

Profile Fitting for Analysis of XRPD Data using HighScore Plus v3

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Profile fitting is a technique used to extract precise information about the position, intensity, width, and shape of each individual peak in a diffraction pattern

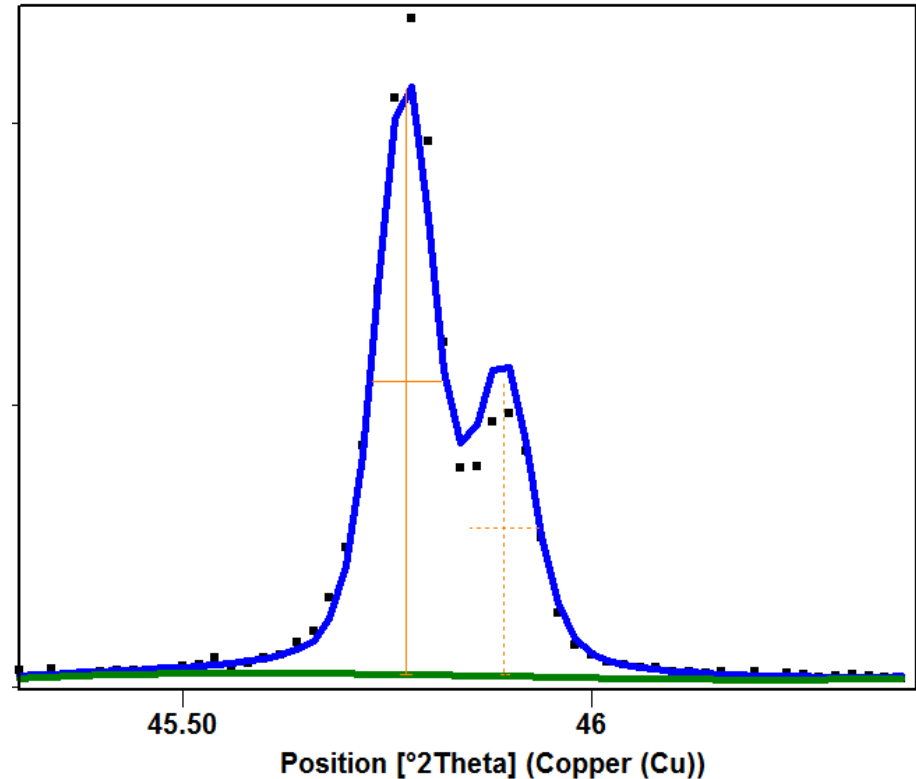
- Profile fitting provides more precise peak information than any peak search algorithm
- The peak information can be used in several calculations to quantify sample parameters such as unit cell lattice parameters, crystallite size and microstrain, and relative weight fractions
- Many programs provide profile fitting capabilities
 - These slides describe how to use HighScore Plus, published by PANalytical Inc, to profile fit diffraction data
 - The general procedure can be used with other programs
 - Other commercial programs that offer profile fitting capabilities are: MDI Jade, Bruker Topas, Rigaku PDXL, X Powder
 - Free programs, some of which are a bit older, include Xfit, Fourya, Winfit, Fullprof, Fit

Techniques to Quantify Diffraction Data

- Profile Fitting
 - The position, intensity, width, and shape of each diffraction peak is empirically fit
 - Each diffraction peak is fit independently of others unless constraints are explicitly imposed
 - This is a precise way to determine information about the peaks, but further work is required to extract meaning from the data
- Whole Pattern Fitting
 - An ideal diffraction pattern is calculated from a model of the sample
 - The calculated diffraction pattern is compared to experimental data..
 - The model is refined until the differences between the calculated and experimental diffraction patterns are minimized.
 - The result is a refined model of the sample.
- Rietveld Refinement
 - The position and intensity of diffraction peaks are calculated from the crystal structure
 - The width and shape of diffraction peaks are fit to functions that describes their systematic behavior related to 2θ
 - The result is a refined model of the crystal structure and peak shape functions that can provide information about the microstructure
- Pawly or LeBail Fit
 - The position of the diffraction peaks are calculated from, and constrained by, the unit cell lattice parameters
 - The width and shape of diffraction peaks are fit to a function that describes their systematic behavior related to 2θ
 - The peak intensities are empirically fit

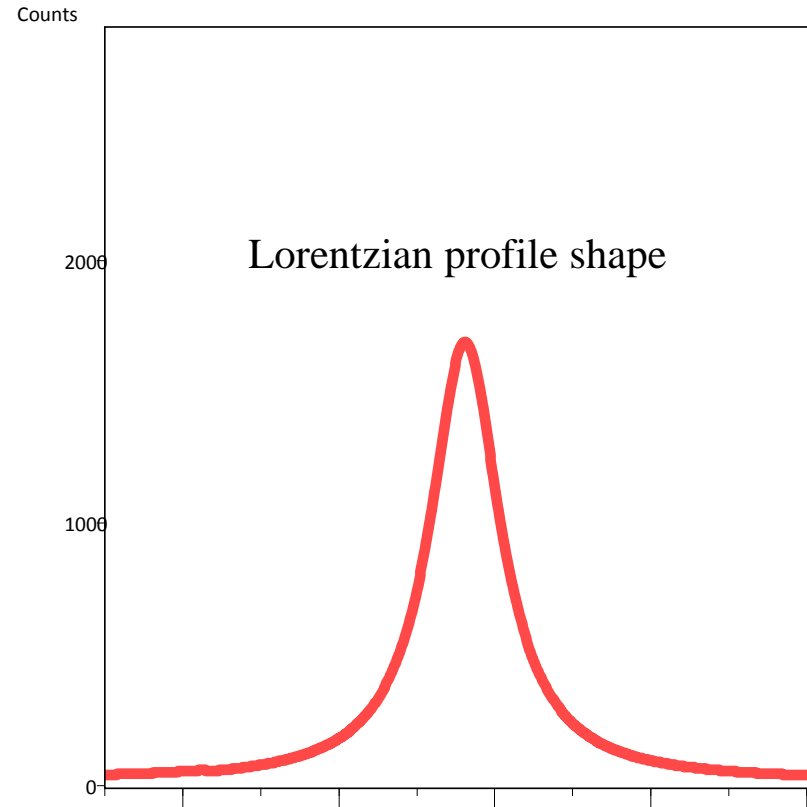
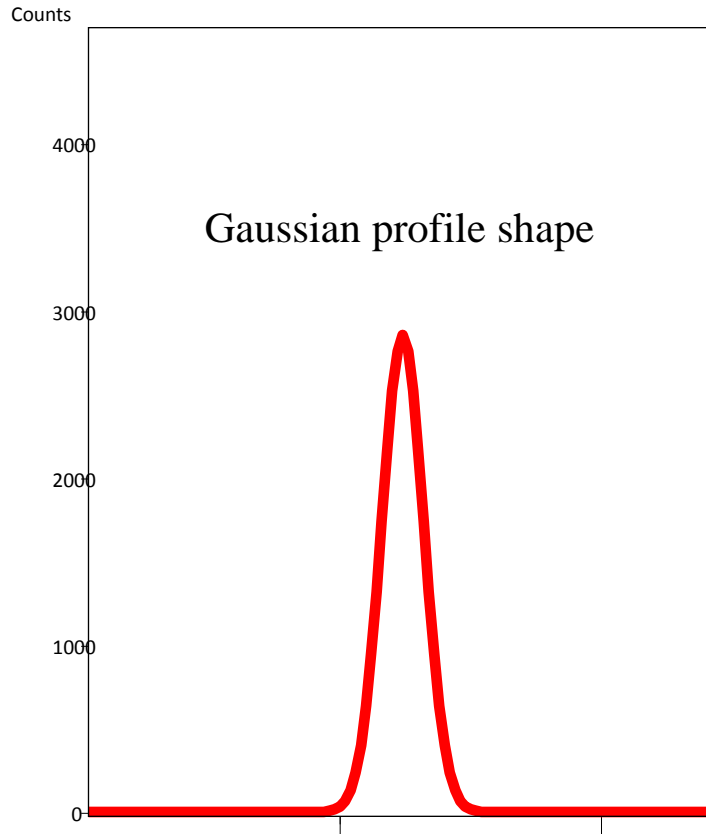
Profile Fitting models each diffraction peak with an empirical equation

- The experimental data are empirically fit with a series of equations
 - Each diffraction peak is fit using a profile function
 - The background is also fit, usually using a polynomial function
 - *this helps to separate intensity in peak tails from background*
- Peak information is extracted from the profile equation rather than numerically from the raw data
- **Profile fitting produces precise peak positions, widths, heights, and areas with statistically valid estimates**



In this example, the profile function models the K alpha-1 & K alpha-2 peak doublet

Diffraction peaks from laboratory diffractometers are a mixture of Gaussian and Lorentzian profiles



- The profile function models this complex peak shape
- The same profile function is used for every peak in the diffraction pattern

Profile functions model the mixture of Gaussian and Lorentzian contributions to the peak shape

- Diffraction data are most commonly modeled using a pseudo-Voigt or Pearson VII function
 - A true Voigt curve is a convolution of the Gaussian and Lorentzian components
 - This function is difficult to implement computationally
 - The pseudo Voigt is a linear combination of Gaussian and Lorentzian components
 - The Pearson VII is an exponential mixing of Gaussian and Lorentzian components
- Some techniques try to deconvolute the Gaussian and Lorentzian contributions to the peak shape- this is difficult
- SA Howard and KD Preston, “Profile Fitting of Powder Diffraction Patterns,” Reviews in Mineralogy vol 20: Modern Powder Diffraction, Mineralogical Society of America, Washington DC, 1989.

Calculations are based on the peak information extracted from profile fitting results

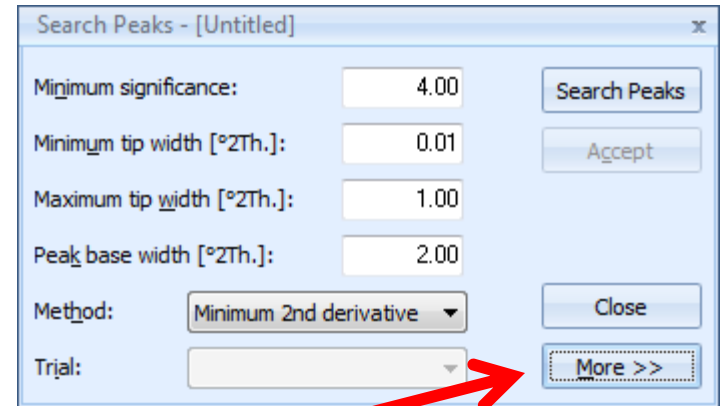
- **Peak positions** are used to calculate **unit cell lattice parameters**
- **Peak widths** are used to calculate **crystallite size** and **microstrain**
 - Peak shapes may also be used in crystallite size and microstrain analysis
- **Peak intensities** are used to calculate the **weight fraction** of each phase in a mixture

Profile fitting procedure for HighScore Plus

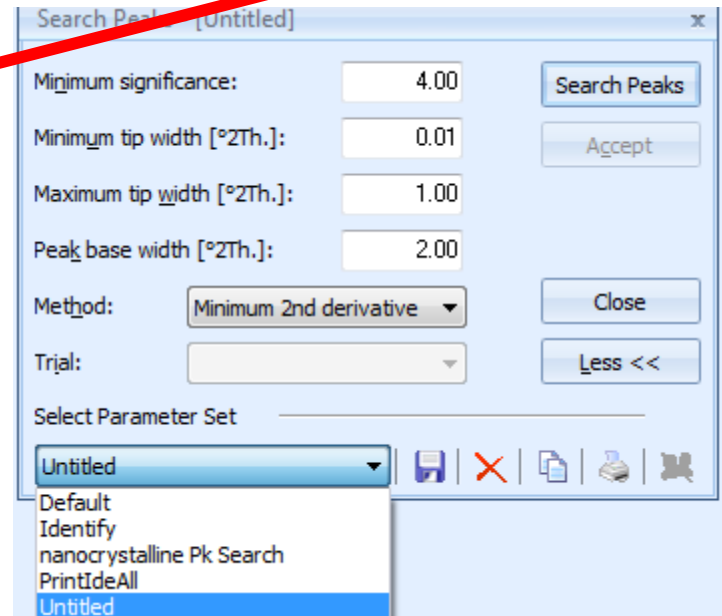
This tutorial assumes that you have a basic familiarity with HighScore Plus. Please review the document <http://prism.mit.edu/xray/HighScore%20Plus%20Guide.pdf> for some guidelines on the basics of HighScore Plus.

Using **Parameter Sets** in HighScore Plus

- Each treatment or analysis in HighScore Plus has several parameters that can be adjusted to modify the behavior of the program.
- “Parameter Sets” are saved values for the parameters that can be used during analysis
- If you do not know what parameters to use, the “**Default**” parameter set is usually a good starting point.



