

Basic instructions for WinX^{POW}

Note: These instructions instruct on how to use the WinX^{POW} software package. An alternative guide specifically on how to use XRD to conduct phase analysis is available from the lab uSpace website.

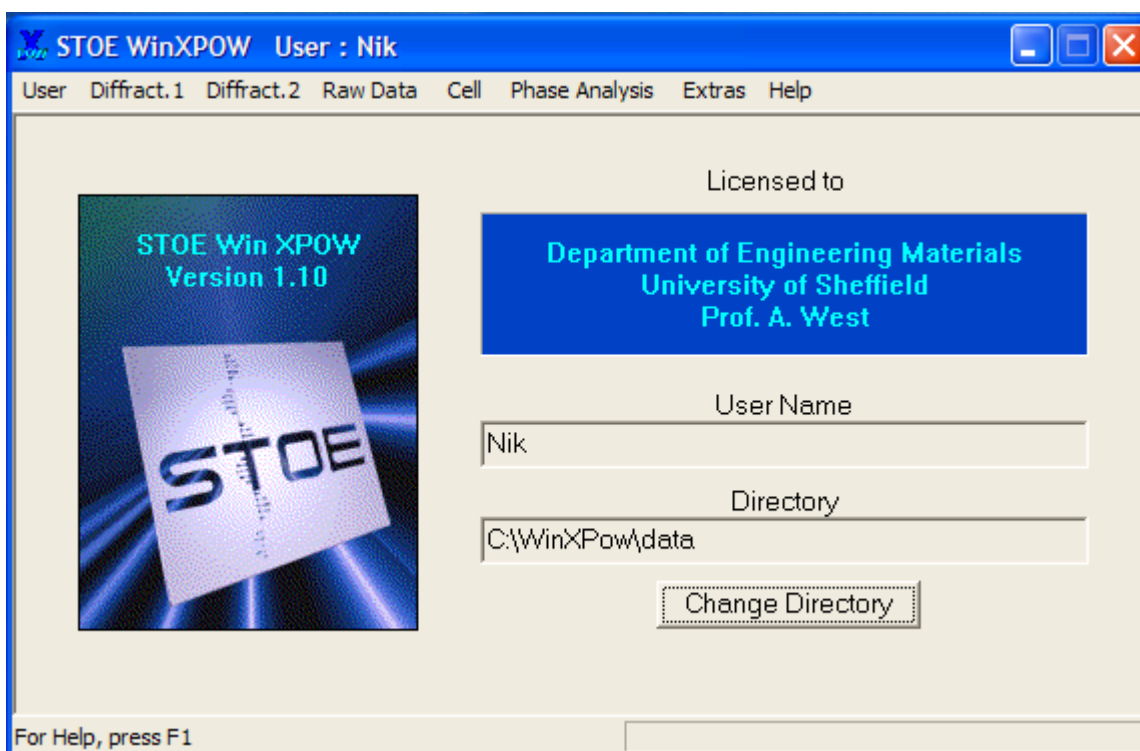
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Basic instructions for WinX^{POW}

The WinX^{POW} software suite contains a number of programs that can be used in the study and analysis of X-ray diffraction data. These instructions will give you a basic understanding of how to use this software. Double-clicking on the WinX^{POW} icon will open up the console menu, from which all the other programs can be accessed.

Figure 1 – The WinX^{POW} console menu.



Each individual program in WinX^{POW} has an extensive help file; please refer to these for more detailed information. Extensive software manuals are also available to read in I6a, though these are for reference only and must not be removed.

1. *Importing *.csv files into WinX^{POW}*

WinX^{POW} can be used to study data files in *.raw format. If you have collected diffraction data using the Stoe diffractometers, your data will most likely already be in *.raw format; however, if you collected your data using the Siemens, or either of the Philips instruments, then your data will be in *.cpi and/or *.csv format.

Files in *.cpi format can be converted into *.csv files using Traces, simply by opening your *.cpi file then saving as (using the 'Save as' option under the 'File' menu) a *.csv file.

To import *.csv files into WinX^{POW}:

1. Go to **Raw Data/Raw Data Handling**
2. Go to **File/Import**
3. Change the entry in the 'Files of Type' box to '**ASCII X/Y Files (*.*)**', select the data file you wish to import, then click '**OK**'.
4. Enter the filename you wish to save the *.raw data file with, and click '**Save**'.
5. By default, copper is chosen as the radiation source used for the experiment. If you collected your data using a different source, *e.g.* cobalt, molybdenum, then go to **Parameters/Wavelength** and select the correct radiation. Ignore any error message that appears.
6. If you wish to edit, or add, a title for your experiment (which will appear later when you display the data), then this may be done in **Parameters/Title**.
7. Any changes must be saved. Click on **File/Save As...** and overwrite the *.raw file created earlier.

