HighScore Plus for Crystallite Size Analysis

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- These instructions will assume that you are working with an external calibration standard
- These instructions will also teach you how to create template file

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Before determining crystallite size the instrument broadening must be corrected for

- Data must be collected from a standard using the same instrument and same configuration as will be used to collect data from the specimen
- The data should be opened in HighScore Plus and the peaks profile fit

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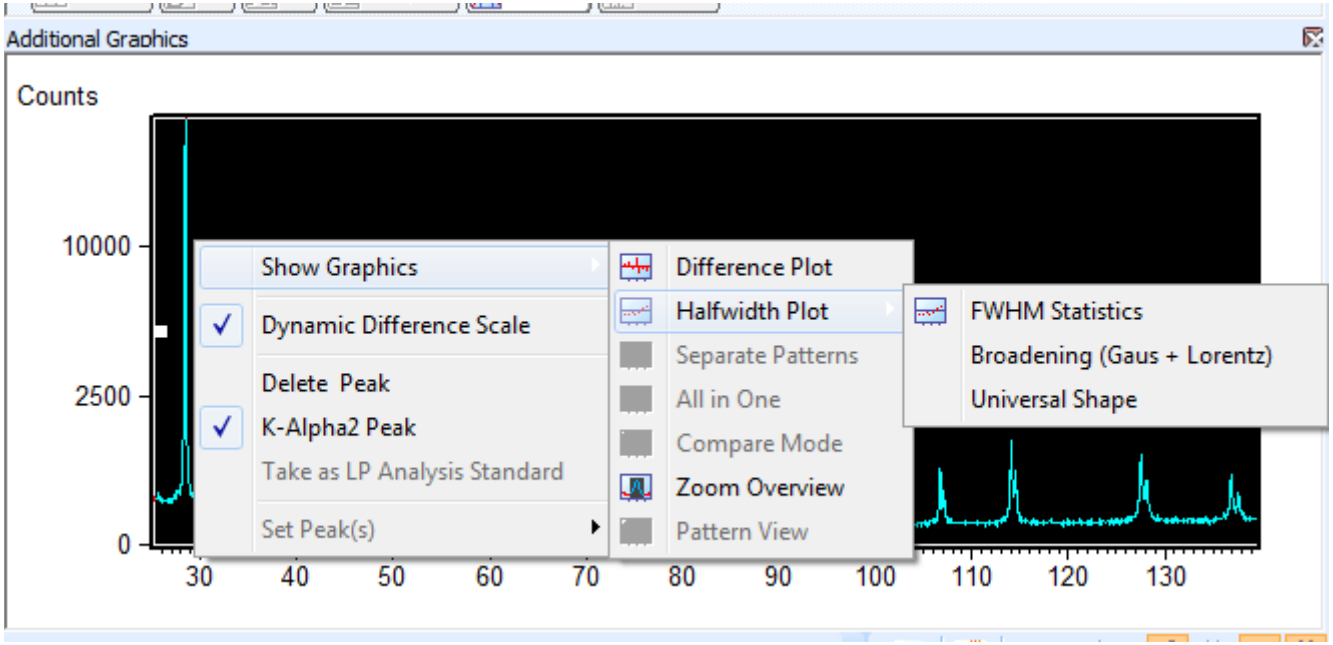
Creating the Instrument Profile Calibration Curve

- Right-click in the **Additional Graphics** pane
- From the menu, select *Show Graphics* > *Halfwidth Plot* > *FWHM Statistics*



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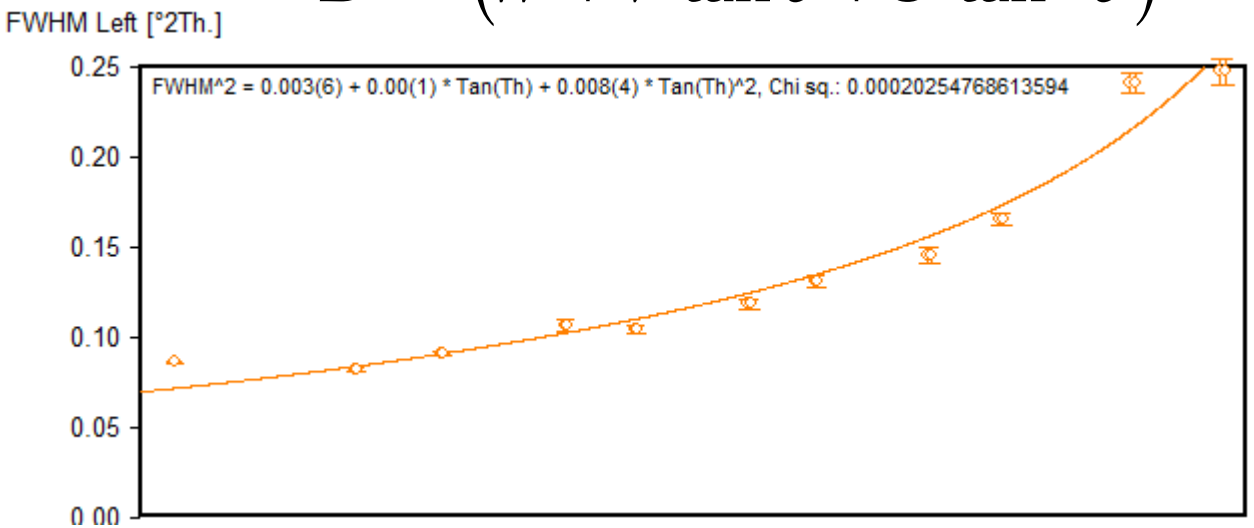
The FWHM Statistics plot will show the FWHM of the profile fit peaks and the best fit Caglioti curve