- To access a parameter set:
 - In any dialogue window, click the “More” button
 - This button is usually in the lower right-hand corner
 - Select the parameter set from the drop-down menu



- To save a parameter set:
 - Set the parameters to values that you want to use
 - Click on the “More” button to open the parameter set area
 - Click the floppy disk icon
 - Give the parameter set a unique name

Do not process the data before profile fitting

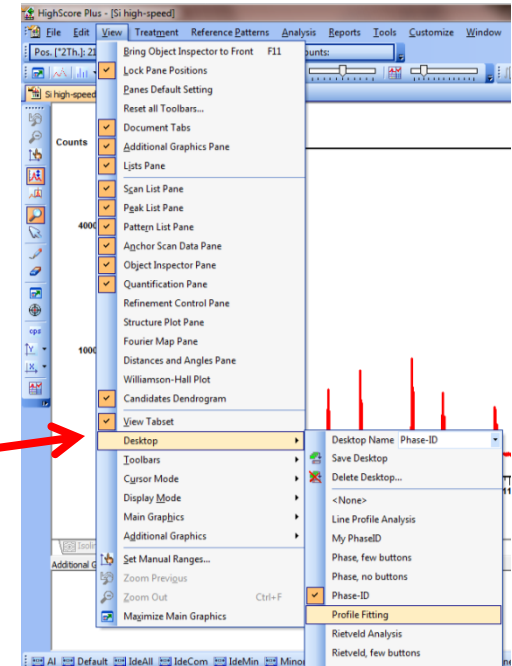
- Do not subtract the background before profile fitting
 - The background will be modeled during the profile fit process
- Do not strip K alpha-2 peaks before profile fitting
 - The K alpha-1 and K alpha-2 peak doublet will be modeled by the profile function
- Do not smooth the data before profile fitting
 - Profile fitting relies on a statistically comparison to your raw data which will be invalid if your data are smoothed

The Steps for Profile Fitting

1. Fit the background
2. Identify the peaks (ie peak search)
3. Profile Fit the data
4. Evaluate the quality of the profile fit
5. Do calculations based on the result

Setting Program Defaults before Profile Fitting

- HighScore Plus has several preconfigured desktop layouts
 - The best desktops for profile fitting are
 - Profile Fitting
 - Line Profile Analysis
 - To change the desktop
 - go to the menu *View > Desktop*
 - Select the desired desktop from the list in the menu
 - *Do not select the desktop from the drop-down menu in the Desktop submenu; this is used for selecting a filename when saving a customized desktop*



You might want to restore Program and Document Settings to default if working on a shared computer

- Go the menu *Customize > Program Settings*
 - Click on the button **Reset All to Default**
 - Click on the **OK** button to close the window
 - *You can also explore Program Settings to modify the look, feel, and performance of the program such as options for display behavior, automatic backing up of analysis files, behavior during pattern simulation or Rietveld refinement, and data treatments applied automatically when you open a file*
- Go to the menu *Customize > Document Settings*
 - Click on the button **Reset All to Default**
 - Click on the **OK** button to close the window
 - *Note: this menu is only available after you have opened a file*
 - *You can also explore the Document Settings to change options for the graphic display, the analyze view, and labeling for legends and peak markers*

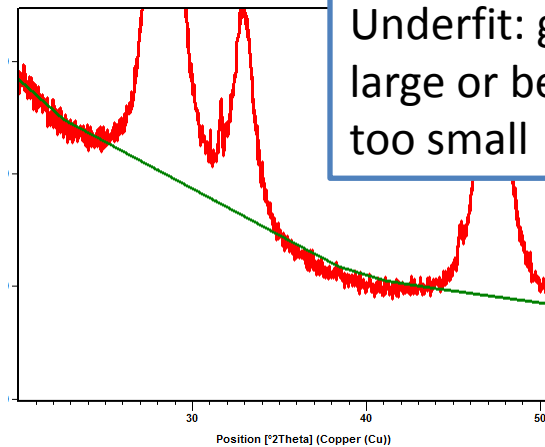
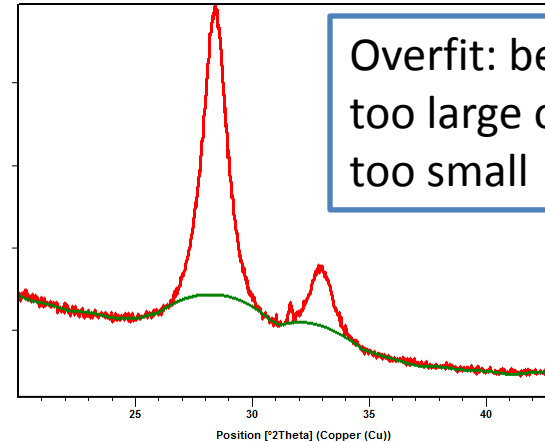
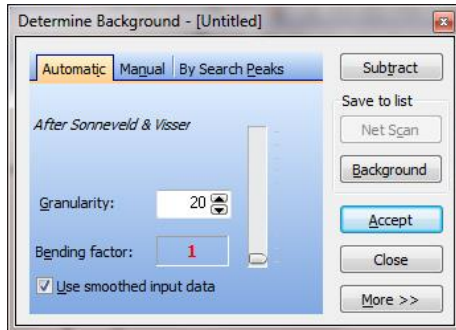
The Steps for Profile Fitting

1. Fit the background
2. Identify the peaks (ie peak search)
3. Profile Fit the data
4. Evaluate the quality of the profile fit
5. Do calculations based on the result

Step 1. Fit the Background

- In most cases, the background fit is only required to aid the peak search
- The background will usually be modeled and refined during the profile fit process
 - A perfect background is not necessary at this point
- To fit the background in HighScore Plus
 - Go to *Treatment > Determine Background*
 - You may want to change the y-axis scale to Square Root so that you can see the background better

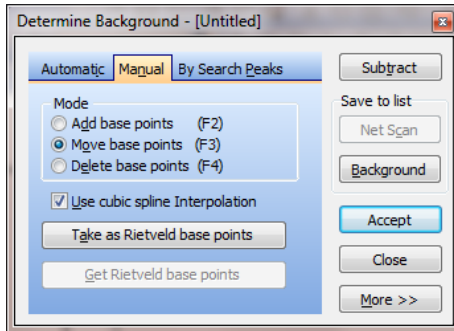
Background Fit Options: Automatic



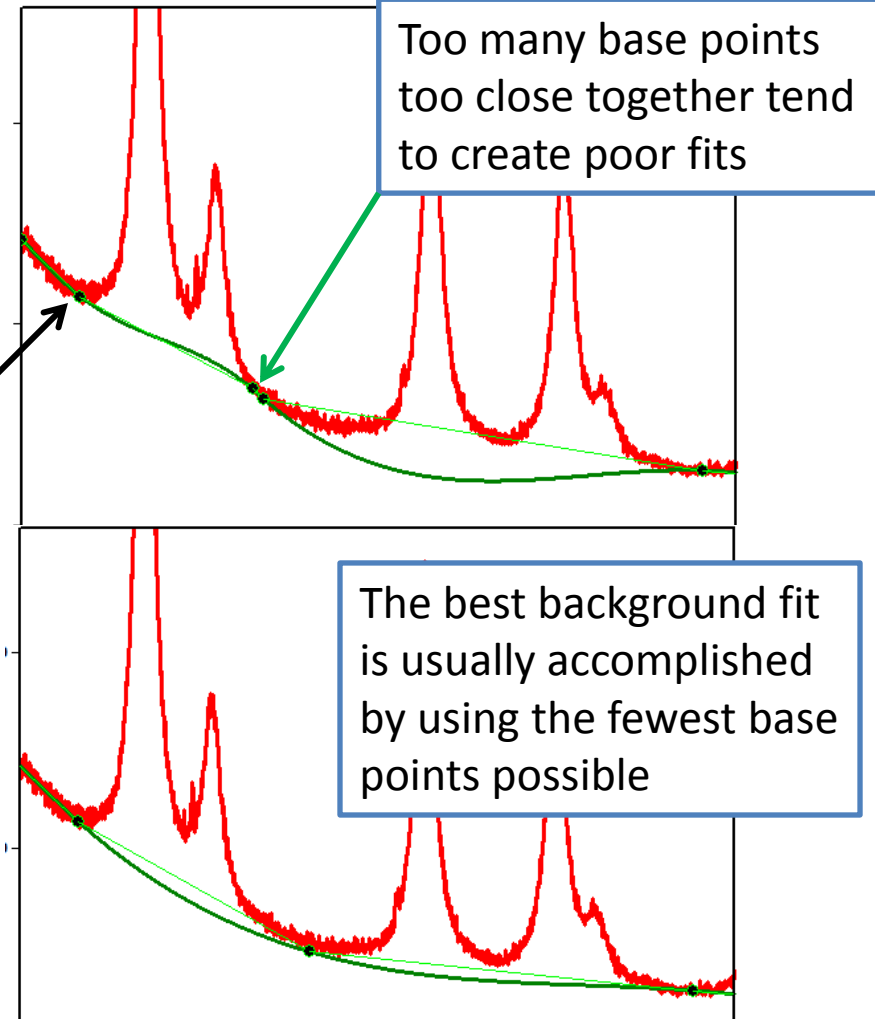
- Adjust parameters until green background line is a good fit to the data, without overfitting the data
- Use the slider to adjust **Bending factor** to fit nonlinearity and curvature
 - If made too large, background may fit peak intensity
- **Granularity** controls the sampling interval
 - A smaller number will fit the data more closely, but may overfit the data
- **Use smoothed input data** to avoid oversampling data and noise
- Typically use parameters:
 - Granularity: 10 to 30
 - Bending Factor: 0 to 2

When the background is a good fit, click **Accept**. Do NOT **Subtract** the background.

Background Fit Options: Manual



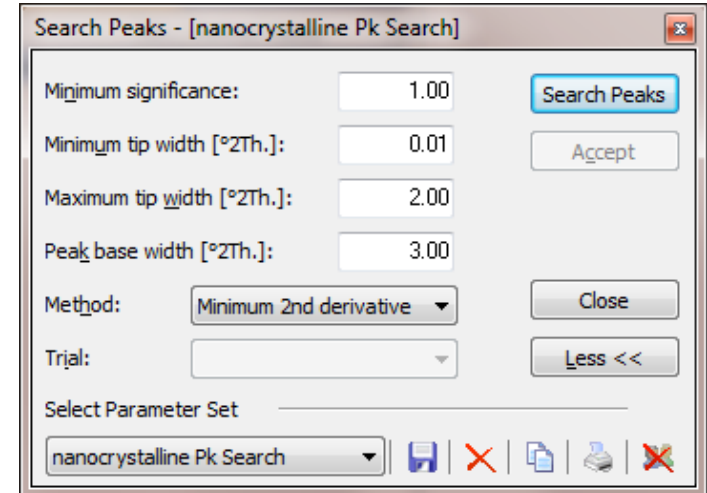
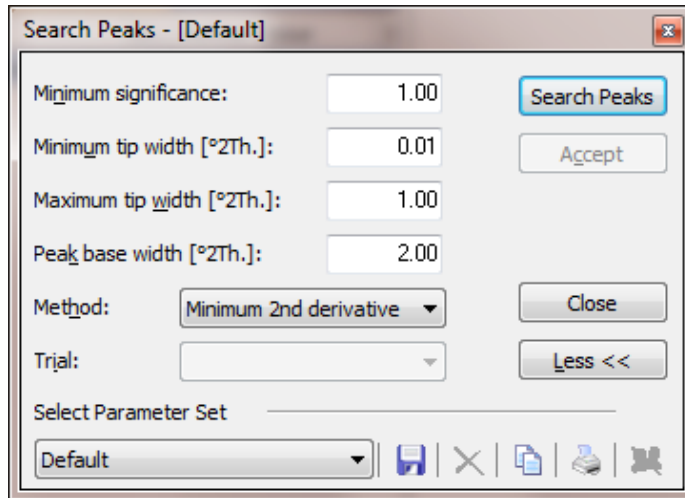
- Use cubic spline interpolation to fit curves between each base point
- The base points are shown as black dots on the **green background curve**
- The **Mode** (add, move, delete) determines what happens when you left-click on the base point
 - **Add** and **Delete** base points to create an accurate background fit
 - The first and last base points can only be **Moved**



When the background is a good fit, click **Accept**. Do not **Subtract** the background.