You may wish to add scan ranges (i.e. 20-25 °2θ, 30-35 °2θ, or from multiple scans on the Stoe Image Plate *etc.*) together. This can also be done in Raw Data Handling:

1. Click **Ranges/Add Ranges** – add ranges 2 and above to range 1.
2. **Extract Ranges** – extract range 1, to a file with format <filename>.ra1.

2. *The 'Graphics' program*

The Graphics (**Raw Data/Graphics**) program can be used to view *.raw files, and to create peak (*.pks) files for indexing/refining unit cells or using in the Search/Match software.

Opening and saving files

To open a *.raw file, click File/Open.

If, after any editing (e.g. comparing a raw file against a PDF card, adding notes *etc.*), you wish to save the graphics you've been working on you can save a graphics file (*.grs) by clicking **File/Save Graphic**. These can be reloaded at a later date by clicking **File/Open Graphic**.

Creating peak files

Peak files may be created for use in unit cell determination (using the Index/Refine software) and phase identification (using the Search/Match software). The first step is to find the peaks in your trace; clicking Options/Find Peaks will bring up a child window where the Peak Search Parameters may be entered:

Estimated Halfwidth – characteristic of both the sample and the instrument the data were collected upon. *Values of ~ 0.1 (for the Stoe PSD) and ~ 0.2 (for all our other instruments) are reasonable.*

Significance Level - sets a lower limit to the peak heights, defined as the ratio of the maximum peak intensity to background. Peaks found by the slope criterion, but with a peak height below the given significance limit, will be discarded. *Default value of 2.5 is fine.*

Intensity Limit - All peaks having an absolute height less than the input value will be discarded. Entering low values significantly increases the chance that the software will find 'peaks' in the random noise of the background!

Remove Alpha2 Peaks - Checking this box will scan the peak list for pairs of Alpha1/Alpha2 peaks and discard the Alpha2 reflection.

Remove Spikes - Peaks of a halfwidth less than 25% of the estimated halfwidth defined above will be discarded as spikes, or electrical noise.

Clicking '**OK**' will perform the peak search. It is important to remember at this stage that not all of the peaks present in your trace necessarily come from one phase, so exercise some caution when writing *.pks files.

Comparison of data sets and PDF cards in Graphics

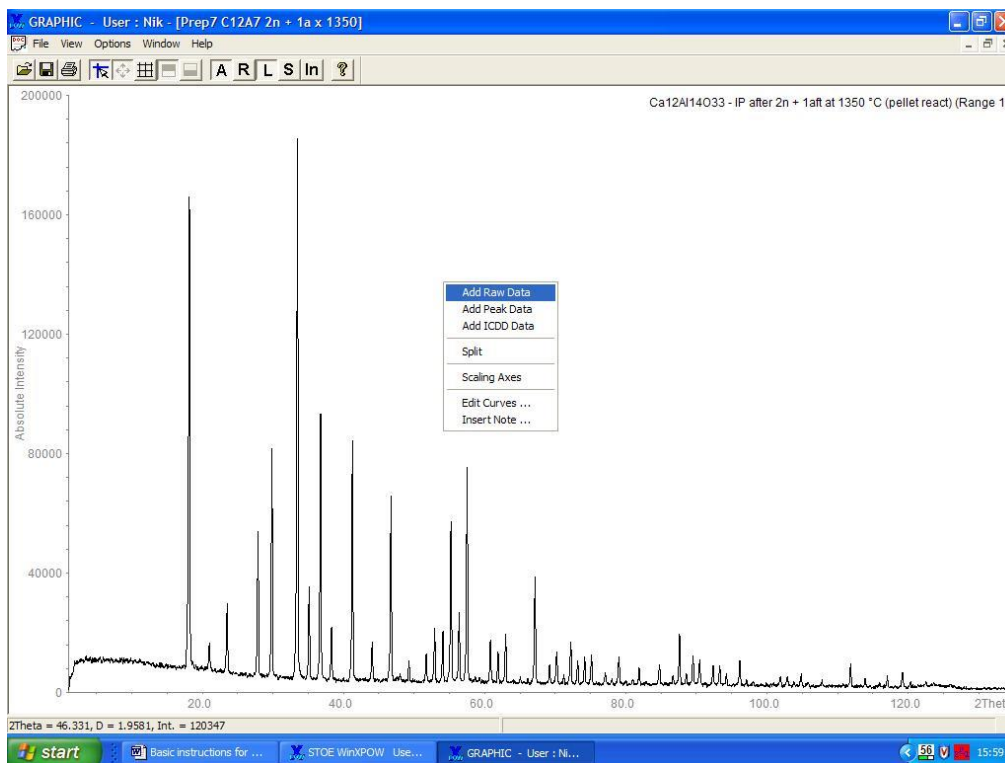
It is easy to overlay many different raw data sets as well as patterns from the Powder Diffraction File. To overlay a pattern, right-click on the main window. This will bring up a menu, as shown in Figure 2. It should then be obvious how to overlay other *.raw files, *.pks files or PDF cards!

