

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 Decomposition

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

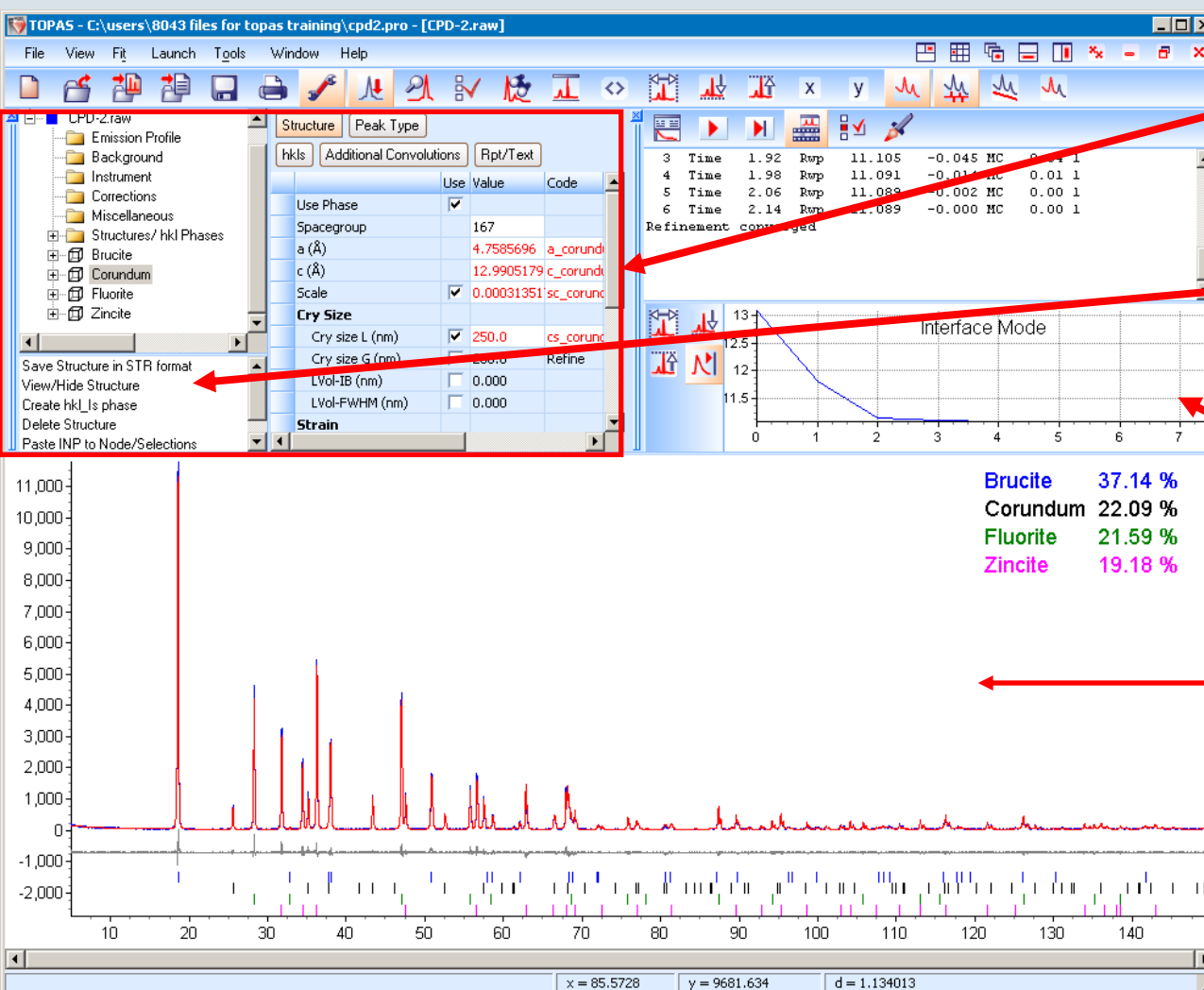
Tutorial example files

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



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
quantitative Rietveld
refinements)

Parameter values

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

	Use	Value	Code	Error	Min	Max
Background						
Chebyshev	<input checked="" type="checkbox"/>		@			
Order		1				
1/X Bkg	<input type="checkbox"/>	1000	Refine	0		
Goniometer radii						
Primary radius (mm)		217.5				
Secondary radius (mm)		217.5				
Equatorial Convolutions						
Point detector	<input checked="" type="checkbox"/>					
Receiving Slit Width (mm)	<input checked="" type="checkbox"/>	0.1	Fix	0		
FDS Shape, angle(°)	<input checked="" type="checkbox"/>	0.5	Fix	0		
Beam spill, sample length	<input type="checkbox"/>	50	Fix	0		
VDS irradiated length (mm)	<input type="checkbox"/>	12	Fix	0		
VDS Scale Intensity	<input type="checkbox"/>					
Capillary	<input type="checkbox"/>					
Linear PSD	<input type="checkbox"/>					
Tube Tails	<input type="checkbox"/>					
Axial Convolutions						
Full Axial Model	<input checked="" type="checkbox"/>					
Source length (mm)		12	Fix	0		
Sample length (mm)		15	Fix	0		
RS length (mm)		12	Fix	0		
Prim. Soller (°)	<input checked="" type="checkbox"/>	2.3	Fix	0		
Sec. Soller (°)	<input checked="" type="checkbox"/>	2.3	Fix	0		
N Beta		30				
Finger_et_al	<input type="checkbox"/>					
Simple Axial Model (mm)	<input type="checkbox"/>	12	Fix	0		

TOPAS GUI: Fit window



Start Refinement (Step by step)

Refinement until convergence

Residual of the Refinement at every refinement step

graphical output of the residual as a functions of iteration number

Launch mode on/off

The screenshot shows the TOPAS GUI Fit window. The main window displays a table of refinement data and a residual plot. The table shows iterations 13 to 17 with columns for Time, Rwp, and other parameters. The residual plot shows the residual decreasing over iterations, with a red arrow pointing to the data point at iteration 4. The 'Refinement Options' dialog box is open, showing various settings for the refinement process.

Iteration	Time	Rwp	Other Parameters
13	1.84	6.882	-0.004 MC 0.01 1
14	1.86	6.880	-0.002 MC 0.00 1
15	1.89	6.877	-0.003 MC 0.00 1
16	1.91	6.876	-0.001 MC 0.02 1
17	1.94	6.876	-0.001 MC 0.01 1

Refinement converged

*** Parameter(s) close to limit(s).
Check for LIMIT_MIN and LIMIT_MAX in Grid/Text

Interface Mode

Graphics Response Time (secs) 0.02

Ok

Profile Fitting Methods

■ Analytical Profile Fitting

- Empirical description of observed line profile shapes through analytical functions such as Lorentian, Gaussian or mixtures such as Pseudo Voigt 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:
 $Y(2q) = (W \times G) \times S$, where $I = (W \times G)$
 - Measured I : Conventional Approach
 - Calculated I : Fundamental Parameters Approach (FPA)

Deconvolution / Convolution Methods

Basic Principle



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

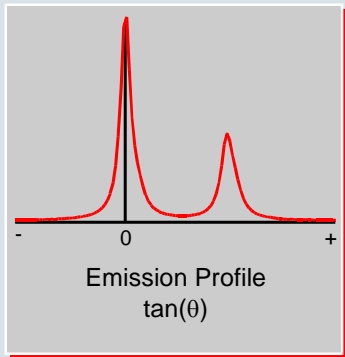
$$Y(2\theta) = (W \times G) \times S$$

W: Emission profile **G:** Instrument contribution

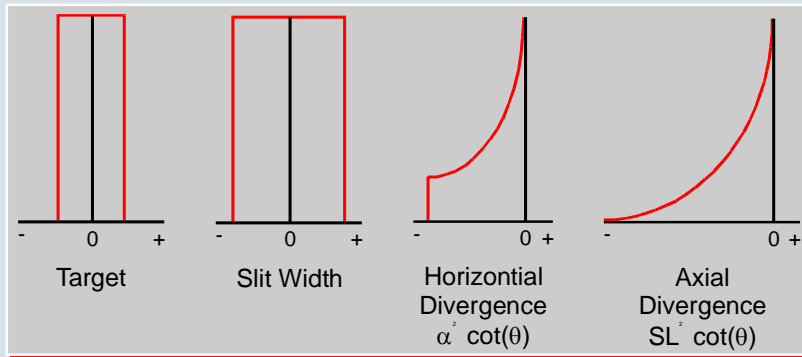
S: Sample contribution

- 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.

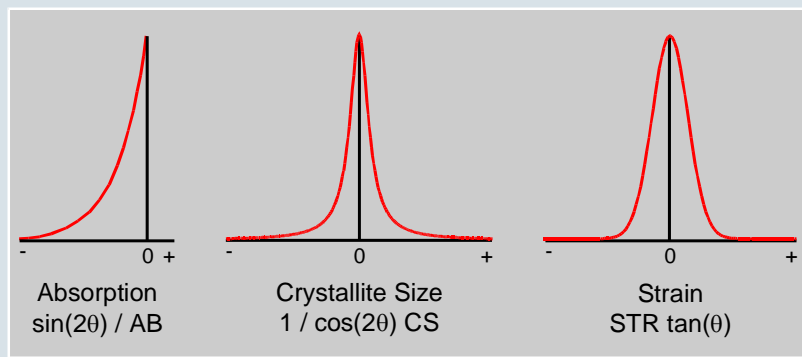
Convolution Synthesis of Line Profiles



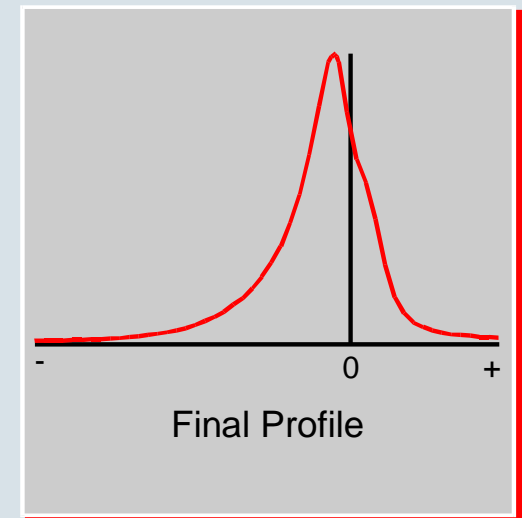
W



G



S



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

Data collection

Bragg-Brentano Geometry



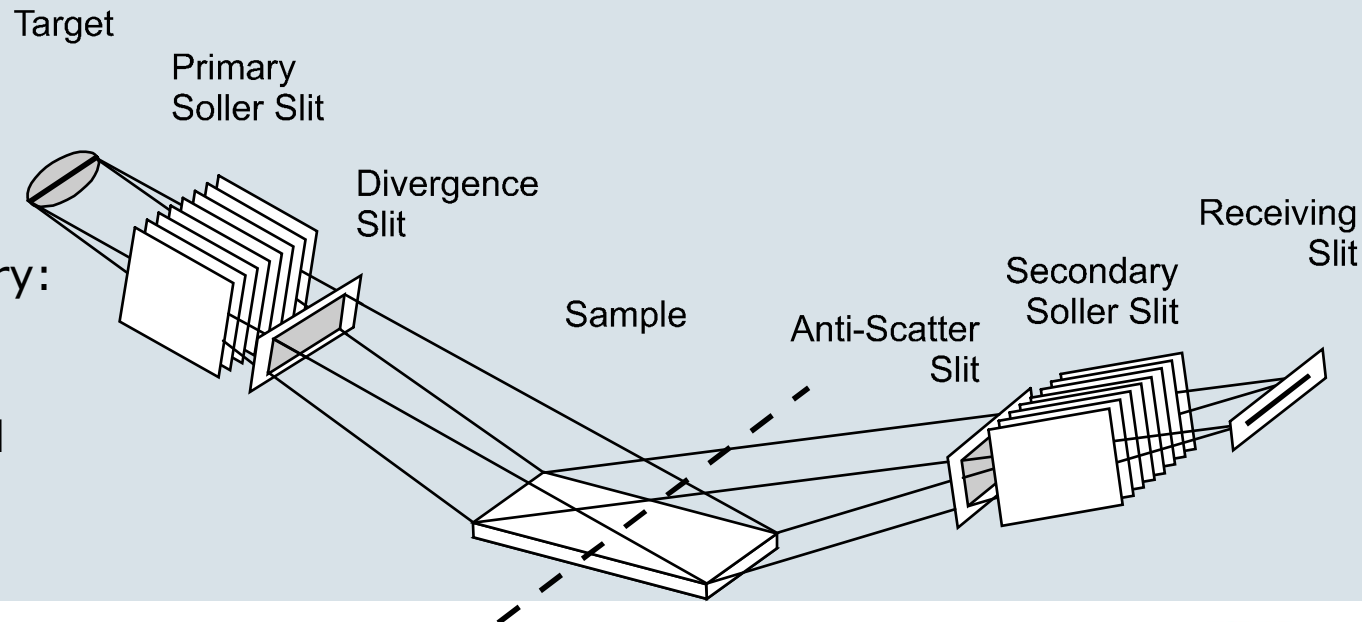
Instrument parameter notation in TOPAS:

- 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

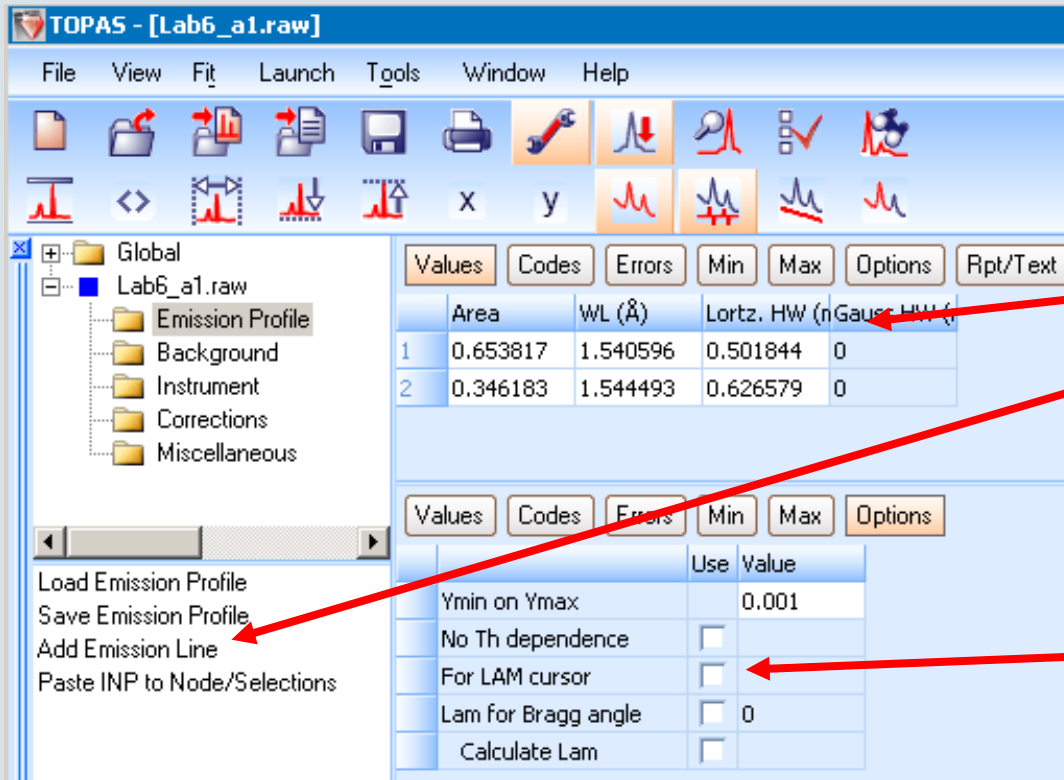
Tube tails: Default settings correspond to fine focus tubes and rarely need to be refined or changed

Parafocussing Geometry:
Error because of flat specimen

Errors because of axial and equatorial divergence



Choose an Emission Profile



TOPAS - [Lab6_a1.raw]

File View Fit Launch Tools Window Help

Global
Lab6_a1.raw
Emission Profile
Background
Instrument
Corrections
Miscellaneous

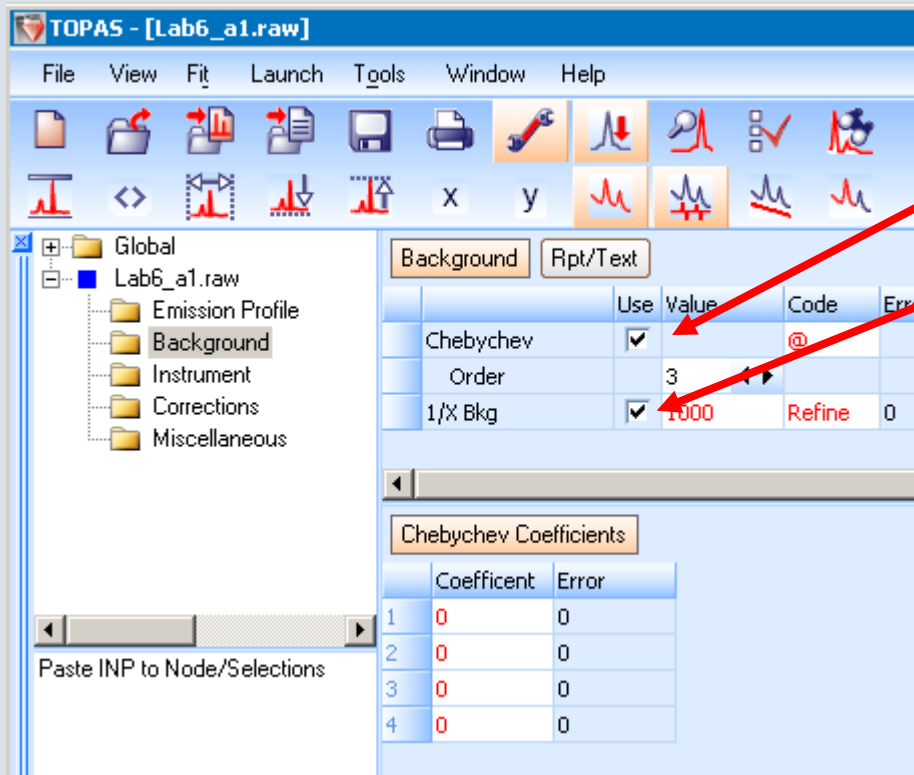
	Area	WL (Å)	Lortz. HW (nGauss)	HW (Å)
1	0.653817	1.540596	0.501844	0
2	0.346183	1.544493	0.626579	0

	Use	Value
Ymin on Ymax		0.001
No Th dependence	<input type="checkbox"/>	
For LAM cursor	<input type="checkbox"/>	
Lam for Bragg angle	<input type="checkbox"/>	0
Calculate Lam	<input type="checkbox"/>	

Load Emission Profile
Save Emission Profile
Add Emission Line
Paste INP to Node/Selections

- 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, $Cu\alpha_1$ and $Cu\alpha_2$.
- If a residual of the $k\beta$ line is visible for measurements with Ni filter and very intense peaks, an emission line with 1.39222Å 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



	Use	Value	Code	Err
Chebychev	<input checked="" type="checkbox"/>		@	
Order		3		
1/X Bkg	<input checked="" type="checkbox"/>	1000	Refine	0

	Coefficient	Error
1	0	0
2	0	0
3	0	0
4	0	0

- 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



TOPAS - [Lab6_a1.raw]

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Divergent beam Additional Convolutions Hpt/Text

	Use	Value	Code	Erro
Goniometer radii				
Primary radius (mm)		217.5		
Secondary radius (mm)		217.5		
Equatorial Convolutions				
Point detector	<input checked="" type="checkbox"/>			
Receiving Slit Width (mm)	<input checked="" type="checkbox"/>	0.1	Fix	0
FDS Shape, angle(°)	<input checked="" type="checkbox"/>	1	Fix	0
Beam spill, sample length (mm)	<input type="checkbox"/>	50	Fix	0
VDS irradiated length (mm)	<input type="checkbox"/>	12	Fix	0
VDS Scale Intensity	<input type="checkbox"/>			
Capillary	<input type="checkbox"/>			
Linear PSD	<input type="checkbox"/>			
Tube Tails	<input type="checkbox"/>			
Axial Convolutions				
Full Axial Model	<input checked="" type="checkbox"/>			
Source length (mm)		12	Fix	0
Sample length (mm)		15	Fix	0
RS length (mm)		12	Fix	0
Prim. Soller (°)	<input checked="" type="checkbox"/>	2.3	Fix	0
Sec. Soller (°)	<input checked="" type="checkbox"/>	2.3	Fix	0
N Beta		30		
Finger_et_al	<input type="checkbox"/>			
Simple Axial Model (mm)	<input type="checkbox"/>	12	Fix	0

Load Instrument Details
Save Instrument Details
Paste INP to Node/Selections

- 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

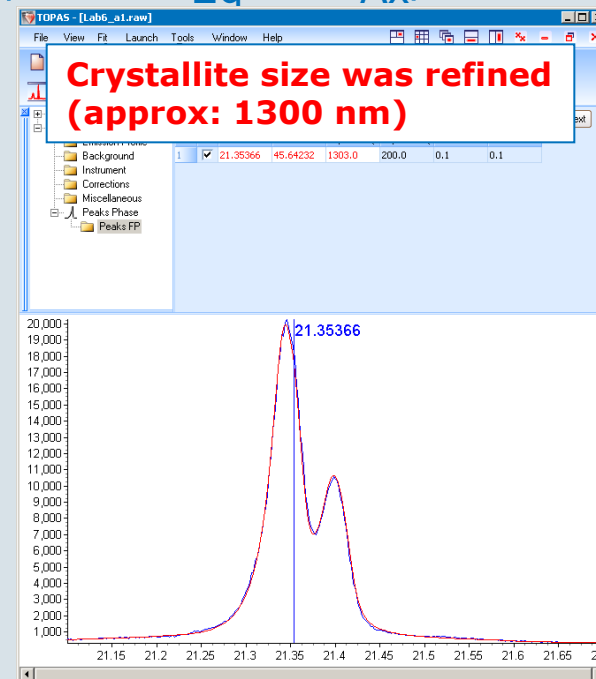
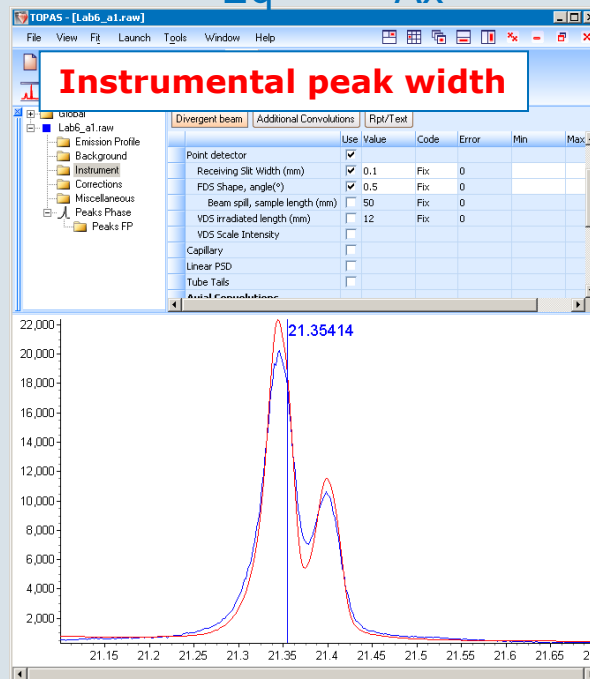
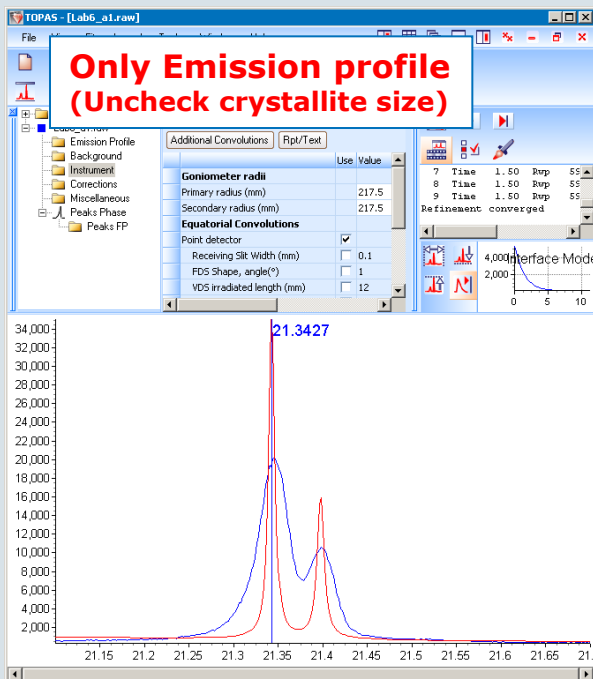
FPA Example for LaB₆ (111)

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°

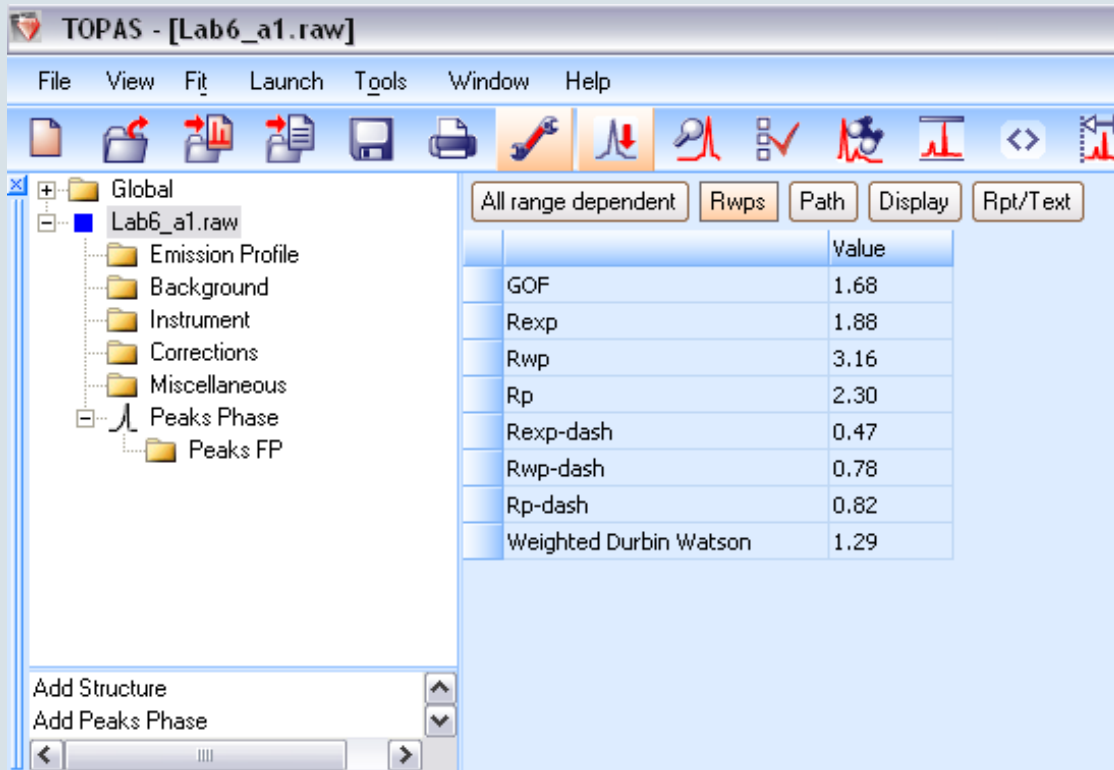
Receiving slit: 0.1mm

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.