- Examine the curve fit to the FWHM data points
- Make sure that the Caglioti curve fits the FWHM plot
  - Closely examine any outliers
- The equation that is displayed is the Caglioti equation with parameters W, V, and U

$$B^2 = \left(W + V \tan\theta + U \tan^2\theta\right)$$



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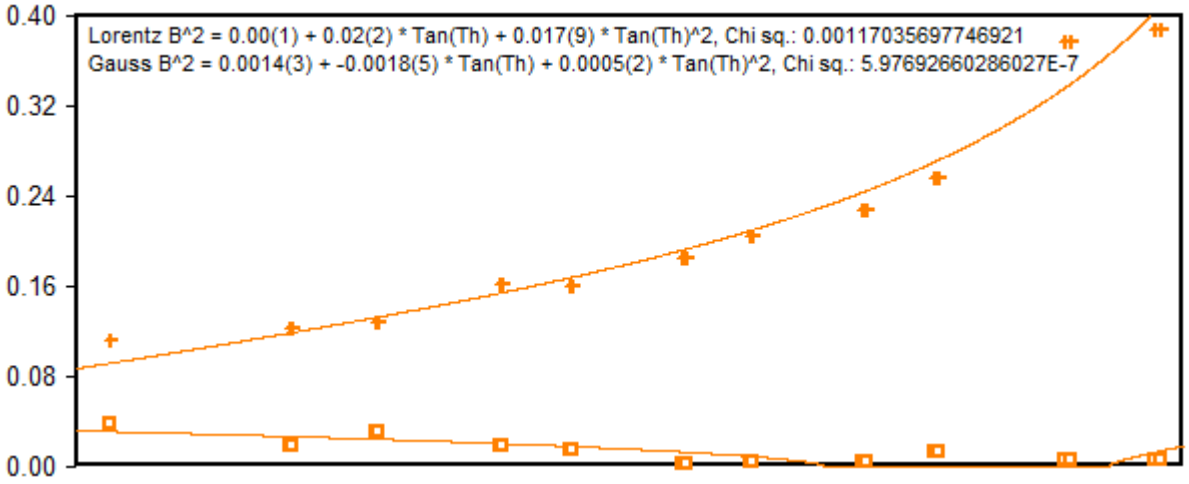
Creating the Instrument Profile Calibration Curve

- Right-click in the **Additional Graphics** pane
- From the menu, select *Show Graphics* > *Halfwidth Plot* > *Broadening (Gaus+Lorentz)*
- In this plot, the Gaussian and Lorentzian components of the peak profiles are plotted in individual Caglioti curves
  - This is the calibration curve required for proper line profile analysis
  - These Caglioti equations must be converted into an instrument profile
- Right-click in the Additional Graphics pane
- From the menu, select *Show Graphics* > *Take as LP Analysis Standard*



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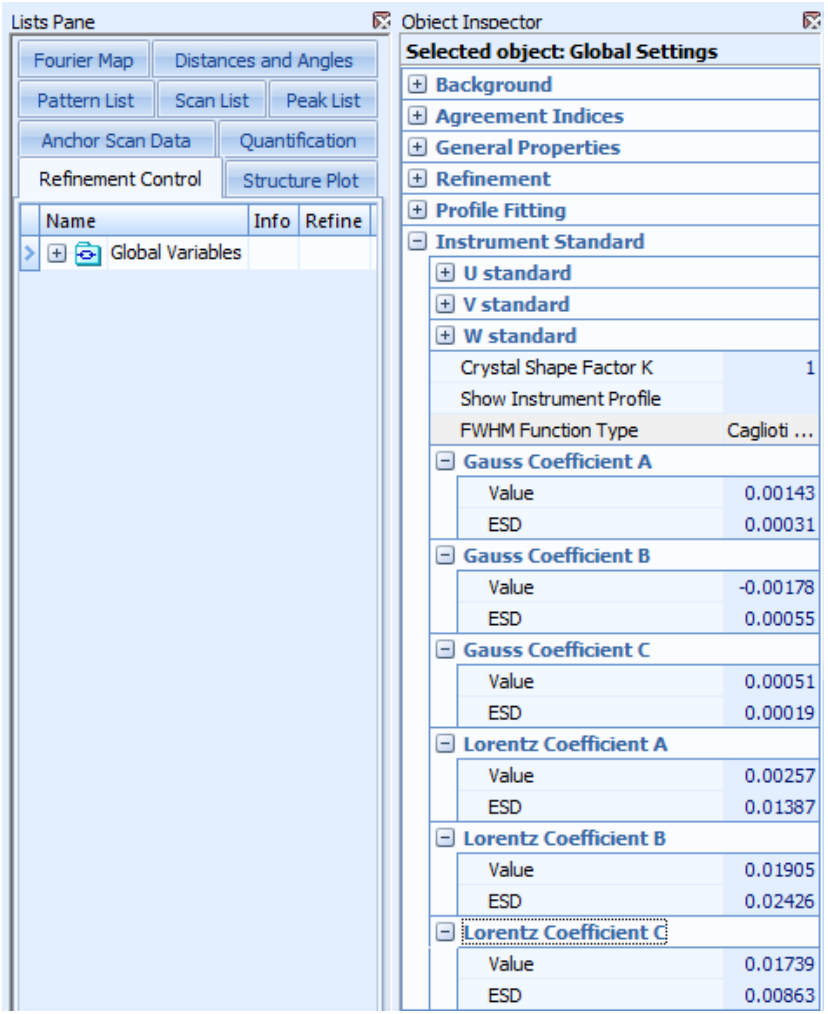
The Caglioti coefficients for the calibration curve can be seen in the Global Settings