Comparing files collected using different wavelengths is also possible, by using a $1/d$ x-axis (since the d-spacings are independent of wavelength). Changes to the scaling axes can be made by right-clicking and choosing the '**Scaling Axes**' option.

To change the colours of the displayed information, go to **Options/Colours**. Then click on Curve <the number of the trace you wish to change the colour of> and '**Choose Colour**'. Make your selection and click '**OK**'!

The '**Edit Curves**' option in the right-click menu can be very useful. By selecting a trace and hitting delete, you can remove a trace from the display. By double-clicking on an entry, you can also edit the Title information that gets displayed in the top right hand corner of the graphic.

Figure 2 – The right-click menu in Graphics. Options also available in ‘Window’ menu.



It is also possible to insert notes onto the graphics, by selecting the option in the right-click menu. These can be left-dragged into position (check their actual position using print preview!) or deleted by double-clicking on them and pressing ‘Delete’ then ‘OK’.

Publishing data from WinX^{POW}

Once you’ve finally finished analysing your data, and have it presented exactly as you wish, click **File/Write Metafile**. These *.emf files can be inserted into MS Word or Powerpoint as pictures; they can also be manipulated in a graphic editing package (I use the free package Paint.net) to remove the WinX^{POW} header bar that the software places above the data, but which really is unsuitable for publication.

3. *Peak Calibration in WinX^{POW}*

The Calibrate Peaks program allows the user to calculate correction terms for the 2θ scale of data collected with an internal (or external) Si standard. The program calculates a correction term which may be used to correct raw data files in the 'Raw Data Handling' program.

To perform a peak calibration on your data set, you will need a copy of the **si-icdd.pks** file, a peak file for the Si standard powder. You will also need a Si peak file, created from data collected on the same day as your data (in the case of the Stoe PSD) or from a Si internal standard (i.e. Si powder added to your sample). This latter course of action is recommended if you wish to refine lattice parameters from data collected on any instrument other than the Stoe PSD.

To perform the peak calibration:

1. Run **Raw Data/Peak Calibration**
2. Click **File/Open**. A child window will appear; enter the location of the **si-icdd.pks** file in the upper box, and your Si file in the lower box.
3. From the menubar, select **Calibrate/Match Peaks**. In the child window that appears, there are two options:
 - a. **Intensity limit** - a cutoff-value below which the program will ignore all peaks from both the calibration and the observed peak files. *Set to 0 %*.
 - b. **2-Theta window**: the 2θ range around a calibration peak which the program will search for matching observed peaks. *Set this to 0.05*.

You will need at least three peaks, but more is better.

4. You may need to connect a measured peak to a calibration peak; to do this, left-click the (blue) calibration peak, then attach the measured (grey) peak by left-clicking on it.
5. Once all your measured peaks are attached to calibration peaks, click **Calibrate/Calculate Polynomials**. The results are shown in the lower part of the

main window. The 2θ offsets for all peak pairs are shown as black squares and the calculated correction polynomials as curves of different colours.

6. Click **Calibrate/Calibrate Peakfile**. A child window will appear asking which polynomial should be applied; choose the one with order > 0 with the lowest χ^2 value, and check that this fits the observed data well. Click OK and exit from the Calibrate program *without* saving changes.
7. Go to **Raw Data/Raw Data Handling** and **Open** the file you wish to calibrate. Click **Operations/Angle Correction**. Make sure the ‘**use stored polynomial**’ box is ticked, and click ‘**OK**’.
8. Save your corrected data.

4. *Pattern Fitting*

The Pattern Fitting routine is used to determine profile parameters and integrated intensities from observed powder patterns. A variety of constraints makes it possible to achieve meaningful results even for complicated patterns. This routine does not require any information on the structure of the phase.