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

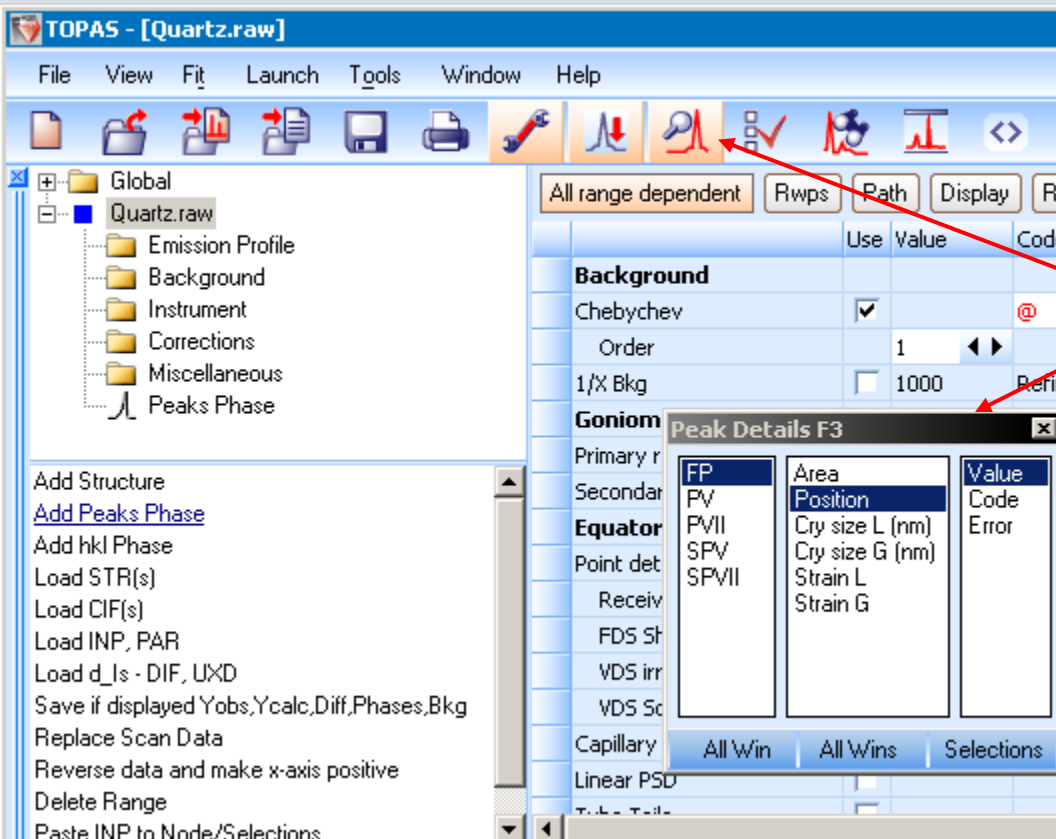
Other numerical indicators:

Goodness of fit: $GOF = Rwp/Rexp$

Rwp-dash: background subtracted residuals

Profile Fitting in TOPAS

Peaks Phases



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 Voigt function

PVII: Pearson VII function

SPV: Split Pseudo Voigt function

SPVII: Split Pearson VII function

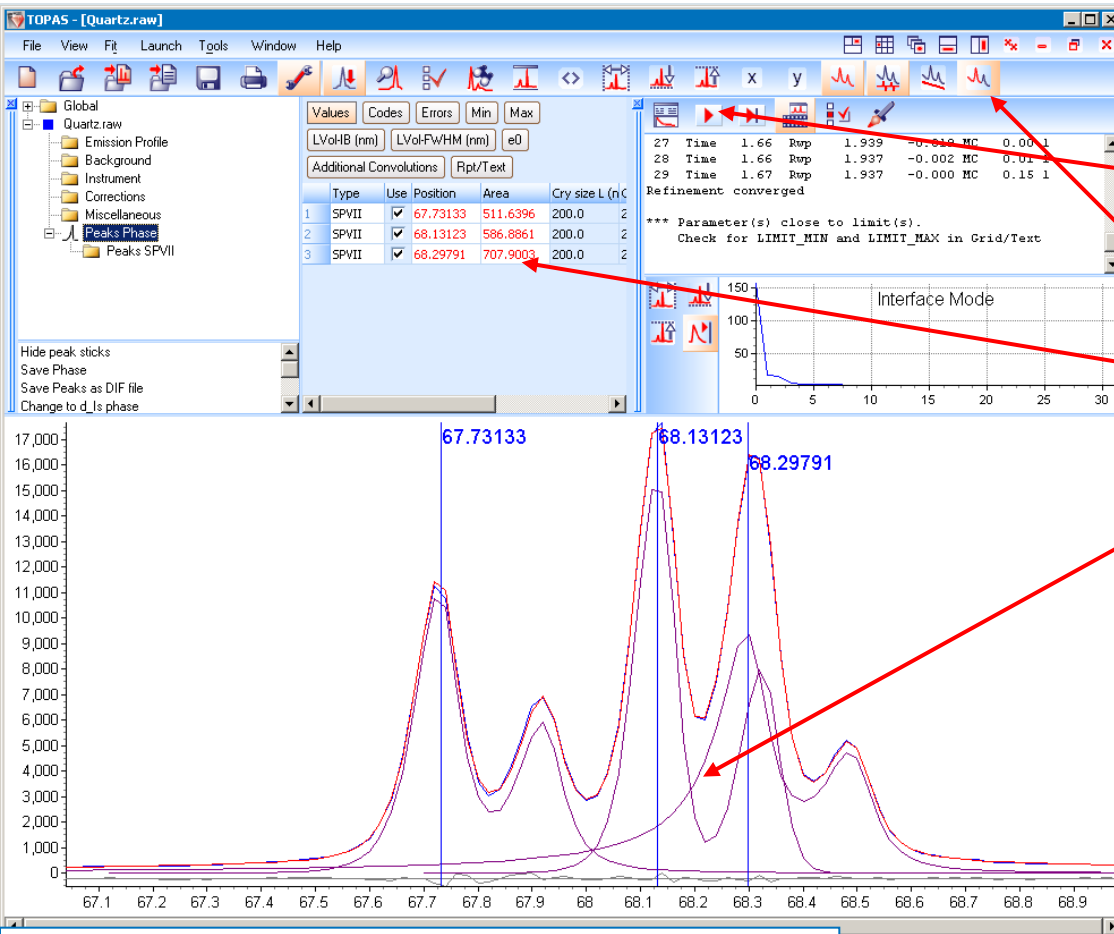
The second column allows display of position, area, crystallite size or strain at the peak

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

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

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

Use	Position	Area	FWHM Left	FWHM Right	M Left	M Right
<input checked="" type="checkbox"/>	67.73133	511.6396	0.05504582	0.03754237	2.506625	1.278807
<input checked="" type="checkbox"/>	68.13123	586.8861	0.04567504	0.03597622	2.915417	9.179479
<input checked="" type="checkbox"/>	68.29791	707.9003	0.06775916	0.04041264	0.7614877	1.232083

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 LVolHB (nm) LVol-FWHM (nm) e0 Rpt/Text

	Use	Position	Area	FWHM Left	FWHM Right	M Left	M Right
1	<input checked="" type="checkbox"/>	67.73133	511.6396	0.05	0.05	1	1
2	<input checked="" type="checkbox"/>	68.13123	586.8861	0.05	0.05	1	1
3	<input checked="" type="checkbox"/>	68.29791	707.9003	0.05	0.05	1	1

Values Codes Errors Min

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

	Use	Position	Position	Area	FWHM Le	FWHM Rig	M Left	M Right
1	<input checked="" type="checkbox"/>	67.73133	Refine	Refine	FWHML	FWHMR	ML	Mr
2	<input checked="" type="checkbox"/>	68.13123	Refine	Refine	FWHML	FWHMR	ML	Mr
3	<input checked="" type="checkbox"/>	68.29791	Refine	Refine	FWHML	FWHMR	ML	Mr

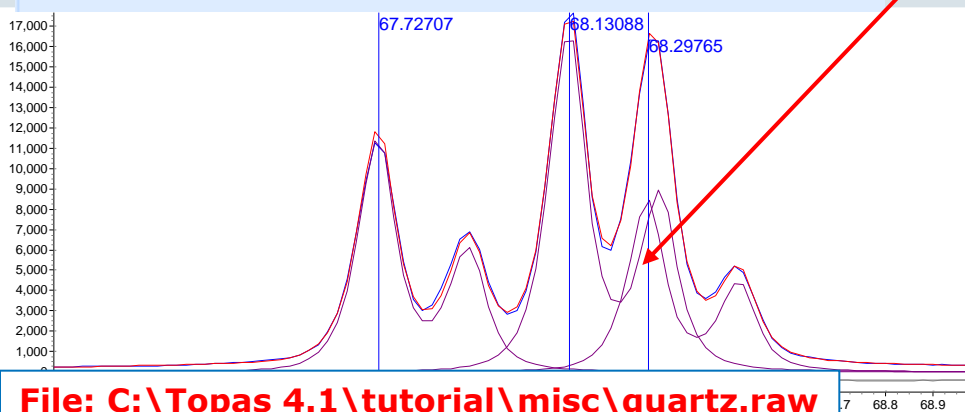
To change a whole column to the same value, click on the upper right corner of the grid

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 LVolHB (nm) LVol-FWHM (nm) e0 Rpt/Text

	Use	Position	Area	FWHM Left	FWHM Right	M Left	M Right
1	<input checked="" type="checkbox"/>	67.72707	532.3152	0.04967582	0.04142547	1.86854	1.421101
2	<input checked="" type="checkbox"/>	68.13088	768.883	0.04967582	0.04142547	1.86854	1.421101
3	<input checked="" type="checkbox"/>	68.29765	385.4827	0.04967582	0.04142547	1.86854	1.421101

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

Profile Fitting in TOPAS

Peaks Phases, Fundamental parameters as an intrinsic constraint

TOPAS - C:\users\8043 files for topas training\test.pro - [Quartz.raw]

File View Fit Launch Tools Window Help

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 Quartz.raw
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 Peaks Phase:0
 Peaks FP

Divergent beam Additional Convolutions Rpt/Text

	Use	Value
Goniometer radii		
Primary radius (mm)		217.5
Secondary radius (mm)		217.5
Equatorial Convolutions		
Point detector	<input checked="" type="checkbox"/>	
Receiving Slit Width (mm)	<input checked="" type="checkbox"/>	0.1
FDS Shape, angle(°)	<input checked="" type="checkbox"/>	1
Beam spill, sample length (mm)	<input type="checkbox"/>	50
VDS irradiated length (mm)	<input type="checkbox"/>	12
VDS Scale Intensity	<input type="checkbox"/>	
Capillary	<input type="checkbox"/>	
Linear PSD	<input type="checkbox"/>	
Tube Tails	<input type="checkbox"/>	
Axial Convolutions		
Full Axial Model	<input checked="" type="checkbox"/>	

Global
 Quartz.raw
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 Peaks Phase:0
 Peaks FP

Values Codes Errors Min

Max LVolHB (nm) LVolFWHM (nm)

	Type	Use	Position
1	FP	<input checked="" type="checkbox"/>	67.7318
2	FP	<input checked="" type="checkbox"/>	68.13618
3	FP	<input checked="" type="checkbox"/>	68.30136

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

Global
 Quartz.raw
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 Peaks Phase:0
 Peaks FP

Values Codes Errors Min Max LVolHB (nm) LVolFWHM (nm) e0 Rpt/Text

	Use	Position	Area	Min	Max	LVolHB (nm)	LVolFWHM (nm)	e0	Rpt/Text
1	<input checked="" type="checkbox"/>	67.7318	595.1021	237.0		200.0	0.1	0.1	
2	<input checked="" type="checkbox"/>	68.13618	833.056	285.8		200.0	0.1	0.1	
3	<input checked="" type="checkbox"/>	68.30136	444.1307	228.4		200.0	0.1	0.1	

Profile Fitting in TOPAS

Peaks Phases

TOPAS - C:\users\8043 files for topas training\test.pro - [Quartz.raw]

File View Fit Launch Tools Window Help

Quartz.raw

- Emission Profile
- Background
- Instrument
- Corrections
- Miscellaneous
- Peaks Phase:0
- Peaks SPVII

Values Codes Errors Min Max

LVolHB (nm) LVol-FWHM (nm) e0 Additional Convolutions

	Type	Use	Position	Area	Cry size L (n	Cry size G
1	SPVII	<input checked="" type="checkbox"/>	67.72927	532.1825	200.0	200.0
2	SPVII	<input checked="" type="checkbox"/>	68.13253	769.1925	200.0	200.0
3	SPVII	<input checked="" type="checkbox"/>	68.29935	386.5809	200.0	200.0

