

RIETVELD EXERCISE GUIDE

Crystallography Basics and Structural Characterization 2023

Introduction

In this exercise, you are provided with an XRD measurement file of a precursor powder for solid state synthesis. Tragically, the chemical storage room is haunted by a ghost that likes to take off the etiquettes of the chemical bottles! Mamma Mia!

Fortunately, the ghost is not able to move around the bottles, and on this shelf we have been keeping only primary oxides for 4th period metals: Cr, Cu, Fe, Mn, and Ni. This helps to limit the possibilities, and it is feasible to try to identify the powder by XRD.

You will need two programs for this exercise: FullProf and Vesta.

<https://www.ill.eu/sites/fullprof/php/downloads.html>

<https://jp-minerals.org/vesta/en/download.html>

some of you may also like Notepad++: <https://notepad-plus-plus.org/downloads/>

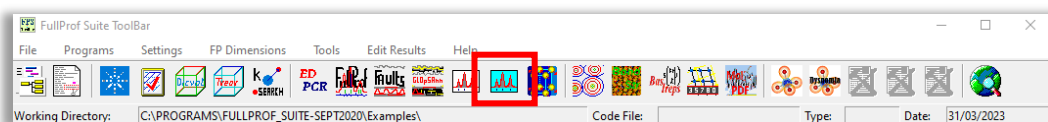
Part 1: space group recognition by Le Bail fitting

Le Bail fitting is a method to evaluate possible space groups for an unknown sample. The method uses peak extinction rules to determine which Bravais lattices are possible (and which are not), and calculates the lattice parameters (a , b , c , α , β , and γ) for the unit cell.

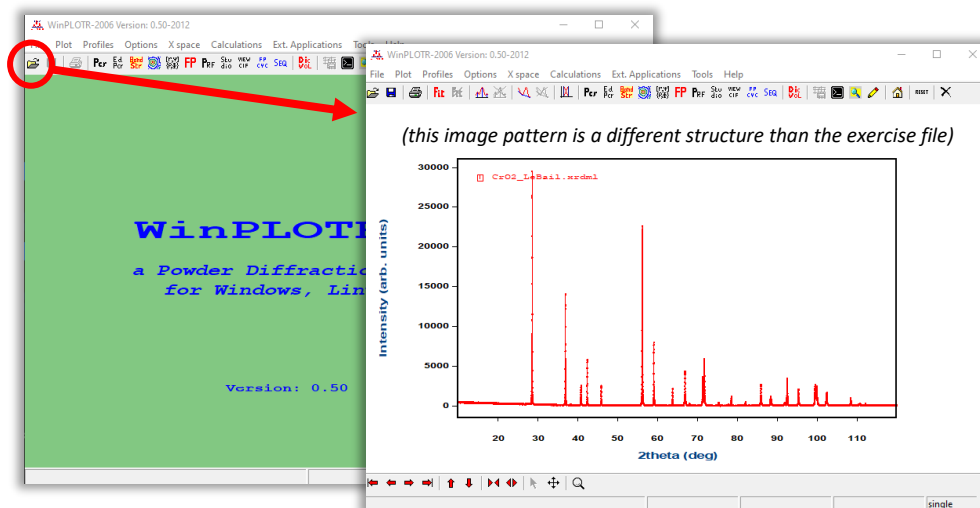
Le Bail fitting requires two steps: peak identification, and pattern fitting.

Peak identification and indexing:

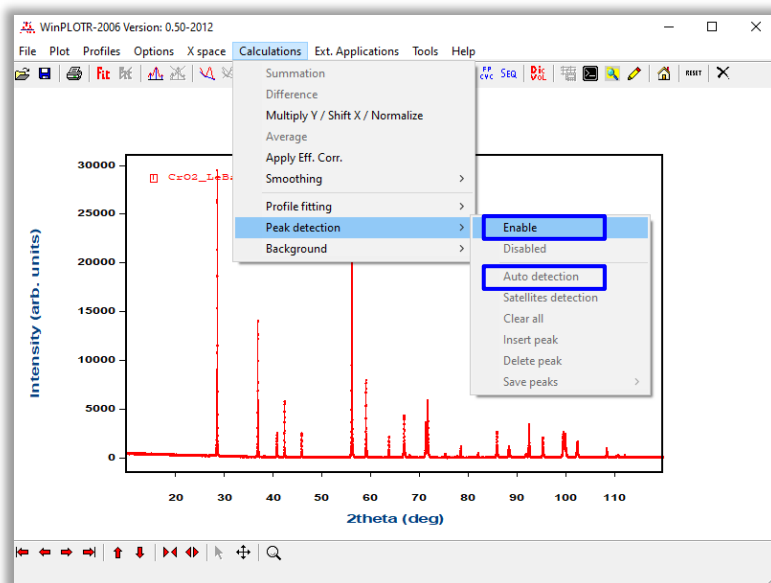
1. Open the FullProf toolbar.



