaluate the systematic absences and refine the cell parameters (<http://www.ccp14.ac.uk/tutorial/lmgp/index.html>)



Autoindexing Tips

How do I know when I have the correct solution?

- ◆ It's hard to say for sure. You would like to have high figure of merits (F_n & M_n) and all of the lines indexed. Generally it is not worth paying attention to solutions which give figure of merits (FOM) less than 10. On the other hand for many cells the correct solution will give a FOM between 10 and 100. Also high symmetry solutions are favored over low symmetry solutions.

How accurate is the output?

- ◆ If the FOM is greater than 50 the solution almost certainly has an element of truth, but not all aspects may be correct. Watch out for:
 - Cell edges that are very similar, where Crysfire may have chosen the symmetry too low.
 - Unnecessary doubling of one or more of the cell edges.
 - Cells with edges related by $\sqrt{2}$, $\sqrt{3}$, etc.



Programs within Crysfire

There are many programs contained within Crysfire, which ones should I use? I recommend to use several programs, as they have different strong points. I highly recommend running the input through several algorithms to look for common solutions. Some of my favorites are:

Dicvol91

- Performs exhaustive searches down to monoclinic.
- Not so good for large monoclinic cells and triclinic cells as the program can run for several days.
- Cannot tolerate impurity lines
- Important to set realistic uncertainties in peak positions

Treor

- Fast
- Tolerates impurities
- Accurate peak positions are more important than with other programs

ITO12

- Optimized for low symmetry