Step 2: Peak Search

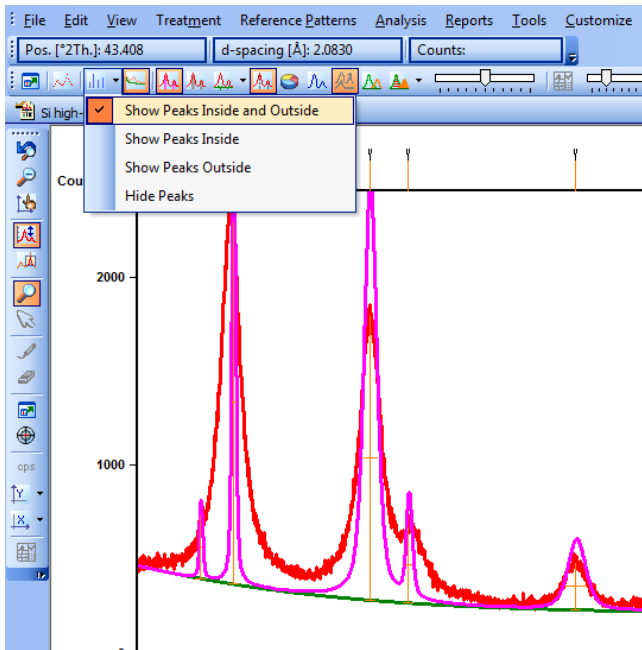
- Start a Peak Search from the menu *Treatment > Search Peaks*
- Use the Default parameter set



When starting with the Default parameter set, you may need to increase the “Minimum Significance” for noisy data

If the sample is nanocrystalline, you will need to increase the **Maximum tip width** and **Peak base width** in order to account for the broader diffraction peaks

Step 2: Peak Search (cont.)



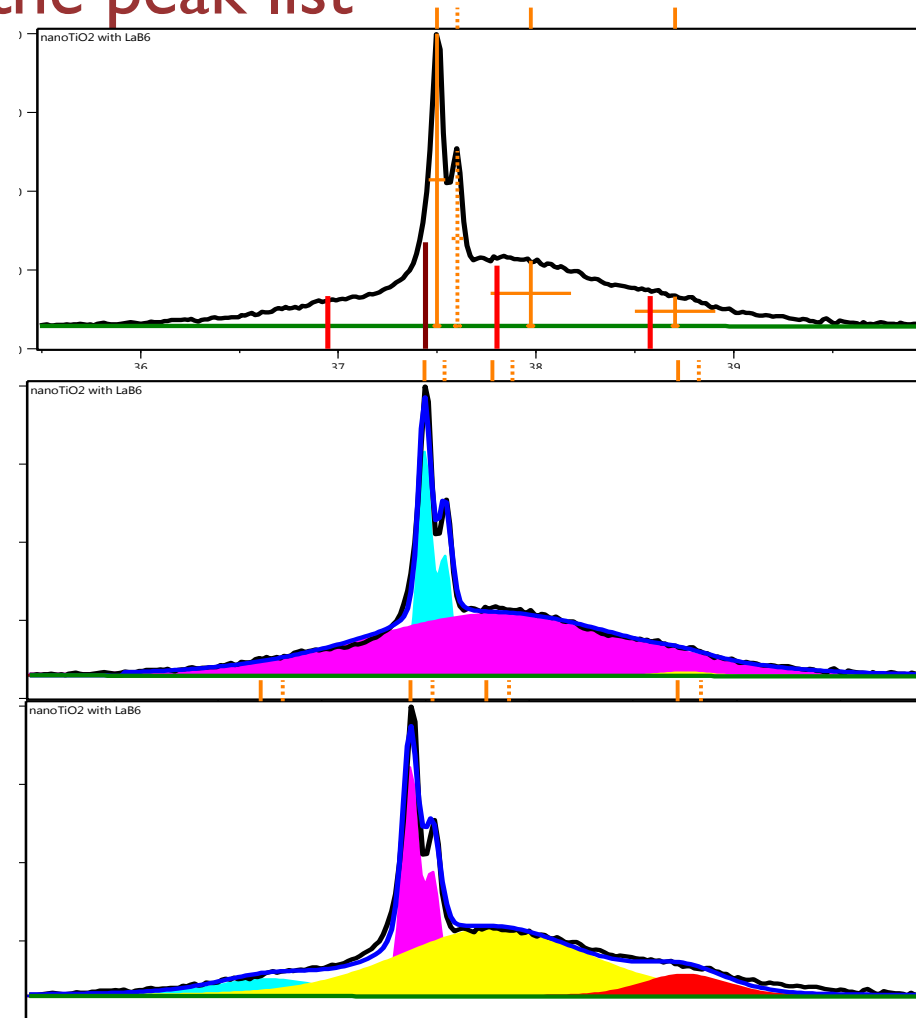
- Click on **Search Peaks** to see a preview of the result
 - A calculated pattern based on the peak search is shown over the experimental data.
 - The “Set Display of Peaks” button will allow you to place the orange peak line markers in the data, above the data, or both.
 - Click on the triangle next to the button in order to see the drop-down menu.
- If necessary, modify the peak search parameters and click **Search Peaks** button to see the new result.
- Click **Accept** when the peak search is satisfactory

If a reference pattern exists for your phase, use it to help you edit the peak list

In this example, the peak search only found 3 peaks (solid orange lines), while the reference card shows that there are 4 peaks (solid red lines).

The profile fitting will use the peaks available to fit the data as best as possible. In this case, the second peak is modeled as much too wide in order to compensate for the missing first peak at $\sim 37^\circ 2\theta$. This also causes the last peak to disappear.

When all four peaks are properly included, the profile fitting accurately separates the contributions of the overlapping peaks.



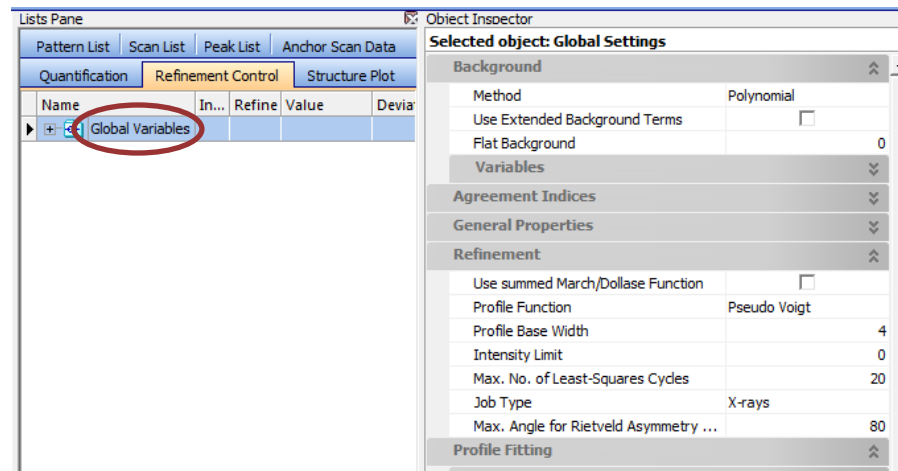
If the peak list is incorrect, the profile fitting will be inaccurate.

If a reference pattern exists for your phase, use it to help you edit the peak list

- Select the Peak List tab in the *Lists Pane*
- To delete a peak, select its line in the Peak List and either:
 - Press Delete on your keyboard
 - Right-click and select **Delete Peak**
 - If you move your mouse cursor above a peak line marker, that peak will automatically be highlighted in the Peak List
 - *Remember that lines shaded gray in the Peak List are K-alpha2 peaks. These are shown as dotted orange lines in the Main Graphics. You do not have to edit these—they will be corrected automatically during profile fitting.*
- To insert a peak:
 - Right-click in the Main Graphics window and select **Insert Peak**
 - Position the cursor to match the height and position of the peak, and then left-click to insert the peak
 - Right-click in the Main Graphics window and select **Insert Peak** to turn the peak insertion cursor off

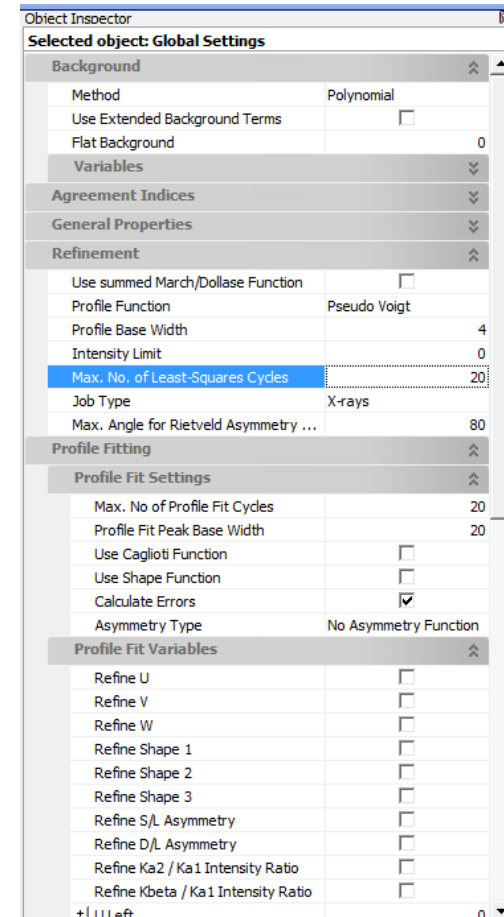
Step 3. Profile Fit the data

- Inspect the Program Settings for the Profile Fitting
 - Select the Refinement Control tab in the *Lists Pane*
 - Left-click on the phrase *Global Variables* in the Refinement Control pane (circled in red)
 - Look in the *Object Inspector* pane for the Global Settings.



Inspect the most relevant profile fitting preferences

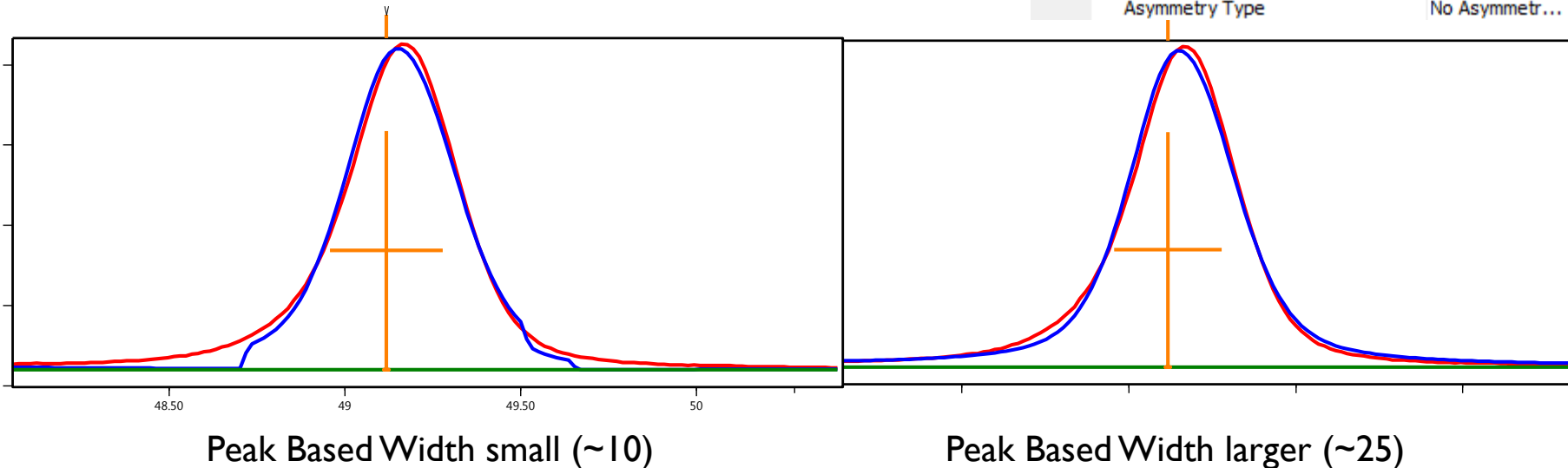
- Background:
 - The Method can be changed using the drop-down menu
 - The most common settings are:
 - Polynomial: fit the background using a polynomial curve
 - Shifted Chebyshev: fit the background using a curve that is useful for samples with amorphous content
 - Use Available Background: fix the background to the curve created in step 1 and do not refine it during profile fitting
 - This is a useful selection when the background is complex or when the pattern features many overlapping peaks.
- Profile Function:
 - The function can be changed using the drop-down menu
 - This determines the equation used to fit each diffraction peak
 - Pseudo Voigt and Pearson VII are the most common
- *For settings with a text-based value, you click on the word describing what is being used (such as the “Polynomial” for Background Method or “Pseudo Voigt” for Profile Function) and a drop-down menu will appear to allow you to change the setting.*



