Introduction to TOPAS
Profile fitting and Rietveld analysis

Holger Cordes, Ph.D.
Applications Scientist, XRD
5465 E. Cheryl Parkway
Madison, WI 53711-5373
608-276-3048
Holger.Cordes@bruker-axs.com

Outline:

TOPAS Introduction

TOPAS Interface

Profile fitting

- Fitting with analytical functions
- Convolution based approaches and Fundamental Parameters
- Empirical determination of instrument funtions
- Whole Powder Pattern Decompostion
- Obtaining information about micro structure
- Anisotropic Refinement models
- Determining Degree of crystallinity with Peaks phases
- Determining Degree of crystallinity with hkl phases

- Quantitative Analysis with Rietveld
  - Introduction
  - Corrections
  - Examples:
    - Round robin example with preferred orientation
    - Cement sample
    - Mixture of minerals, ...
  - PONKCS

TOPAS
TOtal Pattern Analysis Solutions

- Generalized software for profile and structure analysis

  Seamless integration of all currently employed profile fit techniques and related applications

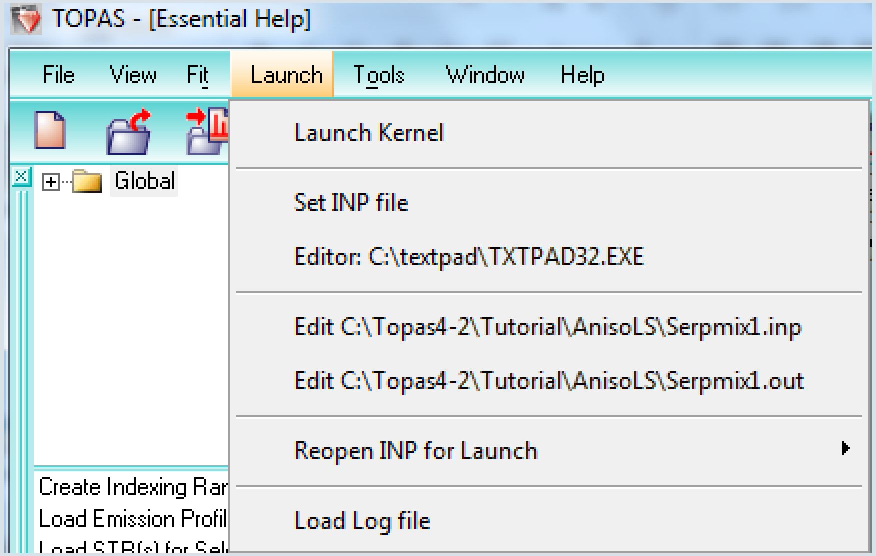
  - Single Line Fitting
  - Indexing
    (LSI, LP-Search)
  - Whole Powder Pattern Decomposition
    (Pawley, Le Bail)
  - Ab initio structure determination
    (Simulated annealing, charge flipping, Fourier analysis)
  - Structure refinement
    (Rietveld)
  - Quantitative phase analysis
    (Rietveld, PONKCS)

Size/ Strain
Degree of crystallinty

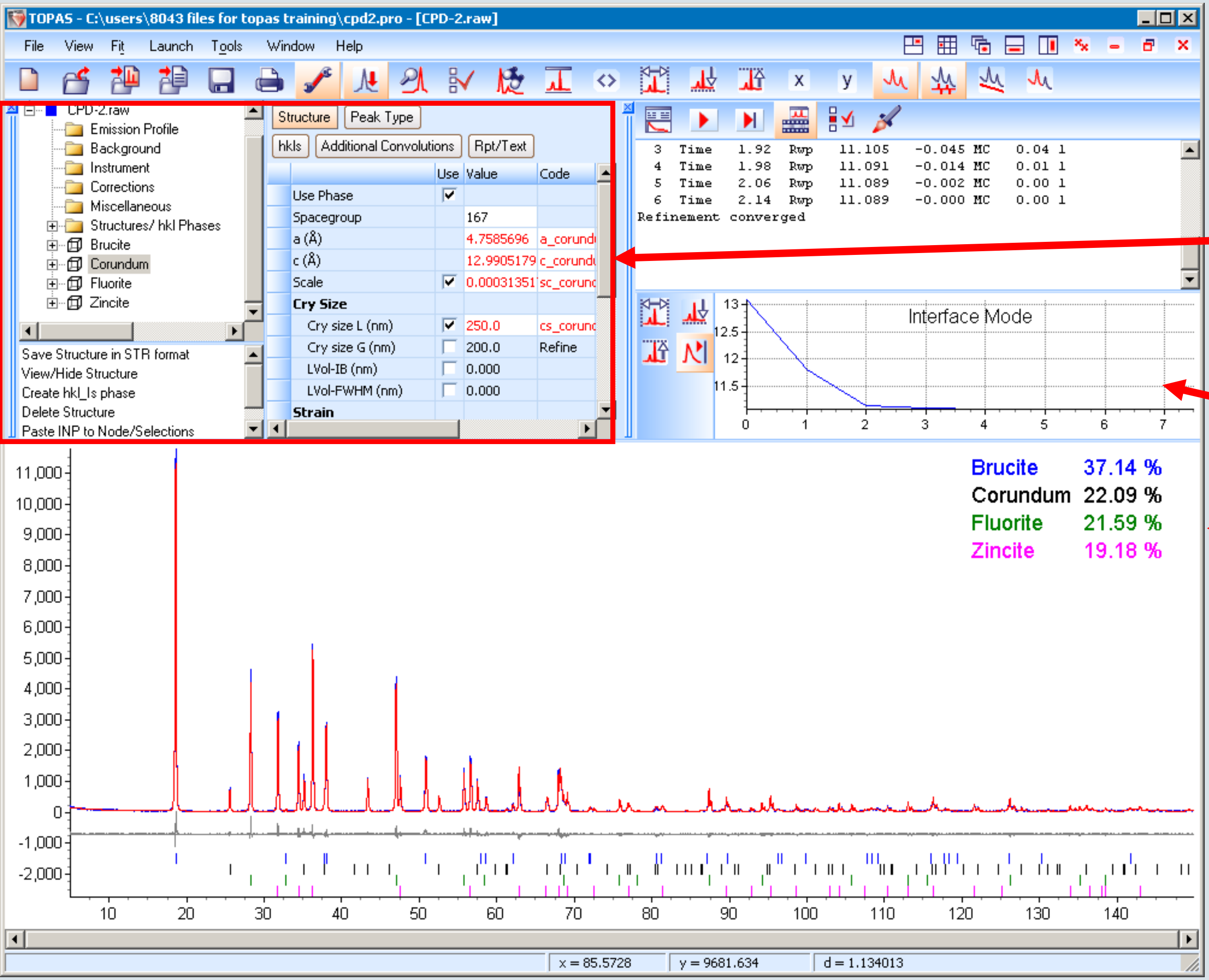
TOPAS Interface:
GUI and Launch mode

- TOPAS has a graphical user-interface (GUI) and a text based (Launch)mode
  - GUI supports most Profile fitting and Rietveld applications
  - Beginners should use this mode of operation.

- LAUNCH MODE
  - More features for advanced users
  - For structure solution
  - For automation or batch operation



TOPAS GUI:
User Interface



	Use	Value	Code
Use Phase	☑		
Spacegroup		167	
a (Å)		4.7585696	a_corund
c (Å)		12.9905179	c_corund
Scale	☑	0.00031351	sc_corun
Cry Size			
Cry size L (nm)	☑	250.0	cs_corun
Cry size G (nm)	☐	200.0	Refine
LVol-IB (nm)	☐	0.000	
LVol-FWHM (nm)	☐	0.000	
Strain			

```
 3  Time  1.92  Rwp  11.105  -0.045 MC  0.04 1
 4  Time  1.98  Rwp  11.091  -0.014 MC  0.01 1
 5  Time  2.06  Rwp  11.089  -0.002 MC  0.00 1
 6  Time  2.14  Rwp  11.089  -0.000 MC  0.00 1
Refinement converged
```

Brucite	37.14 %
Corundum	22.09 %
Fluorite	21.59 %
Zincite	19.18 %

x = 85.5728 y = 9681.634 d = 1.134013

Parameter window with instrument and structure information

Fit window

wt.% for each phase

Measured curve

Calculated curve

Difference curve

TOPAS GUI:
Parameter Window

Parameter values

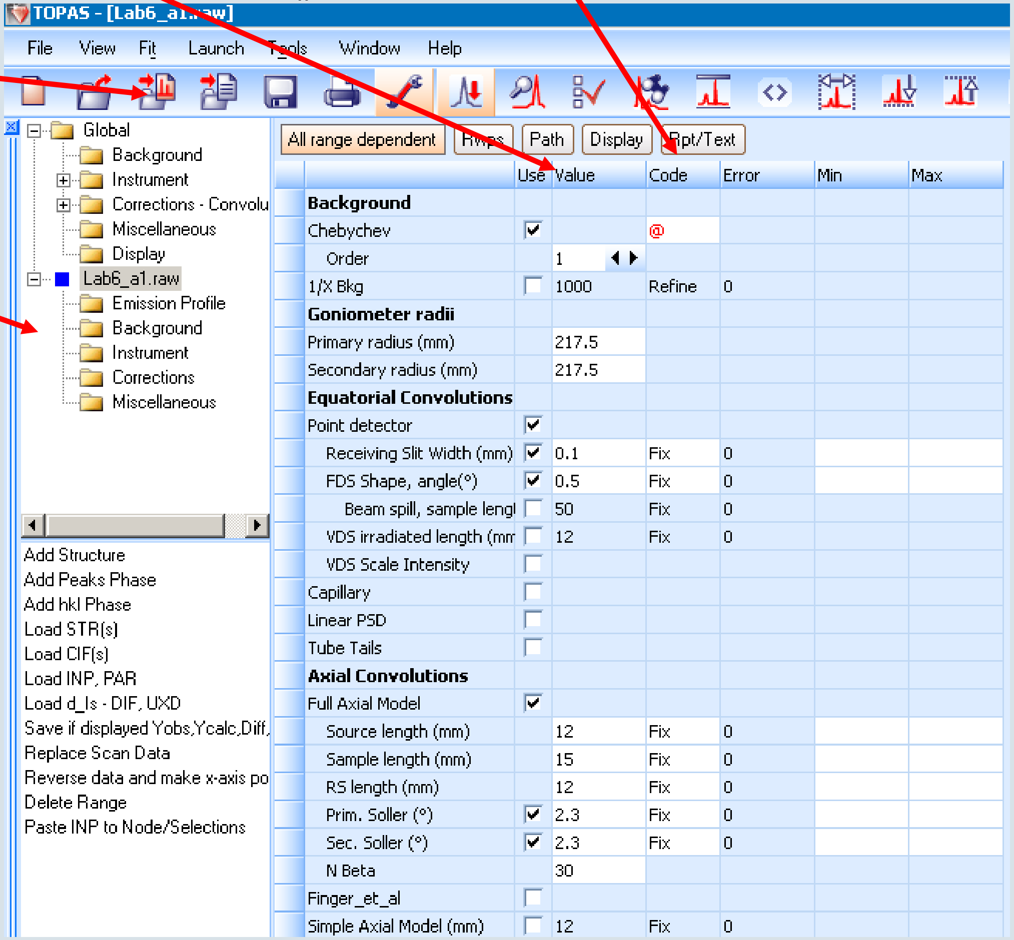
Toggle any parameter between Fix and Refine in „Code“ column

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)



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

TOPAS GUI:
Fit window

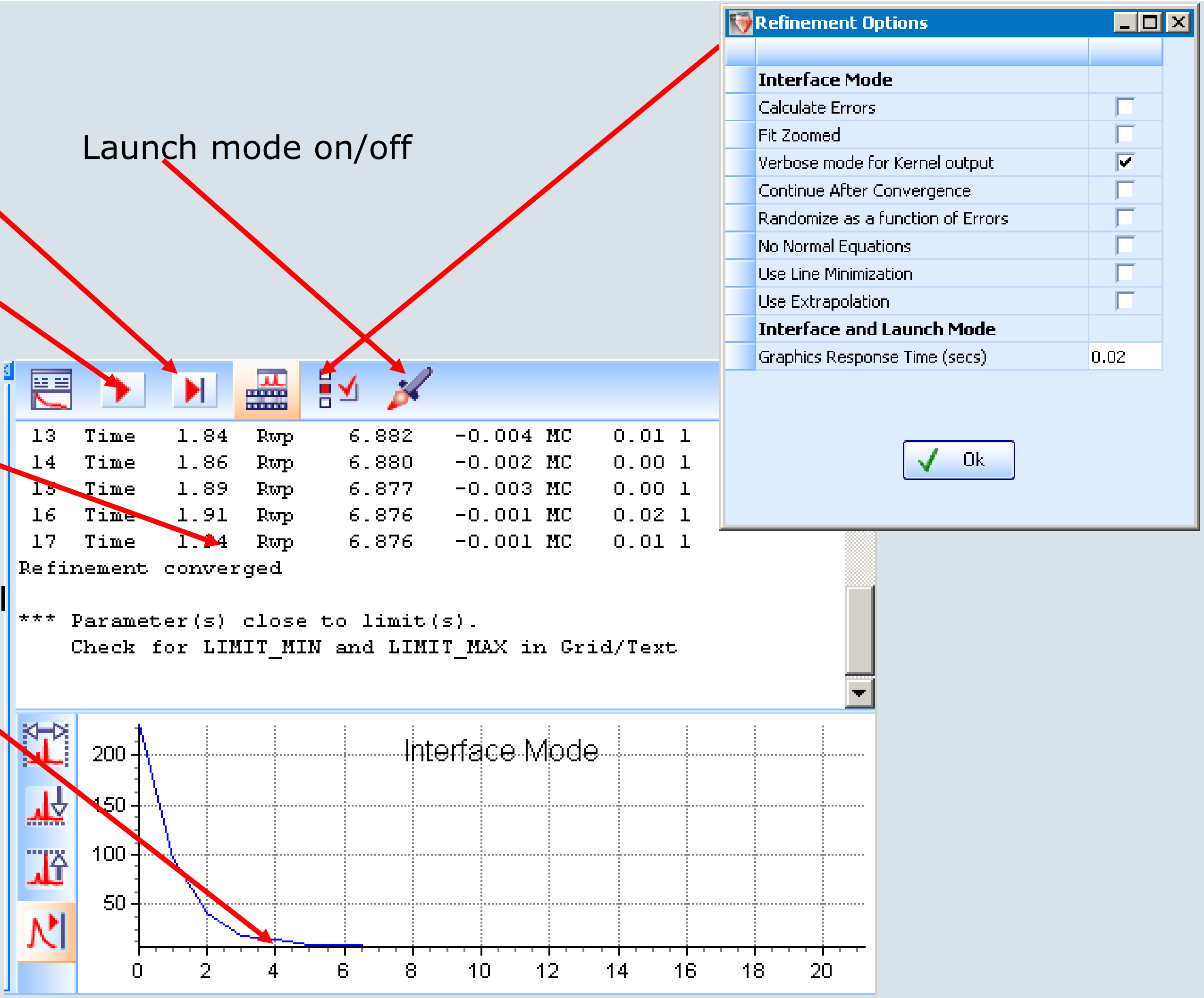
Start Refinement (Step by step)

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



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

Refinement Options

Interface Mode	
Calculate Errors	☐
Fit Zoomed	☐
Verbose mode for Kernel output	☑
Continue After Convergence	☐
Randomize as a function of Errors	☐
No Normal Equations	☐
Use Line Minimization	☐
Use Extrapolation	☐
Interface and Launch Mode	
Graphics Response Time (secs)	0.02

Profile Fitting Methods
How do you describe a Peak?

A peak may be described by the following peak parameters:

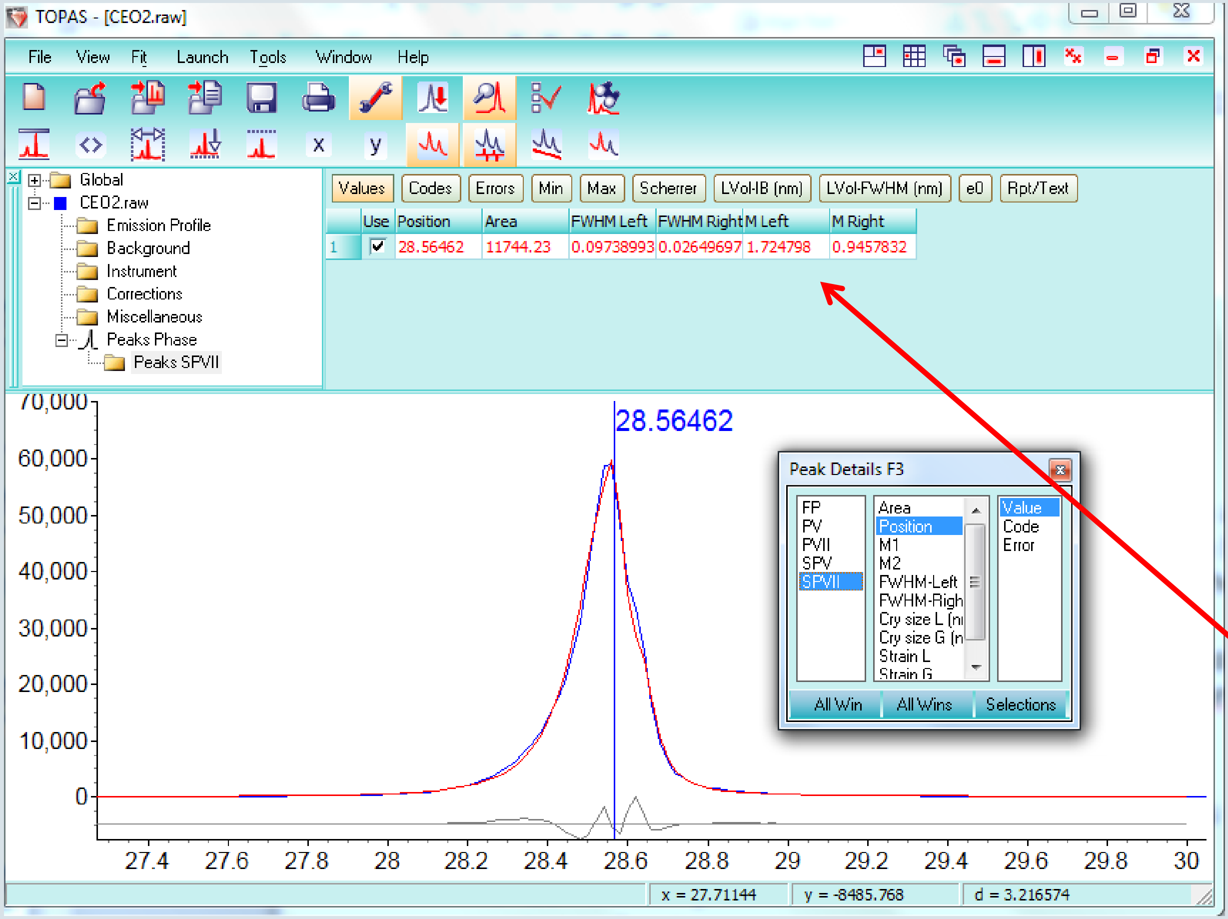
- background (Due to air scatter, fluorescence, overlapping peak tails, diffuse scatter)
- Position (integral intensity depends more on weight fraction, atomic position or other relevant physical parameters than intensity maximum)
- Intensity
- Line width (FWHM)
- Shape (How fast does the intensity drop off?)
- Asymmetry (FWHM, Left and Right)

Profile Fitting Methods
Analytical approach

- Analytical Profile Fitting
  - Characterized by peak shape functions (PSFs) with an explicit and relatively simple mathematical form which can be differentiated analytically with respect to each of the refined parameters
  - Most common are the Gaussian, Lorentzian, sums of Gaussians or Lorentzians Voigt, pseudo Voigt (PV) and PearsonVII functions (PVII)
  - Convenient to use
  - Large number of parameters required to fit profiles well over the whole 2θ range pattern frequently leading to
    - Correlation problems
    - Loss of uniqueness
    - Instability of the refinement procedure

Analytical approach

Example: CeO2



	Use	Position	Area	FWHM Left	FWHM Right	M Left	M Right
1	☑	28.56462	11744.23	0.09738993	0.02649697	1.724798	0.9457832

x = 27.71144 y = -8485.768 d = 3.216574

- Import the raw file and zoom on the main low angle peak
- Open Peak Details window (F3)
- Choose SPVII (Split Pearson VII) peak type and drop a peak on the main peak with the mouse. This adds a Peaks Phase
- Start refinement (F6)
- Get peak parameters

File: C:\Topas 4.2\tutorial\CeO2\CeO2.raw

Profile Fitting Methods

Convolution based methods

- Direct Convolution Approach
  - Discrimination of instrument and sample contributions:
  Y(2q) = (W x G) x S, where I = (W x G)

  W: Emission profile   G: Instrument contribution   S: Sample contribution

TOPAS offers 3 direct convolution approaches:

1. Empirical parametrization of line profile shapes by convolution of appropriate functions
   - Profile parameters have NO physical meaning
2. Explicit discrimination of instrument and sample contributions: Measured Instrument Function
   - Sample related profile parameters have physical meaning: Size/strain/...
3. Explicit discrimination of instrument and sample contributions: Calculated Instrument Function
   - All profile parameters have a physical meaning

     → Fundamental Parameters Approach (Peak Type FP)

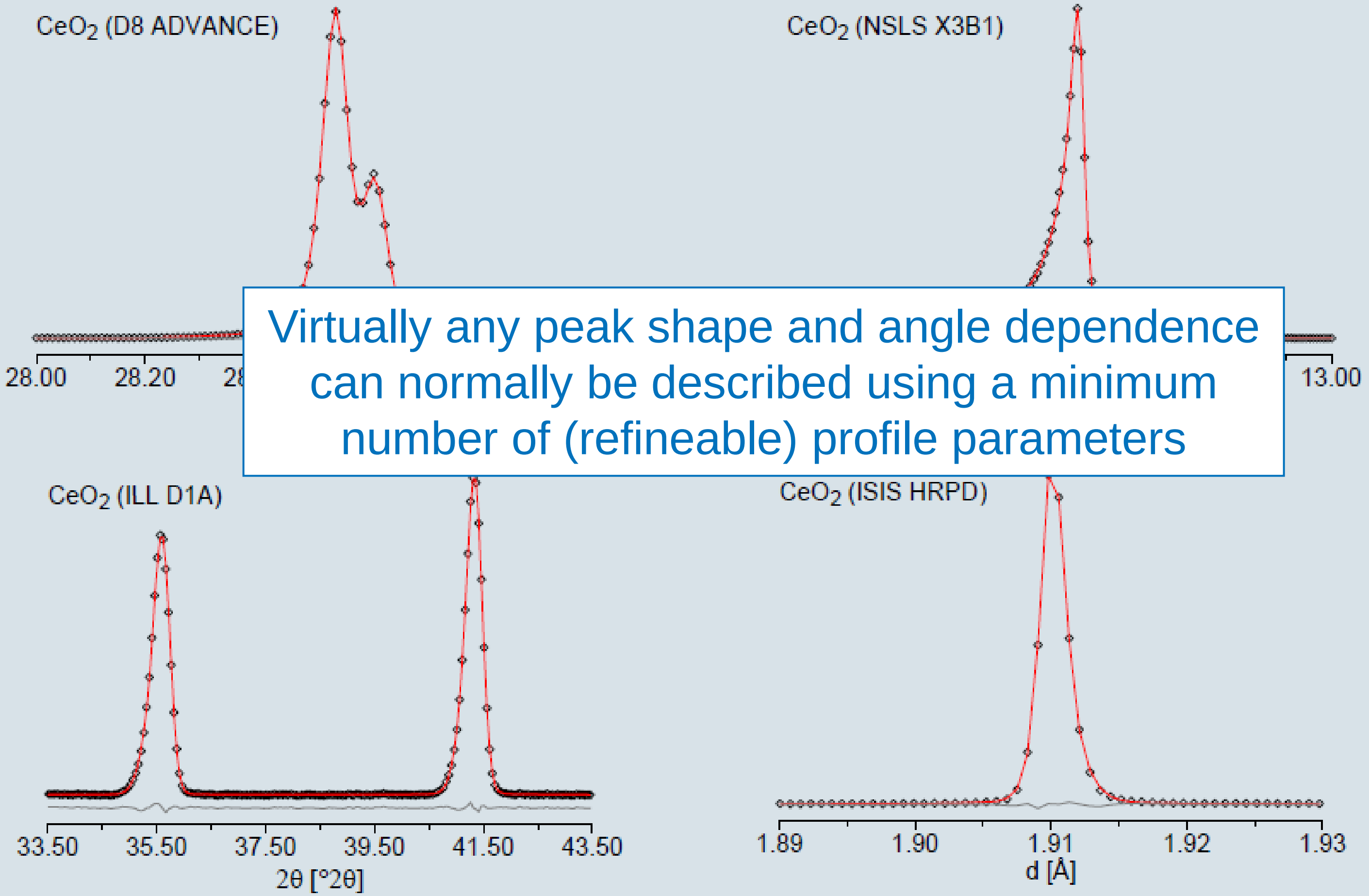
Convolution approach
Empirical parametrization

- Convolute any appropriate functions to achieve a best fit
  - Minimize the number of functions / function parameters to
  - minimize parameter correlation

- An excellent approach for all profile fit applications using any instrument, if micro-structure information is NOT of interest (Refined profile parameters have NO physical meaning)
- Knowledge of the most common contributions to line profile shapes and their dependence on angle helps:

Contribution	*Convolution*	*Angular dependence*
Detector (slit)	Hat	Constant
Crystallite size	Lorentzian	1/cos(Th)
Strain	Gaussian	Tan(Th)
Axial divergence	Circles	-1/Tan(Th)

Convolution approach
Empirical parametrization Examples



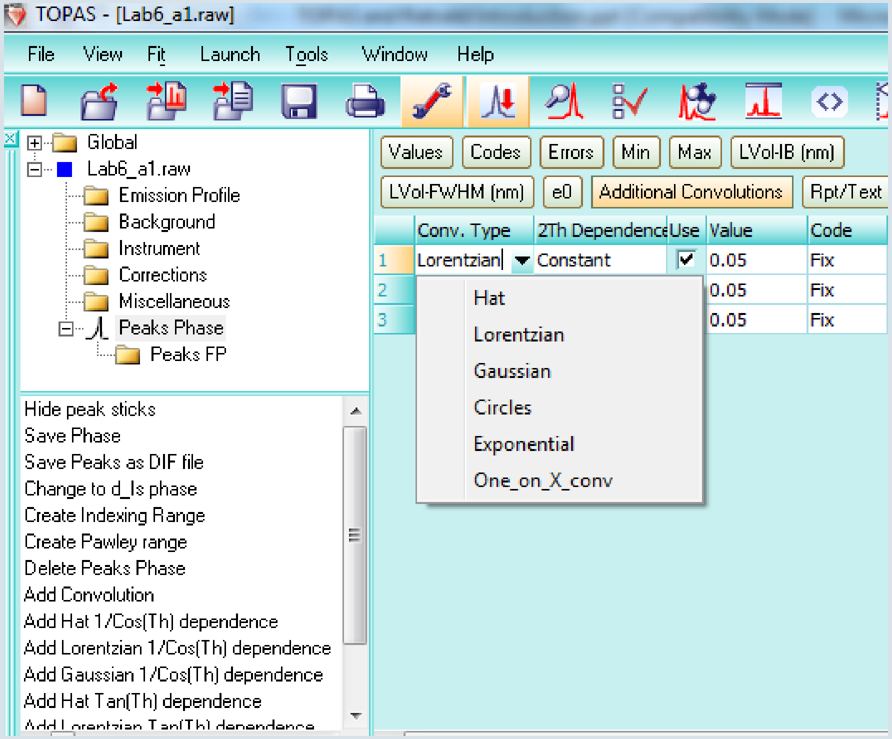
Virtually any peak shape and angle dependence can normally be described using a minimum number of (refineable) profile parameters

Size-Strain Round Robin, Balzar (2004); "sharp data".

Convolution approach
Exercise: Empirical parametrization

File: C:\Topas 4.2\tutorial\misc\Lab6_a1.raw
Emission profile: CuKa2.lam

- Use Peak type FP for any convolution based approach
- For the empirical approach make sure that no instrument parameters are used (uncheck all)
- Add Peaks Phase, uncheck crysize and select “Additional Convolutions”
- “Add a Convolution”
- Select a predefined Convolution function, define a 2Th dependency and set Value to refine
- Add several convolutions until you achieve a good fit
- Trial and Error approach



	Conv. Type	2Th Dependence	Use	Value	Code
1	Lorentzian	Constant	☑	0.05	Fix
2				0.05	Fix
3				0.05	Fix

Convolution approach

Measured instrument function approach

Step 1: Determine an instrument function

- Obtain data from a suitable standard:
  Reflection: LaB6 (SRM 660a)
  Transmission: Si (SRM 640a)
- Convolute any appropriate functions to achieve a best fit (Empirical parameterization!)

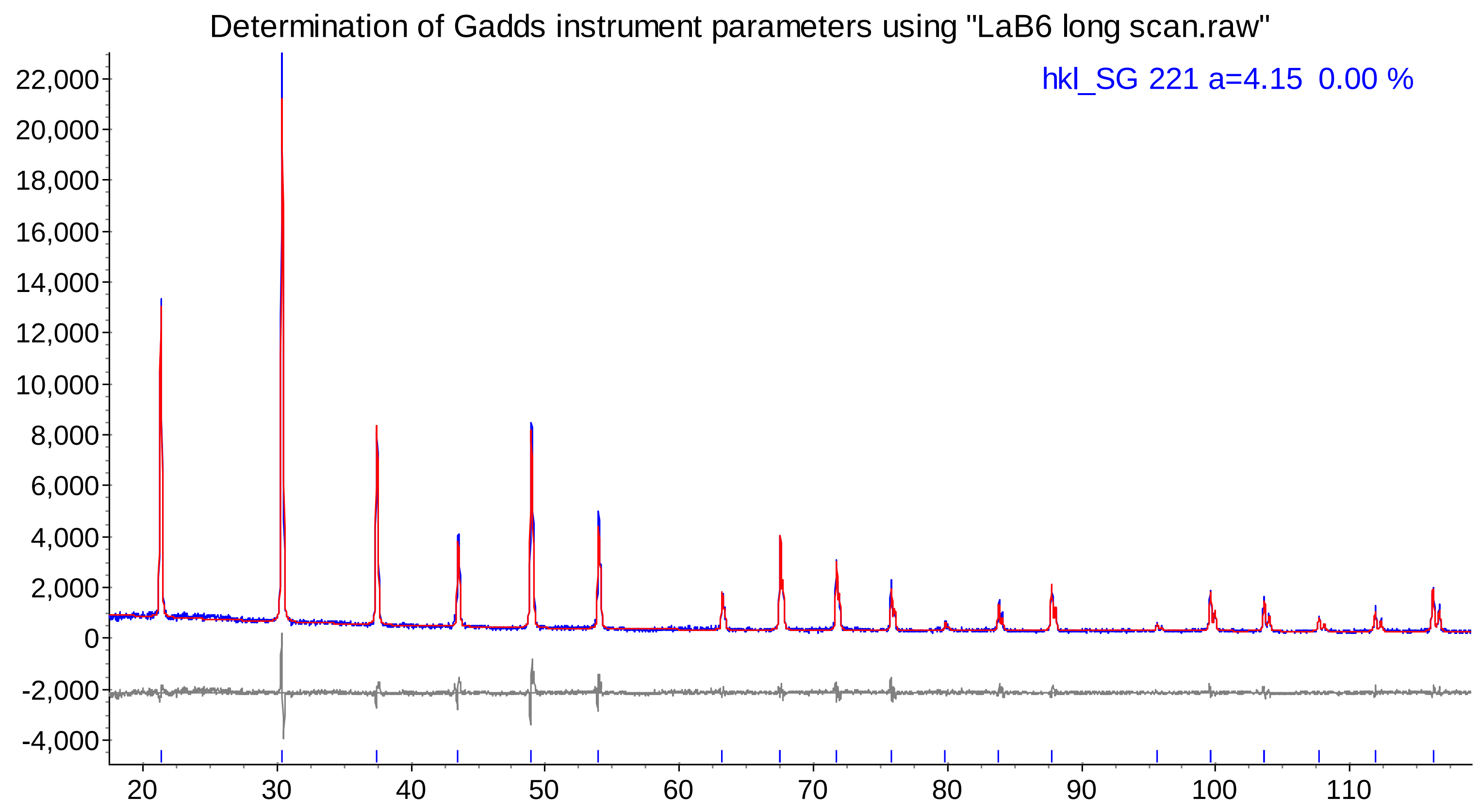
- The number of functions / function parameters is irrelevant, the more the better!
- Fix all refineable profile parameters and save an instrument file

Step 2: Refine the actual data using the instrument function

- Load the instrument file
- Refine on micro-structure parameters as required

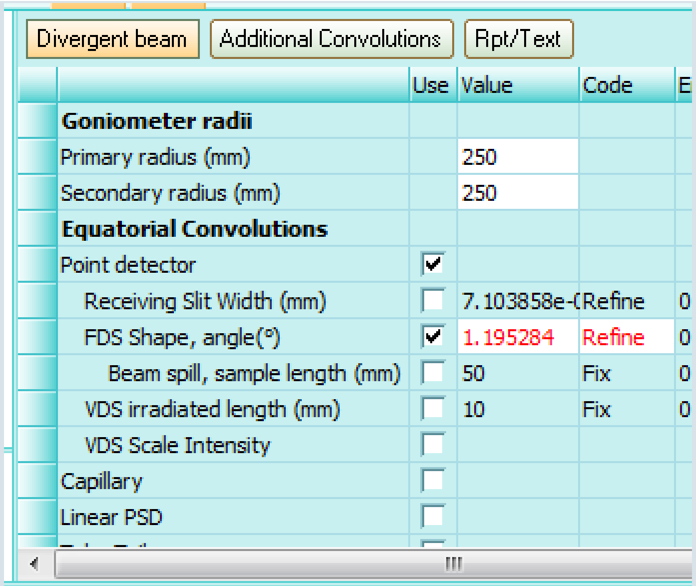
Convolution approach
Measured instrument function

File: C:\Topas 4.2\examples\GADDS LaB6 long scan.raw
Emission profile: CuKa2.lam
Determine instrument function

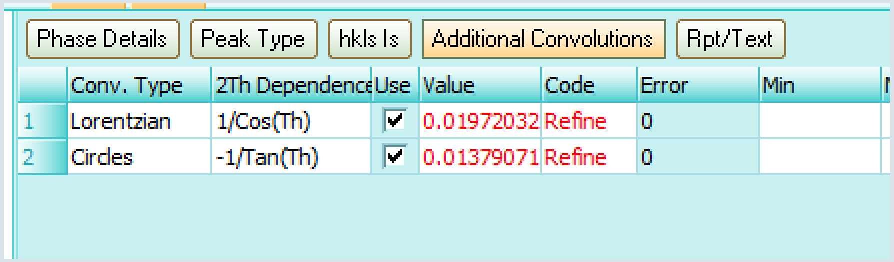


Convolution approach

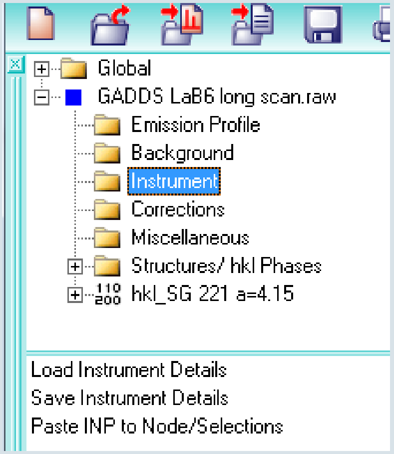
Measured instrument function



	Use	Value	Code	E
Goniometer radii				
Primary radius (mm)		250		
Secondary radius (mm)		250		
Equatorial Convolutions				
Point detector	☑			
Receiving Slit Width (mm)	☐	7.103858e-(	Refine	0
FDS Shape, angle(°)	☑	1.195284	Refine	0
Beam spill, sample length (mm)	☐	50	Fix	0
VDS irradiated length (mm)	☐	10	Fix	0
VDS Scale Intensity	☐			
Capillary	☐			
Linear PSD	☐			



	Conv. Type	2Th Dependence	Use	Value	Code	Error	Min
1	Lorentzian	1/Cos(Th)	☑	0.01972032	Refine	0	
2	Circles	-1/Tan(Th)	☑	0.01379071	Refine	0	



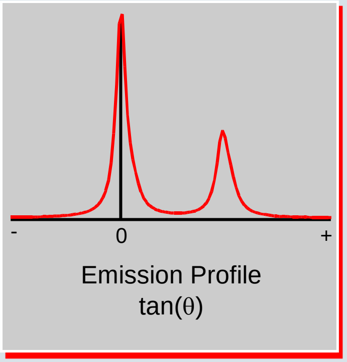
- Global
- GADDS LaB6 long scan.raw
  - Emission Profile
  - Background
  - Instrument
  - Corrections
  - Miscellaneous
  - Structures/ hkl Phases
  - hkl_SG 221 a=4.15

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

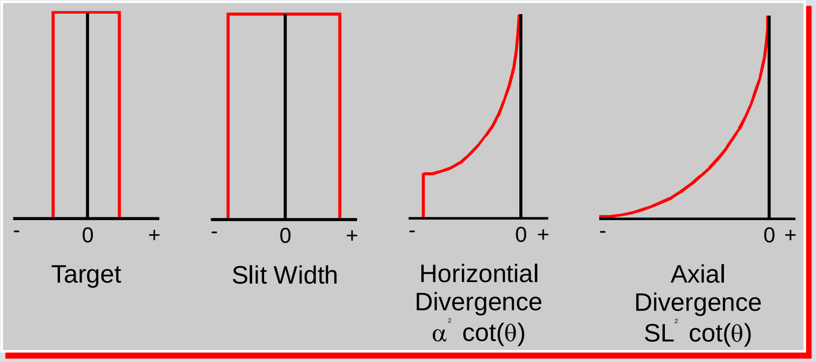
- Any “slit width” or “function” under the Divergent beam tab or any additional convolution can be refined to get the best possible fit for the instrument peak shape.
- No limit to number of functions or paramters, the more the better the fit.
- After refining LaB_6 these parameters they are set to “fixed” and used as an empirical instrument function for refinement of unknown samples.