Hide peak sticks

Save Phase

Save Peaks as DIF file

Change to d_ls phase

Create Indexing Range

Create Pawley range

Delete Peaks Phase

Paste INP to Node/Selections

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

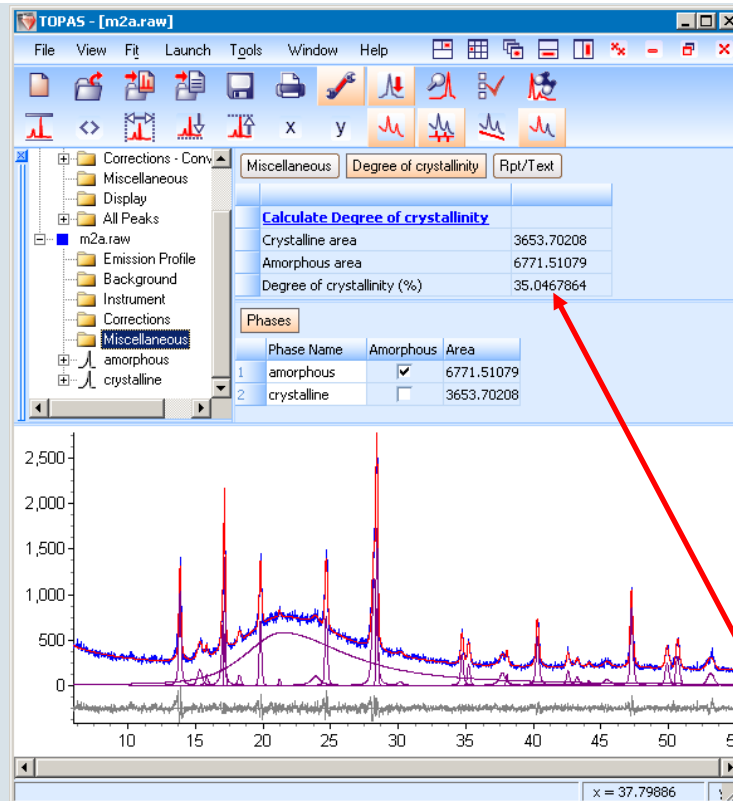
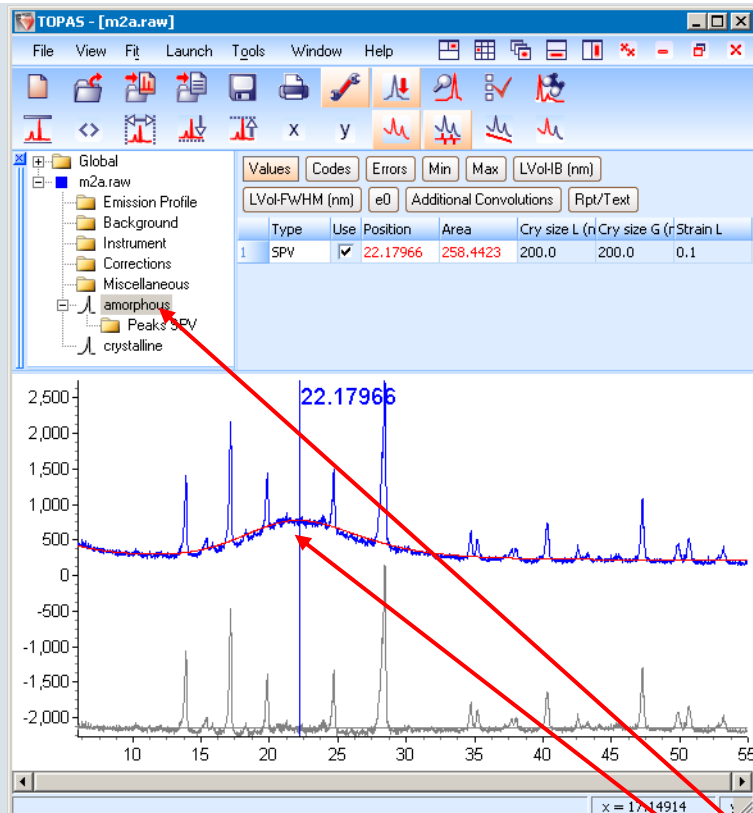
File: C:\Topas 4.1\tutorial\misc\quartz.raw

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

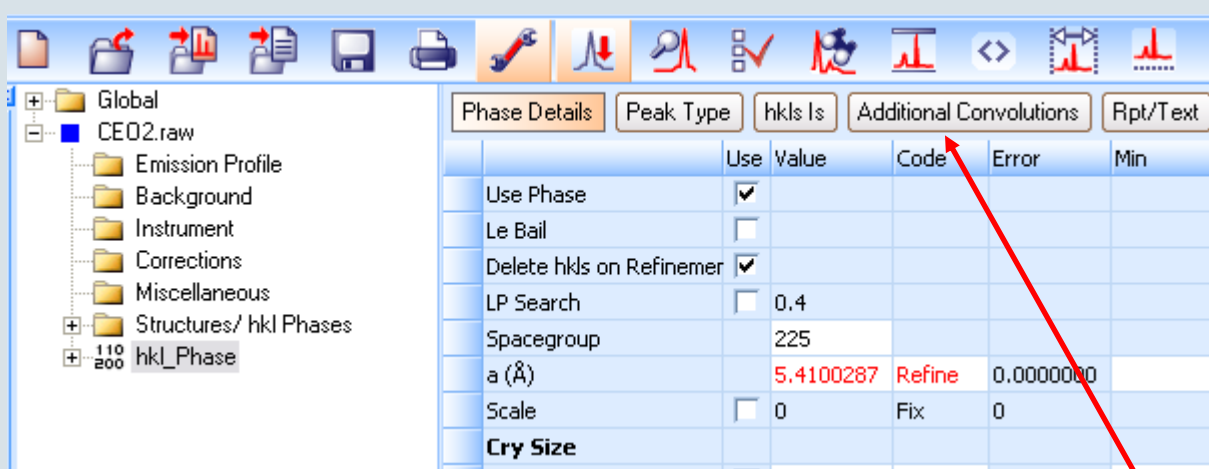
Background order 1

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

Pawley or LeBail fit

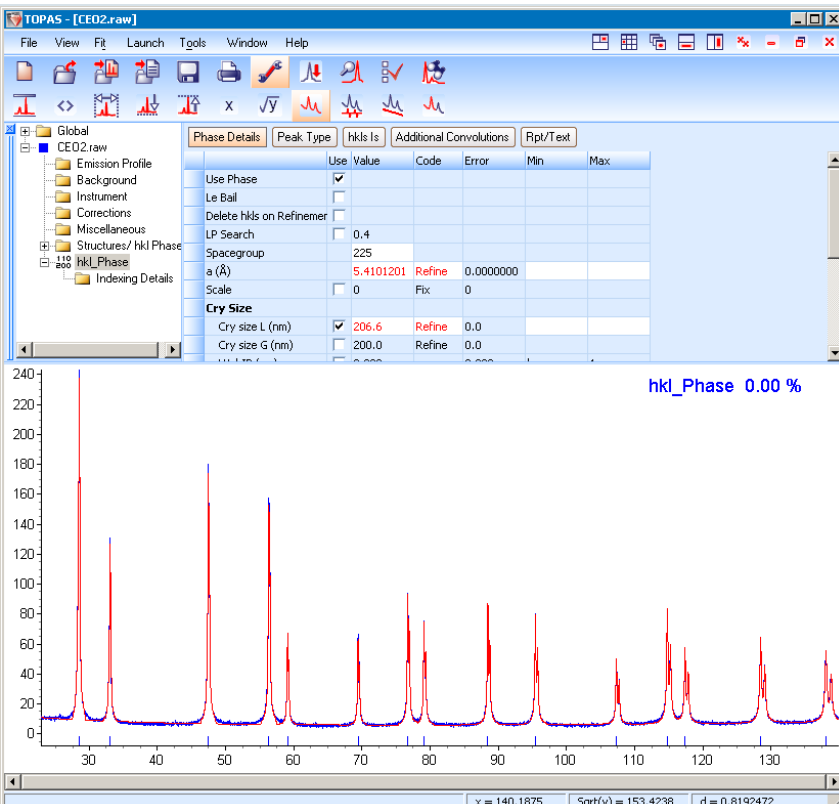
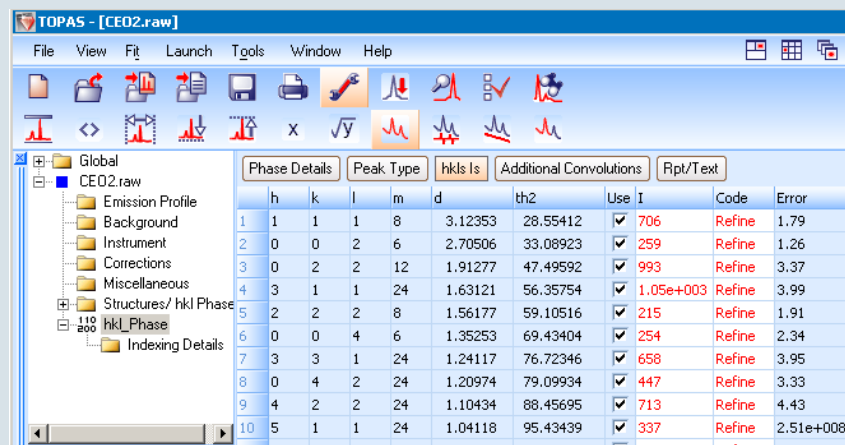


	Use	Value	Code	Error	Min
Use Phase	<input checked="" type="checkbox"/>				
Le Bail	<input type="checkbox"/>				
Delete hkl's on Refinement	<input checked="" type="checkbox"/>				
LP Search	<input type="checkbox"/>	0.4			
Spacegroup		225			
a (Å)		5.4100287	Refine	0.0000000	
Scale	<input type="checkbox"/>	0	Fix	0	
Cry Size					

- 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

h	k	l	m	d	th2	Use	I	Code	Error
1	1	1	1	8	3.12353	<input checked="" type="checkbox"/>	706	Refine	1.79
2	0	0	2	6	2.70506	<input checked="" type="checkbox"/>	259	Refine	1.26
3	0	2	2	12	1.91277	<input checked="" type="checkbox"/>	993	Refine	3.37
4	3	1	1	24	1.63121	<input checked="" type="checkbox"/>	1.05e+003	Refine	3.99
5	2	2	2	8	1.56177	<input checked="" type="checkbox"/>	215	Refine	1.91
6	0	0	4	6	1.35253	<input checked="" type="checkbox"/>	254	Refine	2.34
7	3	3	1	24	1.24117	<input checked="" type="checkbox"/>	658	Refine	3.95
8	0	4	2	24	1.20974	<input checked="" type="checkbox"/>	447	Refine	3.33
9	4	2	2	24	1.10434	<input checked="" type="checkbox"/>	713	Refine	4.43
10	5	1	1	24	1.04118	<input checked="" type="checkbox"/>	337	Refine	2.51e+008

File: C:\Topas 4.1\tutorial\ce02\ce02.raw

Measurement circle radius: 173mm

Emission profile: CuKa5.lam

Background order 3, 1/x function

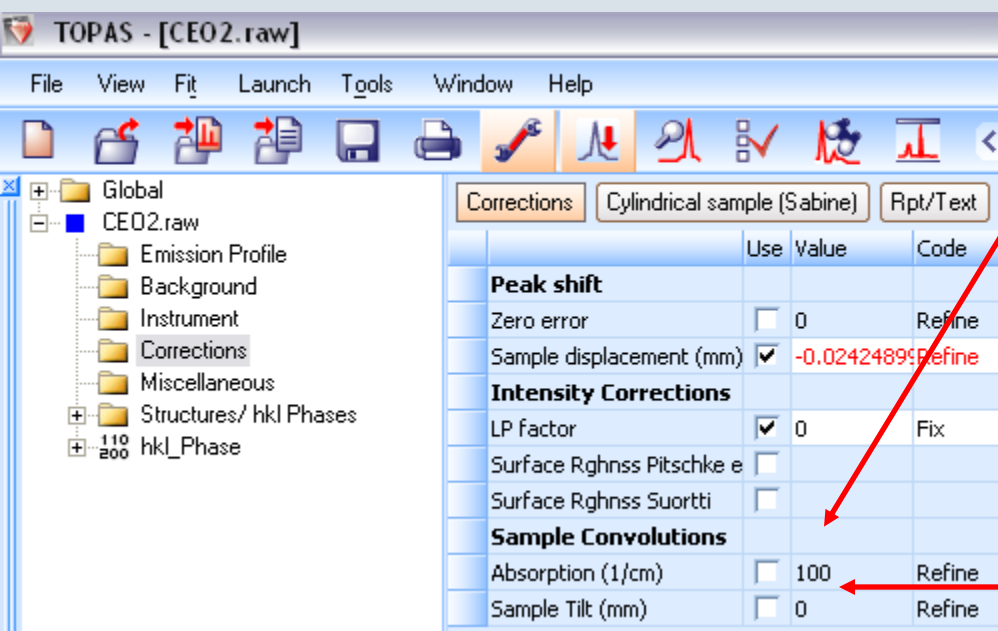
Divergence: 1°, Receiving slit: 0.1mm

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

Phase Details		Peak Type	hkls	Is	Additional Con
	Use	Value			Code
a (Å)	<input checked="" type="checkbox"/>	5.4100287			Refine
Scale	<input type="checkbox"/>	0			Fix
Cry Size					
Cry size L (nm)	<input checked="" type="checkbox"/>	208.7			Refine
Cry size G (nm)	<input type="checkbox"/>	200.0			Refine
LVol-IB (nm)	<input checked="" type="checkbox"/>	132.851			
LVol-FWHM (nm)	<input checked="" type="checkbox"/>	185.727			
Strain					
Strain L	<input type="checkbox"/>	0.1			Refine
Strain G	<input checked="" type="checkbox"/>	0.01210106			Refine
e0	<input checked="" type="checkbox"/>	0.00303			