- Select the Refinement Control tab in the *Lists Pane*
- Left-click on the phrase *Global Variables* in the Refinement Control pane
- Look in the *Object Inspector* pane for the Global Settings.
- The LP Standard coefficients are recorded in the "**Instrument Standard**" field as Gauss Coefficients and Lorentz Coefficients



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A template can be used as a starting point for multiple analyses of experimental data

- You could record the Gauss and Lorentz coefficients from the Instrument Standard field and them enter into every new document
  - If you are not sharing a computer and only use one instrument with one configuration, you could also save them as defaults in the menu *Customize > Defaults*

- In order to save work, you can also create a template file
  - A template file is an empty HPF document that contains several settings
  - We will create a document that contains the LP Standard coefficients determined by the analysis of the standard
  - A template can also contain
    - Reference patterns
    - Peaks in the peak list
    - Phases for refinement

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Creating a template

- After you create the instrument LP Analysis Standard
  - Go to the Peak List tab in the Lists Pane
    - Right-click in the Peak List and select the menu option *Delete* > *Included Peaks*
  - Go to the Refinement Control tab in the Lists Pane
    - Expand the entries Global Variables and Background
    - In every parameter within Background (Flat Background, Coefficient 1, etc), set the value to 0
  - Go to the Pattern List in the Lists Pane
    - Delete all reference patterns loaded in the Pattern List
    - If you are always analyzing the same phase(s), you could load the reference patterns for those phases and save them in the template
  - Go to the Scan List in the Lists Pane
    - Delete all experimental scans loaded in the Scan List
- Save the document in a *.HPF format with a clever name like "LP Analysis Template.hpf

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Begin analysis of the nanocrystalline material

- Open the template file if it is not already open
- Insert the data for the nanocrystalline sample by selecting the menu *File* > *Insert*

- Be sure that you do not save over your empty template. Before you go any further, you can save this file using the menu item *File* > *Save As* …

- Profile Fit the data from them nanocrystalline sample

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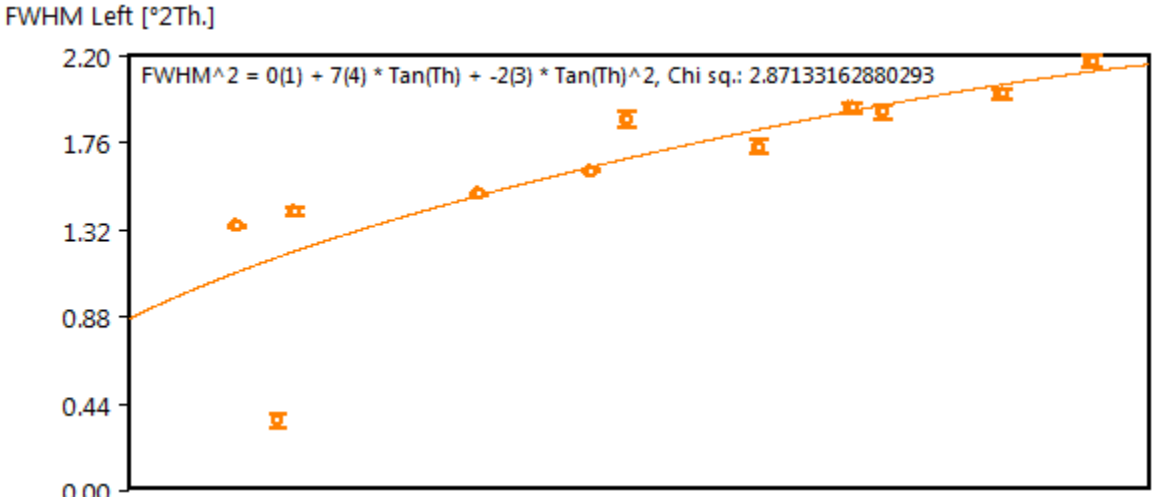
Examine the FWHM Plot for Outliers

- Right-click in the **Additional Graphics** pane
- From the menu, select *Show Graphics* > *Halfwidth Plot* > *FWHM Statistics*
- Examine the FWHM plot for outliers or anomolies
  - In the plot below, one peak does not conform to the general FWHM curve
  - If your sample contains a mixture of phases, you may observe a different FWHM line for each different phase



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Select what peaks you will use in the line profile analysis

- There are two ways to deal with a mixture of phases
  - You could use the ability to mark peaks as included/excluded
  - You could associate all peaks with a specific phase and then analyze the peaks from one phase at a time