Use an “unknown” sample with identical instrument settings
File: C:\Topas 4.2\examples\GADDS Anatase 5pc Rutile.raw

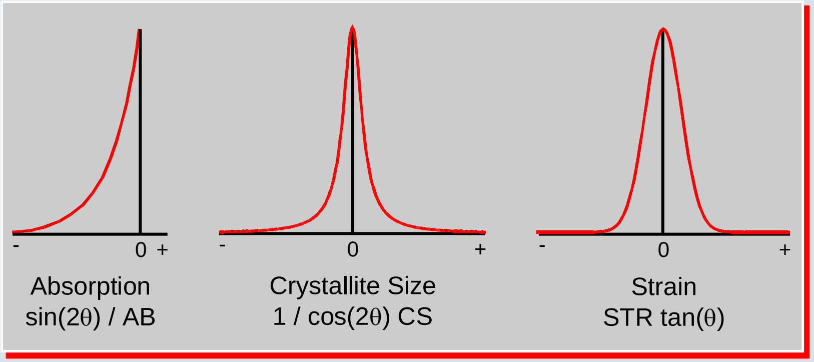
Convolution approach
Calculated Instrument Function
Fundamental Parameters



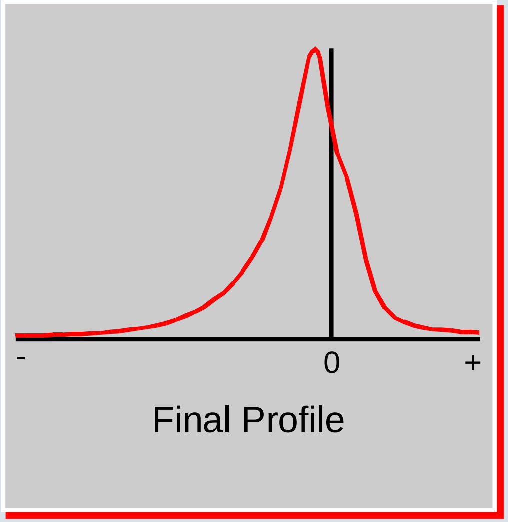
W



G



S



Y(2θ) = (W x G) x S

Convolution approach
Calculated Instrument Function
Fundamental Parameters

Implemented only for Bragg-Brentano Geometry
Notation for slit settings:

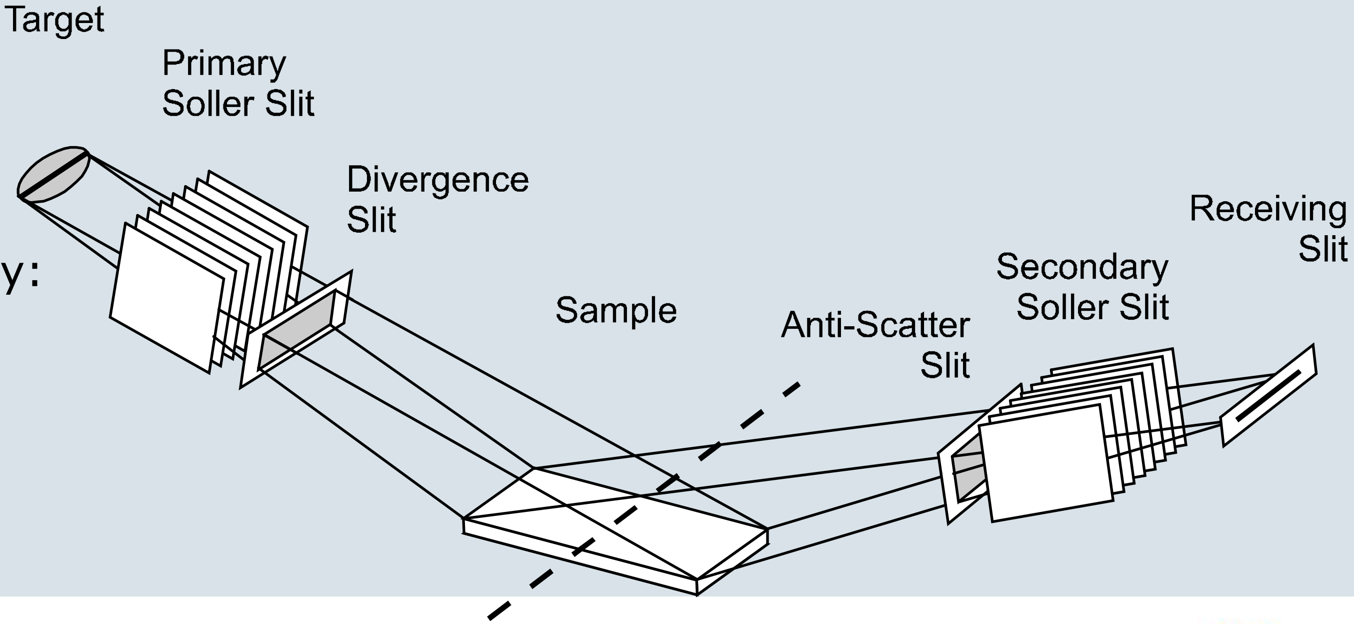
Instrument parameter notation in TOPAS in Divergent beam tab:

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

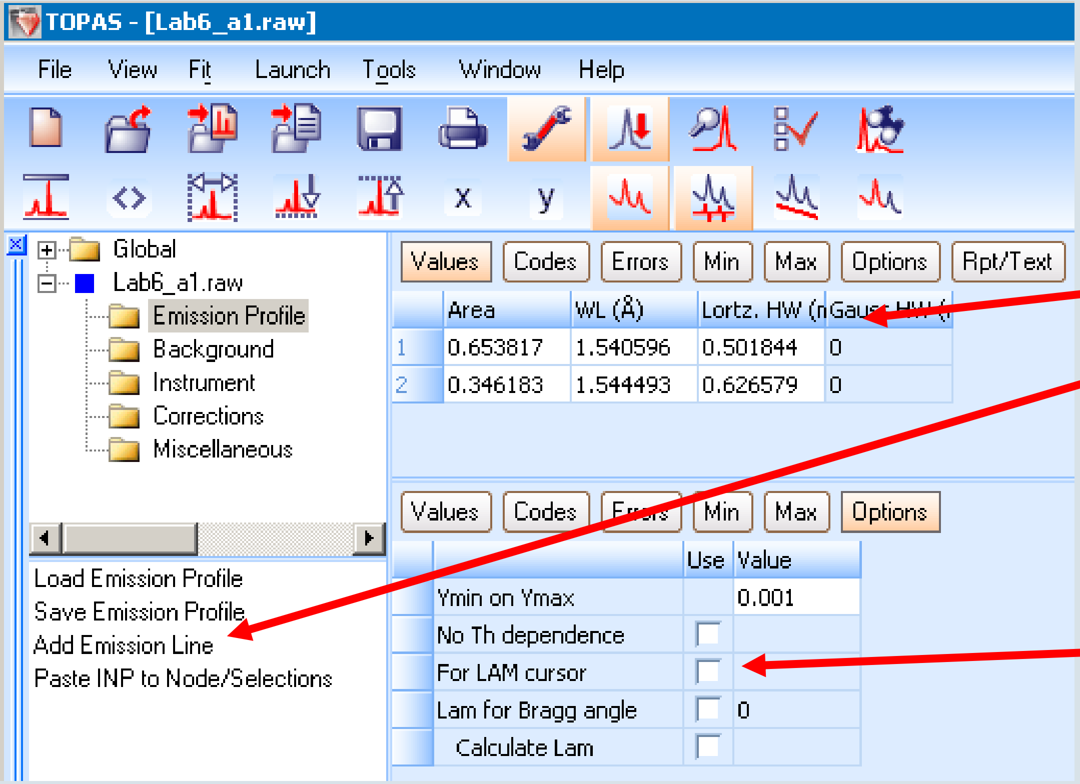


Parafocussing Geometry: Error because fo flat specimen

Errors because of axial and equatorial divergence

Single Line Fitting

Choose an Emission Profile



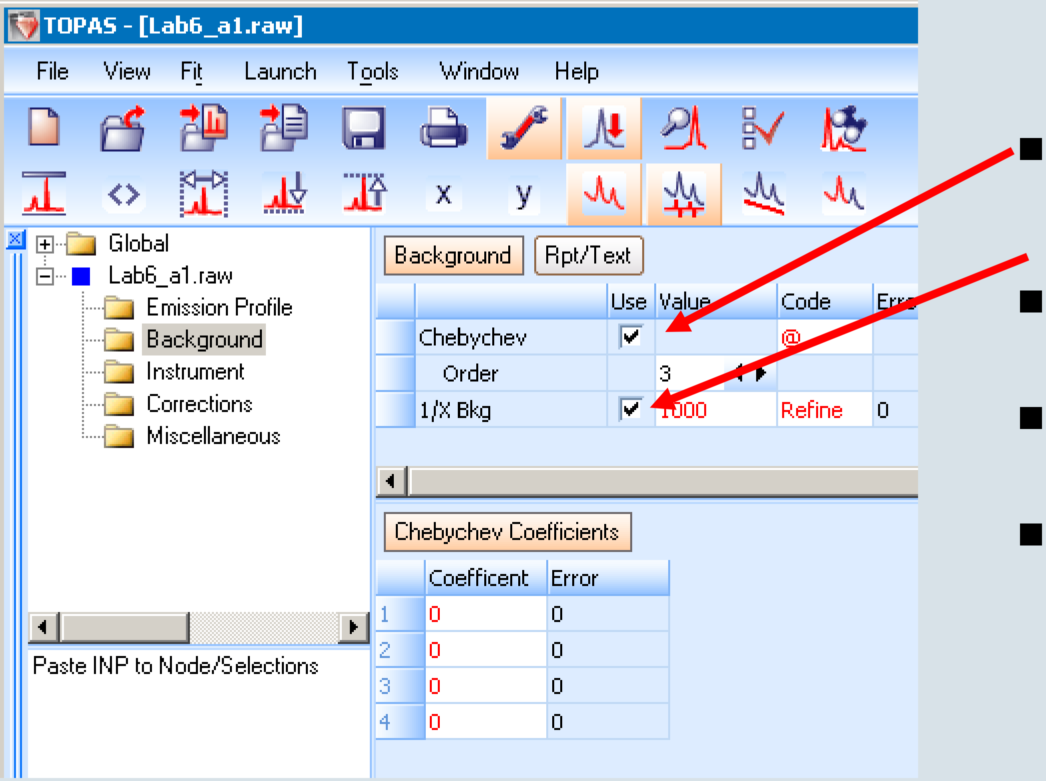
	Area	WL (Å)	Lortz. HW (m	Gauss HW (
1	0.653817	1.540596	0.501844	0
2	0.346183	1.544493	0.626579	0

	Use	Value
Ymin on Ymax		0.001
No Th dependence	☐	
For LAM cursor	☐	
Lam for Bragg angle	☐	0
Calculate Lam	☐	

File: C:\Topas 4.2\tutorial\misc\Lab6_1.raw

- Predefined emission profiles for most common sealed tube systems and radiations are predefined in the directory c:\topas3\lam\
- The default profile Cuka2.lam has 2 lines, Cu$k\alpha 1$ and Cu$k\alpha 2$.
- 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



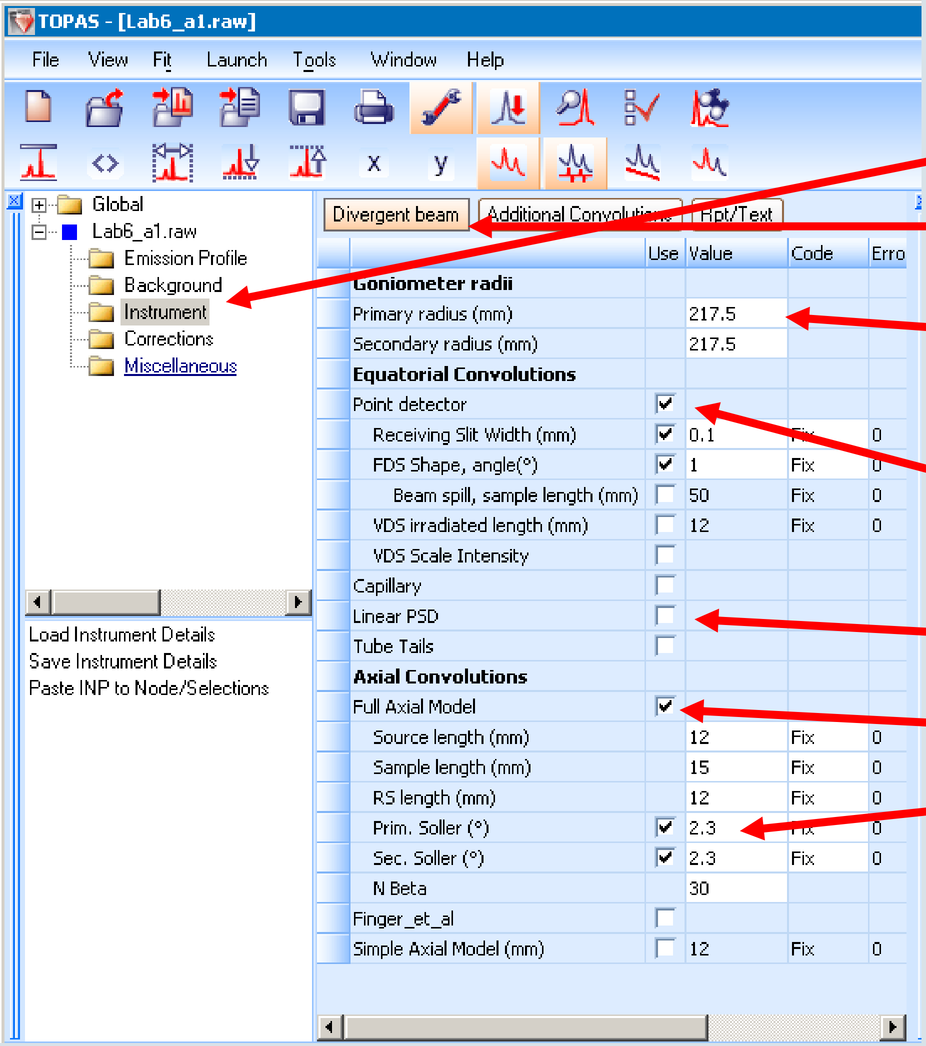
Paste INP to Node/Selections

	Use	Value	Code	Err
Chebychev	☑		@	
Order		3		
1/X Bkg	☑	1000	Refine	0

	Coefficent	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

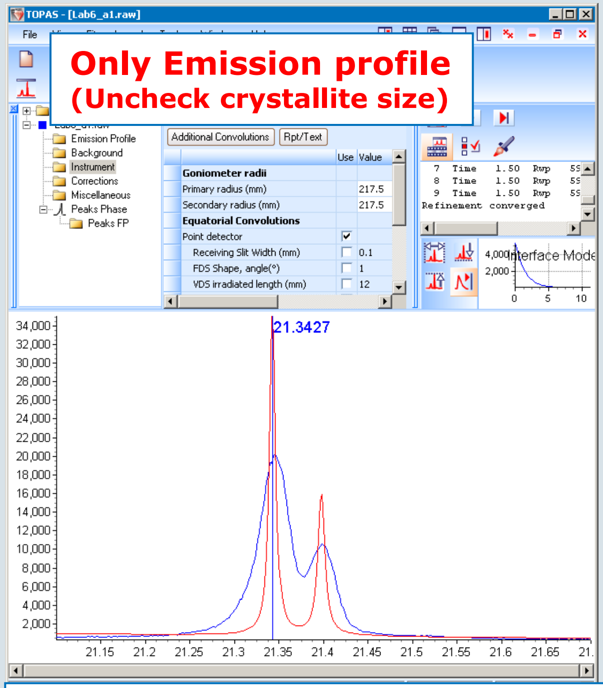


	Use	Value	Code	Erro
Goniometer radii				
Primary radius (mm)		217.5		
Secondary radius (mm)		217.5		
Equatorial Convolutions				
Point detector	☑			
Receiving Slit Width (mm)	☑	0.1	Fix	0
FDS Shape, angle(°)	☑	1	Fix	0
Beam spill, sample length (mm)	☐	50	Fix	0
VDS irradiated length (mm)	☐	12	Fix	0
VDS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

- 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

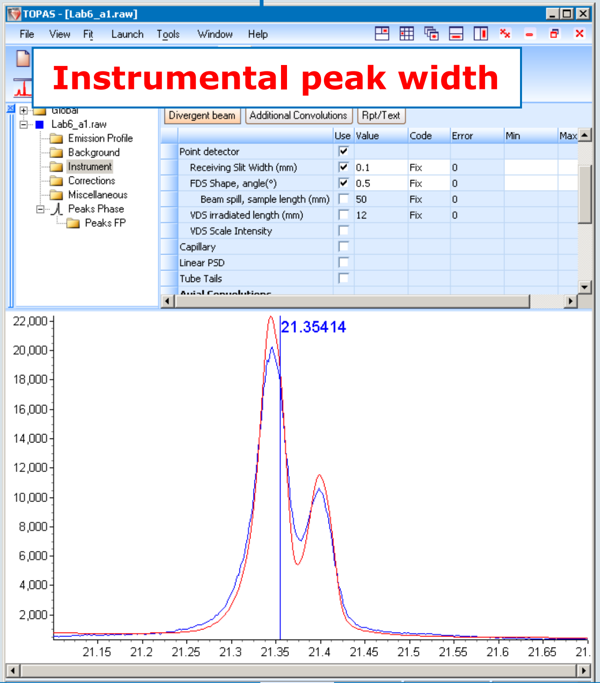


Only Emission profile
(Uncheck crystallite size)

	Use	Value
Goniometer radii		
Primary radius (mm)		217.5
Secondary radius (mm)		217.5
Equatorial Convolutions		
Point detector	☑	
Receiving Slit Width (mm)	☐	0.1
FDS Shape, angle(°)	☐	1
VDS irradiated length (mm)	☐	12

```
 7  Time   1.50  Rwp   59
 8  Time   1.50  Rwp   59
 9  Time   1.50  Rwp   59
Refinement converged
```

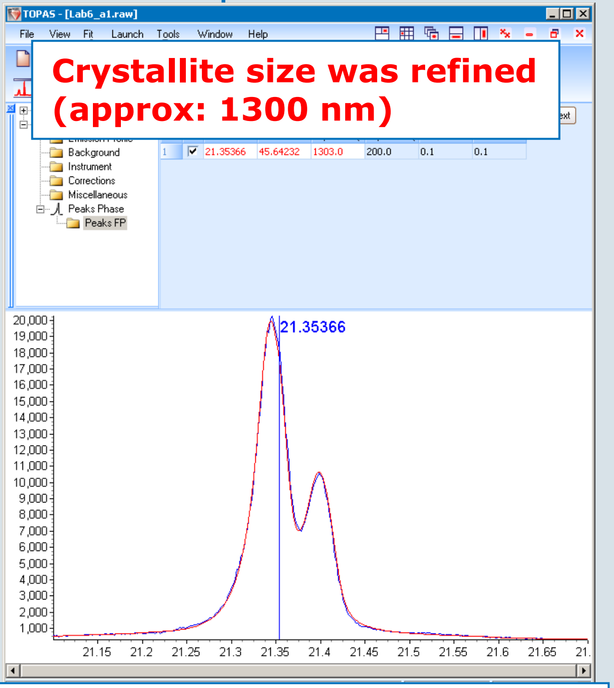
W x G_{Eq} x G_{Ax}



Instrumental peak width

	Use	Value	Code	Error	Min	Max
Point detector	☑					
Receiving Slit Width (mm)	☑	0.1	Fix	0		
FDS Shape, angle(°)	☑	0.5	Fix	0		
Beam spill, sample length (mm)	☐	50	Fix	0		
VDS irradiated length (mm)	☐	12	Fix	0		
VDS Scale Intensity	☐					
Capillary	☐					
Linear PSD	☐					
Tube Tails	☐					

(W x G_{Eq} x G_{Ax}) x S



Crystallite size was refined
(approx: 1300 nm)

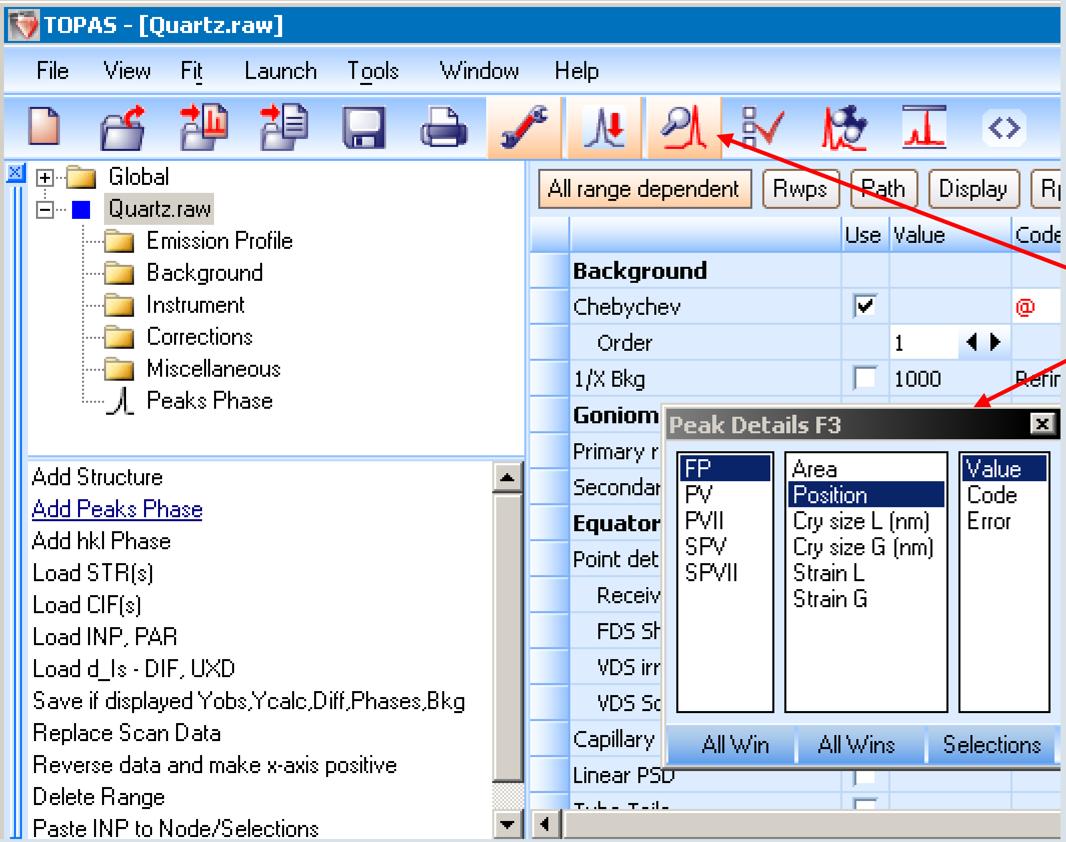
1	☑	21.35366	45.64232	1303.0	200.0	0.1	0.1

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

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

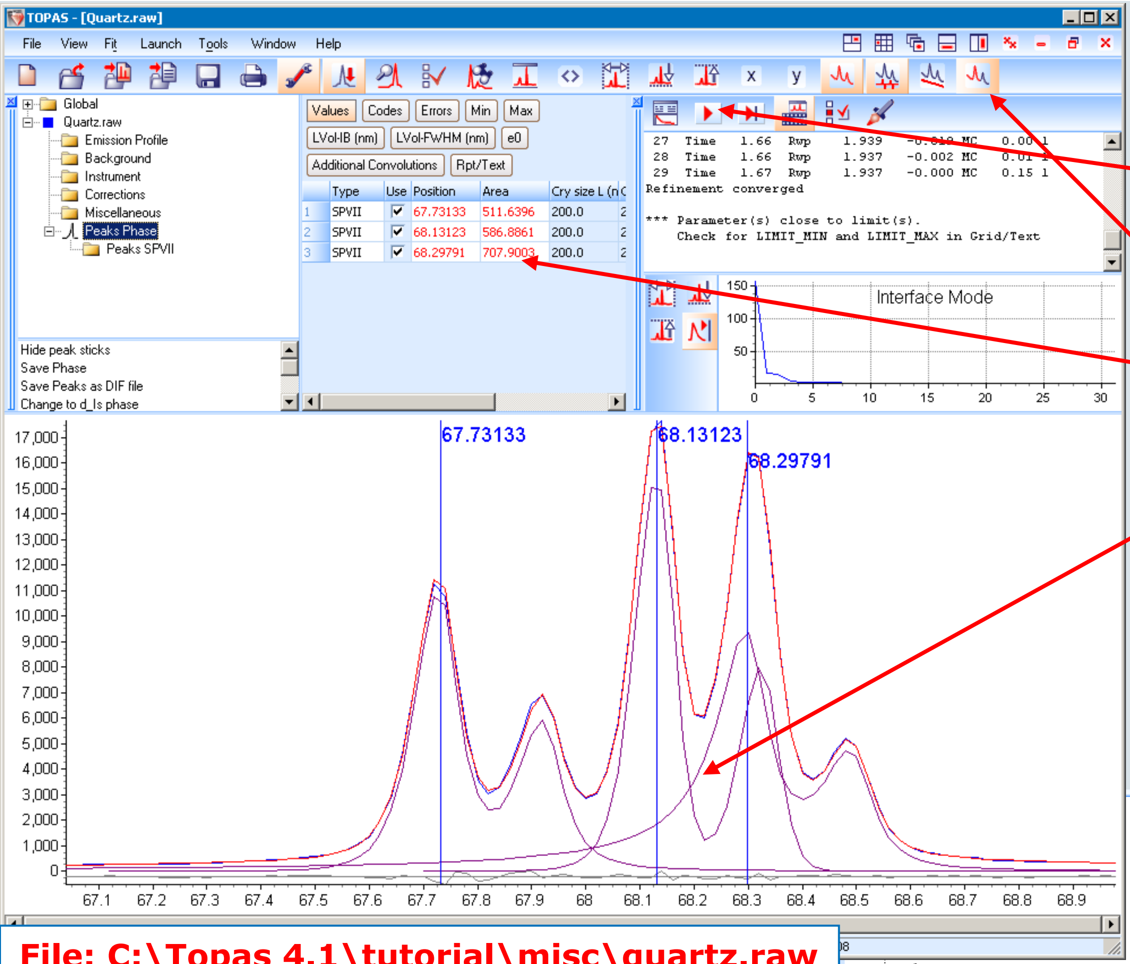
PV: Pseudo Voight function
PVII: Pearson VII function
SPV: Split Pseudo Voight function
SPVII: Split Pearson VII function

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



	Type	Use	Position	Area	Cry size L (n
1	SPVII	☑	67.73133	511.6396	200.0
2	SPVII	☑	68.13123	586.8861	200.0
3	SPVII	☑	68.29791	707.9003	200.0