1. Open up the *.raw and *.pks file for the pattern you wish to fit.
2. Click the **Parameter** menu option. You will notice three choices:
 - a. *Overall* – background and asymmetry functions; unless the background is strange, leave these to the program.
 - b. *Peaks* – Lists the 2θ values, absolute and integrated intensities, and halfwidths of all the peaks.
 - c. *Groups* – Parameters that may be fixed or varied during refinement.
3. Choose the **Group** option. Start by refining the halfwidths only. The initial parameters should be $W = 0.01$, $V = 0$, $U = 0$. Tick '**Halfwidth as function**', and unfix W – make sure that initially all the other parameters are fixed. Click '**Replace**' to enforce any changes you have made, and then '**OK**'.
4. You are now ready to start the refinement: click **Operations/Nonlinear Regression**. Once the refinement has converged, go back to **Groups** and allow U and V to vary. Remember to click '**Replace**' after you've made any changes in the Groups window!
5. Once convergence is achieved, allow the **profile function** to vary. There are two – Pearson and Pseudovoigt – try both to see which fits your data best. The default parameters for the profile function are 0.5 for Pseudovoigt and 2 for Pearson.
6. Inspect the pattern for missed peaks, extra peaks, poorly fitted peaks and edit accordingly by clicking **Operations/Edit Peaks**.
7. Inspect the peak file for negative intensities, halfwidths that are very large (may be two peaks?) or very small (may not be a peak!)
8. Some peaks at low 2θ values may be asymmetric. This can be modelled using the asymmetry function – Click **Parameter/Overall Parameter** and click '**Use**

asymmetry' and untick '**fixed**'. The starting value should be greater than 0.03.

Note: This step will not be necessary if you don't have any peak asymmetry!

9. Once you are happy with the fit, save the fitted peak file as <filename>.pft.

Once again, remember that more detailed help is available from the help files in the Pattern Fitting program.

5. *The Search/Match Software*

The Search/Match routine is used for qualitative phase analysis and browsing through the Powder Diffraction File database. When you want to figure out which crystalline phases are in your sample – this is where you come! Our database licence covers:

PDF1 – Sets 1-54 – Mainly observed data, but some calculated patterns also.

Look out for the quality ratings given for each card entry:

C = Calculated

* = Observed data of high reliability; use these entries wherever possible!

I = Observed data of intermediate reliability.

O = Observed data of low reliability.

None = Observed data; may be of very poor reliability!

PDF2 – Sets 60 (CSD), 65 (NIST), 70 (ICSD), and 71+ (a mixture of all three!) - all calculated patterns, from various databases. Consider whether these cards are meaningful...

The PDF cards also contain a wealth of other information:

- The various names that the phase may be known by
- How the original data were collected, and any reference for the work. Note that many of the older datasets were collected using old photographic film methods, e.g. Hagg-Guinier cameras. While the films are very accurate, the researcher's ability to accurately determine peak positions and intensities visually is less so, so treat these with caution.
- Crystallographic and unit cell information.
- Sample-specific notes about how the sample was prepared, colour *etc.*
- Peak indexing information – miller indices, peak positions and relative intensities. Note that where miller indices are quoted with a '+' symbol, this means that additional indices are possible for this peak.

Step-by-step guide on how to search the PDF

There are a number of basic search options to choose from, available from the ‘Select’ menu option; what you will need to do depends largely on what you suspect is in your sample. Any sort of elemental analysis will also always be a massive help!

1. From the WinX^{POW} console, click **Phase Analysis**, then **Search/Match**.
2. Click **Options/Find** and change to the appropriate radiation type for the instrument used (Cu, Co or Mo).
3. Open up the *.raw file for the sample you wish to perform phase analysis on, by clicking **File/Open**. Note: The default file type is *.pks, so you will need to change this. A second window will appear, displaying the XRD pattern.
4. Click **View/Names** on the top toolbar to see the list of database entries in the original Search/Match window. The database contains over 134,000 entries – looking through each in turn may take some time! However, you should note that you can select to view the pattern for any entry simply by clicking on it. *Double-clicking* will open a third window, displaying the text entry for that card. The arrows on the graphical display window allow the user to easily and rapidly cycle through so-called ‘working sets’ of selected cards.

There are a number of basic search options to choose from, available from the ‘**Select**’ menu option. Which you choose will depend on what information you already have about your sample:

1. **Subfiles** – Choose phases with some common property, e.g. superconducting phases, or with some common usage, e.g. cement phases. Subfiles can be selected after switching off the ‘Full database’ check box.
2. **Elements** – To narrow down the number of possible phases in an unknown sample, the input of chemical information is an essential tool. In the ‘Elements’ window, the periodic table of the elements may be edited by colour-codes : All elements shown in red must be present in a phase to be selected; of all elements shown in yellow, at least one must be present in a phase to be selected; elements

shown in blue must not be present in a selected phase. Elements shown in grey may or may not be present in a phase. The '**Toggle**' button can be used to switch elements between 'Optional' and 'Must not' settings. '**Reset**' resets all elements to the grey optional status. After pressing the OK button, the user is prompted for the requested number of elements in the phases. By accepting the default values by pressing the 'Range' button, no further restriction will be imposed on the phases; by increasing the minimum number or decreasing the maximum number of elements, the number of phases found can be influenced.

