Introduction to TOPAS
Part 1
Profile fitting, Lattice parameter Refinements, Indexing

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Outline:
Part 1

TOPAS Interface

Profile fitting

- Fitting with analytical functions
- Convolution based approaches and Fundamental Parameters
- Determining Degree of crystallinity with Peaks phases
- Whole Powder Pattern Decompostion

Indexing

- LP and LSI Indexing of powder pattern

The applications in part I can all be performed with the TOPAS P variant.

Documentation:

TOPAS Tutorial

TOPAS User manual

TOPAS Reference Manual

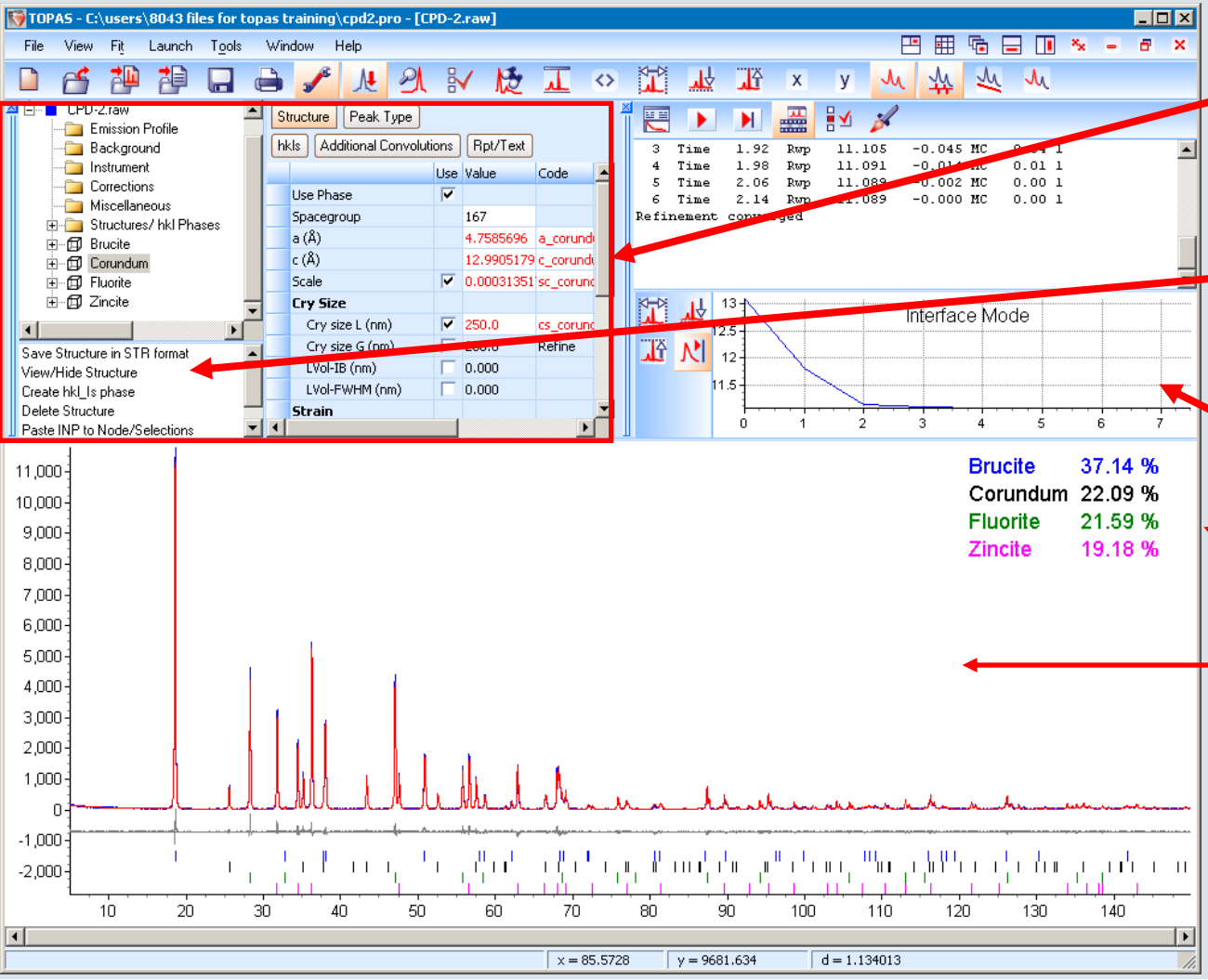
Tutorial example files

TOPAS Interface:
GUI and Launch mode

- TOPAS has a graphical user-interface (GUI) and a text based mode
  - GUI supports most Profile fitting and Rietveld applications
  - Beginners should use this mode of operation
  - Refinement results get stored in .pro project file.

- LAUNCH MODE
  - More features for advanced users but text based
  - For structure solution
  - For automation or batch operation
  - Results and parameter input through .inp input files
  - By default GUI mode is active, Launch mode is activated by setting an in inp file (Launch→ set input file)

TOPAS GUI: User Interface



Parameter window with instrument and structure information

The options in this window is also available in the context menu (right mouse click)

Fit window

wt.% for each phase

Scan window

Measured curve
Calculated curve
Difference curve

TOPAS GUI:
Parameter Window

Parameter values

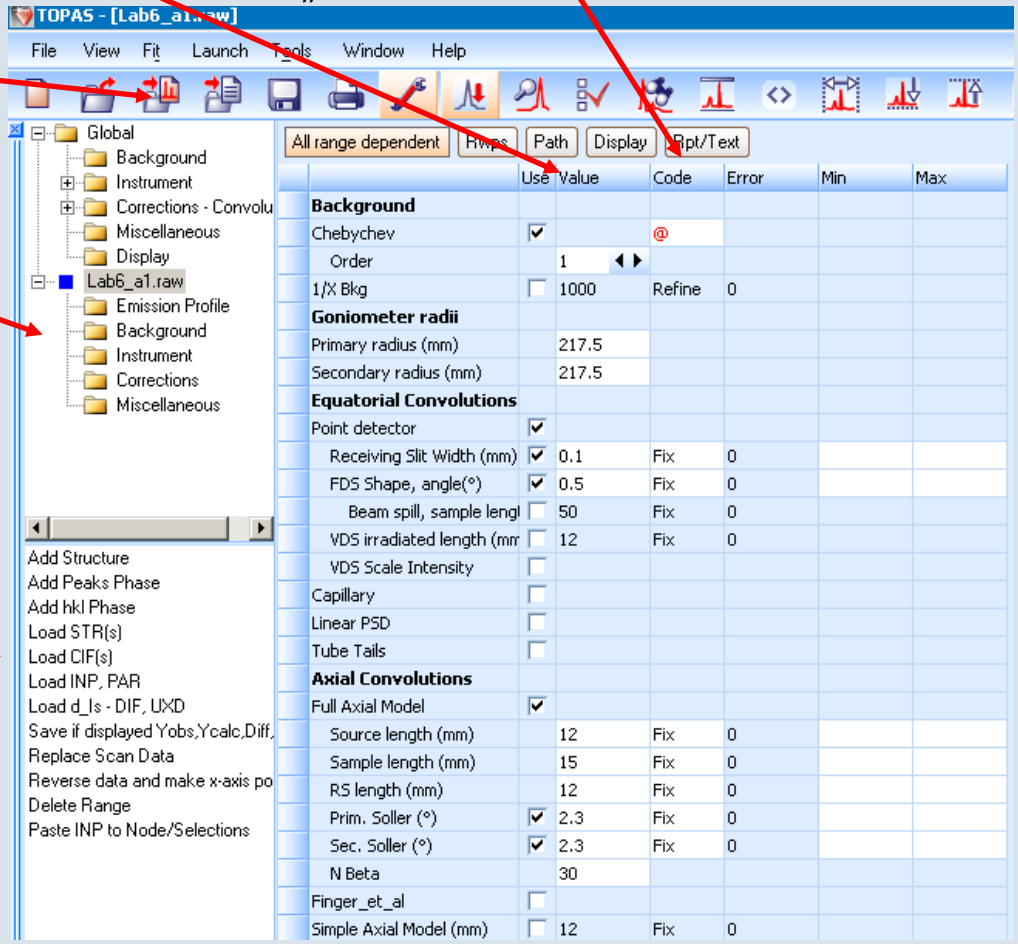
Toggle any parameter between Fix and Refine in „Code" column

Import raw data files

Data files will be displayed in treeview.

Instrument settings have to be entered, if Fundamental Parameters (peak type FP) is used

Add a peak phase (for profile fitting), an hkl-phase (for lattice parameter refinements) or load a structure (for quantitatve Rietveld refinements)



TOPAS GUI:
Fit window

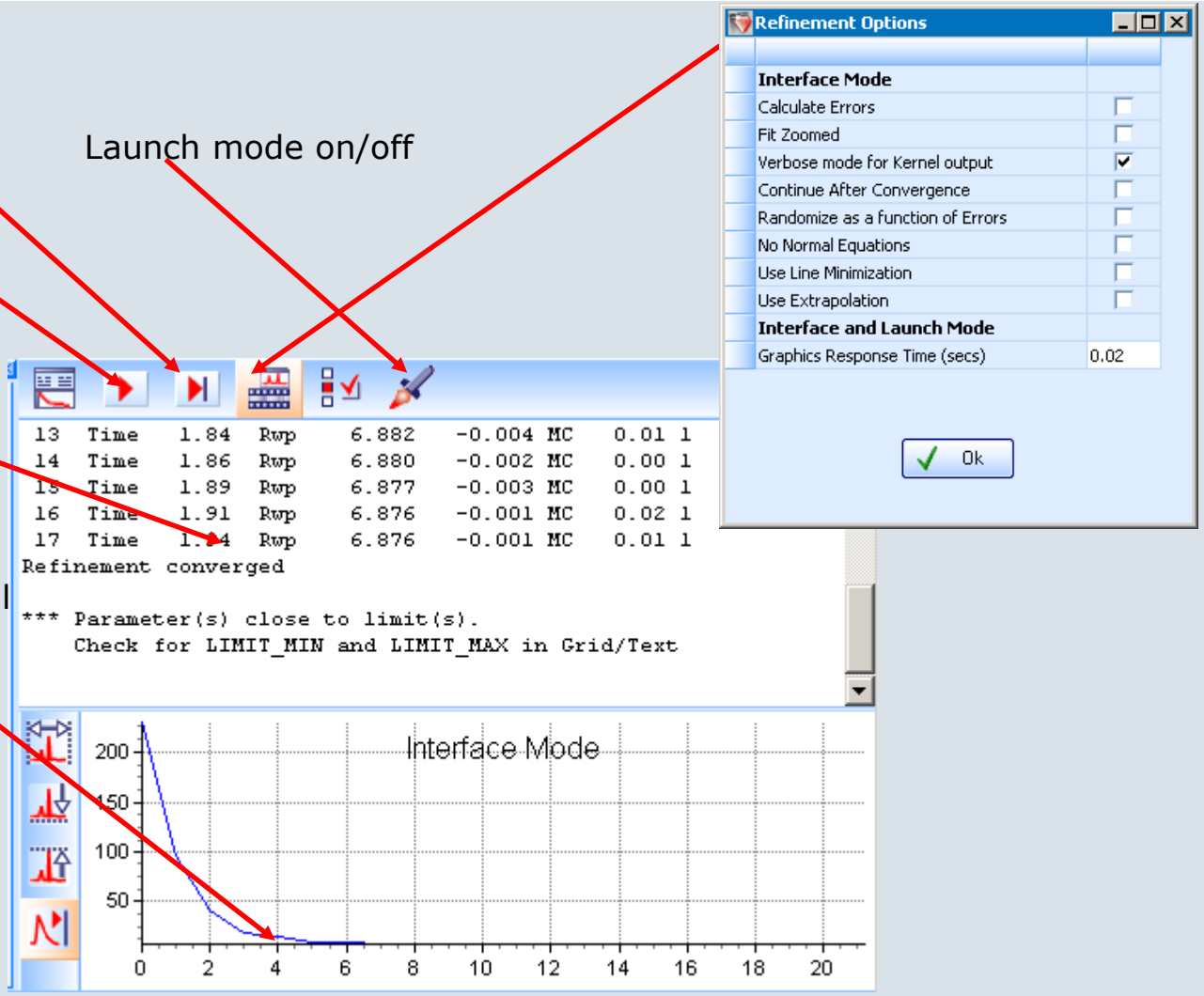
Start Refinement (Step by step)

Launch mode on/off

Refinement until convergence

Residual of the Refinement at every refinement step

graphical output of the residual as a functions of interation number



Profile Fitting Methods

Analytical Profile Fitting

- Empirical description of observed line profile shapes though analytical functions such as Lorentian, Gaussian or mixtures such as Pseudo Voight or Pearson VII functions

Function	Refinables	n_{max}
Gaussian	J, $2\theta_0$, B	3
Lorentian	J, $2\theta_0$, B	3
Pseudo Voigt	J, $2\theta_0$, B, η	4
Voigt	J, $2\theta_0$, B_G, B_L	4
Pearson VII	J, $2\theta_0$, B, m	4
Split pseudo-Voigt	J, $2\theta_0$, B+, B-, η+, η-	6
Split pseudo-Voigt, common shape factor	J, $2\theta_0$, B+, B-, η	5

Direct Convolution Approach

- Empirical description of observed line profile shapes, or
- Discrimination of instrument and sample contributions:
  Y(2q) = (W x G) x S, where I = (W x G)
  - ➔ Measured I : Conventional Approach
  - ➔ Calculated I : Fundamental Parameters Approach (FPA)

Deconvolution / Convolution Methods
Basic Principle

- Well known approach since at least Klug & Alexander, 1954

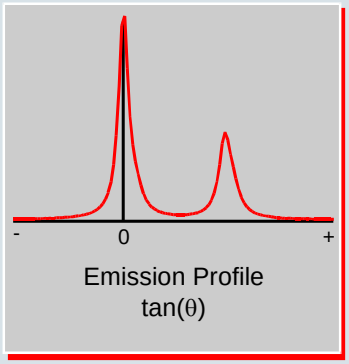
$$Y(2\theta) = (W \times G) \times S$$

W: Emission profile G: Instrument contribution

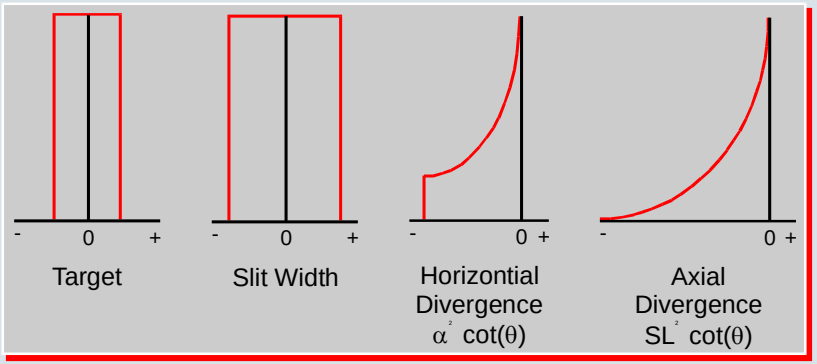
S: Sample contribution

- For the Bragg-Brentano geometry the instrument contribution can be calculated directly from the instrument parameters and slit settings. (Fundamental Parameters) These parameters are not refined and lead to a significant reduction in the number of refinable parameters
- For other geometries (like parallel beam) only the conventional approach can be used. In that case the parameters can be refined on a standard sample like LaB6 and the resulting parameters are fixed for the refinement of the sample.