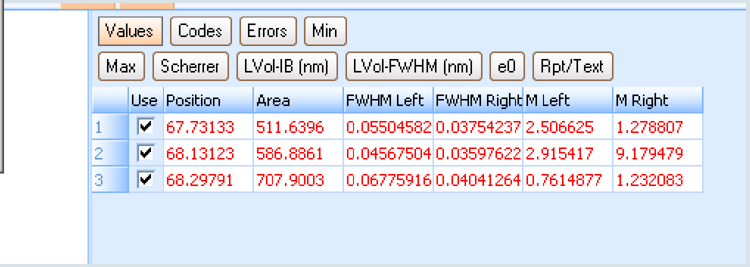
```
 27  Time   1.66  Rwp    1.939  -0.010 MC   0.00 1
 28  Time   1.66  Rwp    1.937  -0.002 MC   0.01 1
 29  Time   1.67  Rwp    1.937  -0.000 MC   0.15 1
Refinement converged

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

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
1	☑	67.73133	511.6396	0.05504582	0.03754237	2.506625	1.278807
2	☑	68.13123	586.8861	0.04567504	0.03597622	2.915417	9.179479
3	☑	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

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

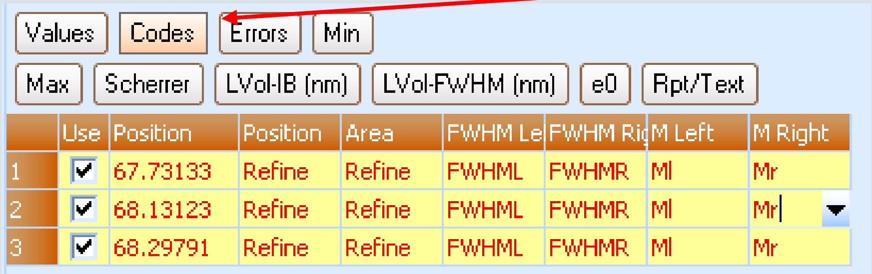
Type identical start value for FWHM and M

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

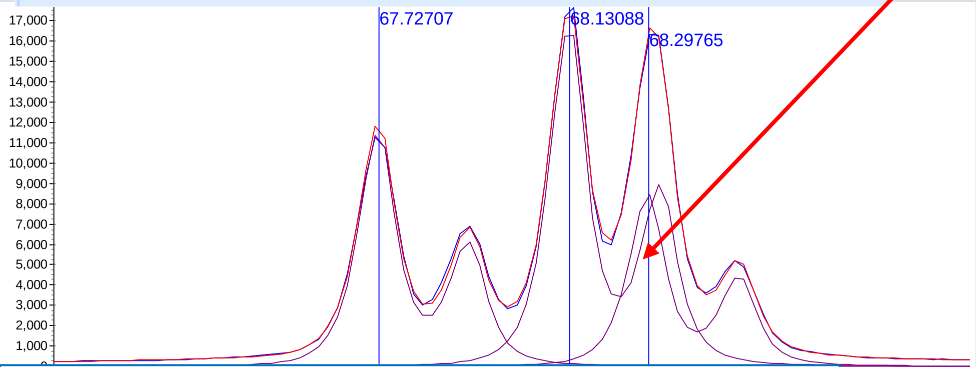
Run the Refinement again

The peaks now have identical shapes and correct intensities

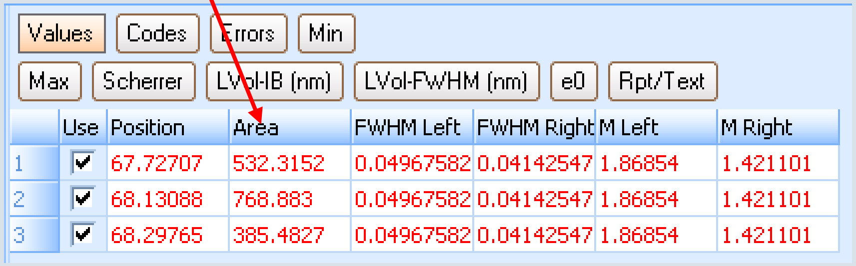
	Use	Position	Area	FWHM Left	FWHM Right	M Left	M Right
1	☑	67.73133	511.6396	0.05	0.05	1	1
2	☑	68.13123	586.8861	0.05	0.05	1	1
3	☑	68.29791	707.9003	0.05	0.05	1	1



	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



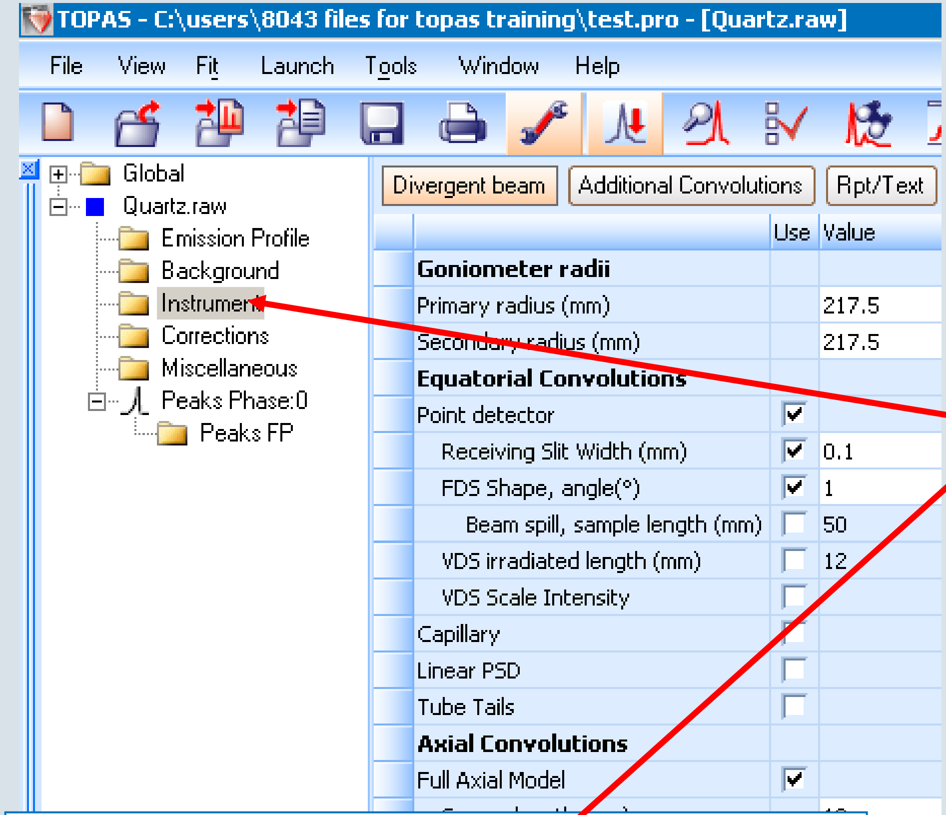
File: C:\Topas 4.1\tutorial\misc\quartz.raw
Emission profile: CuKa2_analyt.lam
Background order 3



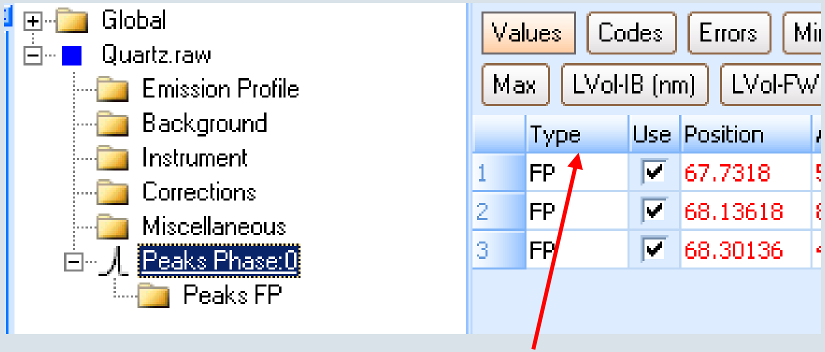
	Use	Position	Area	FWHM Left	FWHM Right	M Left	M Right
1	☑	67.72707	532.3152	0.04967582	0.04142547	1.86854	1.421101
2	☑	68.13088	768.883	0.04967582	0.04142547	1.86854	1.421101
3	☑	68.29765	385.4827	0.04967582	0.04142547	1.86854	1.421101

Profile Fitting in TOPAS

Peaks Phases, Fundamental parameters as an intrinsic constraint



	Use	Value
Goniometer radii		
Primary radius (mm)		217.5
Secondary radius (mm)		217.5
Equatorial Convolutions		
Point detector	☑	
Receiving Slit Width (mm)	☑	0.1
FDS Shape, angle(°)	☑	1
Beam spill, sample length (mm)	☐	50
VDS irradiated length (mm)	☐	12
VDS Scale Intensity	☐	
Capillary	☐	
Linear PSD	☐	
Tube Tails	☐	
Axial Convolutions		
Full Axial Model	☑	

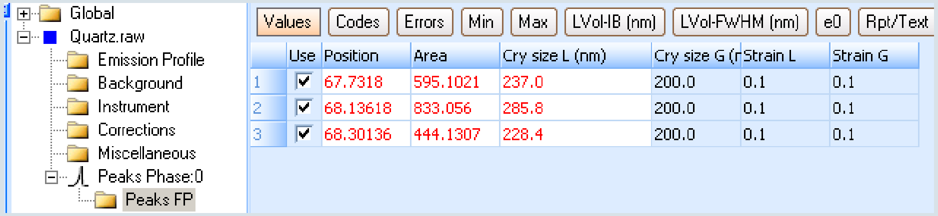


	Type	Use	Position
1	FP	☑	67.7318
2	FP	☑	68.13618
3	FP	☑	68.30136

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

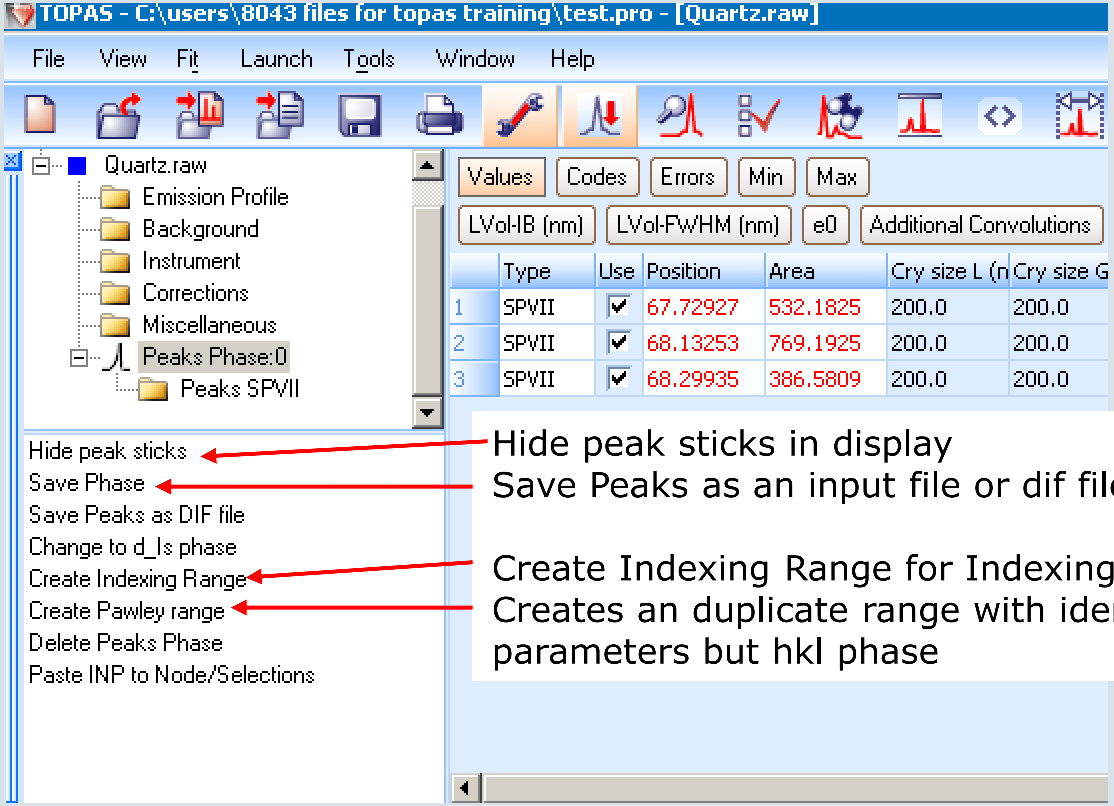


	Use	Position	Area	Cry size L (nm)	Cry size G (r	Strain L	Strain G
1	☑	67.7318	595.1021	237.0	200.0	0.1	0.1
2	☑	68.13618	833.056	285.8	200.0	0.1	0.1
3	☑	68.30136	444.1307	228.4	200.0	0.1	0.1

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



	Type	Use	Position	Area	Cry size L (n	Cry size G
1	SPVII	☑	67.72927	532.1825	200.0	200.0
2	SPVII	☑	68.13253	769.1925	200.0	200.0
3	SPVII	☑	68.29935	386.5809	200.0	200.0

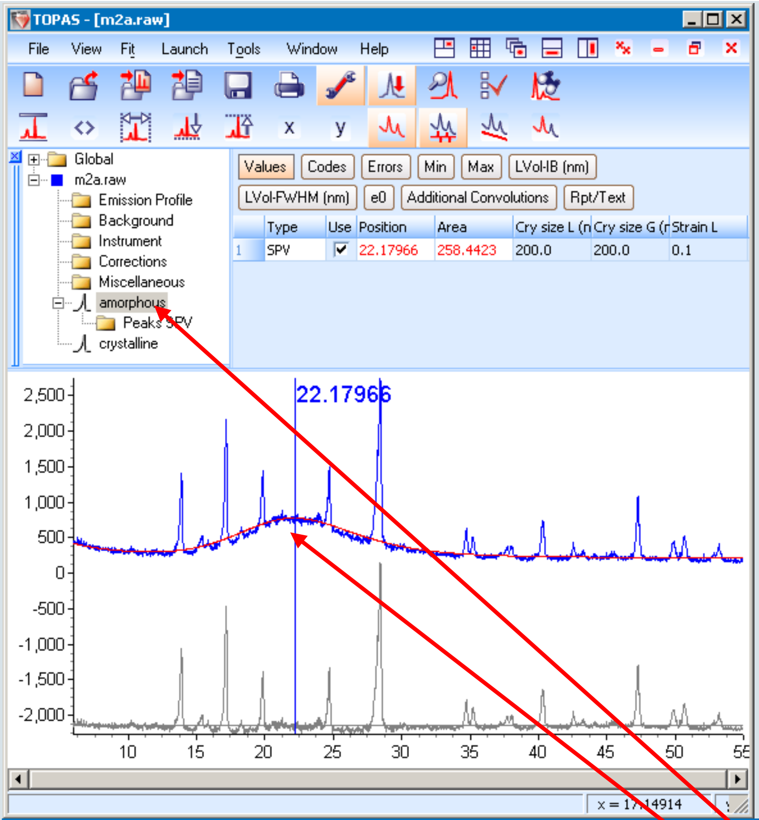
Hide peak sticks in display
Save Peaks as an input file or dif file

Create Indexing Range for Indexing single phase samples
Creates an duplicate range with identical instrument parameters but hkl phase

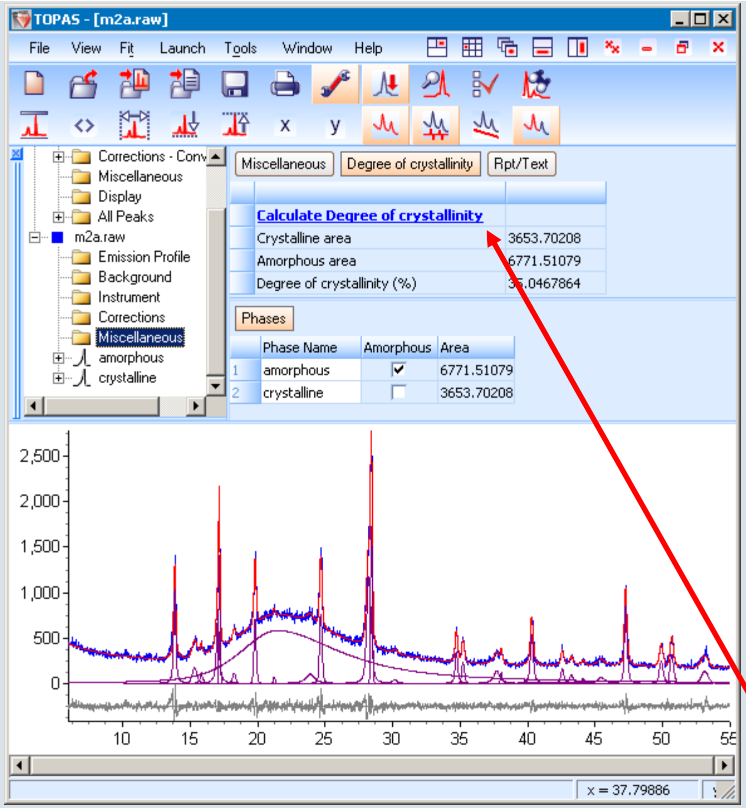
File: C:\Topas 4.2\tutorial\misc\quartz.raw
Emission profile: CuKa2_analyt.lam
Background order 3

Profile Fitting in TOPAS

Peaks Phases, Calculating Areas for crystallinity determination



	Type	Use	Position	Area	Cry size L (n	Cry size G (r	Strain L
1	SPV	☑	22.17966	258.4423	200.0	200.0	0.1



	Calculate Degree of crystallinity	
	Crystalline area	3653.70208
	Amorphous area	6771.51079
	Degree of crystallinity (%)	35.0467864

	Phase Name	Amorphous	Area
1	amorphous	☑	6771.51079
2	crystalline	☐	3653.70208

File: C:\Topas 4.2\tutorial\doc\m2a.raw

Emission profile: CuKa2_analyt.lam

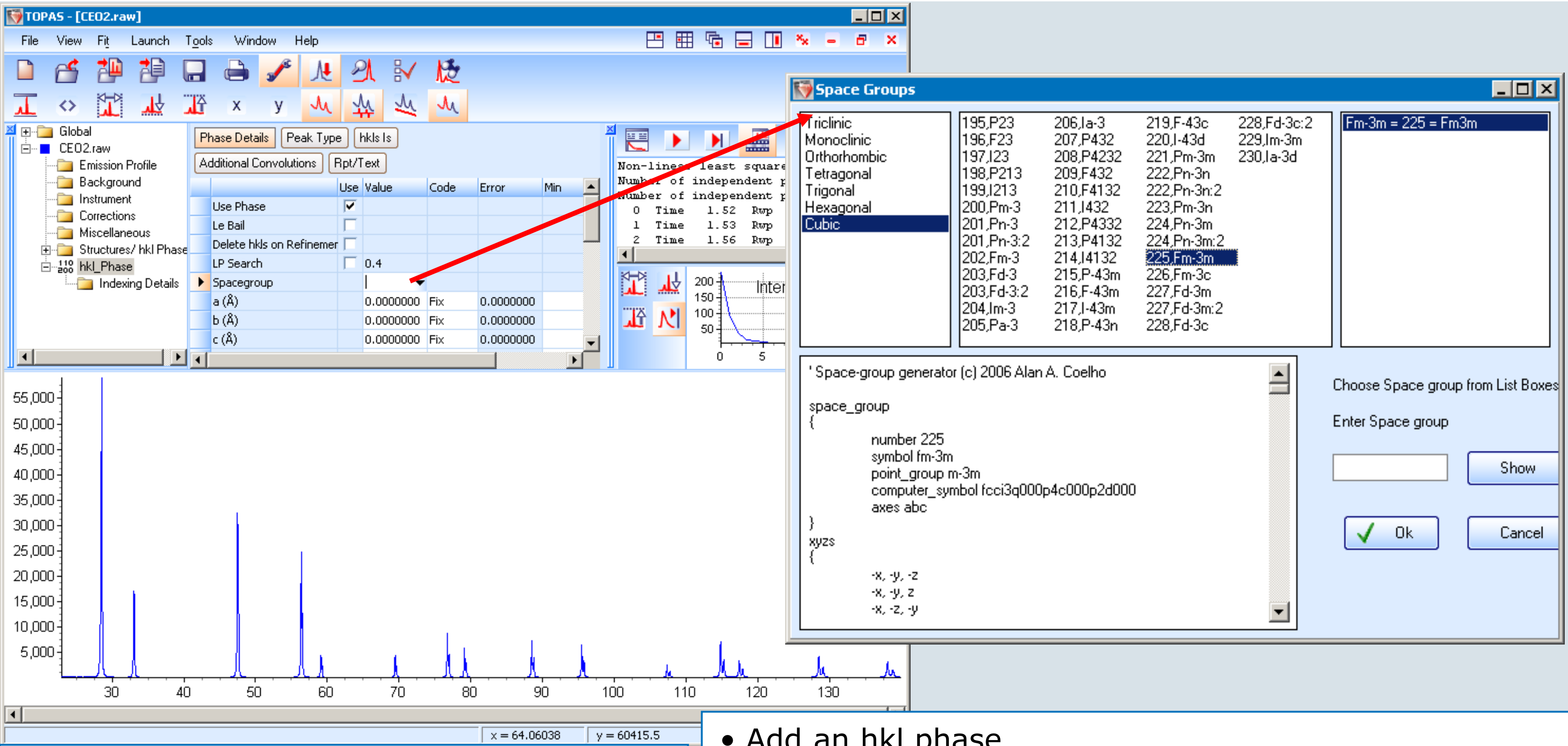
Background order 1

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



	Use	Value	Code	Error	Min
Use Phase	☑				
Le Bail	☐				
Delete hkls on Refinemer	☐				
LP Search	☐	0.4			
Spacegroup					
a (Å)		0.0000000	Fix	0.0000000	
b (Å)		0.0000000	Fix	0.0000000	
c (Å)		0.0000000	Fix	0.0000000	

```
Non-linear least square
Number of independent p
Number of independent p
   0  Time    1.52  Rwp
   1  Time    1.53  Rwp
   2  Time    1.56  Rwp
```

```
' Space-group generator (c) 2006 Alan A. Coelho

space_group
{
        number 225
        symbol fm-3m
        point_group m-3m
        computer_symbol fcci3q000p4c000p2d000
        axes abc
}
xyzs
{
        -x, -y, -z
        -x, -y, z
        -x, -z, -y
```

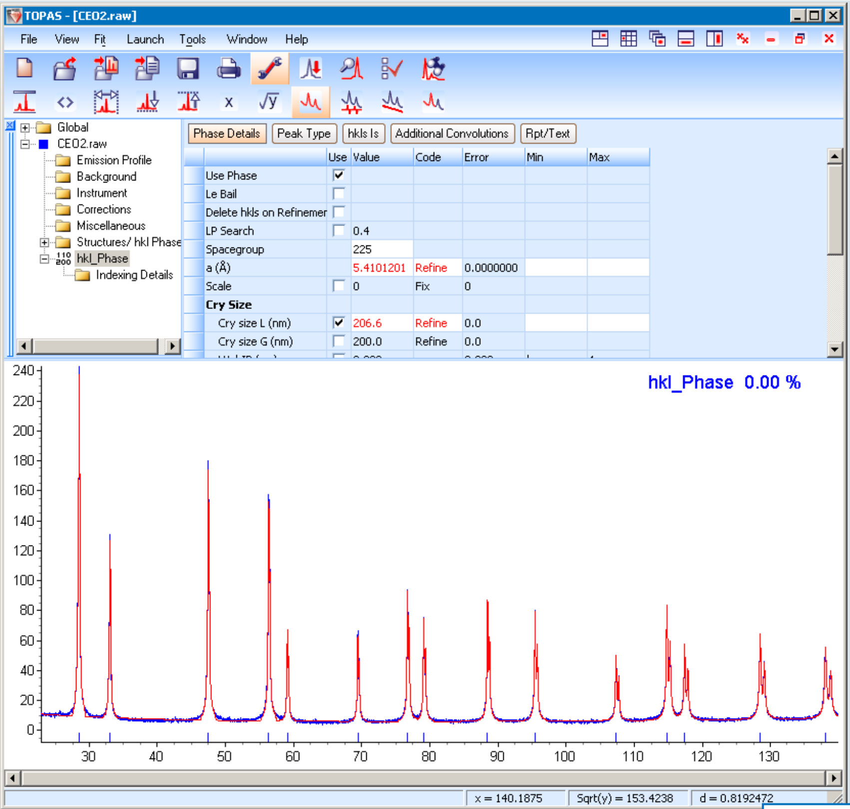
x = 64.06038   y = 60415.5

File: C:\Topas 4.2\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

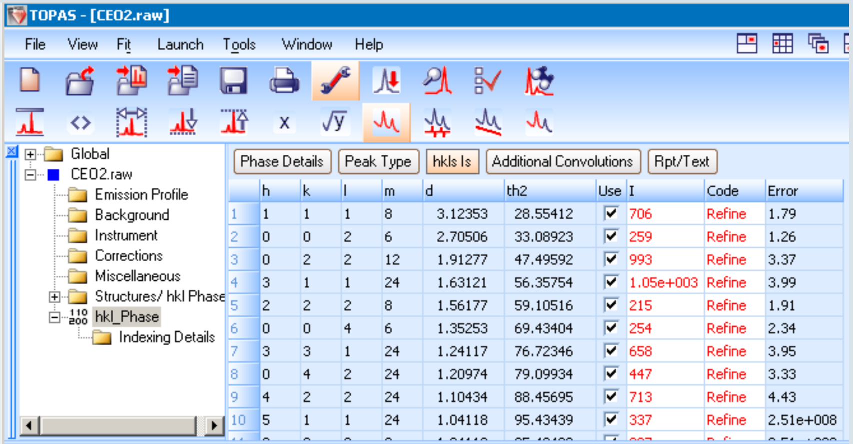
Profile Fitting in TOPAS

hkl Phases for Lattice Parameter Refinement



	Use	Value	Code	Error	Min	Max
Use Phase	☑					
Le Bail	☐					
Delete hkls on Refinemer	☐					
LP Search	☐	0.4				
Spacegroup		225				
a (Å)		5.4101201	Refine	0.0000000		
Scale	☐	0	Fix	0		
Cry Size						
Cry size L (nm)	☑	206.6	Refine	0.0		
Cry size G (nm)	☐	200.0	Refine	0.0		

x = 140.1875 Sqrt(y) = 153.4238 d = 0.8192472



	h	k	l	m	d	th2	Use	I	Code	Error
1	1	1	1	8	3.12353	28.55412	☑	706	Refine	1.79
2	0	0	2	6	2.70506	33.08923	☑	259	Refine	1.26
3	0	2	2	12	1.91277	47.49592	☑	993	Refine	3.37
4	3	1	1	24	1.63121	56.35754	☑	1.05e+003	Refine	3.99
5	2	2	2	8	1.56177	59.10516	☑	215	Refine	1.91
6	0	0	4	6	1.35253	69.43404	☑	254	Refine	2.34
7	3	3	1	24	1.24117	76.72346	☑	658	Refine	3.95
8	0	4	2	24	1.20974	79.09934	☑	447	Refine	3.33
9	4	2	2	24	1.10434	88.45695	☑	713	Refine	4.43
10	5	1	1	24	1.04118	95.43439	☑	337	Refine	2.51e+008

File: C:\Topas 4.2\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°

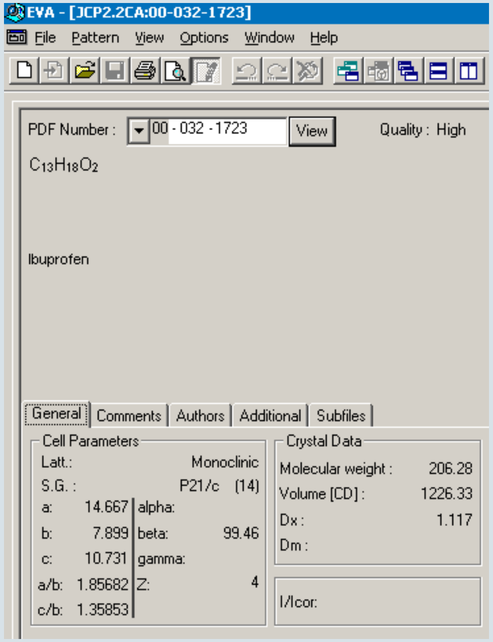
- Refined lattice parameter
- Refined average crystallite size (Scherrer equation)
- Peak list with intensities under the hkl Is tab

Profile Fitting Methods in TOPAS

Exercise: Refine Lattice parameter 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 EVA



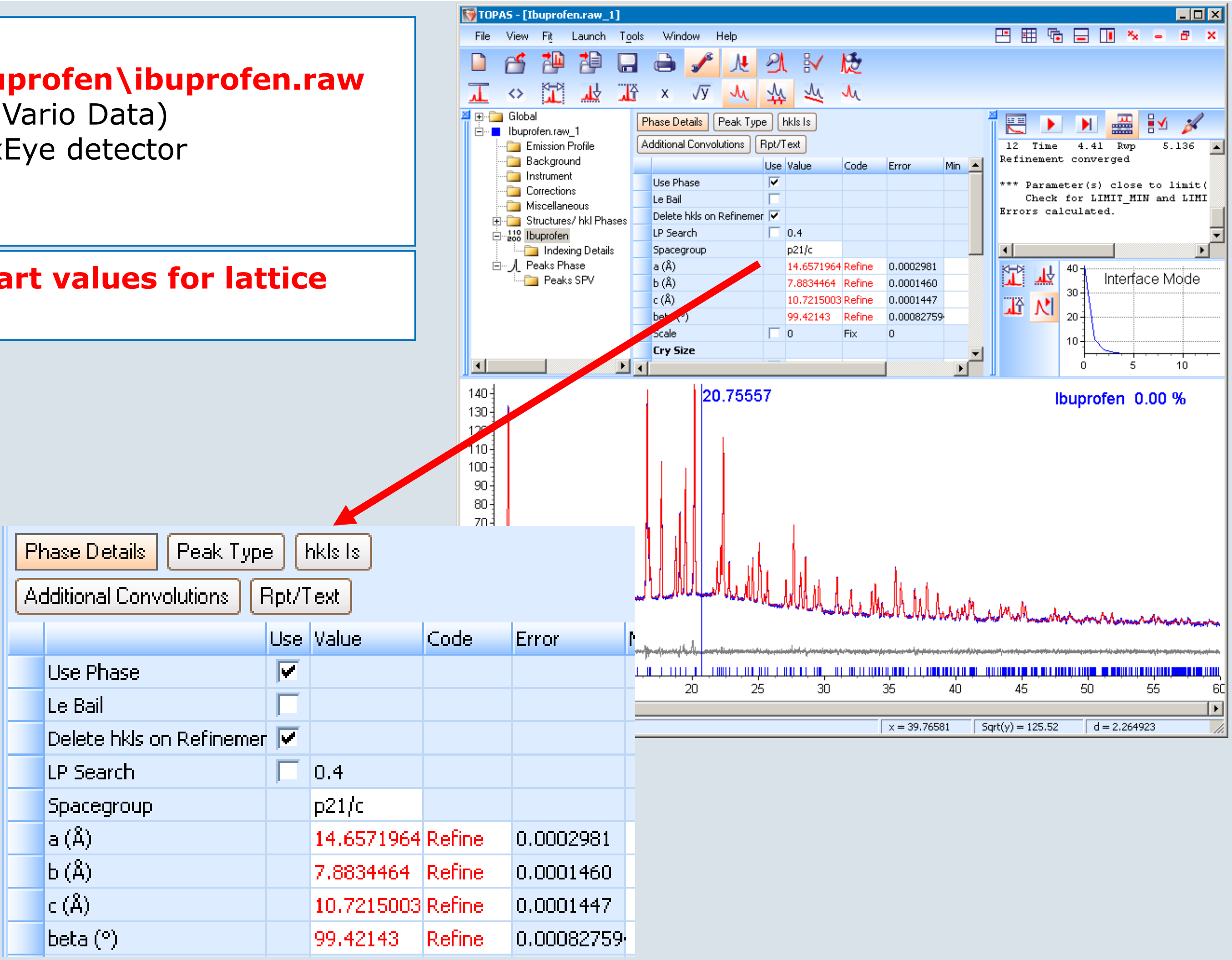
PDF Number : 00 - 032 -1723
Quality : High

$C_{13}H_{18}O_2$

Ibuprofen

Latt.: Monoclinic
S.G. : P21/c (14)
a: 14.667 alpha:
b: 7.899 beta: 99.46
c: 10.731 gamma:
a/b: 1.85682 Z: 4
c/b: 1.35853

Molecular weight : 206.28
Volume [CD] : 1226.33
Dx : 1.117
Dm :
I/Icor:

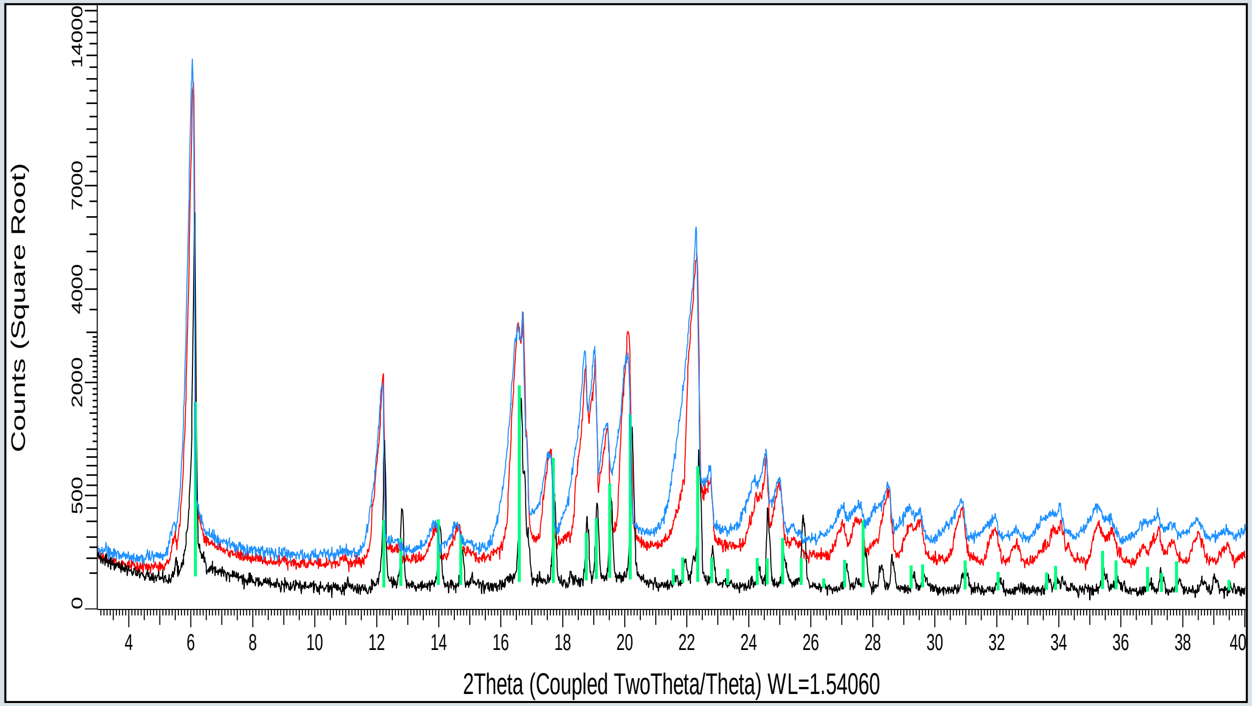


```
 12  Time   4.41  Rwp    5.136
Refinement converged

*** Parameter(s) close to limit(
    Check for LIMIT_MIN and LIMI
Errors calculated.
```

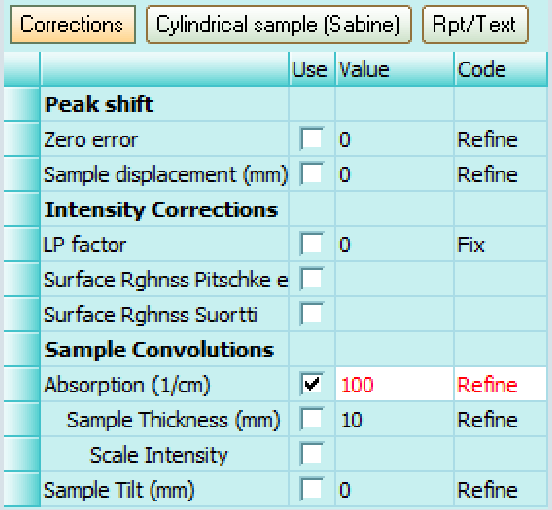
	Use	Value	Code	Error
Use Phase	☑			
Le Bail	☐			
Delete hkls on Refinemer	☑			
LP Search	☐	0.4		
Spacegroup		p21/c		
a (Å)		14.6571964	Refine	0.0002981
b (Å)		7.8834464	Refine	0.0001460
c (Å)		10.7215003	Refine	0.0001447
beta (°)		99.42143	Refine	0.00082759

Peak Shape corrections

Absorption in low density or loosely packed samples



- 🟦 Identical Ibuprofen samples measured with identical scan parameters but different sample holders
- ⬛ Flat low background holder
- 🟥 Low background holders with 0.4mm deep cavity
- 🟦 PMMA holder with 1mm depth
- 🟦 For low density samples absorption correction is necessary



	Use	Value	Code
Peak shift			
Zero error	☐	0	Refine
Sample displacement (mm)	☐	0	Refine
Intensity Corrections			
LP factor	☐	0	Fix
Surface Rghnss Pitschke e	☐		
Surface Rghnss Suortti	☐		
Sample Convolutions			
Absorption (1/cm)	☑	100	Refine
Sample Thickness (mm)	☐	10	Refine
Scale Intensity	☐		
Sample Tilt (mm)	☐	0	Refine

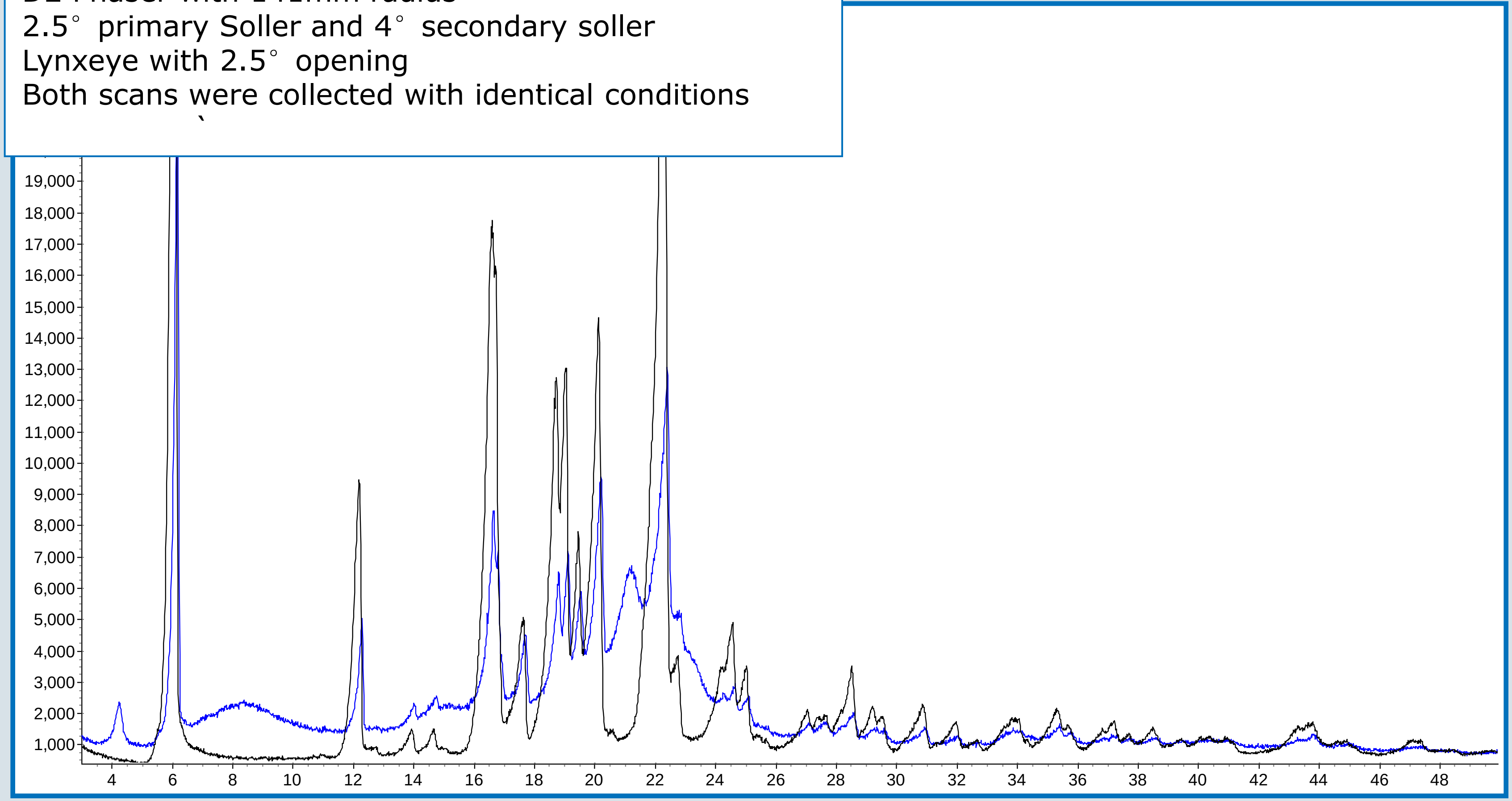
File: C:\Topas 4.2\examples\Ibuprofen D2.raw
Emission profile: CuKa2.lam
Try out Absorption correction

Profile Fitting Methods in TOPAS

Exercise: Determine degree of crystallinity in Ibuprofen testmixture

File: C:\Topas 4.2\Examples\testmixture D2.raw and …\Ibuprofen D2.raw
Emission profile: CuKa2.lam
D2 Phaser with 141mm radius
2.5° primary Soller and 4° secondary soller
Lynxeye with 2.5° opening
Both scans were collected with identical conditions

Obtain degree of crystallinity of testmixture D2.raw (assume that all excipients are amorphous and Ibuprofen D2.raw scan is 100% crystalline)



Microstructural information
Size and Strain

TOPAS default (in GUI)

Size/Strain Component functions (Double Voight Approach)

- CrySize_L: lor_fwhm = 0.1 λ/ cs1 cos(Th);
- CrySize_G: gauss_fwhm = 0.1 λ/ cs2 cos(Th);

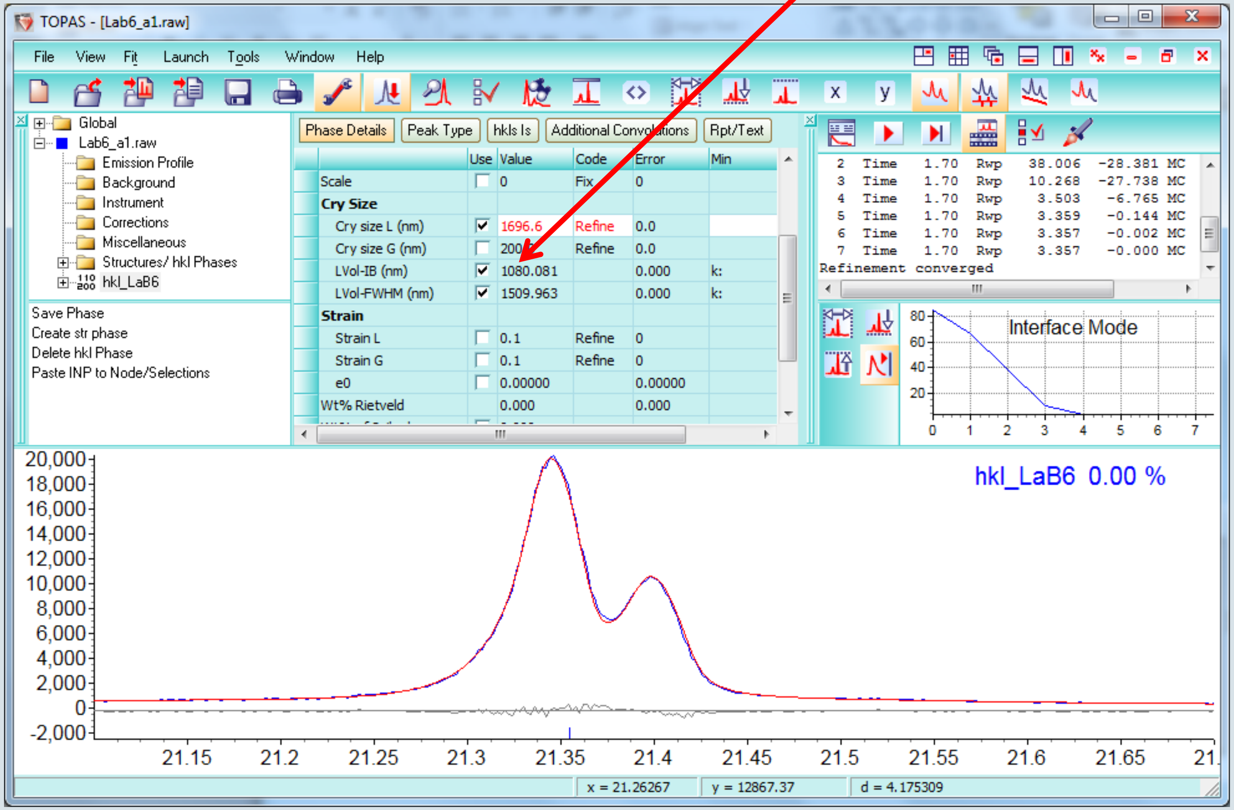
- Strain_L: lor_fwhm = str1 Tan(Th);
- Strain_G: gauss_fwhm = str2 Tan(Th);

cs1, cs2, str1, str2: Refineable parameters, arbitrary parameter names!

Microstructural information
Size/Strain

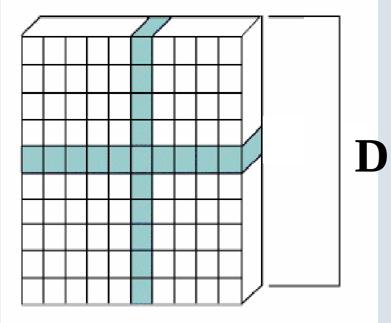
File: C:\Topas 4.2\tutorial\misc\Lab6_1.raw

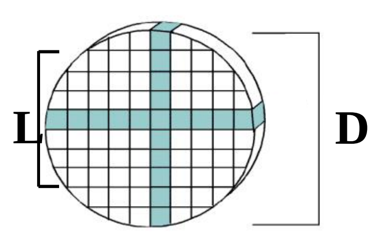
Lvol: Volume weighted mean column height
Size is shape dependent: Simple relationship for cubes and spheres but not anything else



	Use	Value	Code	Error	Min
Scale	☐	0	Fix	0	
Cry Size					
Cry size L (nm)	☑	1696.6	Refine	0.0	
Cry size G (nm)	☐	200	Refine	0.0	
LVol-IB (nm)	☑	1080.081		0.000	k:
LVol-FWHM (nm)	☑	1509.963		0.000	k:
Strain					
Strain L	☐	0.1	Refine	0	
Strain G	☐	0.1	Refine	0	
e0	☐	0.00000		0.00000	
Wt% Rietveld		0.000		0.000	