- These slides will first demonstrate how to include/exclude peaks

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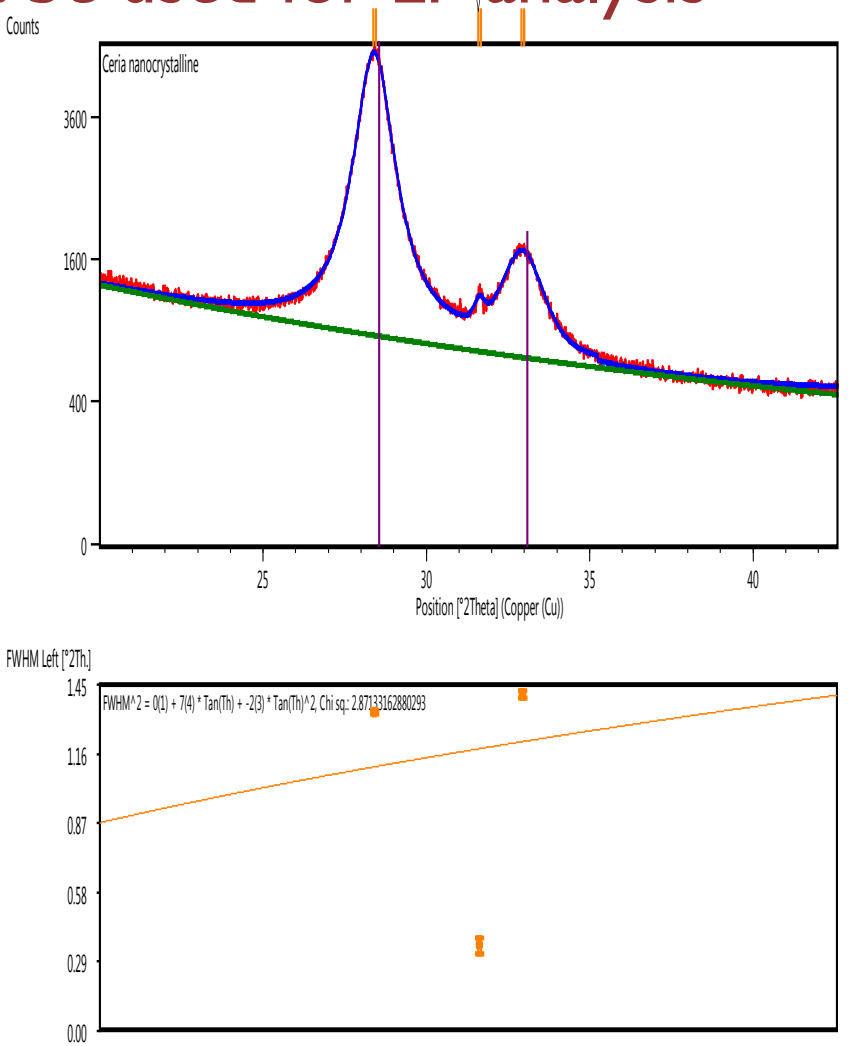
Examine the data, peak list, and FWHM plot and exclude peaks that should not be used for LP analysis

- In the data shown to the right, there is a small impurity phase
  - The peak from this phase is not indexed by the reference card lines (solid purple lines)
  - The peak from this phase is an outlier on the FWHM plot
- We want to exclude the peak(s) from the impurity phase



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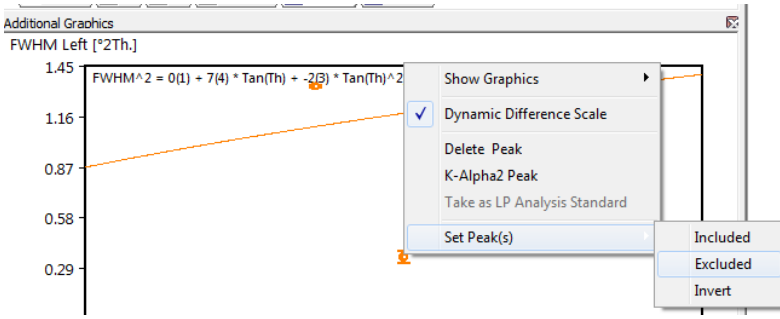
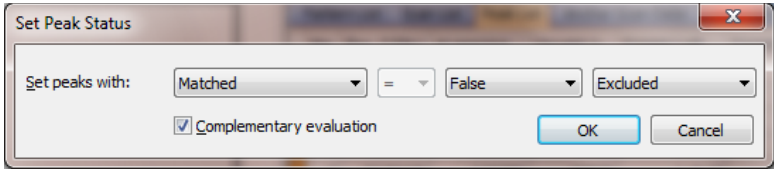
There are a few ways to exclude a peak

- Right-click on the data point for the peak in the FWHM plot
  - From the context sensitive menu, select *Set Peak(s) > Excluded*
- In the Peak List in the lists pane, right-click on the line for the peak
  - From the context sensitive menu, select *Set Peak(s) > Excluded*
- Go to the menu *Tools > Set Peak Status*
  - Build the filter to a setting such as "Set Peaks with: Matched=False to Excluded".
  - All peaks that are not matched by a reference pattern will be excluded
  - You could also exclude all matched peaks instead