- 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.

$$\beta_{int_s} = \frac{\lambda}{L_{vol} \cdot \cos \theta}$$

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

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: CuK α 1.lam (Vario Data)

1mm Capillary data with LynxEye detector

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

EVA - [JCP2.2CA:00-032-1723]

File Pattern View Options Window Help

PDF Number: 00-032-1723 View Quality: High

C₁₃H₁₈O₂

Ibuprofen

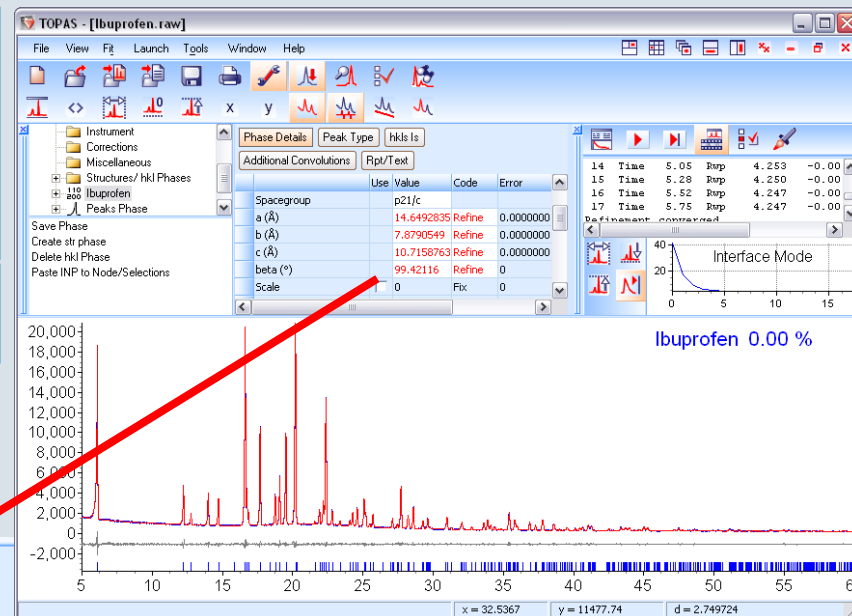
General Comments Authors Additional Subfiles

Cell Parameters		Crystal Data	
Latt.:	Monoclinic	Molecular weight:	206.28
S.G.:	P21/c (14)	Volume [CD]:	1226.33
a: 14.667	alpha:	Dx:	1.117
b: 7.899	beta: 99.46	Dm:	
c: 10.731	gamma:	Z:	4
a/b: 1.85682	Z:	I/Cor:	
c/b: 1.35853			

Phase Details Peak Type hkl's

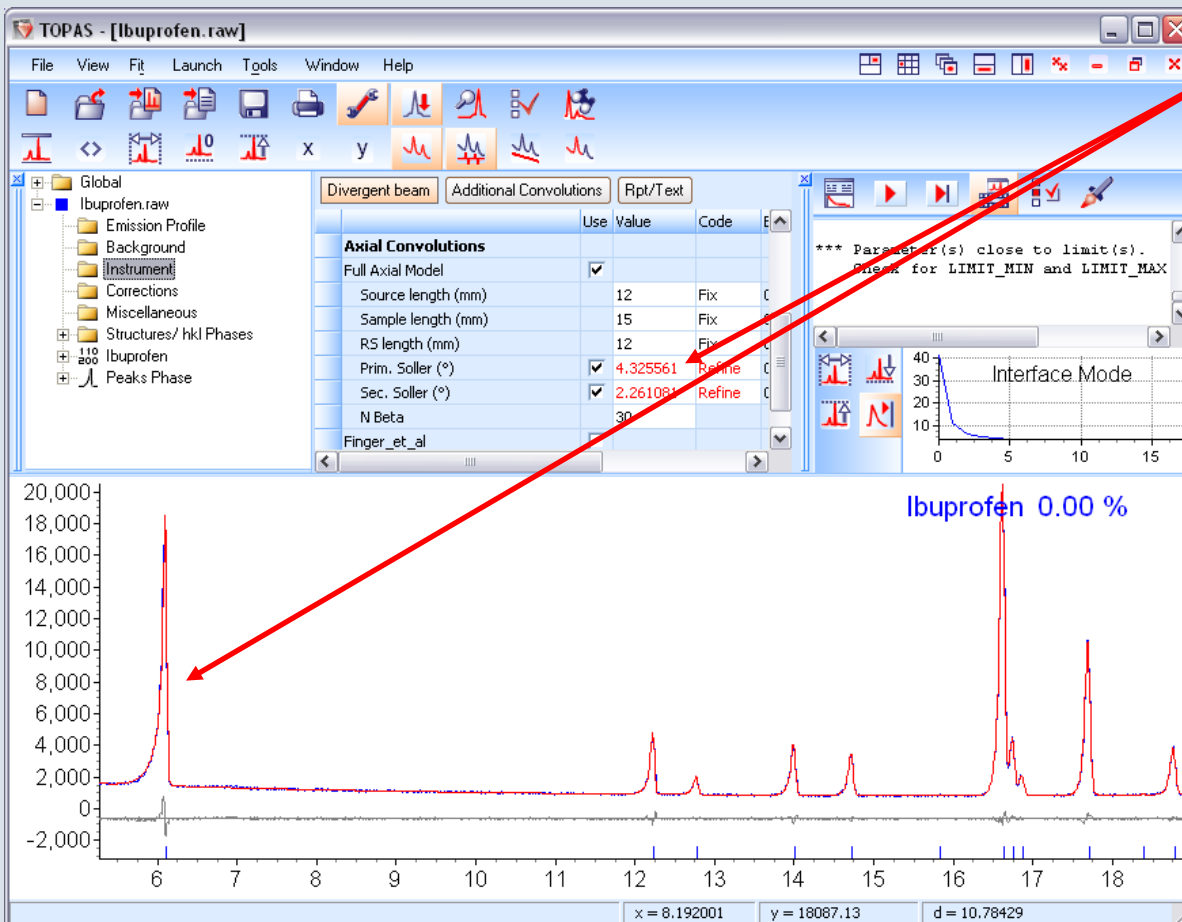
Additional Convolutions Rpt/Text

	Use	Value	Code
Use Phase	<input checked="" type="checkbox"/>		
Le Bail	<input type="checkbox"/>		
Delete hkl's on Refinement	<input checked="" type="checkbox"/>		
LP Search	<input type="checkbox"/>	0.4	
Spacegroup		p21/c	
a (Å)		14.6492835 Refine	
b (Å)		7.8790549 Refine	
c (Å)		10.7158763 Refine	
beta (°)		99.42116 Refine	
Scale	<input type="checkbox"/>	0	Fix



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-Voigt was selected as peak type

Phase Details	Peak Type	hkl's
Ibuprofen	PV_TCHZ	
U	-0.139598	Refine
V	0.05492111	Refine
W	-0.00357546	Refine
Z	0	Fix
X	0.02598721	Refine
Y	0	Fix

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
$$\text{FOM} = \sum_j \sum_i I(2\theta_i) |2\theta_i - 2\theta_{0,j}|$$
 - 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

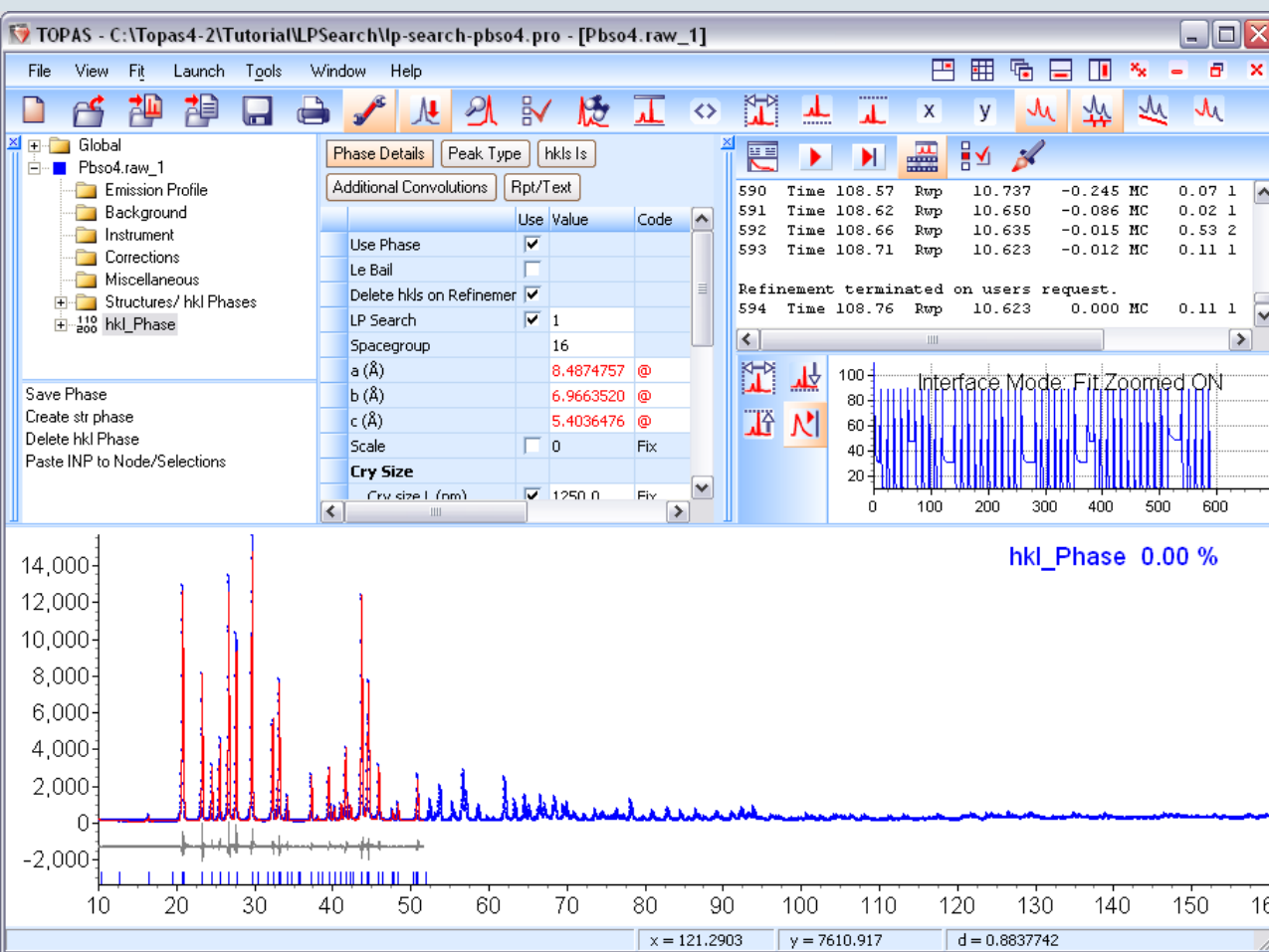
■ LSI-Index Approach

- Perform a Peak profile fitting preferably using the **Fundamental Parameters Approach**
- 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



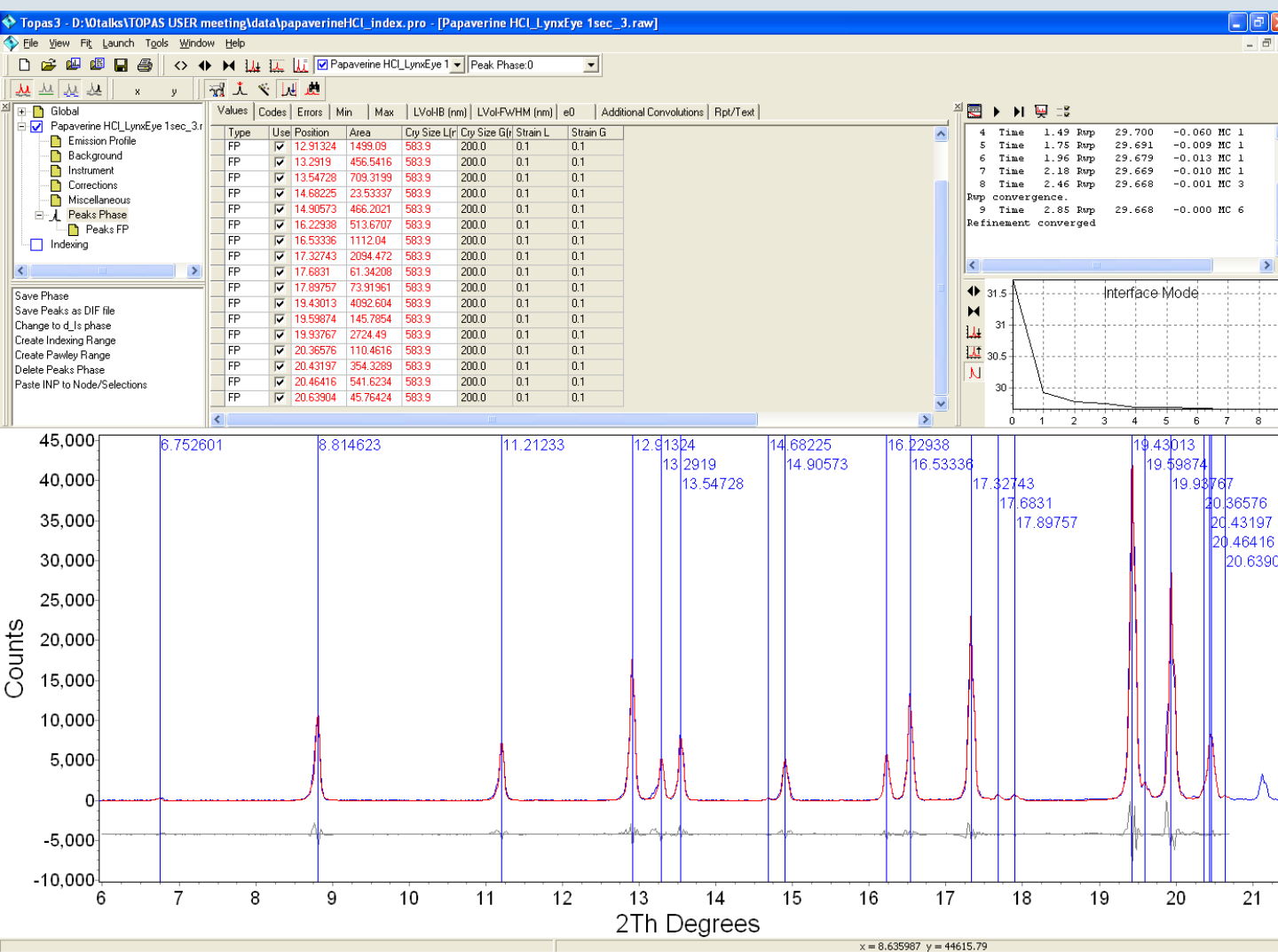
■ A solution is often found within seconds sometimes it takes minutes