```
  2  Time   1.70  Rwp   38.006  -28.381 MC
  3  Time   1.70  Rwp   10.268  -27.738 MC
  4  Time   1.70  Rwp    3.503   -6.765 MC
  5  Time   1.70  Rwp    3.359   -0.144 MC
  6  Time   1.70  Rwp    3.357   -0.002 MC
  7  Time   1.70  Rwp    3.357   -0.000 MC
Refinement converged
```





Microstructural information
Size/Strain

Common assumption:

- Lorentzian part is Size broadening and Gaussian part is Strain.

Better:

-Model each broadening mechanism with Voight functions (Balzar and Ledbetter 1995)

-If the data is measured in large range, the component can still be separated by angular dependencies (tanΘ for strain and 1/cos Θ for size)

-If any Gaussian size broadening is present, it will lead to better fit

-Size distribution can be attempted in Launch Mode by calculating the integral breadth of Lorentzian (Cauchy) size contribution. Works in simple cases and if instrumental function is well known.

Anisotropic Refinement Models

Anisotropic shifts, broadenings and peak assymmetries

General Considerations

- In most applications, the objective is primarily to improve the fit, with an expectation to improve indexing, structure determination and structure refinement
- Anisotropic micro-structure parameters can be derived
- Example functions
  - Spherical harmonics (Popa, 1998)
  - 2nd rank tensors (Le Bail & Jouanneaux, 1997)
    - Multi-dimensional distribution of lattice metrics (Stephens, 1999)

- TOPAS Tutorial Examples:
  - Norbonane Fitch & Jobic, 1993
  - LT-ZrMo2O8 Allen et al., 2003
  - NaBenzo R. Dinnebier et al., 1999
  - Clay S. Hillier, 2003
  - SerpMix1 M. Raudsepp, 2004

File: C:\Topas 4.2\tutorial\anisoLS\...

Anisotropic Refinement models

- Keywords that can be hkl dependent

th2_offset E	(anisotropic peak shifts - macrostrain)
scale_pks E	(preferred orientation)

----

lor_fwhm E	(anisotropic line width)
gauss_fwhm E	(anisotropic line width)
hat E	(anisotropic line width)
one_on_x_conv E	(anisotropic line asymmetry)
exp_conv_const E	(anisotropic line asymmetry)
circles_conv E	(anisotropic line asymmetry)
user_defined_convolution	

Anisotropic Refinement models

- Example: Spherical harmonics

  Anisotropic line width

```
prm p1 0.01 min 0.0001
spherical_harmonics_hkl sh1
sh_order 2
lor_fwhm = sh1 p1 / Cos(Th);
```

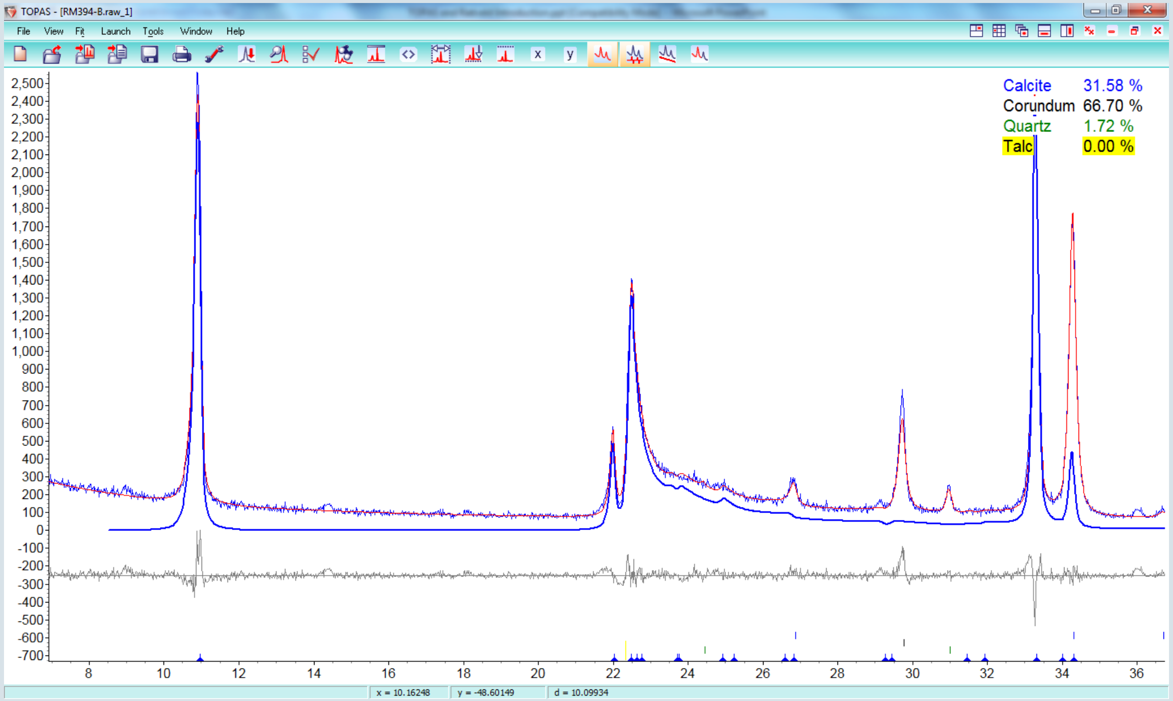
- Anisotropic line asymmetry

```
prm p2 0.01 min 0.0001
spherical_harmonics_hkl sh2
sh_order 2
circles_conv = sh2 p2 / Cos(Th);
```

p1, sh1, p2, sh2: Refineable parameters, arbitrary parameter names!

Anisotropic Refinement models

Example:
Set C:\Topas 4.2\tutorial\anisoLS\clay.inp in Launch mode
Run the Refinement
Edit the text file in text editor, uncomment Spherical_harmonics_hkl lines and run again



Calcite 31.58 %
Corundum 66.70 %
Quartz 1.72 %
Talc 0.00 %

x = 10.16248 y = -48.60149 d = 10.09934

```
spherical_harmonics_hkl   sh
sh_order  8
exp_conv_const = (sh-1) / Sin(Th);
```

The Rietveld method

- is a standard-less full-profile approach to quantitative phase analysis
- uses every datapoint as a unique observation and least square methods to minimize the difference between calculated and measured intensities
- Residual of Least Square Refinement

  $R = \Sigma\, w_i(y_i - yc_i)^2$

Rietveld Analysis requires:

- The crystal structure data for every phase in a mixture (unit cell and atomic positions)
- a model for the peak shapes and widths and a model for any aberrations
- a model for the background

The relative masses of all phases contributing to the diffraction pattern can be derived from the refinement using the simple relationship:

$$W_r = S_r\,(ZMV)_r \,/\, \sum_t S_t\,(ZMV)_t$$

W_r is the *relative* weight fraction of phase *r* in a mixture of *t* phases
S is the scale factor derived from Rietveld refinement
Z is the number of formula units per unit cell
M is the mass of the formula unit (atomic mass units)
V is the volume of the unit cell (Å^3).

Data collection

Measurement parameters:

Depend on sample properties: Determine peak width with a short test scan

- Adjust step size for sufficient amount of data points (6 data points above FWHM)
- Adjust time/step for sufficient counting statistics (at least a few thousand counts on the most intense peaks for basic quantitative analysis)

Typical measurement parameters for analysis of mineral samples:

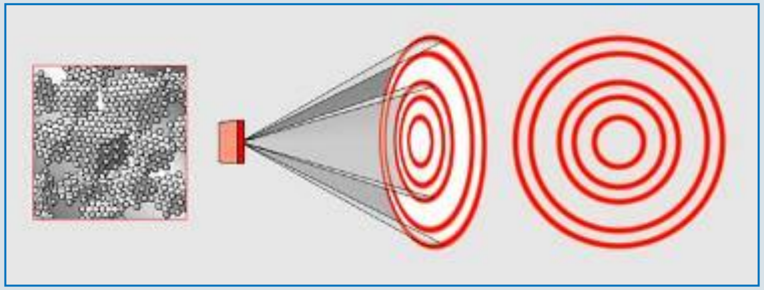
- With Point detector:
- 1° divergence slit
- 4° Soller slits
- 0.02 step size and at least 1 sec/step

- With 1-D detector:
- 0.3° divergence slit and anti-airscatter screen
- 4° Soller slits
- 0.015 step size and at least 0.1 sec/step

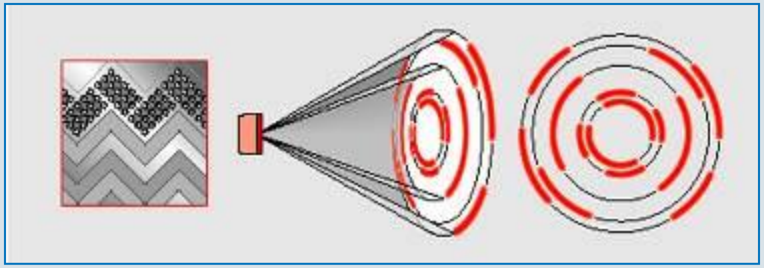
Data collection
General sample preparation requirements

- Good mixing, powder sample should be representative for bulk sample (no segregation)
- Smooth flat surface
- Sufficient particles to cover the x-ray beam area
- Sample thickness should be sufficient for correct intensities (infinite thickness for correct intensities)
- For low density materials thin layers will result in more accurate peak positions (transparancy effect), often better for indexing
- Sufficient number of particles for good statistics (increase number of measured particles by rotation)

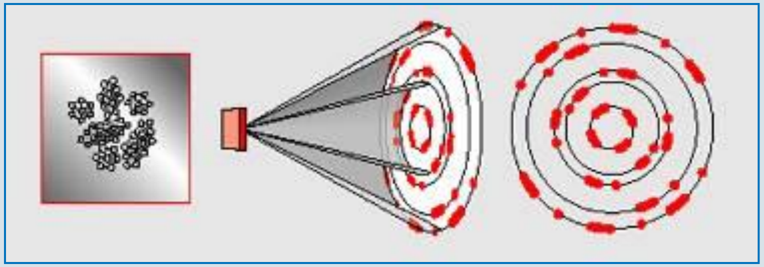
Sample Preparation
Powder Diffraction Basics



Diffraction of an ideal powder



Diffraction of textured materials



Diffraction of a small number
of crystallites ("spotiness effect")

Sample Preparation
Powder Diffraction Basics

- Accurate, reproducible diffraction intensities require small crystallite size

  typical intensity reproducibility for Quartz (113) reflection with CuKα: is

15-20 µm	5-50 µm	5-15 µm	<5 µm
18.2%	10.1%	2.1%	1.2%

- The number of crystallites diffracting is related to size

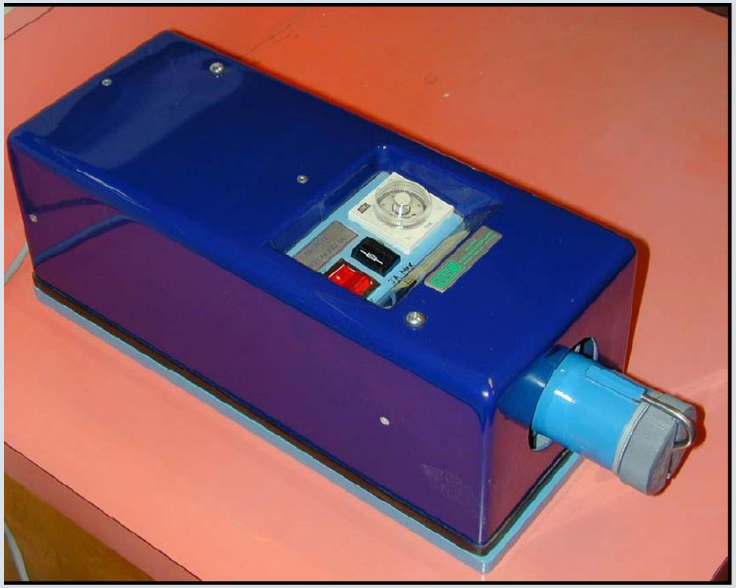
diameter	40 µm	10 µm	1 µm
crystallites / 20mm^3	597.000	38.000.000	3.820.000.000
number diffracting	12	760	38.000

Smith, 1992

General Sample preparation requirements

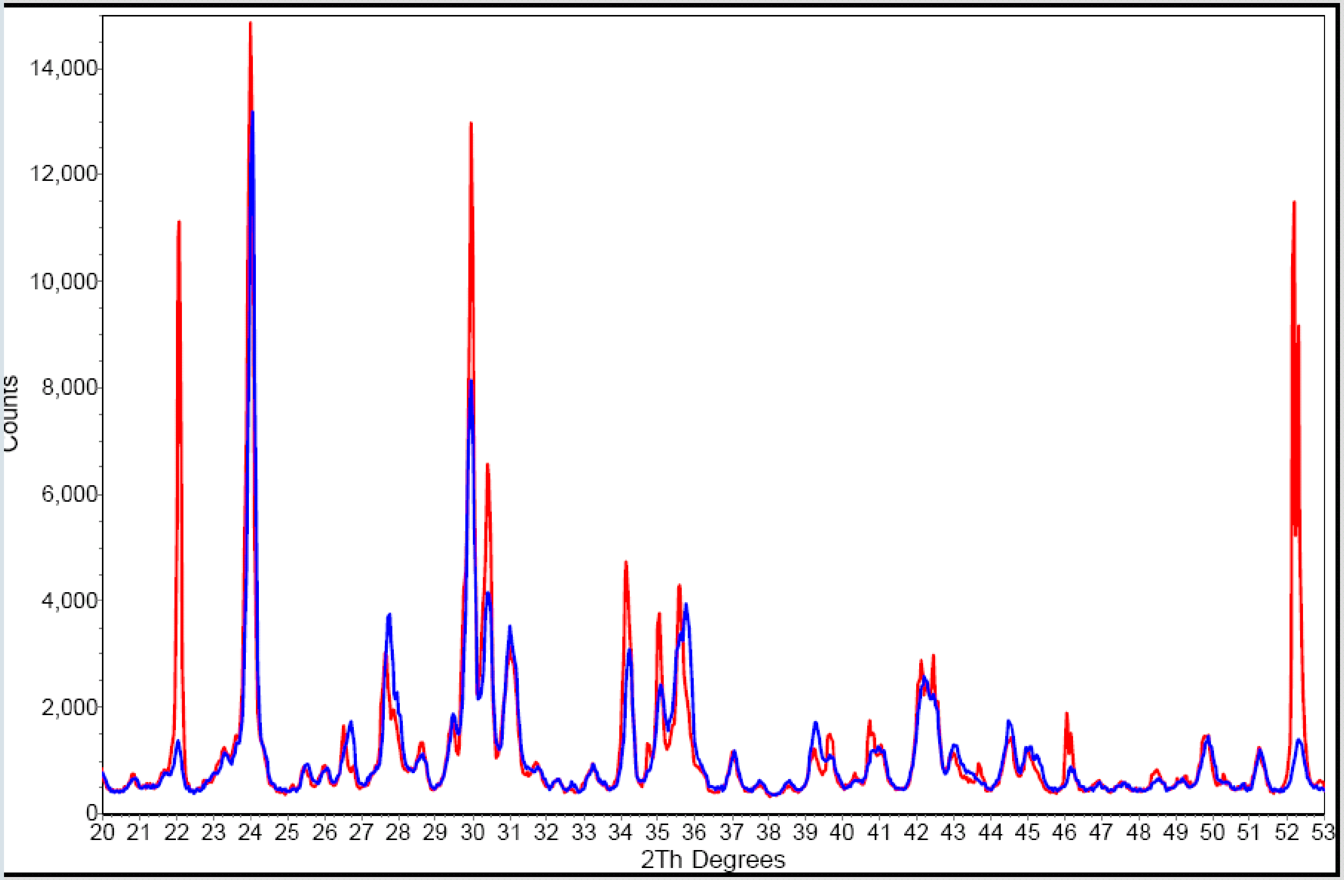
Sufficient Grinding

- Powder preparation
  - Reduce particle size with mortar and pestle (or automatic mill) to smaller than 10 μm to increase number of crystallites and avoid spotiness effect
  - Wet grinding with alcohol in MrCrone Mill is ideal for many geolocial samples.
  - Too coarse grinding also effects preferred orientation



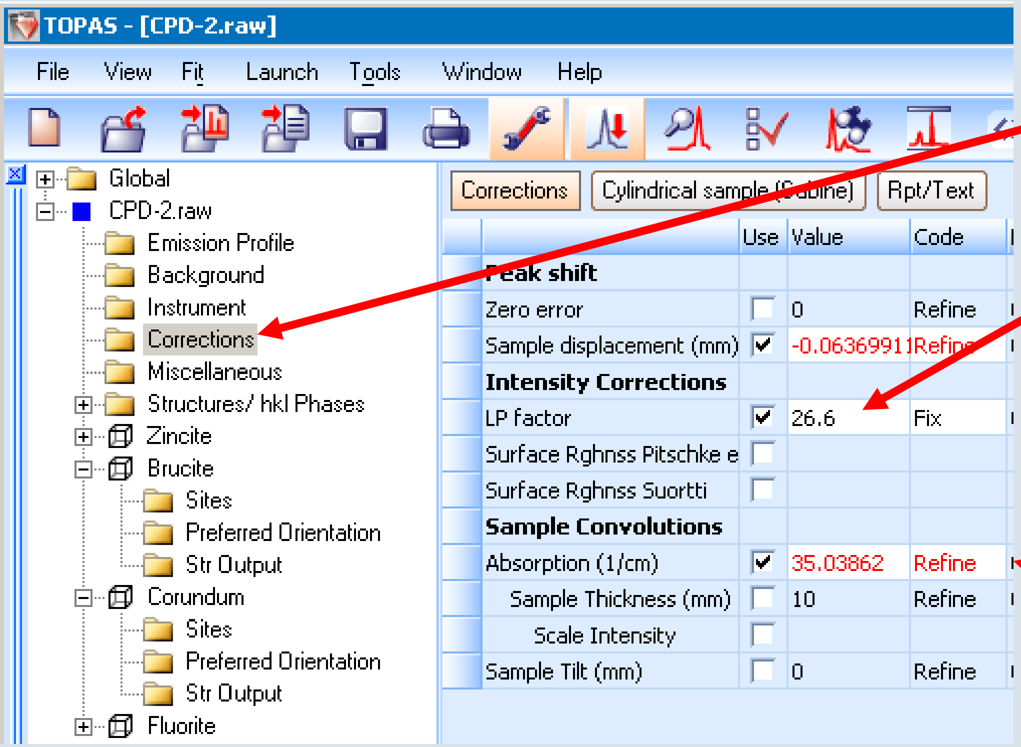
General requirements

Sufficient Grinding



Comparison of X-ray powder-diffraction patterns of a sample mechanically ground under ethanol to <5 μm (blue) and the same sample dry ground by hand with a mortar and pestle (red) . Note the large differences in intensity.

Rietveld Refinement
Corrections



	Use	Value	Code
Peak shift			
Zero error	☐	0	Refine
Sample displacement (mm)	☑	-0.06369911	Refine
Intensity Corrections			
LP factor	☑	26.6	Fix
Surface Rghnss Pitschke e	☐		
Surface Rghnss Suortti	☐		
Sample Convolutions			
Absorption (1/cm)	☑	35.03862	Refine
Sample Thickness (mm)	☐	10	Refine
Scale Intensity	☐		
Sample Tilt (mm)	☐	0	Refine

- Highlight corrections
- Use either Zero Error or Sample displacement as a peak shift correction
- Always Check Lorentz- Polarization correction
  - Type in the Bragg angle of the monochromator
  - Type 0, if no monochromator is present (Ni-filter, Sol-x detector)
- Depending on the sample you may refine Absorption correction

Using the correct structure file

Phase identification

- Correct phase identification is often more difficult than performing the actual Rietveld refinement.
- Use EVA and any complementary data that are available (e.g. XRF, EDX, thermal analysis, etc) to correctly identify all phases.
- Try to find the corresponding structure file in a database, not all structures are known.
- For complex samples with clays, a clay fraction may be necessary to correctly identify and quantify all phases in the sample.
- Quantitative Rietveld results are always normalized to 100% → If any phases are missed or mis-identified, it will lead to errors in the other phases as well.
- If amorphous phases are present, they can sometimes only be detected by using an internal standard.

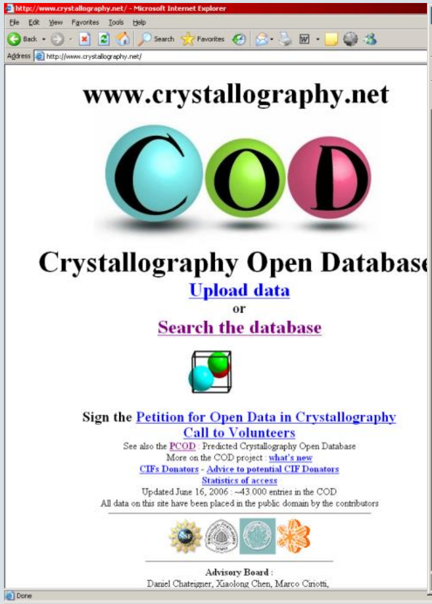
Using the correct structure file
Structure databases

- **Inorganic crystal structure database (ICSD) available at www.nist.gov or at http://icsdweb.fiz-karlsruhe.de/index.php**
- **Bruker-AXS structure database (a few hundred minerals)**

Free databases:

- **www.crystallography.net**
- **American Mineralogist Crystal structure database http://rruff.geo.arizona.edu/AMS/amcsd.php**
- **Min-Chryst http://database.iem.ac.ru/mincryst/**
- **Search for the structure in Google**

Some structures in free data bases may have to be reformatted, if they do not conform to the standard CIF format.


http://www.crystallography.net/ - Microsoft Internet Explorer

http://www.crystallography.net/

www.crystallography.net

Crystallography Open Database

Upload data

or

Search the database

Sign the Petition for Open Data in Crystallography

Call to Volunteers

See also the PCOD : Predicted Crystallography Open Database

More on the COD project : what's new

CIFs Donators - Advice to potential CIF Donators

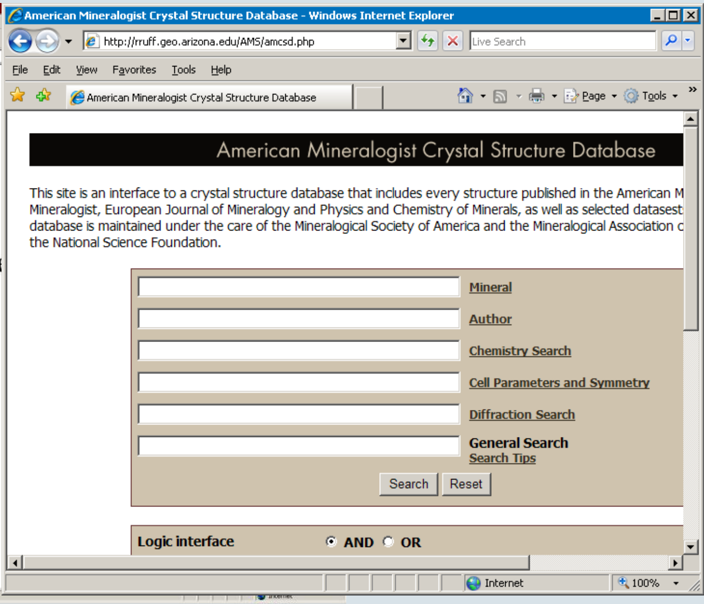
Statistics of access

Updated June 16, 2006 : ~43 000 entries in the COD

All data on this site have been placed in the public domain by the contributors

Advisory Board :

Daniel Chateigner, Xiaolong Chen, Marco Ciriotti,

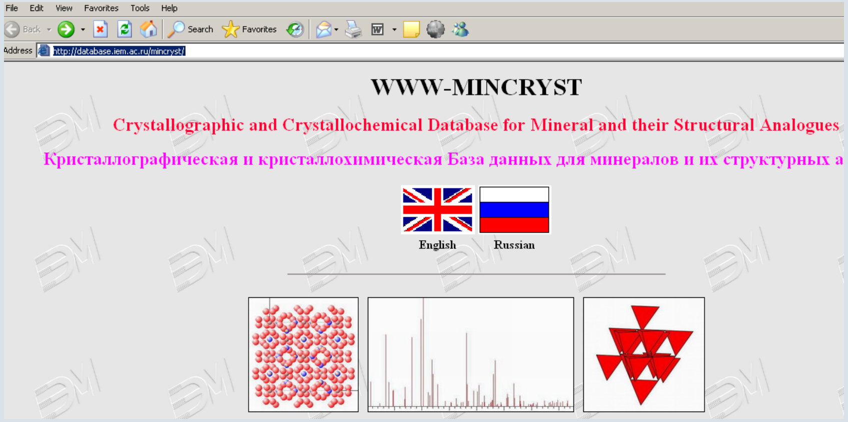

American Mineralogist Crystal Structure Database - Windows Internet Explorer

http://rruff.geo.arizona.edu/AMS/amcsd.php

American Mineralogist Crystal Structure Database

This site is an interface to a crystal structure database that includes every structure published in the American M
Mineralogist, European Journal of Mineralogy and Physics and Chemistry of Minerals, as well as selected datasest
database is maintained under the care of the Mineralogical Society of America and the Mineralogical Association c
the National Science Foundation.

Logic interface ● AND ○ OR



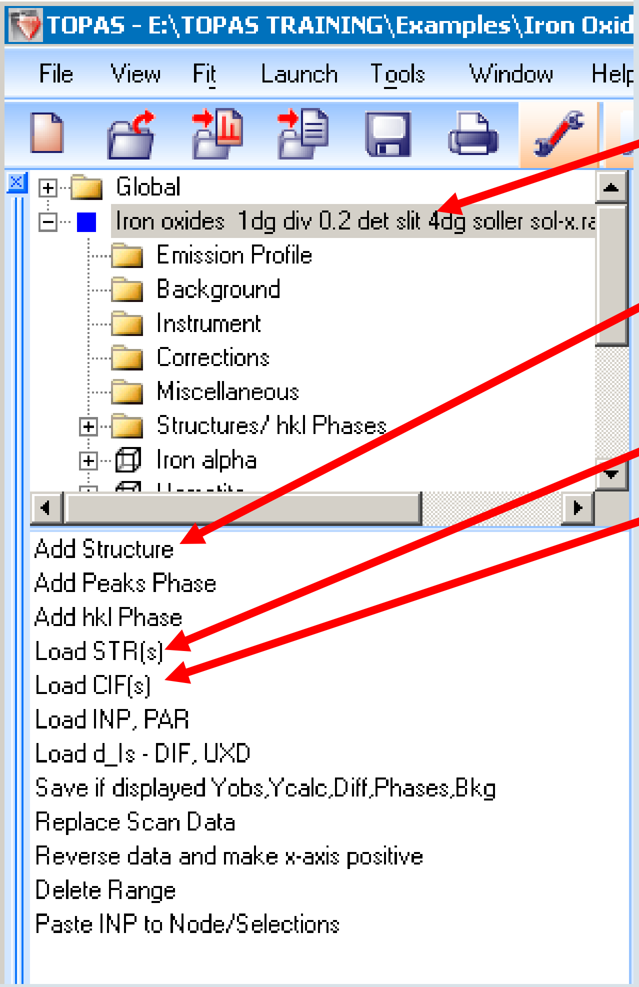
http://database.iem.ac.ru/mincryst/

WWW-MINCRYST

Crystallographic and Crystallochemical Database for Mineral and their Structural Analogues

Кристаллографическая и кристаллохимическая База данных для минералов и их структурных а

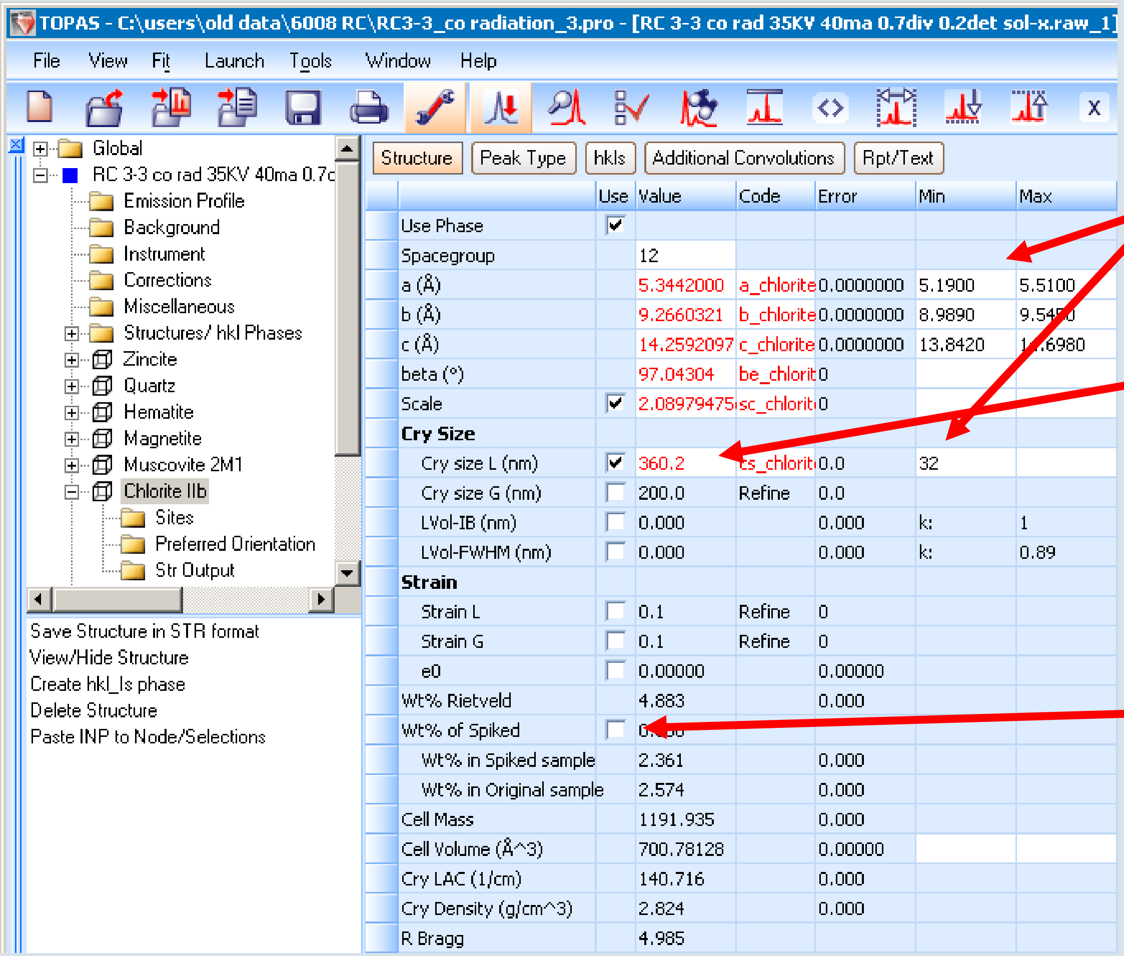
Structure files
Entering the structure into TOPAS



- Highlight the scan file in the parameter window (the window below or in the context menu (right mouse click) allow several options for entering structures.
- Add Structure: Enter a structure manually (lattice parameters and atomic positions). This is sometimes required if the structure is only known from a journal.
- Load STR(s): Load a structure file from the Bruker database
- Load CIF(s): The Crystallographic Interchange Format is a standard format for structures. Most databases or publications have this format for crystal structures.
  Note that not every structure file in cif format that is found online, loads without problems. Occasionly, cif files have to be modified in a text editor to load correctly
- Load INP: Load a structure in Input file format (typically from TOPAS refinements)

Structure files

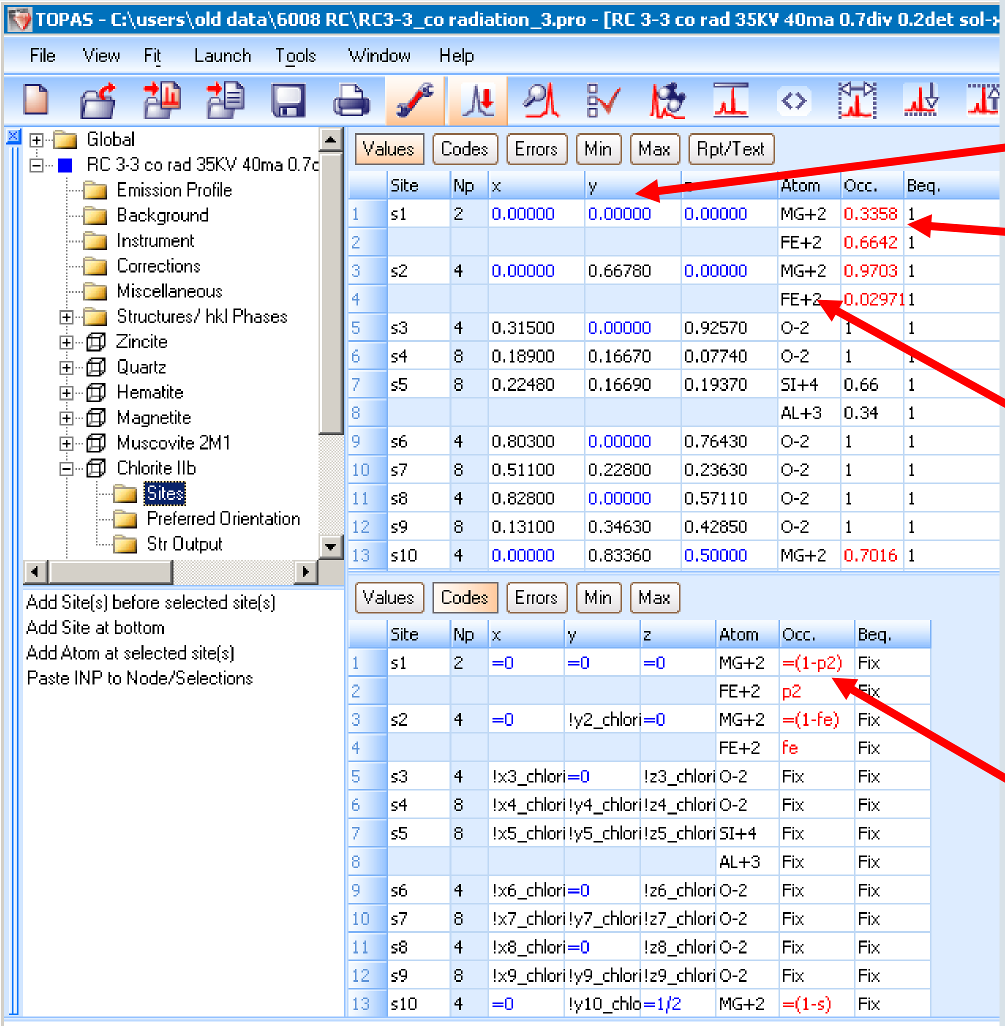
Example: Chlorite
Unit cell parameters



	Use	Value	Code	Error	Min	Max
Use Phase	☑					
Spacegroup		12				
a (Å)		5.3442000	a_chlorite	0.0000000	5.1900	5.5100
b (Å)		9.2660321	b_chlorite	0.0000000	8.9890	9.54[illegible]0
c (Å)		14.2592097	c_chlorite	0.0000000	13.8420	1[illegible].6980
beta (°)		97.04304	be_chlorit	0		
Scale	☑	2.08979475	sc_chlorit	0		
Cry Size						
Cry size L (nm)	☑	360.2	cs_chlorit	0.0	32	
Cry size G (nm)	☐	200.0	Refine	0.0		
LVol-IB (nm)	☐	0.000		0.000	k:	1
LVol-FWHM (nm)	☐	0.000		0.000	k:	0.89
Strain						
Strain L	☐	0.1	Refine	0		
Strain G	☐	0.1	Refine	0		
e0	☐	0.00000		0.00000		
Wt% Rietveld		4.883		0.000		
Wt% of Spiked	☐	0[illegible]				
Wt% in Spiked sample		2.361		0.000		
Wt% in Original sample		2.574		0.000		
Cell Mass		1191.935		0.000		
Cell Volume (Å^3)		700.78128		0.00000		
Cry LAC (1/cm)		140.716		0.000		
Cry Density (g/cm^3)		2.824		0.000		
R Bragg		4.985				

- Values in red are refinable parameters (double click on the code column will change the state to „Fixed")
- Constraining the lattice parameters and crystallite sizes to reasonable values helps with the refinement, especially for impurity phases or phases with broad peaks.
- Average crystallite size values for most minerals are typically above 30 nm and below 1000nm. Clays phases may require smaller crystallite sizes to fit broad peaks.
- Entering the weight of an internal standard in % allows quantification of amorphous materials

Structure files
Example: Chlorite
Atomic sites

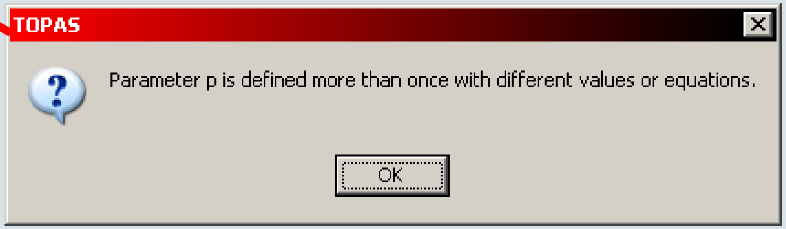


	Site	Np	x	y	z	Atom	Occ.	Beq.
1	s1	2	0.00000	0.00000	0.00000	MG+2	0.3358	1
2						FE+2	0.6642	1
3	s2	4	0.00000	0.66780	0.00000	MG+2	0.9703	1
4						FE+2	0.02971	1
5	s3	4	0.31500	0.00000	0.92570	O-2	1	1
6	s4	8	0.18900	0.16670	0.07740	O-2	1	1
7	s5	8	0.22480	0.16690	0.19370	SI+4	0.66	1
8						AL+3	0.34	1
9	s6	4	0.80300	0.00000	0.76430	O-2	1	1
10	s7	8	0.51100	0.22800	0.23630	O-2	1	1
11	s8	4	0.82800	0.00000	0.57110	O-2	1	1
12	s9	8	0.13100	0.34630	0.42850	O-2	1	1
13	s10	4	0.00000	0.83360	0.50000	MG+2	0.7016	1

	Site	Np	x	y	z	Atom	Occ.	Beq.
1	s1	2	=0	=0	=0	MG+2	=(1-p2)	Fix
2						FE+2	p2	Fix
3	s2	4	=0	!y2_chlori	=0	MG+2	=(1-fe)	Fix
4						FE+2	fe	Fix
5	s3	4	!x3_chlori	=0	!z3_chlori	O-2	Fix	Fix
6	s4	8	!x4_chlori	!y4_chlori	!z4_chlori	O-2	Fix	Fix
7	s5	8	!x5_chlori	!y5_chlori	!z5_chlori	SI+4	Fix	Fix
8						AL+3	Fix	Fix
9	s6	4	!x6_chlori	=0	!z6_chlori	O-2	Fix	Fix
10	s7	8	!x7_chlori	!y7_chlori	!z7_chlori	O-2	Fix	Fix
11	s8	4	!x8_chlori	=0	!z8_chlori	O-2	Fix	Fix
12	s9	8	!x9_chlori	!y9_chlori	!z9_chlori	O-2	Fix	Fix
13	s10	4	=0	!y10_chlo	=1/2	MG+2	=(1-s)	Fix

- For quantitative mineral analysis the atomic sites (x,y,z) of the phase are never refined.
- In solution phases such as Chlorite the occupation factors for the Mg/Fe substitution may be refined.
- The x, y or z positions in blue color designate special positions for this unit cell.
- The atom or ion must be part of the drop down list in the atom column (with imported cif files this could lead to an error message)

- Parameter names like „p" or „s" have to be unique within a TOPAS project. If not, it will lead to this error message → rename parameters



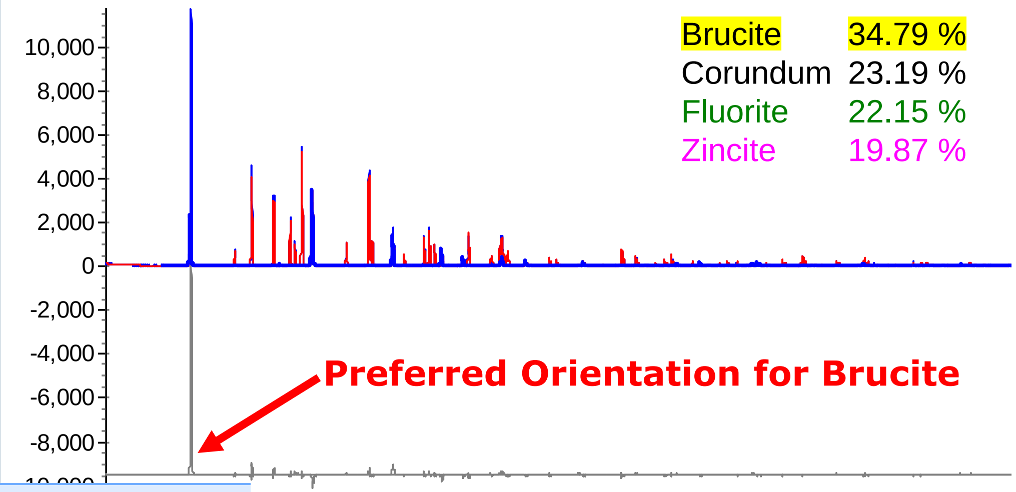
Parameter p is defined more than once with different values or equations.

Quantitative Rietveld Analysis

Exercise: Round-Robin example

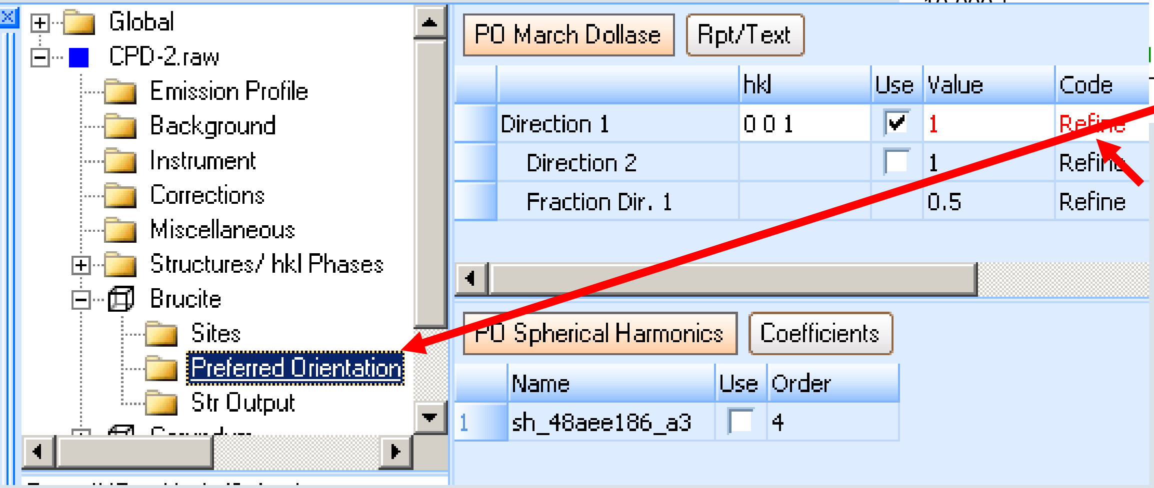
File: C:\Topas 4.1\tutorial\qparr\cpd2.raw
Measurement circle radius: 173mm
Emission profile: CuKa5.lam
Background order 3, 1/x function
Divergence: 1° , Receiving slit: 0.3mm
Soller slits: prim. 4.6° , sec. 4.6°
LP factor: 26.6 (graphite monochromator)

Corundum, Brucite, Fluorite and Zincite Structures in str format in same directory



Brucite	34.79 %
Corundum	23.19 %
Fluorite	22.15 %
Zincite	19.87 %

Preferred Orientation for Brucite



	hkl	Use	Value	Code
Direction 1	0 0 1	☑	1	Refine
Direction 2		☐	1	Refine
Fraction Dir. 1			0.5	Refine

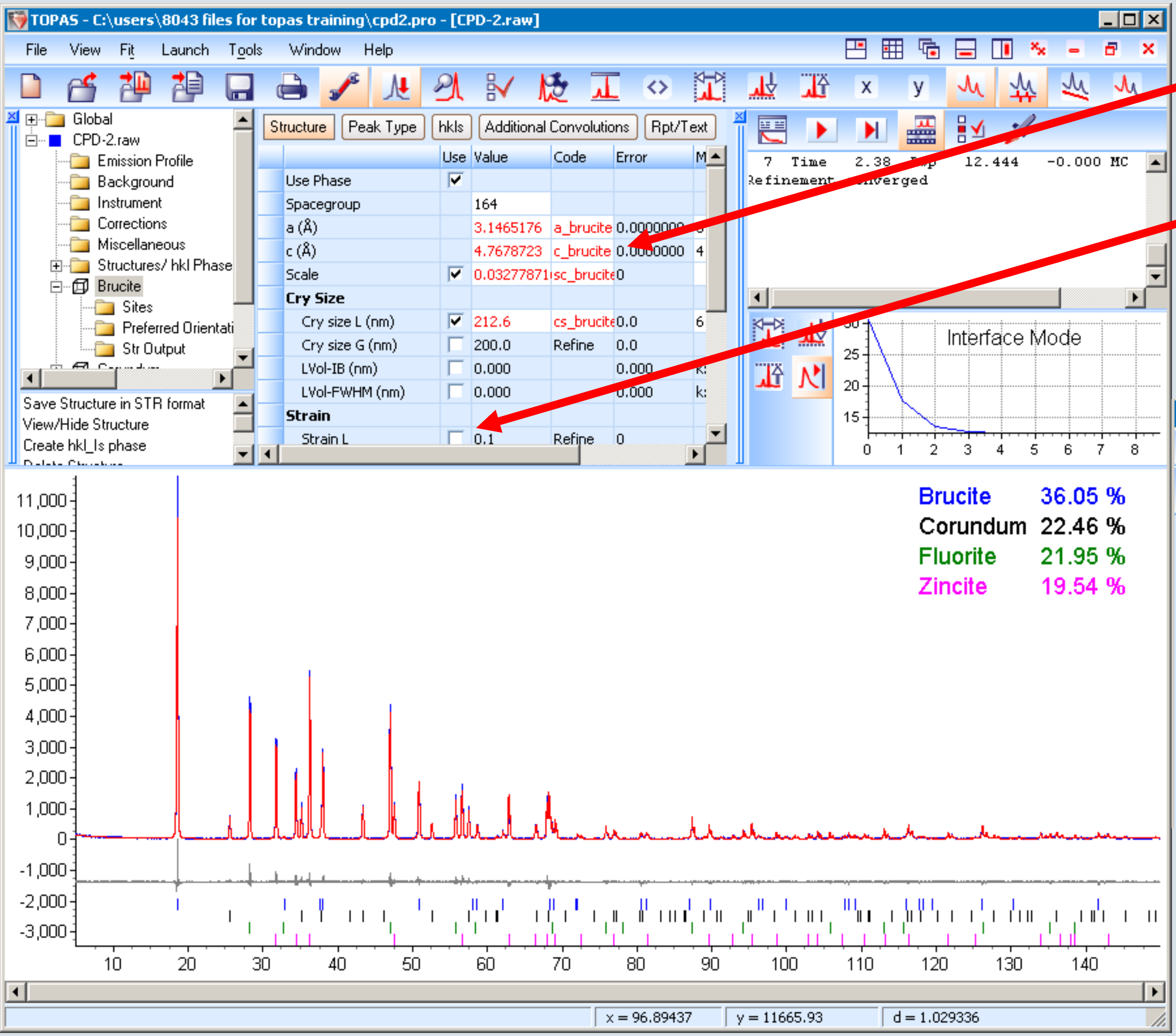
	Name	Use	Order
1	sh_48aee186_a3	☐	4

Highlight Preferred Orientation in Brucite structure

Toggle Code column to Refine and Run Refinement again

Quantitative Rietveld Analysis

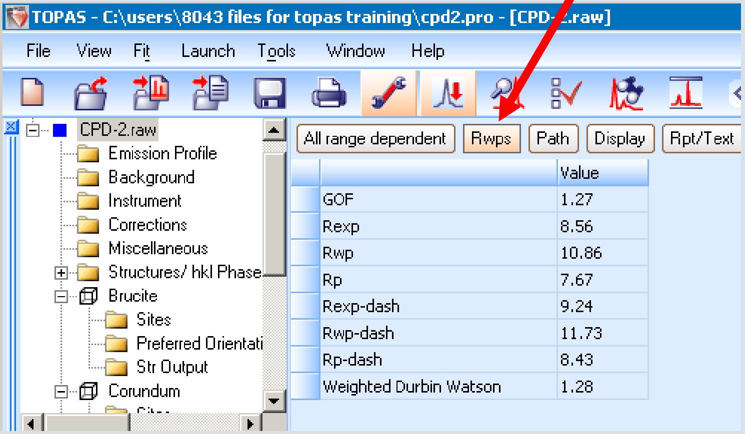
Exercise: Round-Robin example



	Use	Value	Code	Error
Use Phase	☑			
Spacegroup		164		
a (Å)		3.1465176	a_brucite	0.0000000
c (Å)		4.7678723	c_brucite	0.0000000
Scale	☑	0.03277871	sc_brucite	0
Cry Size				
Cry size L (nm)	☑	212.6	cs_brucite	0.0
Cry size G (nm)	☐	200.0	Refine	0.0
LVol-IB (nm)	☐	0.000		0.000
LVol-FWHM (nm)	☐	0.000		0.000
Strain				
Strain L	☐	0.1	Refine	0