Inspect the most relevant profile fitting preferences

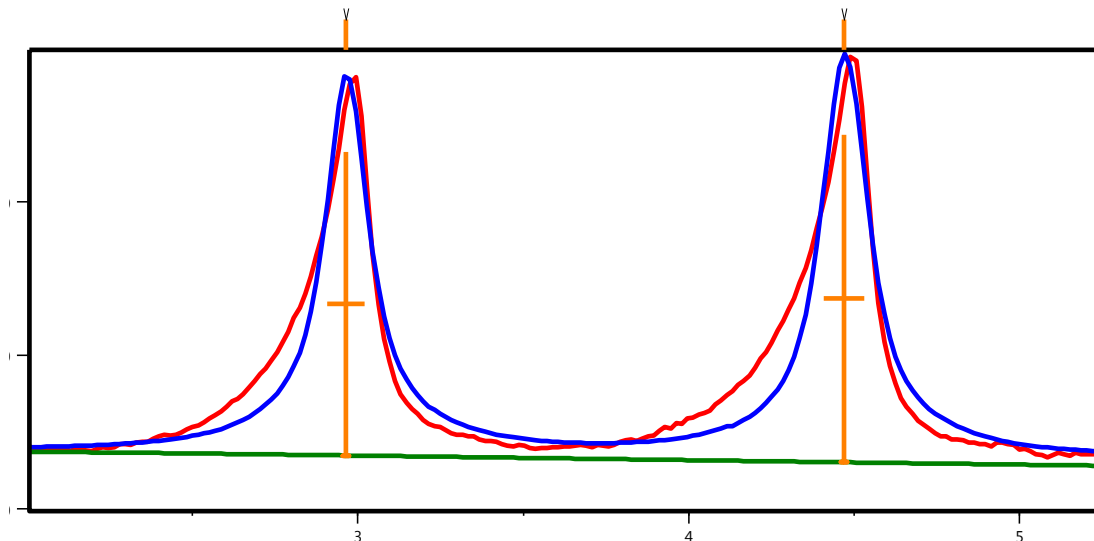
- Profile Fit Peak Base Width
 - This number determines the cut-off where the peak intensity is no longer calculated
 - If the profile fit does not extend for the full length of the tails of the peak, then increase this number

| Object Inspector | |
|----------------------------------|-------------------------------------|
| Selected object: Global Settings | |
| Background | ▼ |
| Agreement Indices | ▼ |
| General Properties | ▼ |
| Refinement | ▼ |
| Profile Fitting | ▲ |
| Profile Fit Settings | |
| Max. No of Profile Fit Cycles | 20 |
| Profile Fit Peak Base Width | 20 |
| Use Caglioti Function | <input type="checkbox"/> |
| Use Shape Function | <input type="checkbox"/> |
| Calculate Errors | <input checked="" type="checkbox"/> |
| Asymmetry Type | No Asymmetr... |



Inspect the most relevant profile fitting preferences

- Asymmetry Type
 - When set to “No Asymmetry Function”, the peaks will be modeled as symmetric
 - If peaks are asymmetric (usually at low angle), you can model using Split Width (most common), Split Shape, or both.
- *For settings with a text-based value, you click on the word describing what is being used (such as “No Asymmetry Function” for Asymmetry type) and a drop-down menu will appear to allow you to change the setting.*



Object Inspector

Selected object: Global Settings

| Background | |
|-------------------------------|--------------------------|
| Method | Polynomial |
| Use Extended Background Terms | <input type="checkbox"/> |
| Flat Background | 0 |
| Variables | |

Agreement Indices

General Properties

Refinement

| | |
|---------------------------------------|--------------------------|
| Use summed March/Dollase Function | <input type="checkbox"/> |
| Profile Function | Pseudo Voigt |
| Profile Base Width | 4 |
| Intensity Limit | 0 |
| Max. No. of Least-Squares Cycles | 20 |
| Job Type | X-rays |
| Max. Angle for Rietveld Asymmetry ... | 80 |

Profile Fitting

Profile Fit Settings

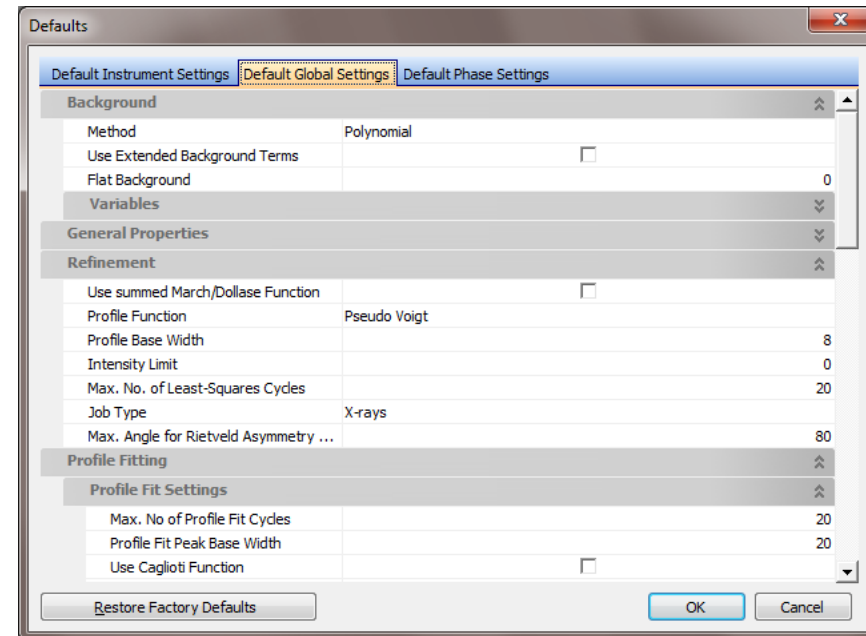
| | |
|--------------------------------|-------------------------------------|
| Max. No. of Profile Fit Cycles | 20 |
| Profile Fit Peak Base Width | 20 |
| Use Caglioti Function | <input type="checkbox"/> |
| Use Shape Function | <input type="checkbox"/> |
| Calculate Errors | <input checked="" type="checkbox"/> |
| Asymmetry Type | No Asymmetry Function |

Profile Fit Variables

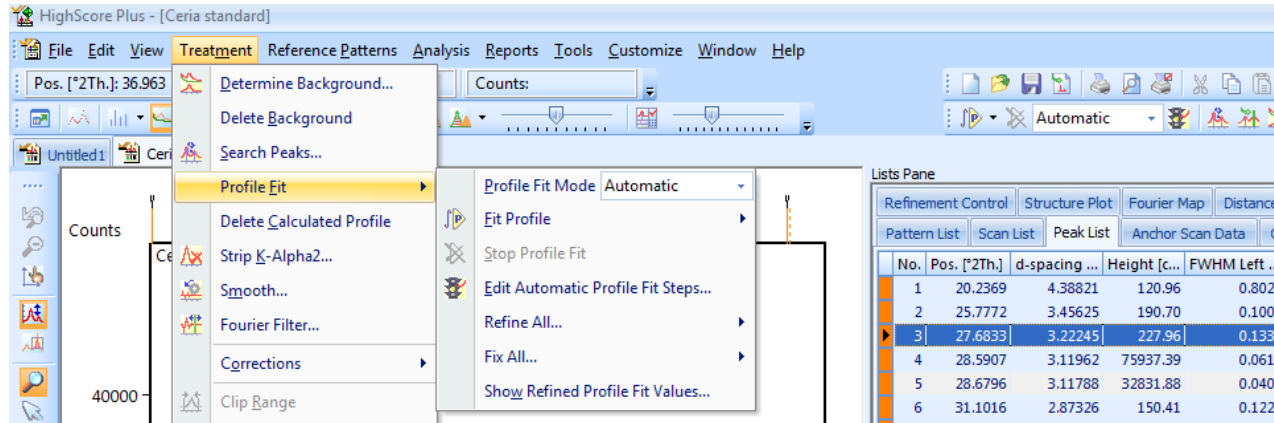
| | |
|------------------------------------|--------------------------|
| Refine U | <input type="checkbox"/> |
| Refine V | <input type="checkbox"/> |
| Refine W | <input type="checkbox"/> |
| Refine Shape 1 | <input type="checkbox"/> |
| Refine Shape 2 | <input type="checkbox"/> |
| Refine Shape 3 | <input type="checkbox"/> |
| Refine S/L Asymmetry | <input type="checkbox"/> |
| Refine D/L Asymmetry | <input type="checkbox"/> |
| Refine Ka2 / Ka1 Intensity Ratio | <input type="checkbox"/> |
| Refine Kbeta / Ka1 Intensity Ratio | <input type="checkbox"/> |

You can customize or restore default values for profile fitting preferences

- Go to the menu *Customize* > *Defaults*
- Select the Default Global Settings tab
- The Profile Fitting Preferences, such as background method and asymmetry type, are listed here.
- Changes made to these preferences will change the default starting values for all new profile fitting analyses



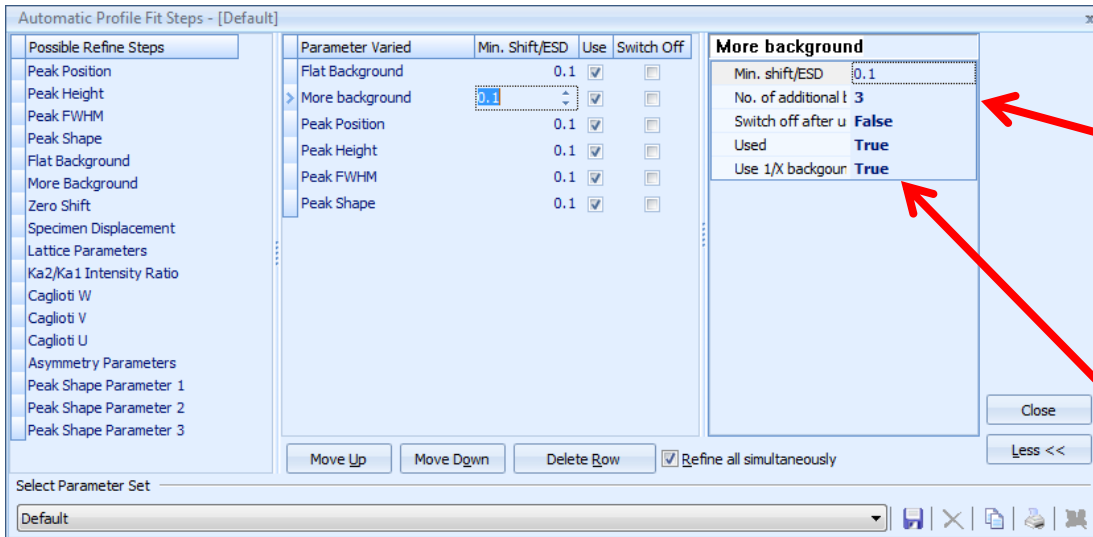
Adjust the Automatic Profile fit parameters



- Many items for profile fitting are found in the menu *Treatment > Profile Fit*
- Make sure the *Profile Fit Mode* is set to **Automatic**
- Select “Edit Automatic Profile Fit Steps” to adjust the way that your data will be fit

Edit the profile fit parameters

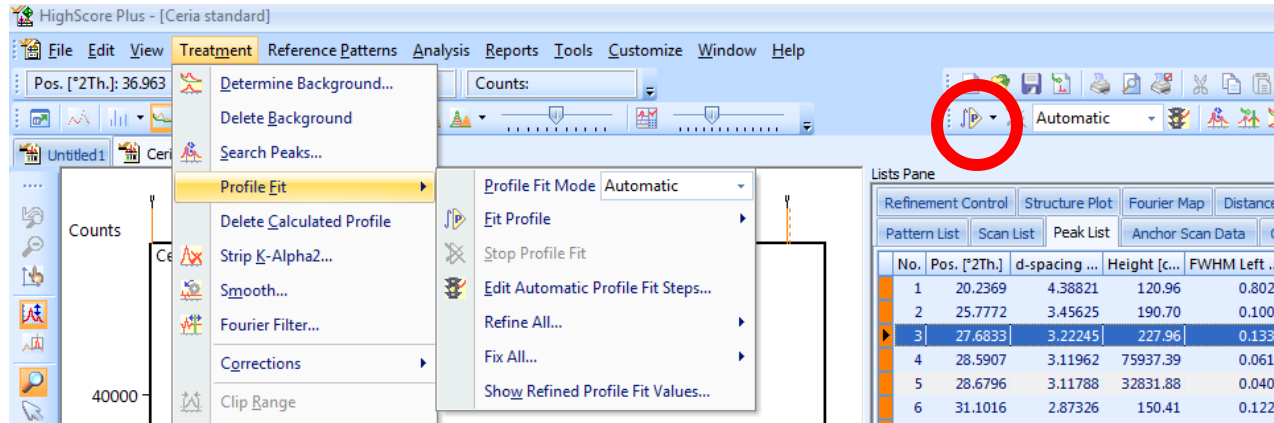
- Go to the menu *Treatment > Profile Fit > Edit Automatic Profile Fit Steps*
- For normal profile fitting, select the Default parameter set
- The only item to modify is the More Background term
 - You can change the No. of Additional Background Terms
 - You can choose whether or not to use the 1/x background term
- If you changed the parameter set, you will need to save it as a new parameter set





When using a background function such as a polynomial, the “No of additional background terms” will determine the order of the polynomial