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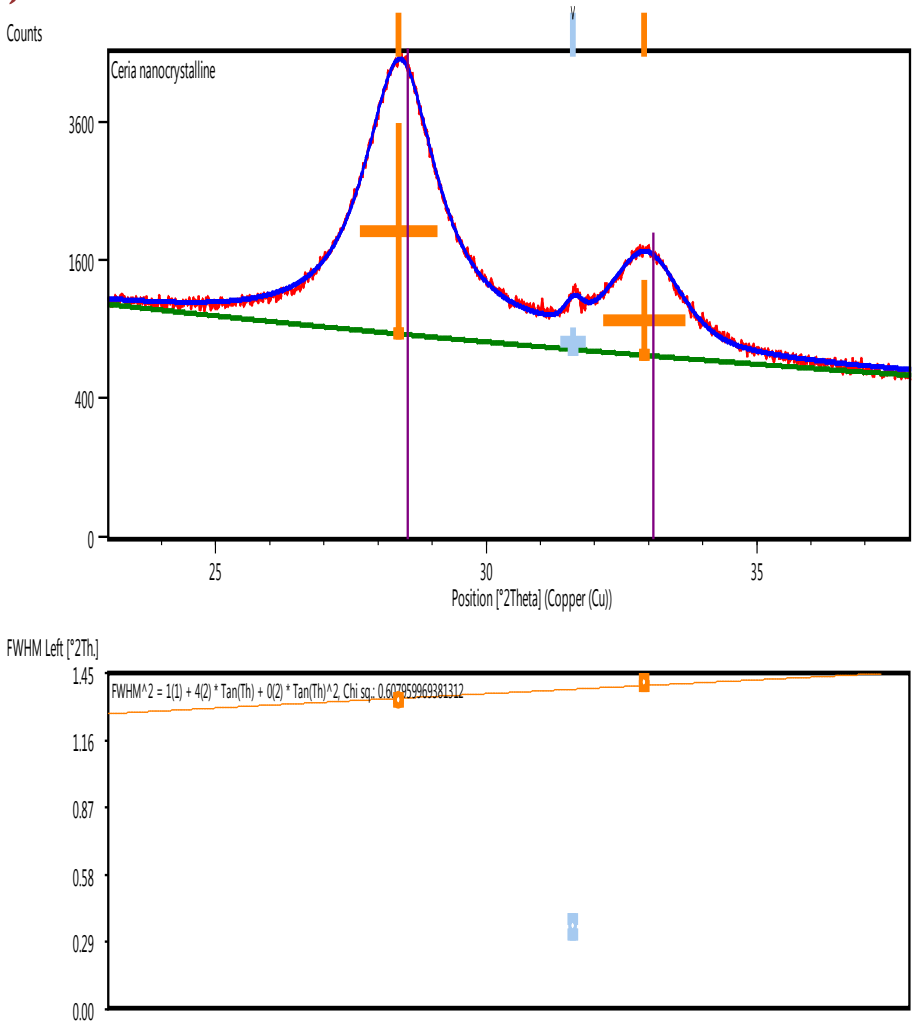
Excluded peaks are highlighted in light blue in the Peak List, the FWHM plot, and the line markers

- The advantage to excluding peaks, rather than deleting them, is that they can be included again if you need to use them for additional analyses (such as repeating the profile fitting)



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You can now use the Peak List to evaluate the crystallite size and microstrain of the sample

Lists Pane

Refinement Control	Structure Plot	Fourier Map	Distances and Angles

Pattern List	Scan List	Peak List	Anchor Scan Data	Quantification

[cts*2...	Backgr.[cts]	Status	Micro Strain [%]	Crystallite Size [Å]	Crystallite Size only [Å]	Micro Strain only [%]
5404.05	874.63	Incl...	0.691696	49.452670	46.818250	3.356183
59.19	745.59	Excl...	0.433694	583.995500	235.457000	0.600810
1213.92	699.10	Incl...	1.382057	73.996330	49.355590	2.754409
3100.59	371.36	Incl...	0.443137	46.329620	43.959820	2.185756
2531.87	284.58	Incl...	0.300946	42.874830	41.765840	1.960599
460.85	269.52	Incl...	0.933475	58.086350	40.186550	1.949222
335.60	248.07	Incl...	0.885946	104.746300	50.540080	1.342845
774.56	251.75	Incl...	0.869333	100.361700	47.679600	1.305896
526.88	254.08	Incl...	0.865021	122.644700	50.271940	1.206935
601.25	258.67	Incl...	0.787526	141.966800	52.519820	1.054280
586.62	247.39	Incl...	0.679052	95.901020	48.959880	1.065957

Object Inspector

Selected object: Peak(s)

Shape Right	0
Integral Breadth [°2Th.]	2.0343
Area [cts*°2Th.]	5404.05
d-spacing	3.14261
Sine^2 Theta	0.06008
Relative Intensity [%]	100
Background [cts]	874.6316
FWHM Asymmetry Ratio	0
FWHM Asymmetry [%]	0
Shape Asymmetry Ratio	0
Shape Asymmetry [%]	0
Significance	63.32574
Tip Width	1.60134
Line Profile Analysis	
Obs. Lorentz B [°2Th.]	1.91548
Obs. Gauss B [°2Th.]	0.40347
Obs. B [°2Th.]	2.0343
Instr. Lorentz B [°2Th.]	0.07438
Instr. Gauss B [°2Th.]	0.04638
Instr. B [°2Th.]	0.10298
Struct. Lorentz B [°2Th.]	1.8411
Struct. Gauss B [°2Th.]	0.40079
Struct. B [°2Th.]	1.9447
Universal Shape	0.65597
Micro Strain [%]	0.6917
Micro Strain only [%]	3.35618
Crystallite Size [Å]	49.45267
Crystallite Size only [Å]	46.81825