```
 7  Time   2.38  Rwp   12.444   -0.000 MC
Refinement converged
```

Brucite	36.05 %
Corundum	22.46 %
Fluorite	21.95 %
Zincite	19.54 %



	Value
GOF	1.27
Rexp	8.56
Rwp	10.86
Rp	7.67
Rexp-dash	9.24
Rwp-dash	11.73
Rp-dash	8.43
Weighted Durbin Watson	1.28

Refined Lattice parameters and crystallite size for each phase

You may try to further improve the fit by introducing strain

Residuals and Goodness of Fit

Save your results in a TOPAS project file (.pro)

Quantitative Rietveld Analysis

More Examples:

Cement Clinker
File: C:\Topas 4.1\tutorial\qa\8486.raw
Measurement circle radius: 217.5mm
Emission profile: CuKa2.lam
Divergence: 1° , Receiving slit: 0.2mm
Soller slits: prim. 4° , sec. 4°
LP factor: 0 (Nickel filter)
Structures: C3Smono_nishi.str, C3acub.str, C2sbmu.str, C4af.str, CaO.str, Periclase.str

Iron Oxides
File: C:\Topas 4.1\tutorial\examples\Iron oxides iron oxides.raw
Measurement circle radius: 217.5mm
Emission profile: CuKa2.lam
Divergence: 1° , Receiving slit: 0.2mm
Soller slits: prim. 4° , sec. 4°
LP factor: 0 (Sol-x detector)
Structures: in same directory

Aggregate with 11.4% Zincite as internal standard
File: C:\Topas 4.1\tutorial\Examples\Aggregate\aggregate with 11.4ZnO.raw
Measurement circle radius: 217.5mm
Emission profile: CuKa2.lam
Divergence: 0.3° , LynxEye detector with 3° opening
Soller slits: prim. 4° , sec. 4°
Structures: determine phases with Eva and use structures in **c:\topas 4.1\structure database**

Natural Granodiorite
File: C:\Topas 4.1\tutorial\examples \cpd-gronodiorite\granodio.raw
Measurement circle radius: 173mm
Emission profile: CuKa2.lam
Divergence: 1° , Receiving slit: 0.3mm
Soller slits: prim. 4.6° , sec. 4.6°
LP factor: 26.6 (graphite)
Structures: in same directory, Quartz, Feldspar, Albite, Biotite, less Chlinochlore, Hornblende, Zircon

Quantitative Rietveld Analysis

More Examples:

Paint panel
File: C:\Topas 4.1\tutorial\Examples\Paint\paint panel.raw
Measurement circle radius: 217.5mm
Emission profile: CuKa2.lam
Divergence: 0.3° , LynxEye detector with 3° opening
Soller slits: prim. 4° , sec. 4°
Structures: determine phases with Eva and use structures in **c:\topas 4.1\structure database**

Shale sample
File: C:\Topas 4.1\tutorial\Examples\Shale\Shale D4 06mm div 4dg soller 3dg LE_10pc ZnO.raw
Measurement circle radius: 201.5mm
Emission profile: CuKa2.lam
Divergence: 0.3° , LynxEye detector with 3° opening
Soller slits: prim. 4° , sec. 4°
Structures: determine phases with Eva and use structures in **c:\topas 4.1\structure database**

General error sources and trouble shooting:

- Check crystallite size of all phases for reasonable values. (it should not converge to zero or infinity), Constrain with min and max values.

-Check visually by highlighting the individual phase names, if trace phases are really present.

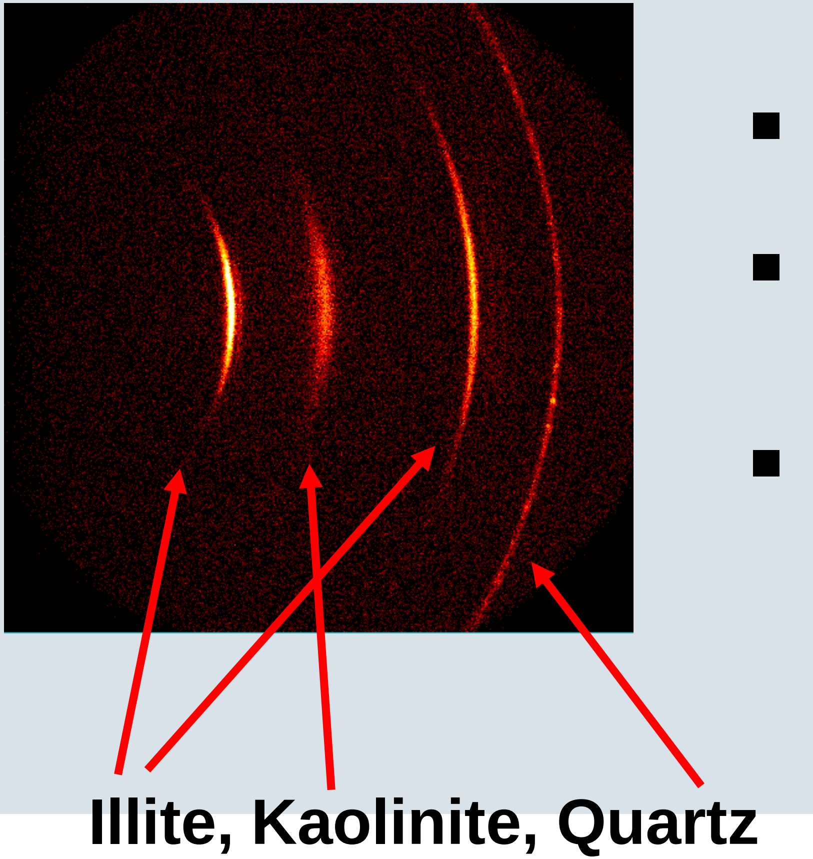
- Avoid correcting for preferred orientation when peaks of different phases are overlapping and both phases have preferred orientation (always try to minimize preferred orientation by better sample preparation)

- For complex multiphase sample, release parameters subsequently.

- Use internal standard to refine for displacement error, then fix it and only refine lattice parameters of other phases.

Corrections for non-ideal powder samples
Texture or preferred orientation

Slate Tile, as an example for strong texture

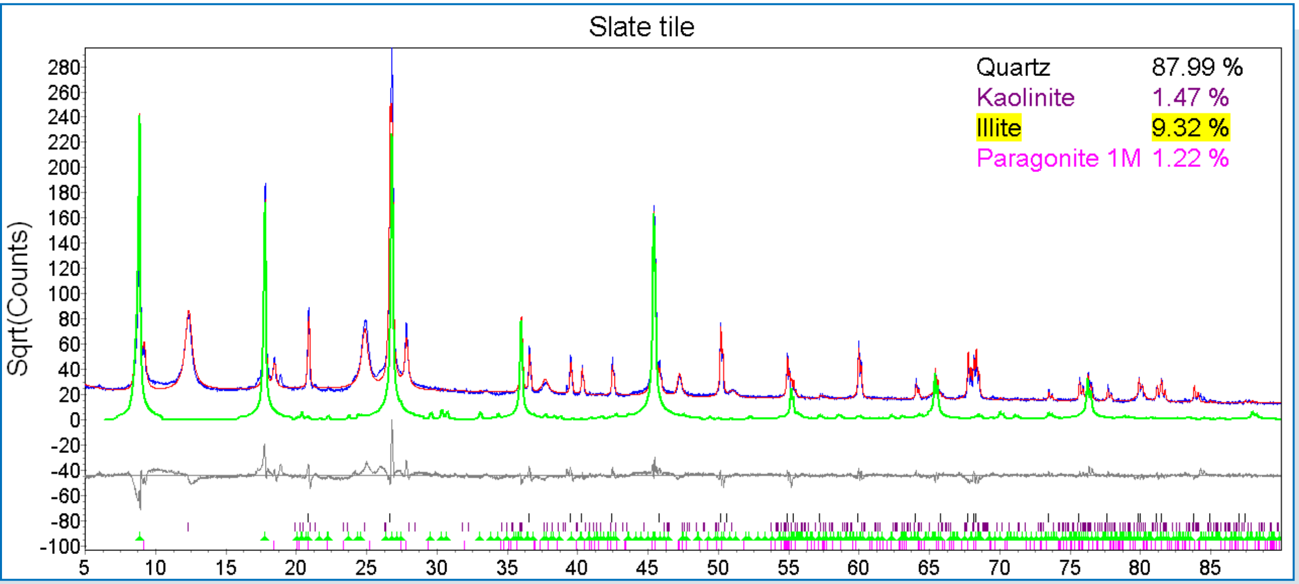

Illite, Kaolinite, Quartz

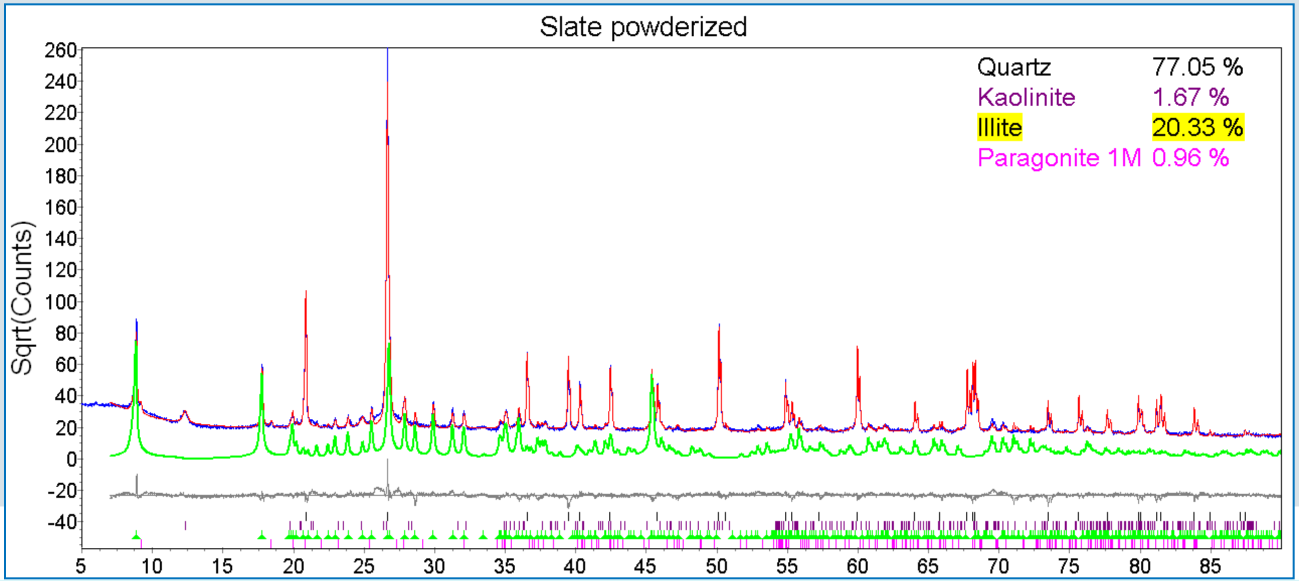
- Preferred orientation of needle or plate-like crystallites can often be corrected with the March-Dollase function
- For minerals with multiple cleavage directions a spherical harmonics correction can be applied.

- Acceptable limits of preferred orientation corrections should ideally be tested with a standard mixture

Correction for non-ideal powder samples

Texture or preferred orientation





← Unground sample

- Comparison of slate tile and ground slate (Calculated Illite patterns are highlighted)
- The (001) directions of Illite, Kaolinite and Paragonite were corrected with the March-Dollase model for both sample

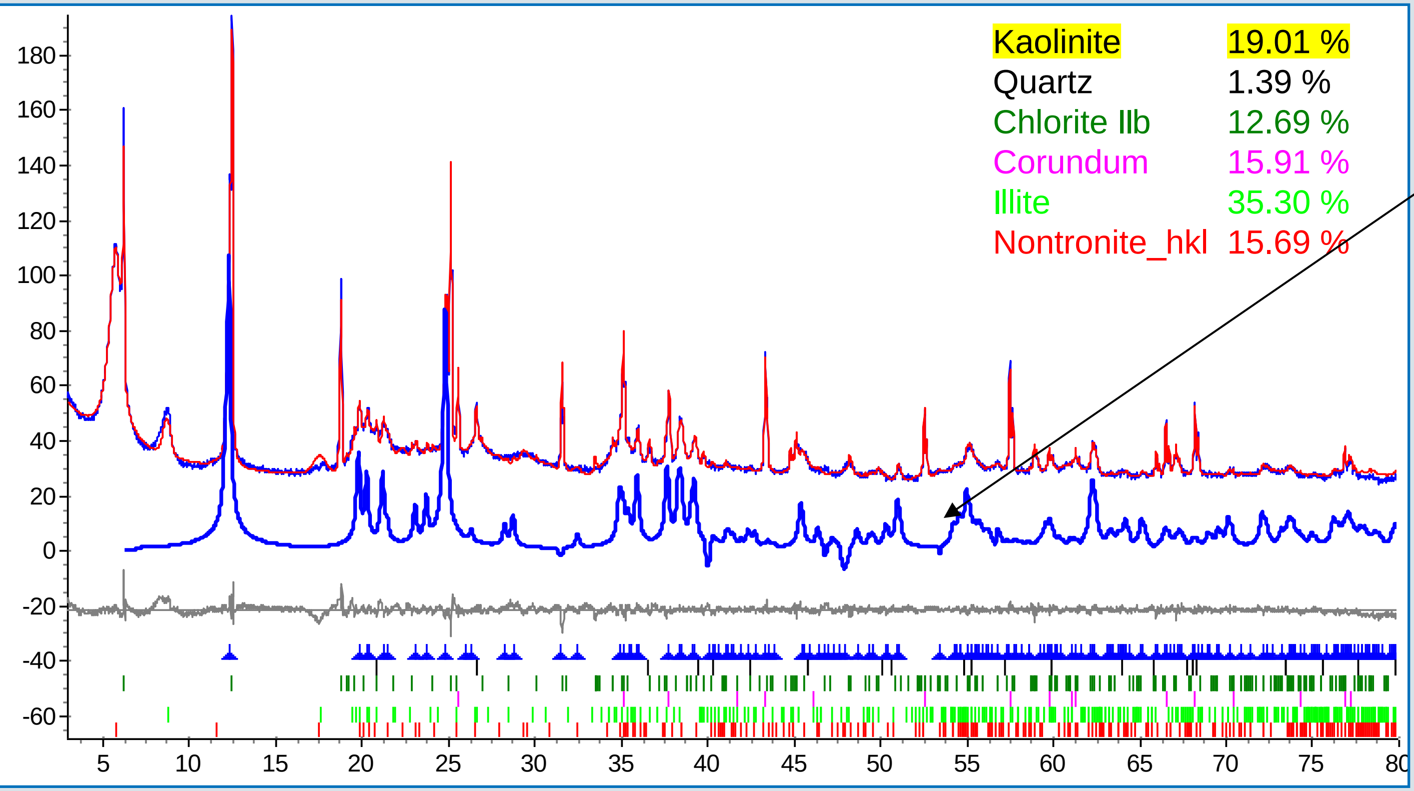
← Ground sample

- Preferred Orientation is too severe to be corrected with March Dollase model

Samples measured with Vantec-1 detector 0.1sec/step

Preferred orientation correction

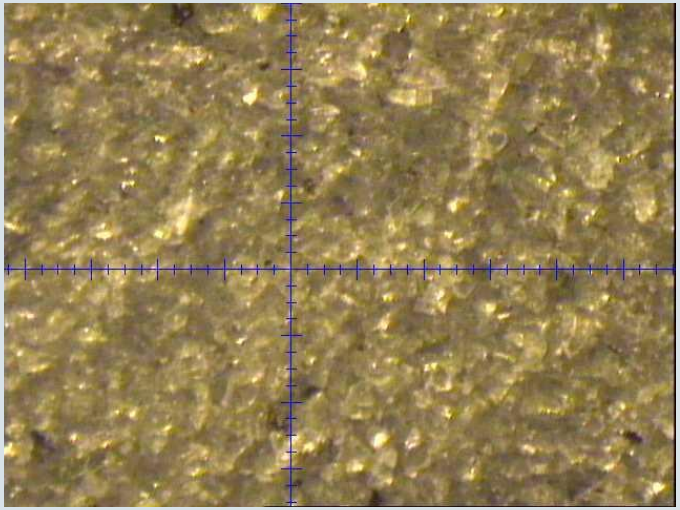
Spherical harmonics correction using too many parameters

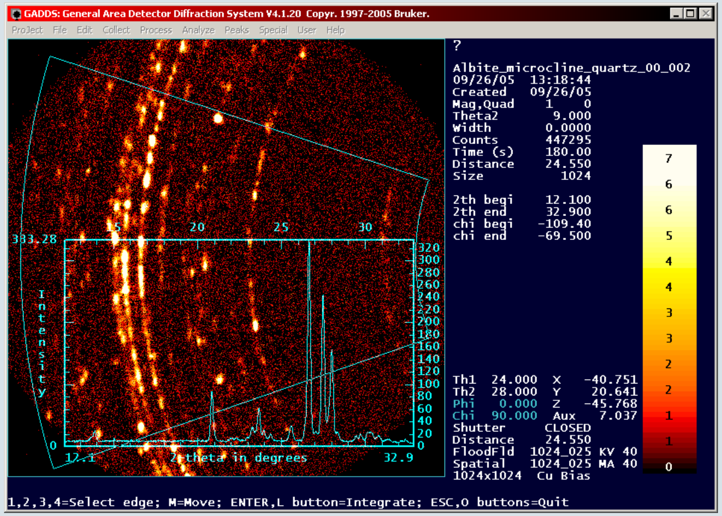


Negative peak intensities as a result of using the spherical harmonics correction for preferred orientation for Kaolinite

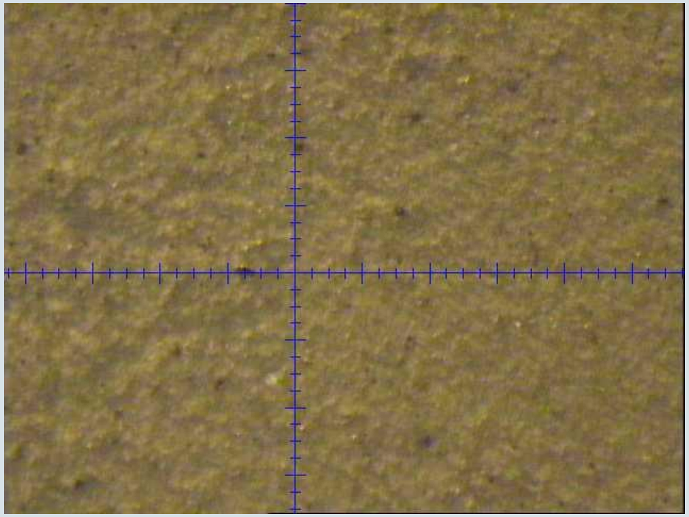
Corrections for non-ideal powder samples

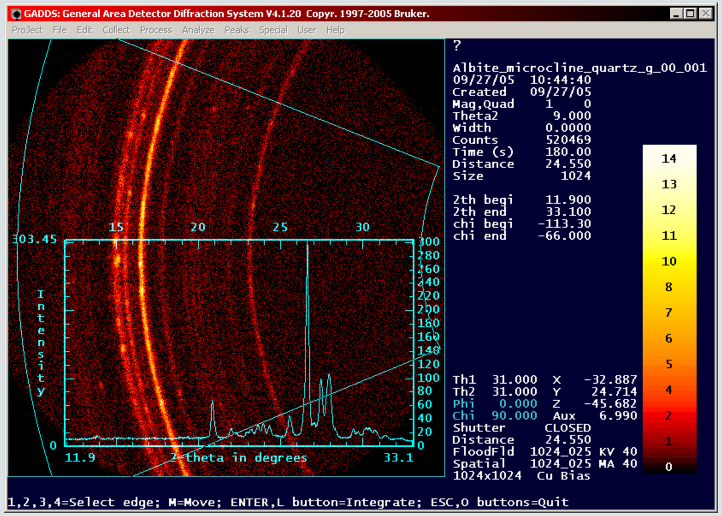
Large grains lead to spotiness effect and Micro absorption (demonstrated with area detector and weighted test mixture)





```
?
Albite_microcline_quartz_00_002
09/26/05  13:18:44
Created   09/26/05
Mag,Quad    1    0
Theta2       9.000
Width       0.0000
Counts      447295
Time (s)    180.00
Distance    24.550
Size          1024