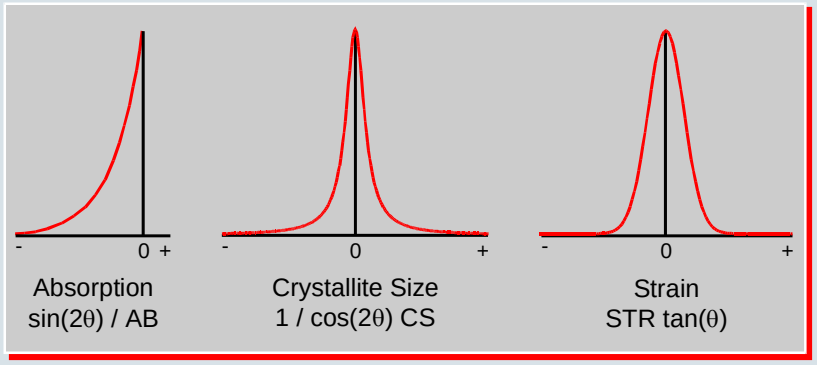
Convolution Synthesis of Line Profiles



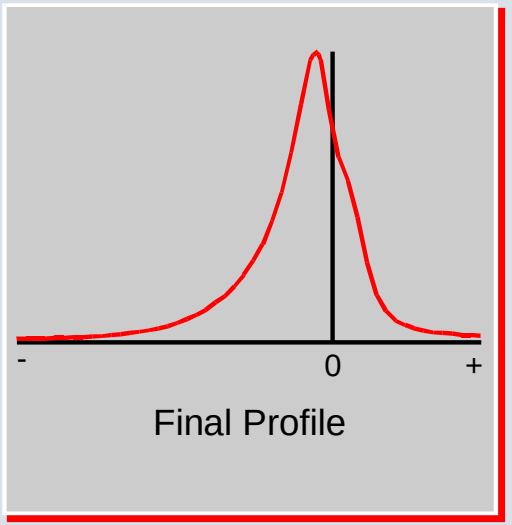
W



G



S



$$Y(2\theta) = (W \times G) \times S$$

Data collection
Bragg-Brentano Geometry

Instrument parameter notation in TOPAS:

RS: Receiving Slit (entered in mm)

FDS: Fixed Divergence Slit (entered in degrees)

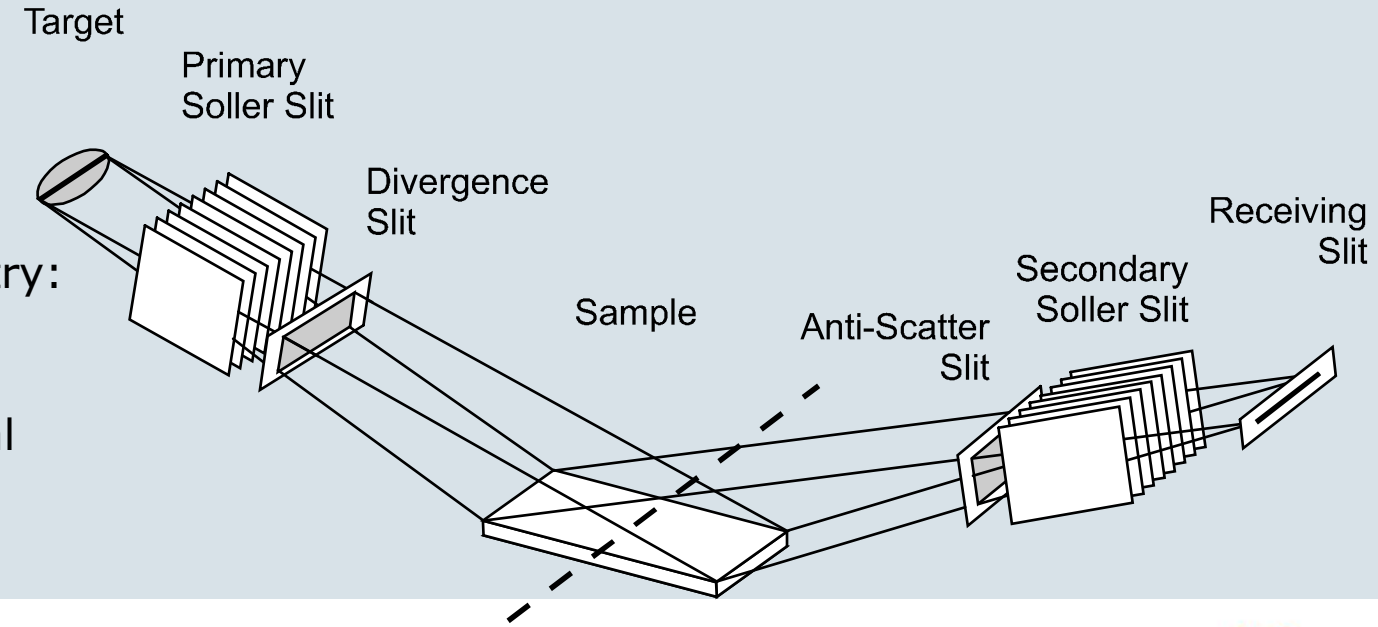
VDS Length: Variable Slit (mm correspond to beam width on sample)

Full Axial Model: enter primary and secondary Soller slit sizes here

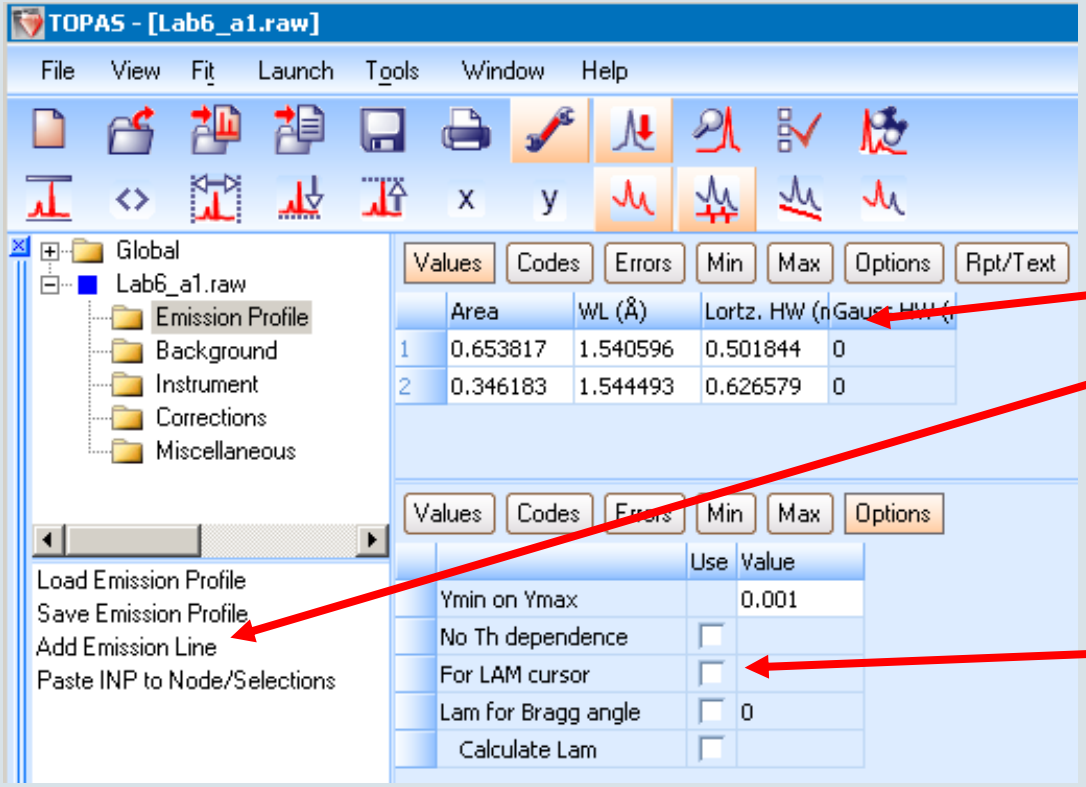
Tube tails: Default setings correspond to fine focus tubes and rarely need to be refined or changed

Parafocussing Geometry: Error because fo flat specimen

Errors because of axial and equatorial divergence



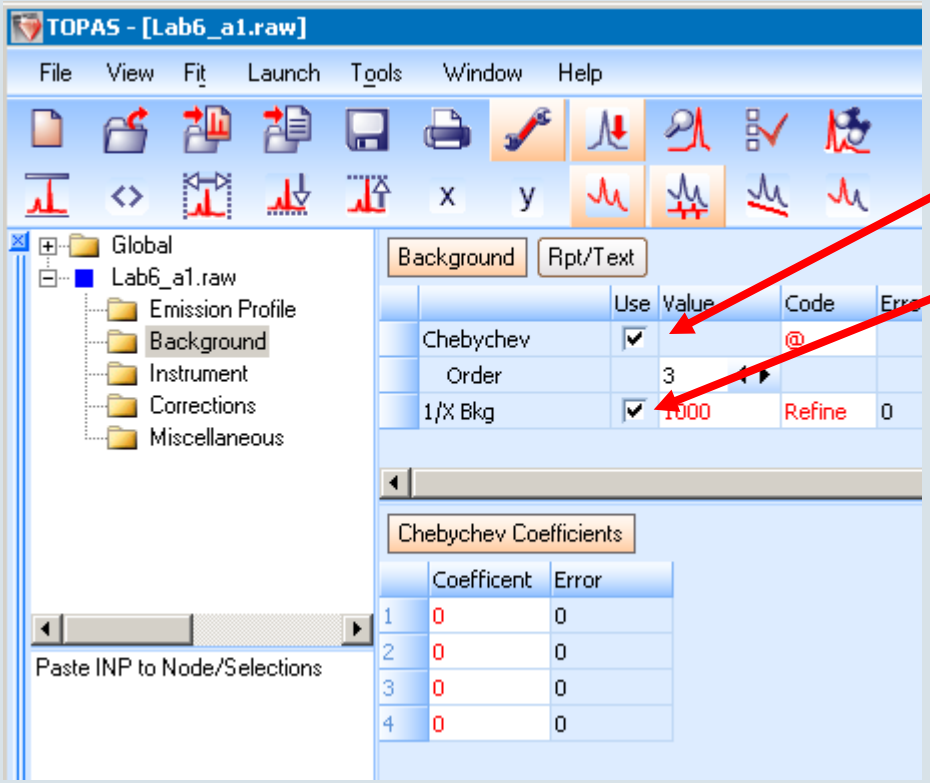
Choose an Emission Profile



- Predefined emission profiles for most common sealed tube systems and radiations are located in the directory c:\topas4\lam\
- The default profile Cuka2.lam has 2 lines, Cukα1 and Cukα2.
- If a residual of the kβ line is visible for measurements with Ni filter and very intense peaks, an emission line with 1.39222A can be added and its intensity be refined.
- For data with very sharp peaks the profile Cuka5.lam will give slightly better refinements.
- Check the „For LAM cursor" box to visualize the emission profile with the cursor

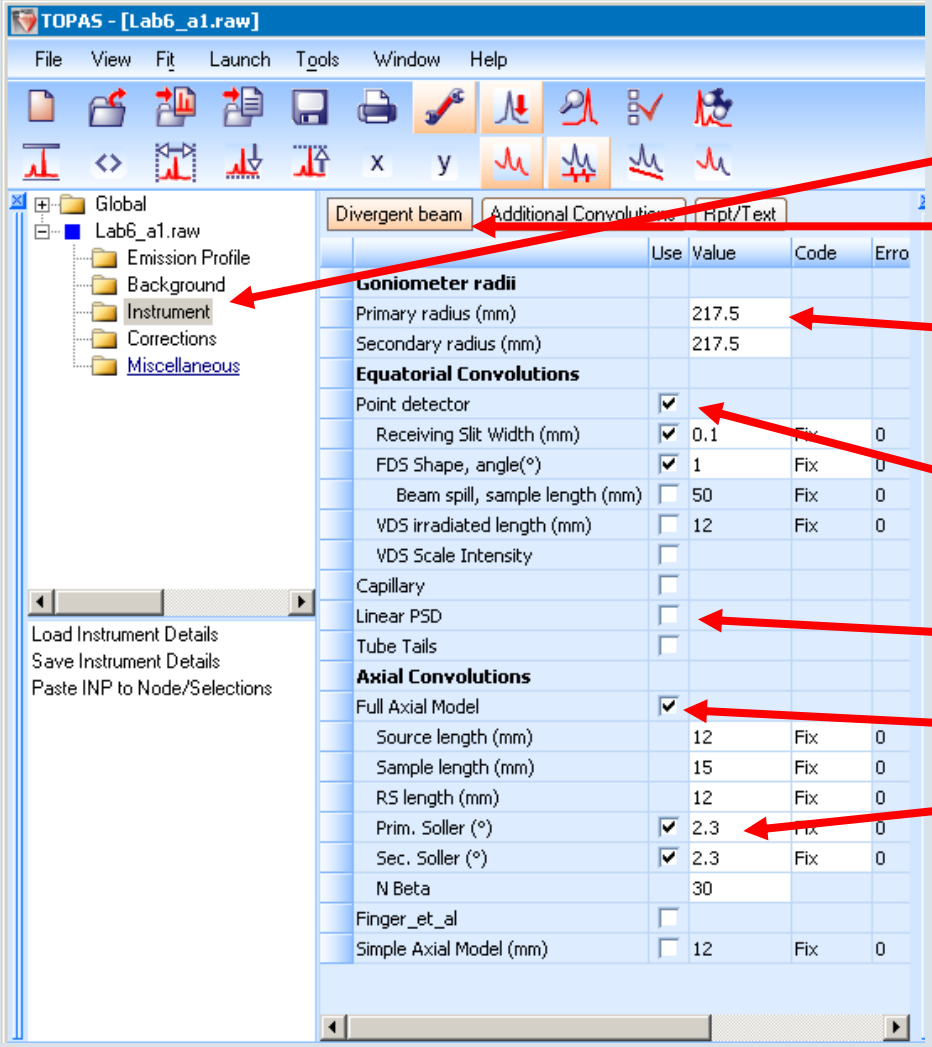
- For optics that may distort the wavelength spectrum (e.g. Goebel mirrors, Polycaps), the emission profile can be refined.

Modeling the background in TOPAS



- Most backgrounds can be fitted with a polynomial function (Chebychev Polynomial) and relatively few parameters
- The 1/x function is used to fit the rise the background at low angles caused by scatter from the direct beam
- Too few (<3) or too many parameters (>6) can be a source for serious errors, especially if broad peaks are present
- If an amorphous halo is present, it can often be fitted by entering a peak phase with a single peak

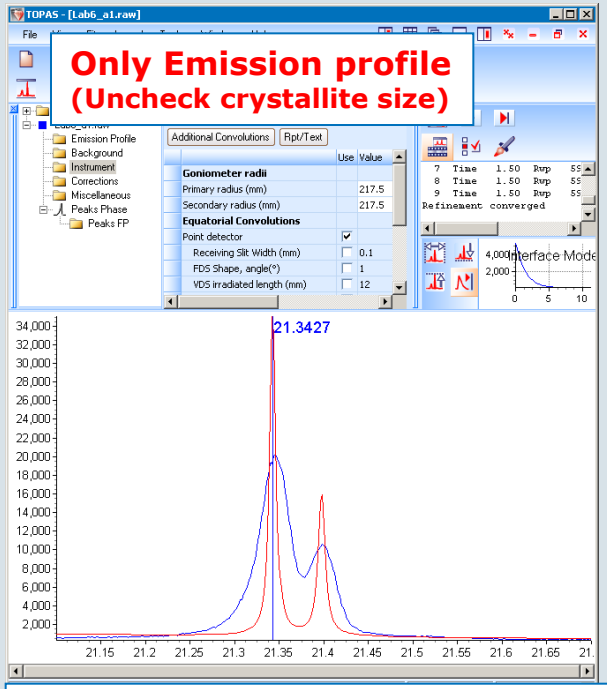
Entering instrument parameters in TOPAS

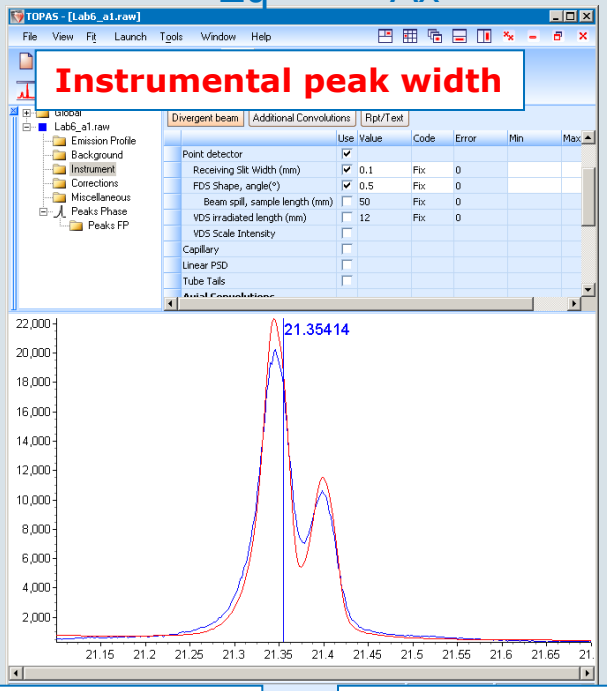


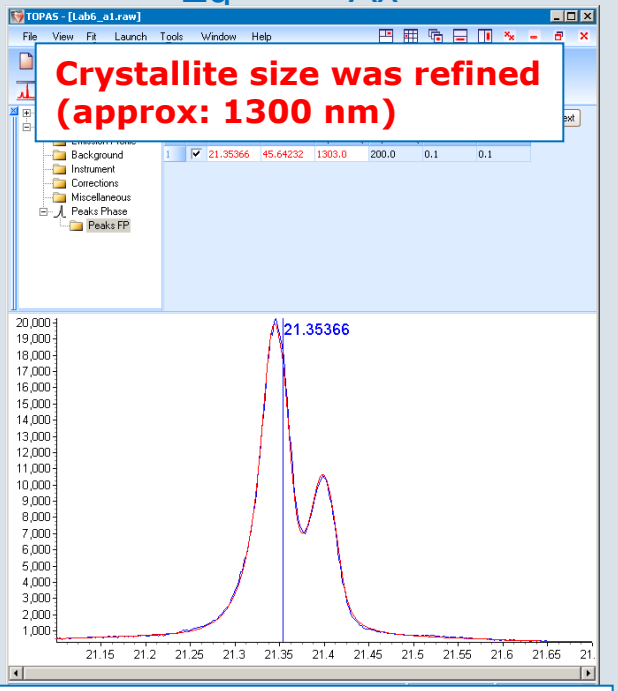
- Highlight the instrument item in the treeview below the scan file
- In the tab „divergent beam“ the slit sizes for Bragg-Brentano geometry are entered in either mm or degrees.
- Radius depends on measurement circle of diffractometer
  - D4, D500, D5000: 200.5mm
  - D8: usually 217.5 or 250mm
- For Point detector: Check the use column for point detector and enter settings for receiving and divergence slit
- For Linear PSDs (LynxEye and Vantec-1) check here and enter angular 2Θ range and divergence
- Soller slits sizes are entered under Full Axial model
  Default size for D8: 2.5°
  Default size for D4: 4°
- Instrument settings can be saved, loaded or made a default setting