- There are four columns with crystallite size and microstrain information available in the Peak List
- Additional information is shown in the Object Inspector for each individual peak in the Line Profile Analysis area
  - This information can be viewed by left-clicking on a peak in the Peak List and then looking at the Object Inspector

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Different calculations reported in the peak list use different values of the peak breadth

- In the Object Inspector, you can see peak information for the peak breadth "B"
  - HighScore Plus uses breadth instead of FWHM for LP analysis
- Calculations use the Structural Breadth
  - Obs B is the breadth of the experimental diffraction peak for the sample being analyzed
  - Inst B is the breadth calculated from the LP Analysis Standard created when the calibration data was used to analyze the instrument profile
  - Struct B is the peak broadening due to the sample
    - Struct B= Obs B – Inst B
- The Breadth is reported as three components
  - B is the overall breadth of the entire peak
  - Lorentz B is the breadth of the Lorentzian component of the peak
  - Gauss B is the breadth of the Gaussian component of the peak

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The difference between "Crystallite Size" vs "Crystallite Size Only' (and "Microstrain" vs "Microstrain Only")

- The values Crystallite Size Only and Microstrain Only are determined using the Struct B, ie the overall breadth of the entire diffraction peak
  - Crystallite Size Only is calculated assuming there is no Microstrain broadening
    - This is the classis application of the Scherrer equation
  - Microstrain Only is calculated assuming there is no crystallite size broadening

- The values "Crystallite Size" and "Microstrain" are calculated using a less conventional shape deconvolution
  - The assumption is that all Crystallite Size broadening has as Lorentzian shape and that all Microstrain broadening has a Gaussian shape
  - Therefore, it is assumed that
    - "Struct Lorentz B" quantifies the peak broadening due to crystallite size and can be used in the Scherrer equation to determine the crystallite size
    - "Struct Gauss B" quantifies the peak broadening due to microstrain
  - This analysis might be valid if there is low dislocation density in the sample
    - Dislocations area type of Microstrain broadening that have a Lorentzian shape profile

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The values for Crystallite Size and Microstrain in the Peak List are calculated based on individual peaks

Pattern List | Scan List | Peak List | Anchor Scan Data | Quantification | Refinement Control | Structure Plo

No.	Pos. [°2Th.]	Crystallite Size only [Å]	Micro Strain only [%]	Crystallite Size [Å]	Micro Strain [%]
1	28.377(2)	46.818250	3.356183	49.452670	0.691696
2	32.916(5)	49.355590	2.754409	73.996330	1.382057
3	47.261(2)	43.959820	2.185756	46.329620	0.443137
4	56.114(3)	41.765840	1.960599	42.874830	0.300946
5	58.90(1)	40.186550	1.949222	58.086350	0.933475
6	69.15(1)	50.540080	1.342845	104.746300	0.885946
7	76.42(1)	47.679600	1.305896	100.361700	0.869333
8	78.81(1)	50.271940	1.206935	122.644700	0.865021
9	88.148(8)	52.519820	1.054280	141.966800	0.787526
10	95.121(9)	48.959880	1.065957	95.901020	0.679052

- To determine if the assumption of Crystallite Size Only (ie no microstrain) or Microstrain Only (ie no crystallite size broadening) are true, evaluate how they change with the 2Theta position of the peak
  - In the example above, the value Crystallite Size Only does not change systematically with 2Theta.
  - The value Microstrain Only does change systematically with 2Tehta
  - This means that the assumption that there is no Microstrain is more likely to be correct

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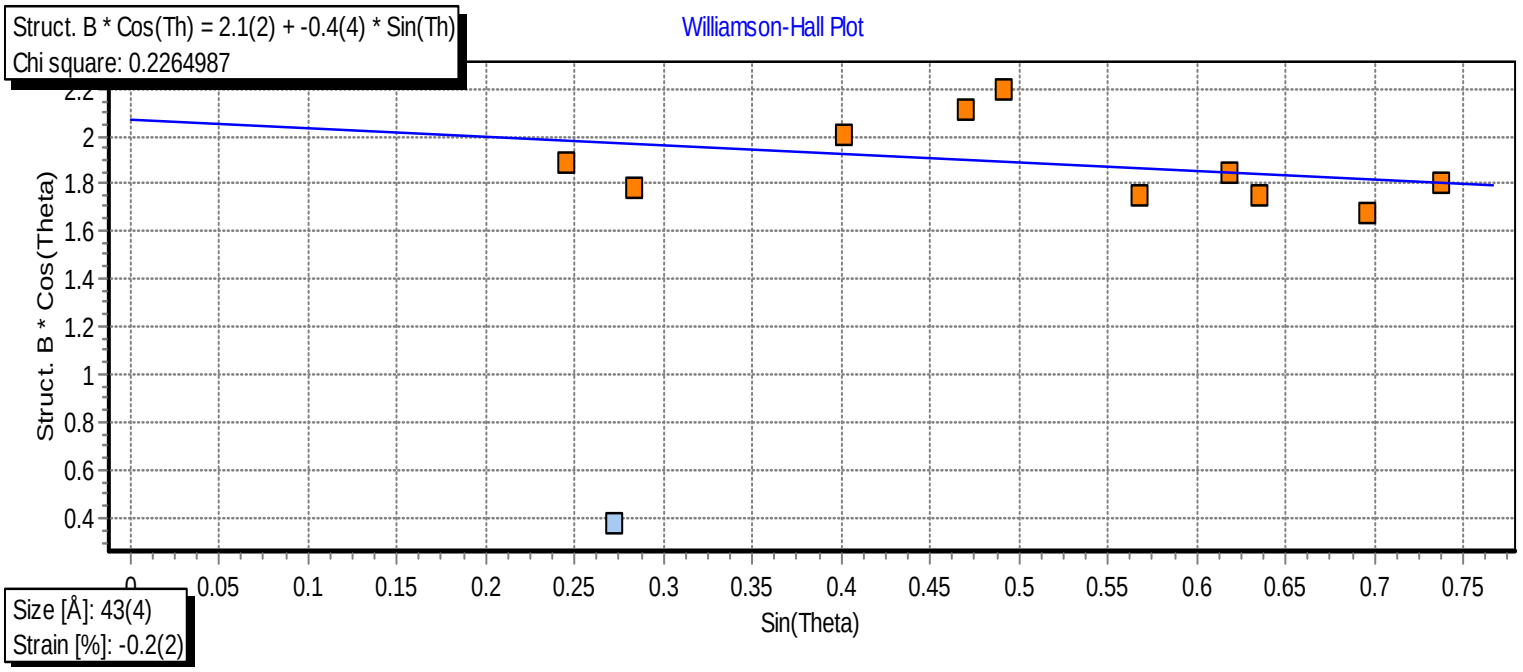
A more accurate evaluation can be determined by using all peaks for the calculation in a Williamson-Hall plot