2th begi    12.100
2th end     32.900
chi begi   -109.40
chi end    -69.500

Th1  24.000  X    -40.751
Th2  28.000  Y     20.641
Phi   0.000  Z    -45.768
Chi  90.000  Aux    7.037
Shutter     CLOSED
Distance    24.550
FloodFld  1024_025 KV 40
Spatial   1024_025 MA 40
1024x1024  Cu Bias
1,2,3,4=Select edge; M=Move; ENTER,L button=Integrate; ESC,O buttons=Quit
```



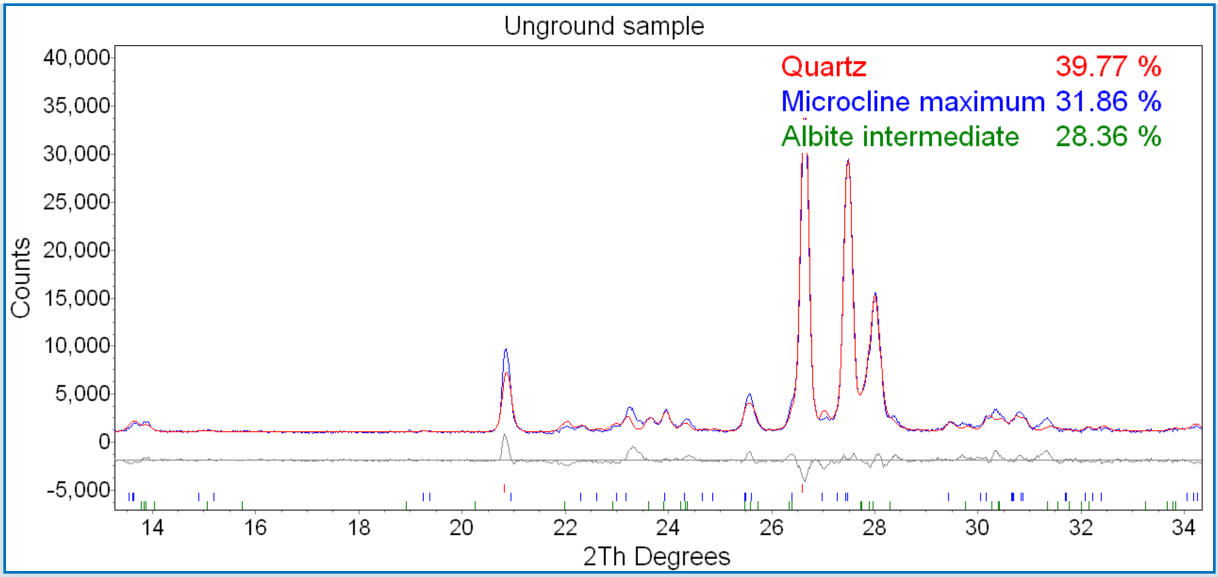


```
?
Albite_microcline_quartz_g_00_001
09/27/05  10:44:40
Created   09/27/05
Mag,Quad    1    0
Theta2       9.000
Width       0.0000
Counts      520469
Time (s)    180.00
Distance    24.550
Size          1024

2th begi    11.900
2th end     33.100
chi begi   -113.30
chi end    -66.000

Th1  31.000  X    -32.887
Th2  31.000  Y     24.714
Phi   0.000  Z    -45.682
Chi  90.000  Aux    6.990
Shutter     CLOSED
Distance    24.550
FloodFld  1024_025 KV 40
Spatial   1024_025 MA 40
1024x1024  Cu Bias
1,2,3,4=Select edge; M=Move; ENTER,L button=Integrate; ESC,O buttons=Quit
```

- Coarse powder of Albite, Microcline and Quartz (some grains are larger than 50μm)
- Identical Powder, wet ground in Micronising Mill for 30 minutes

Gadds data at 25cm sample-detector distance

Corrections for non-ideal powder samples
Large grains, spottiness effect, Micro absorption

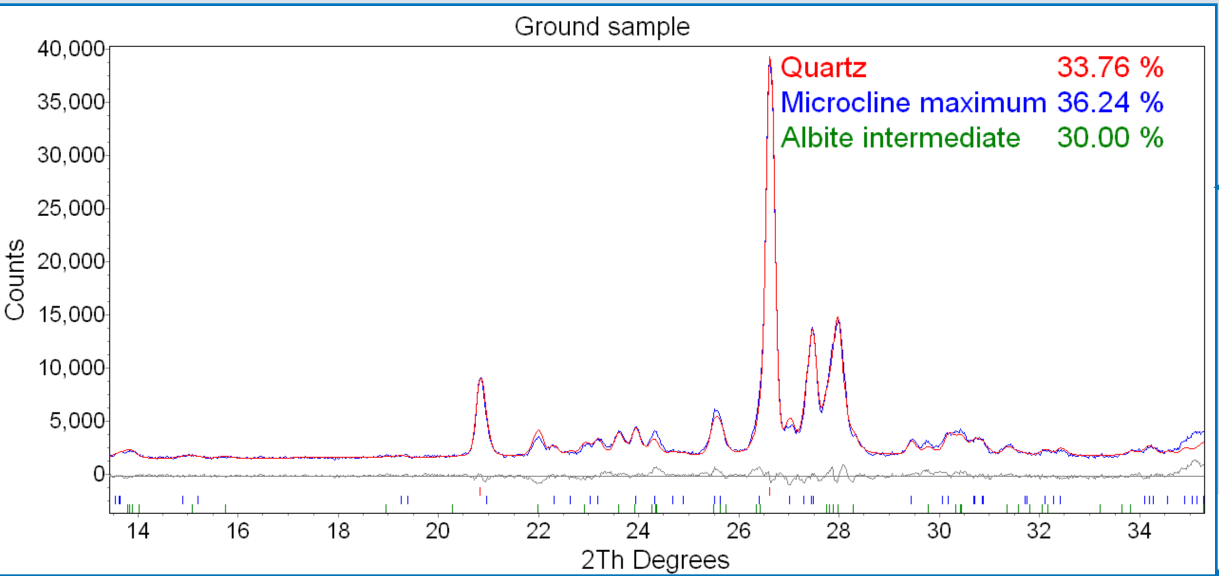


Unground sample

Weighted compositions:

Albite	29.64 wt.%
Microcline	36.63 wt.%
Quartz	33.73 wt.%

- For both samples, preferred orientation for Albite and Microcline were refined



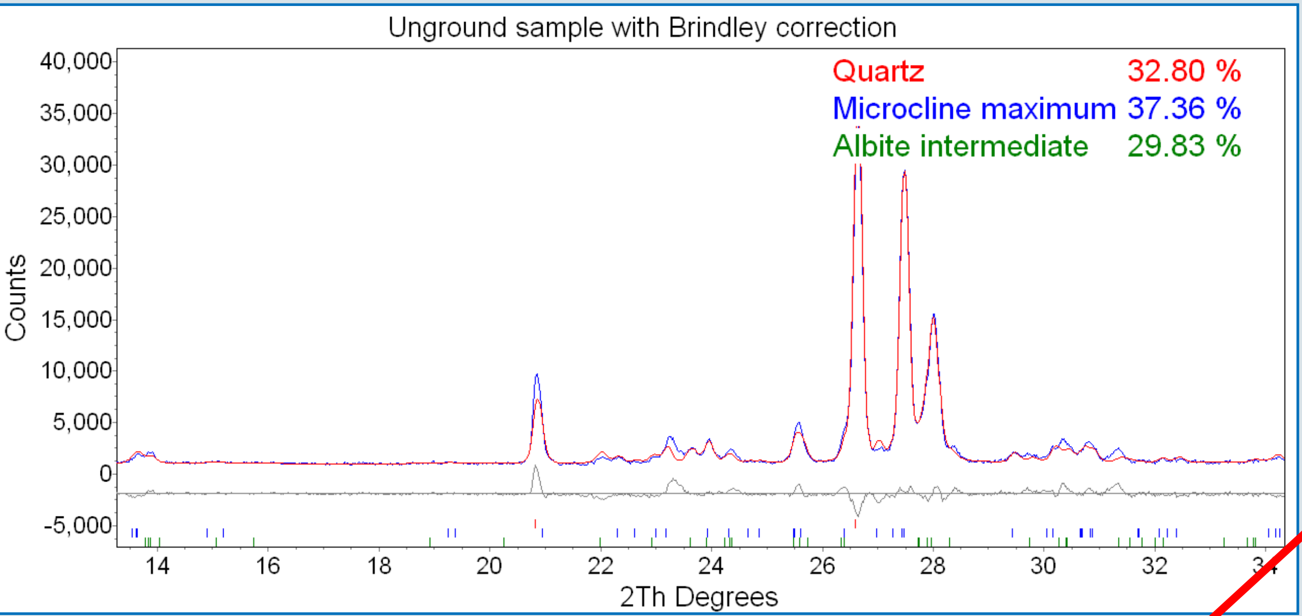
Ground sample

Gadds data at 25cm sample-detector distance

Corrections for non-ideal powder samples

Micro absorption

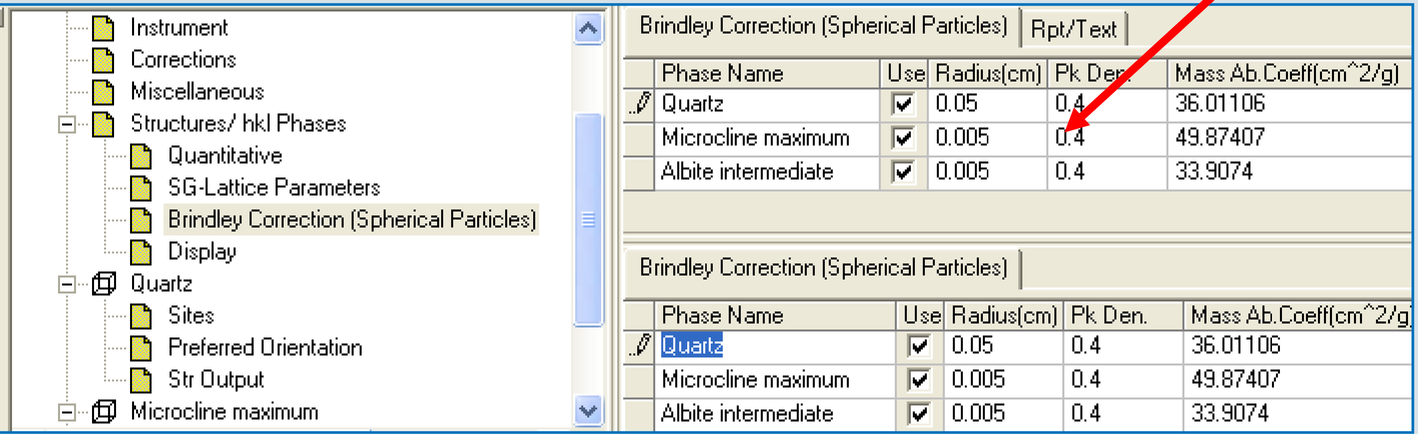
Brindley correction



Weighted compositions:

Albite	29.64 wt.%
Microcline	36.63 wt.%
Quartz	33.73 wt.%

- Larger Quartz grains of 50µm were assumed.



Phase Name	Use	Radius(cm)	Pk Den	Mass Ab.Coeff(cm^2/g)
Quartz	☑	0.05	0.4	36.01106
Microcline maximum	☑	0.005	0.4	49.87407
Albite intermediate	☑	0.005	0.4	33.9074

Brindley Correction (Spherical Particles)

Phase Name	Use	Radius(cm)	Pk Den.	Mass Ab.Coeff(cm^2/g
Quartz	☑	0.05	0.4	36.01106
Microcline maximum	☑	0.005	0.4	49.87407
Albite intermediate	☑	0.005	0.4	33.9074

Note that the error would be considerably larger for phases with higher absorption contrast!

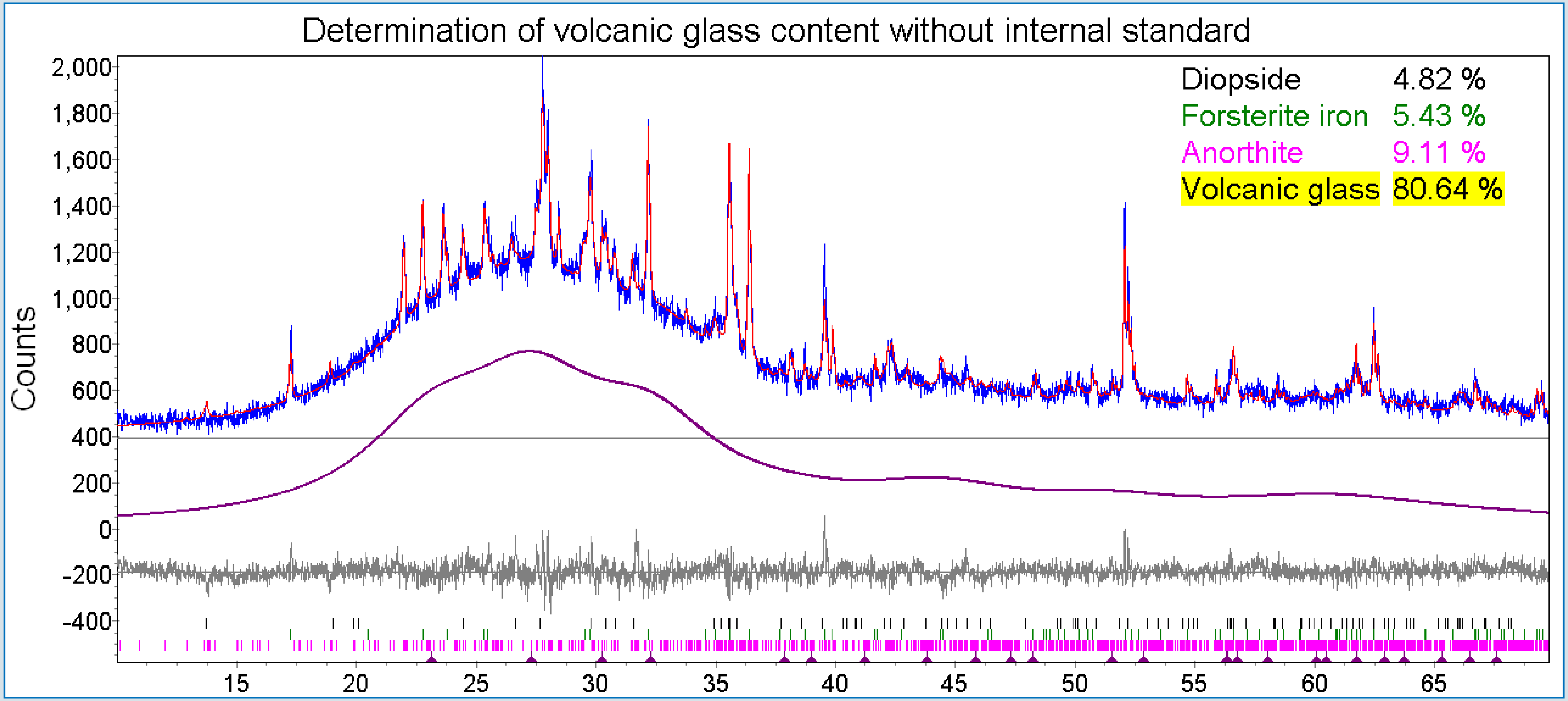
Corrections for non-ideal powder samples

- Preferred orientation effects
  - March Dollase
  - Spherical harmonics
- Micro absorption
  - Brindley correction for spherical particles
- Surface roughness
  - Correction according to Pitschke or Suortti

Corrections for these effects are available in TOPAS, but it is best to avoid or minimize these effects by good sample preparation!

- Flat samples with powder grain sizes below approx. 5µm.
- If possible, minimize preferred orientation by using back or side loaded sample holders

Quantifying Amorphous Phases
Traditional Rietveld Method



Quantifying Amorphous Phases
Traditional Rietveld Method

Benefits

- Requires no standards or calibration
- More than one amorphous phase can be analyzed

Limitations

- Direct method
- Cannot correct for microabsorption errors
- Some amorphous material will not have a representative crystal structure
  - Available crystal structures (with long-range order) may not accurately represent material which only has short-range order (e.g. glasses).

Quantifying Amorphous Phases
Internal Standard Method

- The sample is "spiked" with a known mass of standard material and the QPA normalized accordingly
- The weight fractions of the crystalline phases present in each sample are estimated using the Rietveld methodology
- Concentrations to be corrected proportionately according to:

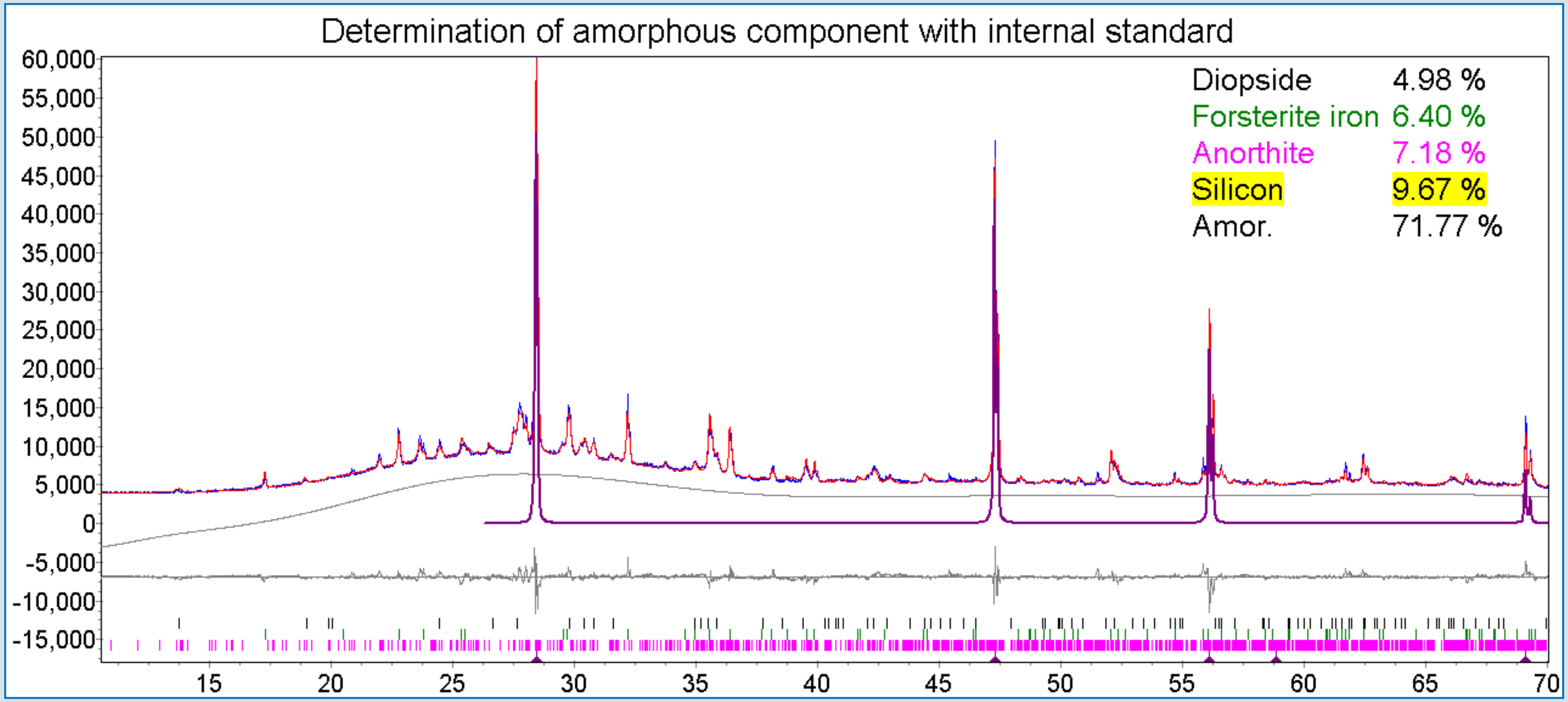
$$Corr(W_\alpha) = W_\alpha \frac{STD_{known}}{STD_{measured}}$$

where $Corr(W_\alpha)$ is the corrected weight percent, STD_{known} the weighed concentration of the standard in the sample and $STD_{measured}$ the analyzed concentration

- The amount of amorphous material $W_{amorphous}$ can then be derived from:

$$W_{amorphous} = 1 - \sum_{j=1}^{n} Corr(W_j)$$

Quantifying Amorphous Phases
Internal Standard Method



Determination of amorphous component with internal standard

Phase	Wt.% in spiked sample	Wt.% in original sample	Wt.% det. without standard
Diopside	4.98	5.52	4.82
Forsterite	6.40	7.09	5.43
Anorthite	7.18	7.95	9.11
Volcanic glass	71.76	79.45	80.64

Quantifying Amorphous Phases
Internal Standard Method

Benefits

- Indirect method
- The Internal Standard Method is enabled in many Rietveld analysis packages

Limitations

- Only the sum of all amorphous and unidentified phases can be reported
- Cannot correct for microabsorption errors
- The sample is contaminated
- The standard addition process is laborious (weighing, mixing), and not feasible in industrial, automated sample preparation environments
- The method relies upon obtaining a standard of appropriate absorption contrast to prevent the introduction of a microabsorption problem

Quantifying Amorphous Phases
PONKCS Method

- Phases with Partial Or No Known Crystal Structure are characterized by measured rather than calculated structure factors
- Follows the same general form as that used in the Rietveld Method but now includes all crystalline and amorphous phases characterized by either calculated or empirical structure factors
- For all phases α using empirically derived structure factors ZMV "calibration constants" must be derived, e.g. via an internal standard *s*

$$(ZMV)_\alpha = \frac{W_\alpha}{W_s}\frac{S_s}{S_\alpha}(ZMV)_s$$

- A one time calibration per phase with a single standard mixture is usually sufficient

Quantifying Amorphous Phases PONKCS Method

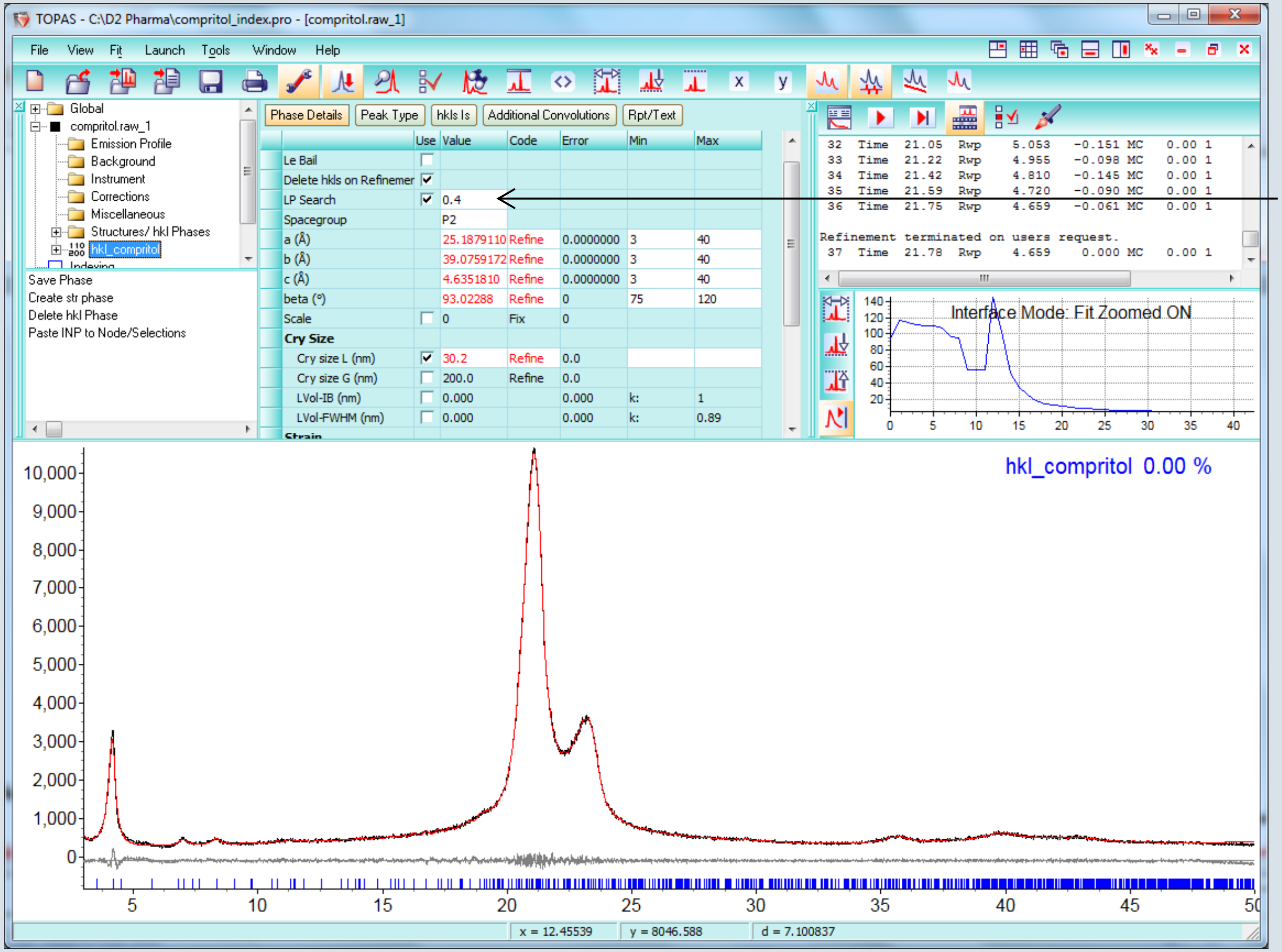
Benefits

- The amorphous phase is included in the analysis model
- More than one amorphous phase can be analyzed
- Potential to minimize errors related to microabsorption, when ZMVs have been calibrated for all phases
  - Consider to use the PONKCS methodology also for all crystalline phases with known crystal structures are known
  - It is highly recommended to create a database with "PONKCS phases"; such a database can be used in full analogy to crystal structure databases

Limitations

- Direct method
- Requires availability of a standard mixture to derive an empirical ZMV

Quantifying Amorphous Phases
PONKCS Method-walk through for Compritol

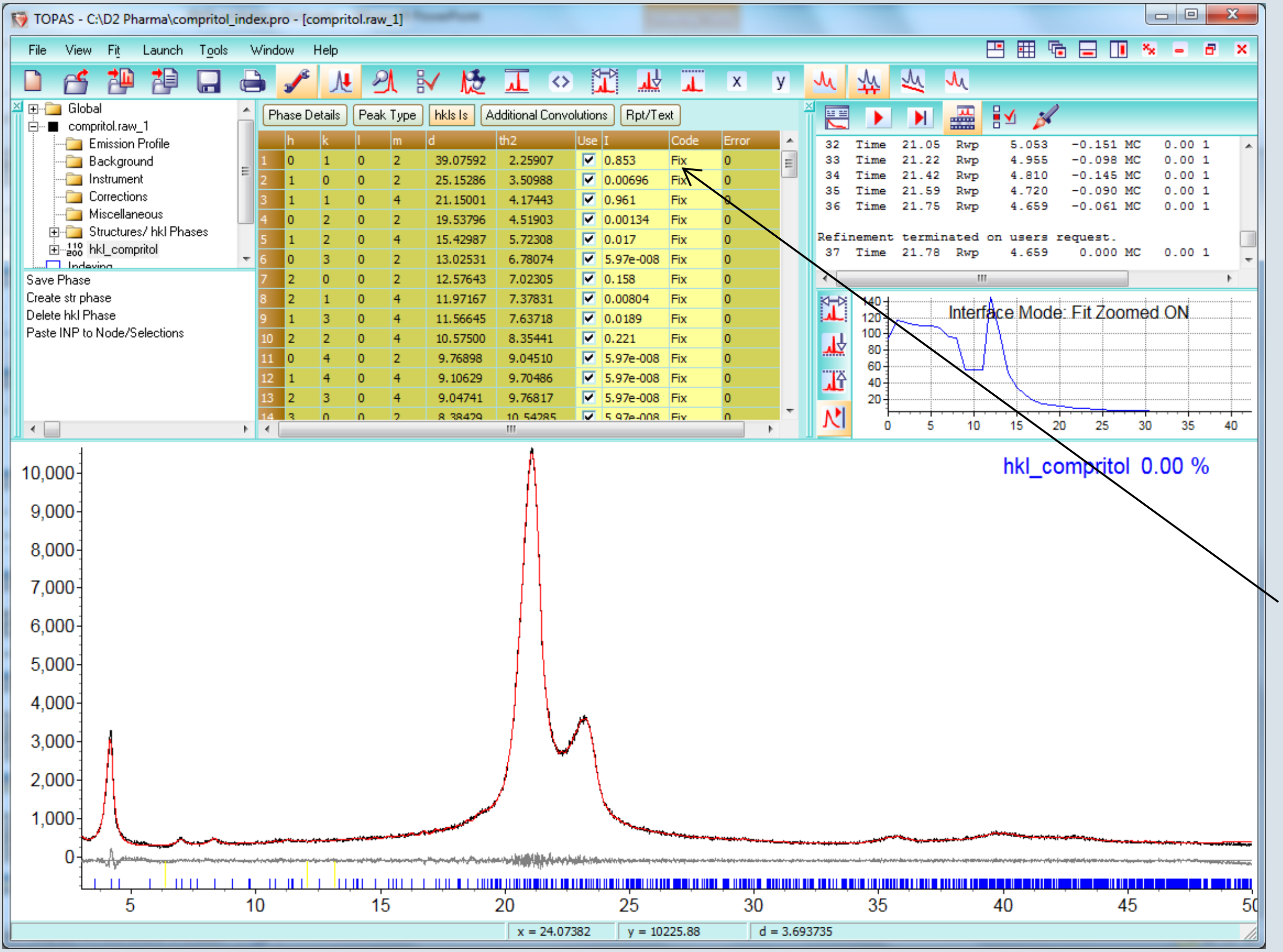


	Use	Value	Code	Error	Min	Max
Le Bail	☐					
Delete hkls on Refinemer	☑					
LP Search	☑	0.4				
Spacegroup		P2				
a (Å)		25.1879110	Refine	0.0000000	3	40
b (Å)		39.0759172	Refine	0.0000000	3	40
c (Å)		4.6351810	Refine	0.0000000	3	40
beta (°)		93.02288	Refine	0	75	120
Scale	☐	0	Fix	0		
Cry Size						
Cry size L (nm)	☑	30.2	Refine	0.0		
Cry size G (nm)	☐	200.0	Refine	0.0		
LVol-IB (nm)	☐	0.000		0.000	k:	1
LVol-FWHM (nm)	☐	0.000		0.000	k:	0.89
Strain						

```
 32  Time  21.05  Rwp    5.053   -0.151 MC   0.00 1
 33  Time  21.22  Rwp    4.955   -0.098 MC   0.00 1
 34  Time  21.42  Rwp    4.810   -0.145 MC   0.00 1
 35  Time  21.59  Rwp    4.720   -0.090 MC   0.00 1
 36  Time  21.75  Rwp    4.659   -0.061 MC   0.00 1

Refinement terminated on users request.
 37  Time  21.78  Rwp    4.659    0.000 MC   0.00 1
```

- Scan of pure Compritol
- Step 1: try to find a “unit cell” that will fit the scan. If not enough peaks are present for LSI algorithm, try LP search
- Step 2: after getting a satisfactory fit, fix all peak intensities and uncheck “Delete hkls on refinement”

Quantifying Amorphous Phases
PONKCS Method-walk through for Compritol

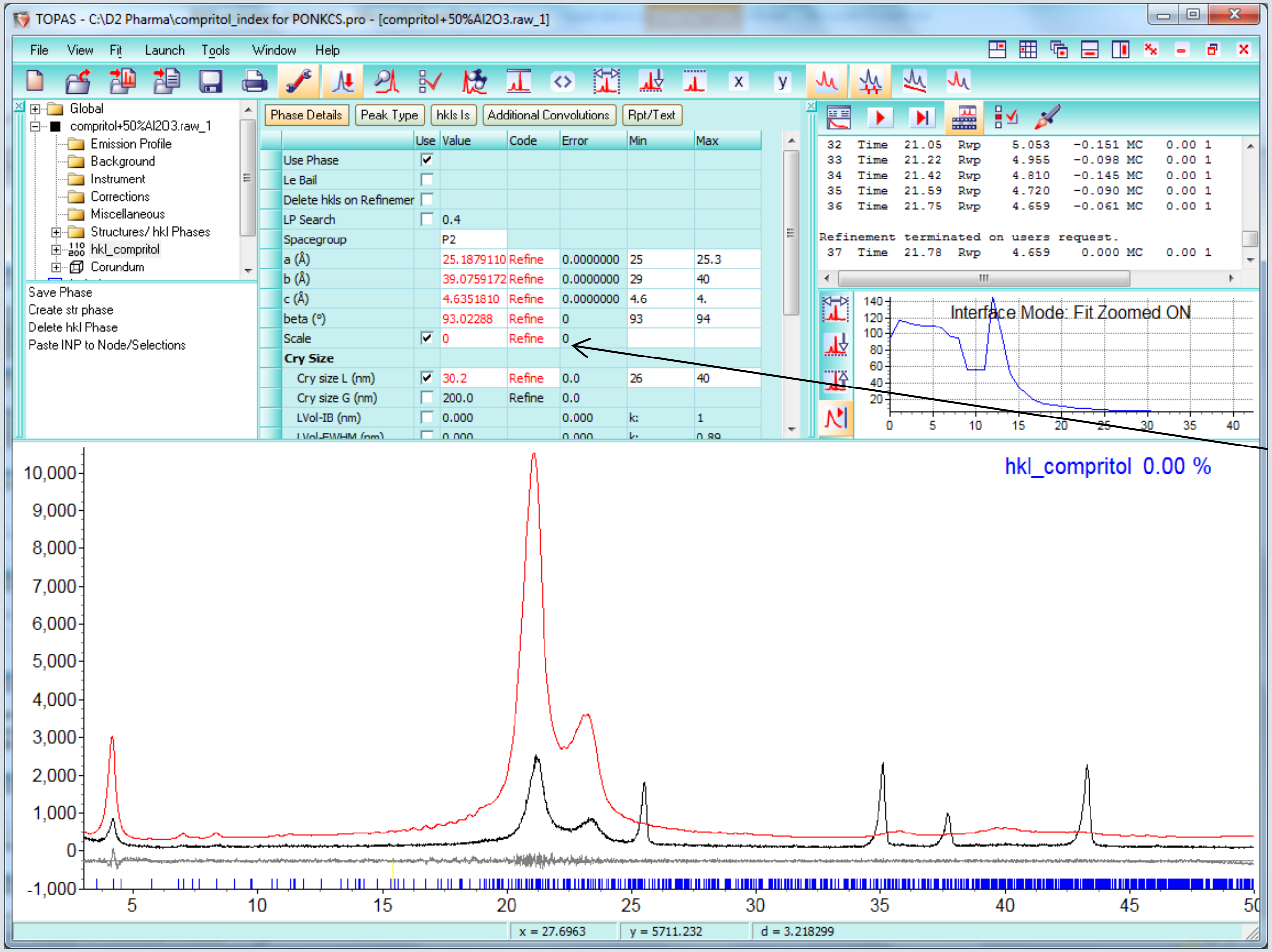


	h	k	l	m	d	th2	Use	I	Code	Error
1	0	1	0	2	39.07592	2.25907	☑	0.853	Fix	0
2	1	0	0	2	25.15286	3.50988	☑	0.00696	Fix	0
3	1	1	0	4	21.15001	4.17443	☑	0.961	Fix	0
4	0	2	0	2	19.53796	4.51903	☑	0.00134	Fix	0
5	1	2	0	4	15.42987	5.72308	☑	0.017	Fix	0
6	0	3	0	2	13.02531	6.78074	☑	5.97e-008	Fix	0
7	2	0	0	2	12.57643	7.02305	☑	0.158	Fix	0
8	2	1	0	4	11.97167	7.37831	☑	0.00804	Fix	0
9	1	3	0	4	11.56645	7.63718	☑	0.0189	Fix	0
10	2	2	0	4	10.57500	8.35441	☑	0.221	Fix	0
11	0	4	0	2	9.76898	9.04510	☑	5.97e-008	Fix	0
12	1	4	0	4	9.10629	9.70486	☑	5.97e-008	Fix	0
13	2	3	0	4	9.04741	9.76817	☑	5.97e-008	Fix	0
14	3	0	0	2	8.38429	10.54285	☑	5.97e-008	Fix	0

```
 32  Time  21.05  Rwp    5.053   -0.151 MC   0.00 1
 33  Time  21.22  Rwp    4.955   -0.098 MC   0.00 1
 34  Time  21.42  Rwp    4.810   -0.145 MC   0.00 1
 35  Time  21.59  Rwp    4.720   -0.090 MC   0.00 1
 36  Time  21.75  Rwp    4.659   -0.061 MC   0.00 1