FPA Example for LaB_6 (111) Single line fitting: Exercise

W | $W \times G_{Eq} \times G_{Ax}$ | $(W \times G_{Eq} \times G_{Ax}) \times S$



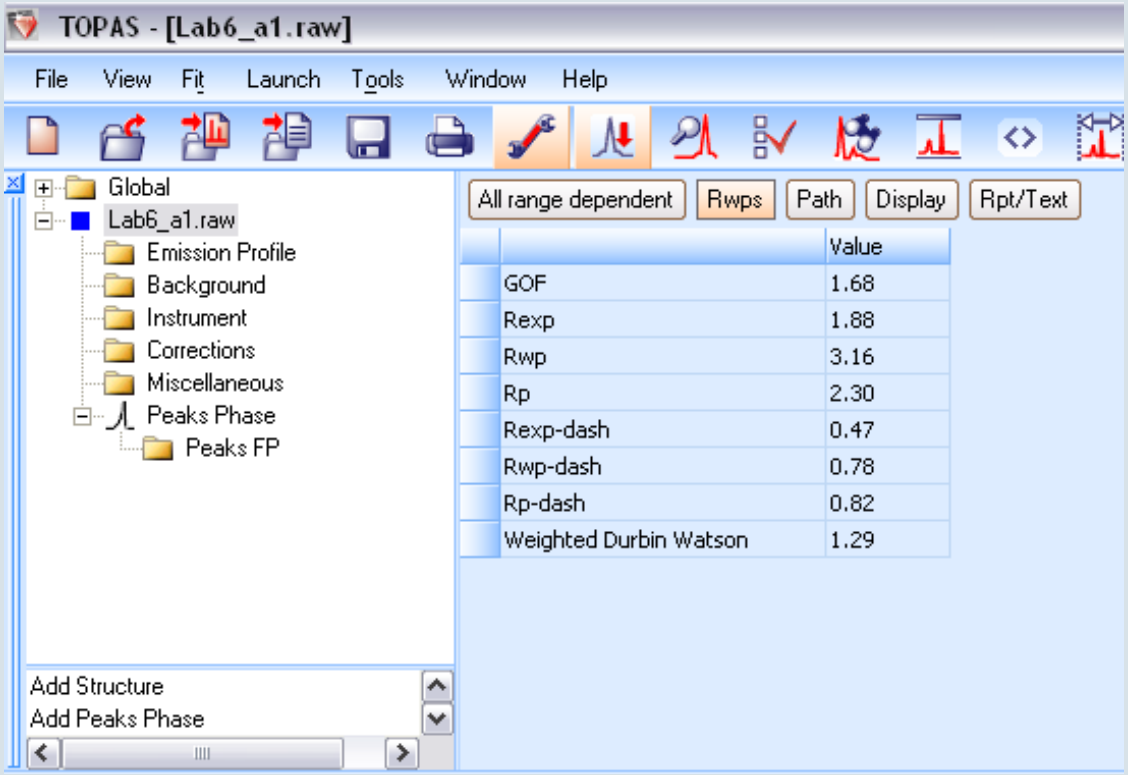




File: C:\Topas 4.1\tutorial\misc\Lab6_a1.raw
Emission profile: CuKa2.lam
Background order 3
Radius: 217 mm
Divergence: 0.5°
Receiving slit: 0.1mm
Soller slits: 2.3°

Advantages of FPA:
- Identical instrument contribution to every peak
- Fewer parameters: Faster, more stable computation
- No parameter turn-on sequence for refinements
- Average crystallite size/strain for each phase

How good is my Fit?



Rwp is the parameter that is being minimized during the least square fit.

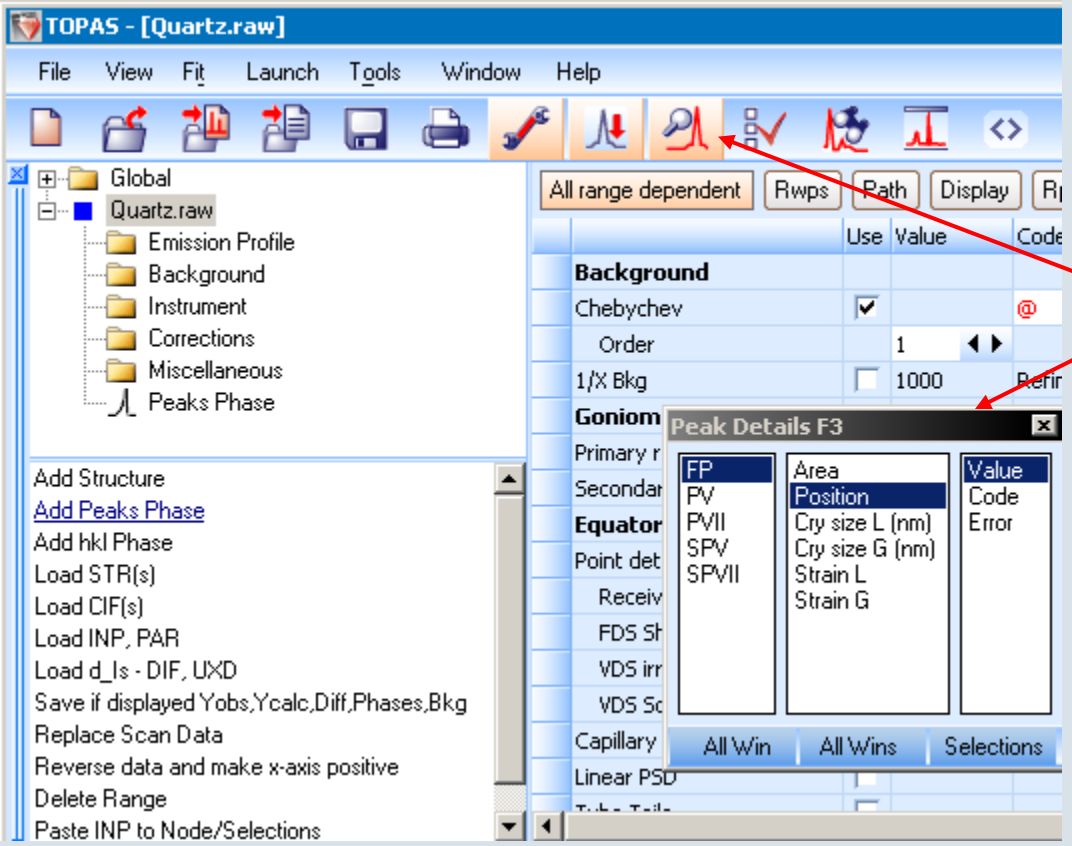
$$R_{wp} = \sum_i w_i [y_i(o) - y_i(c)]^2 / \sum_i w_i y_i^2$$

Other numerical indicators:

Goodness of fit: GOF = Rwp/Rexp

Rwp-dash: background subtracted residuals

Profile Fitting in TOPAS
Peaks Phases



File: C:\Topas 4.1\tutorial\misc\quartz.raw

Adding a Peaks Phase will add a phase without any position or intensity constraints

This is typically used to determine accurate peak positions for Indexing, peak areas or micro-structural parameters

Select the Peak Details window (F3)

Several Peak Types are available

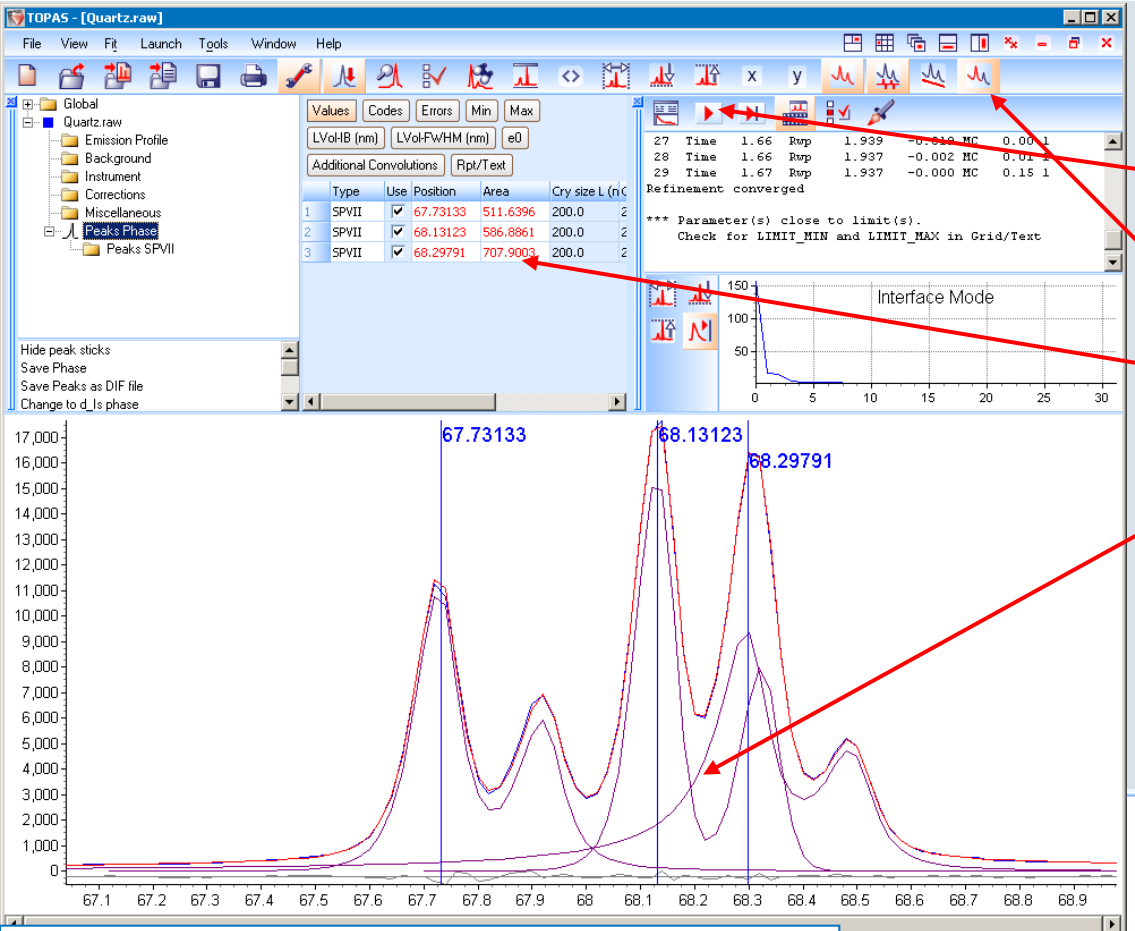
FP: Fundamental Parameters

PV: Pseudo Voight function
PVII: Pearson VII function
SPV: Split Pseudo Voight function
SPVII: Split Pearson VII function

The second column allows display of position, area, crystallite size or strain at the peak

Select the peak type SPVII and click with the mouse near the peak maxima of your scan

Profile Fitting in TOPAS
Peaks Phases, Peak types

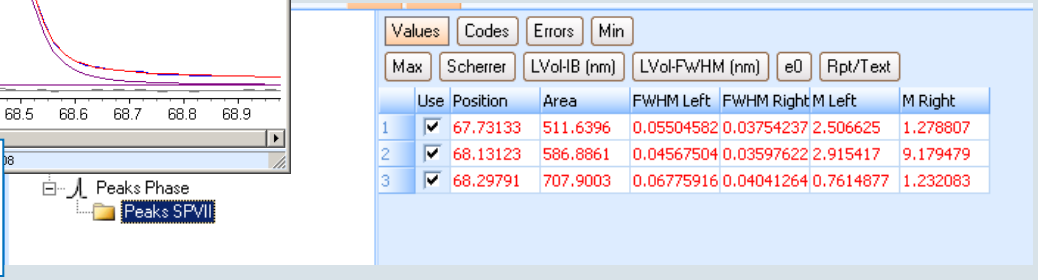


Select SPVII peak type and click near the maximum of the three peaks with the mouse.
Run the Refinement

Select individual peak display

The third peak has almost 50% more intensity than the others, even though the maximum intensity is visually lower
Also note the considerably higher asymmetry

This is caused by parameter correlation and can be avoided by using constraints that ensure the same peak width for all peaks



File: C:\Topas 4.1\tutorial\misc\quartz.raw
Emission profile: CuKa2_analyt.lam
Background order 3

Profile Fitting in TOPAS
Peaks Phases, Constraining parameters

Values | Codes | Errors | Min

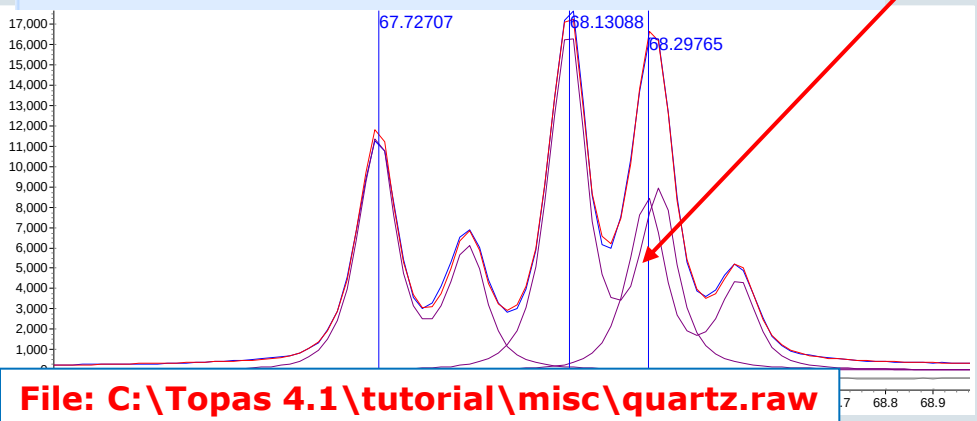
Max | Scherrer | LVol-IB (nm) | LVol-FWHM (nm) | e0 | Rpt/Text

	Use	Position	Area	FWHM Left	FWHM Right	M Left	M Right
1	☑	67.73133	511.6396	0.05	0.05	1	1
2	☑	68.13123	586.8861	0.05	0.05	1	1
3	☑	68.29791	707.9003	0.05	0.05	1	1

Values | Codes | Errors | Min

Max | Scherrer | LVol-IB (nm) | LVol-FWHM (nm) | e0 | Rpt/Text

	Use	Position	Position	Area	FWHM Le	FWHM Ri	M Left	M Right
1	☑	67.73133	Refine	Refine	FWHML	FWHMR	Ml	Mr
2	☑	68.13123	Refine	Refine	FWHML	FWHMR	Ml	Mr
3	☑	68.29791	Refine	Refine	FWHML	FWHMR	Ml	Mr



File: C:\Topas 4.1\tutorial\misc\quartz.raw
Emission profile: CuKa2_analyt.lam
Background order 3

To change a whole column to the same value, click on the upper right corner of the grid

Type identical start values for FWHM and M

Select Codes tab and enter the parameter names for FWHM and M

Run the Refinement again

The peaks now have identical shapes and correct intensities

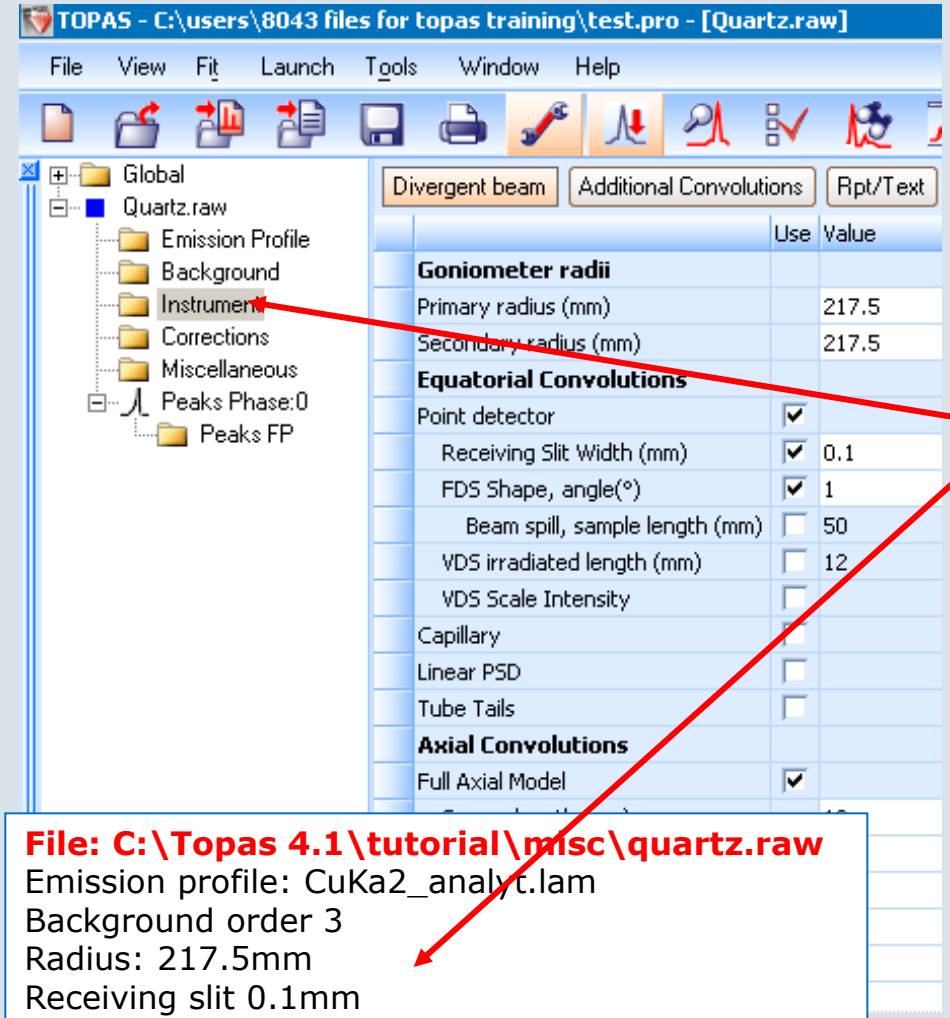
Values | Codes | Errors | Min

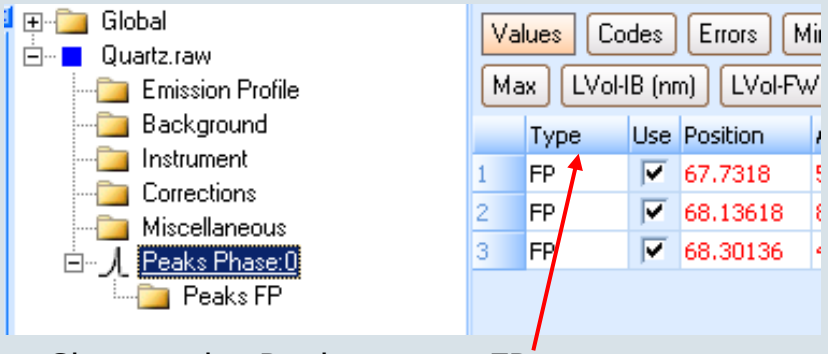
Max | Scherrer | LVol-IB (nm) | LVol-FWHM (nm) | e0 | Rpt/Text

	Use	Position	Area	FWHM Left	FWHM Right	M Left	M Right
1	☑	67.72707	532.3152	0.04967582	0.04142547	1.86854	1.421101
2	☑	68.13088	768.883	0.04967582	0.04142547	1.86854	1.421101
3	☑	68.29765	385.4827	0.04967582	0.04142547	1.86854	1.421101

Profile Fitting in TOPAS

Peaks Phases, Fundamental parameters as an intrinsic constraint

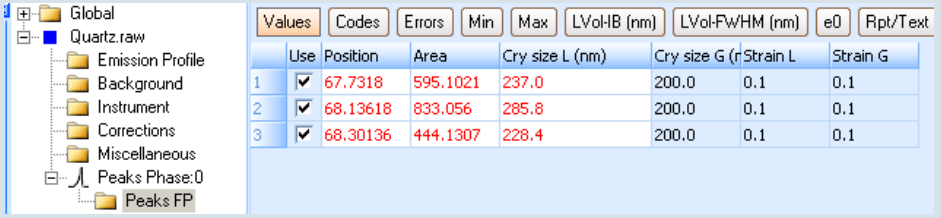




Change the Peak type to FP
Enter Instrument parameters for that scan.