2. Open the toolbar program WinPLOTR2006 (blue pattern icon). Then click the folder icon in the top right corner to open the XRD data file *oxide.xrdbl* from the folder *Indexing*.

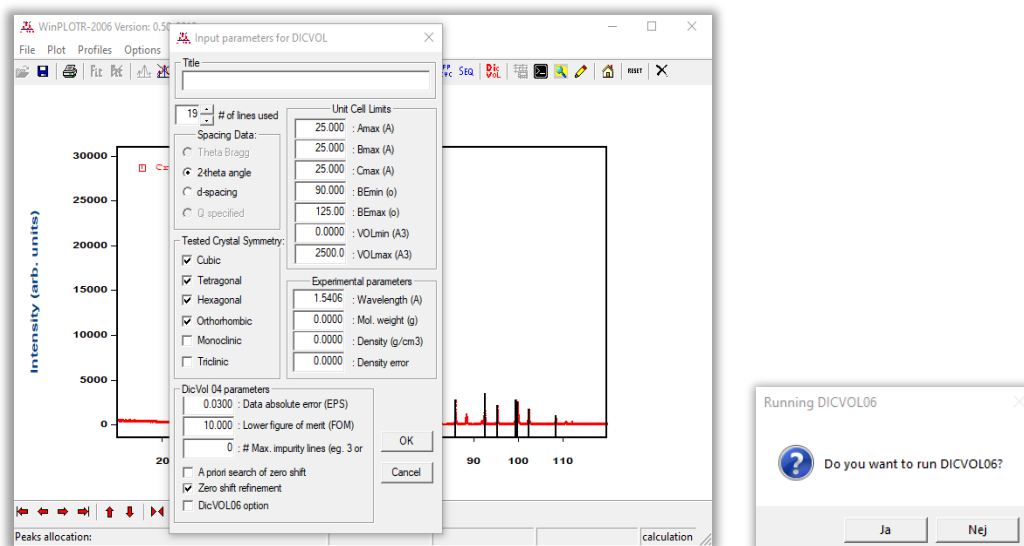


- Search for the peaks: open the menu **Calculations** → **Peak detection** → **Enable**. Then, in the same menu, click on **Auto detection** to run the peak detection (use the default settings).



The program identifies the peaks, possibly not all of them but that is ok – the indexing program is designed to handle this. It is more important that no extra peaks are falsely detected, because this would be problematic for the program.

- When the peaks are detected, save the peak list: open the menu **Calculations** → **Peak detection** → **Save peaks** → **DICVOL format**. In the window 'Input parameters for DICVOL1' you can accept the default settings without adjustment. Name the file (for example *sample1.dic*) and save it in the *Indexing* folder.



The program asks if you want to run DICVOL → press **Yes**

- Dicvol program for unit cell recognition appears in a new window. The algorithm checks through the basic peak patterns for the different crystallographic systems and selects the best fitting crystal systems. Finally, it presents the chosen crystal system options with a crude estimation of lattice parameters.

```

DICVOL05
SEARCH OF ORTHORHOMBIC SOLUTION(S)
*****
VOLUME DOMAIN BEING SCANNED :
-----
LOVER BOUND = 0.00 Å**3 HIGHER BOUND = 56.97 Å**3
41 29 9 4 3 5 4
ITERATION NUMBER AT EACH DICHOTOMY LEVEL:
--- T O T A L  C A L C U L A T I O N  T I M E : 0.270 SEC
>>>> PLEASE READ THE DICVOL OUTPUT FILE: name_LeBail.ind <<<<<
-----
D I C V O L 0 4  S O L U T I O N ( S )

```

When the code has run, the program asks about saving the result into a PCR file → click **NO**.
(this feature would be useful but unfortunately it's not working properly)

The result window will close, and an odd little window appears, just click 'Kenavo'

- The results of peak recognition and Dicvol script analysis have now created a bunch of new documents in your *Indexing* folder, which you can inspect:

name.dic	list of peaks detected
name.ind	report of the indexing calculation steps
name.ord	<u>list of solutions including peaks with indexes</u>
<u>name.ucp</u>	<u>summary of Dicvol calculation results</u>
name_dicvol_cell.sum	empty document for collecting future calculation results
name_1-n.cry	for each solution, a document listing (a, b, c, α , β , γ)

Choose the best structure model

You will find these in the folder named 'Structure suggestions'.