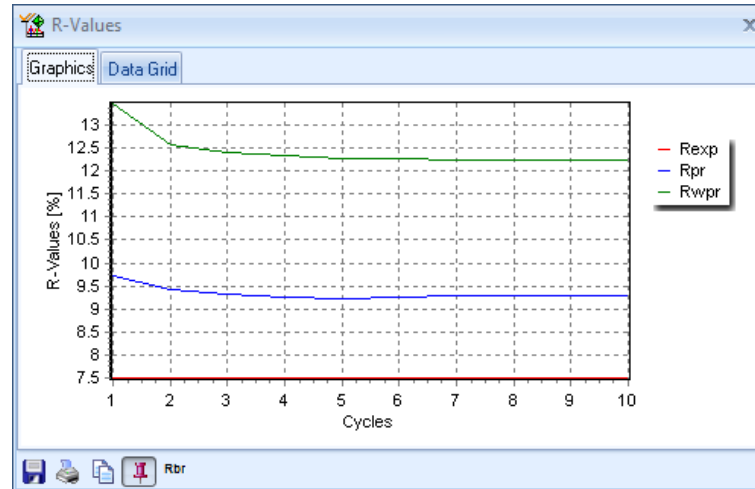
The 1/x background term is effective at modeling background the increases exponentially at low angles

To execute the profile fit



- Many items for profile fitting are found in the menu *Treatment* > *Profile Fit*
- You can execute different profile fitting treatments from the menu *Treatment* > *Profile Fit* > *Fit Profile* or by using the toolbar (circled in red above, which is from the Line Profile Analysis desktop)
 - If you click on the  icon, HSP will run the “Default” parameter set
 - If you click on the black triangle to the right of the  icon, you will be able to select which parameter set you want to run

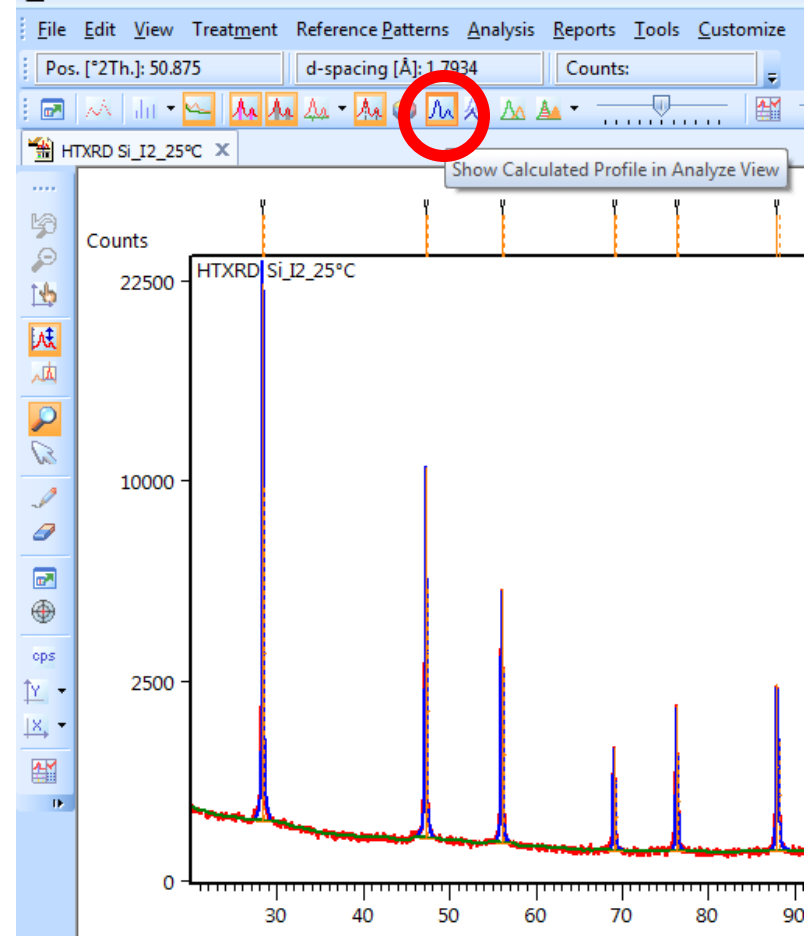
The Residual Plot shows how many refinement cycles ran and how the residual fit improved



- By default the profile fit is limited to 20 refinement cycles.
- If the profile fitting ran for 20 cycles and then stopped, it may not have reached the optimal refinement. You should run the profile fit again.
- If the profile fitting stops before it reaches 20 cycles (as shown above), then it found a minimum in the least-squares residual

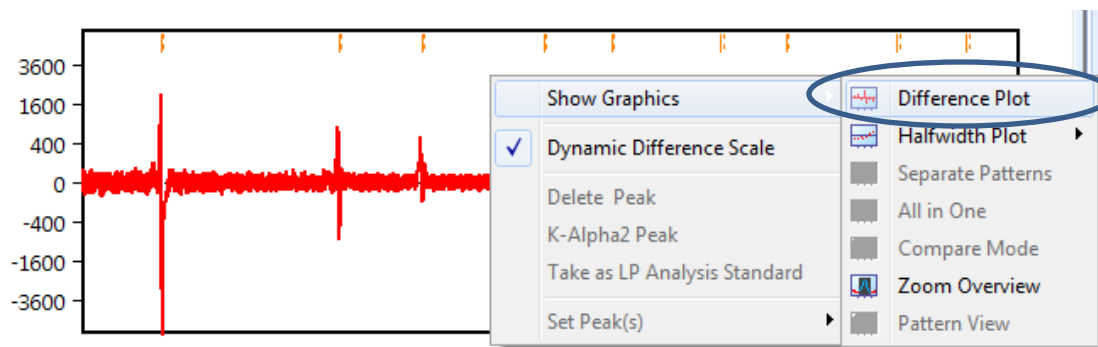
How to determine if the profile fit is good

- First, compare the calculated profile to the experimental data
- In HSP, make sure that the option “Show Calculated Profile in Analyze View is selected” (circled in red).
- The experimental data is usually plotted in red and the calculated profile in blue, though this color scheme can change.
- There should be good agreement between both of these plots.

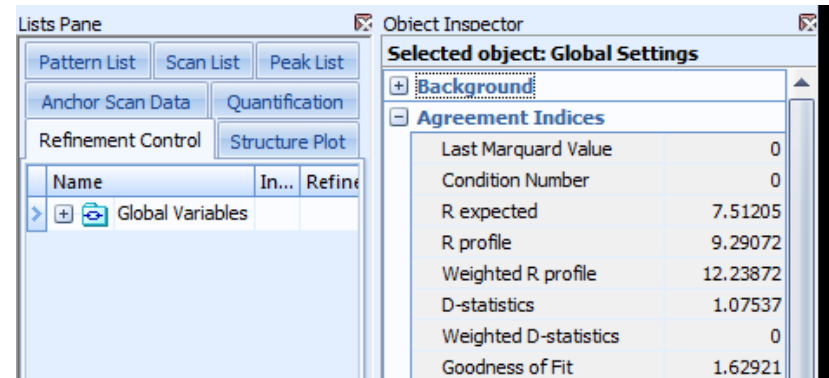


Use the difference plot to determine if the fit is good

- The difference plot shows is a plot of $(I_{\text{exp}} - I_{\text{calc}})$ vs 2θ , and shows where the greatest differences between the experimental and calculated plots are.
- The difference plot is shown in the Additional Graphics area
 - Right-click in the Additional Graphics area.
 - Select the menu *Show Graphics > Difference Plot*



Agreement Indices quantify the difference between the experimental and calculated profiles

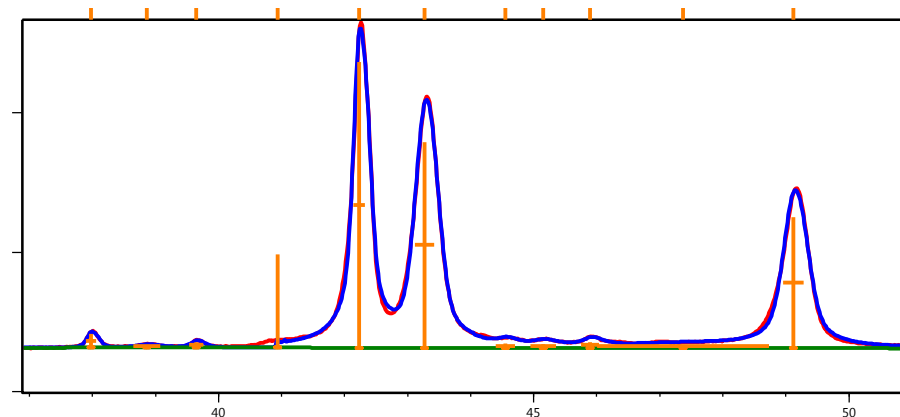


- To see the Agreement Indices
 - Select the Refinement Control tab in the *Lists Pane*
 - Left-click on the entry *Global Variables*
 - Look in the *Object Inspector* pane
 - Expand the area “Agreement Indices”
- R_{expected} is a statistical evaluation of the noise of the data. A smaller R_{expected} indicates better quality data.
- R_{profile} is the residual difference between observed and calculated plots.
- Weighted R_{profile} (R_{wp}) uses a weighting function to place more emphasis on good fit between high intensity data points (such as intense peaks) and less emphasis on low intensity data points (such as background).
 - In a good fit, R_{wp} should be less than 10
- Goodness of Fit is $\frac{R_{\text{wp}}^2}{R_{\text{exp}}^2}$. In a good fit, the GOF should be less than 4.

Look at the Peak List for anomalous values, such as large FWHM values

- For each phase in a sample, values such as FWHM and Shape should be similar, with slight variations as a function of 2θ .
- If one peak in a group that are close together has a larger FWHM, it might mean that there are two overlapping peaks that you fit with a single profile function
- In the peak list to the right, the typical FWHM is 0.16 to 0.4 and the typical shape is 0.5 to 1.
- The peaks with a width of 0 or 3 are atypical and should be inspected.
- The peaks with a shape of 0 are atypical.

| Quantification | | Refinement Control | | Structure Plot | |
|----------------|----------------------------|--------------------|--------------|------------------|-------------|
| Pattern List | | Scan List | Peak List | Anchor Scan Data | |
| No. | Pos. [$^{\circ}2\theta$] | d-spacing ... | Height [c... | FWHM Lef... | Shape... FV |
| 1 | 31(3) | 2.90771 | 81(757) | 0(16) | 0(342) |
| 2 | 37.19955... | 2.44595 | 0(194537... | 0(1608288... | 0(1112... |
| 3 | 37.975(1) | 2.36750 | 2872(162) | 0.16(2) | 0.5(1) |
| 4 | 38.86(2) | 2.31533 | 426(38) | 0.4(1) | 1(1) |
| 5 | 39.643(3) | 2.27164 | 1110(47) | 0.22(7) | 1(1) |
| 6 | 40.9388(3) | 2.20270 | 35586(14... | 0.003(5) | 1(2) |
| 7 | 42.2330(4) | 2.13814 | 224212(2... | 0.1821(6) | 0.58(1) |
| 8 | 43.269(2) | 2.08931 | 127033(2... | 0.302(1) | 0.42(1) |
| 9 | 44.55(2) | 2.03198 | 864(145) | 0.30(1) | 1(1) |
| 10 | 45.15(4) | 2.00664 | 743(66) | 0.4(1) | 1(1) |
| 11 | 45.897(5) | 1.97561 | 1138(85) | 0.3(1) | 1.0(2) |
| ▶ 12 | 47.4(5) | 1.91752 | 571(12) | 3(1) | 0.8(4) |
| 13 | 49.118(6) | 1.85334 | 60133(170) | 0.326(6) | 0.54(3) |
| 14 | 53(1) | 1.72681 | 58(31) | 2.50(9) | 0(1) |



Other Profile fit methods

Individual peak fitting:

Each peak is treated independently. The Position, Height, FWHM and Shape of each peak is an independent variable.

Constrained peak fitting:

The position and height of each peak is an independent parameter. However, the width, shape and asymmetry of all peaks are described by an equation that slowly varies as a function of 2θ . This constraint of the width and shape of peaks is useful when peaks are highly overlapping or data are noisy.

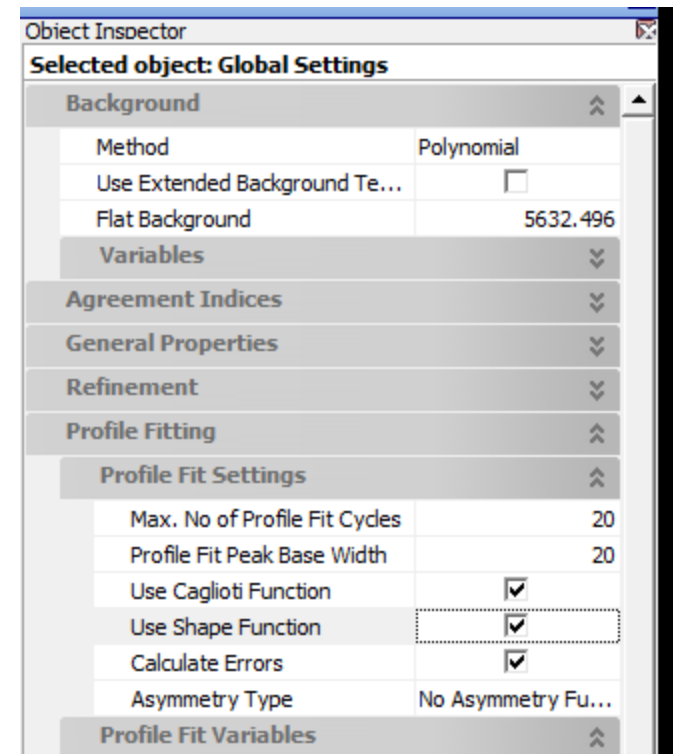
This method may not work well in a mixture, since the different phases may have different peak shapes and widths.