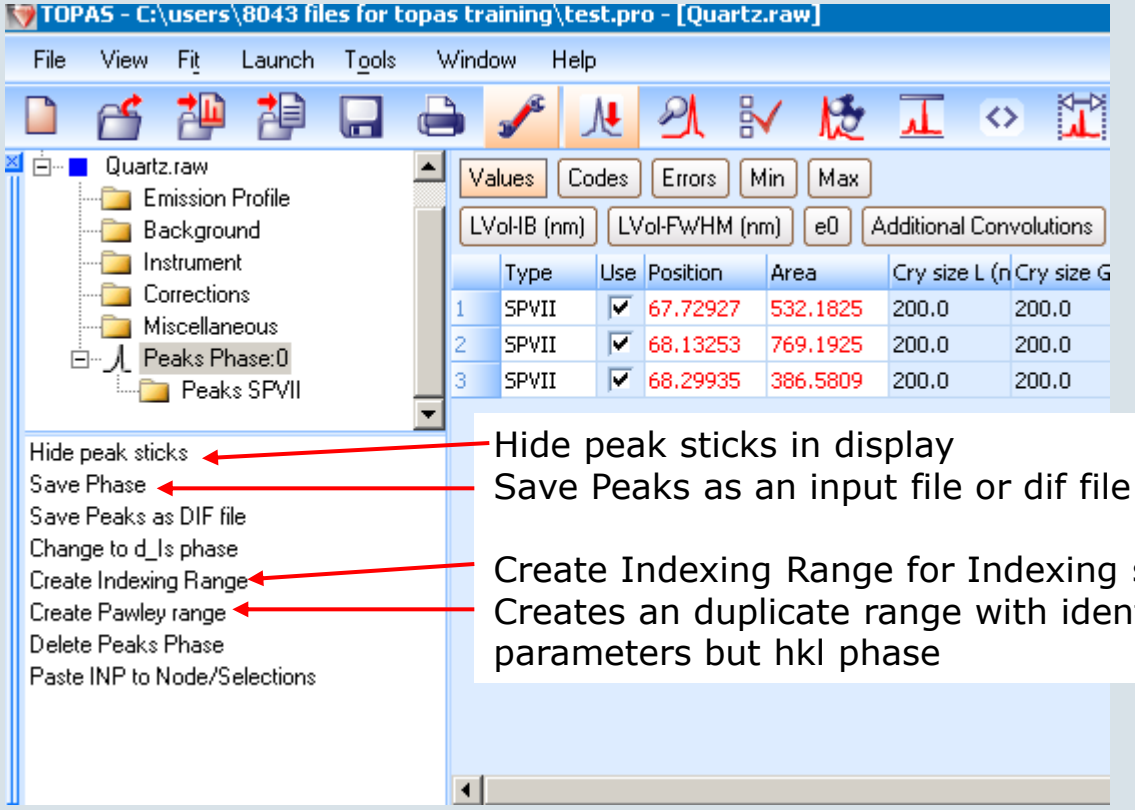
Instrumental contribution to all peaks is identical → intrinsic constraint, however anisotropic effects can be refined individually

Difference between instrumental width and measured width is caused by microstructure such as size broadening or strain



File: C:\Topas 4.1\tutorial\misc\quartz.raw
Emission profile: CuKa2_analyt.lam
Background order 3
Radius: 217.5mm
Receiving slit 0.1mm
FDS 1°
4° Soller slits

Profile Fitting in TOPAS
Peaks Phases



Hide peak sticks in display

Save Peaks as an input file or dif file

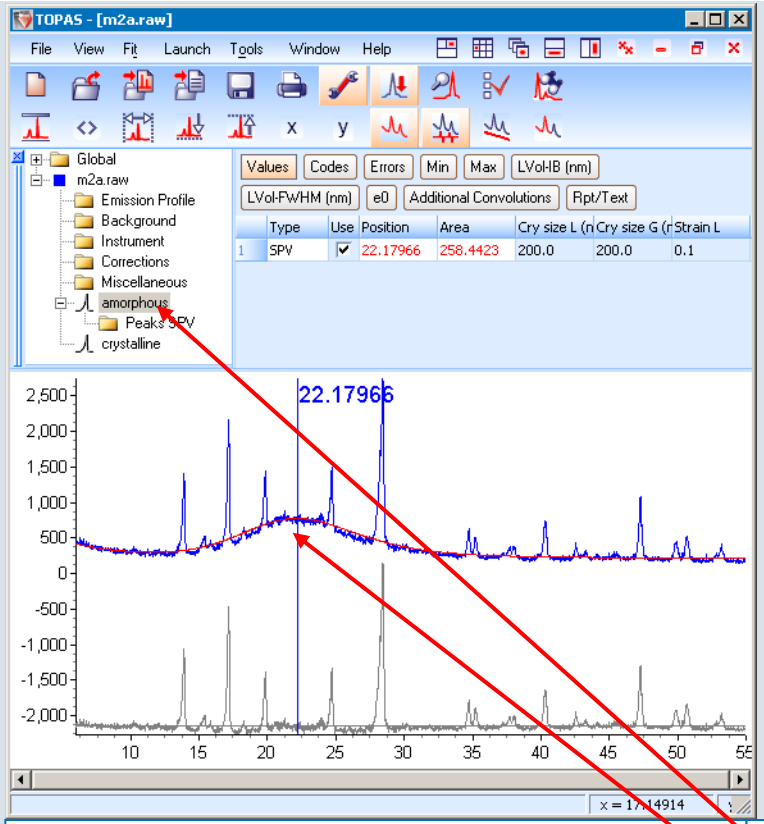
Create Indexing Range for Indexing single phase samples

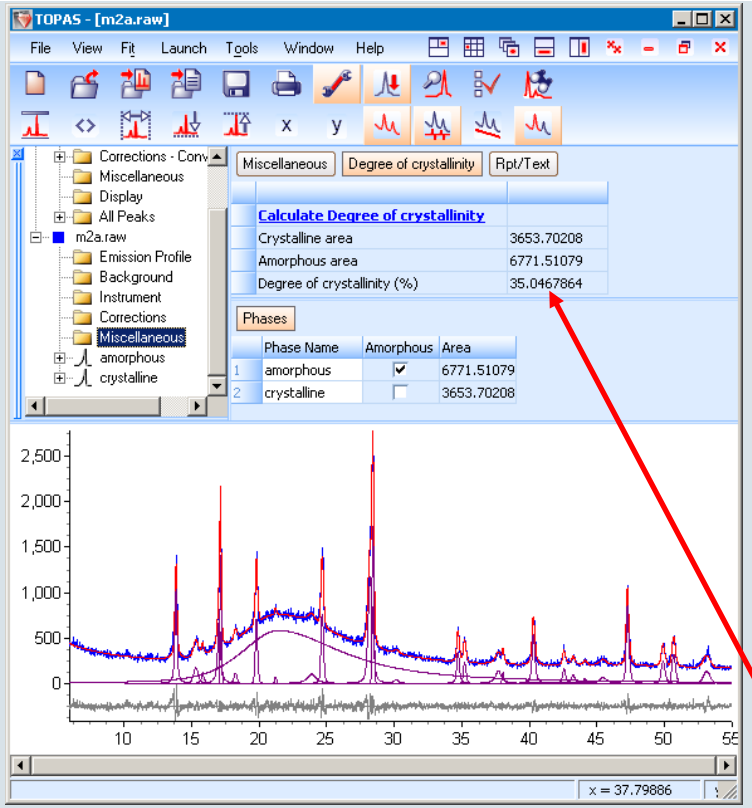
Creates an duplicate range with identical instrument parameters but hkl phase

File: C:\Topas 4.1\tutorial\misc\quartz.raw
Emission profile: CuKa2_analyt.lam
Background order 3

Profile Fitting in TOPAS

Peaks Phases, Calculating Areas for crystallinity determination



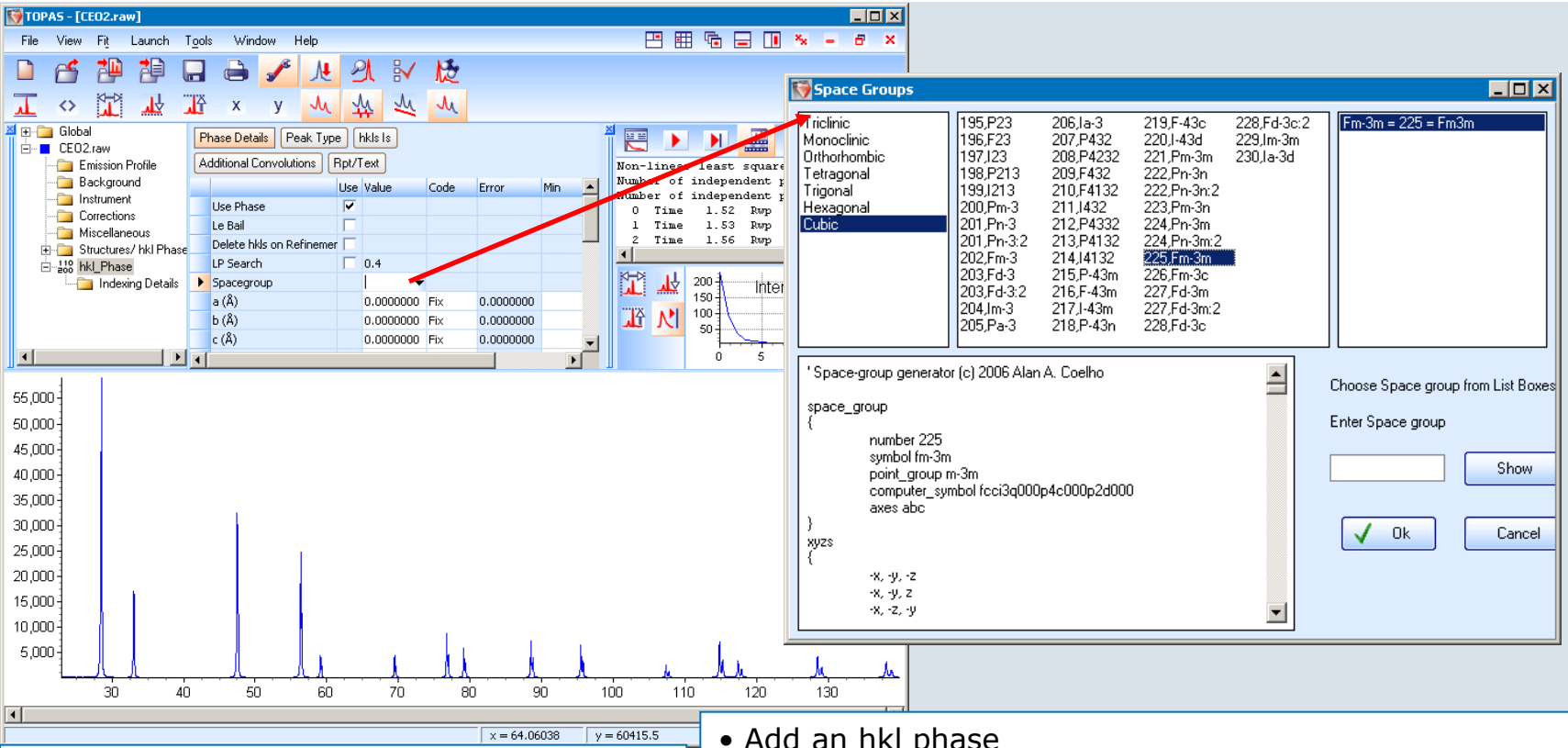


File: C:\Topas 4.1\tutorial\doc\m2a.raw
Emission profile: CuKa2_analyt.lam
Background order 1
1/x function

- Add two peak phases, rename them amorphous and crystalline
- Use one SPV peak for the amorphous hump
- Select crystalline and insert a peak for each reflection (Verify that you are not fitting the background with these peaks otherwise use symmetric functions or constraints)
- Highlight Miscellaneous and Calculate Degree of Crystallinity

Profile Fitting in TOPAS

hkl Phases for Lattice Parameter Refinement

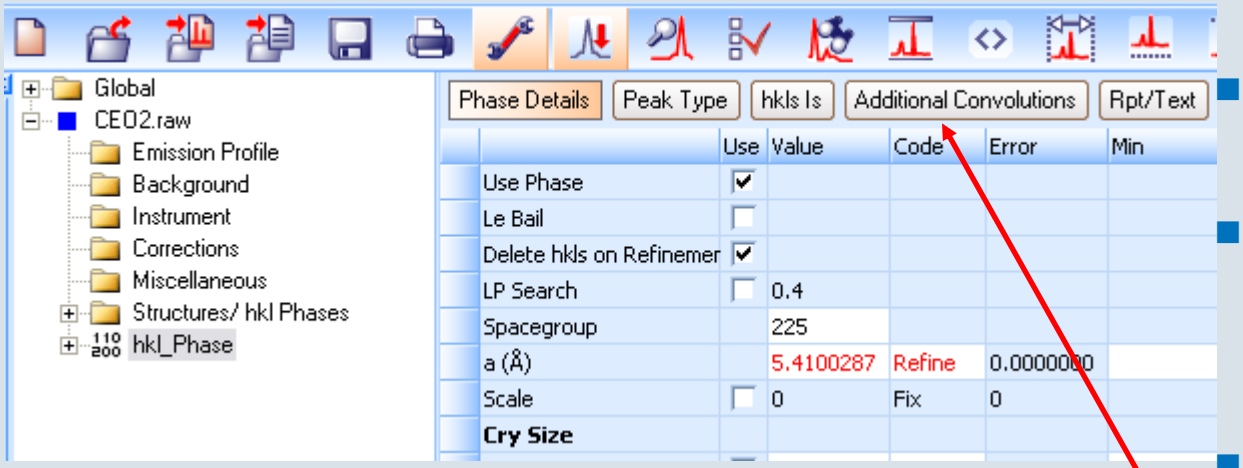


File: C:\Topas 4.1\tutorial\ceo2\ceo2.raw
Measurement circle radius: 173mm
Emission profile: CuKa5.lam
Background order 3, 1/x function
Divergence: 1° , Receiving slit: 0.1mm
Soller slits: prim. 5.1° , sec. 8.6°

- Add an hkl phase
- Enter a space group number or symbol or pick a group from the space group editor
- Enter approx. lattice parameter (5.4 for CeO2) and set to refine
- Enter instrument parameters
- Check zero error correction under Corrections
- Run refinement