Open the provided cif-files (for example in Vesta, or in a text editor) and compare the lattice parameters and crystal system with the listed results from Dicvol (the .ucp file).

Tip: in Vesta, the lattice parameters can be inspected in the Summary tab at the window bottom, or via the menu path Edit → Edit Data → Unit cell

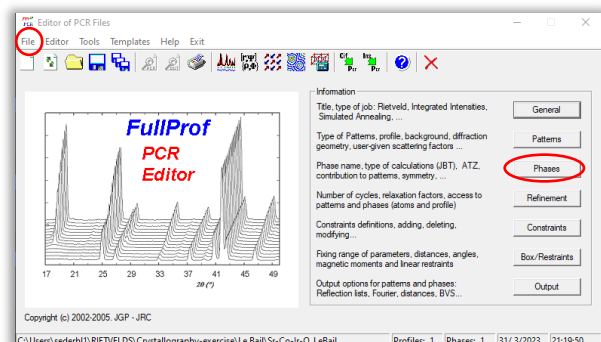
Which structure seems to be the best fit? (you might have to make a choice)


Tip: the crystallographic axes can be interchanged depending on the choice of setting; the combination of values is the important thing

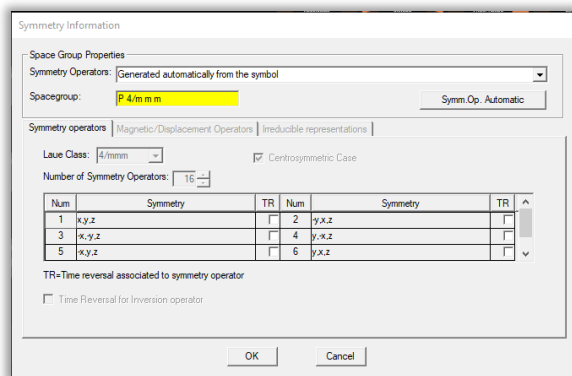
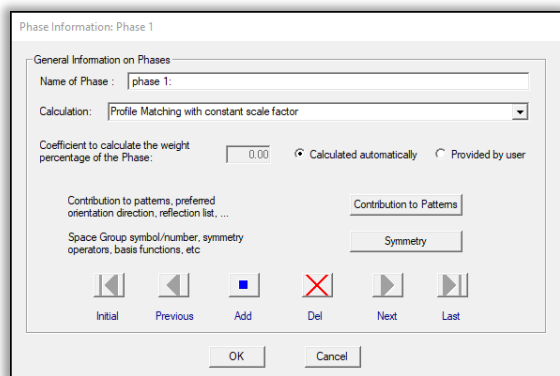
Le Bail fitting


Now we have a guess of the crystal system and an estimate for the lattice parameters (and structure!) Next, we will calculate the unit cell parameters more precisely using Le Bail fitting equations.

- Open the refinement document (pcr-file):
in a text editor such as Notepad++;
or using the graphic editor **EdPCR** from the FullProf toolbar, and then menu **File** → **Open** and find the pcr document "oxide.pcr" in the LeBail folder.

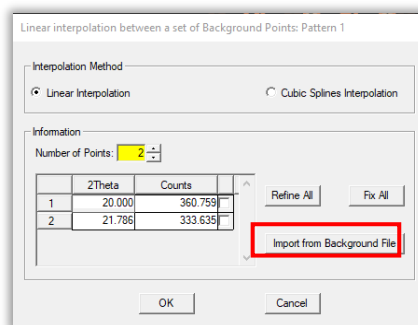
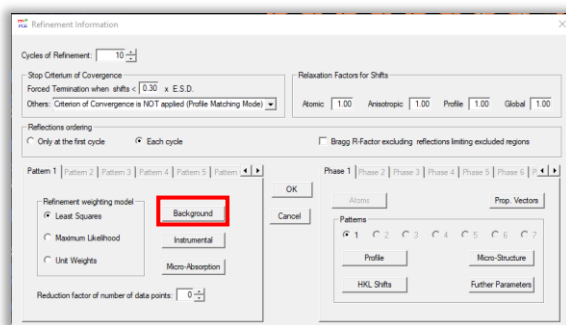