3. **Strong Peaks** – similar to the Hanawalt technique, the 'Strong Peaks' window allows the input of peak positions, either in 2θ or d-spacing. Since the position of observed peaks may differ slightly it is best to allow a range either side of the peak maximum, i.e. if you have an observed peak at $28.443^\circ 2\theta$, then you could input the 2θ range as:

28.33 28.53, or

28.43

The second option automatically enters a 2θ window of 0.1 either side; you may want to replace this with a bigger window and click '**Replace**'. The 'Method' list box is used to select whether to use the three strongest lines for every phase, all peaks above 70% relative intensity, or all lines above 30% relative intensity.

4. **Cards** – single PDF Cards or card lists may be entered in the same way as peaks in the 'Strong Peaks' window. Every entry in the database is identified by a unique card number. The same phase may be present with different card numbers. To search for specific cards, just input the card number in [Set] [Card number] format, i.e. for the standard Si pattern, enter 27 1402.
5. **Text Search** – useful for the retrieval of phases of a given formula or of a certain chemical or mineral name. If, for example, all phases containing phosphorus and oxygen have been selected by the 'Elements' option, a stricter search for pyrophosphates can be done subsequently by looking for formulas containing the string 'P2O7'. Note that string matching is case sensitive. If 'Search full database' is checked, the text search is performed in the whole PDF database, not only in the current working set of phases. Clicking to search the '**Pdf2.dat**'

indicates that the software should look for the text string anywhere in any of the text in the cards.

To perform a search, input the desired data in one of the search options. When done, click 'OK'. You will be presented with four possible options – 'Replace' the previously chosen set of cards; 'Add' to the previously chosen set of cards; 'Match' the results of this search with those of the previous search; or 'cancel'.

One very common and powerful approach to searching through the database is to combine different types of search – the so-called 'Search/Match' method:

1. Click **Select**, then **Elements**.
2. Press '**Toggle**' to turn all elements blue initially.
3. Press '**All req.**' and choose the elements likely to be in all of the phases in the sample, by colouring them red. Press '**Optional**' and choose the elements most likely to be in some of the phases in the sample. You may consider omitting minority elements if you know your sample consists of less than e.g. 5% of that element. Press '**OK**'.
4. Enter the **minimum** and **maximum** number of elements you want to find in any one phase, i.e. if you have selected oxygen as the only 'required' element, you probably don't have elemental oxygen in your sample! Click '**Range**'.
5. **Replace** the current working set.
6. Click **Select**, then **Strong Peaks**.
7. In the 'Line or Region' box, **enter the position of the strongest unidentified reflection** – with a window of $0.2 \text{ }^\circ 2\theta$ either side, e.g. for a peak at $26.5 \text{ }^\circ 2\theta$, enter the text 26.3 26.7. Click **Add**, then **OK**.
8. If there are peaks that have the selected elements, and a peak in the appropriate place, you will now have the option to '**Match**' the searches, i.e. view the list of phases with both the selected elements, and a peak in the appropriate place. If not, try again – try to broaden the range of possible elements, or the peak window. Try with a different peak...

Again, further help is available from the help files with the Search/Match program. Searching through the PDF can often return a vast array of cards for you to look through; it is a good idea to try and eliminate things that are definitely not right! Your ultimate goal should be to find phase(s) which accurately match both the positions and relative intensities of *all* of the peaks in your observed data.

Common problems

'I have found a card with peaks in similar positions, but shifted to higher/lower angle'

This can have three possible causes:

1. Sample height displacement – even a small error in the height of the sample will have an impact on peak position. This error may appear fairly linear with diffracted angle. This is a very common, but largely avoidable, problem. Run the sample again, with more attention to correct sample height.
2. Wrong wavelength selected – either when importing the data (copper is the default), or in Search/Match (other people may have changed this). If the peak shift is dramatically different, this may be the cause.
3. Change in chemistry – if you can replace an element in the crystal structure with another, this is likely to cause changes in the shape and size of the unit cell. You may get the same pattern of peaks, but shifted to higher or lower angles. In this case, the shift is likely to be small at low angles, and significantly larger at higher angles.

'The intensities on the PDF card are a bit odd – they're all multiples of 10, or 20!'

This would indeed be quite odd for a real sample! Most likely the data have been collected using an old photographic film technique; check the card text entry for the method used – perhaps it says a Guinier diffractometer was used, or that intensities were obtained via 'visual' or 'densitometer' methods. Such techniques are extremely accurate; however, the ability of the researcher to accurately interpret the data is more limited! Use such cards with caution.

Automatic Search/Match with Peak Files – not recommended!

Another option is to try and match the peaks from one pattern with those of a phase listed in the PDF. For this, you will need to prepare a peak file in the ‘Graphics’ program. Bear in mind, of course, that the peaks observed for your sample may be from more than one phase... To load a peak file in Search/Match, click **File/Open**, and open your file. If you know which elements are/may be present, perform an element search as detailed previously. Next, to run the Search routine:

1. Click **Options/Find**.
2. The ‘Find parameters’ dialogue box, shown below, will open, with the following options:

Find parameters

General

Wavelength **Cu** 1.5406

2theta_window +/- 0.15

Pre-selection

Strong peak index 3_strongest

Intensity threshold 0

Null area index lines >70%

Intensity threshold 0

Find parameter

Max. missed 0

PDF_line intensity threshold 30

Min. % unknown matched 1
(1 lines)

OK

Cancel

Regions

F.O.M.