■ 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 volume and rwp

Indexing Example: Papaverine hydrochloride

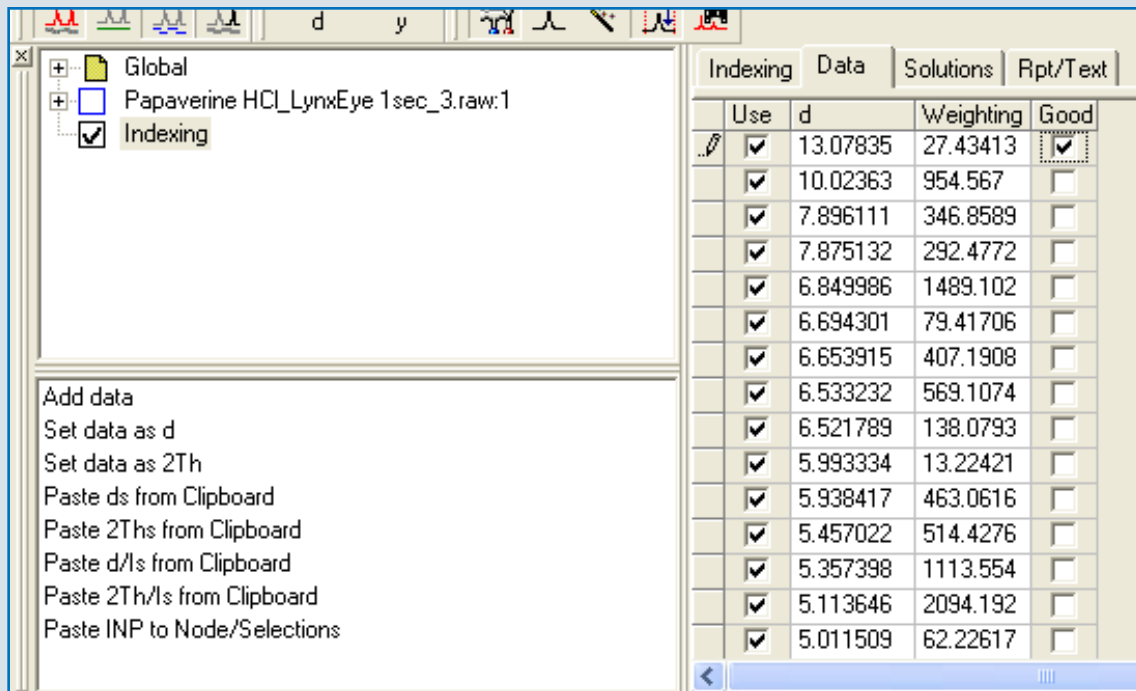


(File: Papaverine HCl_LynxEye 1sec_3.raw)

■ Peak Fit with Fundamental Parameters

■ Creating an Indexing range and paste the 20 highest d-spacing

Papaverine hydrochloride

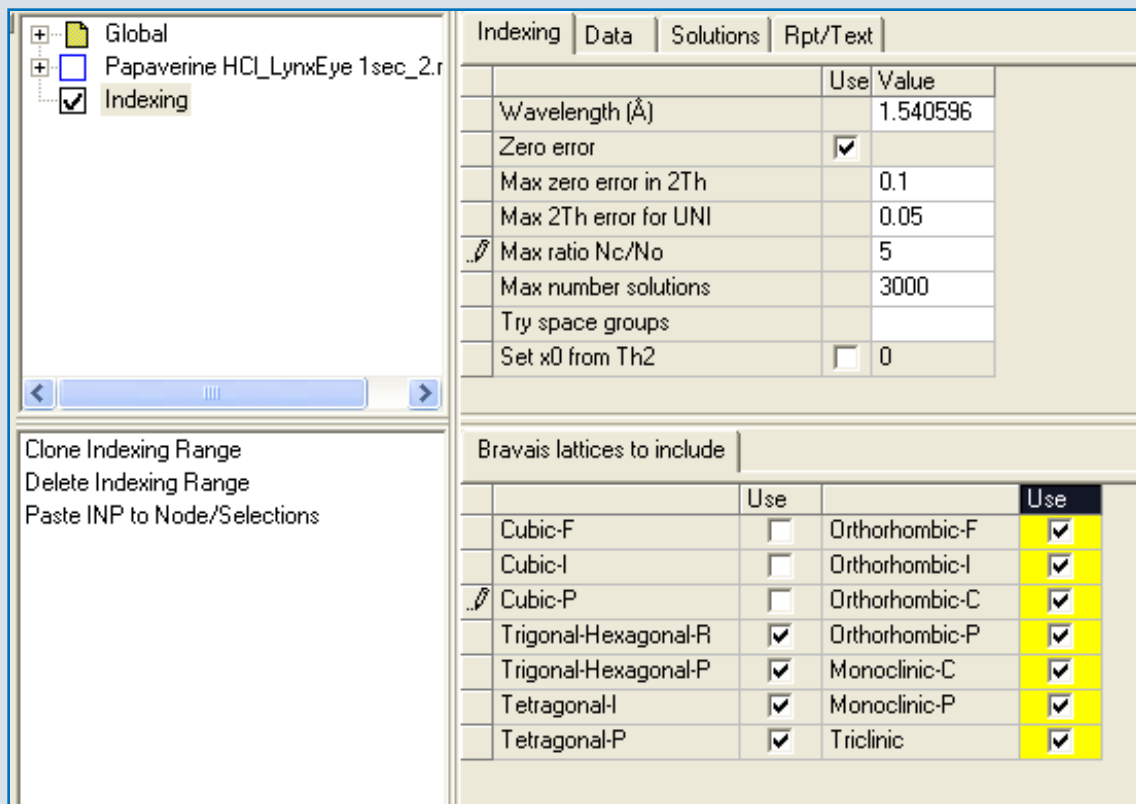


The screenshot shows the Bruker software interface with a table of peak data and a context menu open. The table has columns for 'Use', 'd', 'Weighting', and 'Good'. The context menu is open over the first row, showing options like 'Add data', 'Set data as d', and 'Paste d/ls from Clipboard'.

Use	d	Weighting	Good
<input checked="" type="checkbox"/>	13.07835	27.43413	<input checked="" type="checkbox"/>
<input checked="" type="checkbox"/>	10.02363	954.567	<input type="checkbox"/>
<input checked="" type="checkbox"/>	7.896111	346.8589	<input type="checkbox"/>
<input checked="" type="checkbox"/>	7.875132	292.4772	<input type="checkbox"/>
<input checked="" type="checkbox"/>	6.849986	1489.102	<input type="checkbox"/>
<input checked="" type="checkbox"/>	6.694301	79.41706	<input type="checkbox"/>
<input checked="" type="checkbox"/>	6.653915	407.1908	<input type="checkbox"/>
<input checked="" type="checkbox"/>	6.533232	569.1074	<input type="checkbox"/>
<input checked="" type="checkbox"/>	6.521789	138.0793	<input type="checkbox"/>
<input checked="" type="checkbox"/>	5.993334	13.22421	<input type="checkbox"/>
<input checked="" type="checkbox"/>	5.938417	463.0616	<input type="checkbox"/>
<input checked="" type="checkbox"/>	5.457022	514.4276	<input type="checkbox"/>
<input checked="" type="checkbox"/>	5.357398	1113.554	<input type="checkbox"/>
<input checked="" type="checkbox"/>	5.113646	2094.192	<input type="checkbox"/>
<input checked="" type="checkbox"/>	5.011509	62.22617	<input type="checkbox"/>

- 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/ls from clipboard”
- Apply Weighting “Good” to a low angle peak

Papaverine hydrochloride



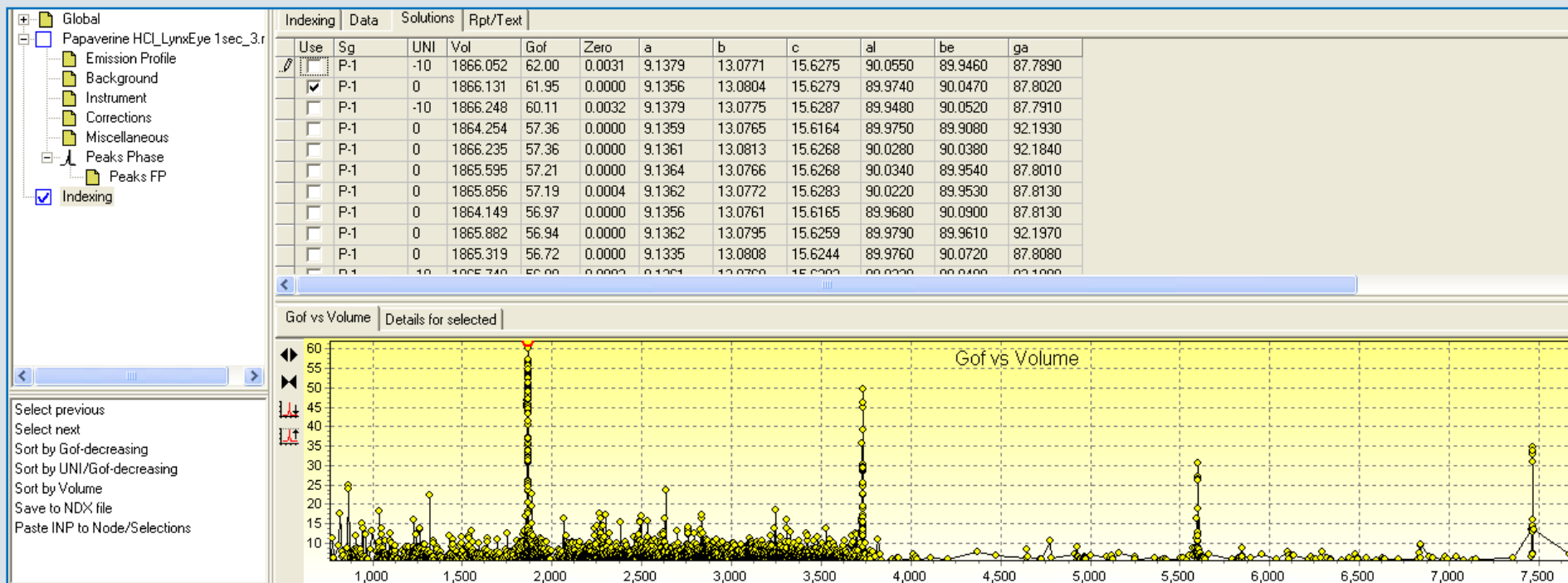
The screenshot shows the 'Indexing' tab in the software interface. The left sidebar shows a tree view with 'Global', 'Papaverine HCl_LynxEye 1sec_2.r', and 'Indexing' (checked). The main area has tabs for 'Indexing', 'Data', 'Solutions', and 'Rpt/Text'. Below the tabs is a table of indexing parameters, and below that is a table of Bravais lattices to include.