2. Enter the correct space group into the refinement document. This is easiest to do by copying the space group symbol from the cif file for the best matching structure
 - a. in Notepad++: scroll down to the line with the text "`--Space group symbol`" and replace the current text with the new space group. Save changes by CTRL+S
 - b. in EdPCR: click on button 'Phases' on the right side to open the window 'Phase information'; then click the button 'Symmetry'; then paste the new space group into the 'Spacegroup' slot (marked in yellow). Click the button 'Symm Op automatic' to load the correct symmetry operations.
Save changes by clicking **OK** → **OK** → save icon  (in the EdPCR window)

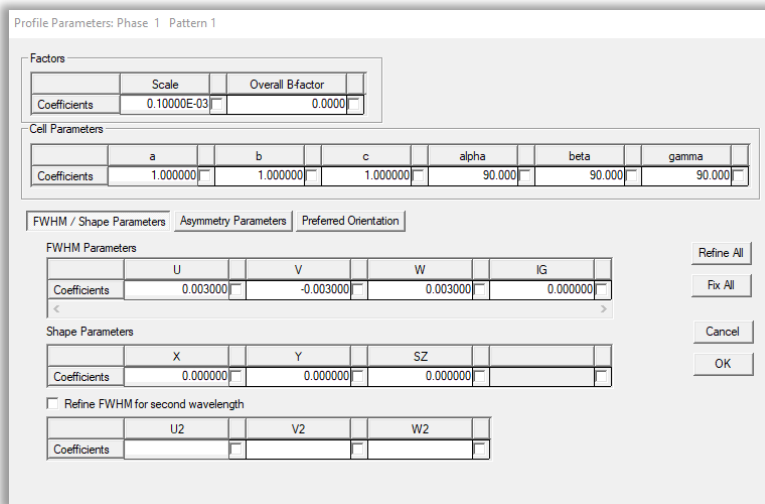


3. Update the background: click on the 'Refinement' button in the *EdPCR* window; then click on the button 'Background' in the *Refinement information* window; then click on 'Import from Background File' and choose the prepared file 'background.bgr' in the Le Bail folder.
Save changes by clicking **OK** → **OK** → save icon 

!Background edits should always be done via the EdPCR window, or you might get errors!



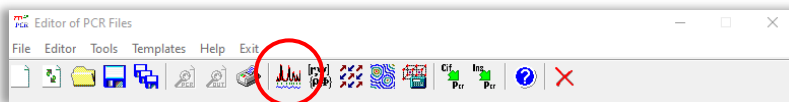
4. Update the lattice parameters: open the cif file (in Vesta or notepad) of your chosen matching structure, and also open the .ucp file from the peak matching. Check which one of the Dicolv suggestions was the best match, and use these values **in the size order as given in the cif file** to replace the old unit cell parameters in the PCR file
 - a. In Notepad: find the row with unit cell data and copy paste the values (be careful to replace only and precisely the old value), then save by CTRL+S
 - b. In EdPCR: click the button 'Refinement' → 'Profile' → edit the text boxes in the Coefficients row → save by clicking **OK** → **OK** → save



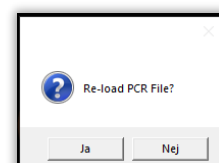
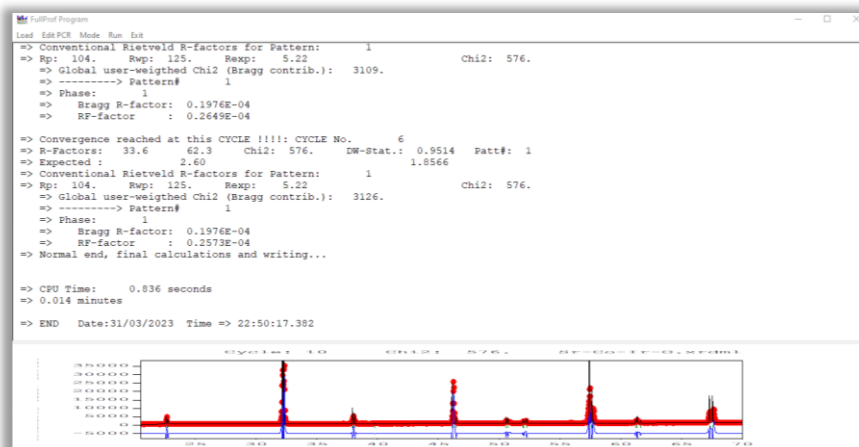
5. Now we have updated all the data in the PCR file. To check that it is working without errors, we will do a 'null' refinement (with no parameters open to be changed):
 - a. Notepad users: from the FullProf toolbar, open (one of) the WinPlotr program, then click on the button 'Run Fullprof' in the top row. In the window that opens, select the PCR file for the refinement and click OK; then select the XRD data file and click OK.