- a. *Wavelength* – Input the kind of X-ray radiation used to calculate 2θ values from tabulated d-spacing values in the PDF cards. The *2theta_window* sets the maximum range in which an observed and calculated peak can be said to match. A value of 0.15 is recommended.

- b. *Pre-selection* – When ticked, the strong Peak index defines a subset of lines for each card in the working set. The first search step will then select all cards for which at least one peak out of this subset matches an observed peak with a relative intensity higher than the ‘Intensity threshold’ value. The ‘Null area index’, when ticked, performs a second search step, rejecting cards left by the first step which have a line belonging to the subset outside of the 2theta_window!
 - c. *Find parameter* – The ‘**maximum number of missed lines**’ is the number of lines in a database card having a relative intensity above the ‘**PDF_line intensity threshold**’ which may not be present in the observed pattern. If this number is exceeded, the card will be rejected. The ‘**Minimum % unknown matched**’ parameter is the percentage of the total number of observed lines which must agree with a database card so that this card is considered a match.
3. The method of figure of merit calculation can be changed in the ‘FOM’ option. The figure-of-merit (FOM) is a tool to select from a maybe long list of possible matches those phases which give the best fit to the observed powder pattern.
 4. Click OK to begin searching, and then View/Names to see the results ranked in order of figure-of-merit, *i.e.* the top one should be the best match!

For a standard diffractogram, the following parameters are suggested for major phases:

2theta window: 0.15	
Strong Peak index: 3 strongest	Intensity threshold: 0
Null area Index: lines > 70 %	Intensity threshold: 0
Max. missed: 0	
PDF_line intensity threshold: 30	
Min. % unknown matched: 1	
Method of figure of merit calculation: Positions & Intensities (scaled).	

To identify spurious phases, the following parameter set may be recommended:

2theta window: 0.15

Strong Peak index: None

Intensity threshold: 0

Null area Index: None

Intensity threshold: 0

Max. missed: 0

PDF_line intensity threshold: 70

Min. % unknown matched: 1

Method of figure of merit calculation: Positions & Intensities (not scaled).

6. *The Index/Refine Software*

The Index & Refine module comprises three indexing routines and a lattice parameter refinement option. The implemented indexing algorithms are based on

- Werner's TREOR program (see e.g. P.-E.Werner, L.Eriksson, M.Westdahl, J. Appl. Cryst. 18 (1985) 367)
- Visser's ITO routine (see e.g. J.W.Visser, J. Appl. Cryst. 2 (1969) 89)
- Louër's DICVOL (see e.g. A.Boultif, D.Louër, J. Appl. Cryst. 24 (1991) 987).

The Index & Refine software can be accessed from the main console window under 'Cell'. This program can be used to analyse peak files in *.pks or*.pth format.

The 'Index' menu options

Under the 'Index' heading, there are four entries. Before running any of the algorithms, however, you first need to define the refinement parameters.

1. Click on **Index/Parameters**. A child window will appear, with three tabs – one for each of the available algorithms. For the algorithm you intend to use, fill in all the boxes you can – a detailed list of what each item means can be found in the help files accessible from the Index program.
2. To run your algorithm of choice (try each one to see which provides the best possible solutions), click **Index/Run <algorithm name>**. This will start the calculation process – this may take some time! You can then try refining your sample based on these solutions.

When Visser's and Louër's routines have finished, they open a child window displaying their output. Werner's routine writes possible solutions into the main window and – after completing the search - the user may double-click on any of them to open a child window showing the indexing of the data with the currently selected cell (highlighted in red in the

main window). Werner's algorithm may be interrupted anytime by clicking the toolbar button with the red traffic light.