Profile Fitting in TOPAS

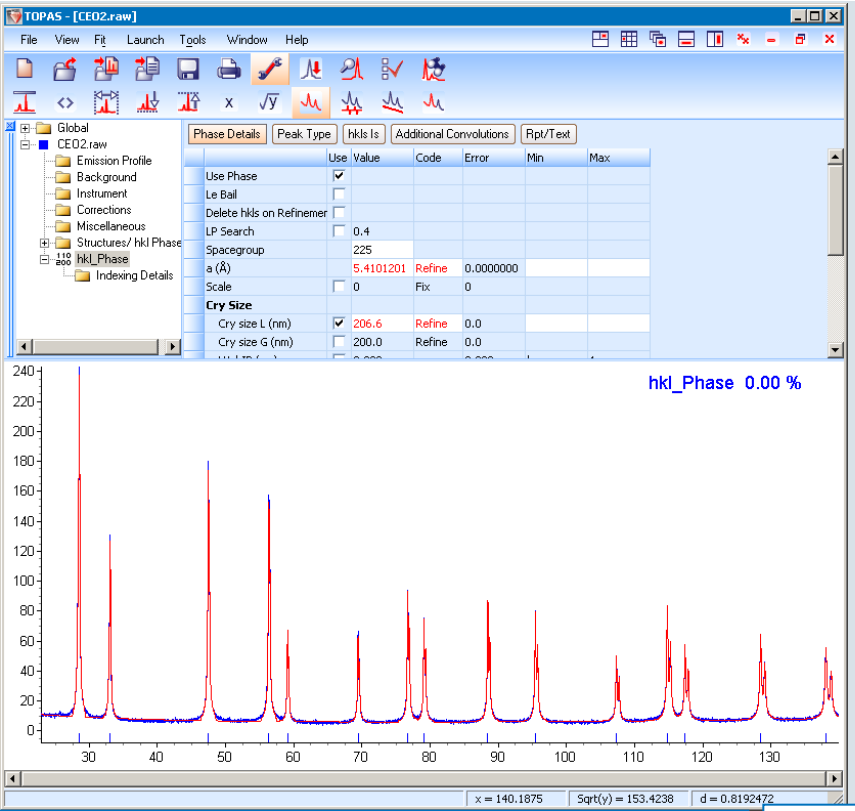
Pawley or LeBail fit

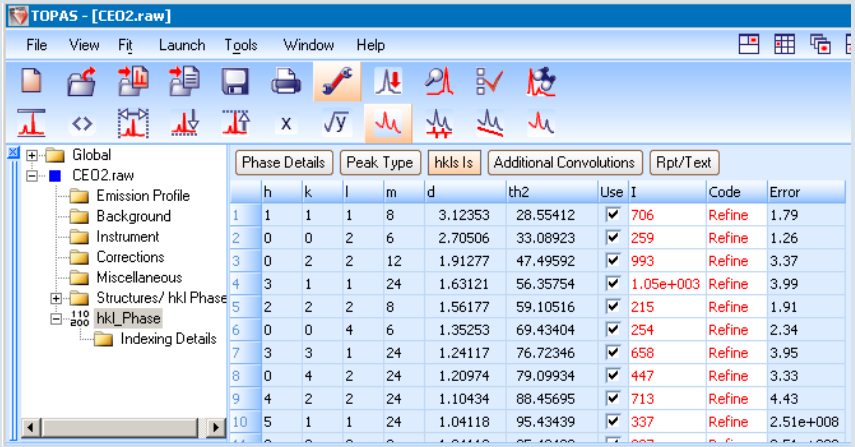


- By default Pawley fit is active, which means that all intensity values are refined independently
- By checking the "le Bail" checkbox is used where new integral intensities are calculated for each refinement step → fewer independent parameters
- Peak type
- hkl Is tab: List of intensities and peak positions
- Additional convolutions: define any additional peak shape convolution that may be necessary for special configurations or synchrotron radiation

Profile Fitting in TOPAS

hkl Phases for Lattice Parameter Refinement

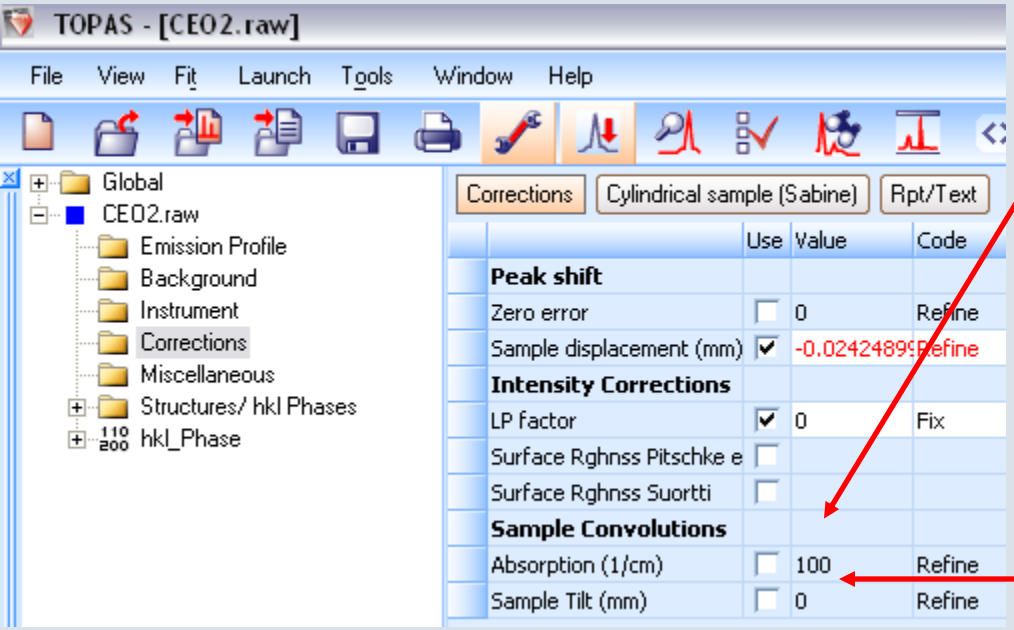




File: C:\Topas 4.1\tutorial\ceo2\ceo2.raw
Measurement circle radius: 173mm
Emission profile: CuKa5.lam
Background order 3, 1/x function
Divergence: 1° , Receiving slit: 0.1mm
Soller slits: prim. 5.1° , sec. 8.6°

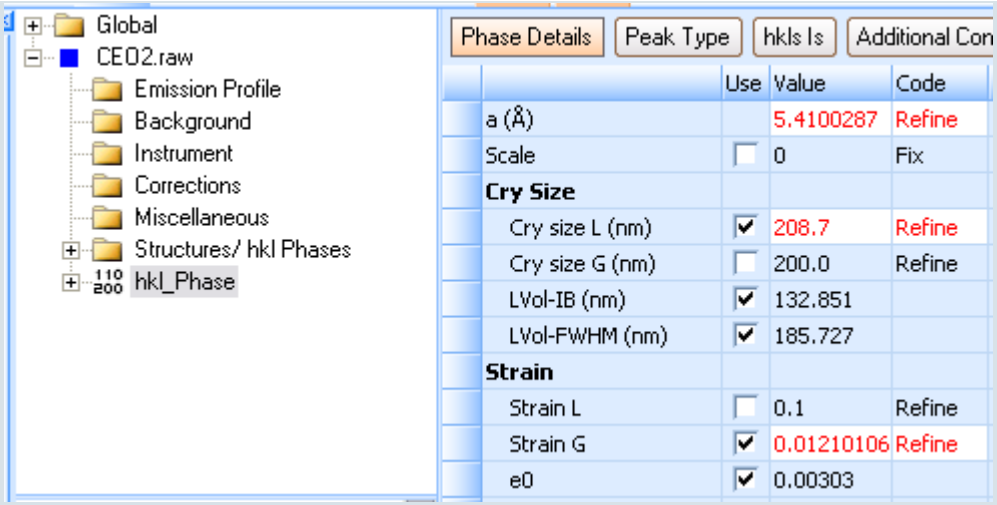
- Refined lattice parameter
- Refined average crystallite size (Scherrer equation)
- Peak list with intensities under the hkl Is tab

Profile Fitting in TOPAS
Sample effects



- The lower the absorption coefficient of the sample, the more the primary beam will penetrate into deeper regions of the specimen.
- This acts like a distribution of sample height displacements and causes peak tails at the low angle side.
- If the sample shows only a limited thickness this effect will be reduced.
- Tilting the sample also acts like a distribution of sample height displacements.
- The height (or length) of the sample also shows an influence because it may lead to beam overflow at low angles and reduced intensities.

Profile Fitting in TOPAS
Microstructure effects



$$\beta_{\mathrm{int}_s} = \frac{\lambda}{L_{vol} \cdot \cos\theta}$$

$$\beta_{1/2_v} = 4 \cdot \varepsilon_0 \cdot \tan\theta$$

- Crystallites of 'unlimited' size and ideal translational periodicity would cause no additional broadening of the peak.
- The smaller the crystallites are, the more severe the broadening will be. This often is given as a 'mean column height' L_{vol}.
- Often crystallite size is confused with (secondary) grain size, domain size and crystal size.
- If locally the d-spacing changes within a crystal this is called micro strain. This is often is described as a quasi-mean value ε_0 parameter.
- Inhomogeneous metric parameters for different crystallites show a similar broadening.
- Anisotropy and domain effects may cause also not only angle dependent broadening.

Profile Fitting in TOPAS

Correcting fit problems in Whole Powder Pattern Fitting applications

Offset in Peak Positions:

- Refine sample displacement or zero error
- Are the lattice parameters being refined or do they hit any min/max constraints?

Peak shape not correct:

- Check instrument parameters. These should be fixed. If the low angle peaks are more asymmetric than the calculated curve, the Soller slit size may be larger
- Crystallite size parameter should be refined and result in reasonable values
- If peaks are broader at higher angles, refine additional micro-strain
- Peak tails at low angle side → refine absorption or measure thinner sample

Additional Peaks:

- Wrong symmetry or crystal system?
- Impurities?

Very asymmetric peaks or single broader peaks:

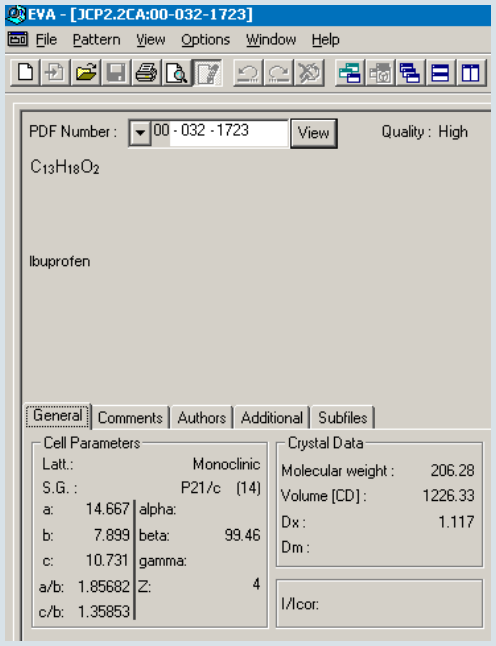
- Try anisotropic corrections in TOPAS Launch mode (e.g. tutorial example: clay.inp)

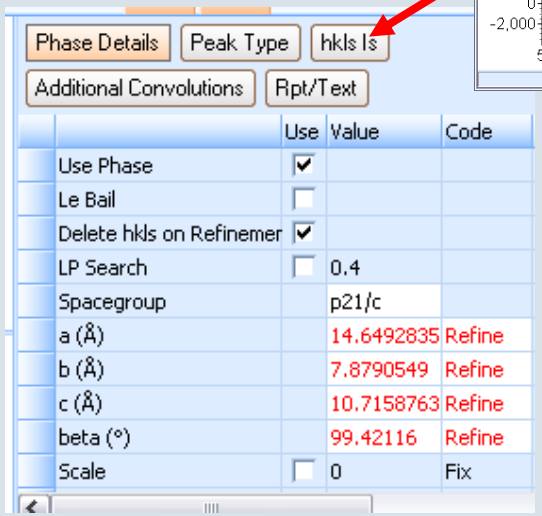
Profile Fitting Methods in TOPAS

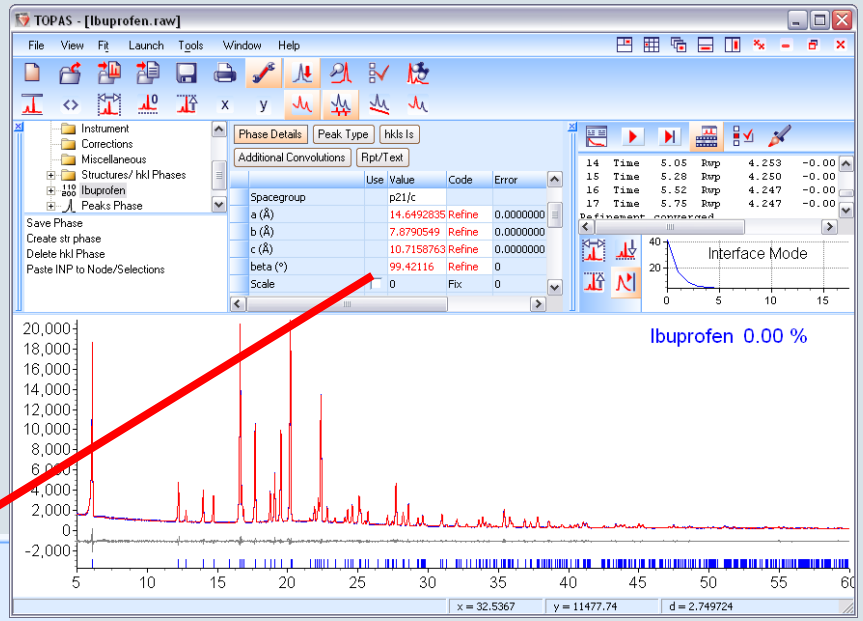
Example: Lattice parameter refinement of Ibuprofen

File: C:\Topas 4.1\tutorial\Examples\ibuprofen\ibuprofen.raw
Emission profile: CuKa1.lam (Vario Data)
1mm Capillary data with LynxEye detector

Obtain space group and start values for lattice parameters from ICDD database

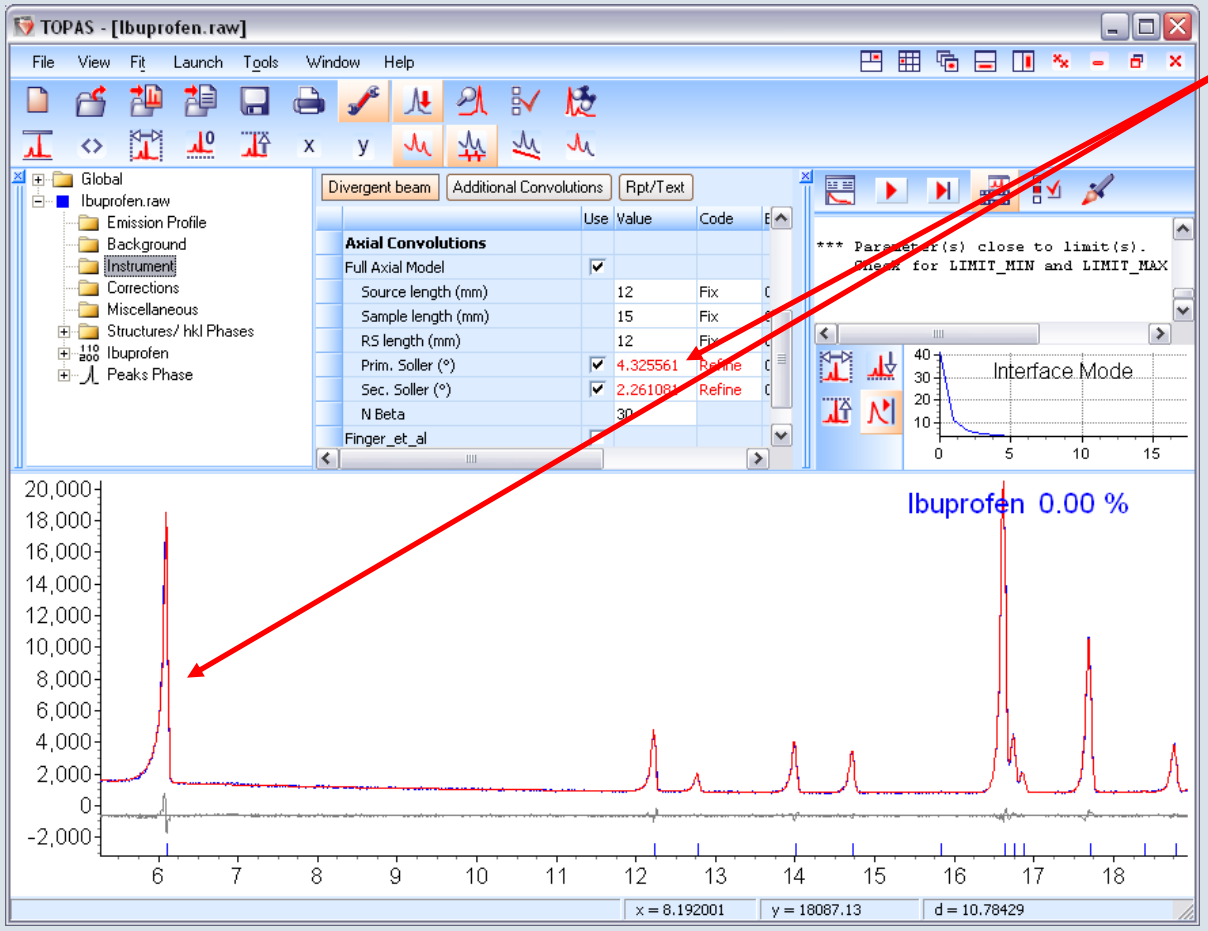




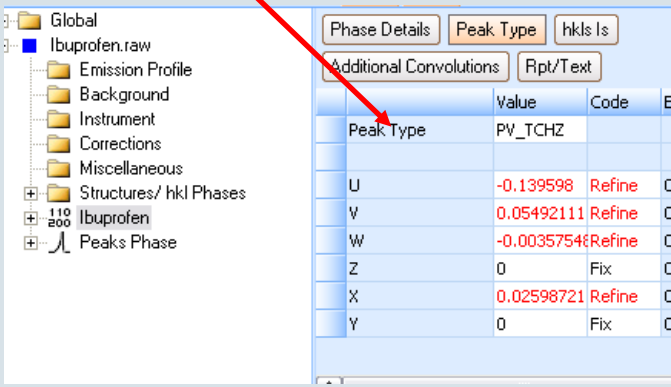


Profile Fitting Methods in TOPAS

Example: Lattice parameter refinement of Ibuprofen



- In this case the low angle asymmetry was modelled by refining both soller slit sizes.
- Refining simple axial model may be used also.
- Pseudo–Voight was selected as peak type