	Use	Value
Wavelength (Å)		1.540596
Zero error	<input checked="" type="checkbox"/>	
Max zero error in 2Th		0.1
Max 2Th error for UNI		0.05
Max ratio Nc/No		5
Max number solutions		3000
Try space groups		
Set x0 from Th2	<input type="checkbox"/>	0

Bravais lattices to include		Use	Use
Cubic-F	<input type="checkbox"/>	Orthorhombic-F	<input checked="" type="checkbox"/>
Cubic-I	<input type="checkbox"/>	Orthorhombic-I	<input checked="" type="checkbox"/>
Cubic-P	<input type="checkbox"/>	Orthorhombic-C	<input checked="" type="checkbox"/>
Trigonal-Hexagonal-R	<input checked="" type="checkbox"/>	Orthorhombic-P	<input checked="" type="checkbox"/>
Trigonal-Hexagonal-P	<input checked="" type="checkbox"/>	Monoclinic-C	<input checked="" type="checkbox"/>
Tetragonal-I	<input checked="" type="checkbox"/>	Monoclinic-P	<input checked="" type="checkbox"/>
Tetragonal-P	<input checked="" type="checkbox"/>	Triclinic	<input checked="" type="checkbox"/>

- 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



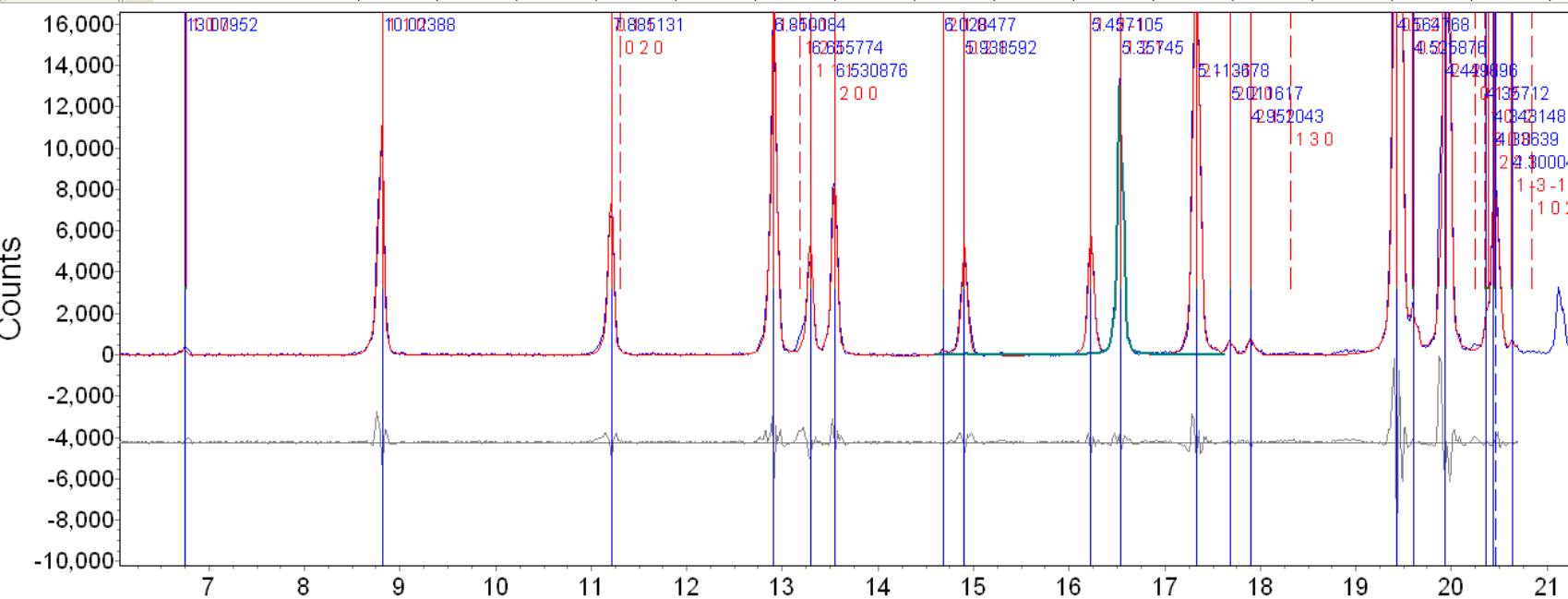
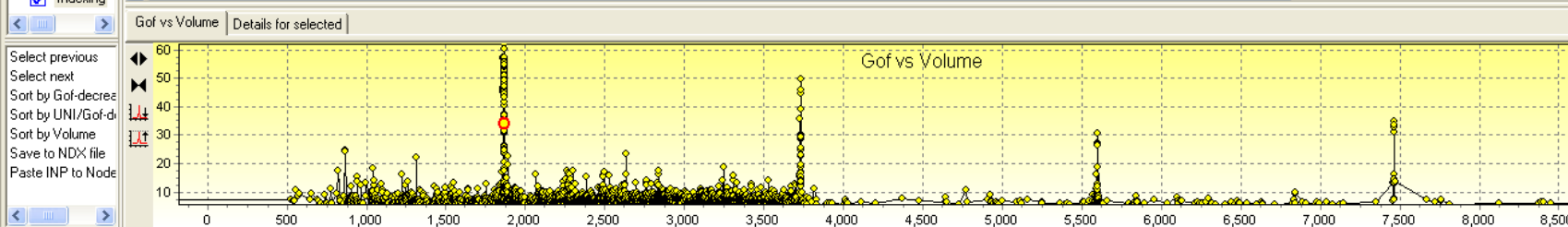
■ The correct cell volume is relatively easy to find, but which unit cell?

→ Click on the various solutions with volume 1866 Å³ and search the overlay with the actual scan for any missed peaks or overlapping peaks (dashed red lines in display)

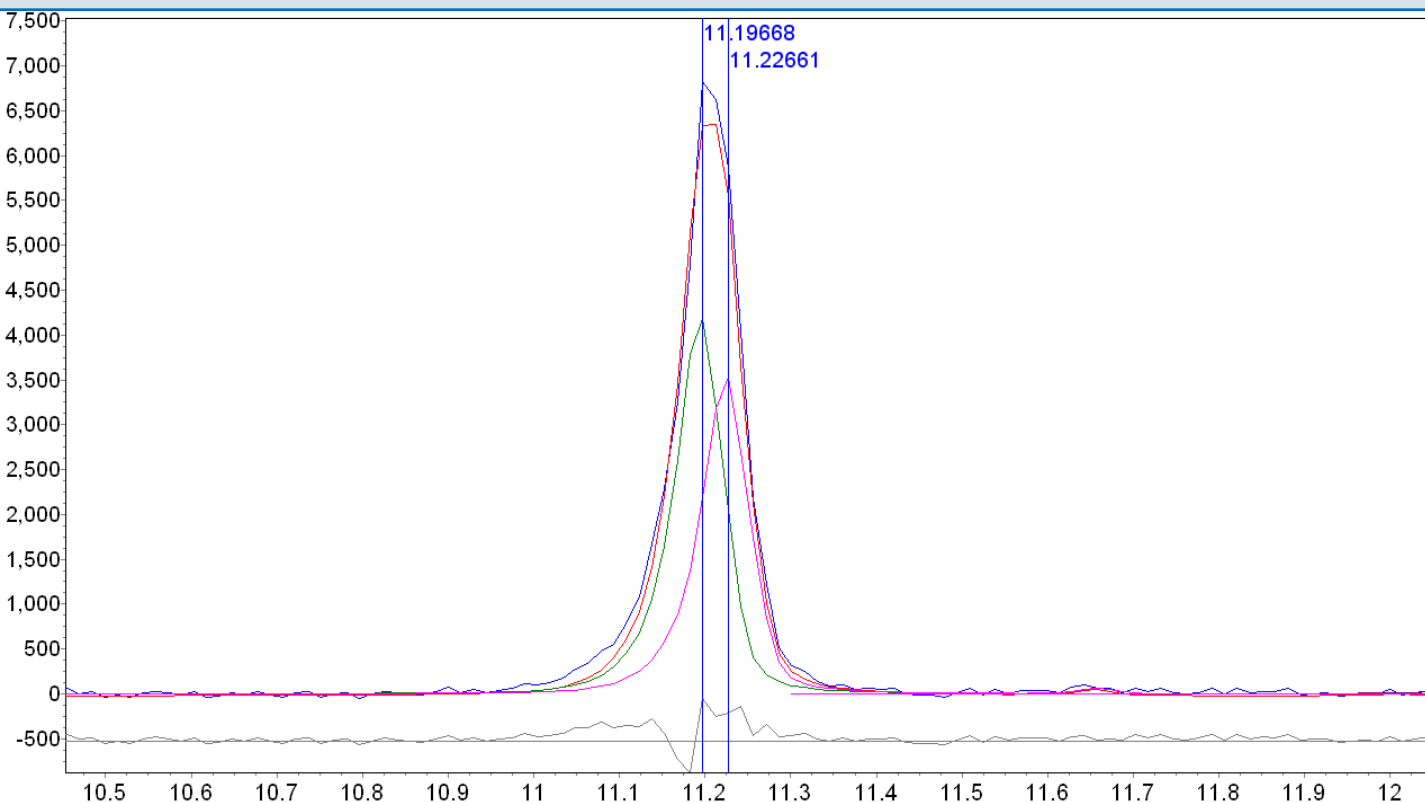
Papaverine hydrochloride



Use	Sg	UNI	Vol	Gof	Zero	a	b	c	al	be	ga
<input type="checkbox"/>	P-1	-10	1866.044	35.67	0.0011	9.1366	13.0745	15.6322	90.0310	89.9760	92.1620
<input type="checkbox"/>	P21/c	-10	1865.751	35.00	0.0000	13.0710	15.6348	9.1362	90.0000	92.1830	90.0000
<input type="checkbox"/>	C2	0	7464.533	34.87	0.0000	18.2800	31.2487	13.0769	90.0000	92.1680	90.0000
<input type="checkbox"/>	P21/c	-10	1866.222	34.12	0.0000	13.0714	15.6349	9.1382	90.0000	87.8370	90.0000
<input checked="" type="checkbox"/>	P21/c	0	1866.059	34.04	0.0000	13.0704	15.6352	9.1379	90.0000	92.1750	90.0000
<input type="checkbox"/>	C2	0	7467.952	33.76	0.0013	18.2740	31.2696	13.0785	90.0000	92.1720	90.0000
<input type="checkbox"/>	P21/c	-10	1866.159	33.70	0.0000	13.0706	15.6391	9.1359	90.0000	92.1760	90.0000
<input type="checkbox"/>	P21/c	1	1866.924	33.68	0.0000	13.0793	15.6344	9.1363	90.0000	87.8420	90.0000

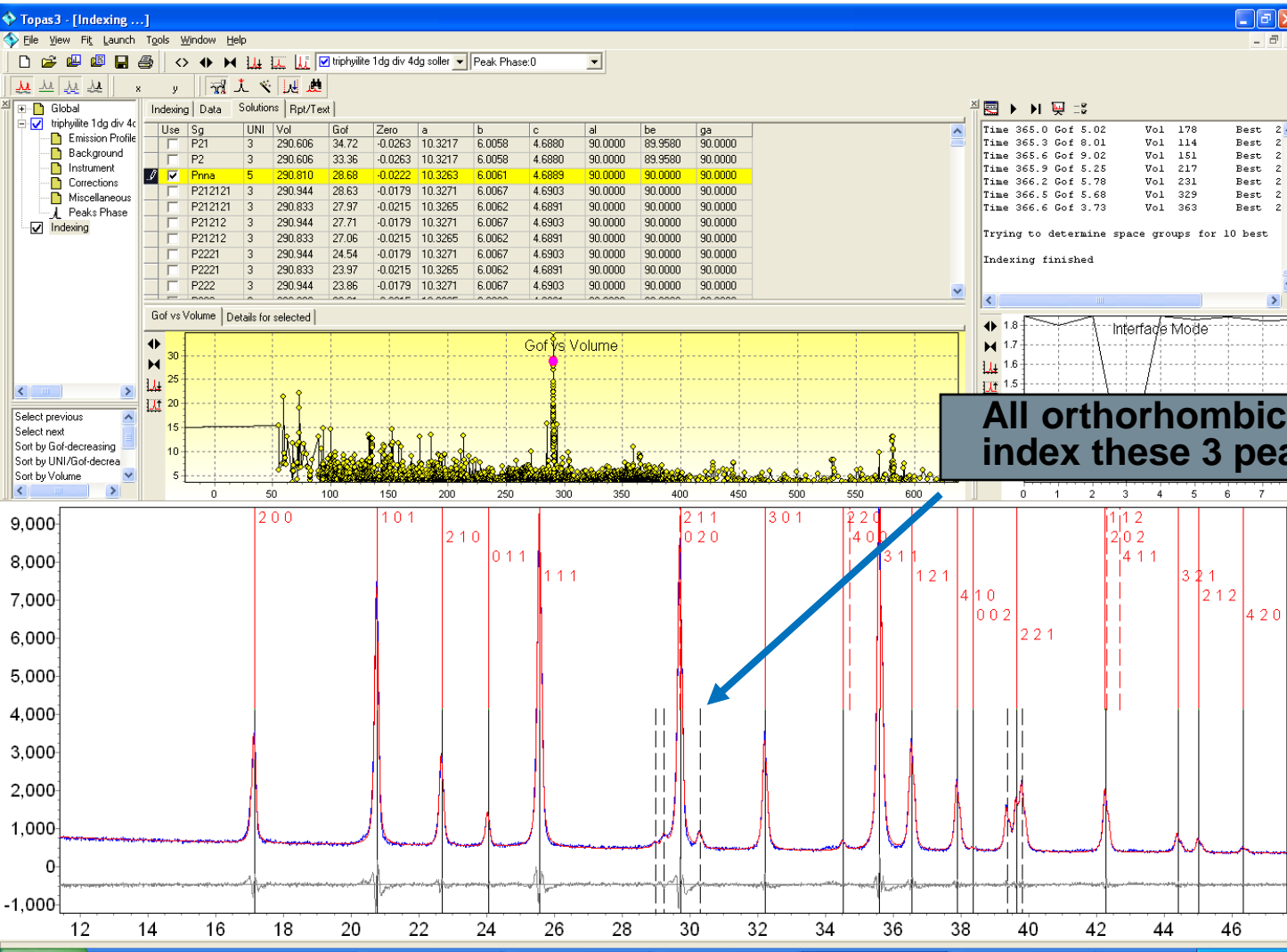


Papaverine hydrochloride



- 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

Global

- triphylite 1dg div 4c
 - Emission Profile
 - Background
 - Instrument
 - Corrections
 - Miscellaneous
 - Peaks Phase
 - Indexing**