Refinement terminated on users request.
 37  Time  21.78  Rwp    4.659    0.000 MC   0.00 1
```

- Scan of pure Compritol
- Step 1: try to find a "unit cell" that will fit the scan. If not enough peaks are present for LSI algorithm, try LP search
- Step 2: after getting a satisfactory fit, fix all peak intensities and uncheck "Delete hkls on refinement" and LP search

Quantifying Amorphous Phases
PONKCS Method-walk through for Compritol

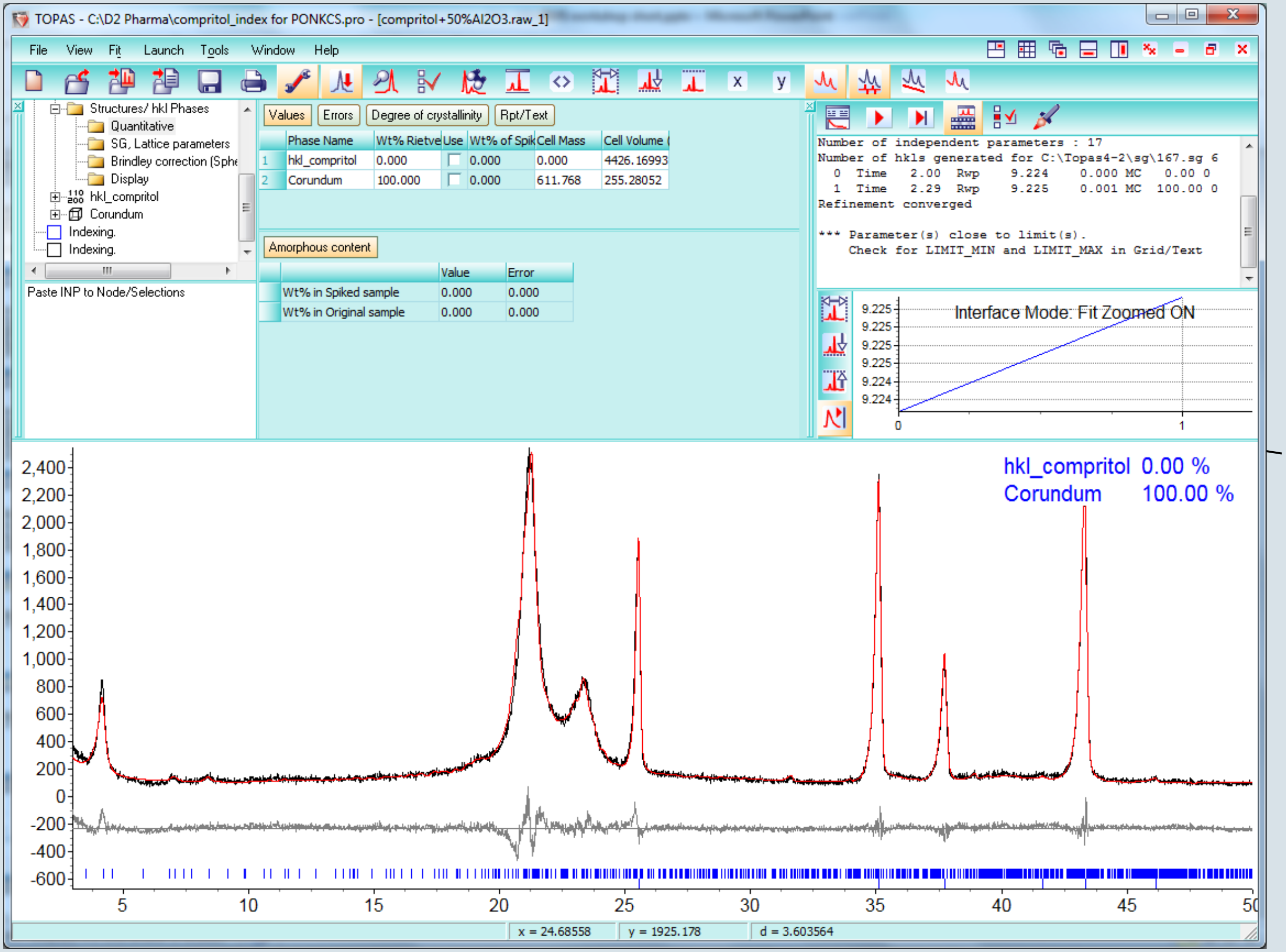


	Use	Value	Code	Error	Min	Max
Use Phase	☑					
Le Bail	☐					
Delete hkls on Refinemer	☐					
LP Search	☐	0.4				
Spacegroup		P2				
a (Å)		25.1879110	Refine	0.0000000	25	25.3
b (Å)		39.0759172	Refine	0.0000000	29	40
c (Å)		4.6351810	Refine	0.0000000	4.6	4.
beta (°)		93.02288	Refine	0	93	94
Scale	☑	0	Refine	0		
Cry Size						
Cry size L (nm)	☑	30.2	Refine	0.0	26	40
Cry size G (nm)	☐	200.0	Refine	0.0		
LVol-IB (nm)	☐	0.000		0.000	k:	1
LVol-FWHM (nm)	☐	0.000		0.000	k:	0.89

```
 32  Time  21.05  Rwp    5.053   -0.151 MC   0.00 1
 33  Time  21.22  Rwp    4.955   -0.098 MC   0.00 1
 34  Time  21.42  Rwp    4.810   -0.145 MC   0.00 1
 35  Time  21.59  Rwp    4.720   -0.090 MC   0.00 1
 36  Time  21.75  Rwp    4.659   -0.061 MC   0.00 1

Refinement terminated on users request.
 37  Time  21.78  Rwp    4.659    0.000 MC   0.00 1
```

- Scan of 50% mix of Compritol and known standard (Corundum)
- Step 3: replace scan of pure compound with known mixture
- Step 4: Constrain all lattice parameters and crystallite size values with reasonable limits and refine scaling factor

Quantifying Amorphous Phases
PONKCS Method-walk through for Compritol



	Phase Name	Wt% Rietve	Use	Wt% of Spik	Cell Mass	Cell Volume (
1	hkl_compritol	0.000	☐	0.000	0.000	4426.16993
2	Corundum	100.000	☐	0.000	611.768	255.28052

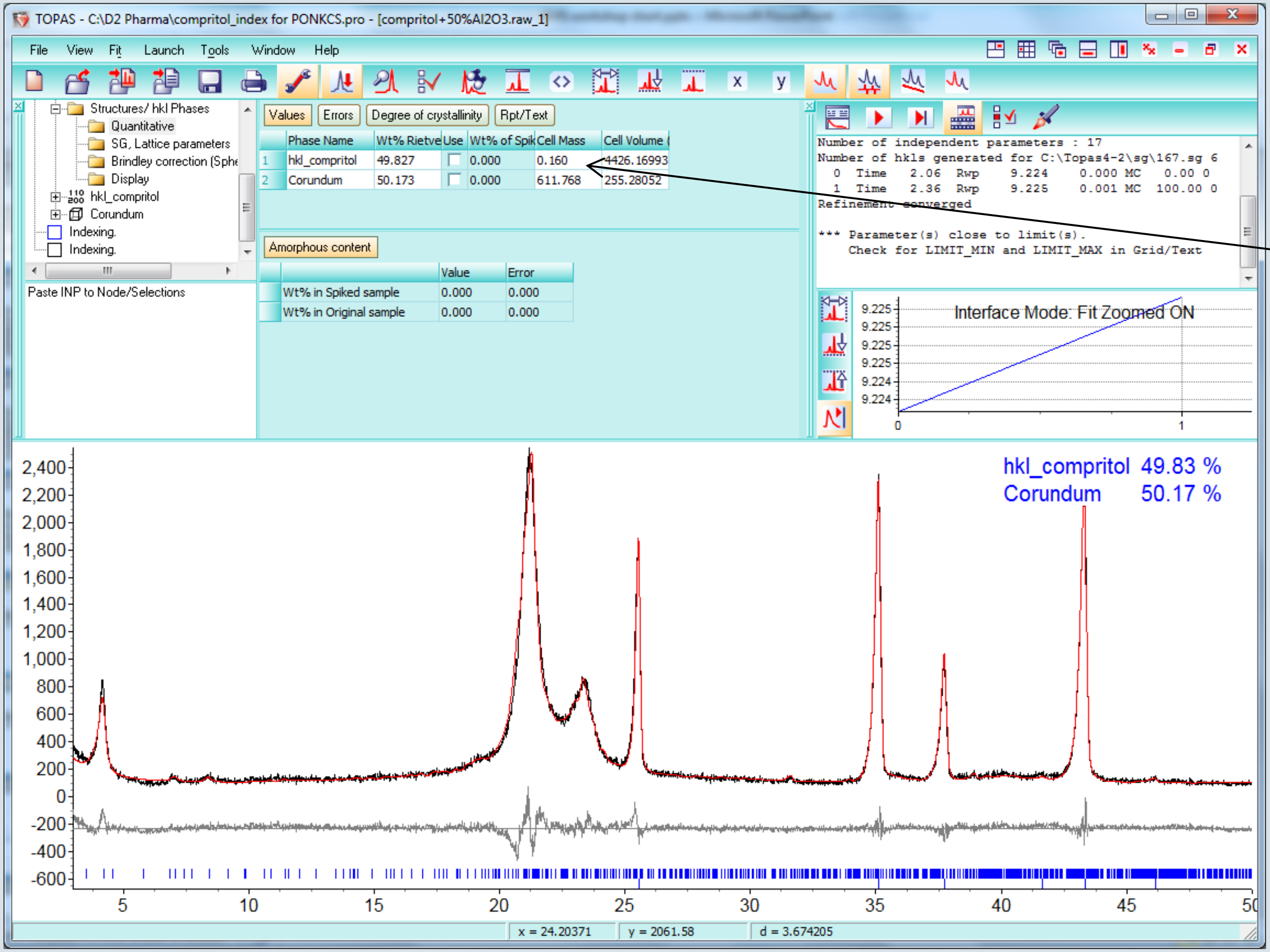
	Value	Error
Wt% in Spiked sample	0.000	0.000
Wt% in Original sample	0.000	0.000

```
Number of independent parameters : 17
Number of hkls generated for C:\Topas4-2\sg\167.sg 6
  0  Time   2.00  Rwp    9.224    0.000 MC   0.00 0
  1  Time   2.29  Rwp    9.225    0.001 MC  100.00 0
Refinement converged

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

x = 24.68558
y = 1925.178
d = 3.603564

- Scan of 50% mix of Compritol and known standard (Corundum)
- Step 3: Empirically determine a value for “mass” to match the known concentration of the mixture

Quantifying Amorphous Phases PONKCS Method-walk through for Compritol



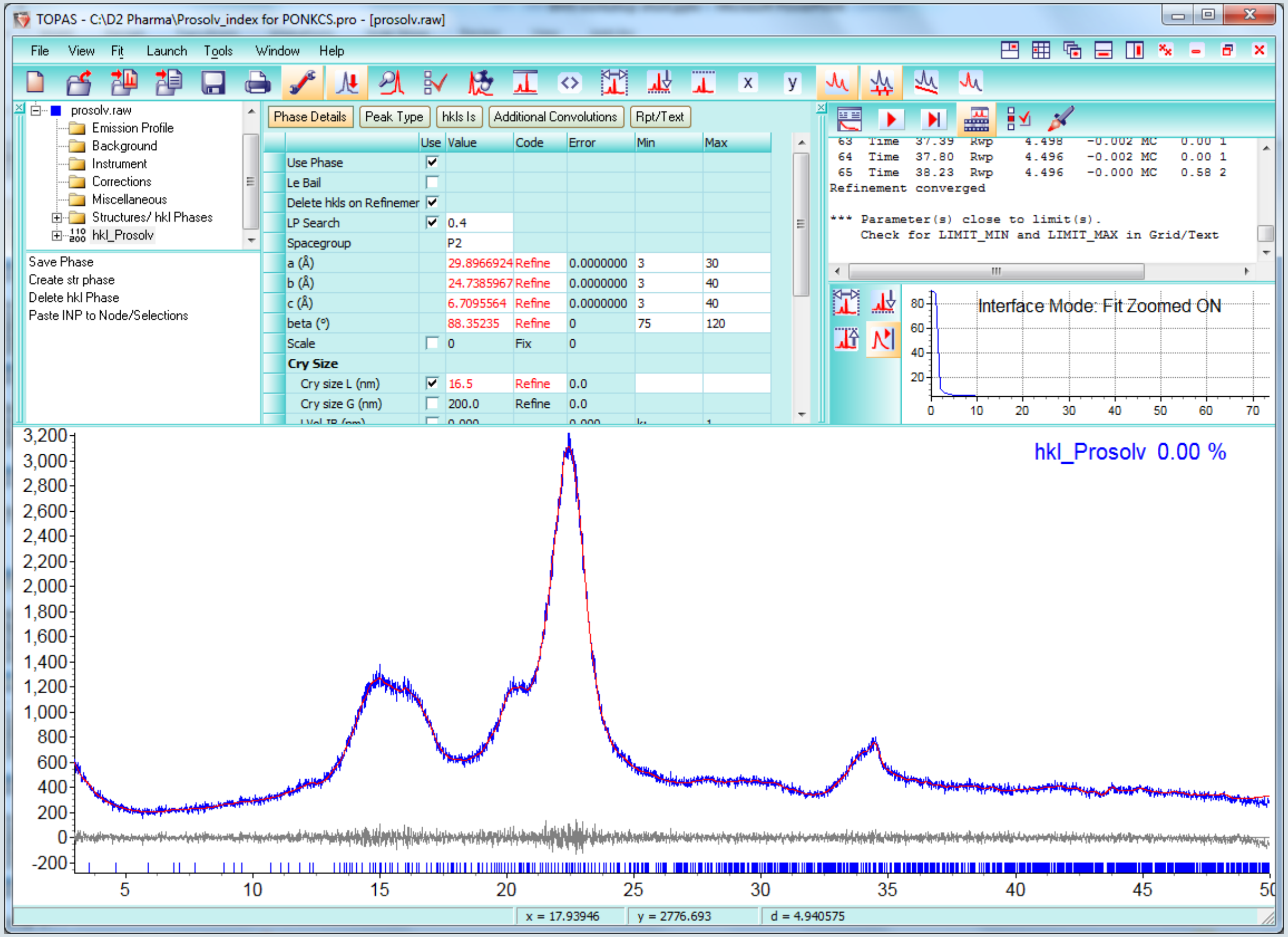
	Phase Name	Wt% Rietve	Use	Wt% of Spik	Cell Mass	Cell Volume (
1	hkl_compritol	49.827	☐	0.000	0.160	4426.16993
2	Corundum	50.173	☐	0.000	611.768	255.28052

		Value	Error
	Wt% in Spiked sample	0.000	0.000
	Wt% in Original sample	0.000	0.000

```
Number of independent parameters : 17
Number of hkls generated for C:\Topas4-2\sg\167.sg 6
  0  Time   2.06  Rwp    9.224    0.000 MC   0.00 0
  1  Time   2.36  Rwp    9.225    0.001 MC  100.00 0
Refinement converged

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

- Step 4: Once that value is known, save the hkl_Compritol phase (in .inp format). It can now be used like a normal structure in any other mixture

Quantifying Amorphous Phases
PONKCS Method-walk through for Prosolv

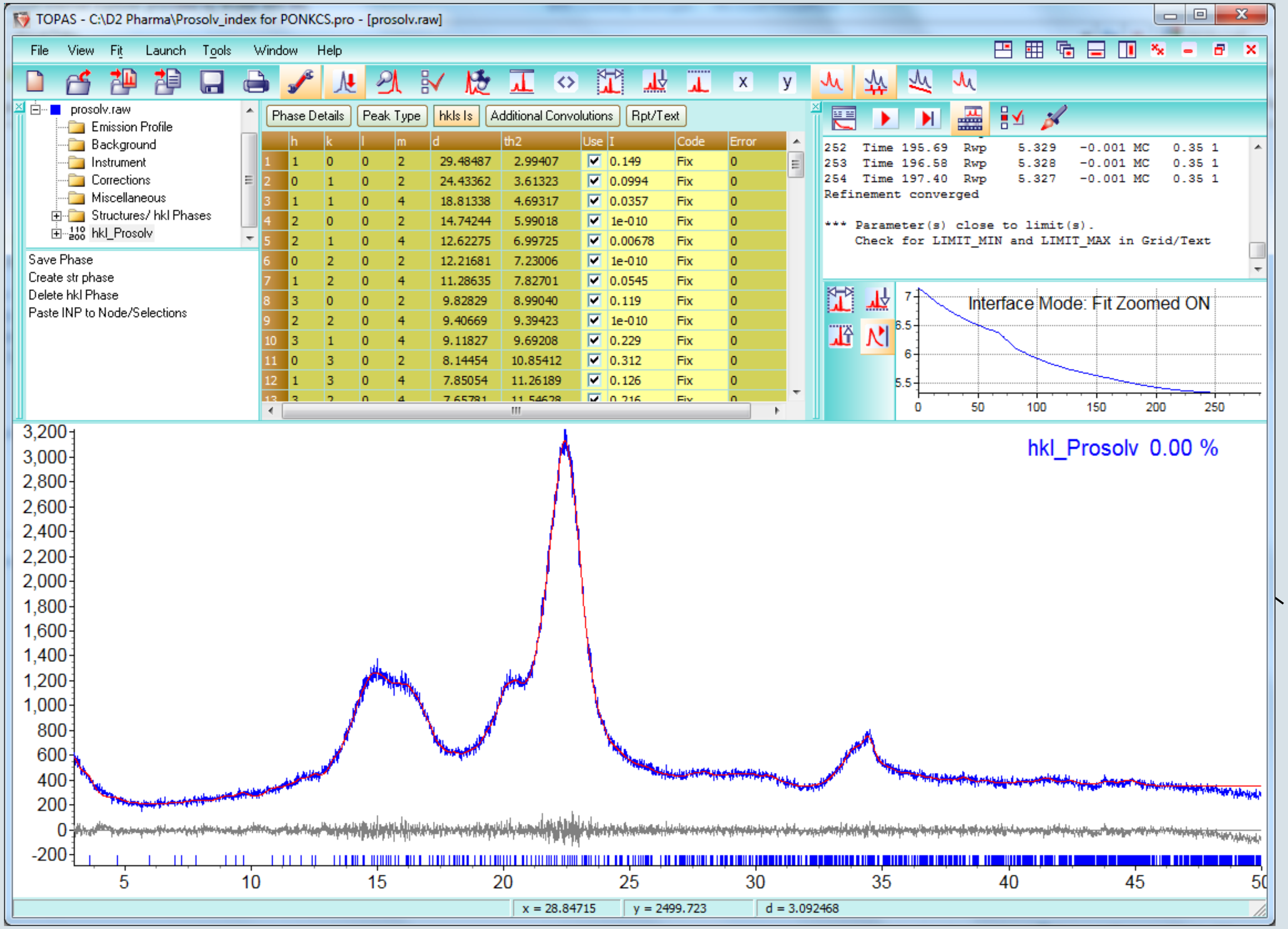


	Use	Value	Code	Error	Min	Max
Use Phase	☑					
Le Bail	☐					
Delete hkls on Refinemer	☑					
LP Search	☑	0.4				
Spacegroup		P2				
a (Å)		29.8966924	Refine	0.0000000	3	30
b (Å)		24.7385967	Refine	0.0000000	3	40
c (Å)		6.7095564	Refine	0.0000000	3	40
beta (°)		88.35235	Refine	0	75	120
Scale	☐	0	Fix	0		
Cry Size						
Cry size L (nm)	☑	16.5	Refine	0.0		
Cry size G (nm)	☐	200.0	Refine	0.0		

```
 63  Time  37.39  Rwp    4.498   -0.002 MC   0.00 1
 64  Time  37.80  Rwp    4.496   -0.002 MC   0.00 1
 65  Time  38.23  Rwp    4.496   -0.000 MC   0.58 2
Refinement converged

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

- Scan of pure Prosolv
- Step 1: try to find a "unit cell" that will fit the scan. If not enough peaks are present for LSI algorithm, try LP search
- Step 2: after getting a satisfactory fit, fix all peak intensities and uncheck "Delete hkls on refinement"

Quantifying Amorphous Phases
PONKCS Method-walk through for Prosolv

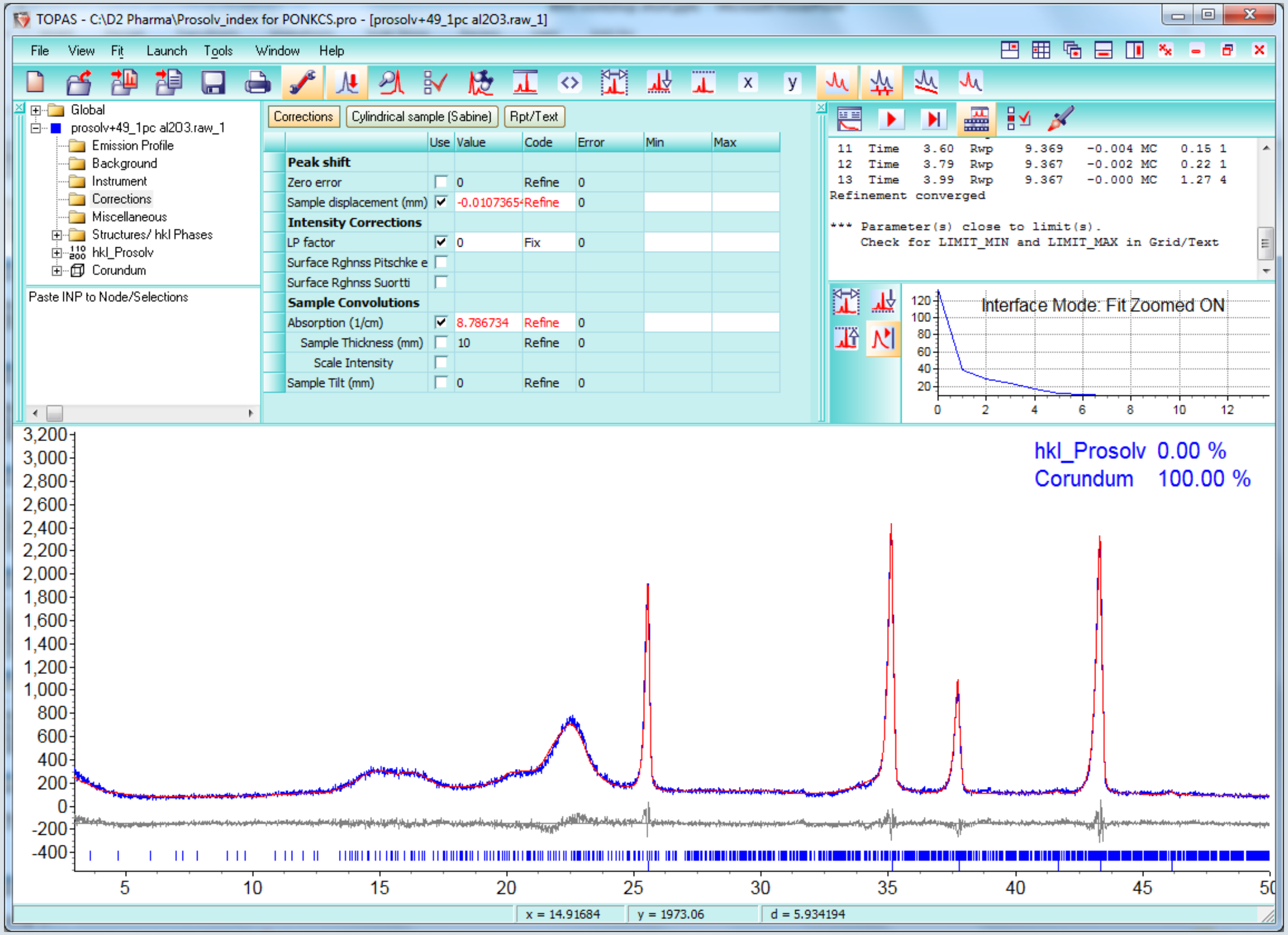


	h	k	l	m	d	th2	Use	I	Code	Error
1	1	0	0	2	29.48487	2.99407	☑	0.149	Fix	0
2	0	1	0	2	24.43362	3.61323	☑	0.0994	Fix	0
3	1	1	0	4	18.81338	4.69317	☑	0.0357	Fix	0
4	2	0	0	2	14.74244	5.99018	☑	1e-010	Fix	0
5	2	1	0	4	12.62275	6.99725	☑	0.00678	Fix	0
6	0	2	0	2	12.21681	7.23006	☑	1e-010	Fix	0
7	1	2	0	4	11.28635	7.82701	☑	0.0545	Fix	0
8	3	0	0	2	9.82829	8.99040	☑	0.119	Fix	0
9	2	2	0	4	9.40669	9.39423	☑	1e-010	Fix	0
10	3	1	0	4	9.11827	9.69208	☑	0.229	Fix	0
11	0	3	0	2	8.14454	10.85412	☑	0.312	Fix	0
12	1	3	0	4	7.85054	11.26189	☑	0.126	Fix	0
13	3	2	0	4	7.65781	11.54628	☑	0.216	Fix	0

```
252  Time 195.69  Rwp    5.329   -0.001 MC   0.35 1
253  Time 196.58  Rwp    5.328   -0.001 MC   0.35 1
254  Time 197.40  Rwp    5.327   -0.001 MC   0.35 1
Refinement converged

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

- Scan of pure Prosolv
- Step 1: try to find a “unit cell” that will fit the scan. If not enough peaks are present for LSI algorithm, try LP search
- Step 2: after getting a satisfactory fit, fix all peak intensities and uncheck “Delete hkls on refinement” and LP search

Quantifying Amorphous Phases
PONKCS Method-walk through for Prosolv

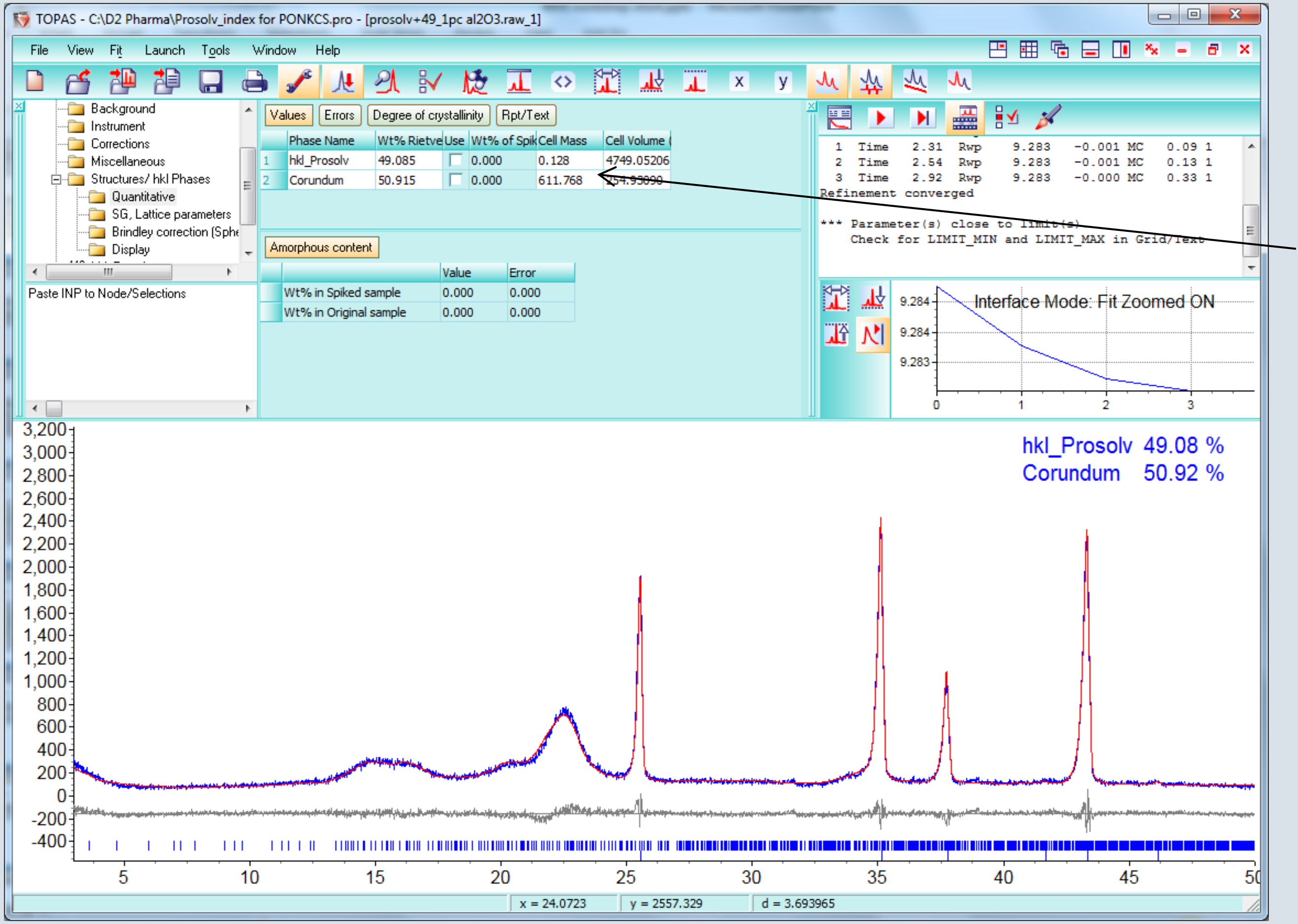


	Use	Value	Code	Error	Min	Max
Peak shift						
Zero error	☐	0	Refine	0		
Sample displacement (mm)	☑	-0.0107365	Refine	0		
Intensity Corrections						
LP factor	☑	0	Fix	0		
Surface Rghnss Pitschke e	☐					
Surface Rghnss Suortti	☐					
Sample Convolutions						
Absorption (1/cm)	☑	8.786734	Refine	0		
Sample Thickness (mm)	☐	10	Refine	0		
Scale Intensity	☐					
Sample Tilt (mm)	☐	0	Refine	0		

```
 11  Time   3.60  Rwp    9.369   -0.004 MC   0.15 1
 12  Time   3.79  Rwp    9.367   -0.002 MC   0.22 1
 13  Time   3.99  Rwp    9.367   -0.000 MC   1.27 4
Refinement converged

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

- Scan of 50% mix of Prosolv and known standard (Corundum)
- Step 3: replace scan of pure compound with known mixture

Quantifying Amorphous Phases
PONKCS Method-walk through for Prosolv



	Phase Name	Wt% Rietve	Use	Wt% of Spik	Cell Mass	Cell Volume (
1	hkl_Prosolv	49.085	☐	0.000	0.128	4749.05206
2	Corundum	50.915	☐	0.000	611.768	254.93090

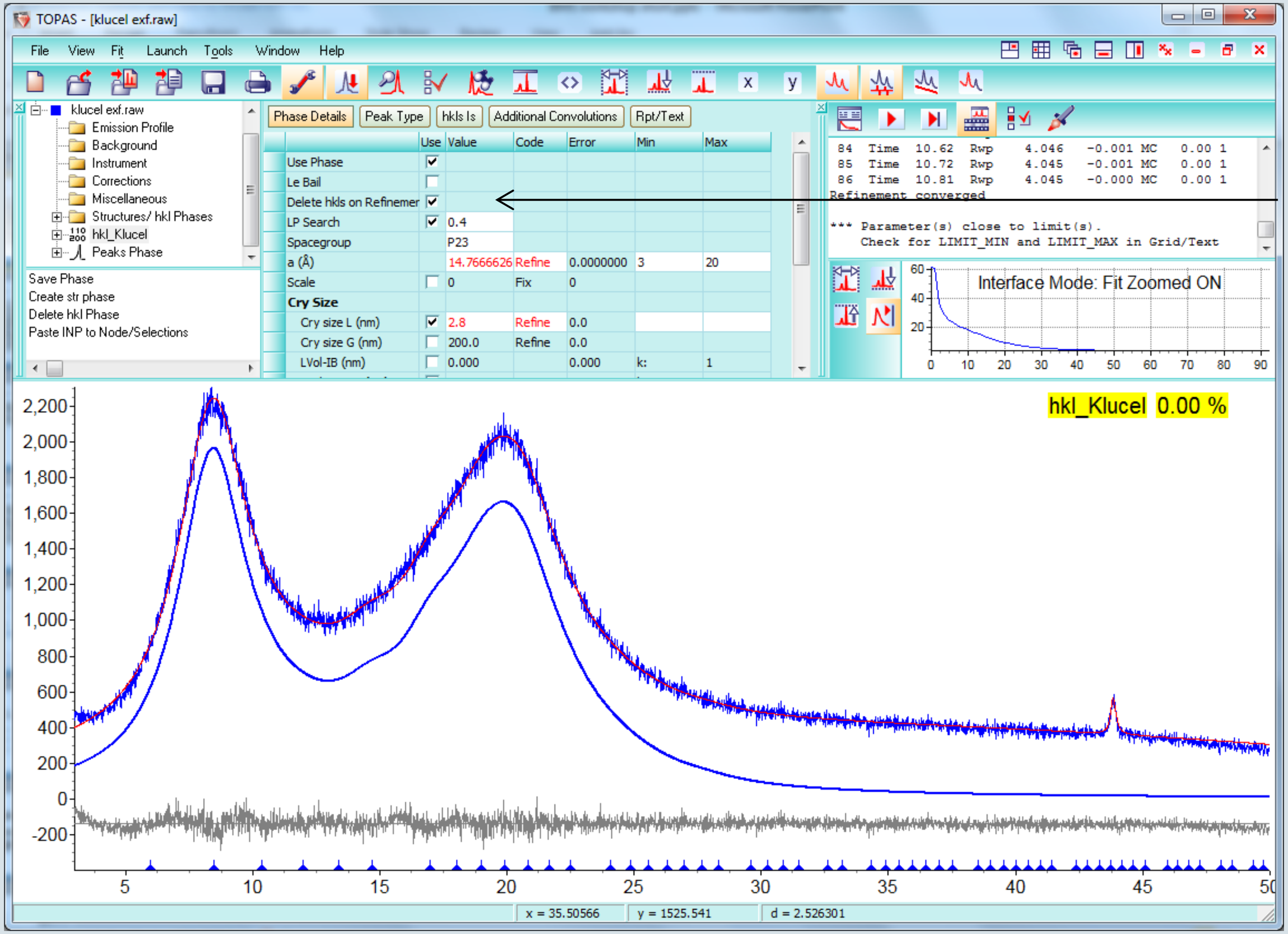
	Value	Error
Wt% in Spiked sample	0.000	0.000
Wt% in Original sample	0.000	0.000

```
  1  Time   2.31  Rwp    9.283   -0.001 MC   0.09 1
  2  Time   2.54  Rwp    9.283   -0.001 MC   0.13 1
  3  Time   2.92  Rwp    9.283   -0.000 MC   0.33 1
Refinement converged

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

hkl_Prosolv 49.08 %
Corundum 50.92 %

- Scan of 49.1% mix of Prosolv and known standard (Corundum)
- Step 3:Once that empirical value is known, save the hkl_Compritol phase (in .inp format). It can now be used like a normal structure in any other mixture

Quantifying Amorphous Phases
PONKCS Method-walk through for Klucel



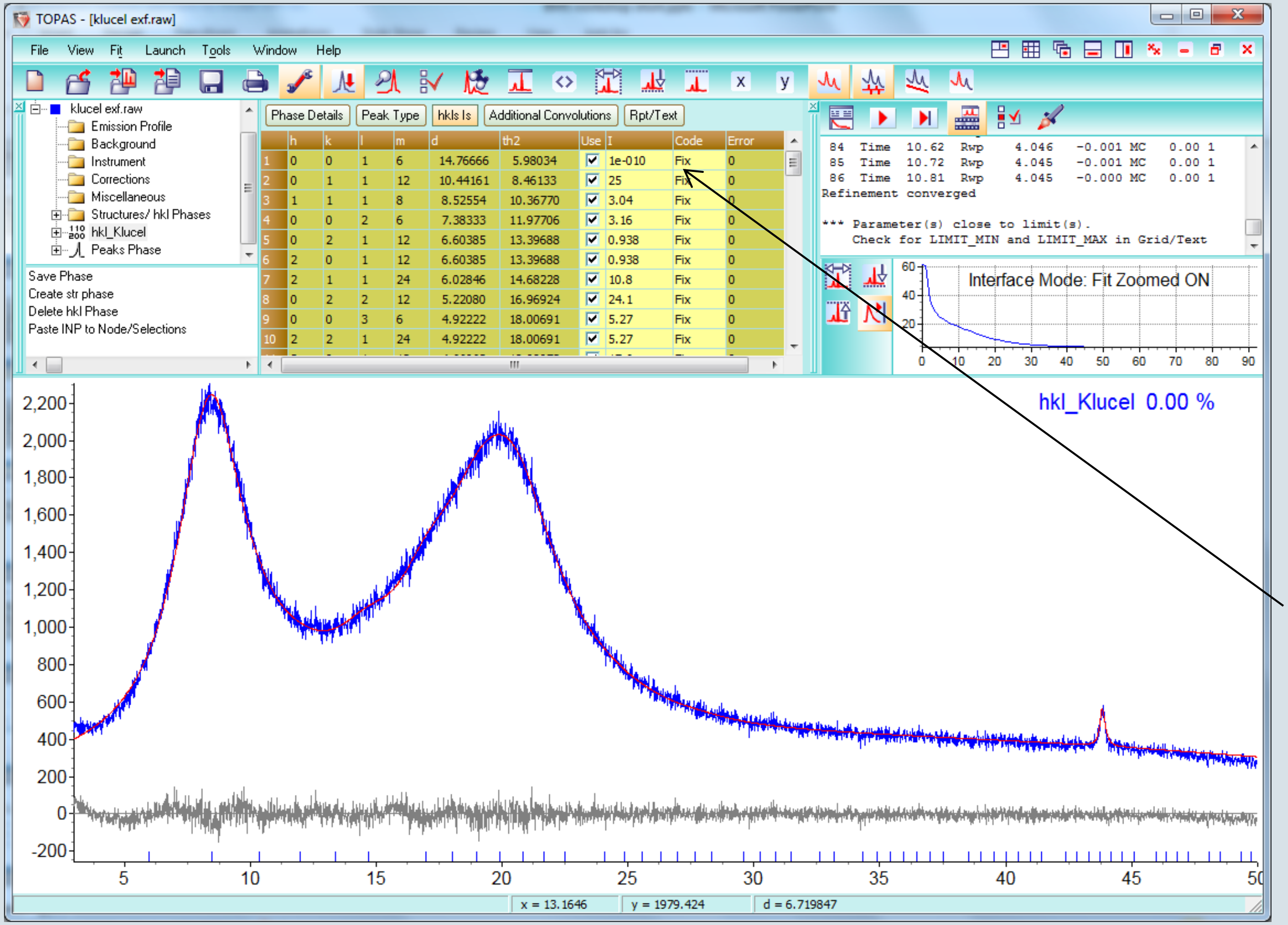
	Use	Value	Code	Error	Min	Max
Use Phase	☑					
Le Bail	☐					
Delete hkls on Refinemer	☑					
LP Search	☑	0.4				
Spacegroup		P23				
a (Å)		14.7666626	Refine	0.0000000	3	20
Scale	☐	0	Fix	0		
Cry Size						
Cry size L (nm)	☑	2.8	Refine	0.0		
Cry size G (nm)	☐	200.0	Refine	0.0		
LVol-IB (nm)	☐	0.000		0.000	k:	1