Powder Pattern Indexing with TOPAS

- TOPAS does not use the well known ITO, Treor or Dicvol algorithms

- LSI method
  - Iterative use of least squares
  - Operates on d-values extracted from reasonable quality powder diffraction data
    - GOF vs. volume plots
    - Automatic Pawley or LeBail fit of all / selected solutions
- LP-Search
  - Monte-Carlo based Whole Powder Pattern Decomposition
  - It minimizes on a new figure of merit function that gives a measure of correctness for a particular set of lattice parameters
  - The figure of merit function assigns parts of the diffraction pattern to calculated peak positions and then sums the absolute values of the products of the diffraction intensities multiplied by the distance to the calculated peak positions

$$\mathrm{FOM} = \sum_{\mathrm{j}} \sum_{\mathrm{i}} \mathrm{I}(2\theta_i) \left| 2\theta_i - 2\theta_{0,\mathrm{j}} \right|$$

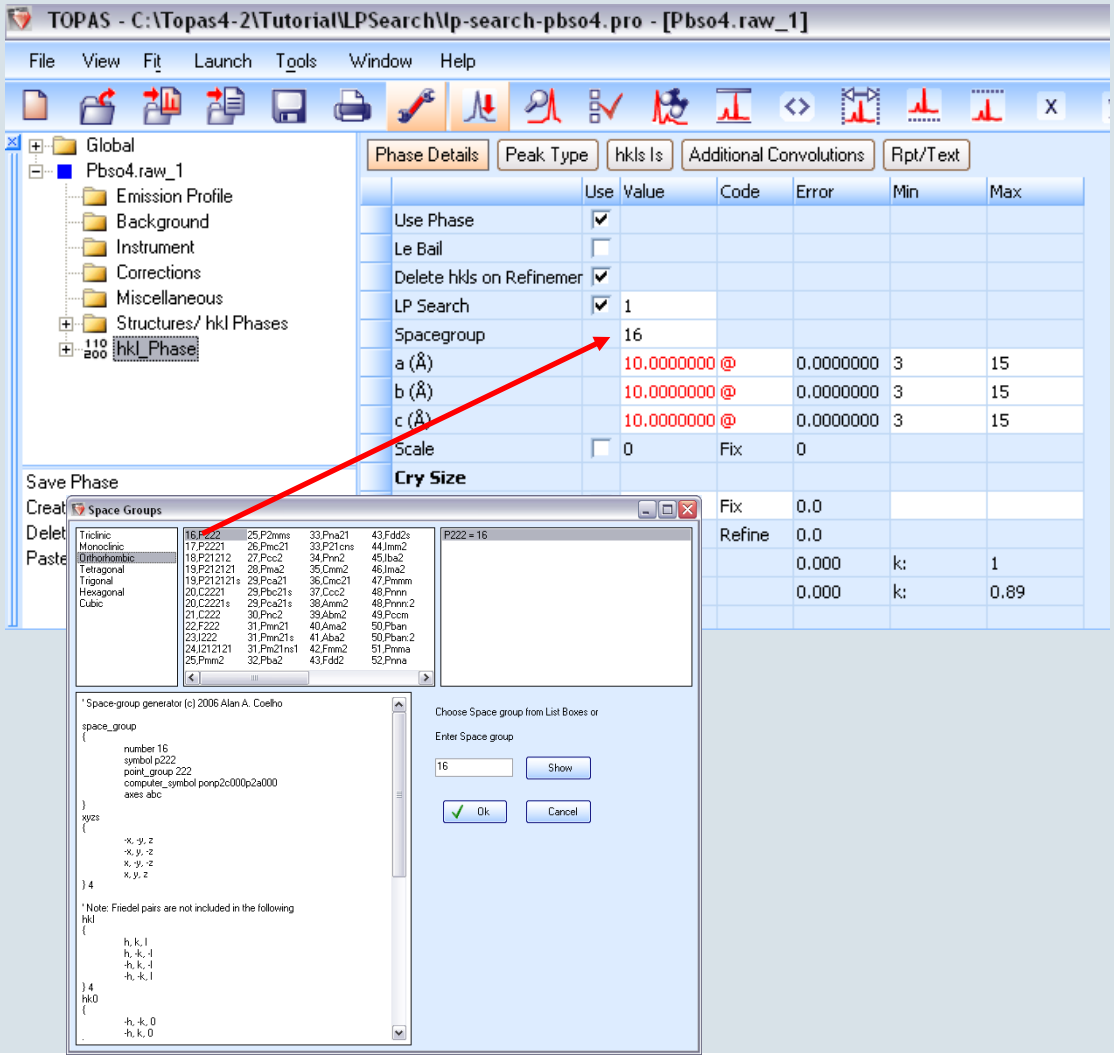
  - Independent of d-spacing extraction and line profile shape and therefore suited for indexing of poor quality powder data (No d-values required!)
  - LP-Search avoids difficulties associated with extracting d-spacings from complex patterns comprising heavily overlapped lines

Indexing Algorithms in TOPAS

- LSI-Index Approach
  - Perform a Peak profile fitting preferably using the **F**undamental **P**arameters **A**pproach
  - Create an indexing range and paste d/I values for the first 20 to 30 peaks into that range
  - Select Indexing parameters and bravais lattices and search the parameter space
  - check possible solutions in the GOF over cell volume plot
  - Paste indexing results into an hkl phase and perform a whole powder pattern fitting for possible solution in the whole data range

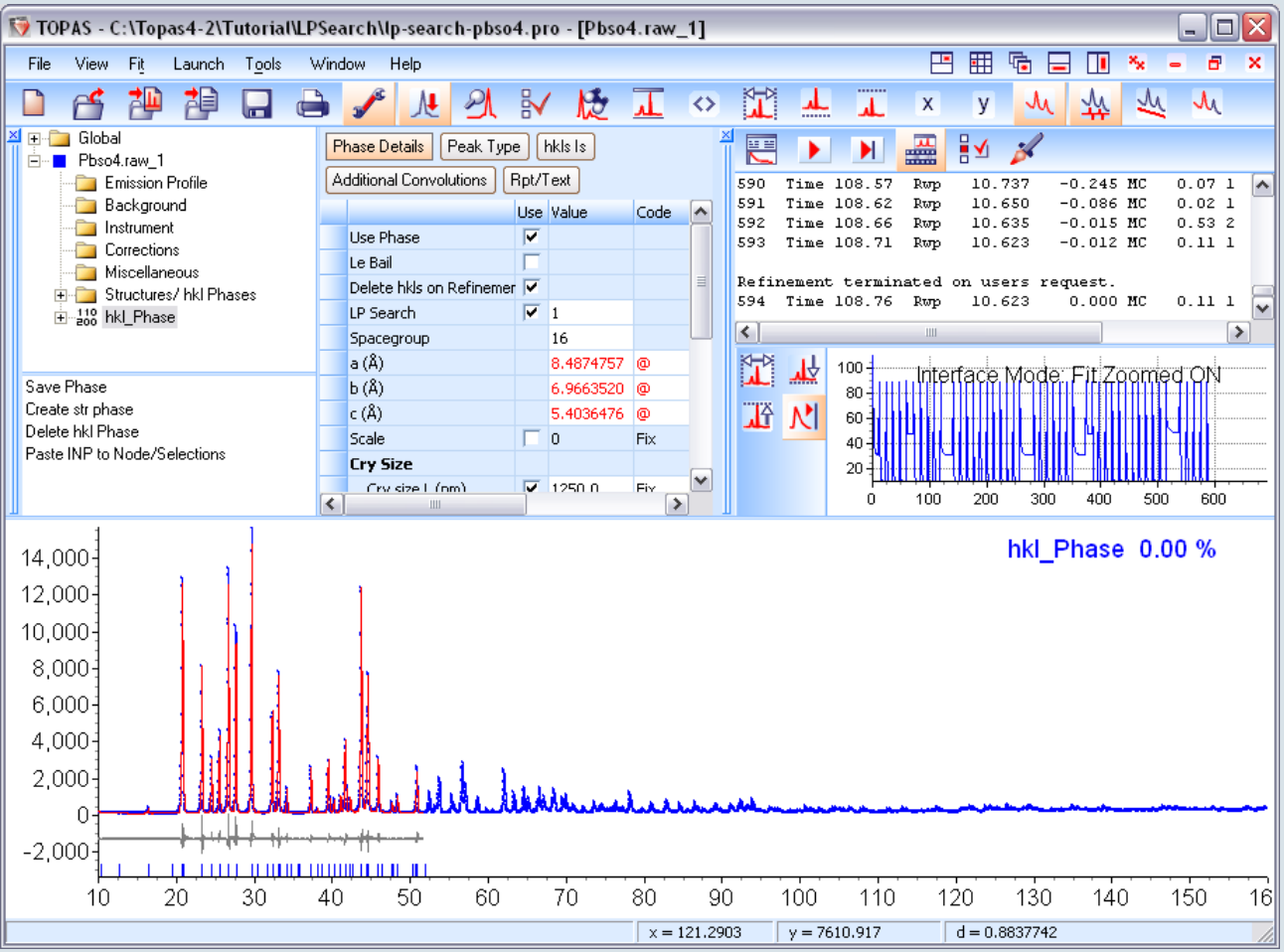
- LP-Search Approach
  - Add an hkl phase to the range and select LP search
  - Guess a crystal system and select the first space group
  - provide start values and constraints for lattice parameters and limit the 2 theta range to speed up the search
  - Check „continue until convergence“ and Run the search

LP- Search example PbSO4



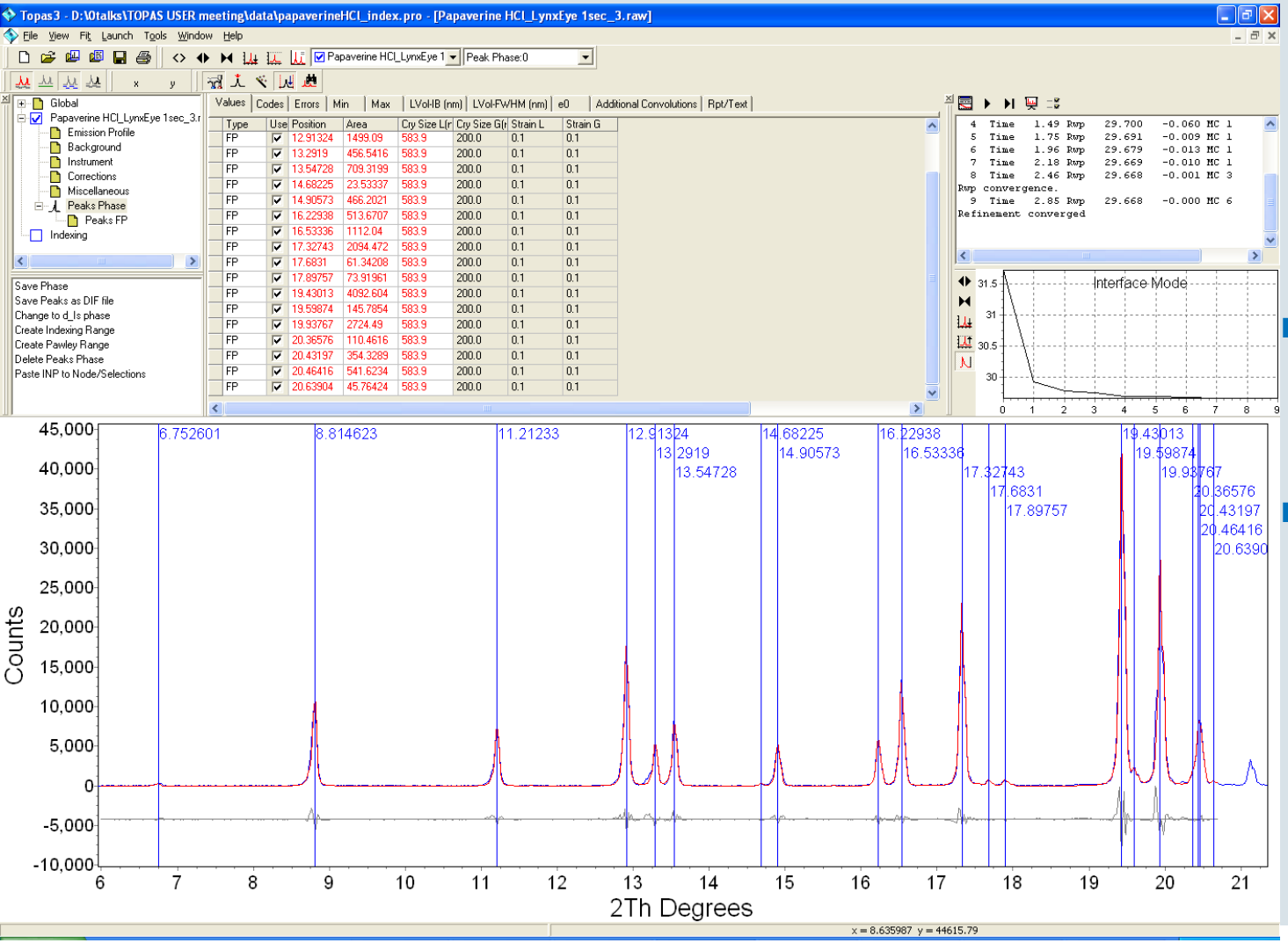
- LP-Search Approach
  - Example: C:\topas4\tutorial\LPsearch\lpsearch-PBSO4.pro
  - •Add an hkl phase and select LP search
  - • Guess a crystal system and select the first space group
  - •Provide peak shape and size strain parameters
  - • provide start values and constraints for lattice parameters and limit the 2 theta range to speed up the search
  - • Check „continue until convergence" and Run the search

LP- Search example PbSO4



- A solution is often found within seconds sometimes it takes minutes
- Peak shape and background parameters can be refined during the search.
- The refinement continues after convergence and needs to be stopped by the user, if a satisfactory solution was found
- All results are written to a log file lp.log containing the best lattice parameters, cell colume and rwp

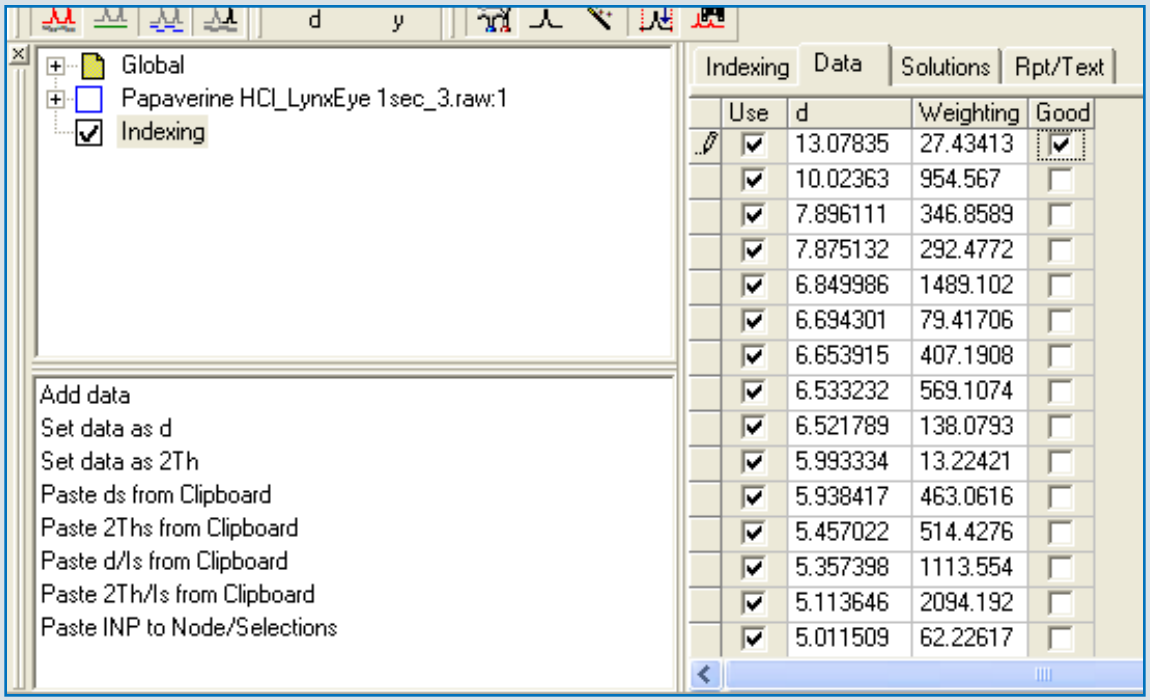
Indexing Example: Papaverine hydrochloride



(File: Papaverine HCl_ LynxEye 1sec_3.raw)

- Peak Fit with Fundamental Parameters
- Creating an Indexing range and paste the 20 highest d - spacing