Add data
 Set data as d
 Set data as 2Th
 Paste ds from Clipboard
 Paste 2Ths from Clipboard
 Paste d/Is from Clipboard
 Paste 2Th/Is from Clipboard
 Paste INP to Node/Selectic

Use	d	Weighting	Good
<input checked="" type="checkbox"/>	5.16859	540.8974	<input checked="" type="checkbox"/>
<input checked="" type="checkbox"/>	4.274985	1290.381	<input type="checkbox"/>
<input checked="" type="checkbox"/>	3.918851	458.0141	<input type="checkbox"/>
<input checked="" type="checkbox"/>	3.699612	176.1475	<input type="checkbox"/>
<input checked="" type="checkbox"/>	3.481962	1751.58	<input type="checkbox"/>
<input type="checkbox"/>	3.080237	29.45132	<input type="checkbox"/>
<input type="checkbox"/>	3.052402	63.27065	<input type="checkbox"/>
<input checked="" type="checkbox"/>	3.005509	1665.399	<input type="checkbox"/>
<input type="checkbox"/>	2.948431	84.83421	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.776868	617.4852	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.59707	53.71675	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.520566	1953.268	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.457586	630.0559	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.372958	416.3256	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.345456	15.18817	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.287968	250.4198	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.271897	279.8314	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.262824	332.3614	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.137225	388.7033	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.039147	118.2511	<input type="checkbox"/>
<input checked="" type="checkbox"/>	2.01261	91.09118	<input type="checkbox"/>
<input checked="" type="checkbox"/>	1.958343	39.00594	<input type="checkbox"/>

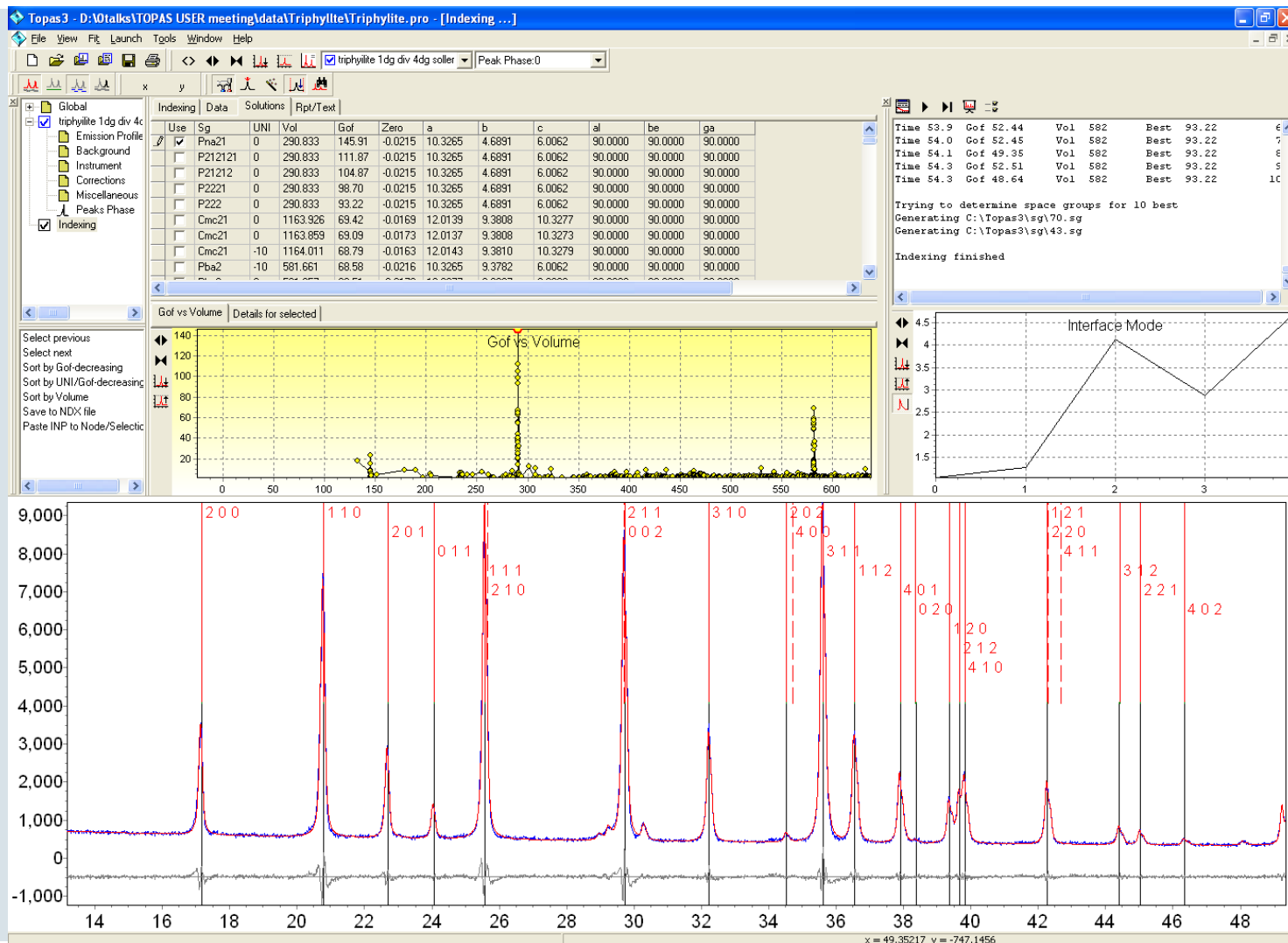
	Use	Value
Wavelength (Å)	<input type="checkbox"/>	1.540596
Zero error	<input checked="" type="checkbox"/>	
Max zero error in 2Th	<input type="checkbox"/>	0.1
Max 2Th error for UNI	<input type="checkbox"/>	0.05
Max ratio Nc/No	<input type="checkbox"/>	5
Max number solutions	<input type="checkbox"/>	3000
Try space groups	<input type="checkbox"/>	
Set x0 from d	<input type="checkbox"/>	0

Bravais lattices to include

	Use		Use
Cubic-F	<input type="checkbox"/>	Orthorhombic-F	<input checked="" type="checkbox"/>
Cubic-I	<input type="checkbox"/>	Orthorhombic-I	<input checked="" type="checkbox"/>
Cubic-P	<input type="checkbox"/>	Orthorhombic-C	<input checked="" type="checkbox"/>
Trigonal-Hexagonal-R	<input type="checkbox"/>	Orthorhombic-P	<input checked="" type="checkbox"/>
Trigonal-Hexagonal-P	<input type="checkbox"/>	Monoclinic-C	<input type="checkbox"/>
Tetragonal-I	<input type="checkbox"/>	Monoclinic-P	<input type="checkbox"/>
Tetragonal-P	<input type="checkbox"/>	Triclinic	<input type="checkbox"/>

Mineral Triphylite (LiFePO₄)

Second Indexing run without impurity peaks



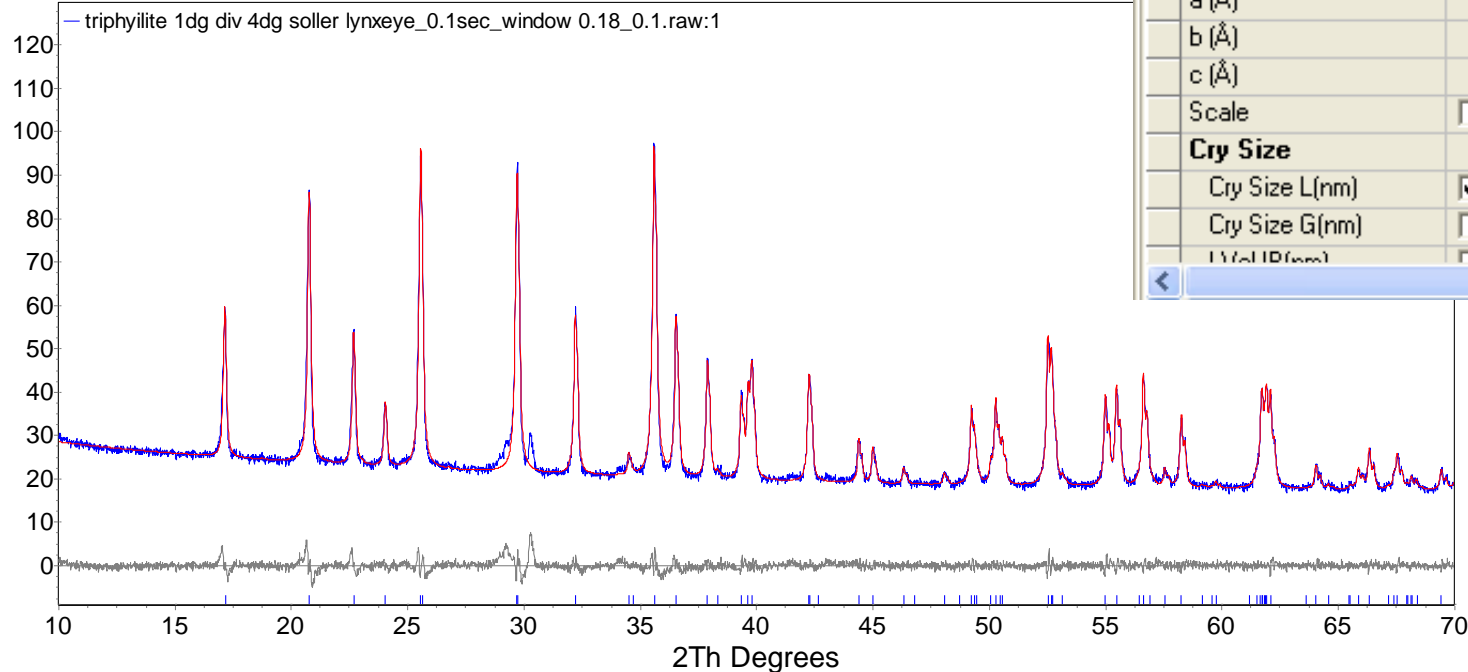
Mineral Triphylite (LiFePO₄)

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 Conv
		Use Value	Code
Use Phase	<input checked="" type="checkbox"/>		
Le Bail	<input type="checkbox"/>		
Delete hkls on Refineme	<input checked="" type="checkbox"/>		
LP Search	<input type="checkbox"/>	0.4	
Spacegroup		Pna21	
a (Å)		10.3324020	@
b (Å)		4.6936578	@
c (Å)		6.0075249	@
Scale	<input type="checkbox"/>	0	Fix
Cry Size			
Cry Size L(nm)	<input checked="" type="checkbox"/>	121.3	Refine
Cry Size G(nm)	<input type="checkbox"/>	200.0	Refine
Cry Size H(nm)	<input type="checkbox"/>	0.000	



- 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
$P-1$	3
$P2_12_12$	3
$Pbca$	3
$Pnma$	3
total	59%

Practical TOPAS demonstrations

As time allows:

- LP-Search Examples

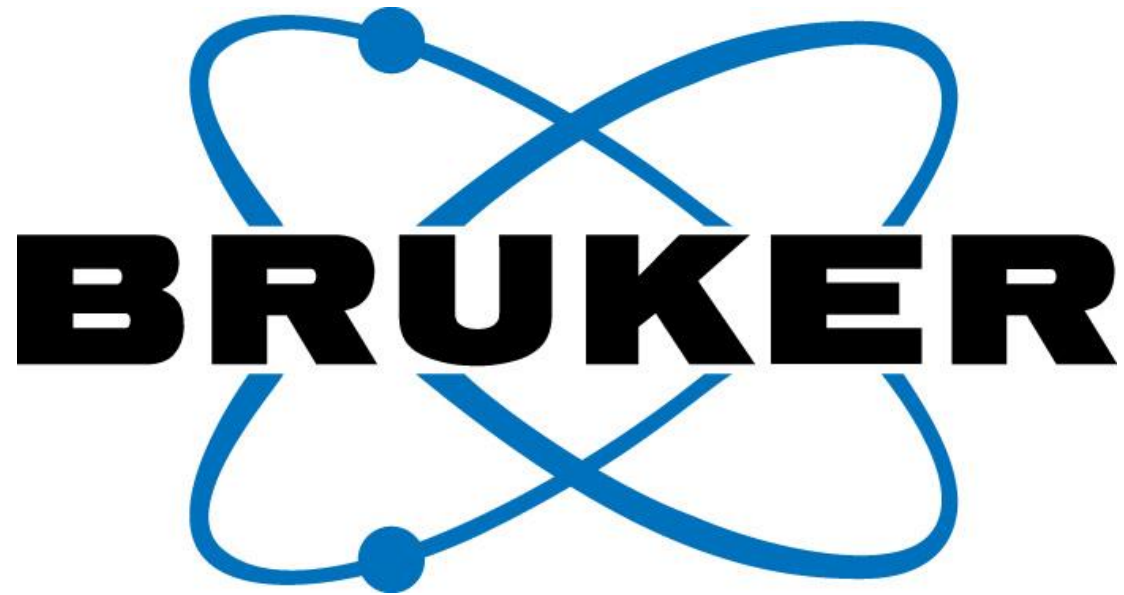
 - [Lp-Zopicone dihydrate.pro](#)

- LSI-Index Examples

 - [.pro](#)

- Whole powder patter fitting Example

 - [AlVO3.pro](#)



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