- The Williamson-Hall plot is shown below the Peak List
- It shows how well the data fit equation



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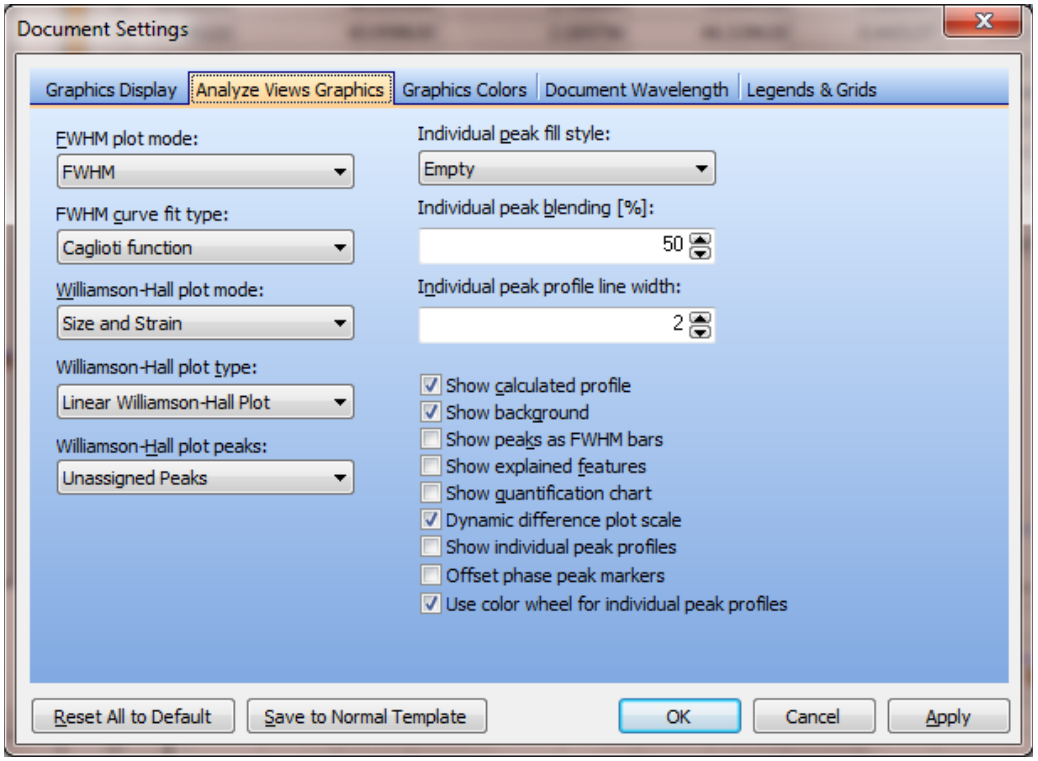
Settings in Customize > Document Settings



- In this dialogue, you can explore different ways to apply Line Profile Analysis to your data.