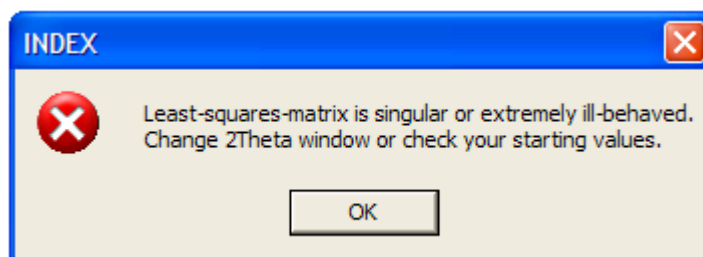
Lattice Constant Refinement

You may already have a possible solution, from literature, the Powder Diffraction File, or one of the algorithms above. The software allows you to refine the lattice constants for your observed data using the 'Refine' menu option. To work through such a refinement:

1. **Open** your peakfile (<filename>.pks) in the '**Index & Refine**' program.
2. Click **Refine**. A child window will appear, offering you various data entry options, all of which should be self-explanatory. Fill these boxes in:
 - a. *Symmetry* - Enter the space group, if you know it, or the crystal system (*e.g.* cubic) and Bravais lattice (*e.g.* Primitive) if you don't.
 - b. *Lattice Parameters* – Enter in the dimensions (in Å) and angles of the cell upon which you wish to refine your data.
 - c. *Settings*
 - i. *2Theta window* - If the absolute difference between an observed peak position and a calculated peak position is less than the 2Theta window (in degrees), the observed peak will be considered indexed. The program will try to reduce the window as much as is possible without observed peaks becoming unindexed. A value of 0.1 is reasonable.
 - ii. *2Theta zero* - allows the input of a constant 2theta-error introduced by poor 2Theta-calibration of the diffractometer. The check box 'Refine 2Theta zero' is used to enable or disable refinement of this value together with the cell parameters (not advised!).
 - iii. *Use peak file indices* - if checked, starting values for refinement are not taken from the 'Lattice parameter' edit fields but are generated from all peaks in the peak file which are indexed. Note:

it is possible to enter hkl values into a peak file using **Notepad** – just place the values directly under the H, K and L headings.

3. Press '**OK**' to perform the refinement.
4. The result of the attempted refinement will now be displayed. There are basically two possible outcomes – success (to some level) or failure.
 - a. *Failure* – You will see a window much like the one below. Your solution is not the answer, or the lattice parameters may be too far from the 'correct' values; try working them out from individual reflections first.



- b. *Success?* – You will be prompted with a list of text, detailing the refined values for your lattice constants. You should now plug these lattice constants back into the 'Refine' window, and try refining again. Keep doing this until the values no longer change. You will also be told how many peaks are fitted by the model; if all of them are fitted, then well done! If there are reflections not accepted by the model, consider possible reasons for this – is the model correct, or could they be from secondary phases? If you know that any unidentified peaks should be there, try indexing these manually in **Notepad** as described above.

Once you have reached a satisfactory answer, you should save your refined peak file (**File/Save As...**). Saving the file also automatically saves a *.lrf file, with the same filename as your *.pks file, with all the lattice refinement data. This *.lrf file can also be viewed in Notepad. You may also wish to print out (**File/Print**) the results of your refinement immediately.

7. *Theoretical patterns with WinX^{POW}*

The Theoretical Pattern generation comprises the calculation of peak positions and Miller indices from given lattice constants and symmetry information (either crystal system, Laue group or space group) as well as the full pattern generation from cell metrics and atomic coordinates. For the full pattern generation, the atomic structure must be entered via the program's editing options.

The Theoretical Pattern program can be started from the **Cell/Theoretical Pattern** option in the main console menu.

To start generating a theoretical pattern:

1. Click **Setup/Crystal Parameters**. This will open a child window, where all the basic crystallographic information may be entered. You should be aware of the following:
 - a. *Formula*: The chemical formula of the phase, with a space between the element and the number, i.e. Li 2 Co Mn 3 O 8. It is also possible to enter ions, i.e. Mn²⁺ 2 Mn³⁺ O 4 for Mn₃O₄. Once you have entered this, the molecular weight will be calculated automatically.
 - b. *Z*: the number of formula units per unit cell.
 - c. *Space Group*: Enter your space group in Herman-Mauguin notation, with spaces between symmetry elements followed by the setting if appropriate, i.e. F d 3 m Z.
 - d. *Cell Parameters*: Enter the unit cell lengths (in Å) and angles.
 - e. *Radiation*: Enter the type of radiation you wish to simulate.
 - f. *Generate Full Pattern*: a check box which is only enabled if atoms have been input in the 'Atom List' dialog box.
 - g. *2Theta (Min, Max)*: describes the 2theta range for which peak positions will be calculated.
 - h. Click **OK** when finished.

This will generate a list of possible peak positions but with no intensity information; for this, you will need to input atoms.