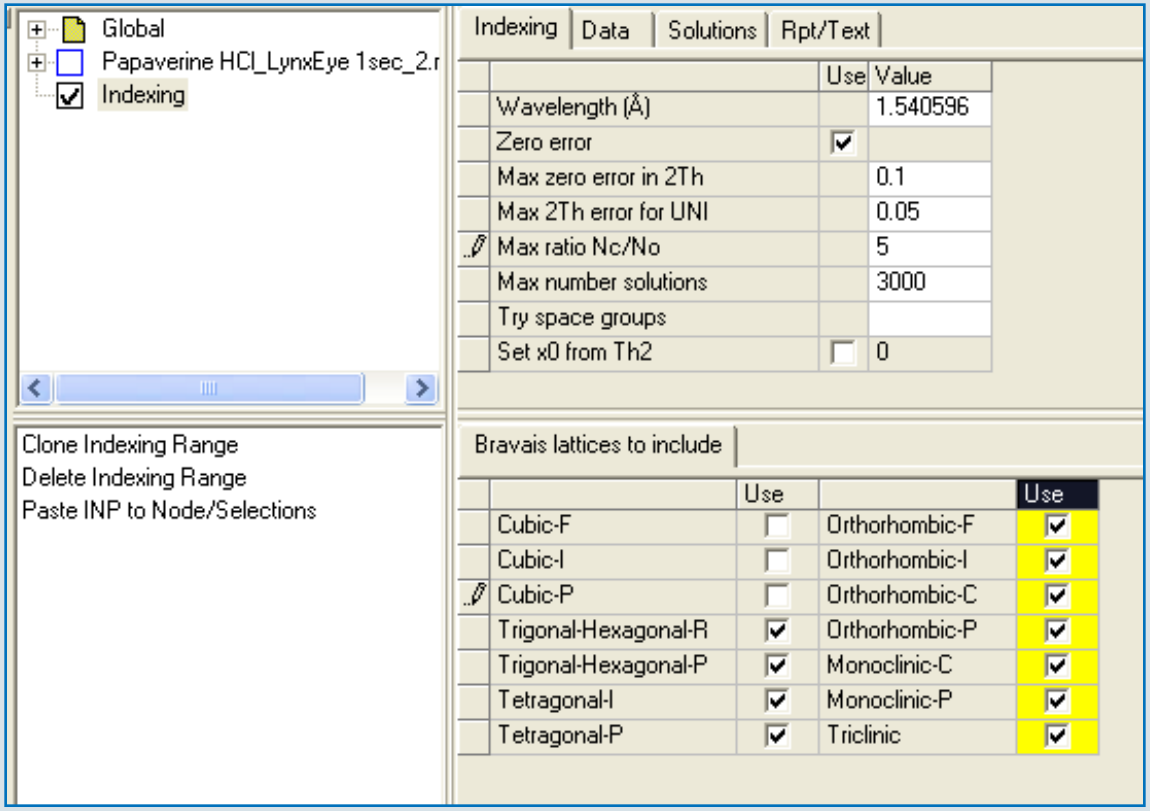
Papaverine hydrochloride



Use	d	Weighting	Good
☑	13.07835	27.43413	☑
☑	10.02363	954.567	☐
☑	7.896111	346.8589	☐
☑	7.875132	292.4772	☐
☑	6.849986	1489.102	☐
☑	6.694301	79.41706	☐
☑	6.653915	407.1908	☐
☑	6.533232	569.1074	☐
☑	6.521789	138.0793	☐
☑	5.993334	13.22421	☐
☑	5.938417	463.0616	☐
☑	5.457022	514.4276	☐
☑	5.357398	1113.554	☐
☑	5.113646	2094.192	☐
☑	5.011509	62.22617	☐

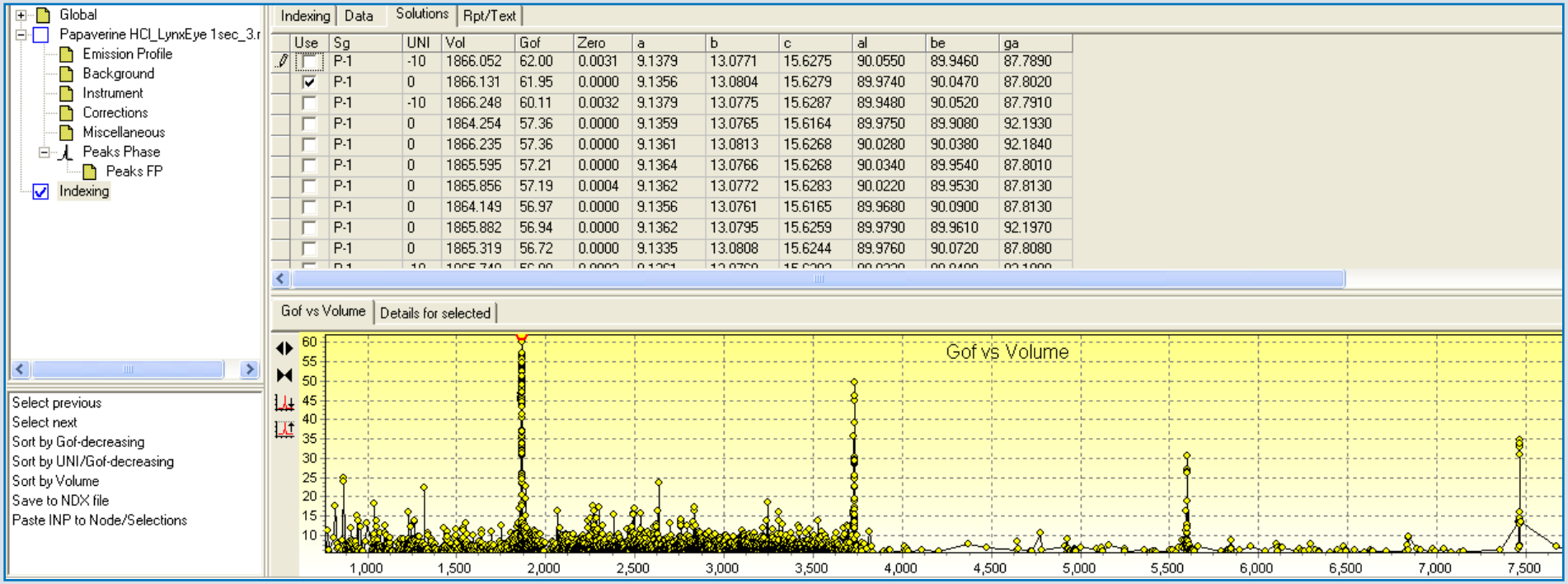
- **Creating an “Indexing Range” (The menu item is in the context menu if you highlight the Peak Phase)**
- **“Set data as d” and “Paste d/Is from clipboard”**
- **Apply Weighting “Good” to a low angle peak**

Papaverine hydrochloride



- **Creating and setting up the indexing range**
- **Enter indexing parameters and constraints**
- **Constrain to list of common space groups if known**
- **Check the bravais lattices that will be included in the search**

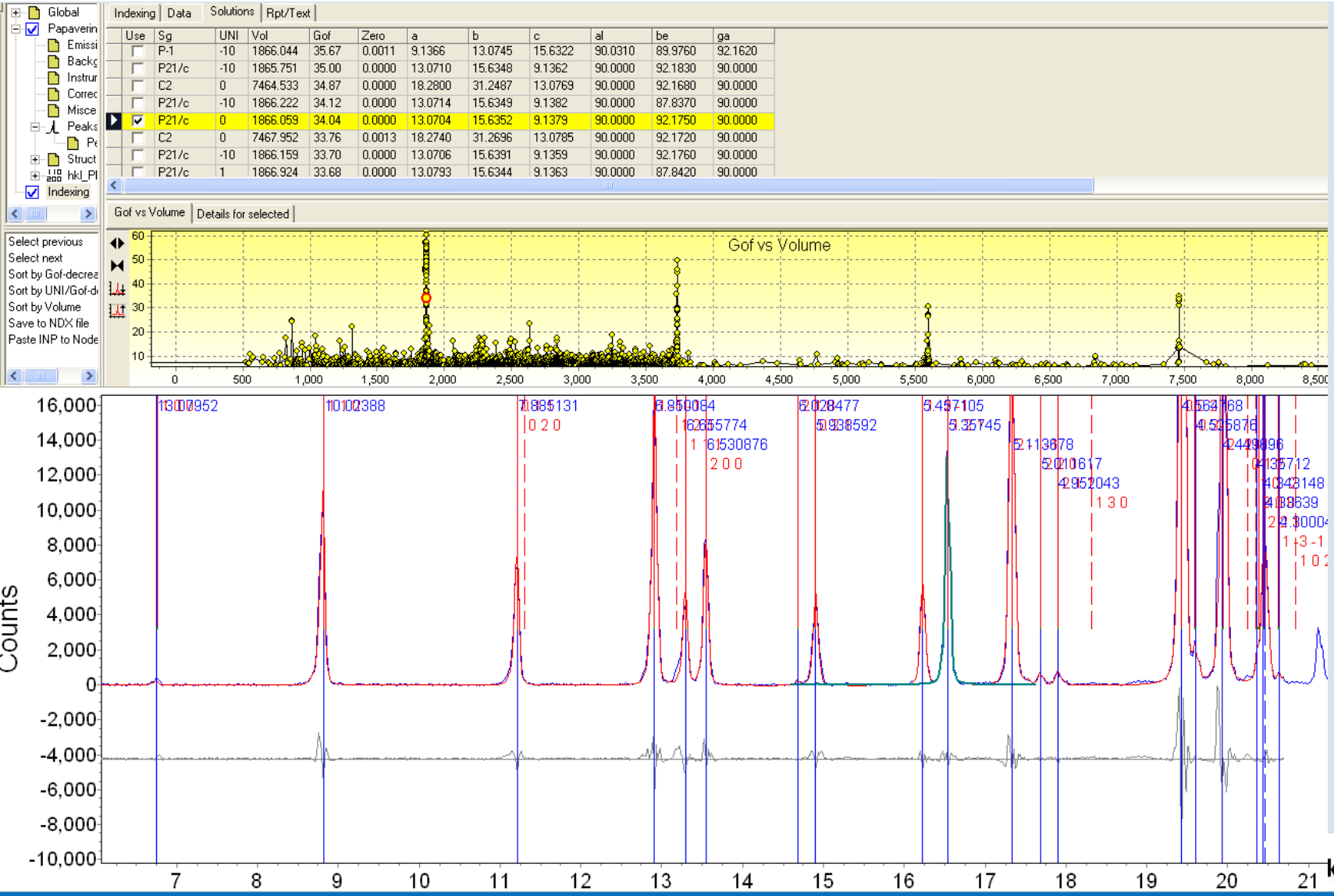
Papaverine hydrochloride



- **The correct cell volume is relatively easy to find, but which unit cell?**

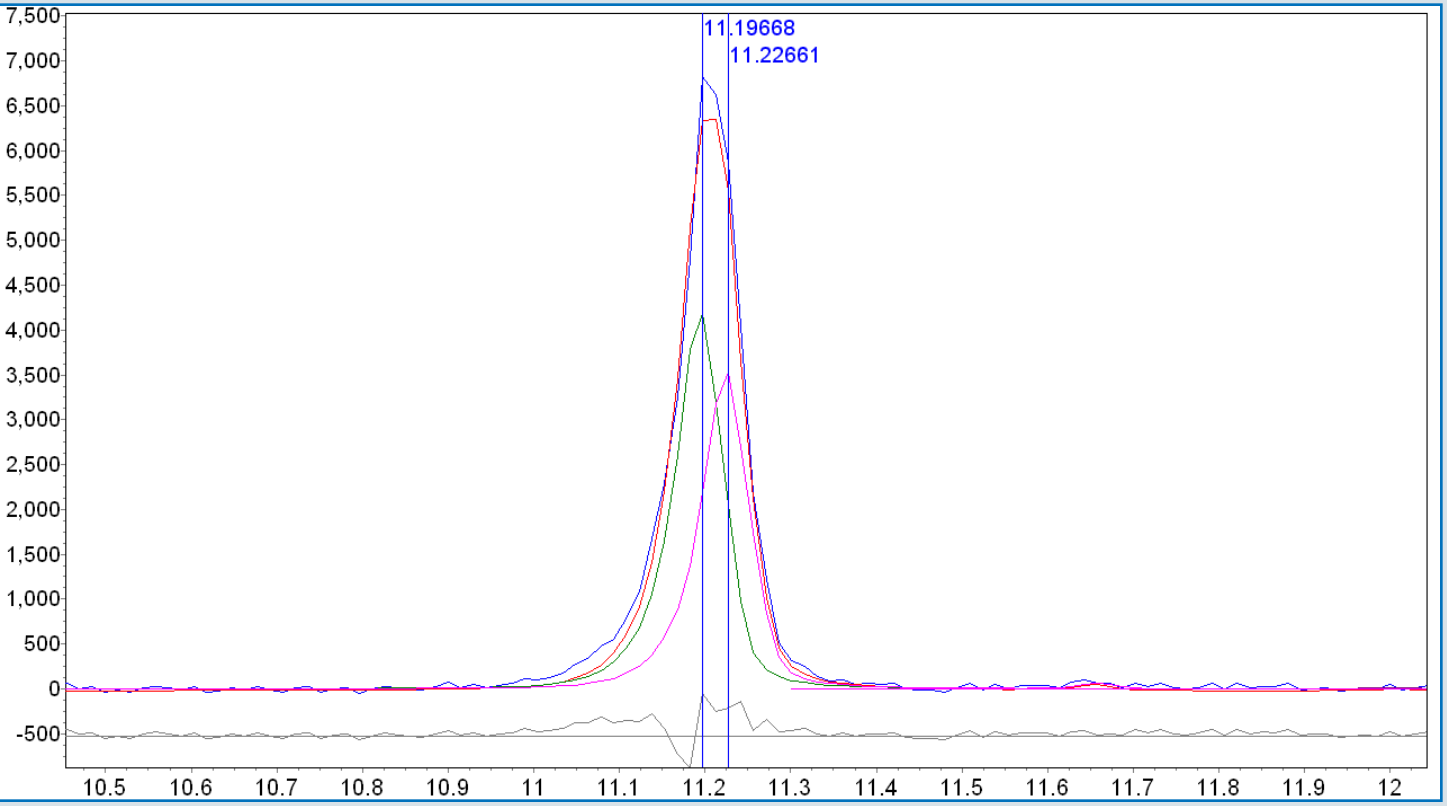
→ **Click on the various solutions with volume 1866 Å^3 and search the overlay with the actual scan for any missed peaks or overlapping peaks (dashed red lines in display)**

Papaverine hydrochloride



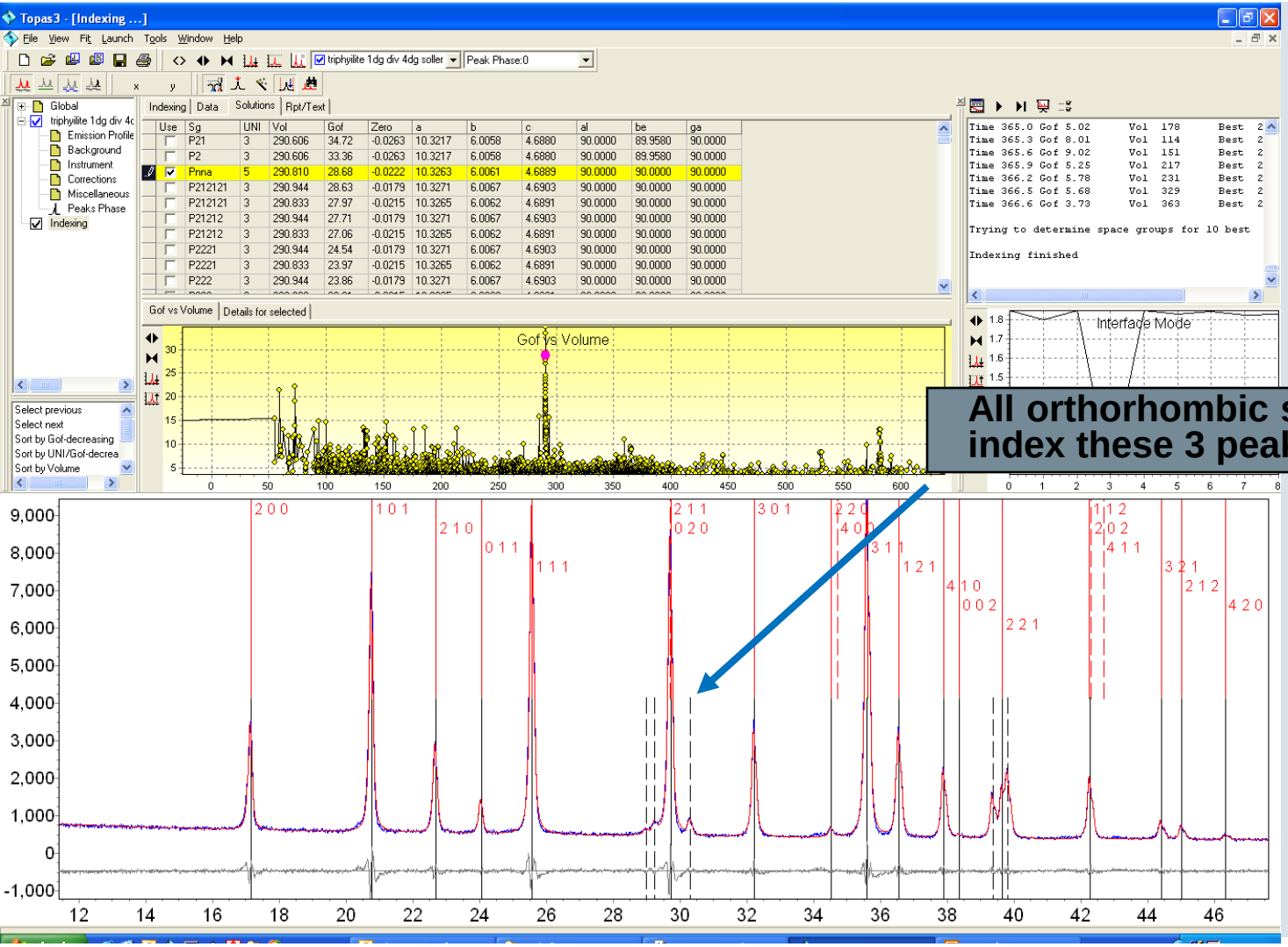
ker AXS

Papaverine hydrocloride



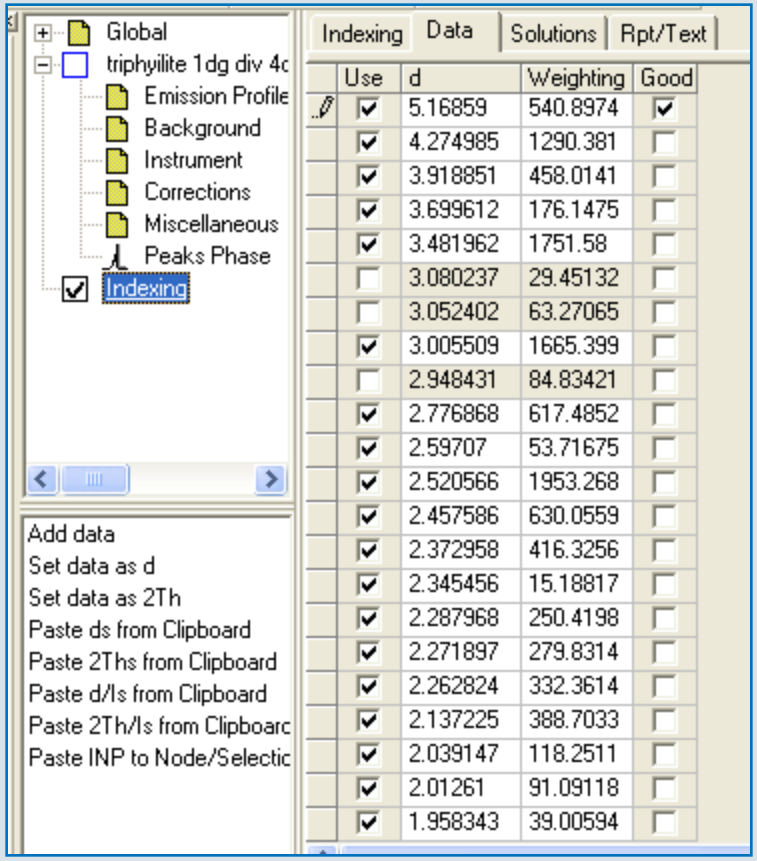
- **Peak Fit with Fundamental Parameters**
- **Constraining the crystallite size allows identification of overlapping peaks**