Pawley fit:

Peak positions are generated and constrained by a unit cell and symmetry information. The unit cell lattice parameter is refined rather than individual peak positions (zero shift or specimen displacement may also be refined). Peak heights are fit independently. The width, shape and asymmetry of peaks are described by a function for each phase in the sample.

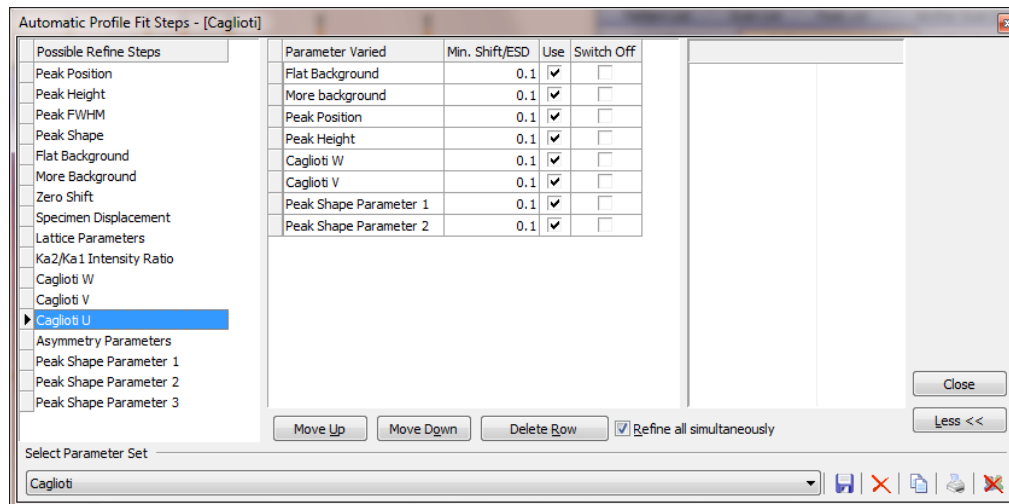
Constrained Peak Fitting: the Caglioti Fit

- Select the Refinement Control tab in the *Lists Pane*
- Left-click on the phrase *Global Variables* in the Refinement Control pane (circled in red)
- Look in the *Object Inspector* pane for the Global Settings.
- In the Profile Fit Settings area, check the boxes for “Use Caglioti Function” and “Use Shape Function”
- All of the peak widths and shapes will be fit with simplified equations
- This reduces the number of independent variables and will improve the stability when profile fitting a pattern with many overlapping peaks.
- *You do not have to use both the Caglioti function and the Shape function- you could use just one or the other*



Edit the profile fit parameters for the Caglioti fit

- Go to the menu *Treatment > Profile Fit > Edit Automatic Profile Fit Steps*
- Select the Default parameter set
- Modify is the More Background term
 - You can change the No. of Additional Background Terms
 - You can choose whether or not to use the 1/x background term
- Select which Caglioti parameters U, V, and W you want to use
 - Always Refine W. Most typical would be to refine U, V, and W.
- Select the number of Peak Shape Parameters
 - Typical is 1. Very strong pattern may be fit with 2
 - If you changed the parameter set, you will need to save it as a new parameter set

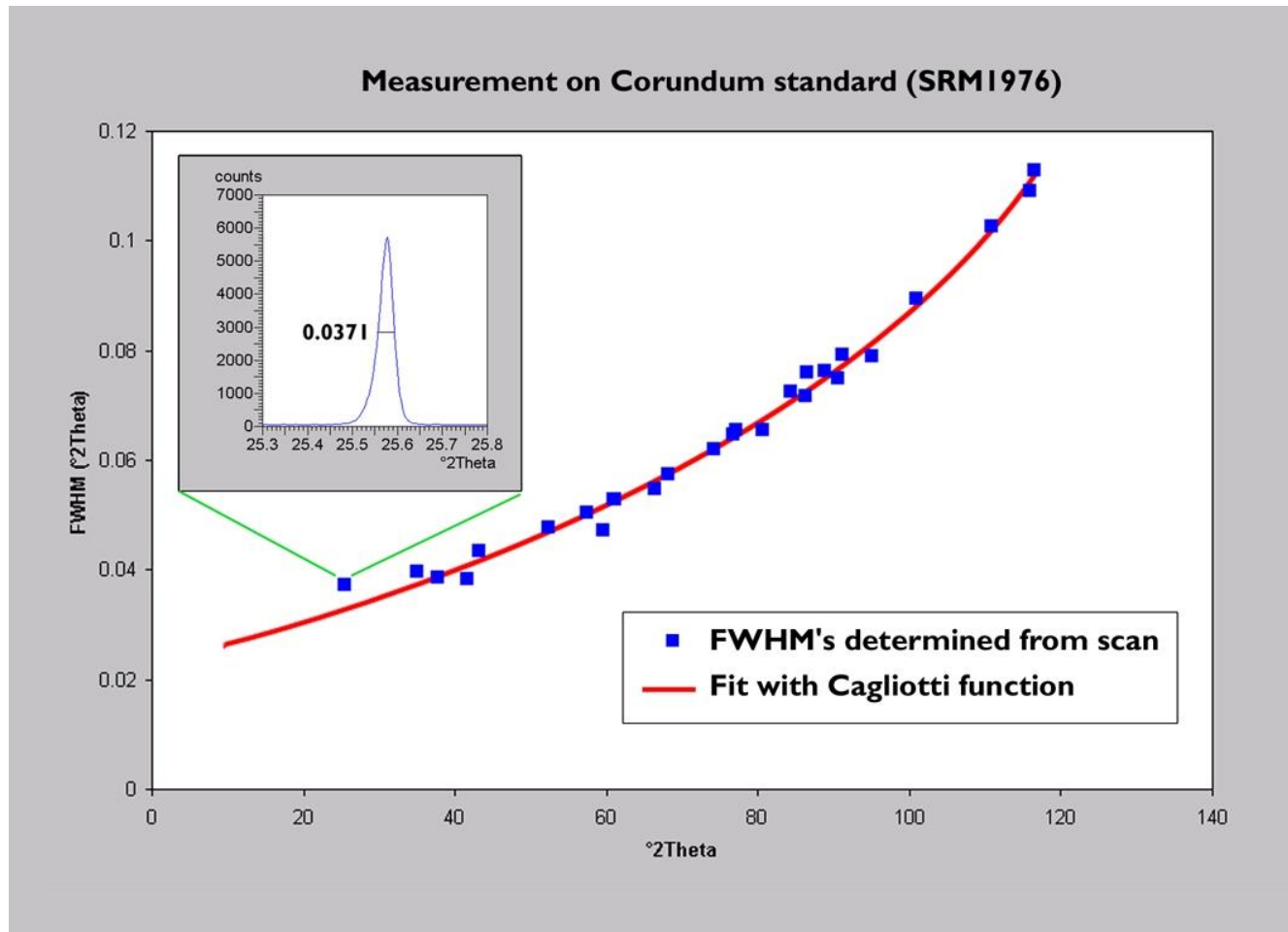


The Cagliotti equation describes how peak width varies with 2θ

$$H_k = \left(U \tan^2 \theta + V \tan \theta + W \right)^{1/2}$$

- H_k is the Cagliotti function where U , V and W are refinable parameters
- HSP treats the Cagliotti equation as a convolution between instrument and sample broadening functions
- The change in U and W between an instrument profile standard (eg NIST 640c) and your sample can indicate the amount of nanocrystallite size and microstrain broadening

The systematic variation of peak width with 2theta

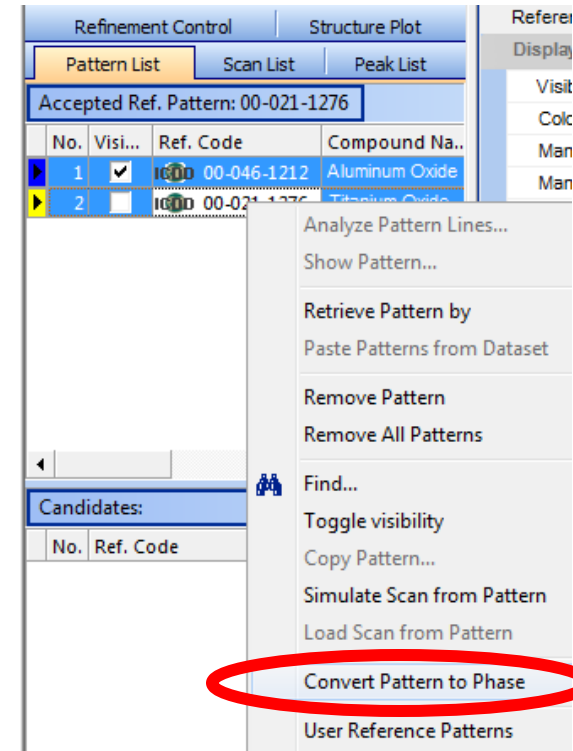


The Pawley Fit

- A unit cell is used to generate the initial peak list
 - The peak positions are adjusted by refining the unit cell lattice parameter rather than the individual peak positions
- Peak heights are individually refined.
- The peak width and shape are constrained with functions such as the Cagliotti equation, as described for the Constrained Peak Fitting

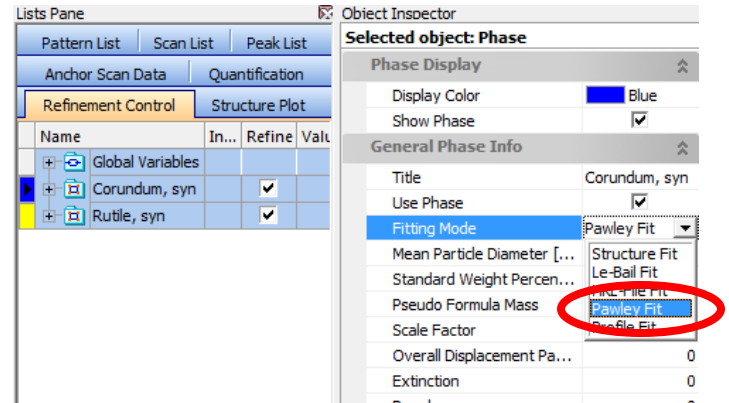
Steps for the Pawley Fit: Load the Reference Patterns

- First, manually fit the background as done previously
- Instead of a Peak Search
 - Retrieve the reference cards for the phase(s) in your sample
 - You may also manually input the unit cell from the menu *Analysis > Rietveld > Enter New Structure*
 - Go to the Pattern List tab in the **Lists Pane**
 - Select the references for your mixture and right-click on the phase(s) that you want to refine
 - Select “*Convert Pattern to Phase*” from the menu
 - The reference(s) that you converted are now listed in the Refinement Control tab of the **Lists Pane**



Steps for Pawley Fit: Set the Fitting Mode

- Go to the Refinement Control in the **Lists Pane**
- Each phase in your mixture should be listed
 - If not, repeat the steps on the previous slide for each phase that is missing



- Click on the name of the first phase in the Refinement Control list
- In the **Object Inspector**, find the entry for “Fitting Mode”
- Change the “Fitting Mode” to Pawley Fit using the drop-down menu
- Repeat for each phase in the Refinement Control List

Steps for Pawley Fit: Create Initial Peak List

- Make sure that you are zoomed out in the **Main Graphics View**
- Execute a Profile Fit using the built-in parameter set “Heights Only”
 - You can select this fitting mode from the menu *Treatment > Profile Fit > Fit Profile > Heights Only* or by using the Profile Fit toolbar
 - This will generate a peak list based on the unit cell(s) of the phase(s) that you loaded into the Refinement Control list
 - In case some peaks are created by the reference card that are not observed in your data, you may need to delete those peaks.