To insert an atom:

1. Click **Setup/Atom List**. Click **New Atom**.
2. A list of each atom you entered in the Crystal Parameters window is given in a menu to the right. Select the type of atom you wish to enter, and click '**Set Type**'.
3. Enter a **name** for the atom (commonly the type, followed by a number, *e.g.* Ba1), the **atomic coordinates** and the **fraction** of the site that is occupied by this particular atom. Leave the thermal parameters at the default values. Finally, to insert the atom press '**Enter**' on your keyboard.
4. Repeat step 3 for all the atoms in your structure, pressing enter to insert each one onto the atom list. When complete, press '**Okay**'.
5. It is now possible to generate a full theoretical pattern, with calculated peak intensities. Go to **Setup/Crystal Parameters** and you will notice that the previously-ghosted 'Generate full pattern' tickbox is now no longer ghosted; tick the box now.
6. The Pattern Parameters window will appear. The geometry of the experiment and presence of a monochromator will have an obvious impact on your data, so options are available here to improve the simulated pattern.
 - a. *Geometry* – the Stoe runs in Transmission mode generally, though capillaries are actually in Debye-Scherrer. All our other instruments have Reflection geometry.
 - b. *Monochromator* – the Stoe has a Germanium monochromator; the other instruments do not have monochromatic radiation.
 - c. *Profile Function* – detailed descriptions of these are given in the help file. These affect the peak shape; try different ones to see which matches the observed data best.
 - d. Finally, it is possible to enter the 2Theta ranges for the calculated pattern, peak halfwidths (should choose similar values to that in your observed

data!) and a maximum intensity (*i.e.* number of counts). It is also possible to generate $K\alpha_2$ peaks.

7. Click '**Okay**' to generate the pattern.

To save your theoretical patterns, click **File/Save**. The program will save three files: a *.tin parameter file, an ASCII list file with *.lth format, and a peak file with *.pth format – all three files will have the same filename, but different extensions. The *.tin file can be opened in Theoretical Pattern; the peak file can be opened in Graphics if you wish to compare against observed data.

Finally, all these files can be edited – if you have a good reason! – in Notepad.

8. *Crystallite Size Analysis by XRD*

The 'Size/Strain' program allows the calculation of crystallite size and microstrain from peak widths. The algorithms used are based on the variation of the integral breadth over 2θ ; the fundamental equations used are given in the help files associated with the program.

The Size/Strain program can be started from the **Extras/'Size/Strain'** option in the main console menu. **Two *.pft files will be needed** for the analysis – one for a standard material without peak broadening, and the experimental data of interest. **These fitted patterns must have been fitted using a Pseudo-Voigt function.** The standard should ideally be of the same composition being studied, but without any peak broadening – you should discuss how to obtain this with your supervisor. The *.pft files must be created in the Pattern Fitting program (see Page 8) – for this you will require the *.raw and *.pks files for the experimental and standard samples you wish to fit.

1. **Open** both of your fitted peakfiles (<filename>.pft) in the '**Size/Strain**' program.
2. A list of peaks will be presented. De-select any peaks of very low relative intensity.
3. The '**Calculation**' radio buttons give you the choice between two different ways of evaluating the 2θ -dependence of the peak broadening effect.
 - I. '**Use functions**' will perform a least-squares-fit according to the Scherrer- and Wilson-formula (using the breadth parameter selected with the next two input options).
 - II. '**Use mean value**' will apply the two formulas independently for every peak, calculate a size-strain parameters for each line and take the average of these parameters. The difference between the results obtained with the two methods is usually small (*e.g.* 1-10% of the calculated value depending on the number of peaks evaluated); if the difference exceeds about 20%, this is an indication that the data do not follow the theoretical prediction at all.

Try studying the effects of each setting on your results, but once you decide which you prefer, stick to that method.

4. Tick the '**use deconvolution**' box if you feel you have good quality data. This box is usually checked as it is the most accurate way of separating the size and strain broadening effects in raw data of very good quality. The background must be defined unambiguously and the peak counting statistics have to be excellent. If these prerequisites cannot be met, you should retreat to a simpler size/strain estimation (i.e. look at the effect of using gamma or beta for calculation) rather than expect correct results from an advanced algorithm fed with insufficient data. Therefore, this box should not be checked for poor data.
5. The '**2Theta window for deconvolution**' controls the assignment of observed peaks to standard peaks. The standard peak used to correct the profiles for instrument broadening must be in the same 2θ region as the broadened peak, since peak width and shape vary with 2θ . Therefore there are two options for this:
 - I. **If the standard is the same substance as the broadened sample but showing no peak broadening effects.** In this case, every broadened peak may be corrected with its unbroadened analogue in the standard. Peak positions would vary very little and *a small 2θ window can be used.*
 - II. **If the use of the very same substance as a standard was not feasible** - another standard, like Si, must be used. In these cases, the permissible width of the 2θ window depends on the size of the broadening effect and may be the larger the larger the broadening is. If the instrumental FWHM is e.g. in the range of 0.1° and the broadened peaks are more than 2° wide, *the 2θ window may be up to 10° without introducing significant error.*
6. Press '**OK**' to start the calculation and display the results on the screen (size/strain results will be presented towards the bottom of the 'output' window.

Note: in general, particle-size broadening leads to a Lorentzian shape, and strain-broadening to a Gaussian shape.