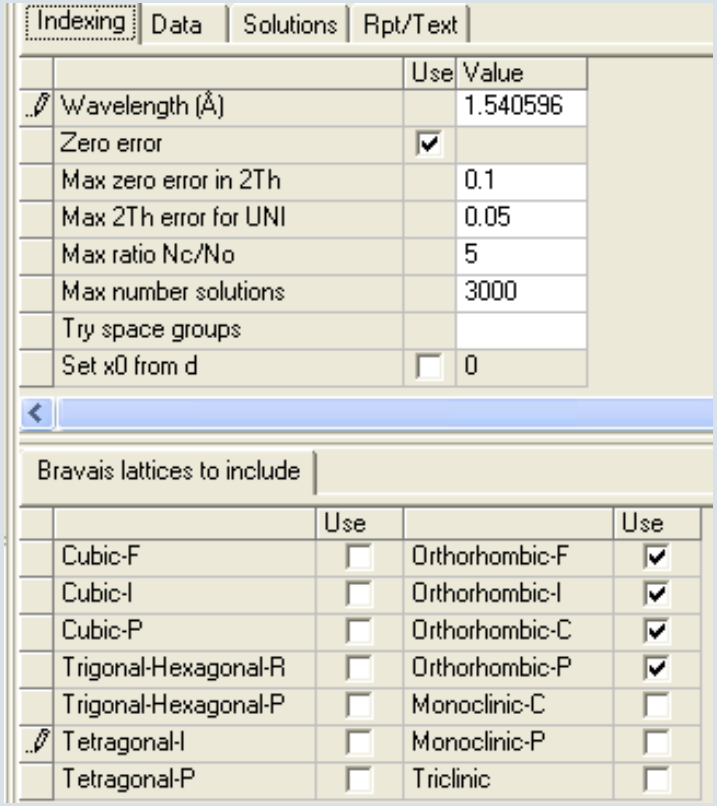
Mineral Triphylite (LiFePO4)



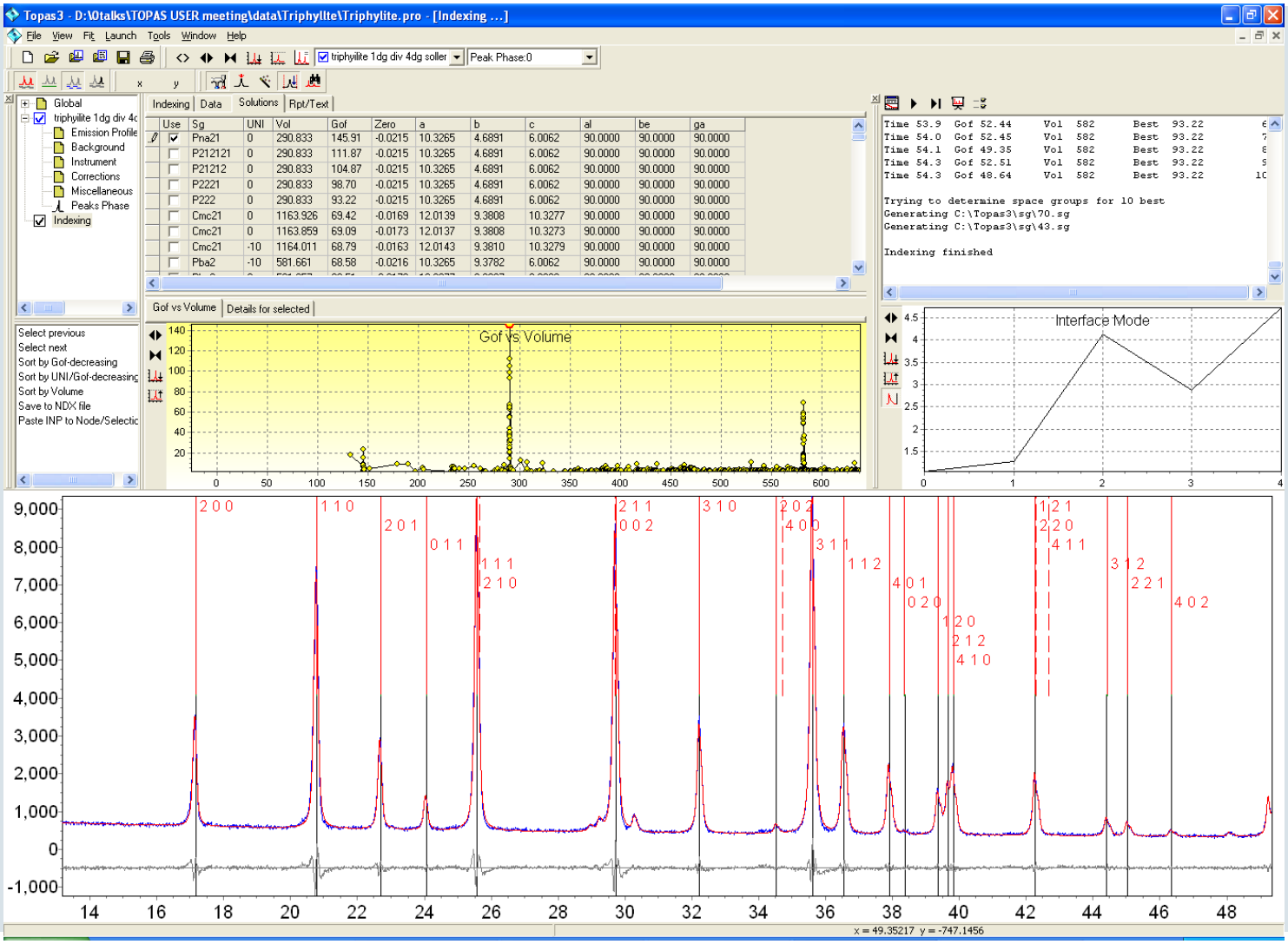
All orthorhombic solutions do not index these 3 peaks → impurity phase

Mineral Triphylite (LiFePO4)
Second Indexing run without impurity peaks





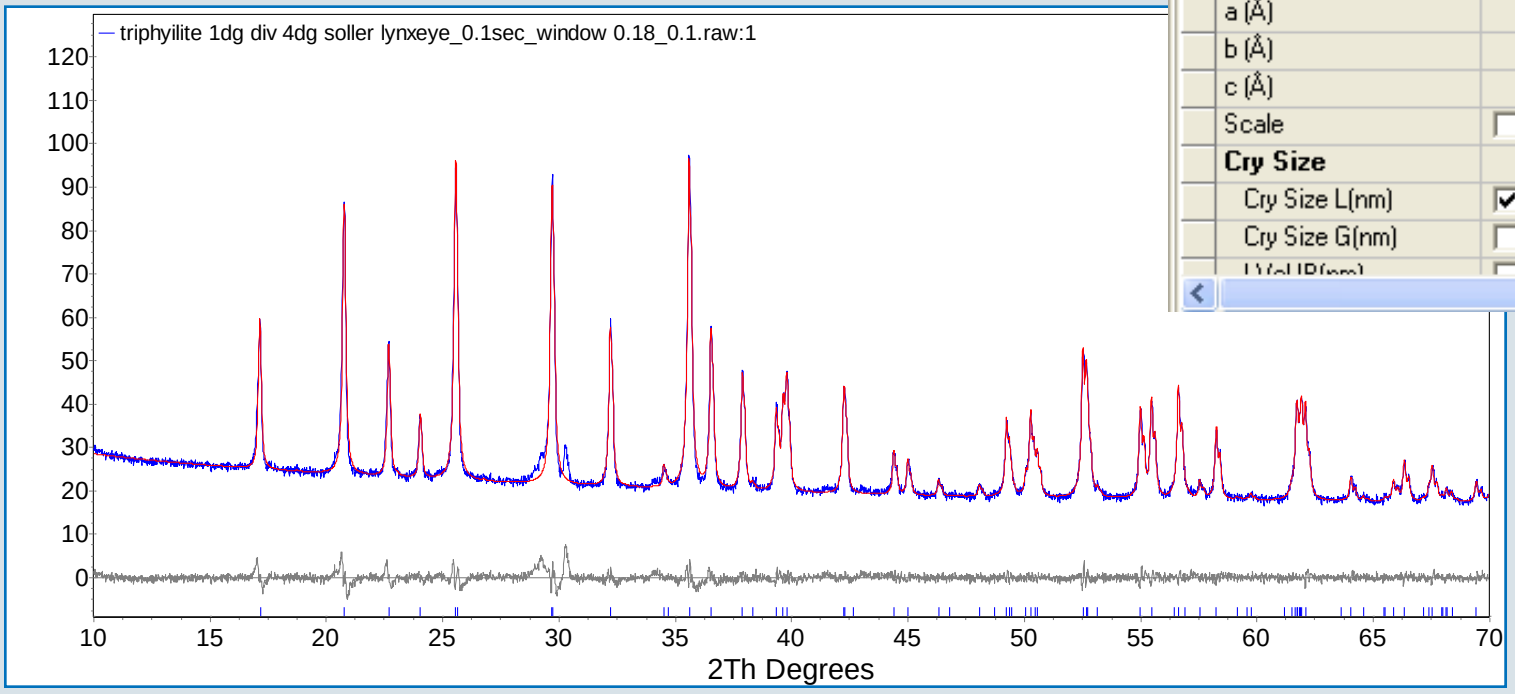
Mineral Triphylite (LiFePO4)
Second Indexing run without impurity peaks



Mineral Triphylite (LiFePO4)
Whole powder pattern fitting

- **Several orthorhombic solutions fit equally well**

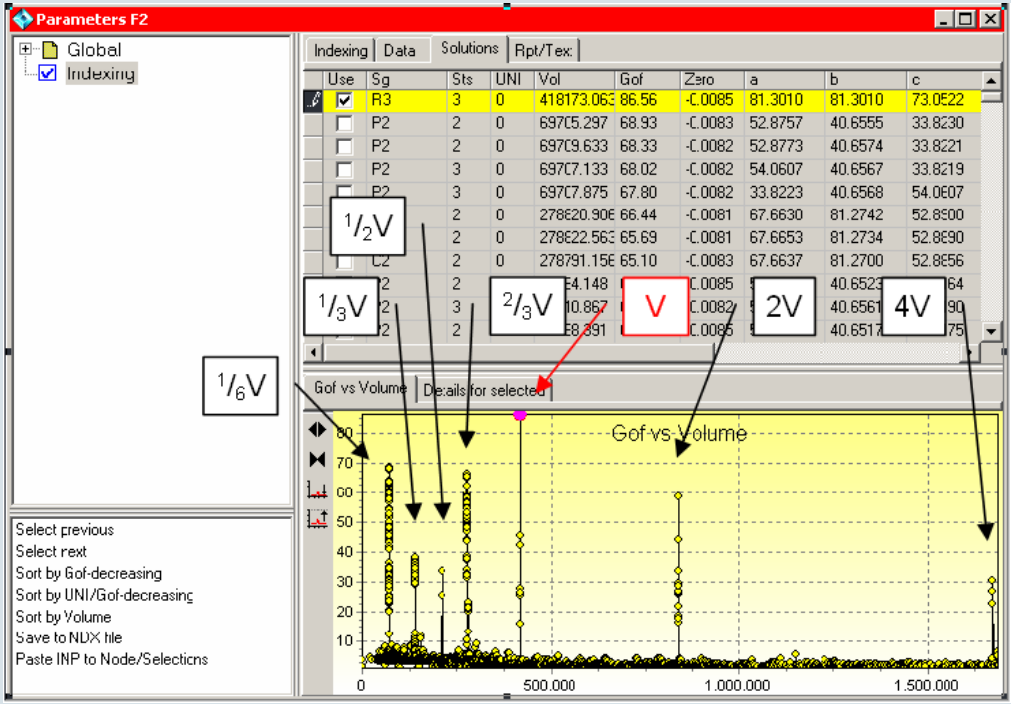
→ **longer measurement range and better quality data necessary to determine space group**



Phase Details	Peak Type	hkls Is	Additional Convo
	Use	Value	Code
Use Phase	☑		
Le Bail	☐		
Delete hkls on Refineme	☑		
LP Search	☐	0.4	
Spacegroup		Pna21	
a (Å)		10.3324020	@
b (Å)		4.6936578	@
c (Å)		6.0075249	@
Scale	☐	0	Fix
Cry Size			
Cry Size L(nm)	☑	121.3	Refine
Cry Size G(nm)	☐	200.0	Refine

Tips and Tricks for Indexing:

- **Indexing will probably never be fool proof**
- **Use 20 to 25 lines for indexing**
- **Use GOF versus volume plot to identify pseudo solutions**
- **Avoid testing all Bravais lattices at the same time**
- **Use intensity weighing, if impurities may be present**
- **You may not be able to find a unique space group in powder diffraction, many space groups have identical hkls.**



- **Trial and error pattern fitting with various space groups can help finding the correct space group**
- **Entering common space groups will make it more likely that the correct space group will be found**

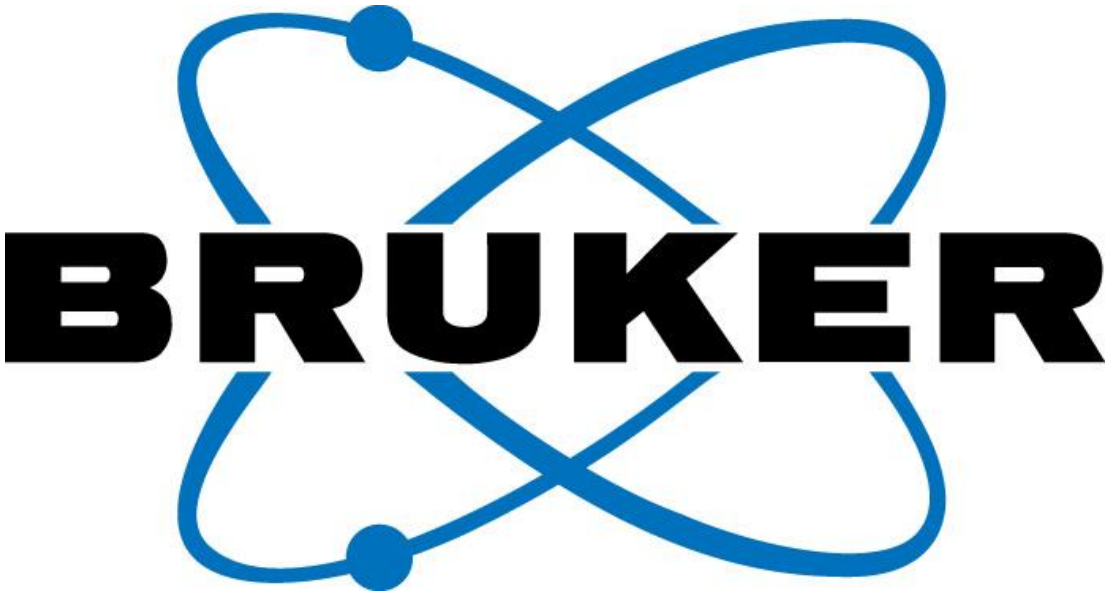
Common Space groups for pharmaceutical samples

Space Group	Frequency
$P2_1/c$	22%
$P2_12_12_1$	10
$P2_1$	10
$C2/c$	5
$P\text{-}1$	3
$P2_12_12$	3
$Pbca$	3
$Pnma$	3
total	59%

Practical TOPAS demonstrations

As time allows:

- LP-Search Examples
  - Lp-Zoplicone dihydrate.pro
- LSI-Index Examples
  - .pro
- Whole powder patter fitting Example
  - AlVO3.pro



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