```
 84  Time  10.62  Rwp    4.046   -0.001 MC   0.00 1
 85  Time  10.72  Rwp    4.045   -0.001 MC   0.00 1
 86  Time  10.81  Rwp    4.045   -0.000 MC   0.00 1
Refinement converged

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

x = 35.50566 y = 1525.541 d = 2.526301

- Scan of pure Klucel
- Step 1: try to find a "unit cell" that will fit the scan. If not enough peaks are present for LSI algorithm, try LP search
- Step 2: after getting a satisfactory fit, fix all peak intensities and uncheck "Delete hkls on refinement"

Quantifying Amorphous Phases
PONKCS Method-walk through for Klucel

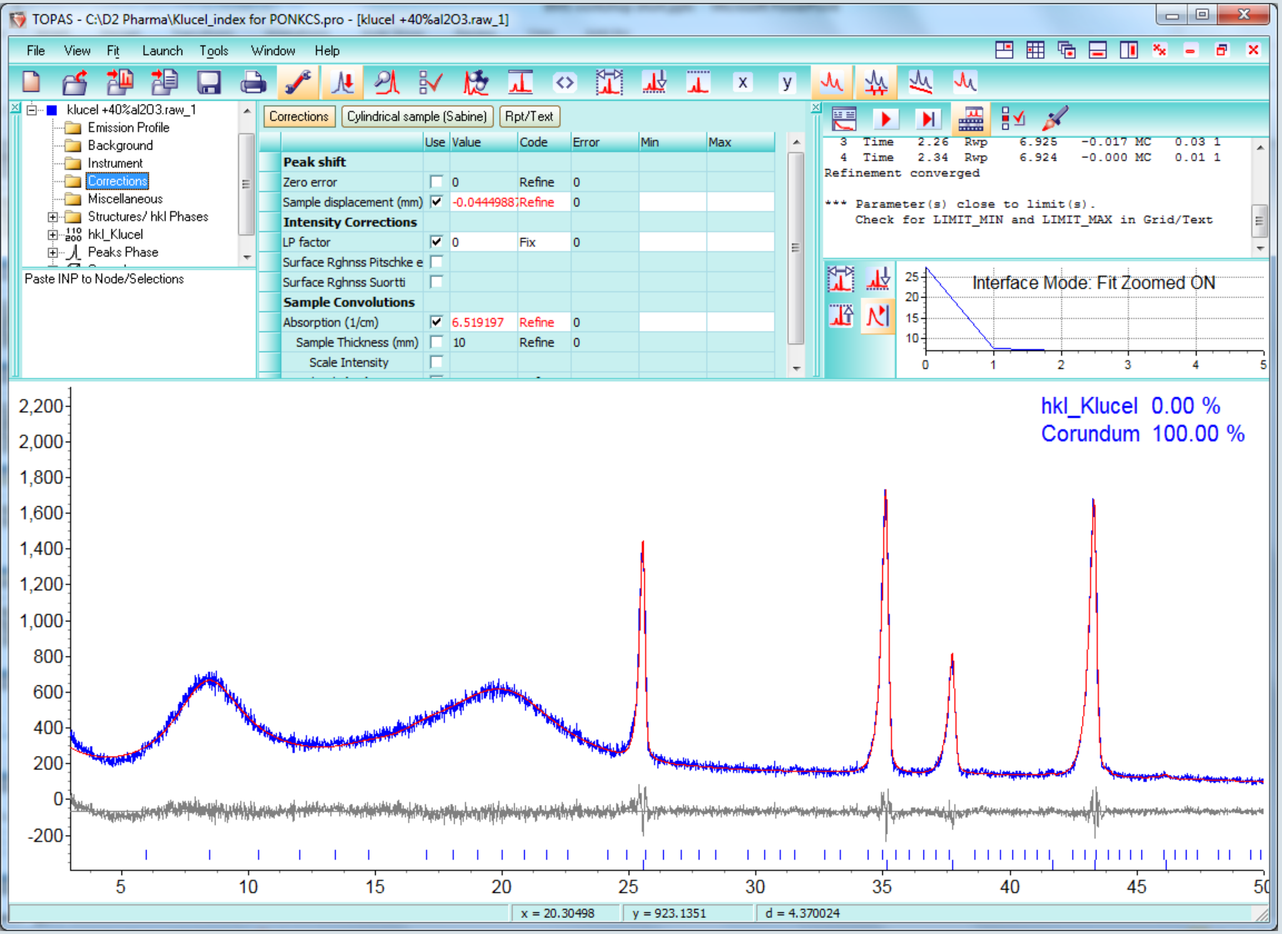


	h	k	l	m	d	th2	Use	I	Code	Error
1	0	0	1	6	14.76666	5.98034	☑	1e-010	Fix	0
2	0	1	1	12	10.44161	8.46133	☑	25	Fix	0
3	1	1	1	8	8.52554	10.36770	☑	3.04	Fix	0
4	0	0	2	6	7.38333	11.97706	☑	3.16	Fix	0
5	0	2	1	12	6.60385	13.39688	☑	0.938	Fix	0
6	2	0	1	12	6.60385	13.39688	☑	0.938	Fix	0
7	2	1	1	24	6.02846	14.68228	☑	10.8	Fix	0
8	0	2	2	12	5.22080	16.96924	☑	24.1	Fix	0
9	0	0	3	6	4.92222	18.00691	☑	5.27	Fix	0
10	2	2	1	24	4.92222	18.00691	☑	5.27	Fix	0

```
 84  Time  10.62  Rwp    4.046   -0.001 MC   0.00 1
 85  Time  10.72  Rwp    4.045   -0.001 MC   0.00 1
 86  Time  10.81  Rwp    4.045   -0.000 MC   0.00 1
Refinement converged

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

- Scan of pure Klucel
- Step 1: try to find a “unit cell” that will fit the scan. If not enough peaks are present for LSI algorithm, try LP search
- Step 2: after getting a satisfactory fit, fix all peak intensities and uncheck “Delete hkls on refinement” and LP search

Quantifying Amorphous Phases
PONKCS Method-walk through for Klucel



TOPAS - C:\D2 Pharma\Klucel_index for PONKCS.pro - [klucel +40%al2O3.raw_1]

	Use	Value	Code	Error	Min	Max
Peak shift						
Zero error	☐	0	Refine	0		
Sample displacement (mm)	☑	-0.0444988	Refine	0		
Intensity Corrections						
LP factor	☑	0	Fix	0		
Surface Rghnss Pitschke e	☐					
Surface Rghnss Suortti	☐					
Sample Convolutions						
Absorption (1/cm)	☑	6.519197	Refine	0		
Sample Thickness (mm)	☐	10	Refine	0		
Scale Intensity	☐					

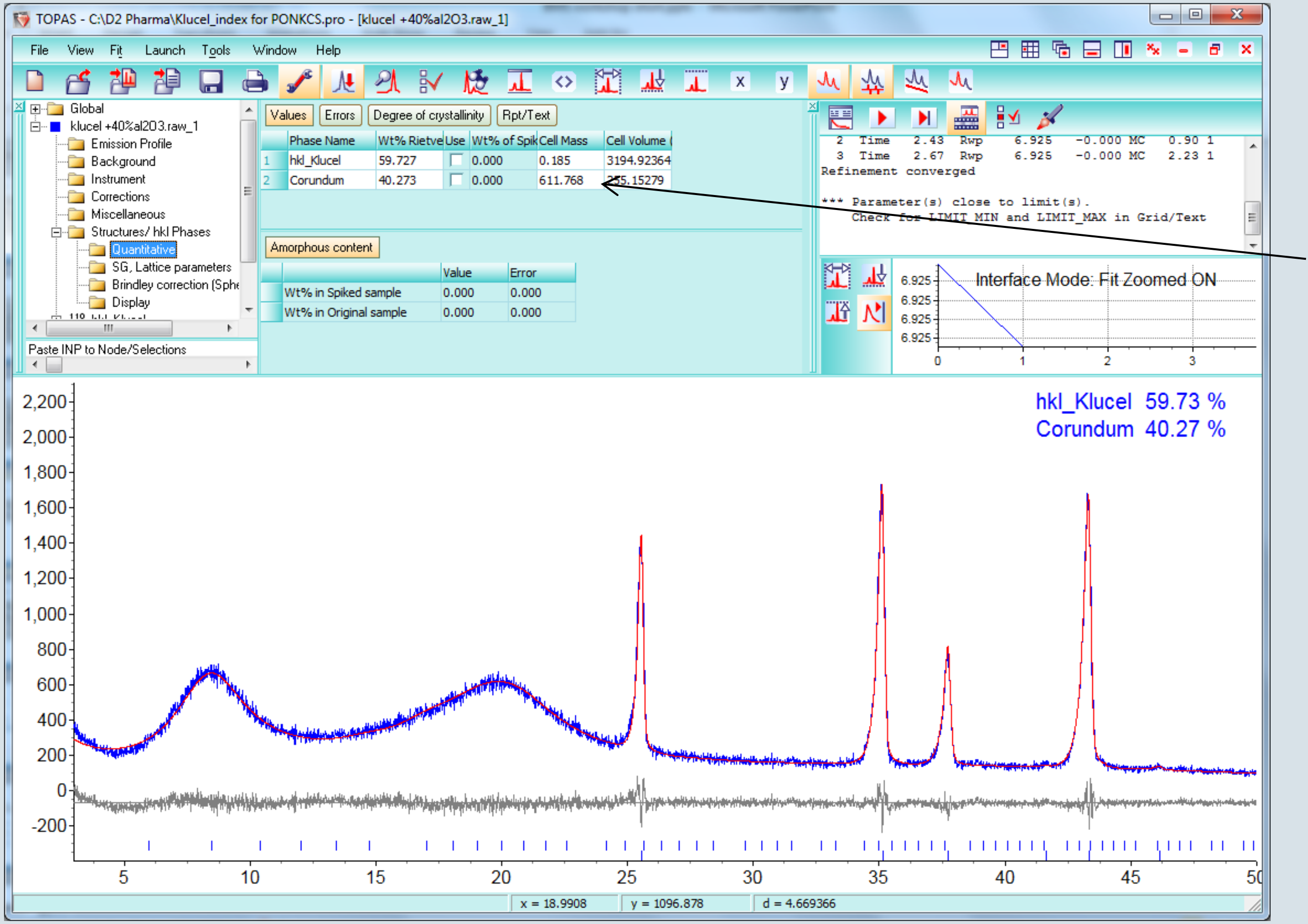
```
  3  Time   2.26  Rwp    6.925   -0.017 MC   0.03 1
  4  Time   2.34  Rwp    6.924   -0.000 MC   0.01 1
Refinement converged

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

hkl_Klucel 0.00 %
Corundum 100.00 %

x = 20.30498 y = 923.1351 d = 4.370024

- Scan of 50% mix of Klucel and known standard (Corundum)
- Step 3: replace scan of pure compound with known mixture

Quantifying Amorphous Phases
PONKCS Method-walk through for Klucel



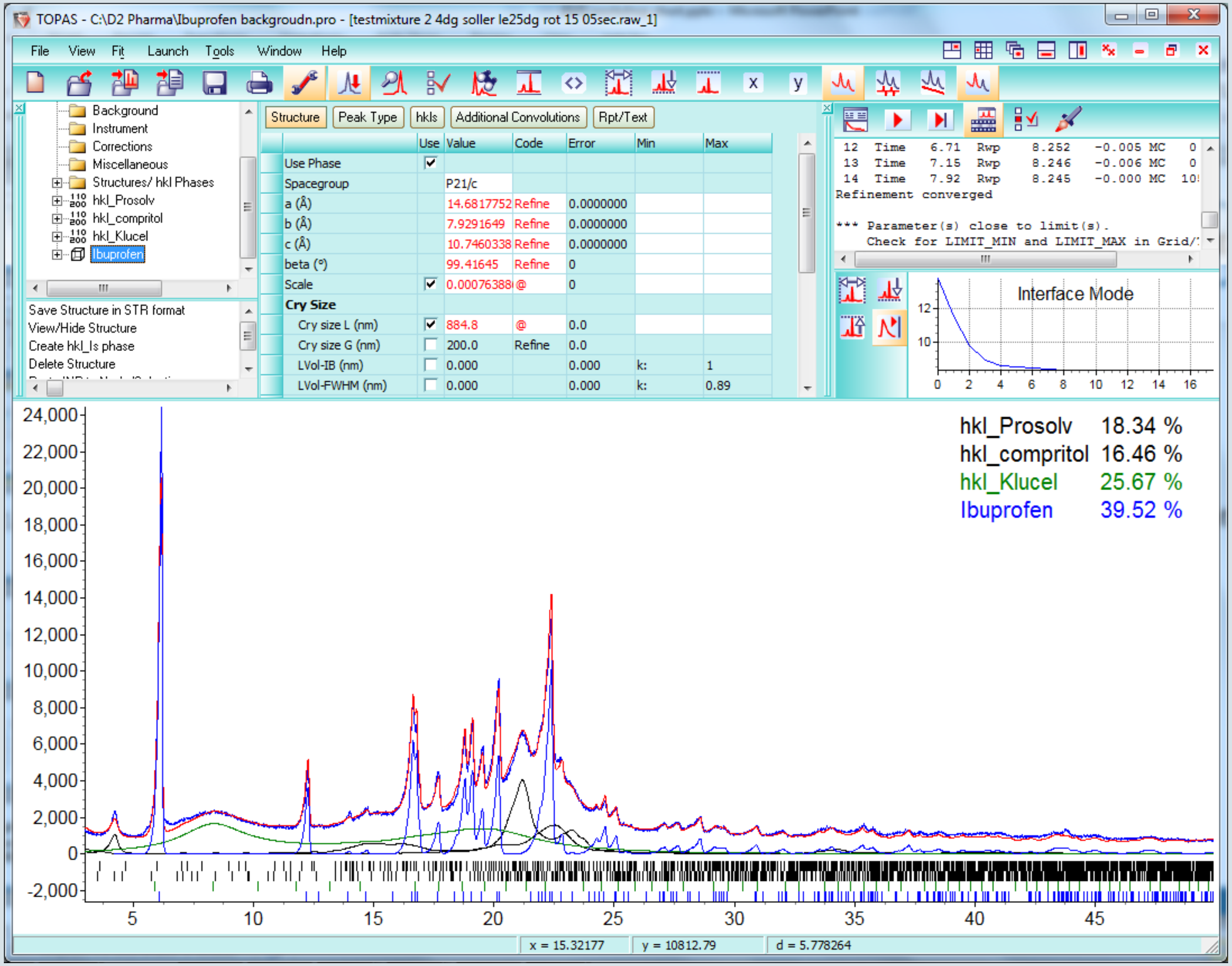
	Phase Name	Wt% Rietve	Use	Wt% of Spik	Cell Mass	Cell Volume (
1	hkl_Klucel	59.727	☐	0.000	0.185	3194.92364
2	Corundum	40.273	☐	0.000	611.768	255.15279

	Value	Error
Wt% in Spiked sample	0.000	0.000
Wt% in Original sample	0.000	0.000

```
  2  Time   2.43  Rwp    6.925   -0.000 MC   0.90 1
  3  Time   2.67  Rwp    6.925   -0.000 MC   2.23 1
Refinement converged

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

- Scan of 60% mix of Klucel and known standard (Corundum)
- Step 3:Once that empirical value is known, save the hkl_klucel phase (in .inp format). It can now be used like a normal structure in any other mixture

Quantifying Amorphous Phases PONKCS Method-Test mixture



	Use	Value	Code	Error	Min	Max
Use Phase	☑					
Spacegroup		P21/c				
a (Å)		14.6817752	Refine	0.0000000		
b (Å)		7.9291649	Refine	0.0000000		
c (Å)		10.7460338	Refine	0.0000000		
beta (°)		99.41645	Refine	0		
Scale	☑	0.00076388	@	0		
Cry Size						
Cry size L (nm)	☑	884.8	@	0.0		
Cry size G (nm)	☐	200.0	Refine	0.0		
LVol-IB (nm)	☐	0.000		0.000	k:	1
LVol-FWHM (nm)	☐	0.000		0.000	k:	0.89

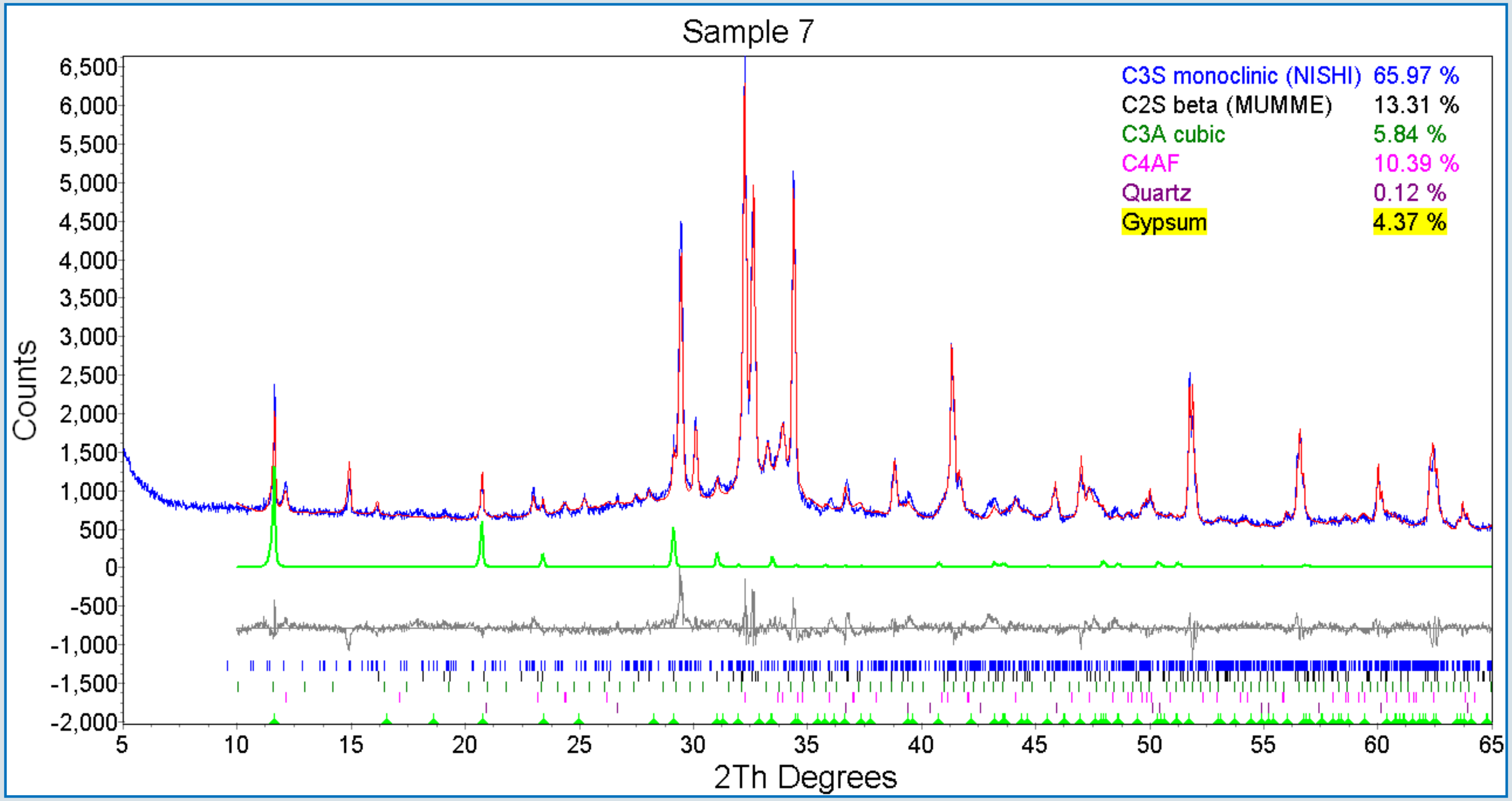
```
 12  Time   6.71  Rwp    8.252   -0.005 MC   0
 13  Time   7.15  Rwp    8.246   -0.006 MC   0
 14  Time   7.92  Rwp    8.245   -0.000 MC  10!
Refinement converged

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

hkl_Prosolv	18.34 %
hkl_compritol	16.46 %
hkl_Klucel	25.67 %
Ibuprofen	39.52 %

x = 15.32177
y = 10812.79
d = 5.778264

- Test mixture
  - 39% Ibuprofen
  - 18.7% Prosolv
  - 18% Compritol
  - 24.24% Klucel
- Background was determined on pure Ibuprofen sample to avoid correlation effects with broad excipient peaks
- Ibuprofen structure was also refined on pure sample to minimize preferred orientation effects → no further correction necessary

Industrial application: Cement + flyash Rietveld refinement with TOPAS, only crystalline components



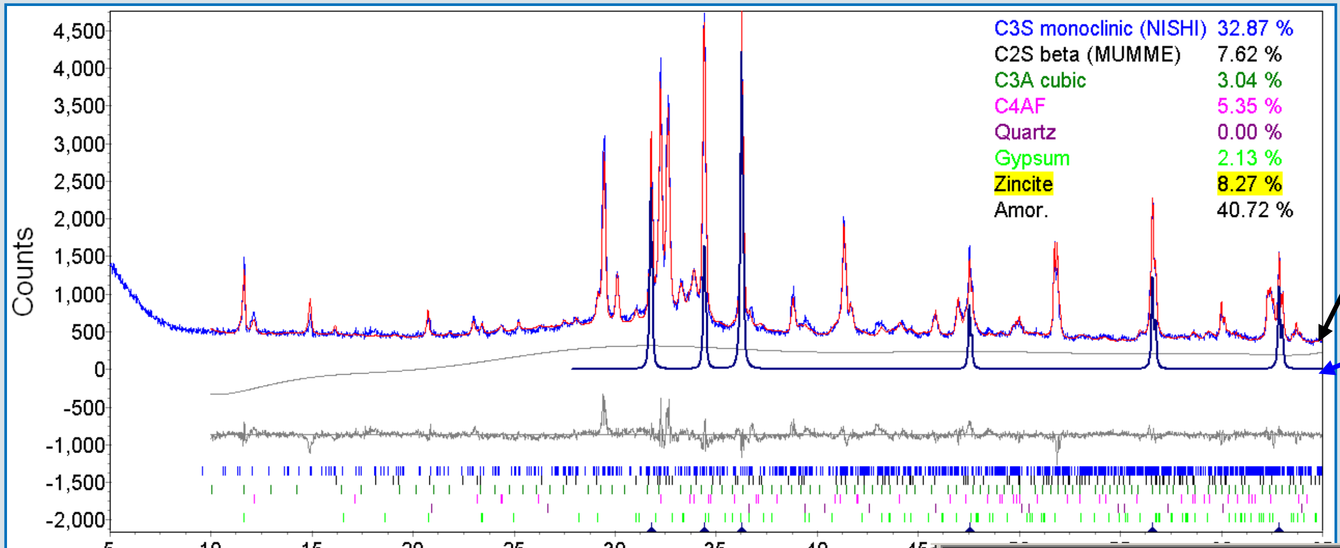
- LynxEye Detector
- 0.3° divergence, 4° Soller slits
- 0.02° /step, 0.2sec/step
- Measurement time: 9 minutes

A high order polynomial function was necessary to fit the background, which is an indication for amorphous material in the sample.

Industrial application: Cement and flyash

Determination of amophous component

Method 1: spiking the sample with an internal standard



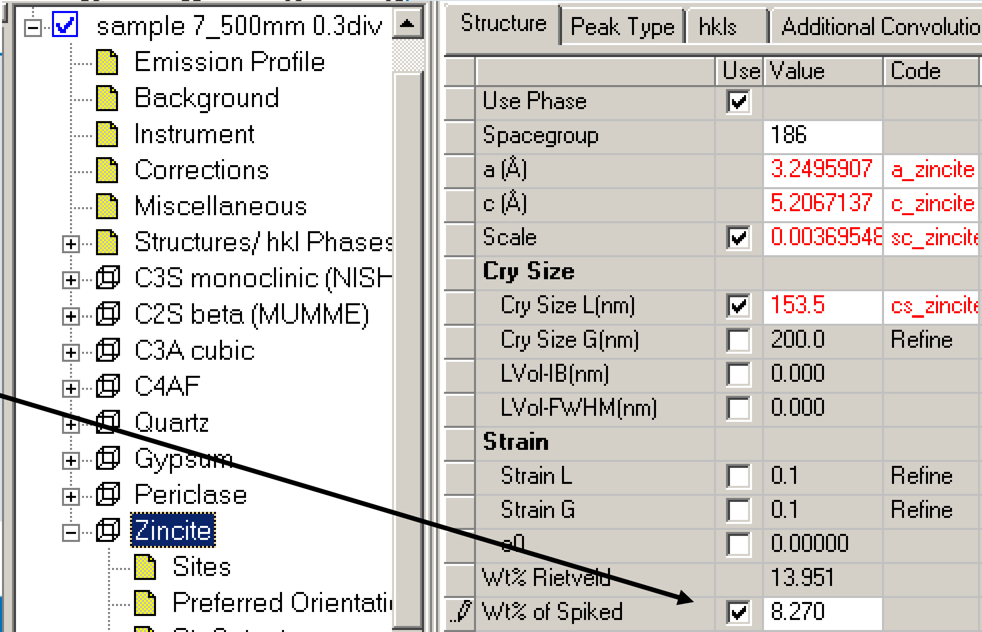
C3S monoclinic (NISHI)	32.87 %
C2S beta (MUMME)	7.62 %
C3A cubic	3.04 %
C4AF	5.35 %
Quartz	0.00 %
Gypsum	2.13 %
Zincite	8.27 %
Amor.	40.72 %

Background was fitted with high-order polynomial function

8.27 wt% Zincite was added to the sample as an internal standard

The elevated background is modeled with high-order polynomial function.

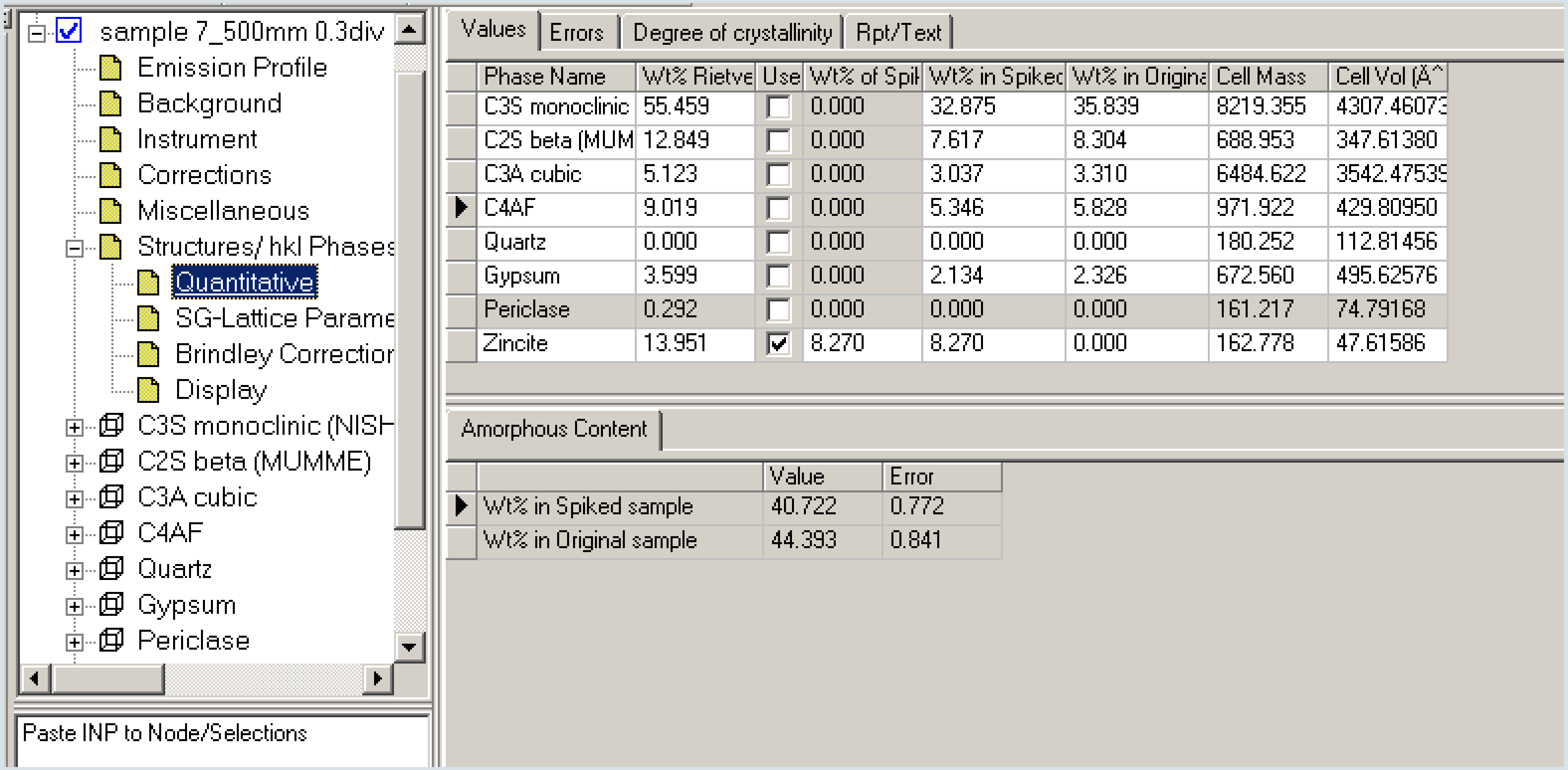
The sample is spiked with an known amount of an internal standard.



- ☑ sample 7_500mm 0.3div
  - Emission Profile
  - Background
  - Instrument
  - Corrections
  - Miscellaneous
  - Structures/ hkl Phases
  - C3S monoclinic (NISH
  - C2S beta (MUMME)
  - C3A cubic
  - C4AF
  - Quartz
  - Gypsum
  - Periclase
  - Zincite
    - Sites
    - Preferred Orientati

	Use	Value	Code
Use Phase	☑		
Spacegroup		186	
a (Å)		3.2495907	a_zincite
c (Å)		5.2067137	c_zincite
Scale	☑	0.00369548	sc_zincit
Cry Size			
Cry Size L(nm)	☑	153.5	cs_zincit
Cry Size G(nm)	☐	200.0	Refine
LVol-IB(nm)	☐	0.000	
LVol-FWHM(nm)	☐	0.000	
Strain			
Strain L	☐	0.1	Refine
Strain G	☐	0.1	Refine
e0	☐	0.00000	
Wt% Rietveld		13.951	
Wt% of Spiked	☑	8.270	

Industrial application: Cement + flyash
Determination of amophous component
Method 1: spiking the sample with an internal standard



Phase Name	Wt% Rietve	Use	Wt% of Spi	Wt% in Spike	Wt% in Origin	Cell Mass	Cell Vol (Å
C3S monoclinic	55.459	☐	0.000	32.875	35.839	8219.355	4307.4607
C2S beta (MUM	12.849	☐	0.000	7.617	8.304	688.953	347.61380
C3A cubic	5.123	☐	0.000	3.037	3.310	6484.622	3542.4753
C4AF	9.019	☐	0.000	5.346	5.828	971.922	429.80950
Quartz	0.000	☐	0.000	0.000	0.000	180.252	112.81456
Gypsum	3.599	☐	0.000	2.134	2.326	672.560	495.62576
Periclase	0.292	☐	0.000	0.000	0.000	161.217	74.79168
Zincite	13.951	☑	8.270	8.270	0.000	162.778	47.61586

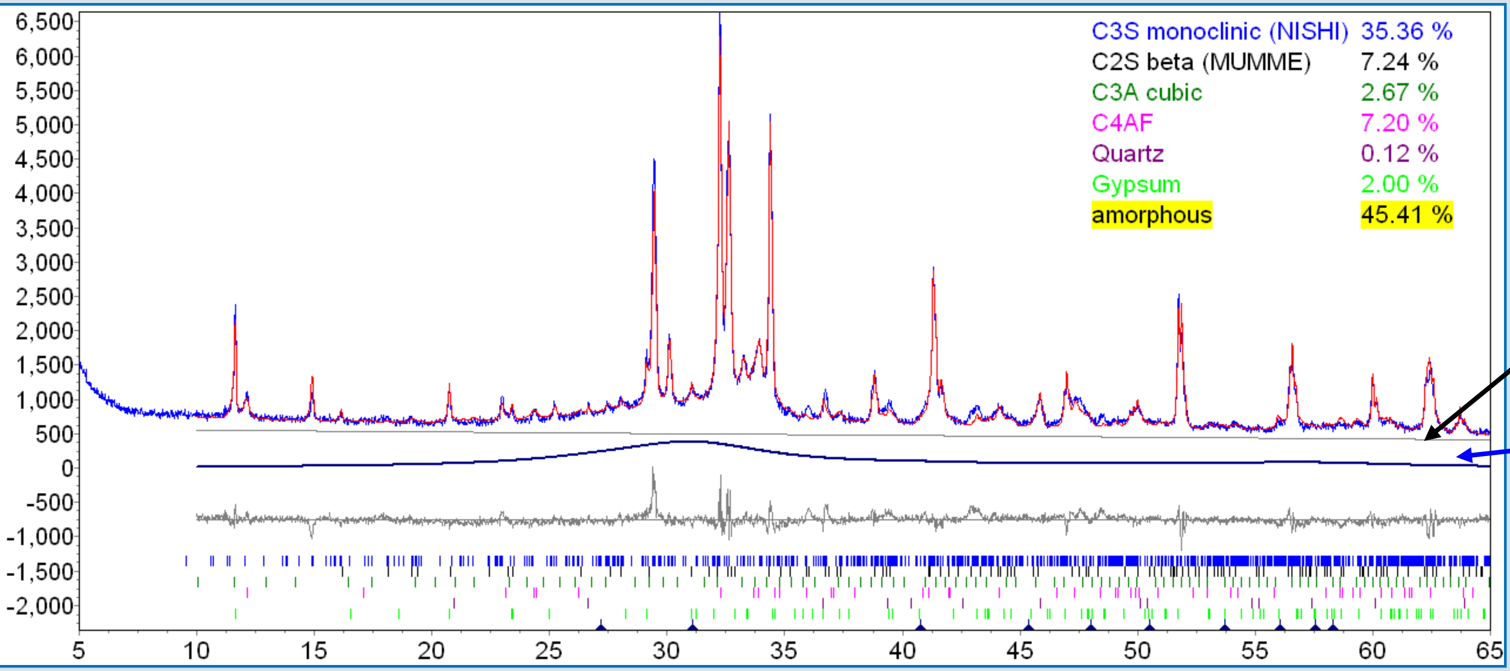
	Value	Error
Wt% in Spiked sample	40.722	0.772
Wt% in Original sample	44.393	0.841

Phase amounts and amorphous content in original sample is calculated in the TOPAS software

Industrial application: Cement + flyash

Determination of amophous component

Method 2: Modeling the background with „amorphous structure"



Background from 0-order polynomial function

Background from amorphous component

The elevated background from the amorphous component is not modeled with a polynomial but mostly with an amorphous "structure". This was achieved by using a normal quartz structure with very small crystallite size and adjusting the lattice parameters to fit the amorphous halo.

This standard less method works reliable and can be automated easier but should be checked for each sample type with the internal standard method.

BRUKER

www.bruker-axs.com