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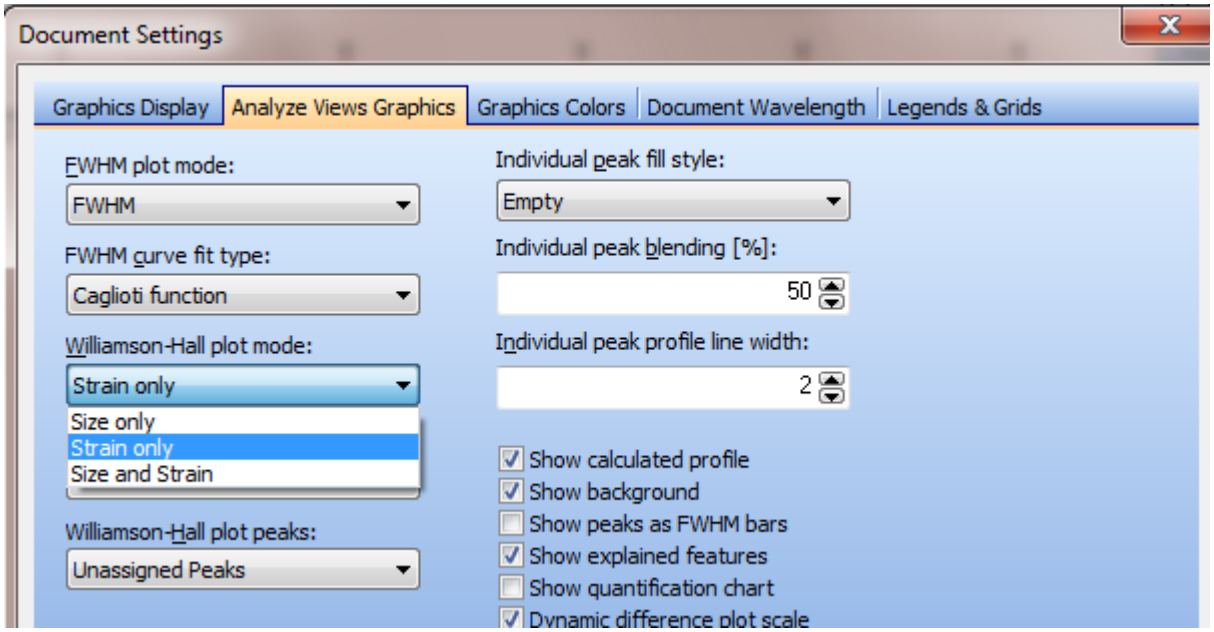
Analyze the Williamson-Hall Plot with Different Assumptions

- You can test your data assuming there is only microstrain broadening or only crystallite size broadening



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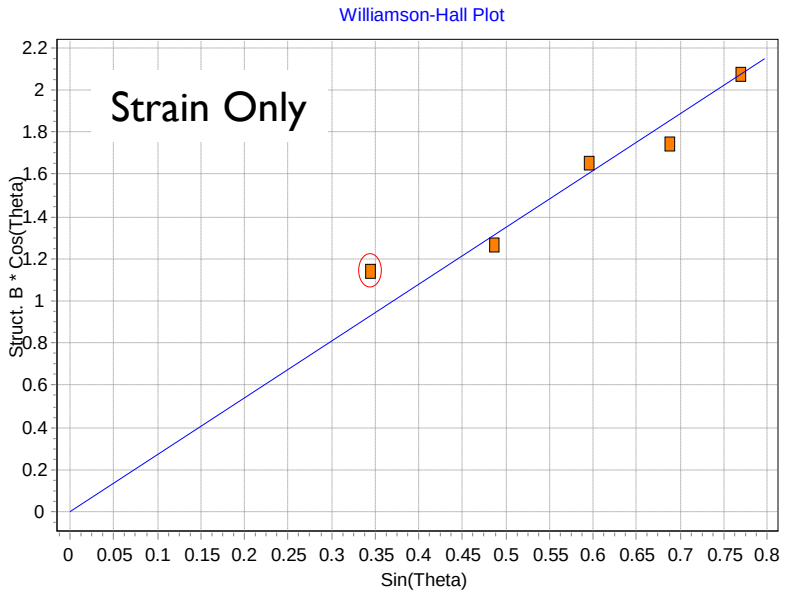
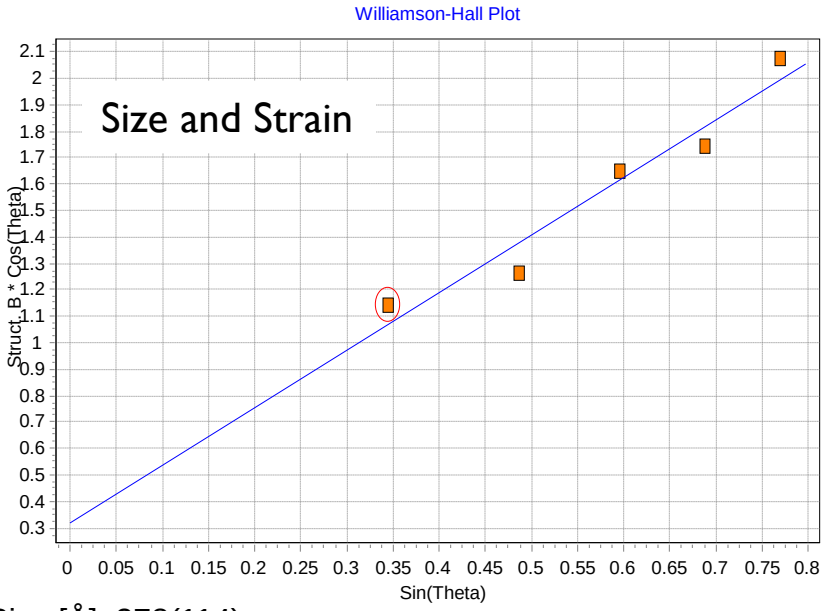
If assuming that there is no crystallite size broadening does not decrease the residual of the linear fit compared to fitting both size and strain, then the amount of crystallite size broadening is insignificant



Strain [%]: 1.18(5)

Chi square: 0.062



Size [Å]: 278(114)

Strain [%]: 1.00(2)

Chi square: 0.058

This does not necessarily mean that there is no crystallite size broadening, just that it cannot be quantified because it is overwhelmed by the amount of microstrain broadening

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