- b. In EdPCR: click on the button 'Run FullProf program' at the top of the window. The program erroneously asks for a file it does not need, so click 'Cancel'. In the next window, select the XRD data file and click OK.



6. The refinement opens a new window and prints its progress while it runs. When it stops printing you should see a preview of the current profile matching status. You can zoom in on the pattern with your mouse to check details. When you close this window, the new data will be saved to the PCR file. EdPCR gives a notification asking to re-load the PCR file: click yes. Notepad shows a corresponding prompt.



7. Now begins the refinement! We will refine the parameters group-wise in order:
 - a. Background (refine once using EdPCR, then deactivate)
 - b. Displacement
 - c. Unit cell parameters
 - d. Peak profile (first W, then X, then U, then V)

The parameters can be activated/deactivated for refinement via either the EdPCR or directly in the pcr document via Notepad:

- In Notepad: activate refinement of a parameter by changing the number shown beneath it; the number formatting is $NNX.xxxx$ where NN is the integer number that denotes the order of calculation and X.xxx describes how 'strongly' the parameter is refined (we use $X.xxxx = 1.000$)

```

51 !-----> Profile Parameters for Pattern # 1
52 !..Scale.....Shapel.....Bov.....Str1.....Str2
53 0.10000E-03...0.00000...0.00000...0.00000...0.000
54 0.00000...0.000...0.000...0.000...0.000...0.0
55 !.....U.....V.....W.....X.....
56 0.003000...0.003000...0.003000...0.000000...0.0
57 0.000...0.000...0.000...0.000...0.000...0.0
58 !.....a.....b.....c.....alpha.....beta
59 5.559299...5.559299...7.809300...90.000000...90.0
60 11.00000...21.00000...31.00000...0.000000...0.0
61 !Prfl1 Prfl2 Asy1 Asy2 Asy3
62 1.00000...0.00000...0.00000...0.00000...0.00000...0.0
  
```

Parameters a, b, c are being refined:
 a first (11.000)
 b next (21.000)
 c third (31.000)

- In EdPCR: click on the 'Refinement' button, then click on 'Instrumental' button to access the displacement parameter; or 'Profile' button to access unit cell and peak shape parameters; tick the boxes next to each parameter to allow refinement of it

8. Activate one parameter at a time, and refine until the calculation converges. Then deactivate the parameter, activate the next one and refine until convergence. When you have refined each parameter in the group to convergence separately, try to refine them together (first pair-wise, then all at once) Repeat the procedure with the next group of parameters. In the end, you should be able to run all parameters at the same time and get convergence.
9. The progress of the refinement is continuously updated into the profile file *.prf* and the output file *.sum* in the refinement folder. Follow the progress of the refinement visually from the WinPLOT2006 window by keeping open the *.prf* file there; if you close it, reopen it from the FullProf toolbar and open the *.prf* file via **File** → **open PRF** → select file Follow the progress numerically by opening the *.sum* file in Notepad++ (shows goodness-of-fit parameters **Chi2**, **Rwp**, and others)

Questions:

1. What is the identity of the powder?
2. After Le Bail fit, what are the unit cell parameters of the powder?
3. What values do you get for the fitness parameters Chi2 and Rwp?

TASK 2: Rietveld refinement.

Now we have a bit more precise values for the unit cell parameters, we can proceed to add atoms into our model.

1. Open the PCR file in the *Rietveld* folder. This is already prepared with the background and other settings for Rietveld refinement, it just needs to be updated with the unit cell data. First enter the values for the unit cell parameters you found by LeBail.
 - a. In Notepad: find the row with unit cell data and copy paste the values (be careful to replace only and precisely the old value), then save by CTRL+S
 - b. In EdPCR: click the button 'Refinement' → 'Profile' → edit the text boxes in the Coefficients row → save by clicking OK → OK → save