Steps for Pawley Fit: Refine the Profile Fit

- You may refine the profile fit by using the built-in Pawley Fit parameter set or by creating your own parameter set
- The parameter set should include:
 - Lattice parameters
 - Background functions
 - Peak Height
 - Caglioti W, V, and maybe U
 - Peak Shape 1, possibly Peak shape 2
 - Zero Shift OR Specimen Displacement
 - Asymmetry Parameters*
 - In order to refine asymmetry parameters, you must set the Asymmetry Type to “Finger, Cox, Jephcoat”
 - The Asymmetry Type is accessed in the Object Inspector: Global Settings, just like the Split Width and Split Shape options.

| Possible Refine Steps | Parameter Varied | Min. Shift/ESD | Use | Switch Off |
|-------------------------|------------------------|----------------|-------------------------------------|--------------------------|
| Peak Position | Lattice Parameters | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Peak Height | Flat Background | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Peak FWHM | More background | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Peak Shape | Peak Height | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Flat Background | Caglioti W | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| More Background | Caglioti V | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Zero Shift | Caglioti U | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Specimen Displacement | Zero Shift | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Lattice Parameters | Peak Shape Parameter 1 | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Ka2/Ka1 Intensity Ratio | Peak Shape Parameter 2 | 0.1 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| Caglioti W | | | | |
| Caglioti V | | | | |
| Caglioti U | | | | |
| Asymmetry Parameters | | | | |
| Peak Shape Parameter 1 | | | | |
| Peak Shape Parameter 2 | | | | |
| Peak Shape Parameter 3 | | | | |

Buttons: Move Up, Move Down, Delete Row, Ref

Select Parameter Set: Pawley

Pawley Fit

- When the Pawley Fit is complete:
 - The unit cell lattice parameters for each phase will have been refined
 - The peak width and peak shape functions for each phase will have been individually refined.
 - These can be found in the Refinement Control List by expanding the entry for a Phase Name and then expanding the Unit Cell and/or Profile Variable entries
 - The Zero Shift or Specimen Displacement error will have been refined.
 - This can be found in the Refinement Control List by expanding the Global Variables entry
 - If you click on a phase name in the Refinement Control List, the peaks for that phase will be highlighted in the **Main Graphics** as long as the “Show Selected Phase Profile” option is enabled.
 - You can enable this option from the menu *View > Display Mode > Show Selected Phase Profile* or from the View toolbar

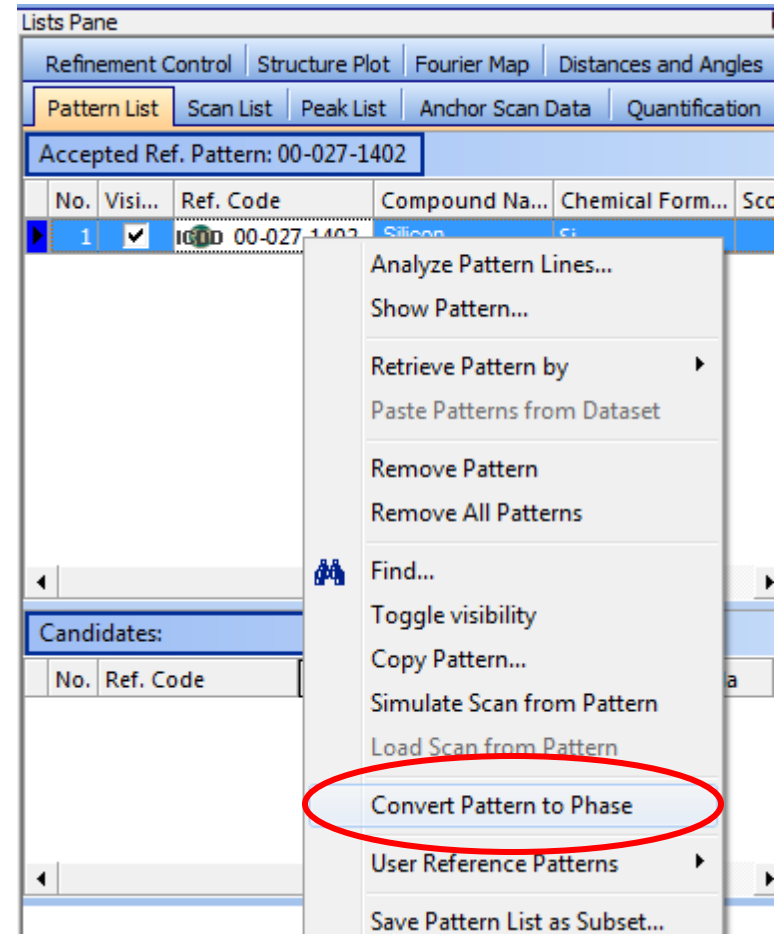
Calculations based on Peak List: Unit Cell Refinement Analysis

Most often you are refining the unit cell lattice parameters based on a known phase

- Most lattice parameter refinements are used to analyze modifications of known materials
 - For example, to quantify the change in the material when it is doped
- The beginning steps for this kind of analysis
 - Load the Reference Card for the Material
 - Profile Fit the data

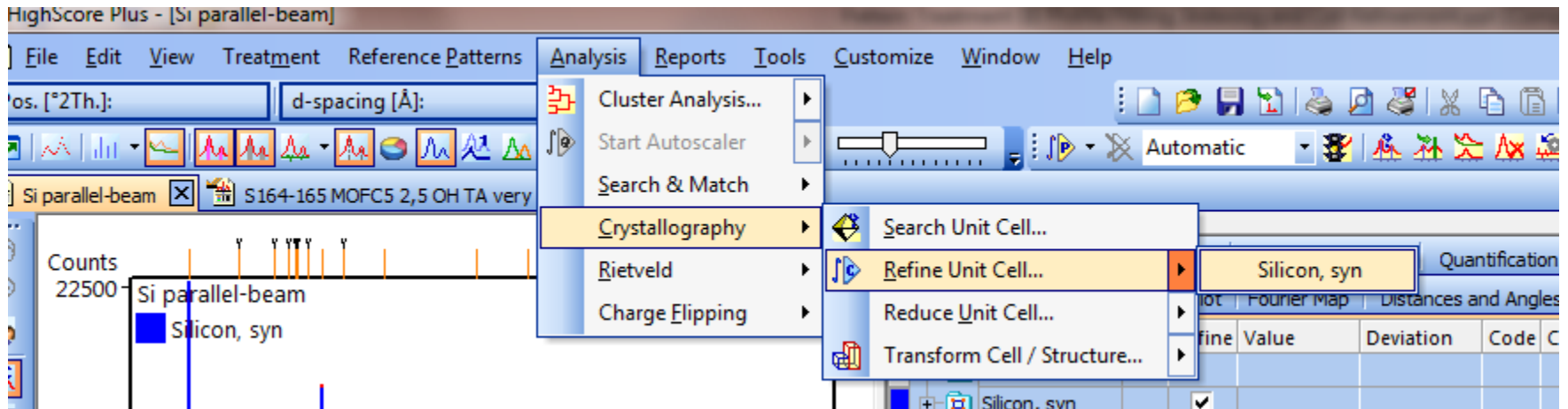
The reference card must be converted before you can use it as the starting basis for unit cell refinement

- After you have loaded the reference card(s), go to the Pattern List tab in the **Lists Pane**
- Right-click on the phase(s) that you want to refine
- Select “*Convert Pattern to Phase*” from the menu
- The reference(s) that you converted are now listed in the Refinement Control tab of the **Lists Pane**



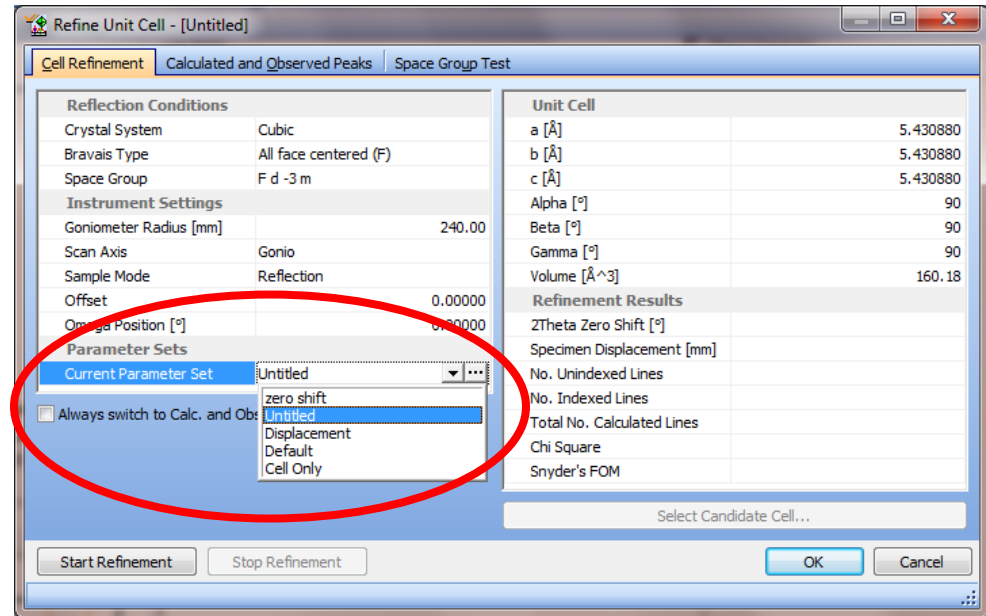
Now you can refine the unit cell lattice parameters

- Go to the menu *Analysis > Crystallography > Refine Unit Cell...*
- Select the entry for the phase that you want to refine first



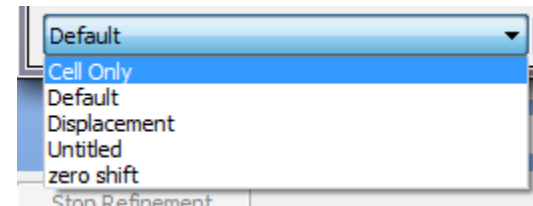
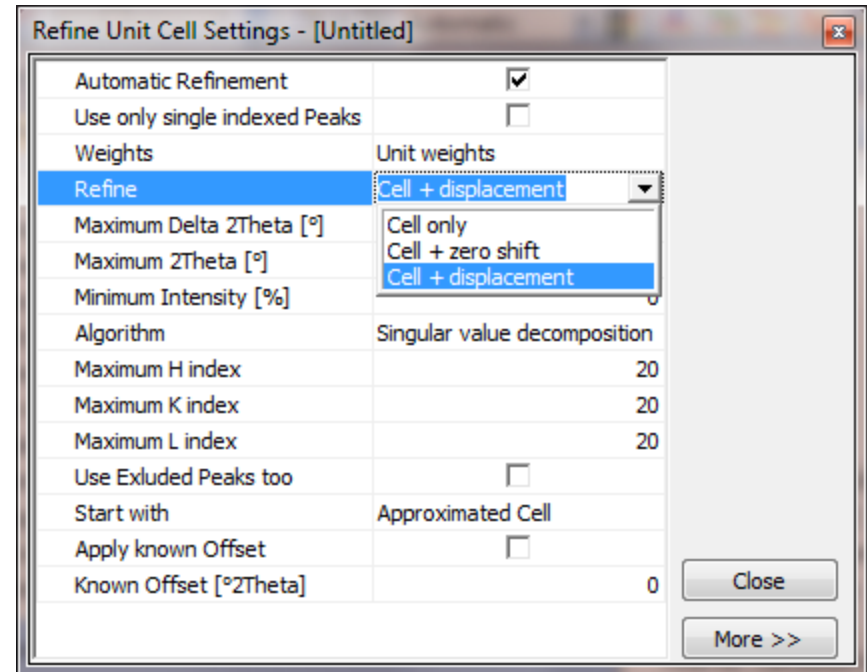
Modify the parameter set for the unit cell refinement

- The parameter set is not found by clicking on the “More” button, like it is in every other dialogue window
- Instead, the parameter set is at the end of the left column (circled in red)
- Select a saved parameter set or click on the “...” button to open the window to edit it



The most important parameter is the “Refine” entry

- In the *Refine Unit Cell Settings*, you can set the **Refine** entry to:
 - Cell only
 - Cell + zero shift
 - Cell + displacement
- This controls the parameters that will be refined
- Zero Shift and Displacement are two common sources of systematic error in the observed peak positions
- If not already created in your copy of HighScore Plus, it is useful to create three saved parameter sets for Cell only, Cell + Zero Shift, and Cell + Displacement



Zero Shift and Displacement are two common sources of systematic error in the observed peak positions