Factors	
Scale	0.10000E-03
Overall B-factor	0.0000

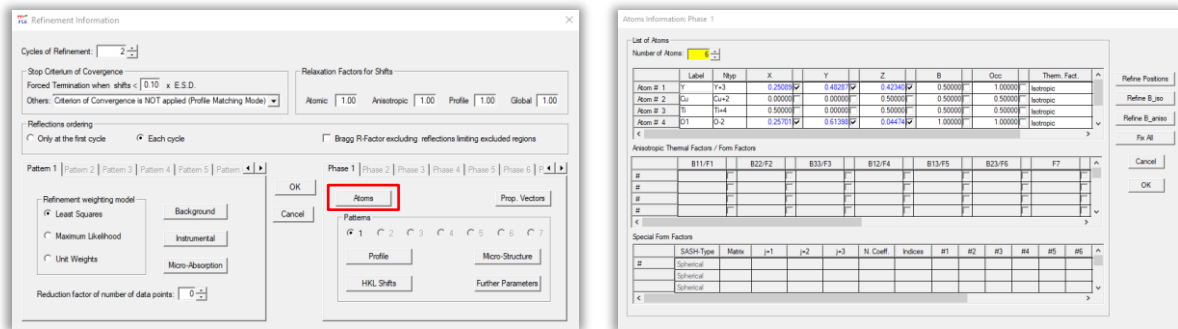
Cell Parameters						
a	b	c	alpha	beta	gamma	
1.000000	1.000000	1.000000	90.000	90.000	90.000	

FWHM / Shape Parameters				
U	V	W	IG	
0.003000	-0.003000	0.003000	0.000000	

Shape Parameters		
X	Y	SZ
0.000000	0.000000	0.000000

Refine FWHM for second wavelength		
U2	V2	W2

2. Update the space group: this is done exactly the same as for the LeBail refinement:
 - a. in Notepad++: scroll down to the line with the text "`<<--Space group symbol`" and replace the current text with the correct space group. Save changes by CTRL+S
 - b. in the PCR editor: click on the button 'Phases' on the right side; the window 'Phase information' will appear, now click on the button 'Symmetry'; the 'Symmetry information' window opens, here paste the new space group into the 'Spacegroup' slot (marked in yellow). Click the button 'Symm Op automatic' to load the correct symmetry operations.
Save changes by clicking **OK** → **OK** → save icon  (in the EdPCR window)
3. Next we add the atoms. Open the cif file that you chose as the best model and check from there what the atoms and their coordinates are.
 - a. In Notepad: find the row where you added the space group. Below this is where the atoms are added. There is one placeholder yttrium atom waiting for you as a model: copy the two-row atom description until you have the right number of atoms for your basis, then update the atomic and ionic symbols, the X Y Z coordinates, and the occupancy factors of the atoms in your model basis.
Make sure to not create any extra rows!
Finally, check a few rows above the space group symbol on the row that says Nat, and update this number to match the number of atoms you have listed.
 - b. In EdPCR: click the button Refinement → Atoms. Adjust the correct number of atoms by clicking the arrows next to the yellow text field, then edit the atom data in the table. Save by clicking OK → OK → save
When refining atomic sites, return to this window to activate/deactivate the refinement of specific atom coordinates using the checkboxes.



4. Test run the refinement to see that there are no errors.
If the refinement runs smoothly, a bunch of documents should appear in the *Rietveld* folder, including a cif-file. Open the structure in Vesta to check if the model looks sensible. Do you need to fix anything?
5. When all looks good, you are ready to start refining! Again, refine one parameter at a time in the beginning, then try refining them group-wise, and finally everyone at once. Follow the refinement progress by keeping the *prf*-file open in WinPLOTR.
 - a. Displacement (SyCos) – refine alone until convergence
 - b. Scale – refine together with displacement, when converged, turn off displacement but leave scale on
 - c. Lattice parameters – first one at a time, then all as a group
 - d. Atom coordinates – those who are Wyckoff position locked will turn off automatically
 - e. Peak shape parameters – these are tricky, proceed carefully
 - f. Asymmetry – should not be needed in this case, but you can try if you want
6. Follow the refinement progress by keeping the *prf*-file open in WinPLOTR.
Follow the progress numerically by opening the .sum file in Notepad++ (**Chi2, Rwp**)

Questions

1. Is there a difference in what goodness-of-fit parameters (Chi2 and Rwp) you can achieve with each method?
Please take a screenshot of how the refinement *prf*-file looks in WinPLOTR when you are finished with the refinement, and add it to your exercise answers document 😊
2. What are the cell parameters of your refined structure? How does the refined structure differ from the model structure that you began with?
3. Any comments/feedback about the exercise?