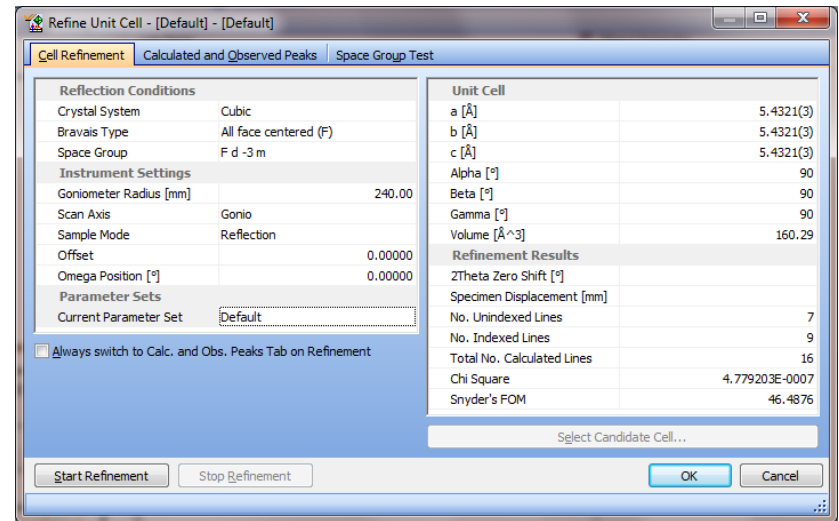
- Specimen Displacement is the most common and most significant source of error in modern diffractometers
 - Specimen displacement is created when the sample is not properly positioned on the focusing circle of the goniometer
 - Specimen displacement varies as $\cos \theta$, according to the equation:

$$\Delta 2\theta = \frac{-2s \cos \theta}{R}$$

- Zero shift is more common in older diffractometers that do not have optical encoders
 - Zero shift is produced when the detector arm of the goniometer is not properly aligned at zero
- Zero shift is better to use when refining data collected over a small angular range, even if the source of error is actual specimen displacement

Refine the Unit Cell using the Parameter set and evaluate the results

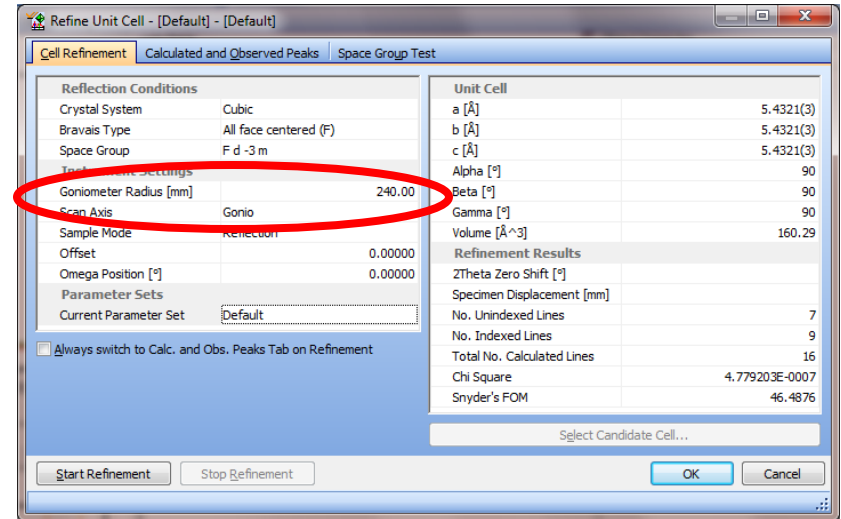
- In the Refine Unit Cell window, click the button “Start Refinement”
- The refined unit cell lattice parameters are shown in the right column



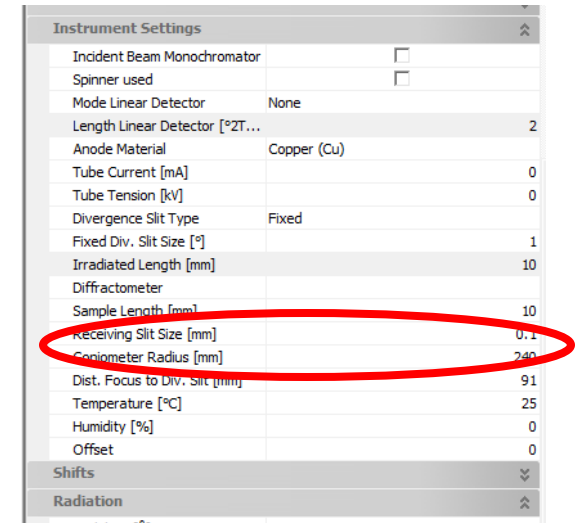
- The ESD shows how precise the refined lattice parameter is
 - The ESD is shown in ()
- A larger Snyder's FOM indicates a better fit.
 - The FOM should be >20 for publishable data
- The No. of Unindexed lines should be zero if the sample was a single phase

Make sure the goniometer radius is correct for displacement correction

- The Goniometer Radius is a part of the specimen displacement calculation
- If your data were not collected on a PANalytical instrument, then HighScore Plus may not know the correct radius of your instrument
 - All PANalytical *.xrdml files include the goniometer radius defined in the data file.

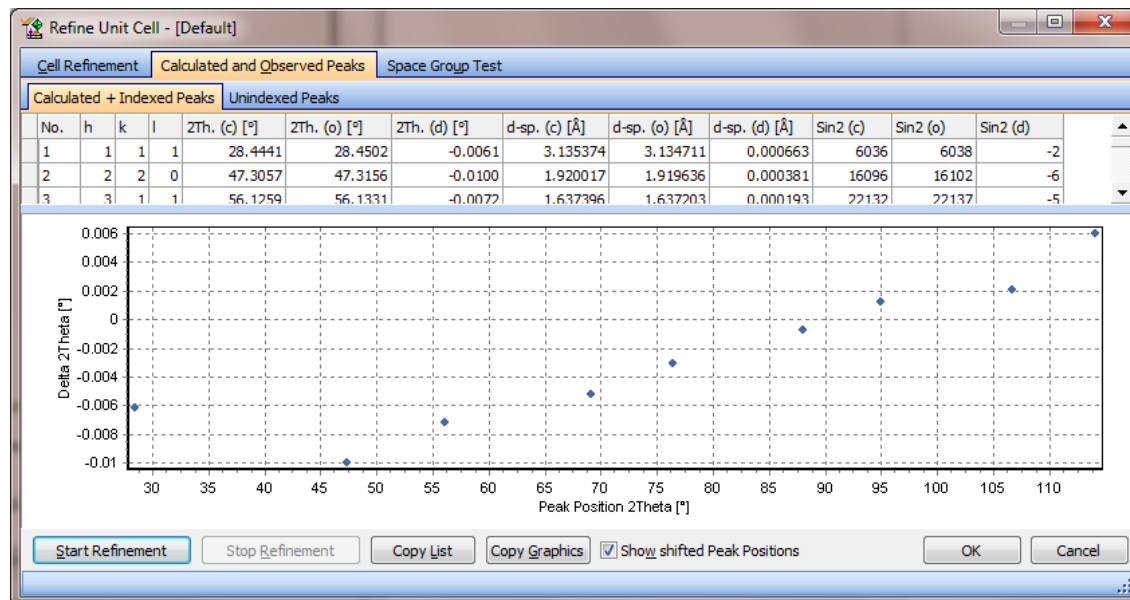


- To change an incorrect radius:
 - Exit the unit cell alignment window (click **Cancel**)
 - Open the Scan Parameters in the Object Inspector tab of the Lists Pane
 - An easy way to do this is to double-click on the scan name in the Scan List
 - Scroll down towards the bottom of the Scan information in the Object Inspector
 - Find the Goniometer Radius entry in the *Instrument Settings* section
 - Type in the correct **Goniometer Radius (mm)**.
 - Press **Enter** key to record the change.
 - Return to the unit cell refinement procedure.



The Delta 2Theta plot will reveal systematic errors in the refinement

- Click on the tab Calculated and Observed Peaks
- The table and plot shows the difference between the experimental peak positions and peak positions calculated based on the refined unit cell
- In a good refinement, **Delta 2Theta** in the plot will be randomly distributed around zero
- A systematic trend may reveal specimen displacement (delta 2theta varies with 2theta) or zero shift (constant delta 2Theta as a function of 2Theta) error



- Once the refinement is acceptable, click OK
- The indexed peaks in the peak list are now associated with new phase
 - The peak profiles can only be further refined with a Pawley fit or phase fit
 - The peaks associated with the phase will be color coded in the Peak List

Lists Pane

Refinement Control | Structure Plot | Fourier Map | Distances and Angles

Pattern List | Scan List | **Peak List** | Anchor Scan Data | Quantification

| No. | Pos. [°2Th.] | d-spacing ... | Height [c...] | FWHM Left ... | FWHM Rig... |
|-----|--------------|---------------|---------------|---------------|-------------|
| 1 | 26.680(1) | 3.33860 | 508(26) | 0.038(4) | |
| 3 | 28.45020(9) | 3.13471 | 55217(174) | 0.0826(4) | |
| 4 | 28.52239(9) | 3.13471 | 27608(174) | 0.0826(4) | |
| 5 | 47.3156(1) | 1.91964 | 37584(122) | 0.0777(4) | |
| 6 | 47.4404(1) | 1.91964 | 18792(122) | 0.0777(4) | |
| 7 | 56.1331(1) | 1.63720 | 19217(86) | 0.0824(5) | |
| 8 | 56.2850(1) | 1.63720 | 9609(86) | 0.0824(5) | |
| 9 | 69.1398(3) | 1.35757 | 4516(40) | 0.093(1) | |
| 10 | 69.3361(3) | 1.35757 | 2258(40) | 0.093(1) | |
| 11 | 76.3846(3) | 1.24583 | 6955(50) | 0.093(1) | |
| 12 | 76.6087(3) | 1.24583 | 3478(50) | 0.093(1) | |
| 13 | 88.0374(2) | 1.10851 | 8420(54) | 0.102(1) | |
| 14 | 88.3128(2) | 1.10851 | 4210(54) | 0.102(1) | |
| 15 | 94.9585(4) | 1.04514 | 4065(35) | 0.116(2) | |
| 16 | 95.2695(4) | 1.04514 | 2032(35) | 0.116(2) | |
| 17 | 106.7154(5) | 0.96002 | 2797(30) | 0.120(2) | |
| 18 | 107.0991(5) | 0.96002 | 1399(30) | 0.120(2) | |
| 19 | 114.0965(4) | 0.91797 | 4470(34) | 0.141(2) | |
| 20 | 114.5371(4) | 0.91797 | 2235(34) | 0.141(2) | |

- The refined cell parameters can be found in the entry for phase in the Refinement Control tab
- Click on the phase name in the Refinement Control tab to see additional information about the phase in the Object Inspector

The screenshot displays two windows from a software application. The left window, titled 'Lists Pane', shows the 'Refinement Control' tab. It contains a table with columns for Name, In..., Refine, Value, Deviation, and Code. The 'Silicon, syn' phase is selected, and its 'Refine' checkbox is checked. Below this, the 'Unit Cell' parameters are listed:

| Name | In... | Refine | Value | Deviation | Code |
|--------------------|-------|--------------------------|-----------|-----------|------|
| Scale fact... | | <input type="checkbox"/> | 0.000100 | 0.000000 | 0.00 |
| Preferred... | 0.... | <input type="checkbox"/> | 1.000000 | 0.000000 | 0.00 |
| B overall | | <input type="checkbox"/> | 0.000000 | 0.000000 | 0.00 |
| Extinction | | <input type="checkbox"/> | 0.000000 | 0.000000 | 0.00 |
| Flat Plate... | | <input type="checkbox"/> | 0.000000 | 0.000000 | 0.00 |
| Porosity | | <input type="checkbox"/> | 0.000000 | 0.000000 | 0.00 |
| Roughne... | | <input type="checkbox"/> | 0.000000 | 0.000000 | 0.00 |
| Unit Cell | | | | | |
| a [Å] | | <input type="checkbox"/> | 5.430628 | 0.000077 | 0.00 |
| b [Å] | | <input type="checkbox"/> | 5.430628 | 0.000077 | 0.00 |
| c [Å] | | <input type="checkbox"/> | 5.430628 | 0.000077 | 0.00 |
| alpha... | | <input type="checkbox"/> | 90.000000 | 0.000000 | 0.00 |
| beta [°] | | <input type="checkbox"/> | 90.000000 | 0.000000 | 0.00 |
| gam... | | <input type="checkbox"/> | 90.000000 | 0.000000 | 0.00 |
| Atomic c... | | | | | |
| Profile Va... | | | | | |

The right window, titled 'Object Inspector', shows the 'Selected object: Phase' for 'Silicon, syn'. It displays various parameters and settings, including:

- Display Color: Blue
- Show Phase:
- General Phase Info:
 - Title: Silicon, syn
 - Use Phase:
 - Fitting Mode: Structure Fit
 - Mean Particle Diameter [...]: -1
 - Standard Weight Percen...: -1
 - Pseudo Formula Mass: -1
 - Scale Factor: 0.0001
 - Overall Displacement Pa...: 0
 - Extinction: 0
 - Roughness: 0
 - Porosity: 0
 - Flat Plate Absorption Co...: 0
- Symmetry / Space Group
- Unit Cell:
 - a [Å]: 5.43063
 - b [Å]: 5.43063
 - c [Å]: 5.43063
 - alpha [°]: 90
 - beta [°]: 90
 - gamma [°]: 90
 - Volume [Å³]: 160.1585
 - Assumed Crystal System: Cubic
 - Crystal System: Cubic
 - Automatic Cell Constraints:
- Indexing
- Preferred Orientation
- Phase Profile:
 - Size Strain Analysis: None
 - Profile Fitting: