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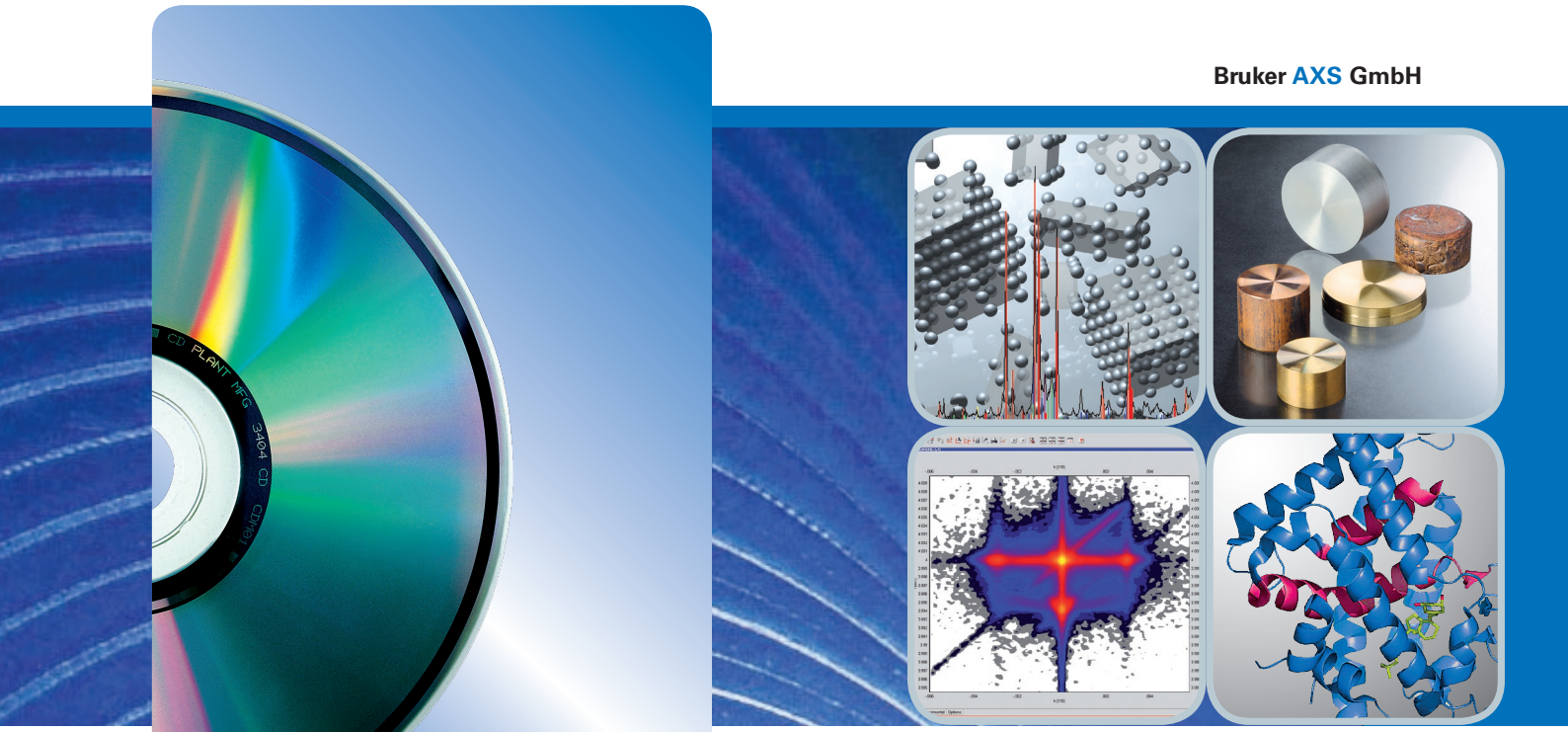

DIFFRAC^{plus}
TOPAS

TOPAS 4.2 Tutorial

think forward

XRD

Order no. DOC-M88-EXX062 V4.2. Updated: Jan 15, 2009.

Printed in the Federal Republic of Germany.

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1 OVERVIEW

TOPAS comes with a large number of selected examples demonstrating much of its functionality in both GUI and Launch Mode. An overview of the application areas covered by the example files is given in Table 1-1.

Table 1-1: Application areas covered by the tutorial example files.

Example	SLF / WPPF	Indexing	WPPD (Pawley & Le Bail)	(Rietveld) Structure refinement	(Rietveld) Quantitative analysis	Structure determination	Misc
				⃠	⃠	⃠	
Ae [1]				✓		✓	
AlVO4 [2]			✓	✓			
AnisoLS [3]			✓		✓		
Batch-UTF							✓
CeO2	✓		✓	✓			
CF [4]						✓	
Cime [5]			✓	✓		✓	
DOC	✓			✓			
FIAn					✓		
KCP [6]			✓	✓		✓	
LSI		✓	✓				
LP-Search		✓	✓				
Min							✓
Misc	✓						
Out							✓
PbSO4 [7]			✓	✓		✓	
Protein [8]			✓				
QA					✓		
QPARR [9]				✓	✓		
SizeStrain [10]	✓		✓				
TOF [11]				✓			

[1] Jin et al. (2003), Karakurt et al. (2003), Li et al. (2003); [2] Göbel (1999);
[3] Fitch & Jobic (1993), Dinnebier et al. (1999), Hillier (2003), Raudsepp (2004);
[4] Schaefer et al. (1998), Fukuoka et al. (2000), Lister et. al. (2004), Von Dreele (2007), Christensen & Thom (1971);
[5] http://www.ccp14.ac.uk; [6] Dinnebier et al. (1997); [7] Hill (1992);
[8] Von Dreele (2000); [9] Madsen et al. (2001), Scarlett et al. (2002);
[10] Balzar (2001); [11] Evans et al. (1999)

⃠ Not available in TOPAS P.

It is assumed that TOPAS has been installed in the default location C:\TOPAS4. Example files are found in the C:\TOPAS4\TUTORIAL\ directory, and are organized as follows:

- C:\
  - TOPAS4
    - Tutorial
      - Ae
      - AlVO4
      - AnisoLS
      - Batch-UTF
      - CeO2
      - CF
      - Cime
      - DOC
      - FlAn
      - KCP
      - LSI
      - LP-Search
      - Min
      - Misc
      - Out
      - PbSO4
      - Protein
      - QA
      - QPARR
      - SizeStrain
      - TOF

Table 1-2. details step by step procedures provided for most common tasks from single line fitting up to structure determination using selected examples.

Table 1-2: Tutorial examples with step by step procedures provided.

General Profile Analysis Techniques (section 2)

- **Single line up to whole powder pattern fitting**
  - Single Line Fitting : CeO_2, LaB_6
  - Simultaneous fitting of two datasets : α-Al_2O_3 (SRM1976)
  - Profile analysis using constraints : Quartz
  - Whole powder pattern fitting : Y_2O_3
- **Indexing**
  - LP-Search : $PbSO_4$
  - LSI : T3R3 human insulin-zinc complex
- **Whole powder pattern decomposition**
  - Pawley and LeBail Fitting : $AlVO_4$, $PbSO_4$
- **Structure determination - Simulated Annealing**
  - Structure determination and refinement of the organic compound Cimetidine (synchrotron X-ray data)
  - Structure determination of the inorganic compound $PbSO_4$ (laboratory X-ray data)
  - Structure determination and refinement of the metal-organic compound KCP (synchrotron X-ray data)
- **Structure determination - Charge Flipping**
  - Structure determination of the organic compound Cimetidine (synchrotron X-ray data)
- **Rietveld structure refinement**
  - Laboratory X-ray data, CW neutron data : $PbSO_4$
- **Quantitative Rietveld analysis**
  - Quantification of a simple mixture : CPD-2
  - Quantification of amorphous phase amounts : CPD-3
  - Quantification of an ordinary Portland clinker : OPC

Miscellanous (section 3)

- **Degree of crystallinity determination**
  - Single line fitting of a polymer
  - Combined Rietveld refinement and single line fitting of KCP
- **Isotropic size-strain analysis**
  - Single line and Pawley fitting : CeO_2
- **Using the rigid body editor**
  - Creation of rigid bodies
  - Torsions
- **TOF neutron data**
  - Rietveld refinement : CeO_2
- **Fourier analysis**
  - Structure completion : $PbSO_4$

2 GENERAL PROFILE ANALYSIS TECHNIQUES

2.1 Single line up to whole powder pattern fitting

2.1.1 Single line fitting

2.1.1.1 Single line fitting with a Split-PVII function

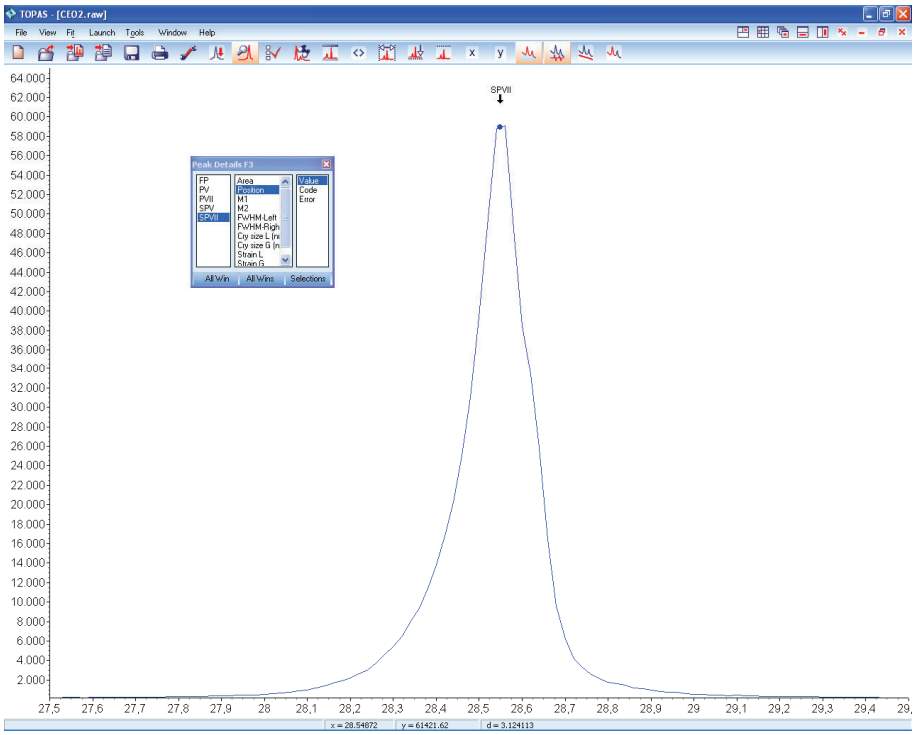
1. Start TOPAS.
2. Load the raw data by importing the file CEO2.RAW. By default this file is located in C:\TOPAS4\TUTORIAL\CEO2.

Menu:	Icon:	Shortcut:	Result:
File - *Import Data File(s)...*		n.a.	Imports measurement data

3. Zoom the first reflection in the region between 27.5° - 29.5° 2θ.

Hint!	The *Chart Options Dialog* (found in the short cut menu of the *Scan Window*) is a powerful alternative for exact zooming. Its use for zooming is described in section 2.1.4.

4. Manually insert one peak at the desired 2θ position: Open the *Peak Details Dialog*, select the split-PVII function (SPVII), and insert one peak at the desired 2θ position by clicking the left mouse button. Note the blue "Bouncing Ball" moving along the scan; the peak will be inserted at the position of the ball. A stick indicates the peak position.

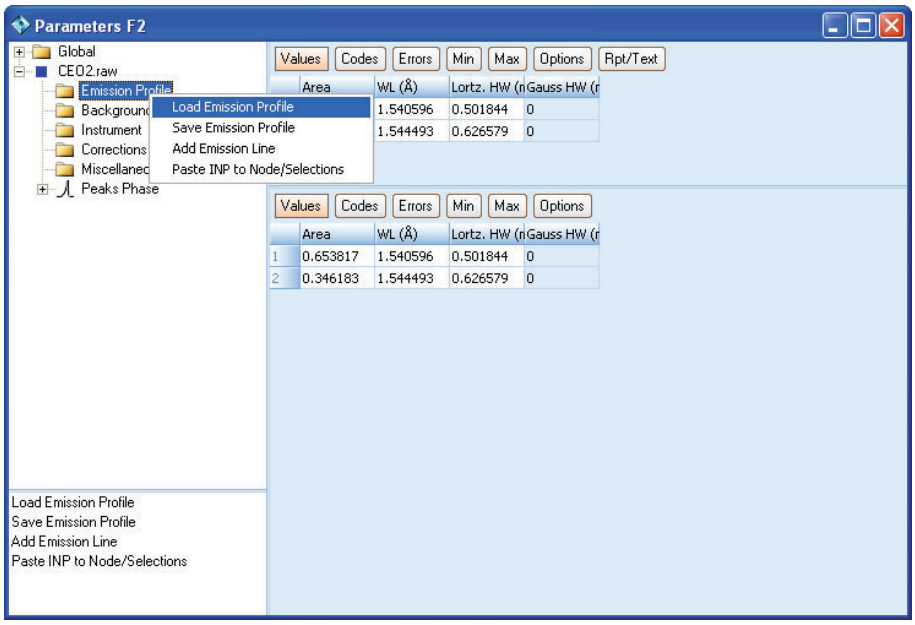


If you incorrectly add a peak, press the "Ctrl" key and drag the mouse over the stick. Then press the "Del" key on your keyboard to delete the peak. You can also press F9 to delete the nearest peak to the mouse pointer or delete the peak in the *Parameters Window*.

Menu:	**Icon:**	**Shortcut:**	**Result:**
View - Peak Details Window		F3	Displays or hides the *Peak Details Window*
View - Parameters Window		F2	Displays or hides the *Parameters Window*

Hint! The *Peak Search Dialog* provides convenient methods for automatic peak finding. Its use is described in section 2.1.4

5. In the *Parameters Window* focus the *Emission Profile* item and load the predefined emission profile CUKA2_ANALYT.LAM. By default this file is located in C:\TOPAS4\LAM.



6. To inspect (and optionally change) the starting values and refinement flags for each parameter you can either use the *Parameters Window* or the *Peak Details Dialog*.
   - In the *Parameters Window* select the *Peaks SPVII* item. The *Values* page lists all parameter values, the *Codes* page allows to define the associated parameter codes.
   - Alternatively open the *Peak Details Dialog* and select the peak property to be displayed or changed. A mouse click on the text displayed nearby the peak using the left mouse button will open an edit field, which allows to change parameter values or codes. Any changes have to be confirmed using the "Enter" key.

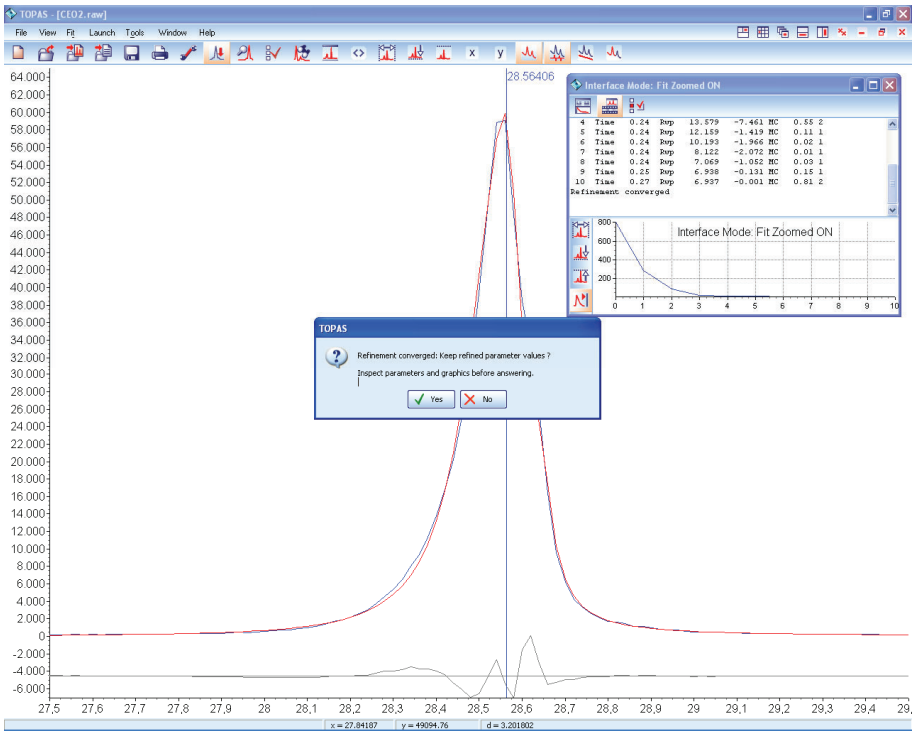
Hint!	For the Split-PVII and the Split-PV functions all profile parameters are always set to individual refinement by default. For more information about refinement flags and the optional use of constraints refer to section 2.1.3.

7. To have errors calculated, check the menu item *Calculate Errors* in the *Fit* menu.
8. To start the refinement switch to the *Fit Window* and click on the *Run* button.

Menu:	**Icon:**	**ShortCut:**	**Result:**
Fit – *Fit Window*		F5	Displays or hides the *Fit Window*
n.a.		F6	Runs the refinement

In the *Scan Window* a calculated pattern based on the start values is shown in red color. The difference to the observed data is represented by the gray curve. After

fitting a dialog informs you, if the refinement has converged or not. Note that this dialog is modeless and allows inspection of the refinement results before accepting any changes.



9. The refinement results can be inspected in the *Parameters Window* or using the *Peak Details Dialog*.

10. Save your work.

Menu:	**Icon:**	**Shortcut:**	**Result:**
File – Save		n.a.	Saves the current work in a document (*.PRO)
File – Export INP file...	n.a.	n.a.	Exports the current work as an input file (*.INP)

Hint! TOPAS documents (PRO files) contain the measurement data, model and refinement parameters, evaluation results, as well as any user-defined GUI settings. Therefore you can load and resume your fit session anytime at any stage or use the document as a template for different data.

Exporting an input file using the Menu *File - Export INP File...* instead allows the use of your refinement model e.g. in an automated environment (using TC) or in Launch Mode. Measurement data and user-defined GUI settings are not saved within an INP file.

2.1.1.2 Single line fitting with fundamental parameters

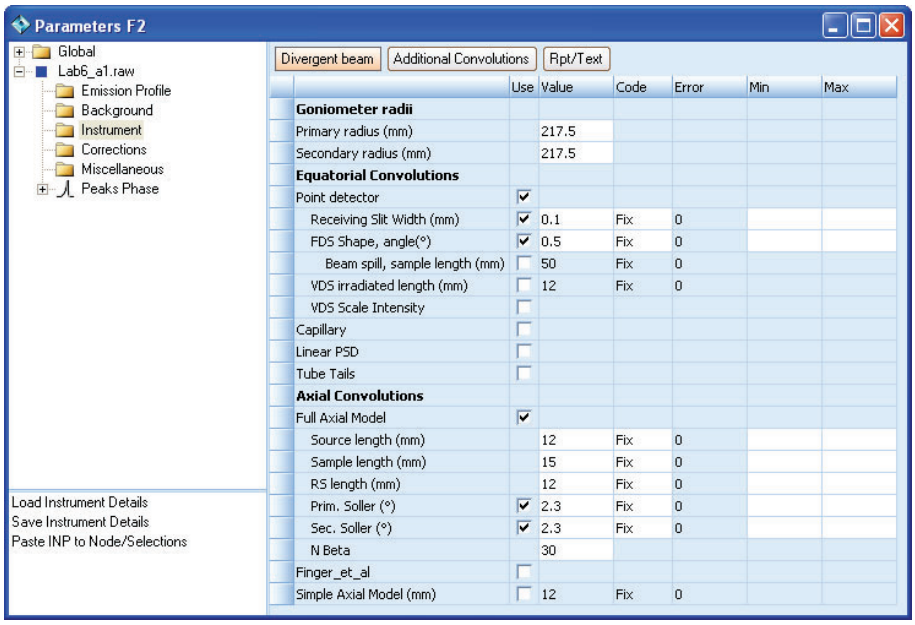
Hint!	The Fundamental Parameter Approach is a convolution based method, where the final profile shape is a composit of several independent model functions. Therefore you have to state explicitely, if i) a model function is to be used, and ii) if the parameters of this function are to be refined or not.

1. Start TOPAS.
2. Import the file LAB6_A1.RAW. By default this file is located in C:\TOPAS4\TUTORIAL\MISC.
3. Select FP (= fundamental parameters) as profile function and insert one peak at the desired 2θ position.
4. Load the predefined emission profile CUKA5.LAM.
5. To use the FPA the instrument configuration has be to known. Focus the *Instrument* item and define the instrument settings according to the following two tables:

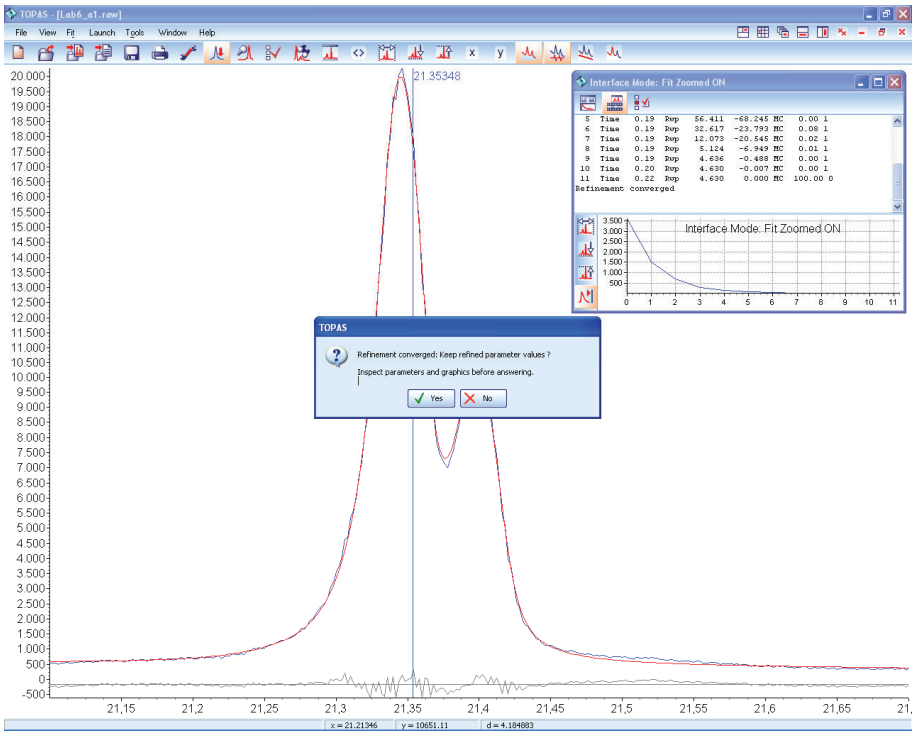
Equatorial Convolutions:		**Axial Convolutions:**	
Receiving Slit Width	☑	Full Axial Model	☑
FDS [1)] Shape, Angle	☑	Primary Soller	☑
		Secondary Soller	☑

Instrument Parameter:		**Value:**
Goniometer Radius	Primary:	217.5 mm
	Secondary:	217.5 mm
Receiving Slit Width	Width:	0.1 mm
FDS [1)] Shape, Angle	Angle:	0.5°
Soller Slits	Primary:	2.3°
	Secondary:	2.3°

[1)] Fixed Divergence Slit



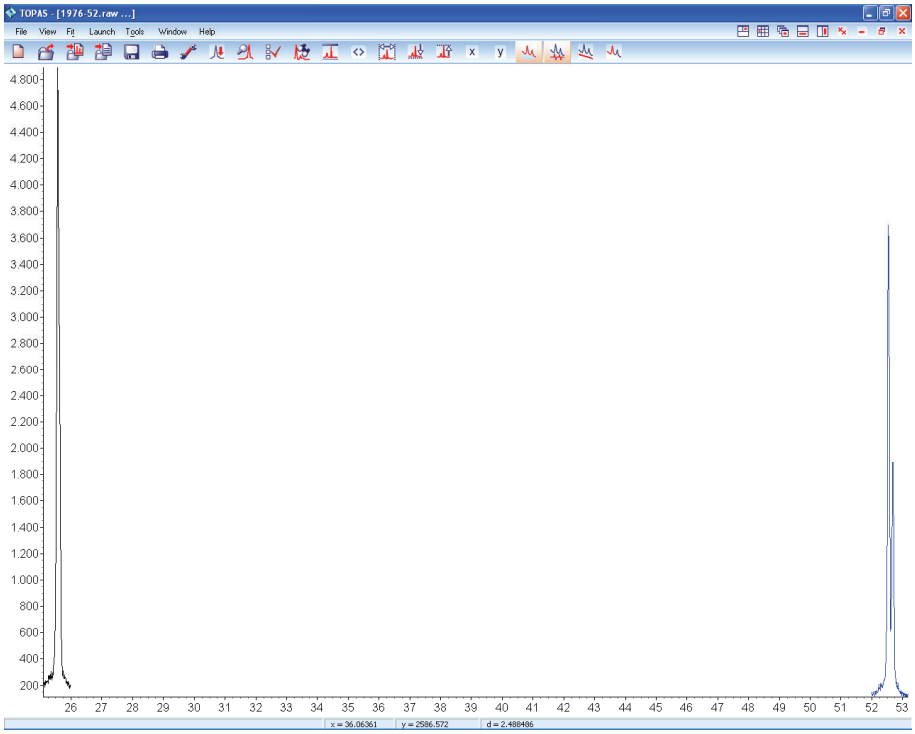
6. Start the refinement.



Hint!	Note that the calculated peak maximum position is offset from the Bragg 2θ position; this is expected and reflects one of the benefits of the FPA: it intrinsically corrects for errors in 2θ due to instrument and sample aberrations. Thus FPA gives a Bragg 2θ position matching that determined as if the data were collected with a "perfect sample" on a "perfect instrument" with monochromatic radiation. Therefore, especially at low angles, the calculated 2θ positions do not generally coincide with the peak maximum.

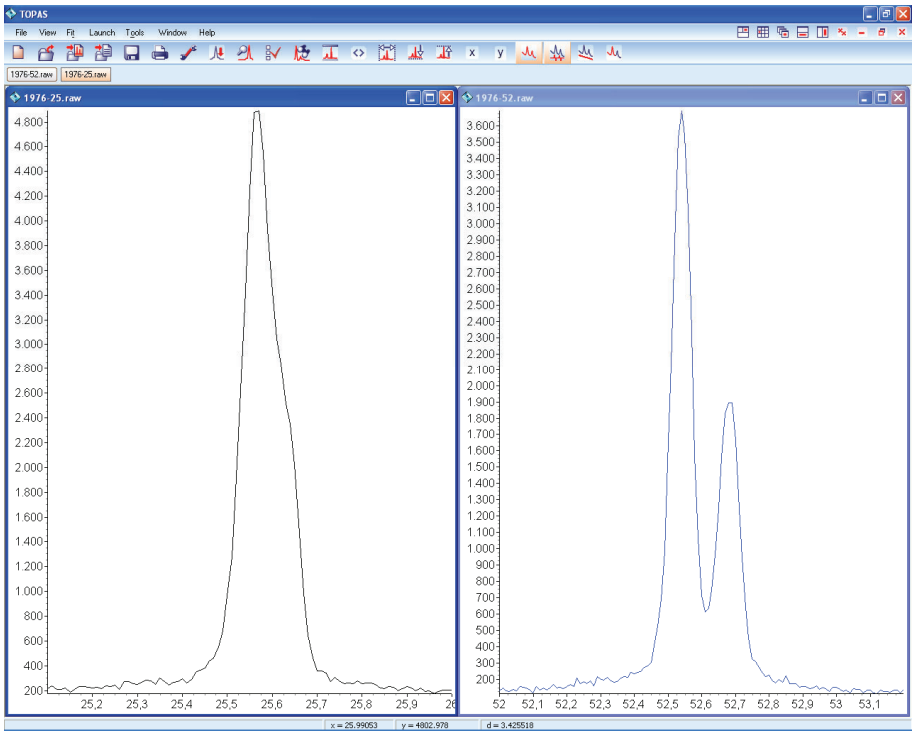
2.1.2 Simultaneous fitting of two datasets

1. Start TOPAS.
2. Import the files 1976-25.RAW and 1976-52.RAW. By default both files are located in C:\TOPAS4\TUTORIAL\MISC.
3. By default both ranges are displayed in one single *Scan Window*.



Display both ranges in separate *Scan Windows*.

Menu:	**Icon:**	**Shortcut:**	**Result:**
Window - *One Range per Window*	n.a.	n.a.	Displays each range in a different *Scan Window*

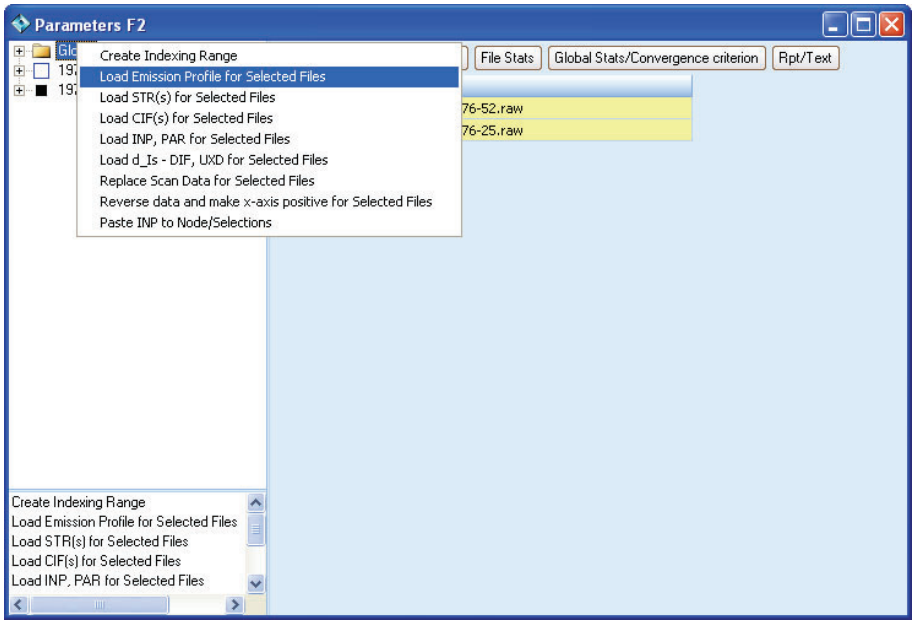


4. Select FP as profile function and insert one peak at the desired 2θ position in each range.

5. In order to define the refinement conditions switch to the *Parameters Window*. In the tree view each range appears as a single *Range* item.

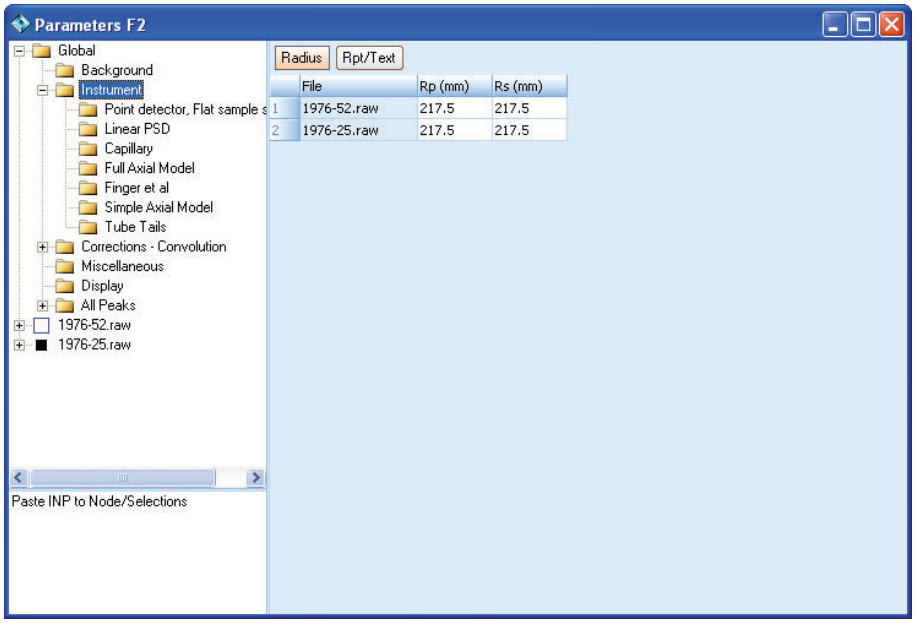
   In this example both ranges have been measured using exactely the same instrumental conditions. Therefore it is possible to define both the emission profile as well as the instrument parameters using the *Global* item of the *Parameter Tree*.

   - Focus the *Global* item, select both data files in the *Path* page, and load the predefined emission profile CUKA5.LAM for all selected files.

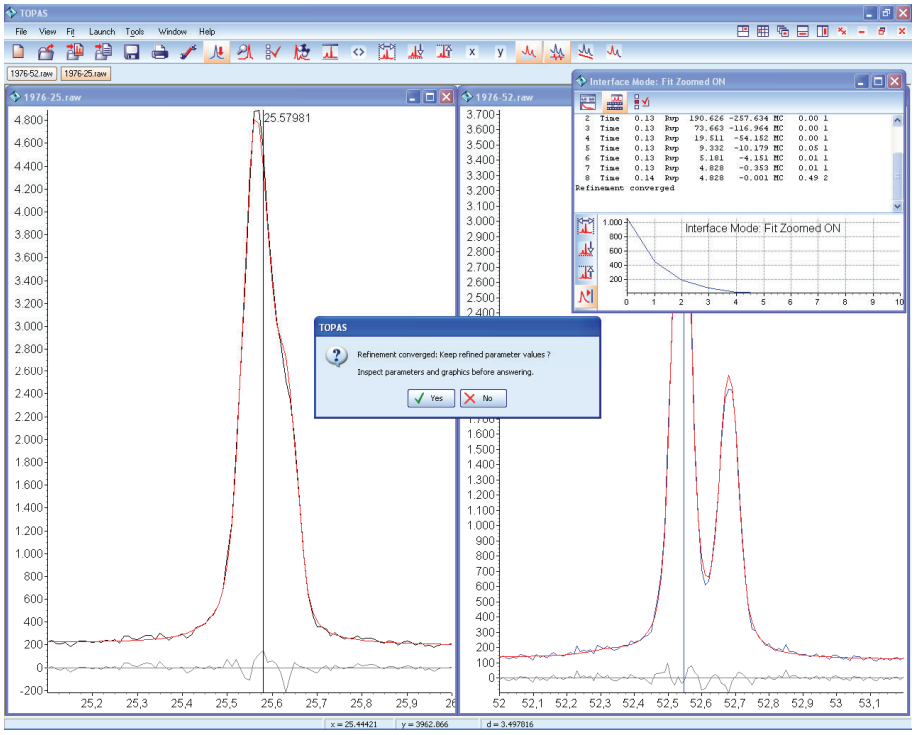


- Expand the *Instrument* item. In the various *Instrument* sub-items and their associated grid pages define the instrument settings according to the following table:

Instrument Parameter:		**Value:**
Goniometer Radius	Primary:	217.5 mm
	Secondary:	217.5 mm
RS	Width:	0.2 mm
FDS	Angle:	1°
Soller Slits	Primary:	2.3°
	Secondary:	2.3°



6. Start the refinement.



2.1.3 Profile analysis using constraints

This lesson is devided into three parts:

I. Unconstrained analytical profile fitting

II. Constrained analytical profile fitting

III. Use of Fundamental Parameters

Part I: Unconstrained analytical profile fitting:

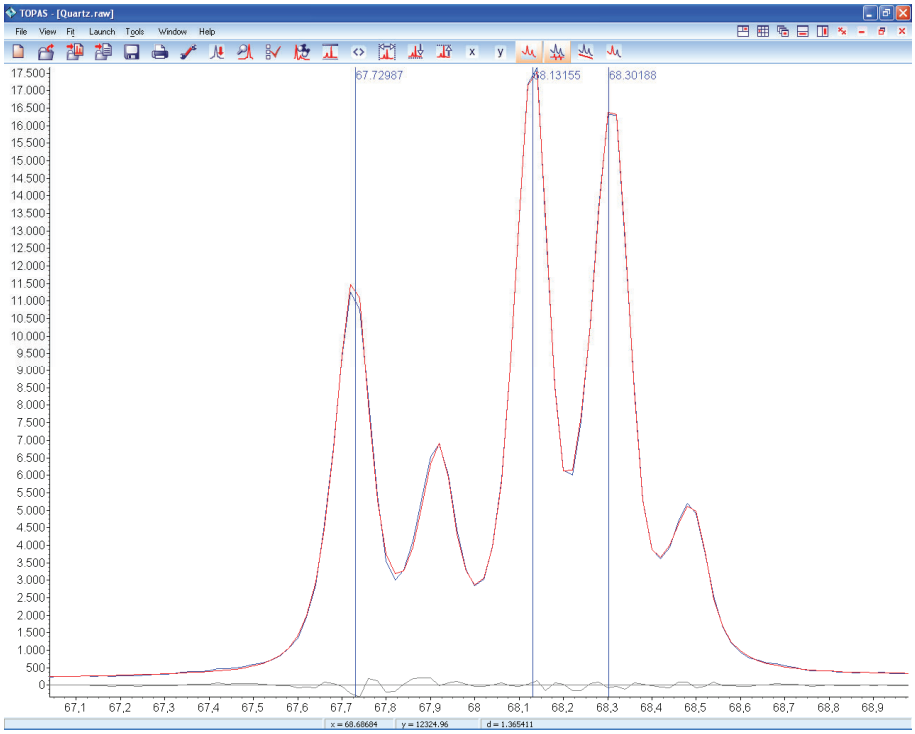
1. Start TOPAS.

2. Import the file QUARTZ.RAW. By default this file is located in C:\TOPAS4\TUTORIAL\MISC.

3. Select SPVII as profile function and insert three peaks at the appropriate 2θ positions.

4. Load the predefined emission profile CUKA2_ANALYT.LAM.

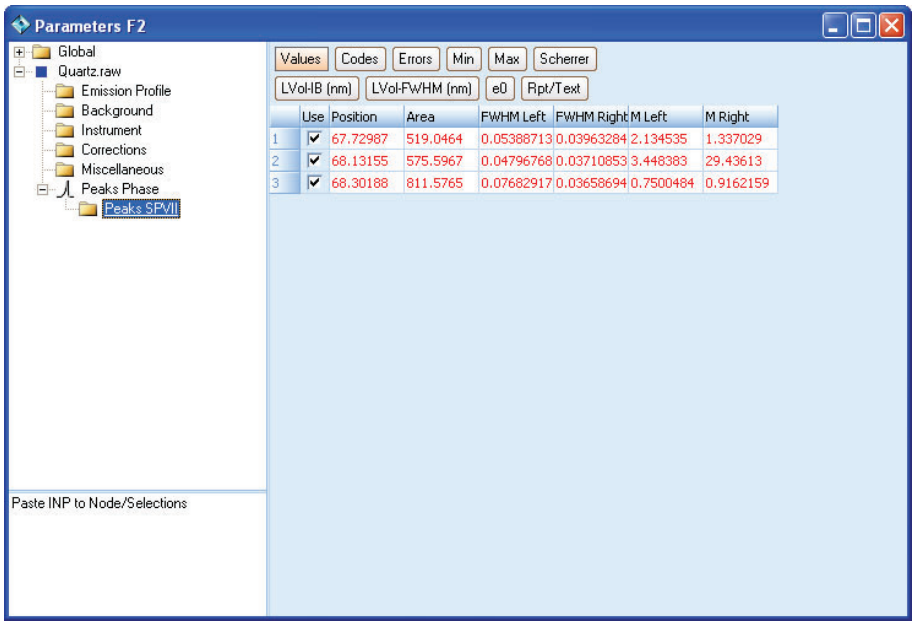
5. Fit the data. After refinement note the excellent match between calculated and observed data. The difference plot as well as the low R_{WP} of about 2.1% indicate a very good refinement.



6. Perform a plausibility control of the refinement results. Check the results for halfwidths, exponents and integrated intensites using the Parameters Window.

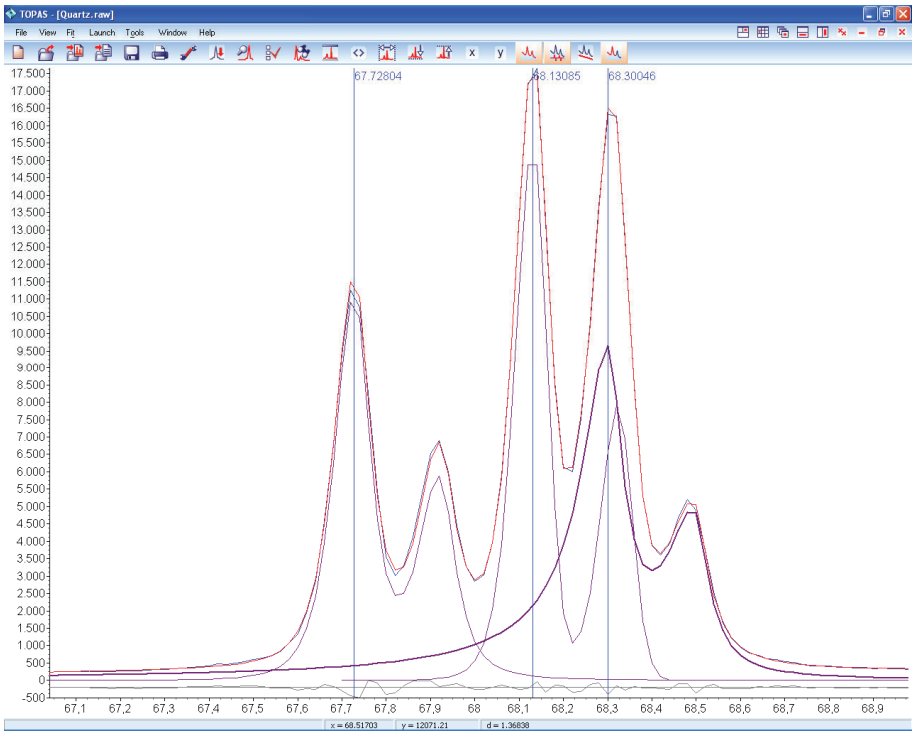
Very inconsistent refinement results for halfwidths and PearsonVII exponents can be seen at the very first sight. A closer review of the refined integrated intensities

shows up a severe refinement error: E.g. the area of the third peak is approximately 50% larger as the area of the second peak, although a visual inspection of the pattern would indicate a reversed ratio.



7. Display all individual peaks and hide the difference curve for more clarity. Move the mouse onto the third peak marker to highlight its calculated intensity. In this representation a severe misfit especially for the third peak shows up directly.

Menu:	**Icon:**	**Shortcut:**	**Result:**
View - Curves - Calculated		n.a.	Displays / hides calculated curves
View - Curves - Background		n.a.	Displays / hides background curves
View - Curves - Difference		n.a.	Displays / hides difference curves
View - Curves - Single Peaks		n.a.	Displays / hides single peaks



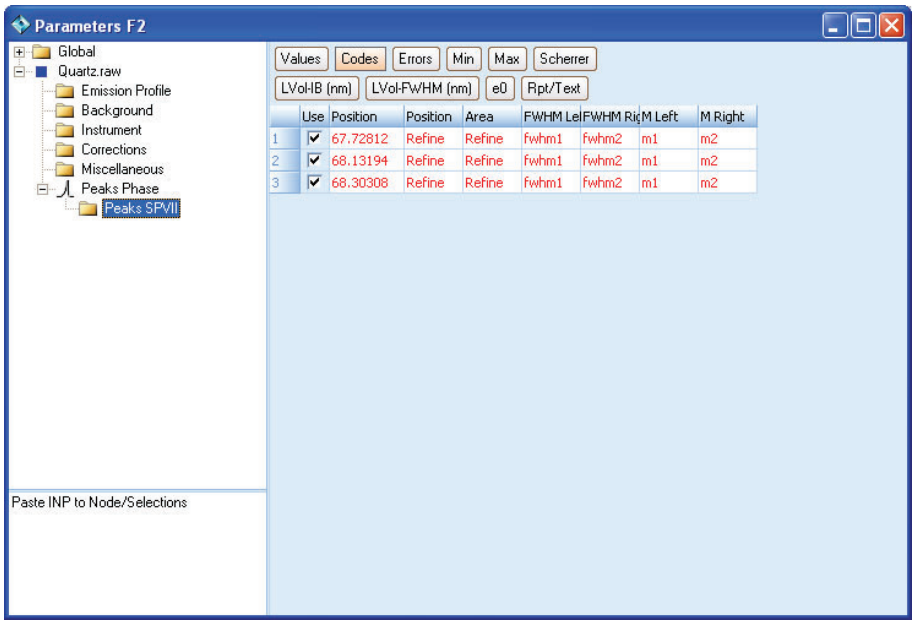
The reason for this misfit are strong corellations particularly between the parameters describing the right wing of the second and the left wing of the third peak. Intensity errors of a magnitude of several 100% are common in cases such as this. For this peak cluster a meaningful decomposition is not possible without the use of constraints.

Part II: Constrained analytical profile fitting:

In analytical profile fitting a successful decomposition of the Quartz Five-Finger-Peak is possible using common peak widths and shapes for all peaks by constraining appropriate profile parameters.

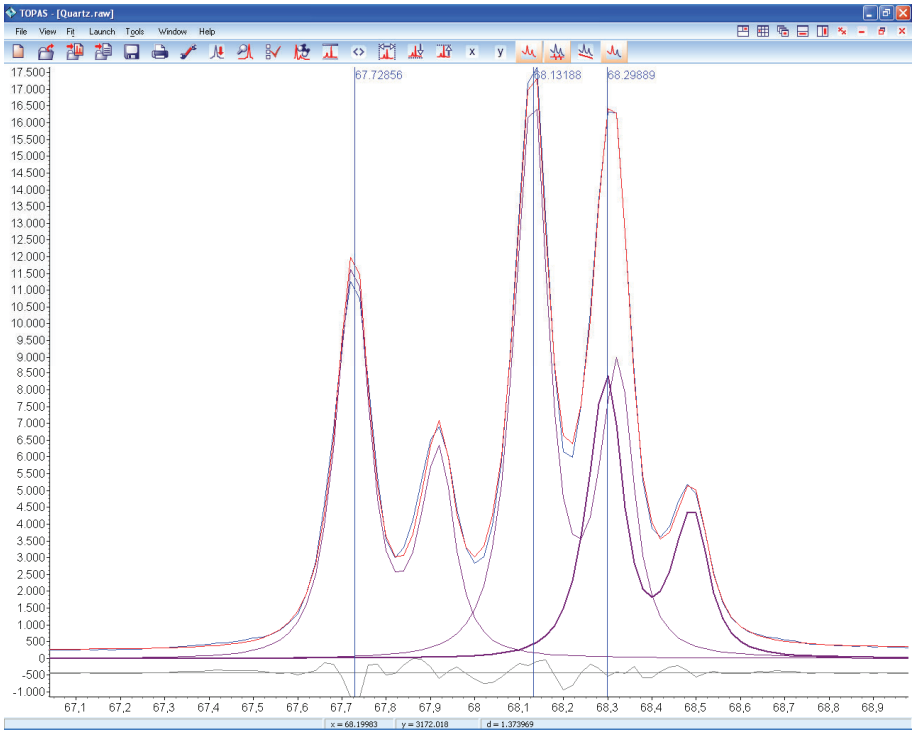
In TOPAS constraints can be introduced into the refinement process either by using "names" or "equations". As in this example the profile parameters shall be constrained to the same value (which is a 1:1 coupling relation), the use of names is sufficient.

8. In the *Parameters Window* focus the SPVII item and select the *Codes* page. To constrain a group of parameters replace their refinement flags by entering any arbitrary text (lower case only!), which must be the same for all parameters within a group. In this example there are 4 parameters groups to be considered: The halfwidths "FWHM left" and "FWHM right" as well as the exponents "M left" and "M right".



As an unconstrained refinement has been carried out before, the values of all parameters are different. Therefore switch to the *Values* page and define identical parameter values within a parameter group, e.g. 0.05 for all halfwidths and 1 for all exponents.

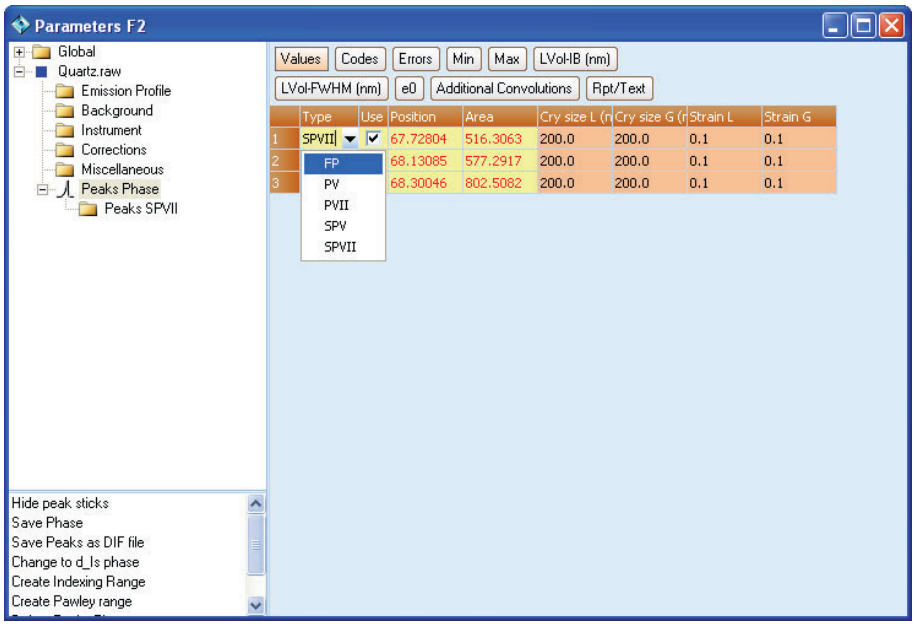
9. Fit the data. Although the R_{WP} of about 4% is significantly worse compared to the unconstrained refinement, the refined profile parameters (particularly intensities) are correct.



Hint!	Constraints are "hard" relationships. As a result a model such as "common width - common shape" does not allow for anisotropic peak shapes, which are common in powder diffractometry.

Part III: Use of Fundamental Parameters:

10. Focus the *Peak Phase* item and select the *Values* page. Change the peak type for all peaks to FP.

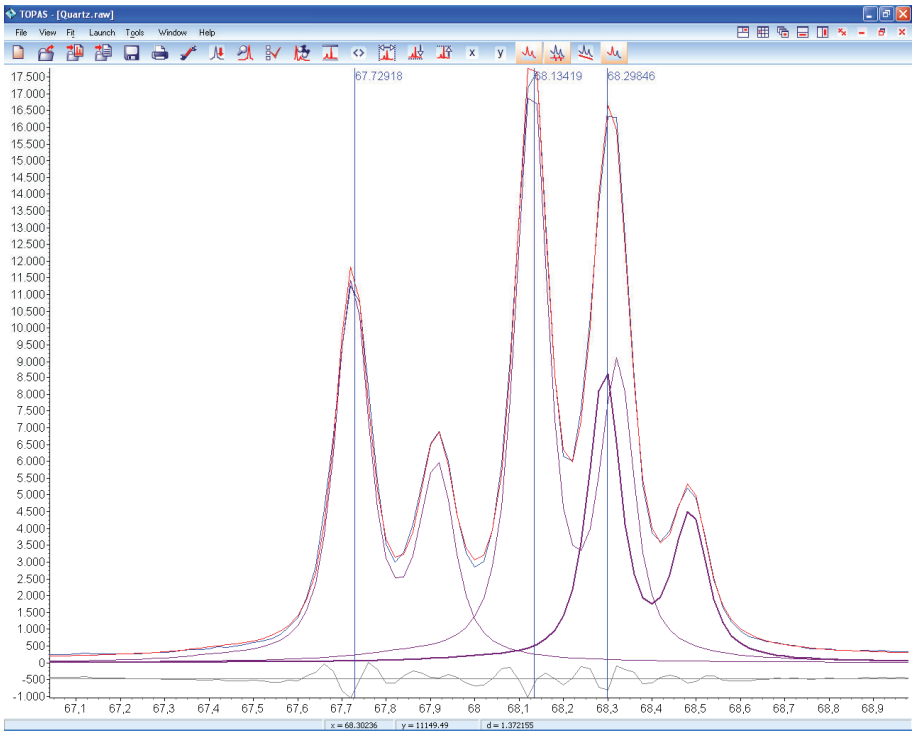


11. Load the predefined emission profile CUKA5.

12. Apply the following instrument settings:

Instrument Parameter:		**Value:**
Goniometer Radius	Primary:	217.5 mm
	Secondary:	217.5 mm
RS	Width:	0.1 mm
FDS	Angle:	1°
Soller Slits	Primary:	4°
	Secondary:	4°

13. Fit the data. You will obtain an R_{WP} of about 3.8%. Although higher than the unconstrained refinement using analytical profile functions, this time the best refinement results possible have been obtained!

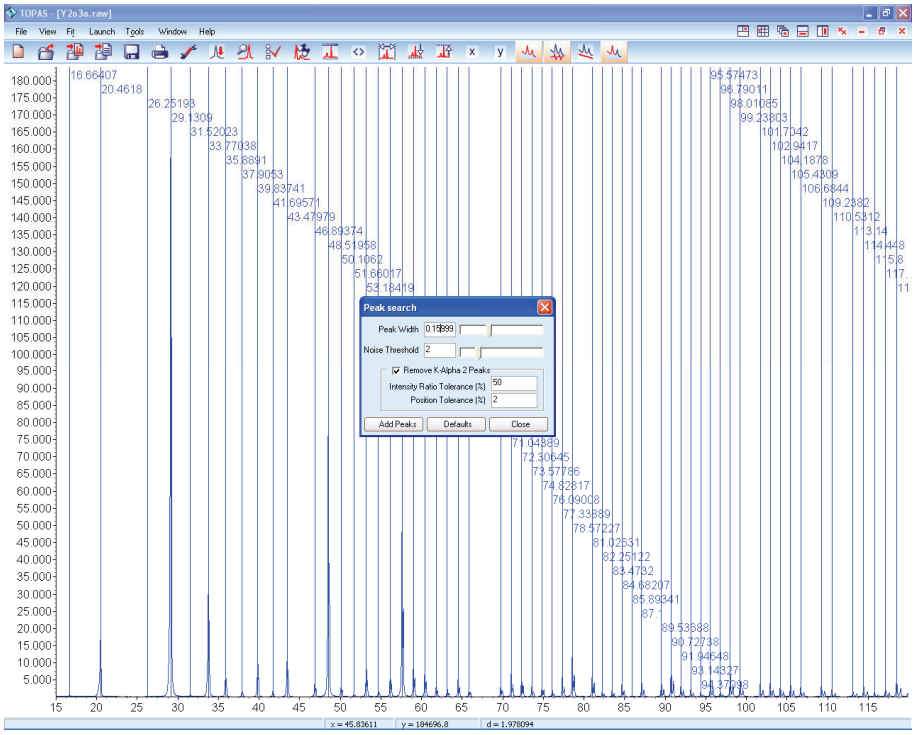


Hint!	The advantage in using Fundamental Parameters instead of constrained analytical functions is based on the fact, that the instrumental contribution to all peaks is the same (which is an intrinsic constraint of the FPA method). In addition, when refining microstructure contributions such as crystallite size for each peak individually, anisotropic peak widths and shapes can be accounted for.

2.1.4 Whole powder pattern fitting

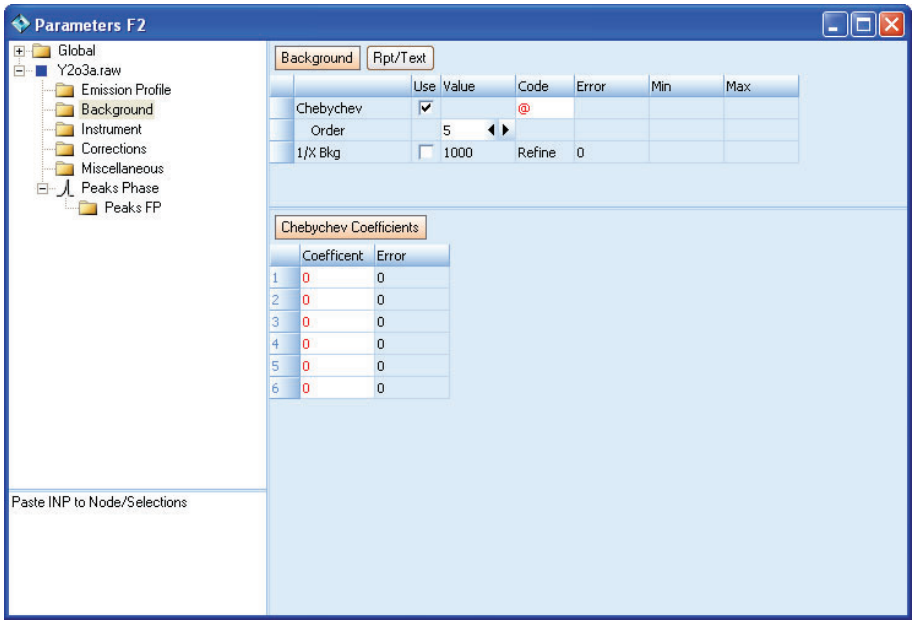
1. Start TOPAS.
2. Importing the file Y2O3A.RAW. By default this file is located in C:\TOPAS4\TUTORIAL\MISC.
3. Select FP as profile function.
4. Perform a peak search using the *Peak Search Dialog*. Define a *Peak Width* of about 0.14 (this value has to correspond approx. to the peak halfwidths) and a *Noise Threshold* of 2. Note the real time preview in the *Scan Window* showing the results of the peak search using peak markers. If you agree with the search result press the *Add Peaks* button. Check for missing or redundant peaks.

Menu:	Icon:	Shortcut:	Result:
View - Search Peaks...		n.a.	Displays the *Peak Search Dialog*



Hint!	It is also possible to import peaks from DIF and UXD files. This feature allows the direct use of PDF data of the ICDD. DIF files can be created e.g. using DIFFRAC*plus* EVA after a search/match operation.

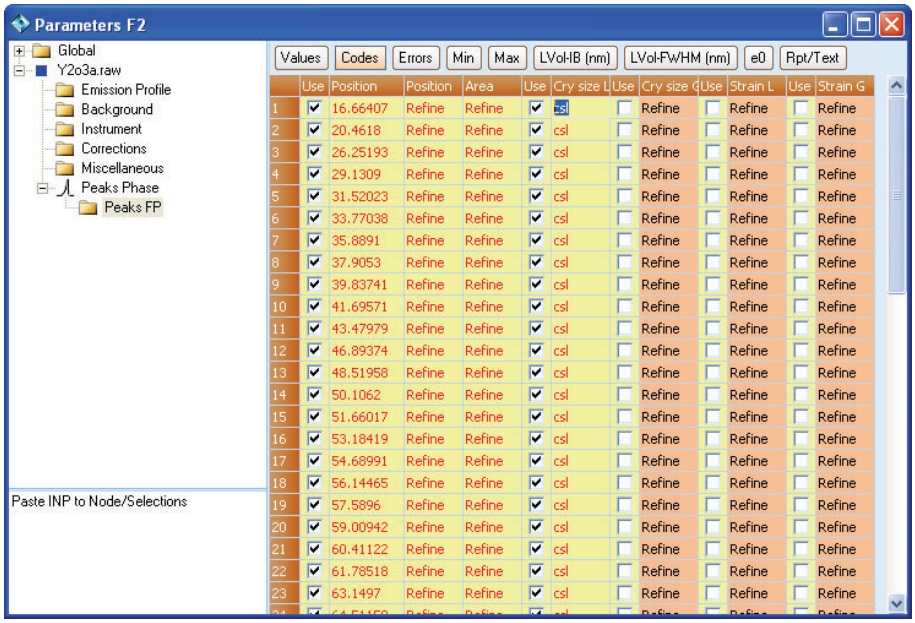
5. Load the predefined emission profile CUKA5. By default this file is located in C:\TOPAS4\LAM.
6. Focus the *Background* item and use a Chebychev Polynomial of 5th order.



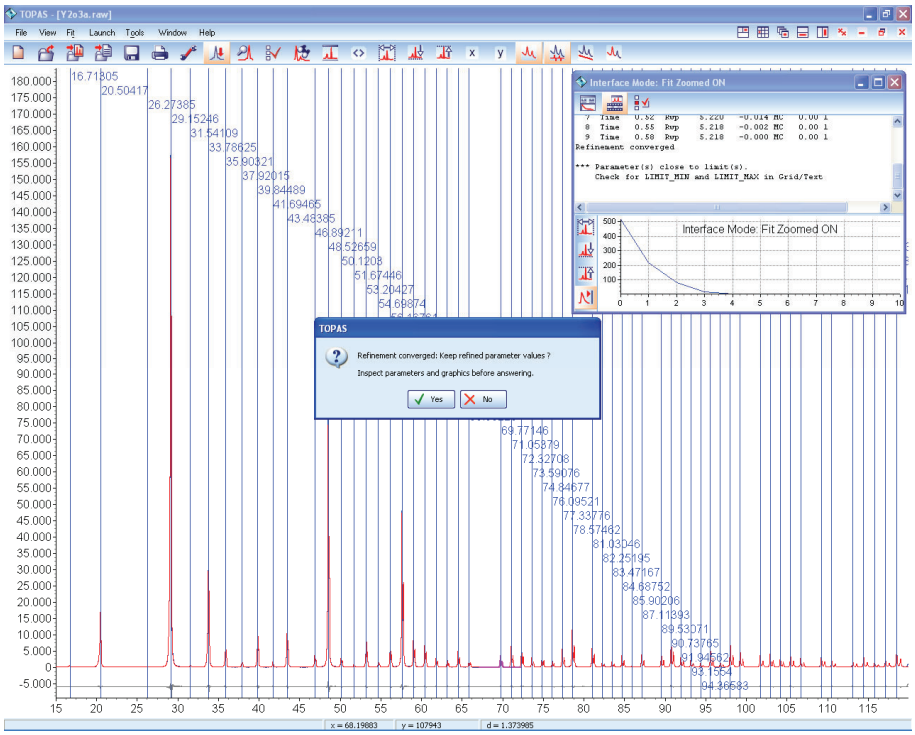
7. Apply the following instrument settings:

Instrument Parameter:		**Value:**
Goniometer Radius	Primary:	173 mm
	Secondary:	173 mm
RS	Width:	0.1 mm
FDS	Angle:	1°
Soller Slits	Primary:	5.1°
	Secondary:	8.6°

8. Refine on an isotropic crystallite size parameter. Focus the *Peak Phase* item, select the *Codes* page and constrain the *Cry Size L* parameter for all peaks to the same value by providing identical parameter codes.



9. Start the refinement.



2.2 Indexing

2.2.1 LSI Indexing

Example files are found in the C:\TOPAS4\TUTORIAL\LSI directory, Table 2-1 provides an overview.

Table 2-1: LSI-Index tutorial examples. R is the ratio of the largest to the smallest lattice-parameter length. Tutorial files Ex1 to Ex12 are discussed in Coelho (2003).

Example	Symmetry	Lattice parameters (Å) / (°)						Vol (Å^3)	R
Ex1 [1)]	Tetragonal	a =	11.190			c =	9.483	1187	1.17
Ex2 [2)]	Rhombohedral	a =	81.306			c =	73.064	420727	1.11
Ex3 [1)]	Orthorhombic	a =	11.333	b =	11.032	c =	9.236	1154	1.23
Ex4 [1)]	Monoclinic	a =	9.188	b =	12.472	c =	6.242	684	2.00
				β =	106.9				
Ex5 [1)]	Monoclinic	a =	10.222	b =	6.497	c =	8.808	583	1.57
				β =	94.7				
Ex6 [3)]	Monoclinic	a =	5.025	b =	5.850	c =	5.065	149	1.16
				β =	91.5				
Ex7 [4)]	Monoclinic	a =	8.213	b =	9.793	c =	9.795	785	1.19
				β =	94.8				
Ex8 [1)]	Triclinic	a =	5.118	b =	5.512	c =	7.034	182	1.37
		α =	73.7	β =	73.9	γ =	90.2		
Ex9 [5)]	Triclinic	a =	7.086	b =	8.788	c =	17.871	984	2.52
		α =	63.0	β =	87.0	γ =	94.1		
Ex10 [6)]	Triclinic	a =	9.920	b =	14.510	c =	9.136	1229	1.59
		α =	90.5	β =	111.7	γ =	90.0		
Ex11 [7)]	Triclinic	a =	12.063	b =	41.714	c =	5.459	2314	7.64
		α =	73.4	β =	100.4	γ =	118.3		
Ex12 [7)]	Triclinic	a =	12.005	b =	51.902	c =	5.445	2879	9.53
		α =	73.8	β =	100.3	γ =	117.7		
PbSO4 [8)]	Orthorhombic	a =	6.959	b =	8.482	c =	5.397	319	1.57
Cime [9)]	Monoclinic	a =	10.395	b =	18.820	c =	6.826	1281	2.76
				β =	106.4				
TPP [10)]	Rhombohedral	a =	37.766			c =	5.729	7055	6.59

[1)] Morris et al. (1980); [2)] Van Dreele et al. (2000); [3)] Swanson et al. (1963);
[4)] Toraya & Yamazaki (2002); [5)] Morris et al. (1979);[6)] Dinnebier et al. (2002);
[7)] Van Langevelde et al. (2001); [8)] Hill (1992); [9)] Cernik et al. (1991);

[10)] Hernandez et al. (2002)

2.2.1.1 Indexing of Ex2 (T3R3 human insulin-zinc complex)

A typical LSI indexing session comprises the following three steps:

I. Peak finding and peak profiling

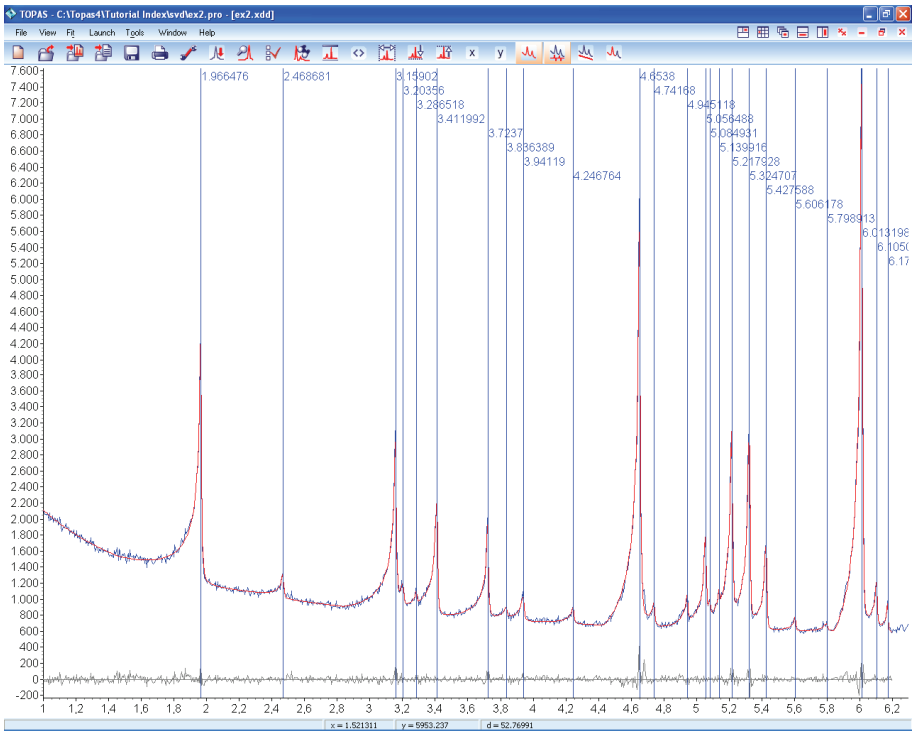
II. Indexing

III. Single or multiple Pawley / Le Bail refinements (see also section 2.3)

Step 1: Peak finding and peak profiling:

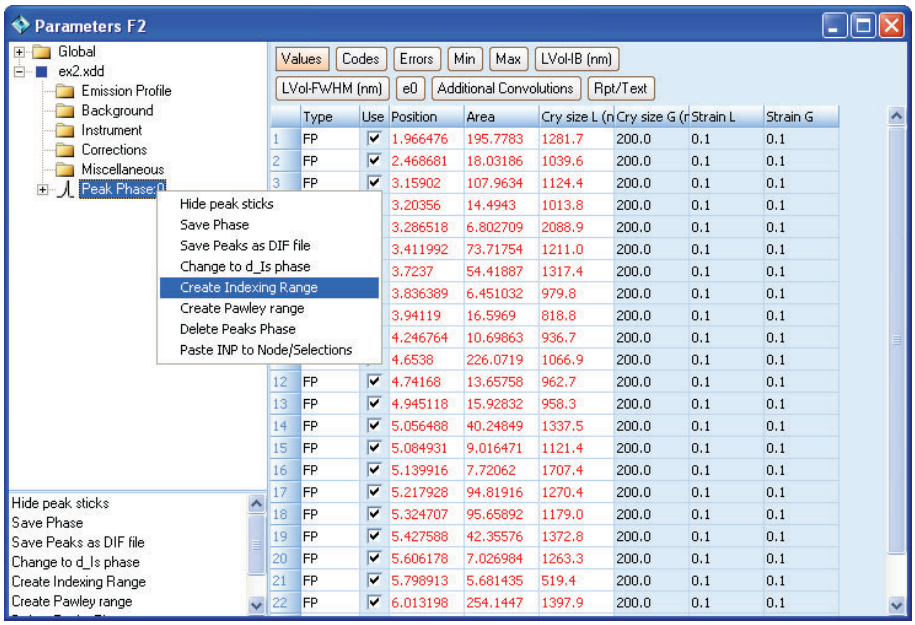
1. Start TOPAS and load the raw data by importing the file EX2.XDD into your document. By default this file is located in C:\TOPAS4\TUTORIAL\LSI.

2. Perform a single line fit using the first about 24 peaks. Note: λ = 1.4011Å. Peak type *FP* with the *Cry Size L* and *Simple Axial Model* parameters refined will yield good results.

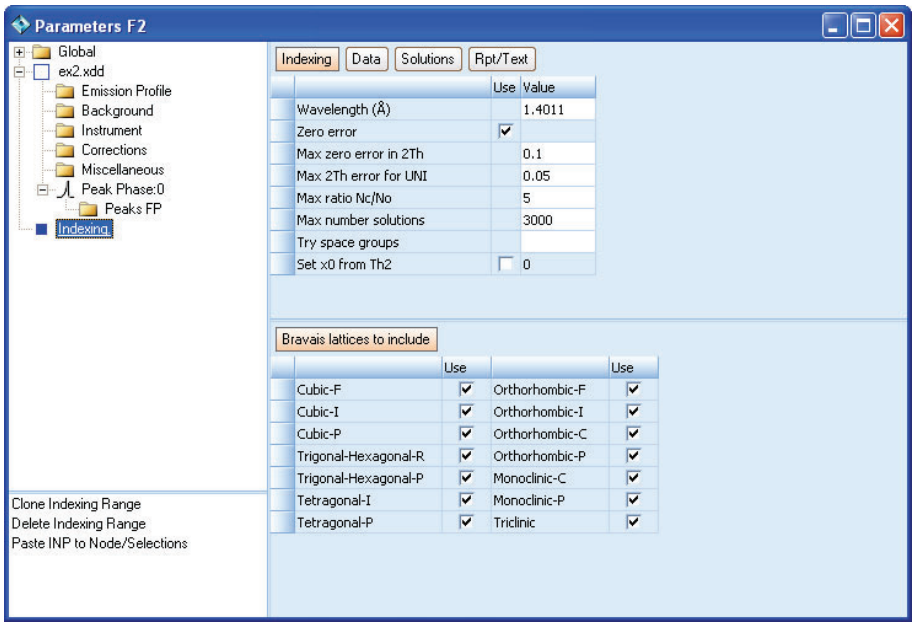


Step 2: Indexing

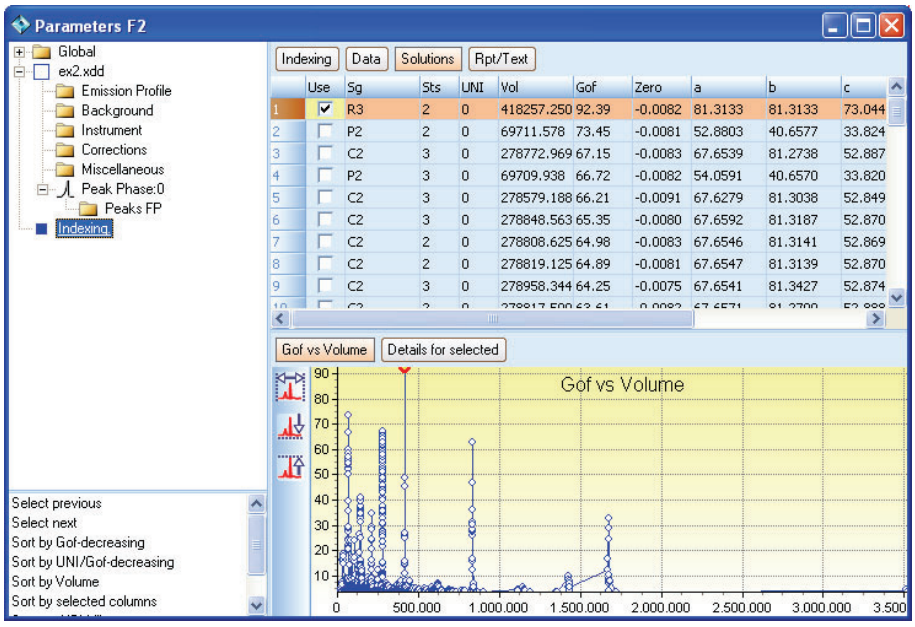
3. Create a new indexing range e.g. using the *Global* item shortcut menu. The wavelength as well as refined peak positions and intensities are automatically placed into the indexing range.



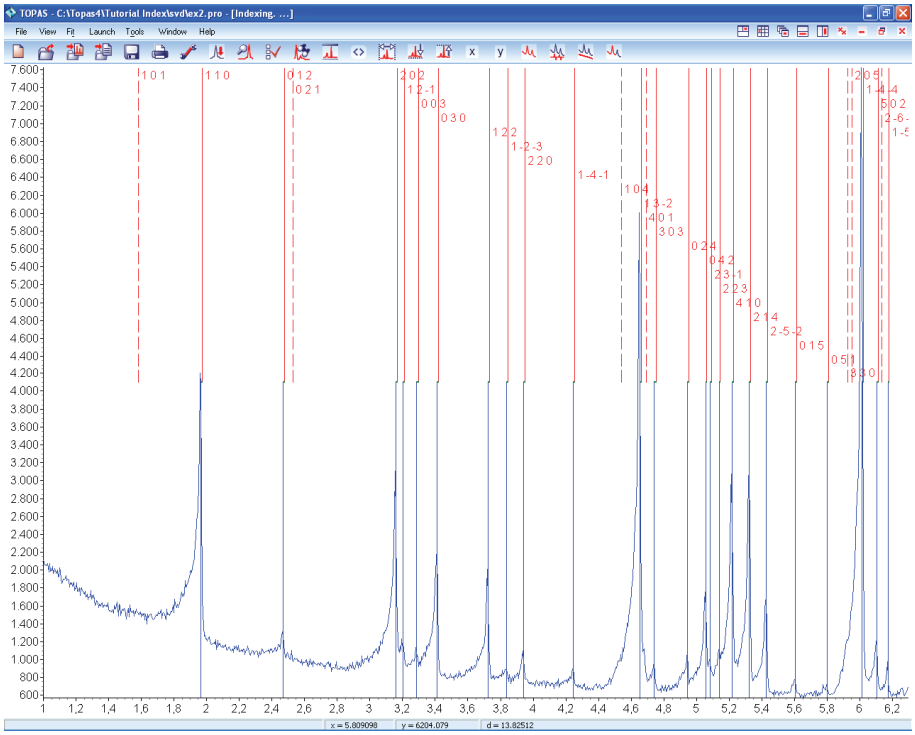
4. Select the *Indexing* range and unselect the "ex2.xdd" range. Unselect all peaks or delete the *Peaks Phase*.
5. Select the Bravais lattices to be included in the indexing run. Default indexing parameters are appropriate for this example.



6. To start the indexing run switch to the *Fit Window* and click on the *Run* button.
7. Indexing details are provided in the *Solutions* page. The correct solution is trigonal R3, a = 81.301Å, c = 73.052Å, Vol = 418173Å^3.

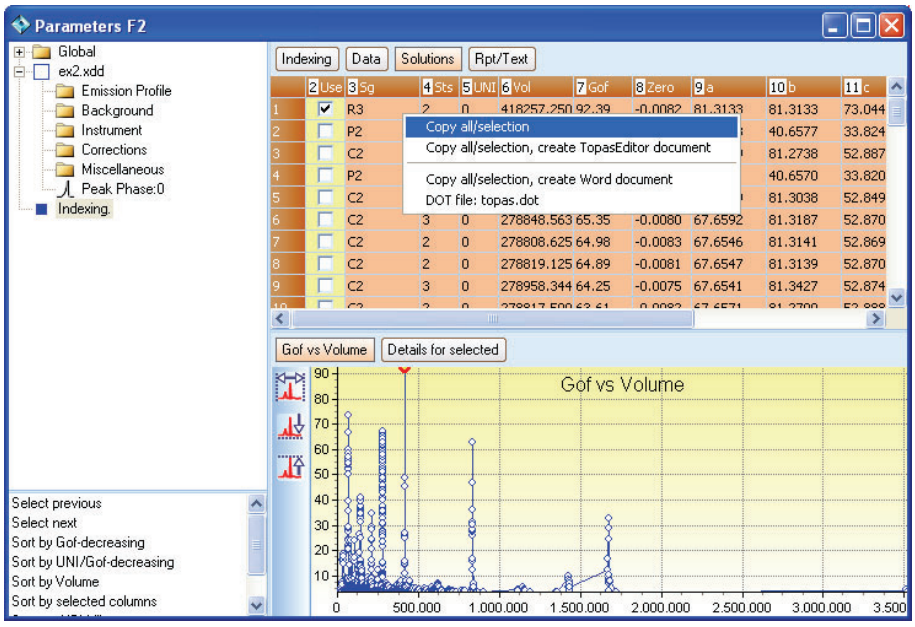


For each selected solution observed and calculated peak positions are shown in the *Scan Window*. Additionally, with the "ex2.xdd" range selected as well, the raw data can be overlaid with or without the single peak fit results.



Step 3: Single or multiple Pawley / Le Bail refinements

8. In the *Solutions* page select all solutions you would like to refine, and copy the indexing details into the clipboard using the data grid shortcut menu.



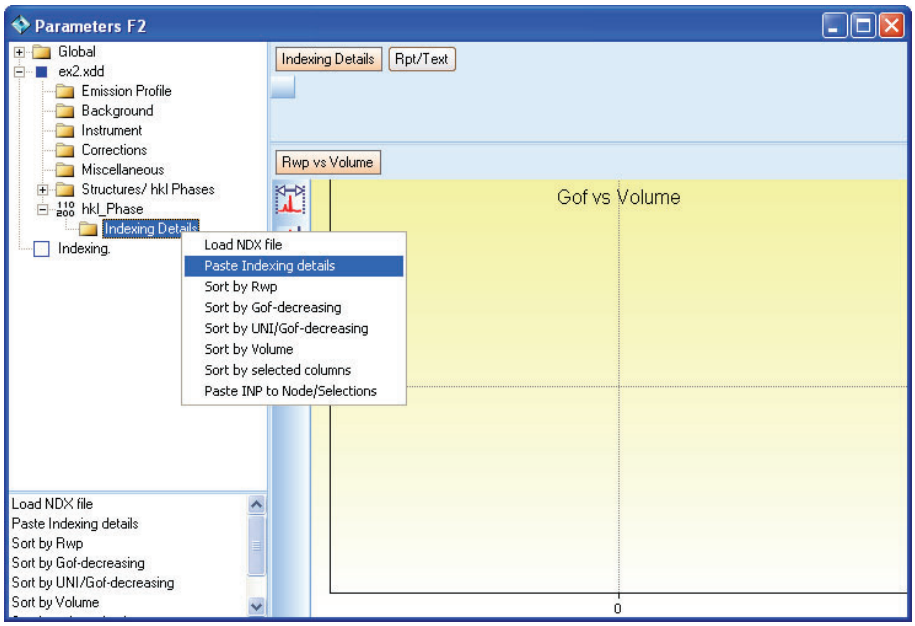
9. Select the "ex2.xdd" range and unselect the *Indexing* range.

10. Insert a new hkl_I phase. Focus the "ex2.xdd" range and select *Add hkl phase*.

11. To account for a zero point error focus the *Corrections* item, check the zero point error and set its code to "Refine".

12. To perform Le Bail instead of Pawley refinements focus the *hkl_Phase* item and check *Le Bail*.

13. Expand the *hkl_Phase* item and focus the *Indexing Details* item. Insert the indexing details by selecting *Paste Indexing details* in the shortcut menu.



14. Switch to the *Fit Window* and click on the *Run* button to automatically refine all selected indexing solutions.

2.2.1.2 Tips and Tricks

Indexing of powder data is a complex problem, which does not permit solutions to be identified with certainty. TOPAS reports possible indexing solutions in the form of complete or partial unit cells. Even if mathematically and physically correct, they will not necessarily be in their simplest or most symmetrical settings. The quality of the indexing solutions will depend on various factors including d-spacing accuracy and completeness, which is typically affected by accidental and systematic peak overlaps as well as peak detection limits. Any trial cells reported can therefore only be suggestions until they are confirmed by structure determination.

In the following a couple of tips and tricks are provided, some of which have been adapted from discussions found on www.ccp14.ac.uk with contributions from Robin Shirley, Armel Le Bail and others.

1. Use 20-25 lines. Too less or too many lines may result into problems

Data need to have 1 to 6 degrees of freedom to be able to define a cubic to triclinic cell, respectively. Note, that the number of required degrees of freedom is not equivalent to the number of required d-spacings:

d-spacings do not contribute any degrees of freedom to define a cell, if they

- belong to the same zone
- are higher order reflections
- are impurity reflections

Using 20 to 25 d-spacings will help to minimize such problems. Furthermore it is more likely to obtain a decent least-squares refinement and to be able to distinguish pseudo-solutions.

Including too many d-spacings is another probable cause of failure. Some of the problems caused by very low d-spacings are:

- The number of calculated lines increases dramatically and thus the maximum ratio of the number of calculated to observed lines, "Max ration Nc/No", will need to be increased
- The low d-spacings are probably inaccurate due to peak overlap at the high angles they are observed at

2. Use the goodness-of-fit versus volume plot to identify pseudo-solutions

Frequently solutions will be found with fractional or multiple volumes of the correct cell: 1/2V, 2/3V, V, 2V, 3V, 4V, ... There are two major reasons for that:

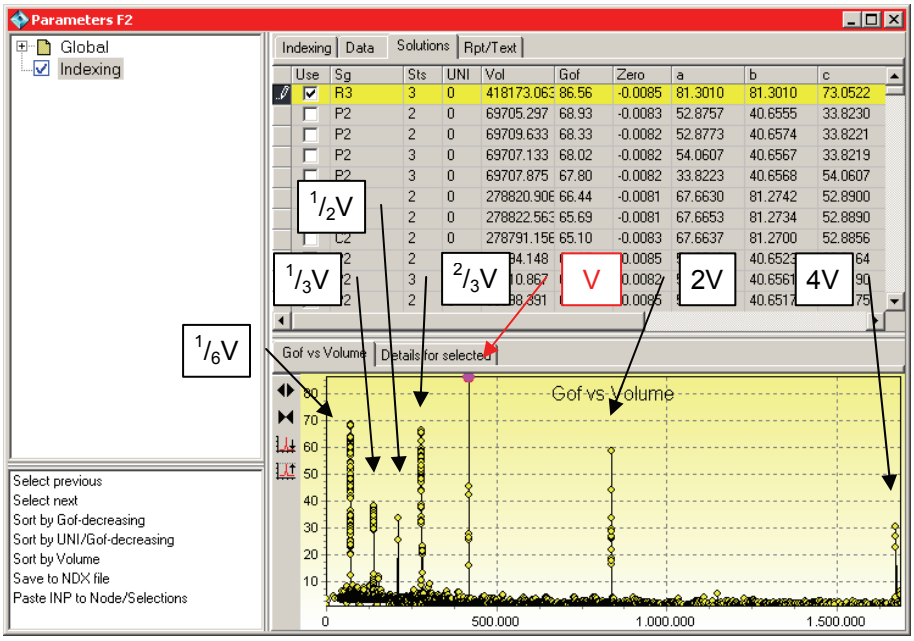
Firstly it is always possible to index d-spacings corresponding to a high symmetry cell with a A, B, C, I, F or R Bravais lattice by a smaller symmetry P cell with smaller volume, and vice versa. Typical examples are:

- A rhombohedral cell can always be described by a monoclinic C-centered cell with 2/3 volume
- A C-centered monoclinic cell is equivalent to a triclinic cell with 1/2 volume

- A hexagonal or trigonal cell can be indexed by an orthorhombic cell with a doubled volume

etc.

Secondly, multiplied volumes are often the result of multiplied lattice parameters.



It is also recommended to test a/b, a/c, etc. ratios in order to check for $\sqrt{2}$ = 1.414 or $\sqrt{3}$ = 1.732 values, which may also indicate pseudo-solutions.

3. Avoid testing all Bravais lattices simultaneously

Testing all Bravais lattices at once may obscure the correct solution due to possible triclinic and monoclinic approximations to actually higher symmetric cells. Identification of higher symmetric lattices is often easier if monoclinic and triclinic lattices are treated independently.

4. Use intensity weighting if impurity peaks might be present

Intensity weighting may help to overcome difficulties due to low intensity impurity peaks. As a last resort consider to run different sets of d-spacings with questionable / low intensity d-spacings excluded.

5. Play with the "Good" and "Max ration Nc/No"options

"Good" indicates that the corresponding d-spacing is not an impurity line. A single use of good on a high d-spacing decreases the number of possible solutions and hence speeds up the indexing process.

- "Max ration Nc/No" determines the maximum ratio of the number of calculated to observed lines:

- Increasing the default value may help for indexing of extreme dominant zone cases or of very large cells, where the number of calculated versus observed d-spacings may become very large (e.g. for proteins)
- Decreasing the default value may help to identify solutions otherwise obscured by low symmetry / high volume solutions

2.2.2 LP-Search

Example files are found in the C:\TOPAS4\TUTORIAL\LP-SEARCH directory, Table 2-2 provides an overview.

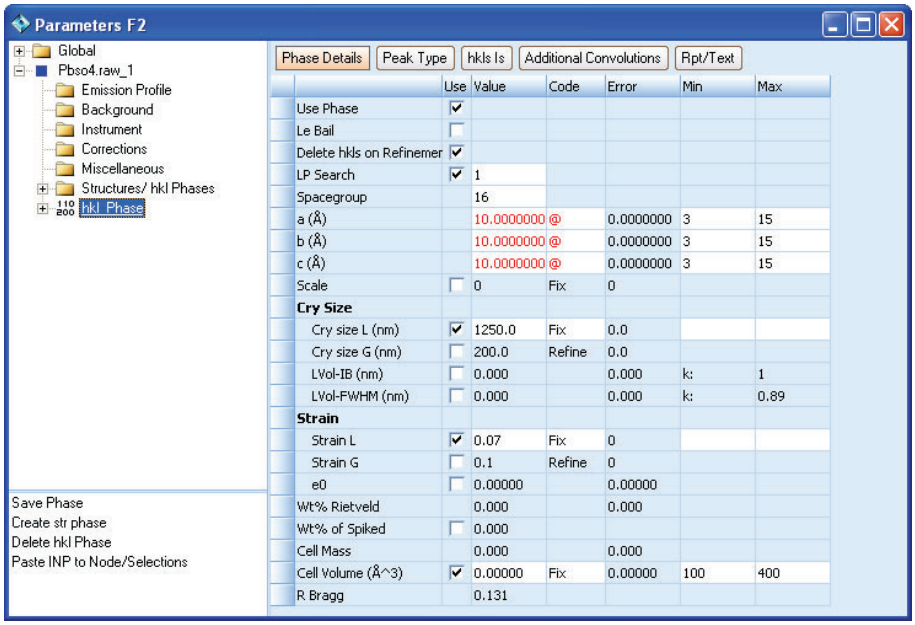
Table 2-2: LP-Search tutorial examples. R is the ratio of the largest to the smallest lattice-parameter length.

Example	Symmetry	Lattice parameters (Å) / (°)						Vol (Å^3)	R
PbSO4 [1)]	Orthorhombic	a =	6.959	b =	8.482	c =	5.397	319	1.57
Captopril [2)]	Orthorhombic	a =	8.811	b =	17.984	c =	6.837	1082	2.63
Cime [3)]	Monoclinic	a =	10.395	b =	18.820	c =	6.826	1281	2.76
				β =	106.4				
Zopiclone Dihydrate [2)]	Monoclinic	a =	16.374	b =	7.030	c =	17.185	1926	2.44
				β =	108.6				

[1)] Hill (1992), [2)] Florence (2002), [3)] Cernik et al. (1991)

2.2.2.1 General guidelines

The LP-Search indexing procedure is a Whole Powder Pattern Decomposition method (section 2.3), and is therefore found as an option in the *Phase Details* data grid of the *hkl Phase* item: *LP Search*.



If checked LP-Search indexing will search the correct lattice parameters starting from dummy values.

LP-Search will test a single crystal system, which is defined by the space group provided. Typically the space group will correspond to one that is of lowest symmetry with the particular crystal system tested, i.e. for triclinic put space group number "1", for monoclinic put "3", for orthorhombic put "16", and so forth.

To limit parameter space it is mandatory to provide Min and Max values for lattice parameters and the cell volume. The upper limits for lattice parameters and the cell volume should be kept as small as possible to avoid finding of doubled / tripled / ... lattice parameters. The d-value of the first reflection often allows to get an approximate idea of the maximum possible lattice parameters dimensions.

The determination of background and peak shape parameters is complicated by the fact, that with random lattice parameters typically not all calculated peaks will lock in, resulting in significant misfits of both background and peak shape.

While the background should be determined as good as possible, the peak shape is uncritical for the indexing success, as LP-Search is peak shape independent. Nevertheless it is recommended to also achieve a good peak shape fit, as this is extremely helpful to identify the correct solution by visual inspection of the fit.

There are two possibilities to determine background and peak shape parameters:

1. Perform a single line fit.

   It is recommended to use the FP peak type with angle dependent profile parameters (e.g. size-strain parameters constrained to the same value), as they can be directly applied to the hkl_Is phase. Fix all profile and background parameters before running LP-Search to minimize parameters space.

   Note that single line fitting is not available in TOPAS R. Users of TOPAS R therefore need to perform the next procedure.

2. Adjust background and peak shape iteratively while LP-Search is running.

   Set the required background and peak shape parameters to "Refine", and run LP-Search. Use as less parameters as possible to minimize parameters space. Stop the refinement, if a good fit has been obtained, and use the refined parameters values as new starting values. Repeat this until satisfactory background and peak shape parameters have been obtained and keep them fixed for the final LP-Search run.

2.2.2.2 Indexing with LP-Search

A typical LP-Search indexing procedure comprises the following steps:

1. Determine background and peak shape parameters as described in section 2.2.2.1.

2. Add a hkl_Is phase

3. Enter a space group and dummy starting lattice parameters

4. Provide *Min* and *Max* values for lattice parameters and cell volume

5. Check the *LP Search* checkbox

6. In the *Refinement Options Dialog* (*Fit Window*) set *Continue After Convergence* on and then run.

2.3 Whole powder pattern decomposition

2.3.1 Pawley fitting

As example X-ray data of the triclinic structure $AlVO_4$ will be used, recorded using a D5000 diffractometer with Ge primary monochromator in capillary mode using Copper radiation. Profile fitting will be performed using the TCHZ pseudo-Voigt function.

1. Start TOPAS.
2. Load the raw data by importing the file ALVO4.RAW into your document. By default this file is located in C:\TOPAS4\TUTORIAL\ALVO4.

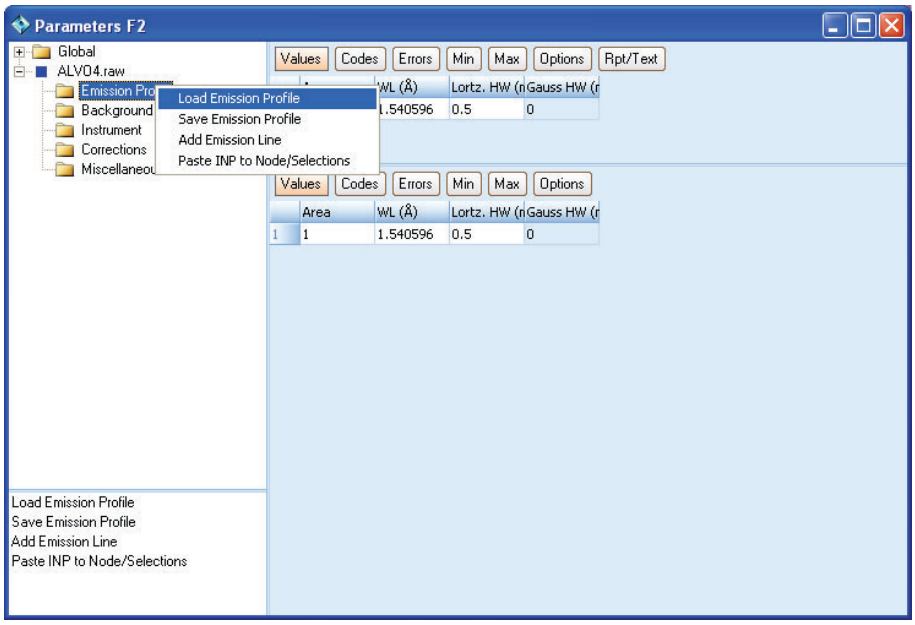
Menu:	Icon:	Shortcut:	Result:
File - Import Data File(s)...		n.a.	Imports measurement data

3. Switch to the *Parameters Window* and define the refinement model.

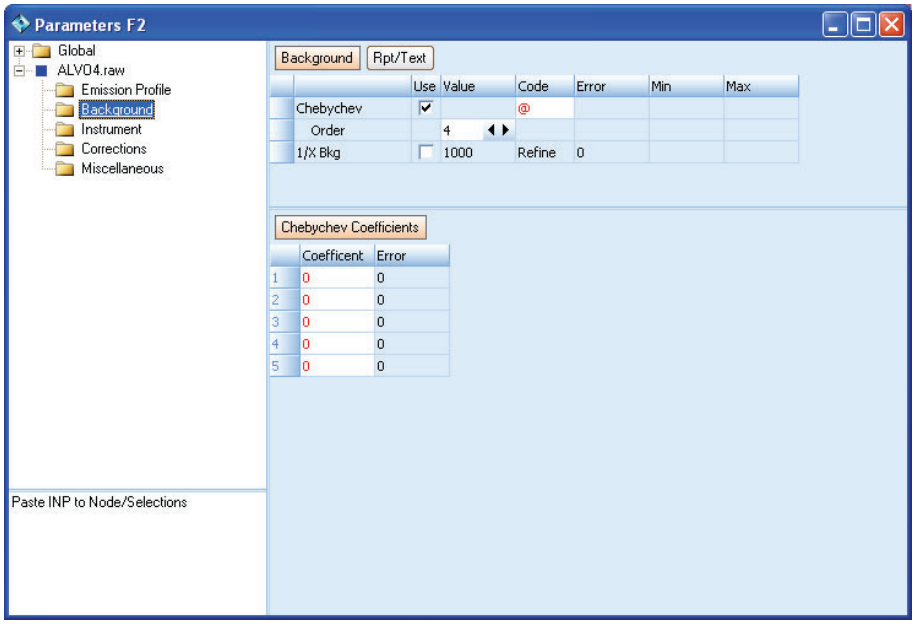
Menu:	Icon:	Shortcut:	Result:
View - Parameters Window		F2	Displays or hides the *Parameters Window*

In the *Parameters Window* expand the range item of ALVO4.RAW and perform the following tasks:

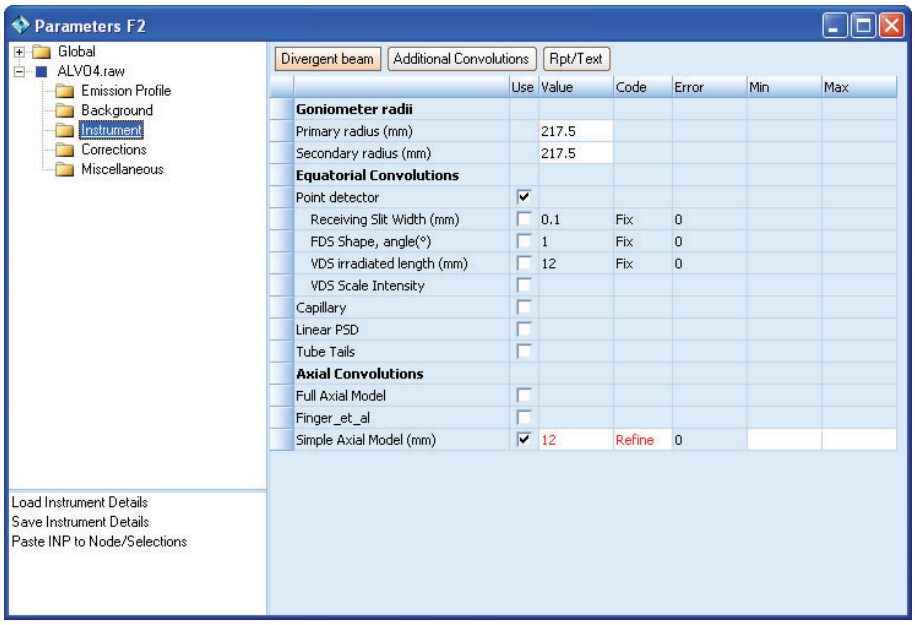
- Focus the *Emission Profile* item and load the predefined emission profile CUKA1.LAM. By default this file is located in C:\TOPAS4\LAM.



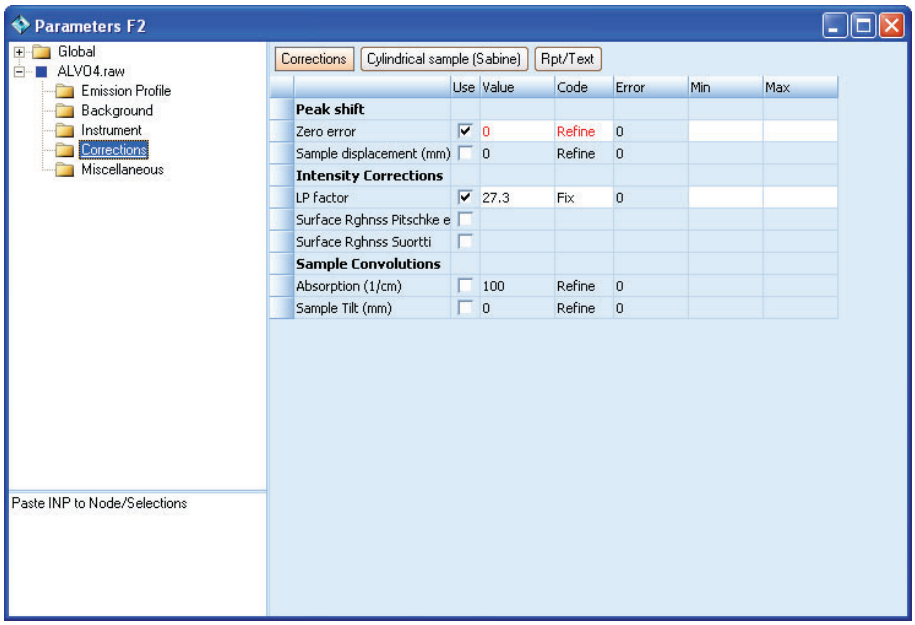
- Focus the *Background* item and use a Chebychev Polynomial of 4th order.



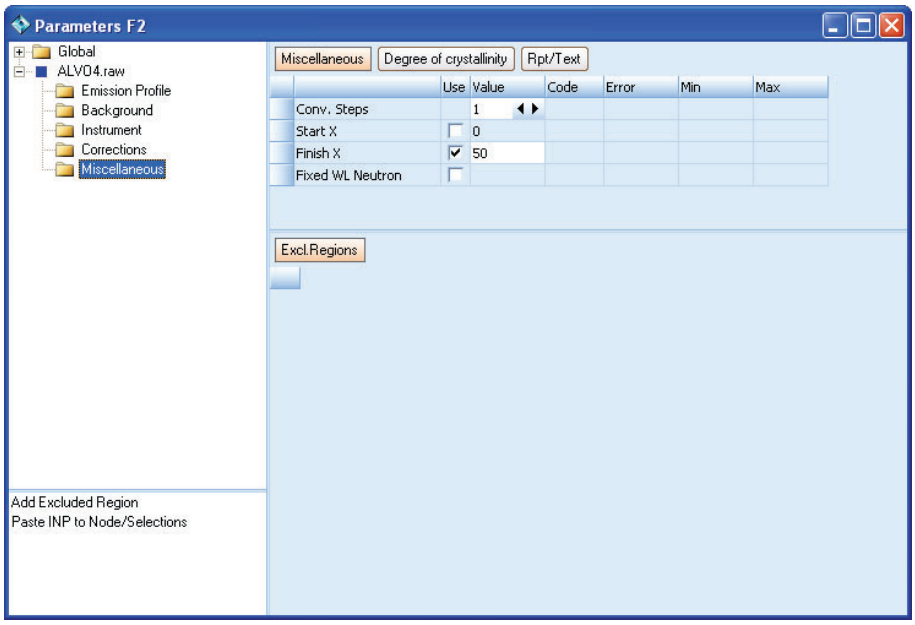
- Focus the *Instrument* item. To describe peak asymmetry, set the instrument radius to 217.5 mm, select the *Simple Axial Model* and set its parameter codes to "Refine".



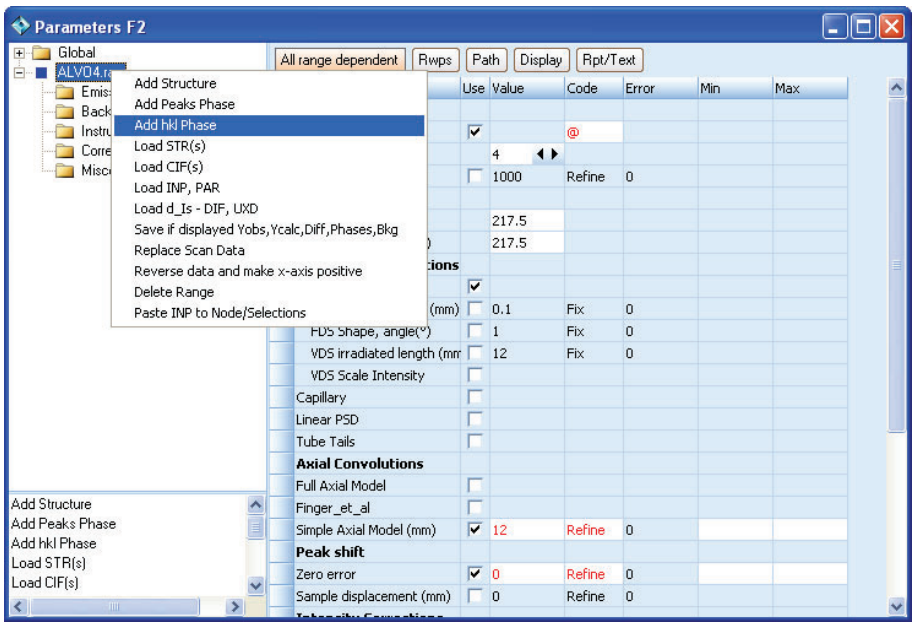
- Focus the *Corrections* item. Check the zero point error and set its code to "Refine". In addition we have to account for the polarization effects coming from the Ge primary monochromator. Therefore check LP factor as well and set the monochromator angle to 27.3° 2θ.



- Focus the *Miscellaneous* item and set *Finish X* to about 50° 2θ.

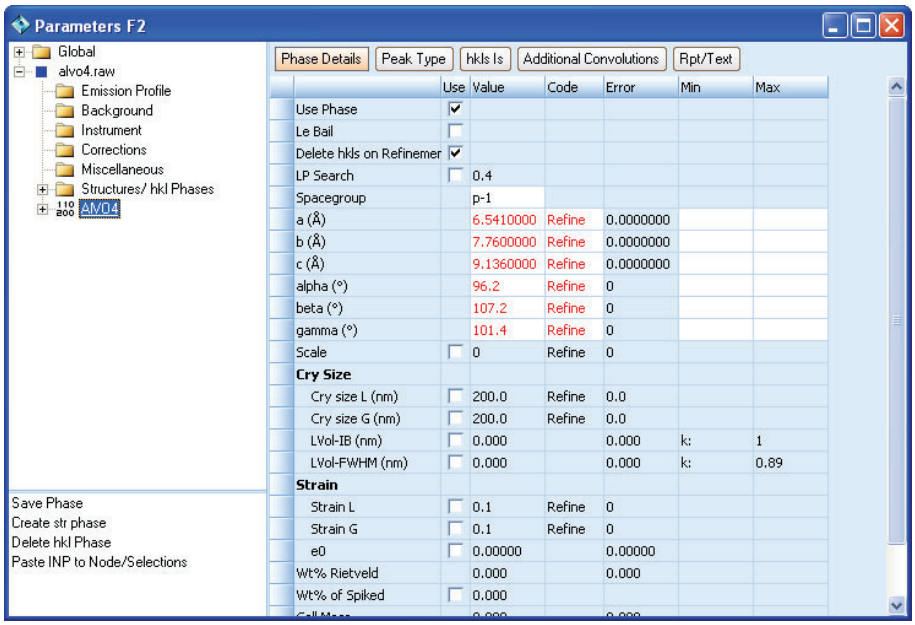


- Insert a new hkl_I phase. Focus the range item for Alvo4.raw and select *Add hkl phase*.

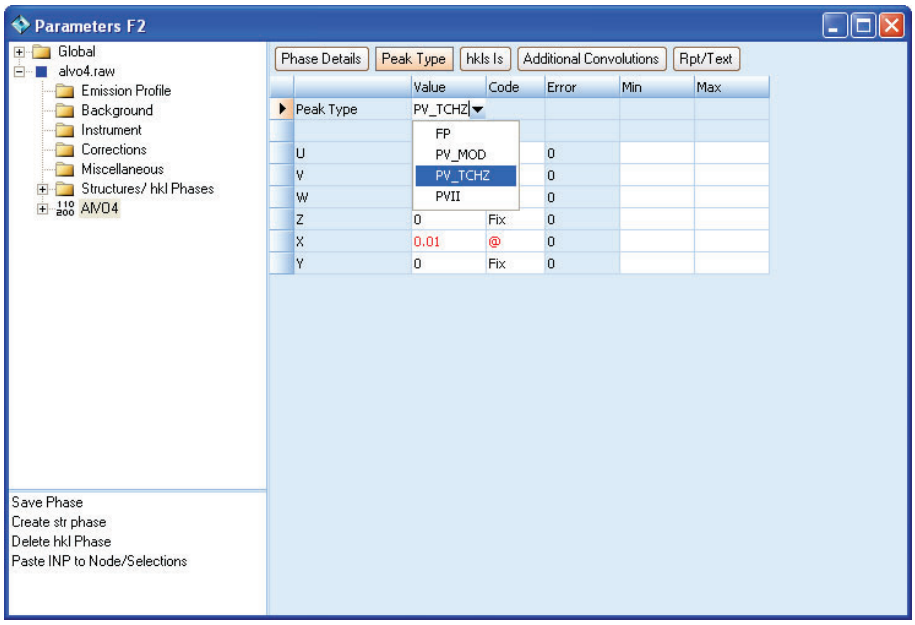


- Focus the *hkl_Phase* item. Input the crystallographic data given below in the *Phase Details* page and change all lattice parameter codes to "Refine". As in this example no instrument function is used, set the *Cry Size L* checkbox to no use.

Crystallographic Data for $AlVO_4$:		
Space group		P-1
Cell parameters	a (Å)	6.541
	b (Å)	7.760
	c (Å)	9.136
	alpha	96.2
	beta	107.2
	gamma	101.4



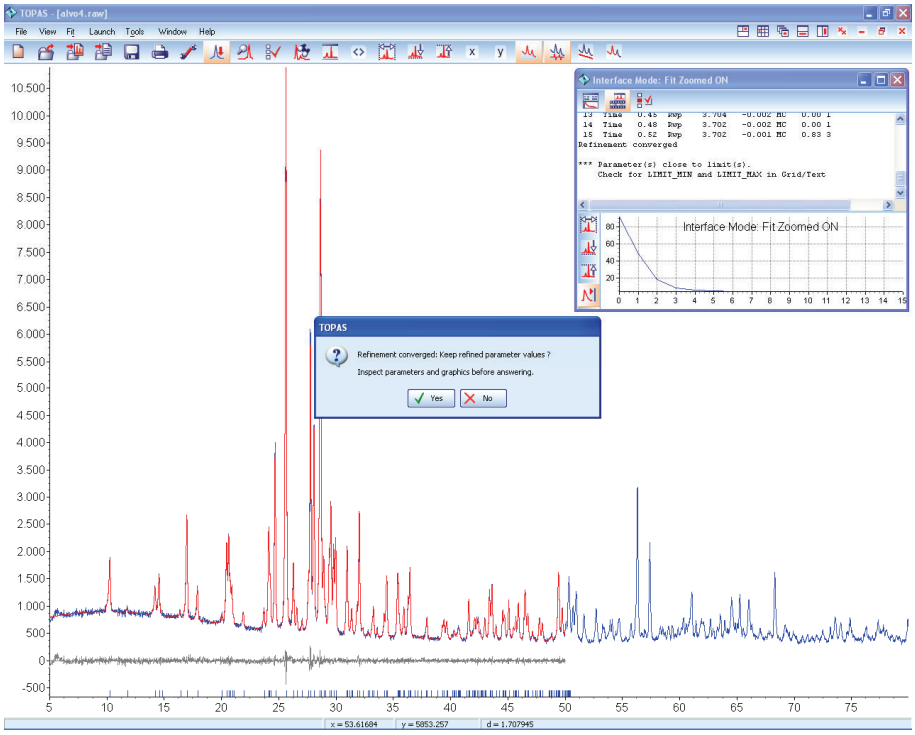
- Switch to the *Peak Type* page and select the TCHZ_PV function.



4. To have errors calculated, check the menu item *Calculate Errors* in the *Fit* menu.
5. To start the refinement switch to the *Fit Window* and click on the *Run* button.

Menu:	Icon:	ShortCut:	Result:
Fit – Fit Window		F5	Displays or hides the *Fit Window*
n.a.		F6	Runs the refinement

In the *Scan Window* a calculated pattern based on the start values is shown in red color. The difference to the observed data is represented by the gray curve. After fitting a dialog informs you, if the refinement has converged or not. Note that this dialog is modeless and allows inspection of the refinement results before accepting any changes.



6. The refinement results can be inspected in the *Parameters Window*.
7. Save your work.

Menu:	Icon:	Shortcut:	Result:
File – Save		n.a.	Saves the current work in a document (*.PRO)
File – Export INP file...	n.a.	n.a.	Exports the current work as an input file (*.INP)

Hint!	TOPAS documents (PRO files) contain the measurement data, model and refinement parameters, evaluation results, as well as any user-defined GUI settings. Therefore you can load and resume your fit session anytime at any stage or use the document as a template for different data. Exporting an input file using the Menu *File - Export INP File...* instead allows the use of your refinement model e.g. in an automated environment (using TC) or in *Launch Mode*. Measurement data and user-defined GUI settings are not saved within an INP file.

Comments and ideas for further working:

- Repeat the refinement using different 2θ regions and different orders for the Chebychev polynomial. Note the strong correlation of intensities with the polynomial coefficients in particular at high angles for Pawley refinement.
- By default hkls are automatically deleted when the refinement is started (*Delete hkls on Refinement* checkbox). This avoids ambiguities when changing the spacegroup or the 2θ range or when switching between Pawley and Le Bail refinement.
- Switching between Pawley and LeBail refinement is easily done by simply checking or unchecking the *Le Bail* checkbox. Compare both methods.

Hint!	When switching between Pawley and Le Bail refinement it is mandatory to consider the following points if *Delete hkls on Refinement* is turned off: • Reset intensities in particular when switching to Le Bail refinement (*hkl Is* page). Setting all intensities to 1 will do it for Le Bail refinement. • In Pawley refinement intensities have to be refined while in Le Bail refinement intensities have to be fixed.

- Note: In Le Bail refinement no errors for intensities are calculated!

2.3.2 Le Bail fitting

As example the orthorhombic structure $PbSO_4$ will be used. The X-ray data supplied are the original data used in the Rietveld Refinement Round Robin Part I conducted by the International Union of Crystallography IUCR (Hill, 1992). Profile fitting will be performed using fundamental parameters.

1. Start TOPAS.

2. Load the raw data by importing the file PBSO4.RAW into your document. By default this file is located in C:\TOPAS4\TUTORIAL\PBSO4.

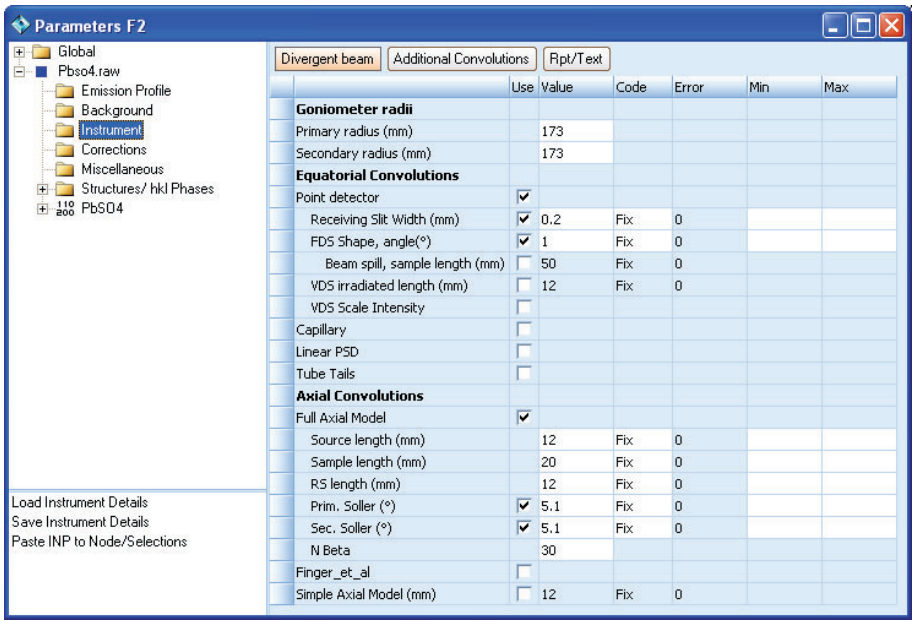
3. Open the parameters window and define the refinement model.

- Focus the *Emission Profile* item and load the predefined emission profile CUKA5.LAM. By default this file is located in C:\TOPAS4\LAM.
- Focus the *Background* item. Use a Chebychev Polynomial of 4th order as well as the *1/X Bkg* function. The latter accounts for increasing background due to airscattering when coming close to the primary beam and also allows to use a Chebychev polynomial with less coefficients.
- Focus the *Instrument* item and define the instrument settings according to the following two tables:

Equatorial Convolutions:		**Axial Convolutions:**	
Receiving Slit Width	☑	Full Axial Model	☑
FDS [1)] Shape, Angle	☑	Primary Soller	☑
		Secondary Soller	☑

Instrument Parameter:		**Value:**
Goniometer Radius	Primary:	173 mm
	Secondary:	173 mm
Receiving Slit Width	Width:	0.2 mm
FDS [1)] Shape, Angle	Angle:	0.1°
Soller Slits	Primary:	5.1°
	Secondary:	5.1°

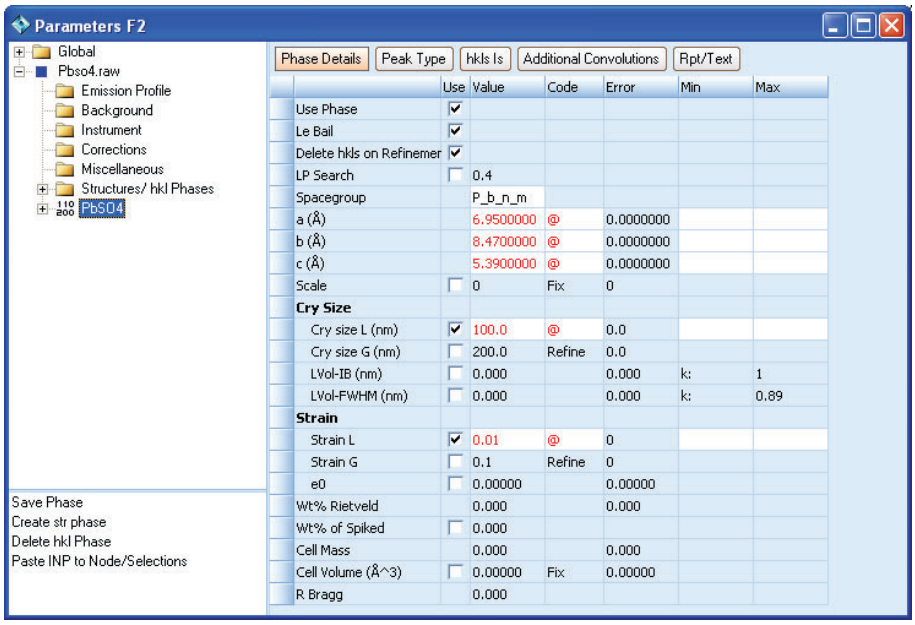
[1)] Fixed Divergence Slit



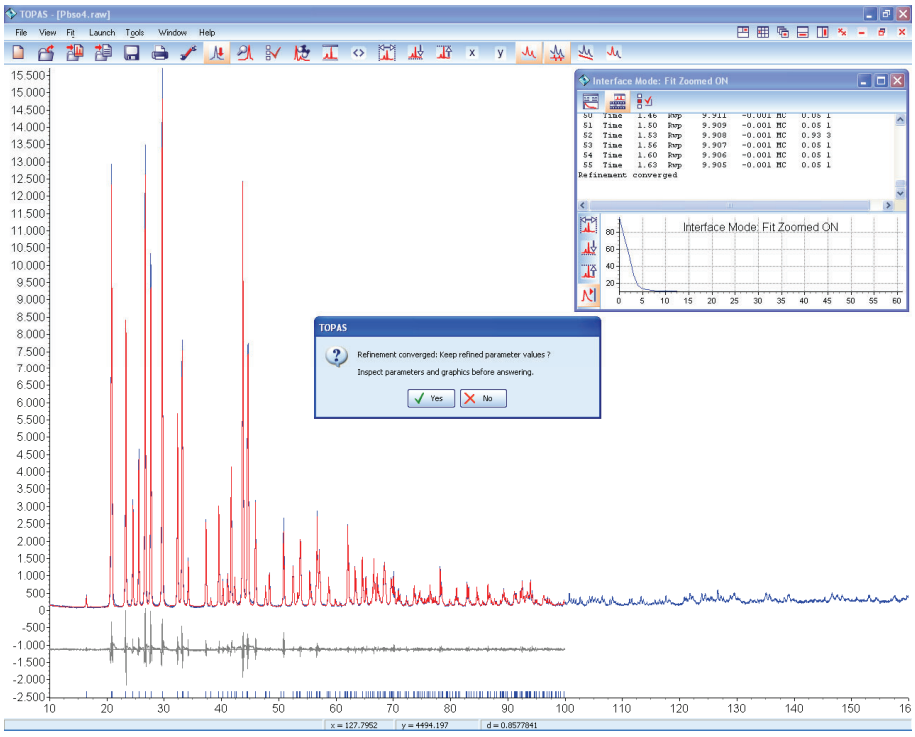
- Focus the *Corrections* item. Check the zero point error and set its code to "Refine". In addition we have to account for the polarization effects coming from the Graphite secondary monochromator. Therefore check LP factor as well and set the monochromator angle to 26.4° 2θ.
- Focus the *Miscellaneous* item and set *Finish X* to about 100° 2θ.
- Insert a new hkl_I phase. Invoke the short cut menu of the range entry for Pbso4.raw and select *Add hkl phase*.
- Focus the *hkl_Phase* item. To perform a Le Bail refinement check the *Le Bail* checkbox. Input the crystallographic data given below in the *Phase Details* page and change all lattice parameter codes to "Refine". Also check the *Cry Size L* and *Strain L* checkboxes and set the parameter codes to "Refine".

Crystallographic Data for $PbSO_4$:

Space group		Pbnm
Cell parameters	a (Å)	6.959
	b (Å)	8.482
	c (Å)	5.397



4. Run the refinement.



2.4 Structure determination - Simulated Annealing


Not available in TOPAS P.

2.4.1 Preliminary considerations

TOPAS is using a direct space approach to structure determination based on simulating. The available diffraction information can be supplemented with prior chemical knowledge of the compound under study, e.g. connectivity in conjunction with tabulated bond lengths, bond angles and bond torsion angles. The relevant parameter space is searched using a simulated annealing algorithm to minimize χ^2. For details please refer to the Technical Reference manual.

The direct space approach to structure determination is straightforward and can be summarized as follows:

1. Construct a trial crystal structure by randomly positioning and orienting individual atoms, molecular fragments or complete molecules taking into account (known or guessed) space group information
2. After calculating diffraction data and comparing it against the measured diffraction data, the variable parameters of the model are adjusted in order to maximise the level of agreement between the observed and calculated data (i.e., minimise χ^2)

Hint!	Structure determination requires TOPAS operation in Launch mode.

2.4.1.1 Data types

Data types that can be used in TOPAS are:

- Integrated intensities
  Integrated intensities from powder data require a preceeding intensity extraction (Pawley or Le Bail fit); good data quality is needed to avoid problems associated with peak overlap (intensity partitioning). Calculations are fast as the number of data points (integrated intensities) is small.
- Step intensity data
  No preceeding intensity extraction required making structure determination from poor quality powder data possible. Calculations are slow as the number of data points (step intensities) is high.
  - Peak maximum intensities
    A powder pattern can be "decomposed" into a new diffraction pattern comprising at most one data point per hkl. Calculations are fast as the number of data points (maximum intensities) is small.

2.4.1.2 Structural degrees of freedom

An atom in general position corresponds to 3 degrees of freedom (DoFs) resulting in a high number of DoFs for large structures. Introducing suitable bond length constraints / restraints can reduce both the number of DoFs as well as the number of local minima in χ^2 and correspondingly increase the chances of obtaining a global minimum. Irrespectively to the number of atoms, each molecular fragment or complete molecule, described as a rigid body, corresponds to 3 positional and 3 orientational DoFs. As a rule of thumb there should be not less than about 5 independent reflections per DoF.

In general the calculation speed as well as the number of local minima in χ^2 correspond to the number of DoFs, so they should be kept small. However, an over use of constraints can in fact hinder the structure determination process in finding the global minimum, if e.g. the movement of atoms or rigid bodies becomes too restricted.

2.4.1.3 General guidelines

The following general guidelines for structure determination with TOPAS are based on the considerations discussed above and have been shown to be adequate in many cases:

- In case of doubt, try step intensity data first. This approach is most straightforward, and avoids problems associated with peak overlap (intensity partitioning). Consider using maximum intensities to speed up calculations, unless data are too noisy.
- Structure determination without or with partial knowledge of connectivity:
  1. Consider to use an unconstrained trial crystal structure (individual atoms only) in first place. Heavy atoms can often be located after some refinement cycles.
  2. Add appropriate constraints step by step. The goal should be to introduce connectivity information and to reduce the number of DoFs. Examples are e.g. limiting the movement of heavy atoms located in the first step, or enforcement of bond distances and angles. The latter can range from general bondlength constraints for selected atom species up to the creation of rigid bodies, where connectivity is known. In general avoid over use of constraints, in particular if the data quality is good.
- Structure determination with knowledge of connectivity:
  1. Create a rigid body and try to position and orient it in the cell. If heavy atoms are present, this process can be significantly simplified by locating them first using an unconstrained trial crystal structure as discussed above. Structure determination success will greatly depend on how accurately the true structure is represented by the rigid body model.
  2. Difficulties typically arise in presence of unknown torsion angles. In many cases it can be sufficient to adjust these simultaneously, but each torsion angle adds one DoF to the problem. An alternative approach is to break up the rigid body into fragments (and even individual atoms) if data quality is good.

Monitor the structure determination process using the *Structure Viewer* window (*view_structure* keyword). This is very useful to

- improve the temperature regime, if displacements of atoms, fragments or molecules are too small or too high
- identify over use of constraints, if movements of atoms, fragments or molecules is too restricted
- identify heavy atom positions, if atoms tend to move repeatedly to the same position

Note, that the use of the *Structure Viewer* window slows down the calculation speed. For maximum calculation speed turn graphics animation off.

2.4.2 Structure determination of the organic compound Cimetidine

This lesson discusses various strategies on how to determine crystal structures using Cimetidine $C_{10}H_{16}N_6S$ (Cernik et al., 1991) with 17 non-Hydrogen atoms on general positions. The measurement data supplied have been taken from http://www.ccp14.ac.uk.

The impact of different data types (integrated intensities, step intensity data, peak maximum intensities) as well as the use of constraints will be evaluated in terms of calculation speed and structure determination success rate.

All example files are located in C:\TOPAS4\TUTORIAL\CIME by default.

2.4.2.1 Whole Powder Pattern Decomposition

Whole powder pattern decomposition is a mandatory part of structure determination in direct space, 2 cases can be distinguished: i) Structure determination using step intensity data requires refined background, zero error, lattice and profile parameters. In this case Pawley refinement is the method of choice. ii) If integrated intensity data shall be used, refined lattice parameters and integrated intensities have to be obtained. In this case both Pawley as well as Le Bail refinements are suitable.

1. Start TOPAS.
2. Perform a Pawley fit. In the Launch menu define the following predefined input file (*Launch - Set INP file*): CIME-PAWLEY.INP. Inspect the input file.
3. Optionally uncomment the *Create_hklm_d_Th2_Ip_file* macro to write refined integrated intensities into the file CIME.SCR.
4. Start the refinement.

2.4.2.2 Structure determination

In the following various strategies to determine the crystal structure of Cimetidine will be demonstrated considering three common cases:

I. Unknown connectivity
   - Use of an unconstrained trial crystal structure (individual atoms), the minimum goal is to find the Sulphur position
   - Use of an trial crystal structure with constrained Sulphur position

II. Known connectivity and molecule conformation
   - Use of an ideal rigid body

III. Known connectivity but unknown torsion angles
   - Use of a rigid body with adjustable torsion angles

For each of these cases predefined INP files are found in the C:\TOPAS4\TUTORIAL\CIME directory based on step intensity data as well as integrated intensities. The following table gives an overview:

	XDD Maximum Intensities	SCR Integrated Intensities
Unknown connectivity		
Individual atoms	CIME-SDPD-XDD-IA1.INP	CIME-SDPD-SCR-IA1.INP
S atom found	<20%	<38%
Structure solved	<12%	<18%
Individual atoms, known S position	CIME-SDPD-XDD-IA2.INP	CIME-SDPD-SCR-IA2.INP
Structure solved	<12%	<20%
Known connectivity and molecule conformation		
Rigid body	CIME-SDPD-XDD-RIGID.INP	CIME-SDPD-SCR-RIGID.INP
Structure solved	~15%	~13%
Known connectivity but unknown torsion angles		
Rigid body with torsions	CIME-SDPD-XDD-Z.INP	CIME-SDPD-SCR-Z.INP
Structure solved	~19%	~27%

Example files containing the string "XDD" in their filename are based on step intensity data, maximum intensities will be used by default to improve calculation speed. Refined background, zero error, lattice and profile parameters have been obtained from the preceeding Pawley refinement.

The string "SCR" denotes example files using integrated intensities. Refined integrated intensities (found in the file CIME.SCR) and lattice parameters have been obtained from the preceeding Pawley refinement.

The table also provides R_{WP} values, at which the structure is normally solved (only valid for the tutorial example files as provided!).

I. Unknown connectivity

1. Start TOPAS

2. In the Launch menu define the following input file: CIME-SDPD-XDD-IA1.INP.

3. Inspect the input file, which is based on the output file of the previous Pawley refinement. The cimetidine trial crystal structure has been defined using individual atoms, the positions of which have been arbitrarily set to x=y=z=0.001.

4. Start the refinement and monitor R_{WP}.

5. If R_{WP} drops below 20% the (approximate) Sulphur position is normally found. You may stop at this point, constrain the Sulphur position (see the comments below), and restart the refinement.

6. If R_{WP} drops below 12% the Cimetidine structure can normally be considered as solved (however see the comments below).

Comments and ideas for further working:

- There are many possibilities to constrain the Sulphur position. The most rigid of which is to use the values found in the refinement and to keep them fixed in subsequent runs. A higher sophisticated and more recommended way is to constrain the Sulphur atom to move within a sphere or a box. The latter, as an example, can be easily defined using the *Keep_Atom_Within_Box* macro as demonstrated in the example file CIME-SDPD-XDD-IA2.INP. The advantage of doing so is that the position of the Sulphur can still be improved within user-defined limits while locating the remaining atoms.
- Due to the lack of connectivity information, the Carbon and Nitrogen atoms will normally be found on swapped sites, as their scattering power is very similar. The correct connectivity needs to be worked out to truly solve the structure.
- Check observed bond lengths and angles (uncomment the *append_bond_lengths* keyword). They need to be constrained for the final structure refinement, as the present diffraction data do not allow for an accurate structure refinement based on unconstrained individual atoms.
- Repeat the exercise using CIME-SDPD-XDD-IA2.INP (constrained Sulphur position). Note the drastically improved success rate (see also section 2.4.2.3). This example clearly demonstrates the advantage of identifying heavy atom positions and to constrain their position for subsequent runs.
- Repeat the exercise with step intensity data (uncomment the *Decompose* macro). Note the significantly increased calculation time.
- Repeat the exercise using CIME-SDPD-SCR-IA1.INP (individual atoms) and CIME-SDPD-SCR-IA2.INP (constrained Sulphur position). Calculation speed and success rate are comparable to those obtained with maximum intensities.

II. Known connectivity and molecule conformation

1. Start TOPAS

2. In the Launch menu define the following input file: CIME-SDPD-XDD-RIGID.INP.

3. Inspect the input file, which is based on the output file of the previous Pawley refinement, and compare it with CIME-SDPD-XDD-IA1.INP.

In this example a rigid body is used describing the actual Cimetidine molecule. Fractional coordinates used to define the rigid body have been taken from Cernik et al. (1991). Individual atoms are no longer adjusted independently, instead the rigid body will be translated and rotated within the cell.

4. Start the refinement and monitor R_{WP}.

5. If R_{WP} drops to ~15% the Cimetidine structure is normally solved.

Comments and ideas for further working:

- Note the drastically improved success rate compared to the individual atom approaches, which is due to the high quality trial structure (i.e. the actual Cimetidine molecule) used in this example (see also section 2.4.2.3). If unknown torsion angles have to be considered, or if the connectivity is not fully known, the success rate will go down significantly.

  Repeat the excercise:

  - Break up the rigid body. E.g. separate the ring and the chain.
  - Use a rigid body only for the ring. Refine all other atoms individually.
  - Use a rigid body only for the ring. Refine all other atoms individually, but constrain the Sulphur position as in CIME-SDPD-XDD-IA2.INP.
- Repeat the exercise with step intensity data (uncomment the *Decompose* macro). Note the significantly increased calculation time.
- Repeat the exercise using CIME-SDPD-SCR-RIGID.INP. Calculation speed and success rate are comparable to those obtained with maximum intensities.

III. Known connectivity but unknown torsion angles

1. Start TOPAS

2. In the Launch menu define the following input file: CIME-SDPD-XDD-Z.INP.

3. Inspect the input file, which is based on the output file of the previous Pawley refinement, and compare it with CIME-SDPD-XDD-RIGID.INP.

In this example a rigid body in Z-matrix notation is used. Note the adjustable torsion angles (turned on by default) and bond lengths (turned off by default).

4. Start the refinement and monitor R_{WP}.

5. If R_{WP} drops to ~19% the Cimetidine structure is normally solved.

Comments and ideas for further working:

- Note the significantly lower success rate compared to the previous example, which is due to the higher number of DoFs (see also section 2.4.2.3). Particularily for more complex examples it is advisable to first to position the molecule in the cell with a minimum number of DoFs, and to refine on torsion angles and eventually bond lengths in separate steps.
- Repeat the exercise with step intensity data (uncomment the *Decompose* macro). Note the significantly increased calculation time.
- Repeat the exercise using CIME-SDPD-SCR-Z.INP. Calculation speed and success rate are comparable to those obtained with maximum intensities.

2.4.2.3 Structure determination success rate

The following results have been obtained on a Pentium III / 1GHz PC (maximum intensities only). The maximum number of iterations was set to 250.000.

CIME-SDPD-XDD-IA1.INP
Nr. of DoFs : 51
Nr. of solutions : 11
Time : 2090 sec.
Success rate : 190 sec / solution

CIME-SDPD-XDD-IA2.INP
Nr. of DoFs : 51
Nr. of solutions : 29
Time : 2118 sec.
Success rate : 73 sec / solution

CIME-SDPD-XDD-RIGID.INP
Nr. of DoFs : 6
Nr. of solutions : 70
Time : 1490 sec.
Success rate : 21 sec / solution

CIME-SDPD-XDD-Z.INP
Nr. of DoFs : 15
Nr. of solutions : 13
Time : 1718 sec.
Success rate : 132 sec / solution

Note the various success rates, which are not simply dependent on the number of DoFs. As expected, the success rate is best when using the actual Cimetidine molecule as trial structure (6 DoFs, CIME-SDPD-XDD-RIGID). Use of unconstrained individual atoms (51 DoFs, CIME-SDPD-XDD-IA1.XDD) results in a success rate comparable to using a rigid body with adjustable torsion angles (15 DoFs, CIME-SDPD-XDD-Z.INP); this is indicative of the fact, that the (over) use of constraints may actually hinder the structure determination process.

2.4.3 Structure determination of the inorganic compound $PbSO_4$

In this lesson the crystal structure of $PbSO_4$ will be determined. The measurement data supplied are the original data used in the Rietveld Refinement Round Robin Part I conducted by the International Union of Crystallography IUCr (Hill, 1992).

In the following maximum intensities and unconstrained individual atoms will be used; identification of special positions will be considered in particular.

All example files are located in C:\TOPAS4\TUTORIAL\PBSO4 by default.

2.4.3.1 Whole Powder Pattern Decomposition

1. Start TOPAS.
2. Perform a Pawley fit. In the Launch menu define the following predefined input file (*Launch - Set INP file*): PBSO4-PAWLEY.INP. Inspect the input file.
3. Start the refinement.

2.4.3.2 Structure determination

1. Start TOPAS
2. In the Launch menu define the following input file: PBSO4-SDPD-IA.INP.
3. Inspect the input file, which is based on the output file of the previous Pawley refinement.
   - According to the chemical formula the $PbSO_4$ trial crystal structure has been defined using 6 individual atoms on general positions arbitrarily set to x=y=z=0.001.
   - Special positions are considered / identified by using the *occ_merge* keyword, see the comments below. Additionally the keywords *append_fractional* and *calculate_bondlengths* are used to calculate equivalent positions as well as bond lengths and angles respectively; this can assist in identifying special positions.
   - The keyword *view_structure* is used to display the structure in the *Structure Viewer* window.
4. Start the refinement and monitor both the *Structure Viewer* window and R_{WP}.

   Watch the atoms moving in the *Structure Viewer* window. It can be easily seen, that the Pb atoms (or clusters of various atoms) repeatedly move to the same positions. Indeed the Pb position is normally found after a few cycles.

   You may stop at this point, appropriately constrain the Pb position (see the comments in section 2.4.2.2) and restart the refinement.
5. If R_{WP} drops down to ~6.5% the $PbSO_4$ structure can normally be considered as solved.
6. In the *Launch* menu open the file PBSO4-SDPD-IA.OUT. Inspect the atomic coordinates (including equivalent positions), occupancies and bond lengths found.

- For 2 Oxygens identical occupancies will be found. Furthermore these 2 Oxygens will be located on the same site (check equivalent positions). Indeed one of the 2 Oxygens is redundant and needs to be deleted from the structure.
- Inspecting the refined coordinates for the remaining atoms shows that the z–coordinates are near values required for a special position (typically values close to 0.25 and / or 0.75) and thus the special position for these sites have been found. This is supported by near zero bond lengths - atoms actually sit almost on top of each other as can be seen clearly in the *Structure Viewer* window. Set the z-coordinates to the special position values and stop refining them.
- Set the occupancies for all atoms to 1.
- Uncomment the occ_merge keywords, as they have become redundant.

7. Restart the calculations to obtain improved results.

Comments and ideas for further working:

- In general it is good practice to obtain information about the number of formula units in the unit cell beforehand, as this can provide valuable information to optimize the trial crystal structure.

  The space group Pbnm generates 8 equivalent positions per general position, that is 8 Pb, 8 S, and 32 O atoms in the present example. This is inconsistent with the actual number of formula units in the unit cell, which is 4 as can be derived e.g. from density measurements or unit cell dimensions. Hence the unit cell can only contain 4 Pb, 4 S, and 16 O atoms; it is therefore inevitable to consider the presence of special positions as otherwise the scattering power for each atom species is exceeded by a factor of 2.

  One possibility to maintain the expected scattering power is to manually set the occupancies for all sites to 0.5. A more straightforward and recommended way is to use the *occ_merge* keyword as demonstrated in the present example, which handles the occupanices automatically. In general this greatly simplifies dealing with more complex cases and supports structure determination, where the number of formula units in the unit cell is unknown or even not required to proceed.

  Note, that in the present example the $PbSO_4$ structure is actually solved with *occ_merge* without knowledge of the number of formula units!

- Repeat the exercise with step intensity data (uncomment the *Decompose* macro). Note the significantly increased calculation time.

2.4.4 Structure determination of the metal-organic compound KCP

The example Cyclopentadienylpotassium KCP (Dinnebier, 1999) represents a small molecular structure containing a heavy atom.

To solve the structure a rigid body for the Cyclopentadienyl ring will be used. Additionally anti-bump restraints will be applied to keep a minimum distance between the rings and Potassium atoms.

All example files are located in C:\TOPAS4\TUTORIAL\KCP by default.

2.4.4.1 Whole Powder Pattern Decomposition:

1. Start TOPAS.
2. Perform a Pawley fit. In the Launch menu define the following predefined input file (*Launch - Set INP file*): KCP-PAWLEY.INP. Inspect the input file.

   The PV function serves as additional background function by defining a single peak to account for the background bump due to an amorphous phase.
3. Start the refinement.

2.4.4.2 Structure determination

1. Start TOPAS.
2. In the Launch menu define the following input file: KCP-SDPD.INP.
3. Inspect the input file, which is based on the output file of the previous Pawley refinement.

   Note the arbitrary "A0" pseudo-atom, which is used to define the center of the Cyclopentadienyl ring. This allows an elegant creation of anti-bump constraints referring to the center of the rings. As the occupancy factor of the pseudo-atom is set to 0, it does not contribute to the calculated intensities.
4. Start the refinement and monitor both the *Structure Viewer* window and R_{WP}.

   Watch the atoms and rings moving in the *Structure Viewer* window. Note the extremely high success rate.

   It can be easily seen, that the Potassium atoms repeatedly move to the same positions. Indeed the Potassium position is normally found after a few cycles.

   You may stop at this point, appropriately constrain the Potassium position (see the comments in section 2.4.2.2) and restart the refinement.
5. If R_{WP} drops below 9% the KCP structure is normally solved.

Comments and ideas for further working:

- Repeat the exercise with step intensity data (uncomment the *Decompose* macro). Note the significantly increased calculation time.
- Repeat the exercise without the anti-bump restraint (uncomment the *Anti_Bumb* macros). Note that success rate decreases.
- This structure can be easily solved using unconstrained individual atoms as well. However note that bond lengths and angles need to be constrained for the final structure refinement, as the present diffraction data do not allow for an accurate structure refinement based on unconstrained individual atoms.

  Repeat the exercise using individual atoms (KCP-SDPD-IA.INP).

2.5 Structure determination - Charge Flipping

Not available in TOPAS P.

TOPAS supports the Charge Flipping method (Oszlányi & Süto, 2004) for structure determination with a number of enhancements (Coelho, 2007), e.g. the inclusion of the tangent formula (Karle & Hauptman, 1956). For details refer to the Technical Reference manual.

Example files are found in the C:\TOPAS4\TUTORIAL\CF directory.

Typical first try INP file template are as follows, see also the example files provided:

- Single crystal data:

```
macro Nr { 100 }

charge_flipping
   cf_hkl_file HKL_FILE.HKL
   space_group $
   a # b # c al # be # ga #
   symmetry_obey_0_to_1 = Ramp(0.5, 1, Nr);
   Tangent(.3, 30)
   min_grid_spacing .3
   Pick (#)
   load f_atom_type f_atom_quantity { … }
```

- Powder data:

```
macro Nr { 100 }

charge_flipping
   cf_in_A_matrix PAWLEY_FILE.A
   space_group $
   a # b # c al # be # ga #
   delete_observed_reflections = D_spacing < #;
   extend_calculated_sphere_to #
   add_to_phases_of_weak_reflections = 90 Ramp(1, 0, Nr);
   flip_regime_2 = Ramp(1, 0, Nr);
   symmetry_obey_0_to_1 = Ramp(0.5, 1, Nr);
   Tangent(.3, 30)
   min_grid_spacing .3
   Pick (#)
   load f_atom_type f_atom_quantity { … }
```

The effects of Charge Flipping keywords can be best investigated by inclusion / exclusion of keywords or by changing equations in the example files provided.

2.6 Rietveld structure refinement

Not available in TOPAS P.

In this lesson the structure refinement of $PbSO_4$ will be demonstrated using measurement data coming from both a laboratory X-ray and a constant wavelength (CW) neutron diffractometer. All data supplied are the original data used in the Rietveld Refinement Round Robin Part I conducted by the International Union of Crystallography IUCR (Hill, 1992).

Observed line profile shapes will be described using Fundamental Parameters for the X-ray data and the TCHZ pseudo-Voigt function for the CW neutron data.

2.6.1 Laboratory X-ray data

1. Start TOPAS.
2. Load the raw data by importing the file PBSO4.RAW into your document. By default this file is located in C:\TOPAS4\TUTORIAL\PBSO4.

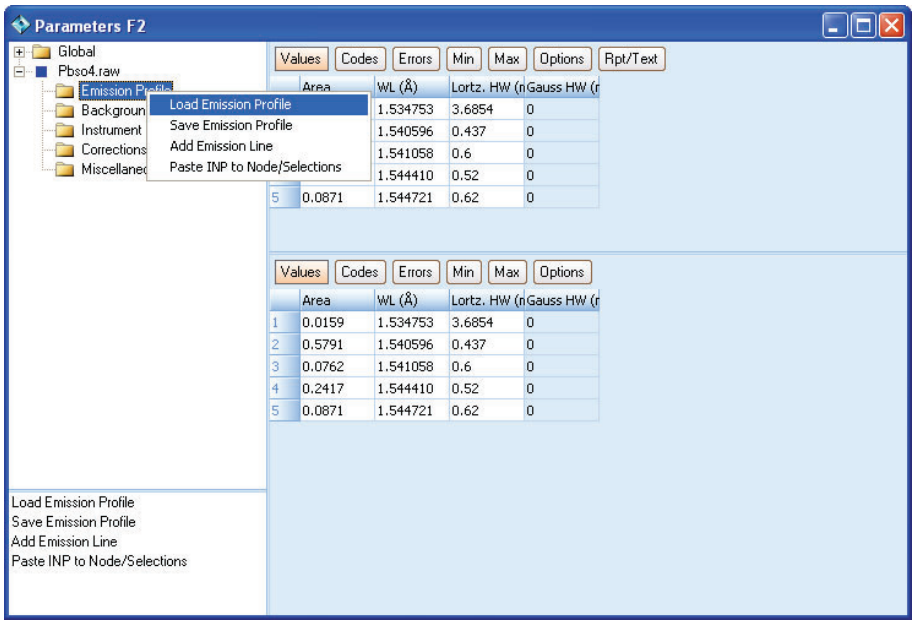
Menu:	Icon:	Shortcut:	Result:
File - *Import Data File(s)...*		n.a.	Imports measurement data

3. Switch to the *Parameters Window* and define the refinement model.

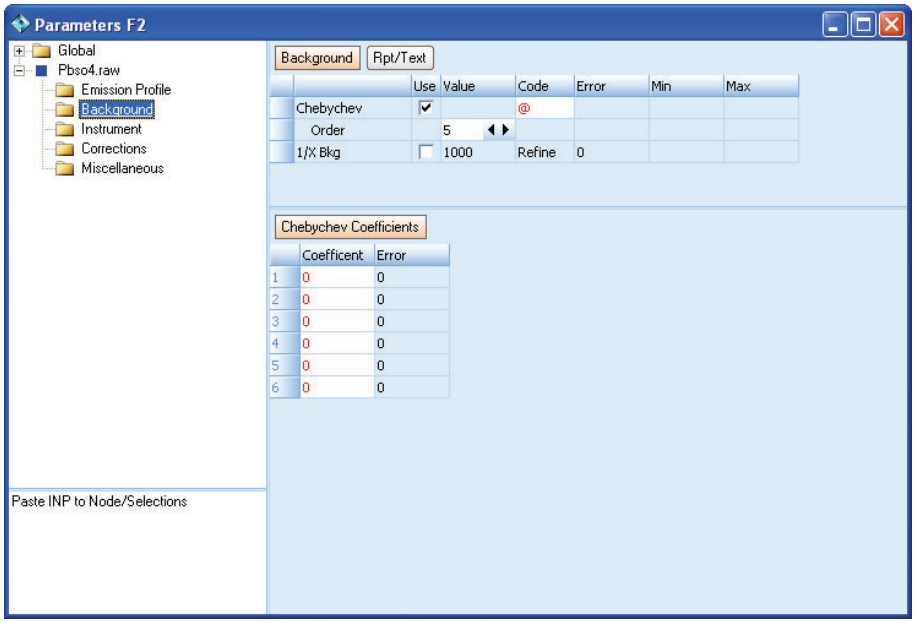
Menu:	Icon:	Shortcut:	Result:
View - *Parameters Window*		F2	Displays or hides the *Parameters Window*

In the *Parameters Window* expand the range item of PBSO4.RAW and perform the following tasks:

- Focus the *Emission Profile* item and load the predefined emission profile CUKA5.LAM. By default this file is located in C:\TOPAS4\LAM.



- Focus the *Background* item. Use a Chebychev polynomial of 5th order and the *1/X Bkg* function. The latter accounts for increasing background due to airscattering when coming close to the primary beam.

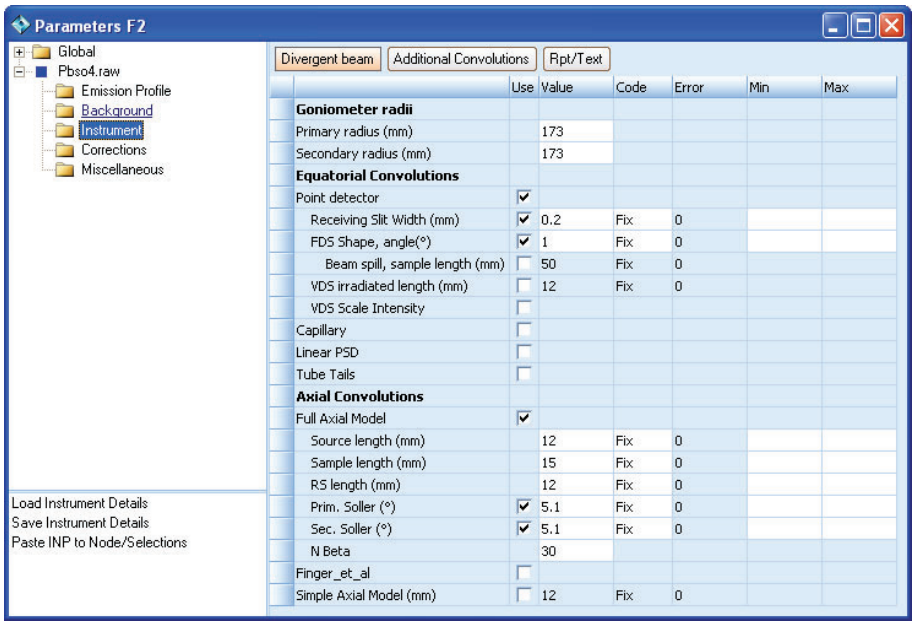


- Focus the *Instrument* item and define the instrument settings according to the following two tables:

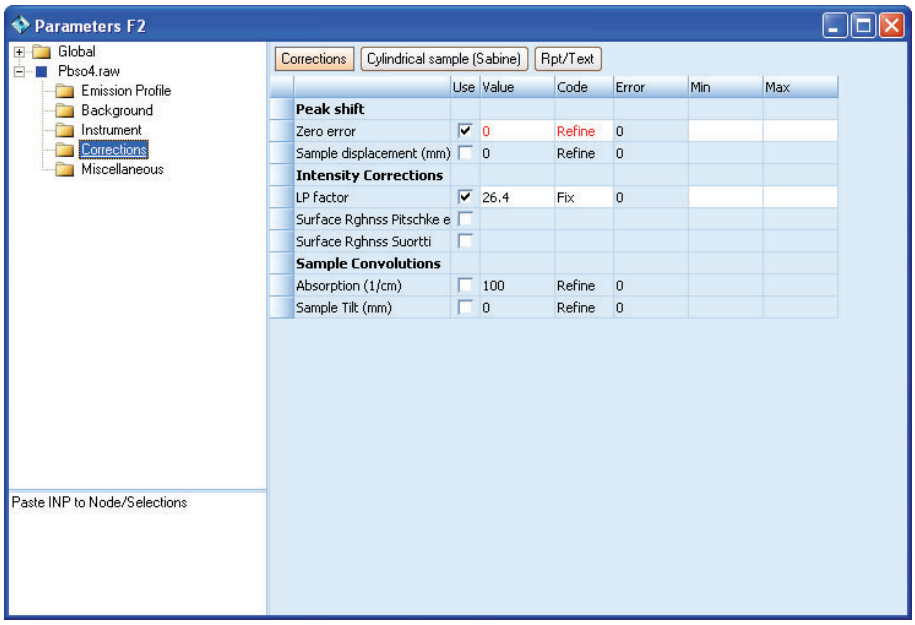
Equatorial Convolutions:		**Axial Convolutions:**	
Receiving Slit Width	☑	Full Axial Model	☑
FDS [1] Shape, Angle	☑	Primary Soller	☑
		Secondary Soller	☑

Instrument Parameter:		**Value:**
Goniometer Radius	Primary:	173 mm
	Secondary:	173 mm
Receiving Slit Width	Width:	0.2 mm
FDS [1] Shape, Angle	Angle:	1°
Soller Slits	Primary:	5.1°
	Secondary:	5.1°

[1] Fixed Divergence Slit



- Focus the *Corrections* item. Check the *Zero error* and set its code to "Refine". In addition polarization effects coming from the secondary Graphite monochromator have to be accounted for. Therefore check *LP factor* as well and set the monochromator angle to 26.4° 2θ.

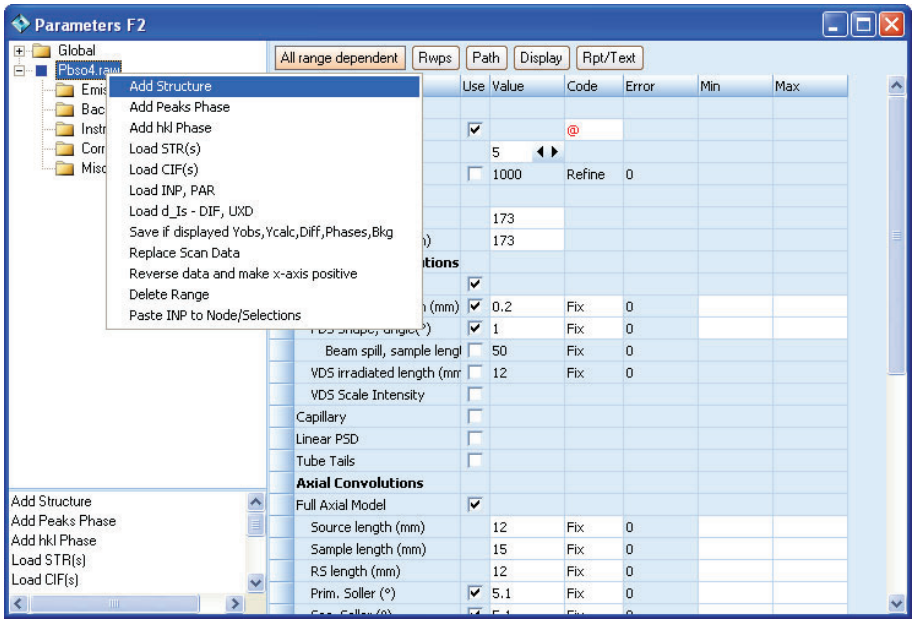


4. In the next step the crystal structure data for $PbSO_4$ has to be provided. In principle there are three different possibilities:

1. Manual input of structure data (Add Structure)
2. Import of TOPAS STR files (*Load STR(s)*, see also section 2.7.1.1)
3. Import of CIF files (*Load CIF(s)*, see also section 2.7.1.2)

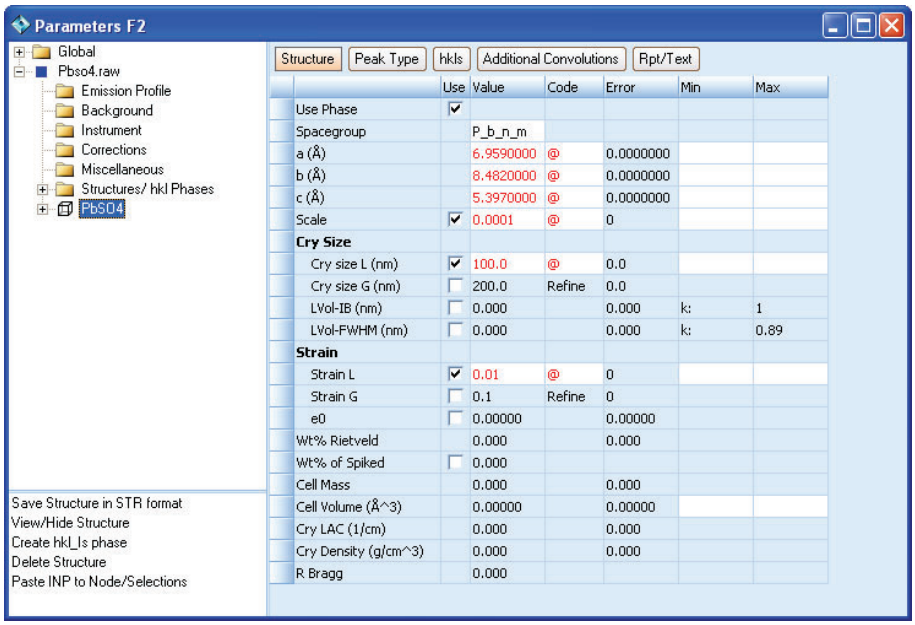
In the following the manual input will be described.

- Insert a new structure. Focus the range item for Pbso4.raw and select *Add Structure*.



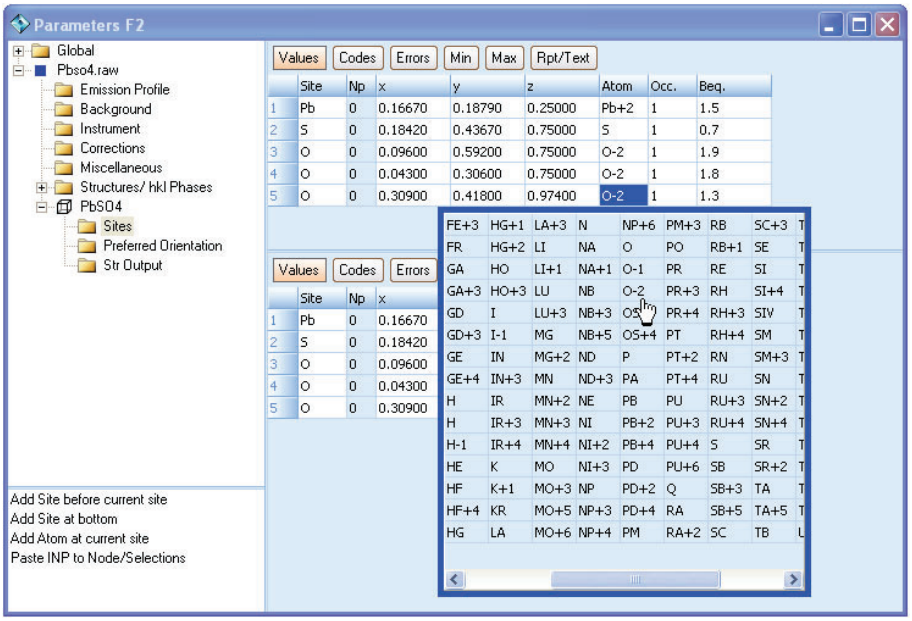
- Focus the *Structure* item. Input the crystallographic data given below in the *Structure* page and change all lattice parameter codes to "Refine". Set the scale factor to 0.0001. Check the *Cry Size L* and *Strain L* checkboxes, set the values to 100 and 0.01 respectively and set the parameter codes to "Refine".

Crystallographic Data for $PbSO_4$:		
Space group		Pbnm
Cell parameters	a (Å)	6.959
	b (Å)	8.482
	c (Å)	5.397

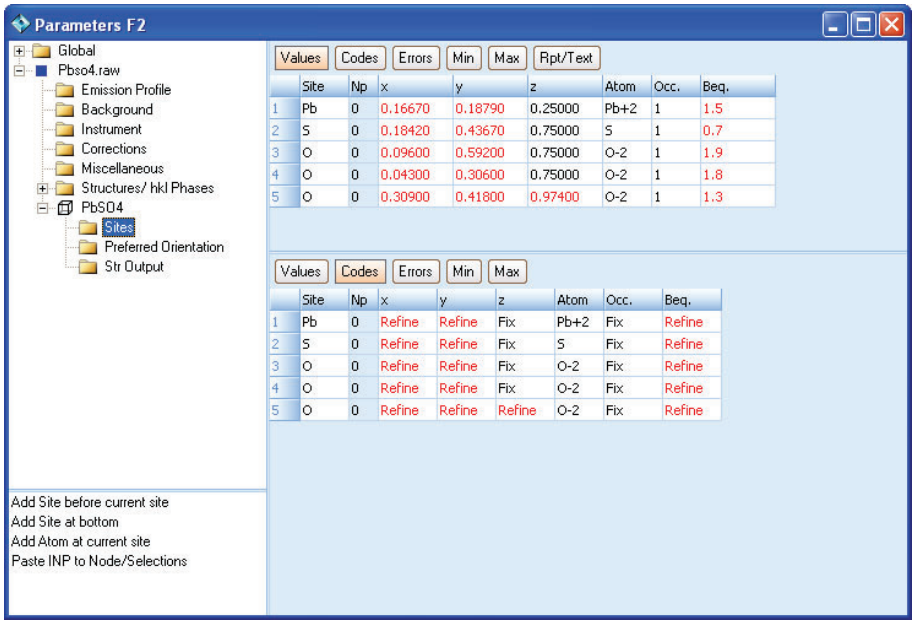


- Expand the *Structure* item and focus the *Site* item. Insert 5 sites by selecting *Add site at bottom* in the short cut menu and input the structure data provided in the table below.
  Note, that Pb-z, S-z, O1-z and O2-z are special positions!

Atom coordinates and isotropic thermal parameters for $PbSO_4$:						
Site:	**x**	**y**	**z**	**Atom**	**Occ**	**B [A^2]**
Pb	0.1667	0.1879	0.2500	Pb+2	1	1.5
S	0.1842	0.4367	0.7500	S	1	0.7
O1	0.0960	0.5920	0.7500	O-2	1	1.9
O2	0.0430	0.3060	0.7500	O-2	1	1.8
O3	0.3090	0.4180	0.9740	O-2	1	1.3



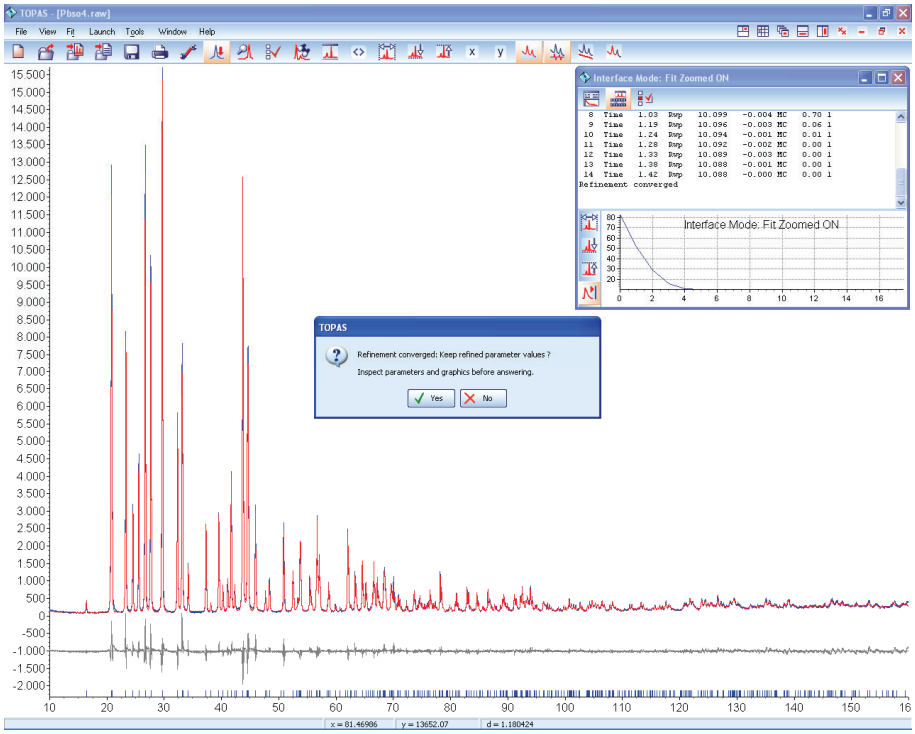
- Switch to the *Codes* page and change the code for all refineable coordinates and for the temperature factors to "Refine". Note: Special positions must not be refined!



5. To have errors calculated, check the menu item *Calculate Errors* in the *Fit* menu.
6. To start the refinement switch to the *Fit Window* and click on the *Run* button.

Menu:	Icon:	ShortCut:	Result:
Fit – Fit Window		F5	Displays or hides the *Fit Window*
n.a.		F6	Runs the refinement

In the *Scan Window* a calculated pattern based on the start values is shown in red color. The difference to the observed data is represented by the gray curve. After fitting a dialog informs you, if the refinement has converged or not.



7. The refinement results can be inspected in the *Parameters Window*.
8. Save your work.

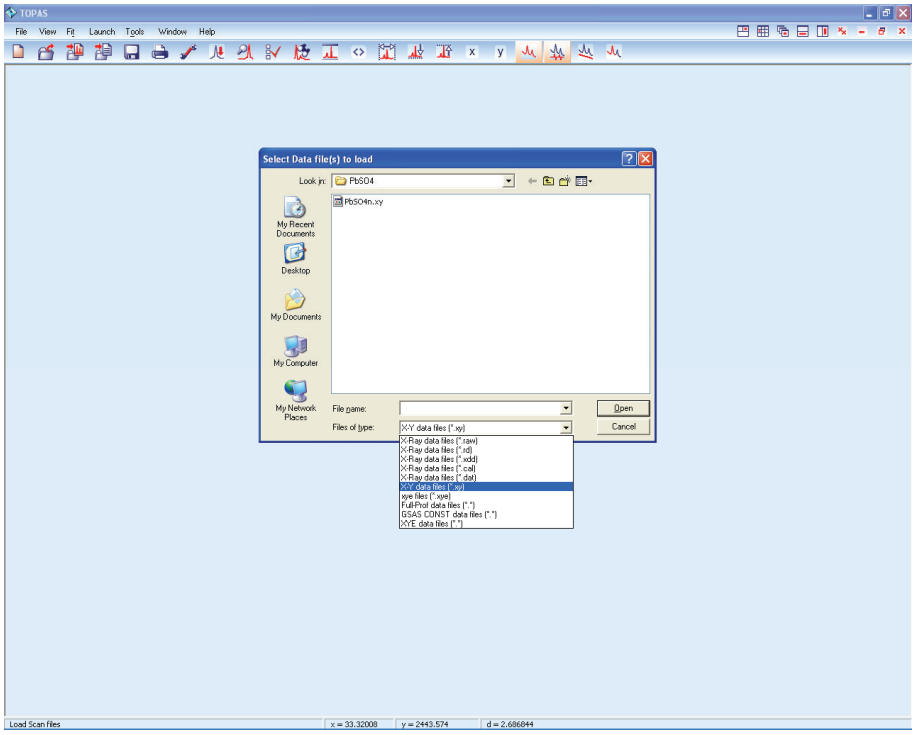
Menu:	Icon:	Shortcut:	Result:
File – Save		n.a.	Saves the current work in a document (*.PRO)
File – Export INP file...	n.a.	n.a.	Exports the current work as an input file (*.INP)

Hint!	TOPAS documents (PRO files) contain the measurement data, model and refinement parameters, evaluation results, as well as any user-defined GUI settings. Therefore you can load and resume your fit session anytime at any stage or use the document as a template for different data. Exporting an input file using the Menu *File - Export INP File...* instead allows the use of your refinement model e.g. in an automated environment (using TC) or in *Launch Mode*. Measurement data and user-defined GUI settings are not saved within an INP file.

Hint!	Fractional coordinates for special positions such as 1/3, 1/6, etc. are expected in the form of an equation such as = 1/3, =1/6, etc. in the *Codes* page, instead of values with re-occuring digits such as 0.3333..., 0.1666..., etc. in the *Values* page. The correct parameter value will be calculated automatically from the equation and displayed in blue color. **Not adhering to this convention may lead to severely wrong refinement results!**

2.6.2 Constant wavelength neutron data

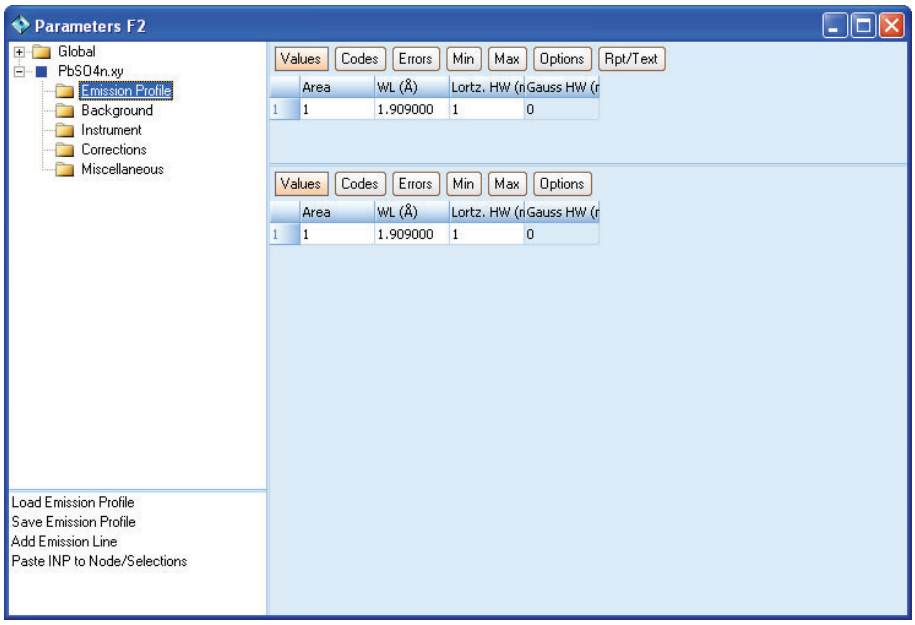
1. Start TOPAS.
2. Load the raw data by importing the file PBSO4N.XY into your document. By default this file is located in C:\TOPAS4\TUTORIAL\PBSO4.



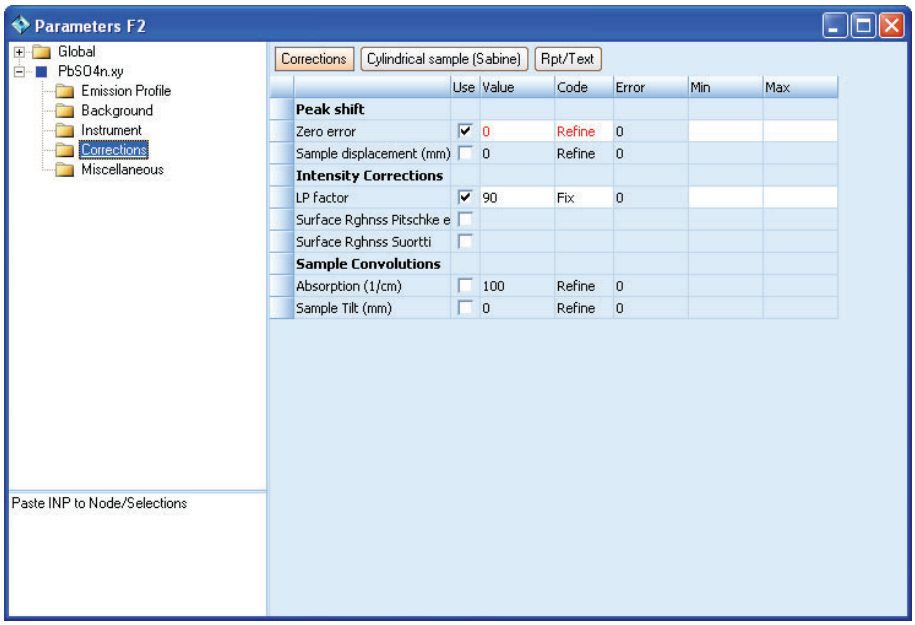
3. Switch to the *Parameters Window* and define the refinement model.

   In the *Parameters Window* expand the range item of PBSO4.RAW and perform the following tasks:

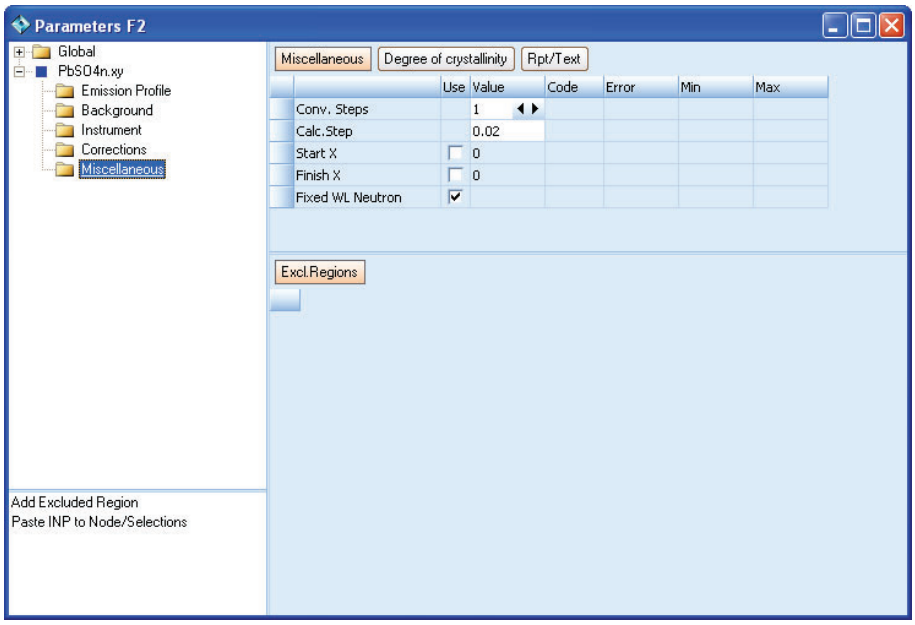
   - Focus the *Emission Profile* item and define a source emission profile using λ = 1.909Å. Setting *Area* and *Lortz. HW* to 1 will do it for this example. For details about emission profiles please refer to the Technical Reference manual.



- Focus the *Background* item. Use a Chebychev polynomial of 3rd order and the *1/X Bkg* function.
- Focus the *Instrument* item. To describe peak asymmetry, select either the *Finger_et_al* or the *Simple Axial Model* and set the asymmetry parameter codes to "Refine". The instrument radii are of no importance for this example.
- Focus the *Corrections* item. Check the *Zero error* and set its code to "Refine". Check *LP factor* and set the monochromator angle to 90° 2θ, as neutron data are unpolarized.

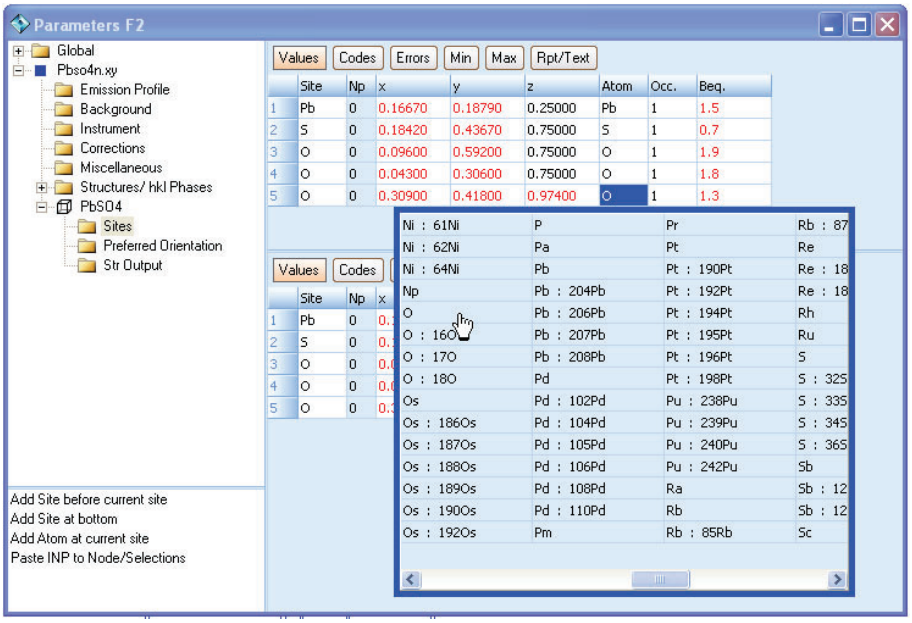


- Focus the *Miscellaneous* item and check *Fixed WL Neutron*.

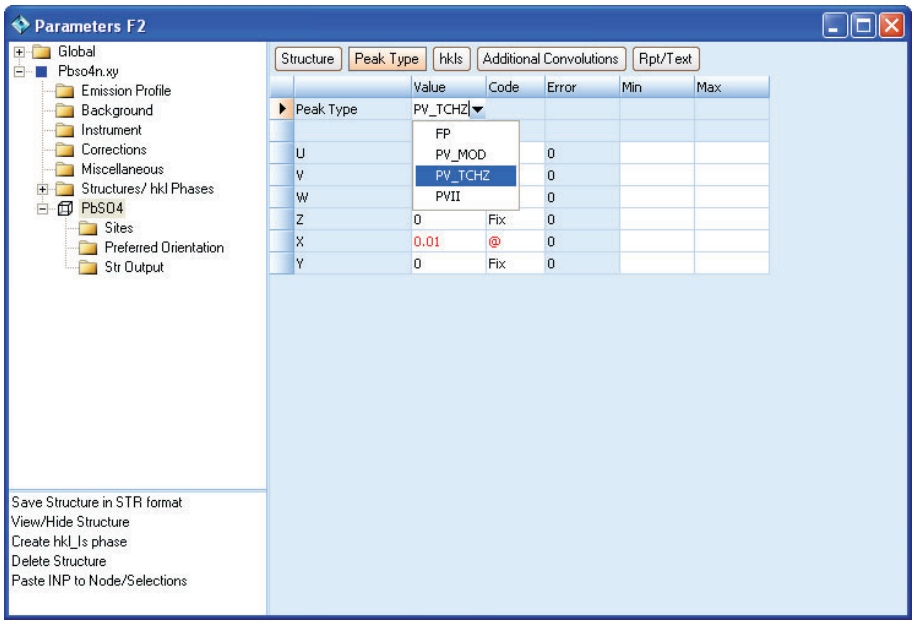


4. In the next step the crystal structure data for $PbSO_4$ has to be provided.

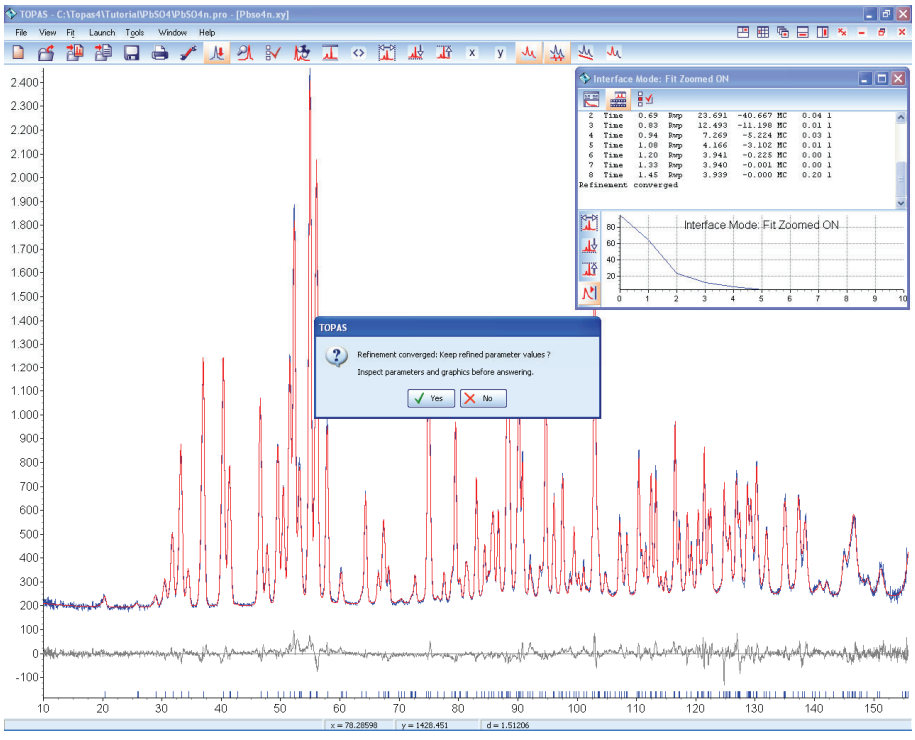
- Repeat step 4 in section 2.6.1 to create the structure model. Note, that scattering lengths will be provided in the *Atom* drop down list, as *Fixed WL Neutron* has been checked in the *Miscellaneous* page.



- In the *Structure* page set the scale factor to about 0.1. Also set the *Cry Size L* checkbox to no use, as there is no instrument function used in this example. Switch to the *Peak Type* page and select the TCHZ_PV function.



5. Start the refinement.



2.7 Quantitative Rietveld analysis


Not available in TOPAS P.

This tutorial demonstrates quantitative Rietveld phase analysis using the following two selected examples:

I. "CPD-2": This sample contains known amounts of the following phases: Corundum, Fluorite, Zincite, and Brucite. It will be shown how to
   - perform a quantitative Rietveld analysis from scratch,
   - optimize a given structure entry with respect to your sample properties, and
   - create templates for interactive (PRO files) as well as automated quantitative Rietveld analysis (INP files).

II. "CPD-3": This sample contains known amounts of the following phases: Corundum, Fluorite, Zincite, and glass. It will be shown how to quantify amorphous phase amounts using a spike phase (Corundum).

III. "OPC": This tutorial example comprises the three NIST ordinary portland clinkers RM 8486, RM 8487, and RM 8488. It is used to demonstrate how to
   - use templates (*.PRO files) for fast, interactive phase quantification, and
   - critically assess the accuracy of quantification results.

This tutorial also provides an introduction into the use of structure databases with TOPAS [1]. This includes the following topics:

- The use of both, the "TOPAS Structure Database" and its specialized version, the "TOPAS Cement Structure Database", respectively [2].
- The use of third party databases such as the ICSD or CSD structure databases using the "Crystallographic Information Files" (CIF) interface.
- The creation of a user-defined structure database using optimized structure entries.

[1] All structure entries required to go through the training examples are included in this tutorial, so it is not necessary to have any database to proceed.
[2] The TOPAS structure databases are optional add-on's to TOPAS, which have to be ordered separately.

2.7.1 Quantification of CPD-2

This exercise is divided into two parts:

I. Introduction into quantitative Rietveld analysis
In the first part the quantification of the CPD-2 sample will be demonstrated using structure entries coming from the "TOPAS Structure Database".

II. Fitting structure entries to your needs
In the second part some important glitches will be discussed when using structure data of unknown quality. It will be shown how to adjust structure data taken from literature using CIF files in order to obtain high quality structure entries for a user-defined structure database.

2.7.1.1 Introduction into quantitative Rietveld analysis

1. Start TOPAS.

2. Load the raw data by importing the file CPD-2.RAW into your document. By default this file is located in C:\TOPAS4\TUTORIAL\QPARR.

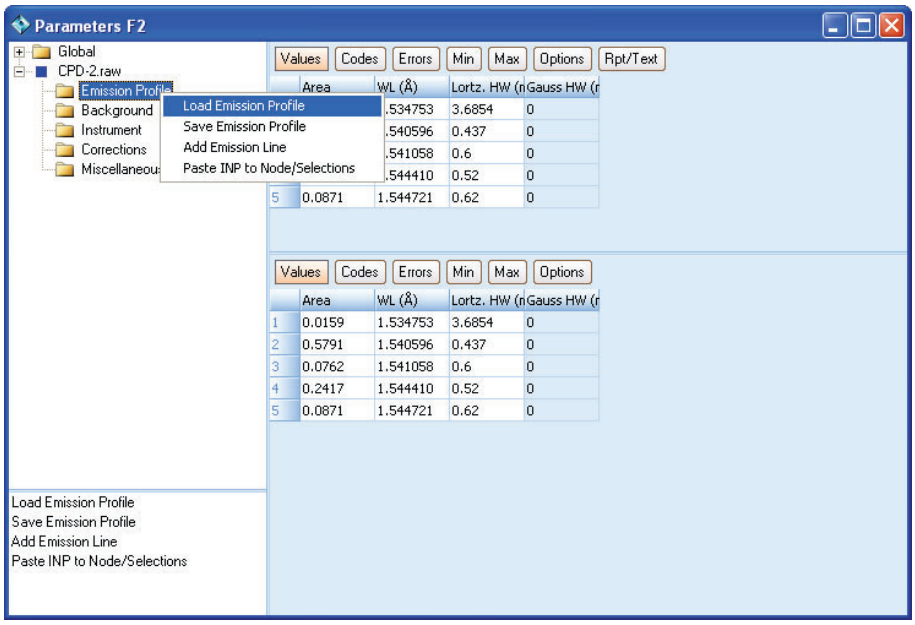
Menu:	Icon:	Shortcut:	Result:
File - *Import Data File(s)...*		n.a.	Imports measurement data

3. Switch to the *Parameters Window* and define the refinement model.

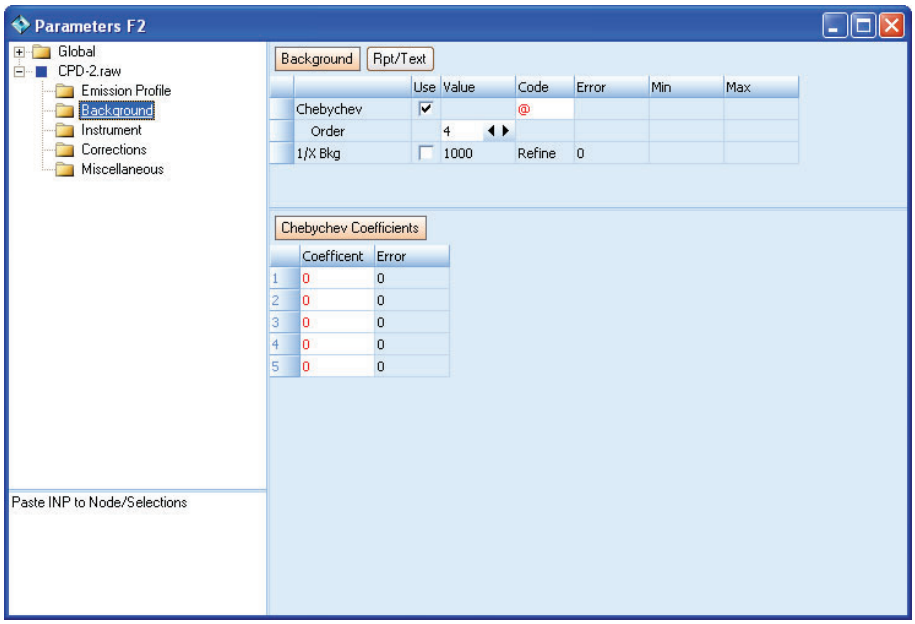
Menu:	Icon:	Shortcut:	Result:
View - *Parameters Window*		F2	Displays or hides the *Parameters Window*

In the *Parameters Window* expand the range item of CPD-2.RAW and perform the following tasks:

- Focus the *Emission Profile* item and load the predefined emission profile CUKA5.LAM. By default this file is located in C:\TOPAS4\LAM.



- Focus the *Background* item. Use a Chebychev polynomial of 4th order and the *1/X Bkg* function. The latter accounts for increasing background due to airscattering when coming close to the primary beam and also allows to use a Chebychev polynomial with less coefficients.

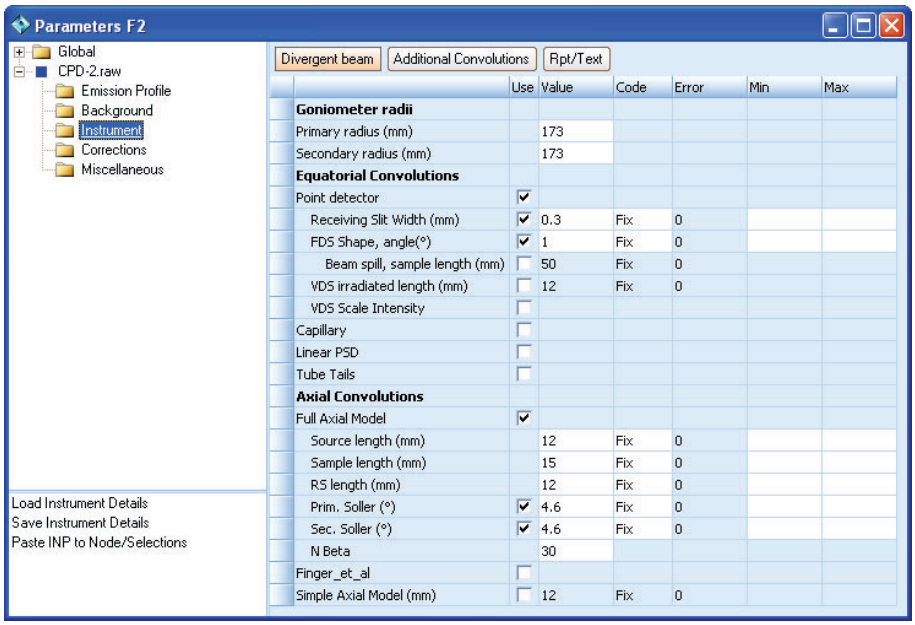


- Focus the *Instrument* item and define the instrument settings according to the following two tables:

Equatorial Convolutions:		Axial Convolutions:	
Receiving Slit Width	☑	Full Axial Model	☑
FDS [1] Shape, Angle	☑	Primary Soller	☑
		Secondary Soller	☑

Instrument Parameter:		Value:
Goniometer Radius	Primary:	173 mm
	Secondary:	173 mm
Receiving Slit Width	Width:	0.3 mm
FDS [1] Shape, Angle	Angle:	1°
Soller Slits	Primary:	4.6°
	Secondary:	4.6°

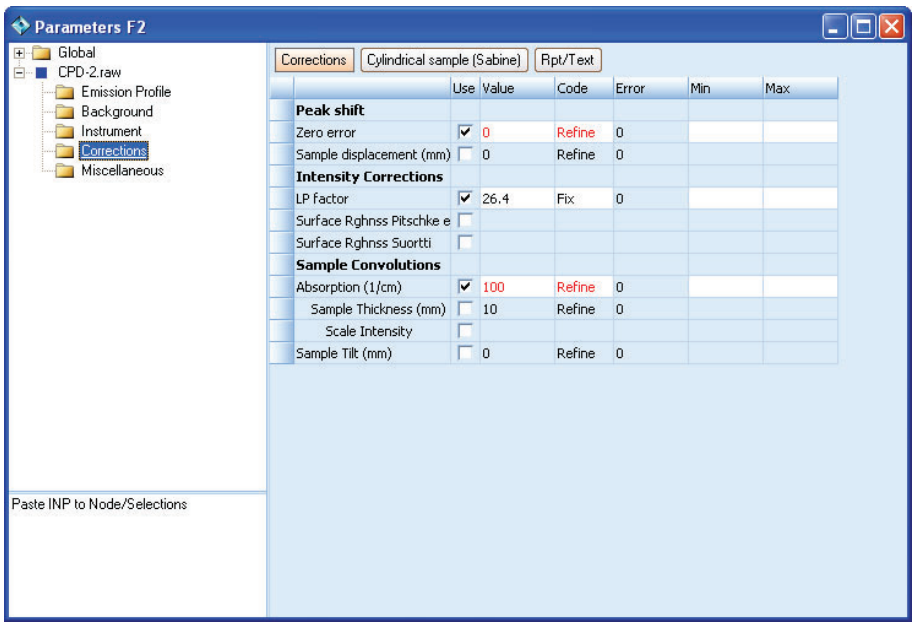
[1] Fixed Divergence Slit



- Focus the *Corrections* item. Check the *Zero error* and set its code to "Refine". In addition polarization effects coming from the secondary Graphite monochromator have to be accounted for. Therefore check *LP factor* as well and set the monochromator angle to 26.4° 2θ. Finally check *Absorption* and set its code to "Refine" in order to correct the significant profile shape distortion caused by the low mass absorption of the sample.

  Note: The absorption correction accounts for the profile distortion due to the sample transparency effect inherent to the Bragg-Brentano geometry. The absorption parameter provides the effective mean absorption coefficient of the sample.
  For the Bragg-Brentano geometry this parameter is a fundamental parameter.

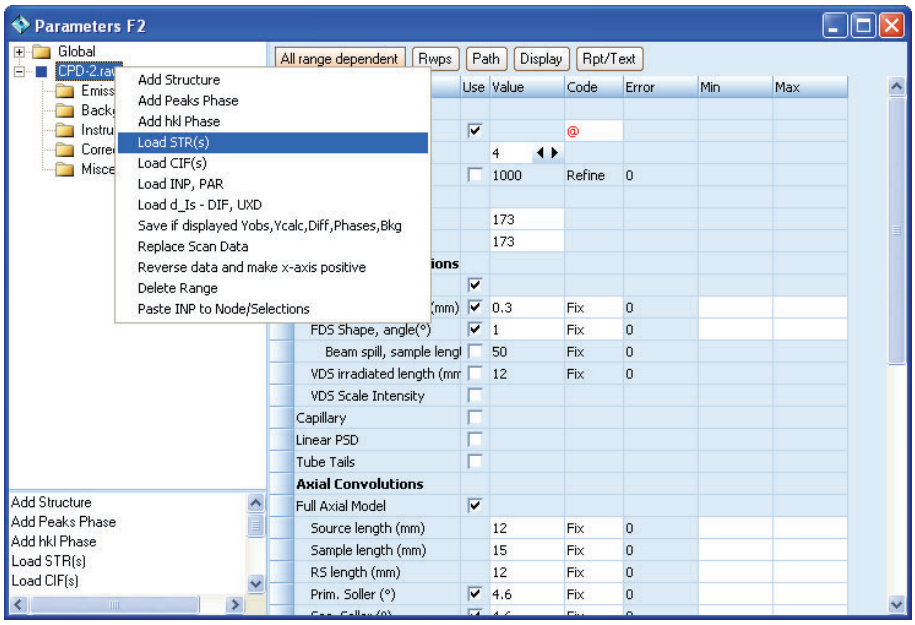
However, absorption results are only meaningful, if the instrument and the microstructure properties of all phases in the sample have been described properly.
If these requirements can not be fulfilled or if a different instrument geometry has been used, the absorption correction can be applied as an additional, empirical function to describe peak asymmetry. In this case the refined absorption parameter does not have a physical meaning.



- Focus the CPD-2.RAW range item and import the structure entries for the four phases Corundum, Fluorite, Zincite and Brucite (multi-selection is supported):

  1. BRUCITE.STR
  2. CORUNDUM.STR
  3. FLUORITE.STR
  4. ZINCITE.STR

By default these files are located in C:\TOPAS4\TUTORIAL\QPARR.

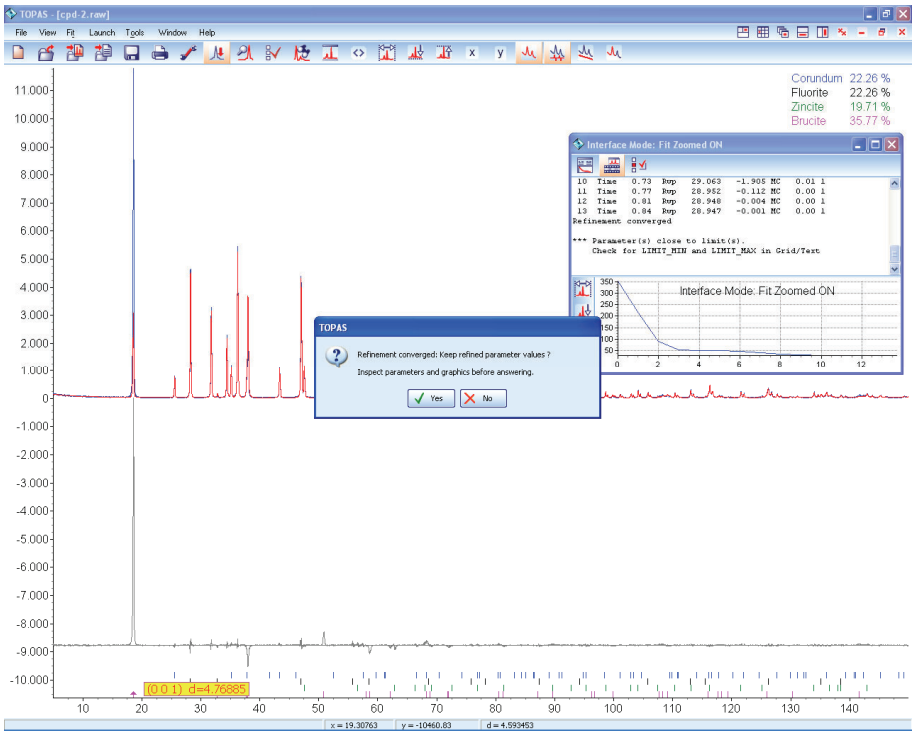


4. To have errors calculated, check the menu item *Calculate Errors* in the *Fit* menu.
5. To run the refinement switch to the *Fit Window* and click on the *Run* button.

Menu:	Icon:	ShortCut:	Result:
Fit – *Fit Window*		F5	Displays or hides the *Fit Window*
n.a.		F6	Runs the refinement

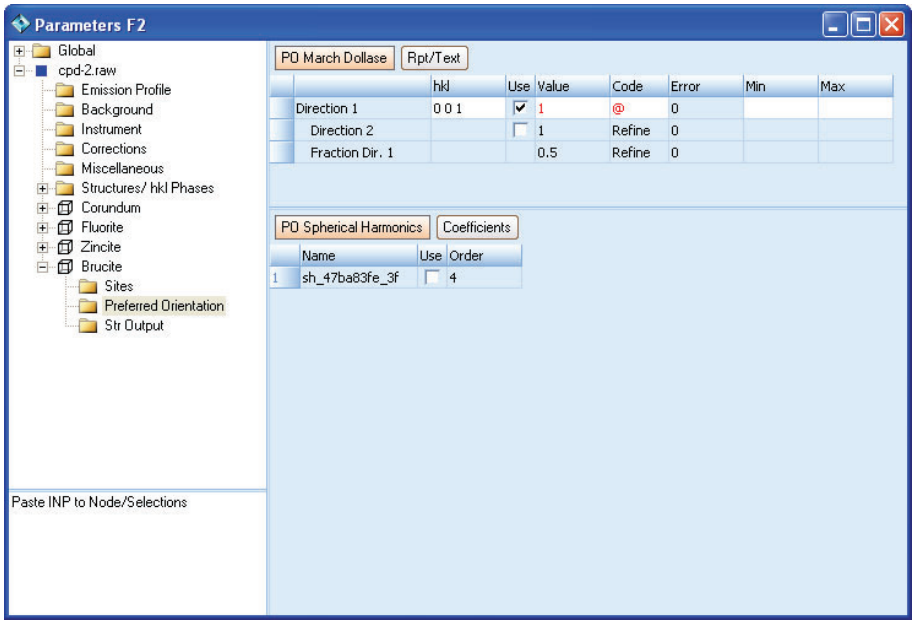
In the *Scan Window* the calculated pattern is shown in red color. The difference to the observed data is represented by the grey curve. After fitting a dialog informs you, if the refinement has converged or not.

Note the poor R_{WP} value of about 30 % and the misfit of the 001 Brucite reflection at about 18.6° 2θ due to preferred orientation.

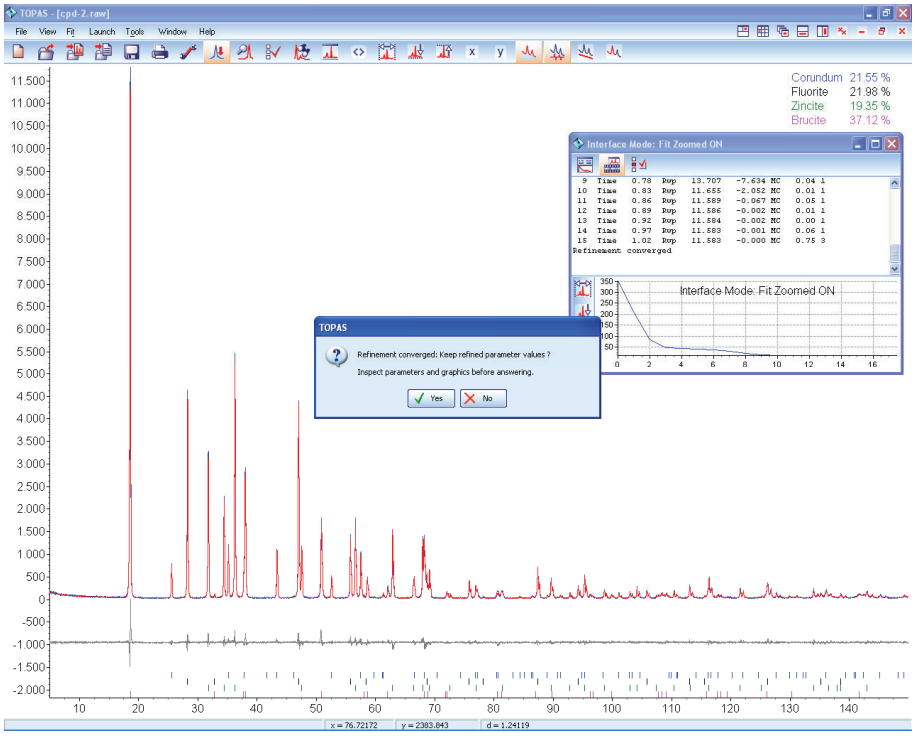


6. To account for the preferred orientation of Brucite switch to the *Parameters Window* again and expand the structure item of Brucite. Select the *Preferred Orientation* item and set the code of the March-Dollase parameter to "Refine".

Note: The TOPAS Structure Database contains the typical preferred orientation direction for most of its entries. For Brucite - as an example - this direction (0 0 1) is included and therefore automatically entered into the hkl field of the *PO March-Dollase* page.



7. Restart the refinement.



8. The quantification results can be inspected in the *Scan Window*, *Weight Percent Pie Chart Window* or in the *Parameters Window*. The expected ("true") values are given in the table below. The accuracy of your results should be about ± 1 % in weight.

CPD-2	Brucite [%]	Corundum [%]	Fluorite [%]	Zincite [%]
Weighed	36,26	21,27	22,53	19,94
XRF	36,14	20,94	22,14	19,49

9. Save your work.

Menu:	Icon:	Result:
File – Save		Saves the current work in a document (*.PRO)
File – Export INP file...	n.a.	Exports the current work as an input file (*.INP)

Hint!	TOPAS documents (PRO files) contain the measurement data, model and refinement parameters, evaluation results, as well as any user-defined GUI settings. Therefore you can load and resume your fit session anytime at any stage or use the document as a template for different data. Exporting an input file using the Menu *File - Export INP File...* instead allows the use of your refinement model e.g. in an automated environment (using TC) or in *Launch Mode*. Measurement data and user-defined GUI settings are not saved within an INP file.

2.7.1.2 Fitting structure entries to your needs

The accuracy of the quantification results as well as the convergence behaviour of a refinement directly depend on

- the quality of the selected refinement models (background, instrument contributions, crystal structure, microstructure, ...), and
- the start values used for the model parameters to be refined, which should be as close to reality as possible.

The description and refinement of background, instrument and microstructure contributions to the powder pattern is straightforward with the comprehensive collection of refinement models offered by TOPAS. Therefore the accuracy of the quantification results is finally determined by the quality of the crystal structure(s) used in the refinement. Often missed is the fact, that even published crystal structure data can be inaccurate or incomplete (e.g. missing atoms or temperature factors). Careful selection as well as critical quality checks of structure data of any origin should be regarded as a matter of course. Synthetic mixtures (as in this exercise) or cross-checks using alternative analysis methods (such as optical microscopy for the OPC samples in section 2.7.2) can be extremely useful to judge structure data quality.

Poor start values e.g. for scale factors (mainly determining calculated peak intensities) or lattice parameters (mainly determining peak positions) may just result in a needless number of refinement cycles, but may also lead to parameter divergence.

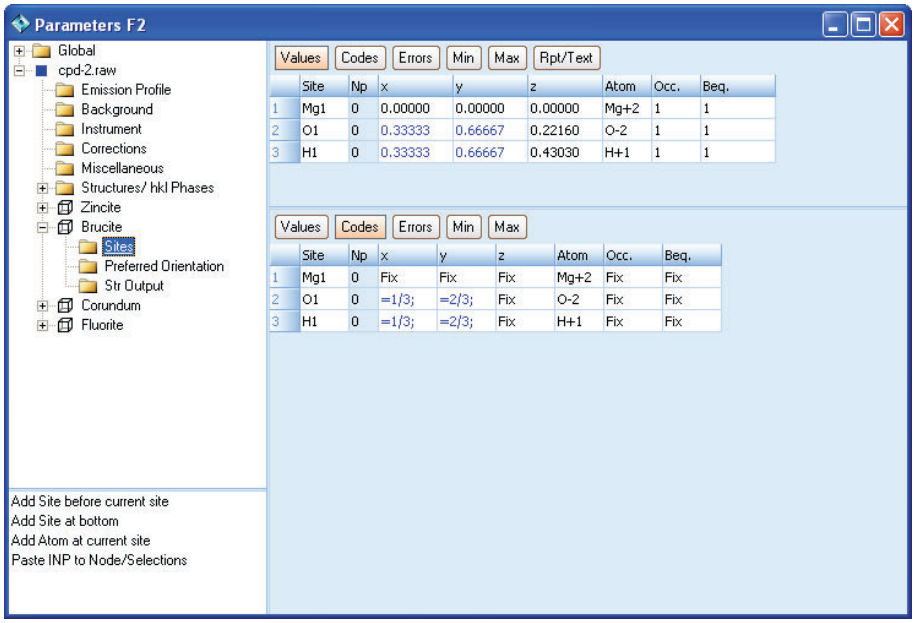
In the following exercise it will be demonstrated, how to deal with some typical problems associated with the use of inaccurate and incomplete third party structure data (provided in CIF format). Discussions include

- poor start values for scale factors,
- low quality lattice parameters, and
- missing temperature factors.

Finally it will be shown how to create new, high quality structure entries for TOPAS.

1. Repeat the refinement of the CPD-2 data from the very beginning. Carry out the steps 1 - 3 as in section 2.7.1.1, but finally load the CIF structure data provided for each phase instead by selecting *Load CIF(s)*.

2. Check the completeness and correctness of the imported structure data. Note, that fractional coordinates for special positions such as 1/3 and 2/3 (see Zincite and Brucite) must be provided in form of an equation, and not with re-occuring digits such as 0.3333 and 0.6667 as given in the CIF files.



Hint!	Fractional coordinates for special positions such as 1/3, 1/6, etc. are expected in the form of an equation such as = 1/3, =1/6, etc. in the *Codes* page, instead of values with re-occuring digits such as 0.3333..., 0.1666..., etc. in the *Values* page. The correct parameter value will be calculated automatically from the equation and displayed in blue color. **Not adhering to this convention may lead to severely wrong refinement results!**

3. The CIF data do not contain the following required information, which therefore has to be entered manually in the *Parameters Window*:

- Parameter attributes such as refinement codes (e.g. "Fix" or "Refine"). Therefore set the lattice parameters codes for all phases to "Refine".
- Preferred orientation model for Brucite. Select the March-Dollase model, enter the preferred orientation direction (0 0 1, blanks between each number are mandatory) and set the code of the March-Dollase parameter to "Refine".

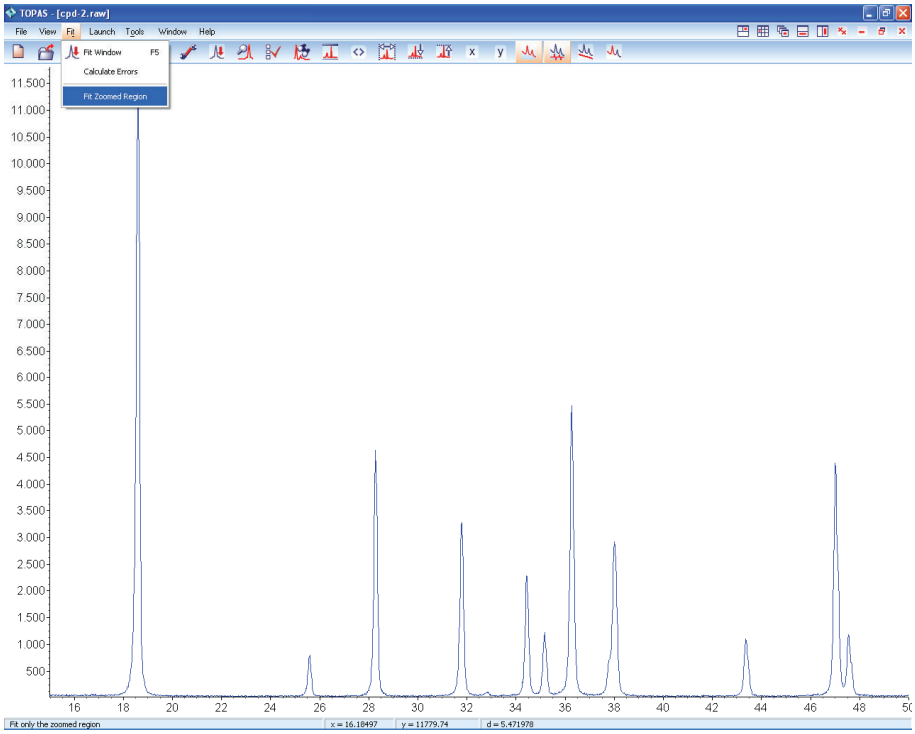
Note, that microstructure information is also not included in the CIF files - default models and default parameter values will be used by TOPAS. A review of these during and after refinement should be regarded as a matter of course.

4. To keep the refinement better under control,

- zoom into the 2θ region ranging from about 15 to 50° 2θ,

- uncheck the menu item *Fit Zoomed* in the *Fit* menu (this is mandatory, as otherwise only the zoomed region is fitted instead of the complete pattern), and
- perform a step by step refinement by clicking on the *Step* button in the *Fit Window*.

Menu:	Icon:	ShortCut:	Result:
n.a.		F7	Runs the refinement step by step



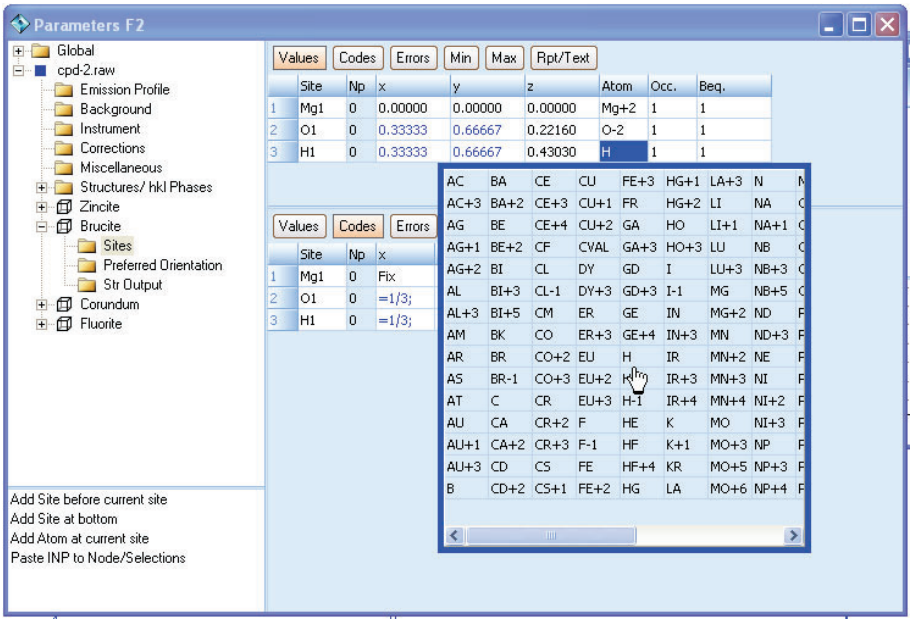
5. Perform a single refinement step.

TOPAS will stop calculations immediately and drop the following error message:

"Atom H+1 not found in atmscat.cpp"

This error is due to the fact, that crystal structure databases frequently provide the atom type "H+1" for Hydrogen. Even if chemically correct, the refinement can not proceed as X-ray scattering data don't exist for protons.
Therefore switch to the *Parameters Window*, expand the structure item for Brucite, select the *Sites* item and set the correct atomic scattering factors for Hydrogen (either enter the character "H" in the text box or select the atom type "H" from the drop down list).

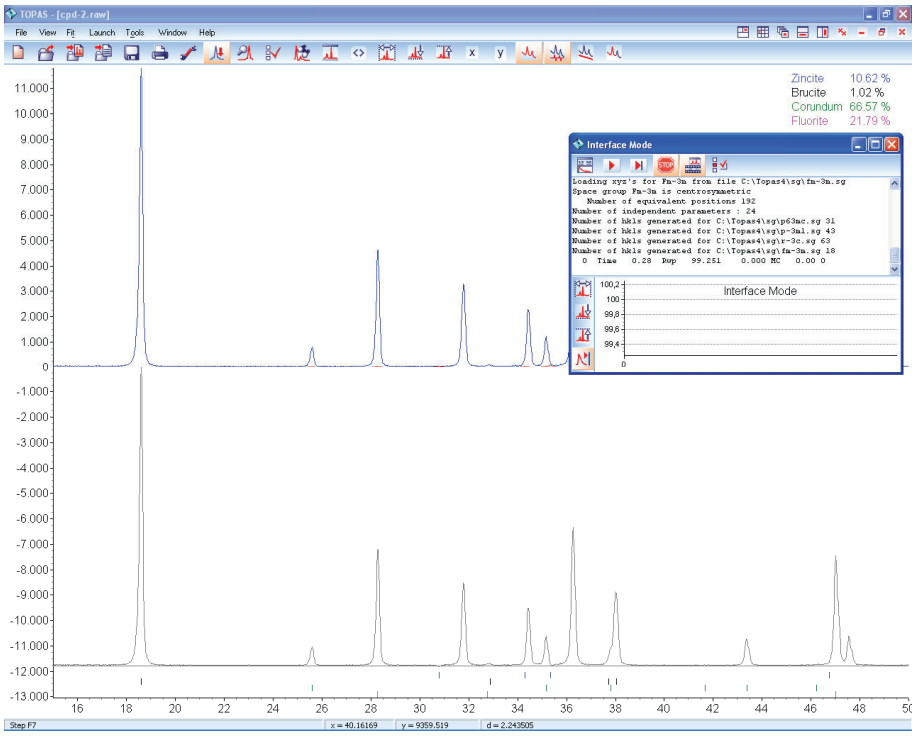
Note: Similar problems may also occur for other atom types. In addition - depending on the character of the bonds in your structure - it may be of concern to choose between atomic and ionic scattering factors.



6. Perform a single refinement step.

Inspect the calculated data in the *Scan Window*. As can be seen clearly, the calculated intensities for all phases are very low, which is due to the default values used for the scale factors.
Cancel the refinement and increase all scale factors from 1E-05 to 0.001.

Note: The purpose of scale factors is to scale the calculated intensities of each phase to the observed intensities of the pattern. It is therefore obvious, that scale factors are directly dependend on external factors such as the intensity of the X-ray beam and measurement time. Consequently it is impossible to provide default values for scale factors, which are globally valid.
Scale factors are linear and very stable parameters and can be off for even some orders of magnitude. However, additional refinement cycles will be required to bring the scale factors in, while complex refinements may become jeopardized. In any case poor scale factors hamper a visual check of the calculated data quality. It is therefore advisable not to stick with poor scale factors but to determine and to apply better start values before proceeding with the refinement.



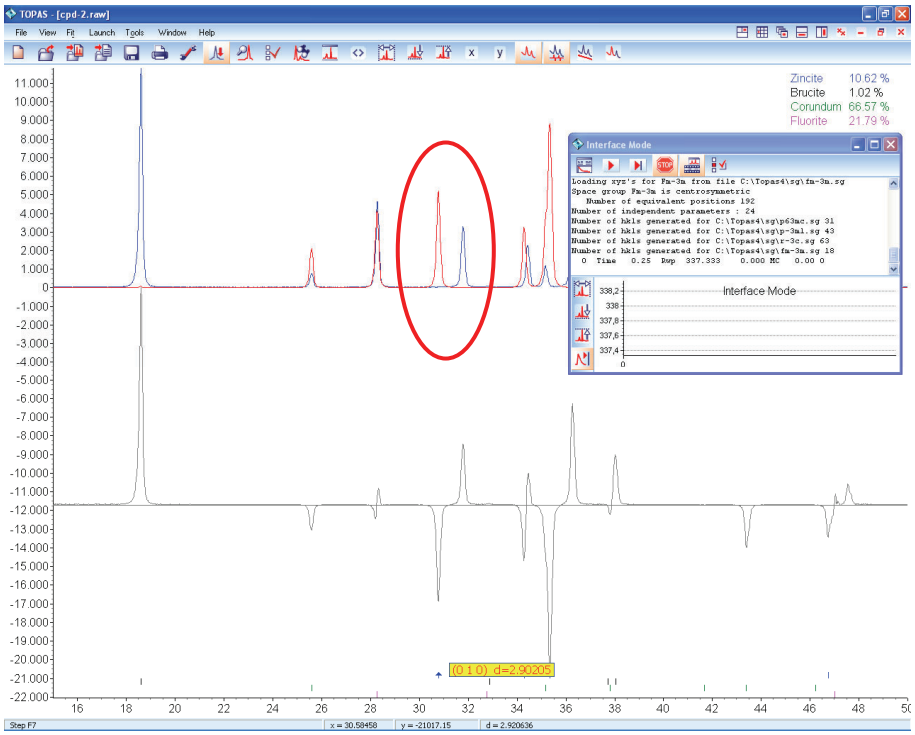
7. Restart the refinement by performing a single refinement step.

Inspect the calculated data in the *Scan Window*. As can be seen clearly, the calculated peak positions for the Zincite peaks are displaced up to 1° 2θ due to poor start values for the lattice parameters.
Continue the refinement step-wise and watch the behaviour of the Zincite peaks. It should be seen, that while the maximum peak intensities decrease the peaks broaden extremely (high risk of parameter divergence (!) as there is no peak intensity at the calculated peak positions). Fortunately the calculated peaks finally lock into the correct observed peaks and the refinement converges.

Note: Although the present refinement converged properly, it is not the recommended procedure to refine "on the off chance" as just demonstrated, but to find better start values. An elegant way is as follows, if there are no better structure data available:

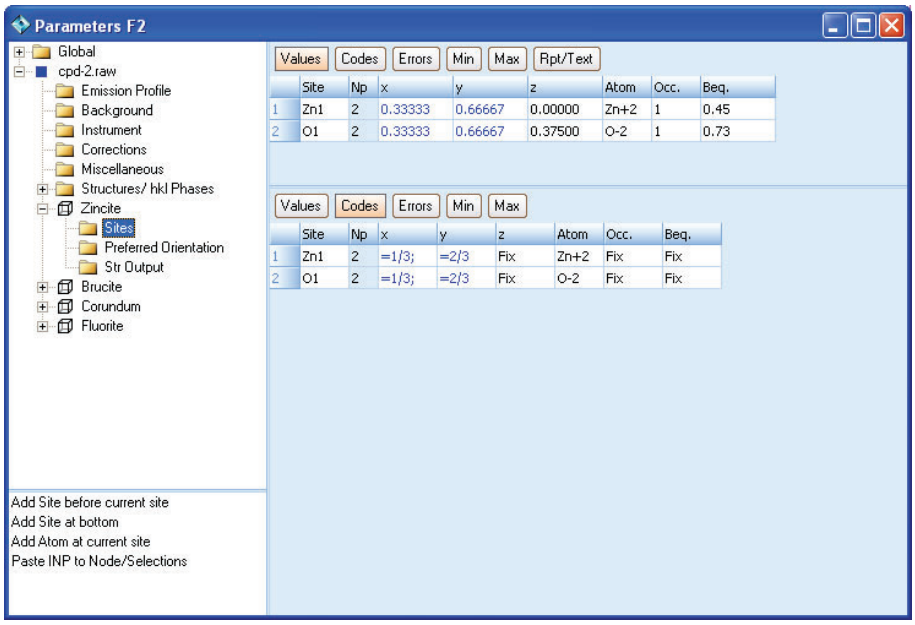
- Cancel the refinement
- Switch the X-axis scale to d-spacings (menu *View - X-Axis Scale - d-spacing*)
- Locate an h00 or 0k0 and an 00l peak and determine their d-values using the mouse cursor (the current mouse position is displayed in the status bar in terms of d).

In the present refinement the 100 / 010 peak at 31.7° 2θ (d ≈ 2.81) and the 002 peak at 34.4° 2θ (d ≈ 2.60) may be used. From these the following lattice parameters can be determined: a = 2.81 / sin(120) ≈ 3.245; b = 2.60 x 2 = 5.2.

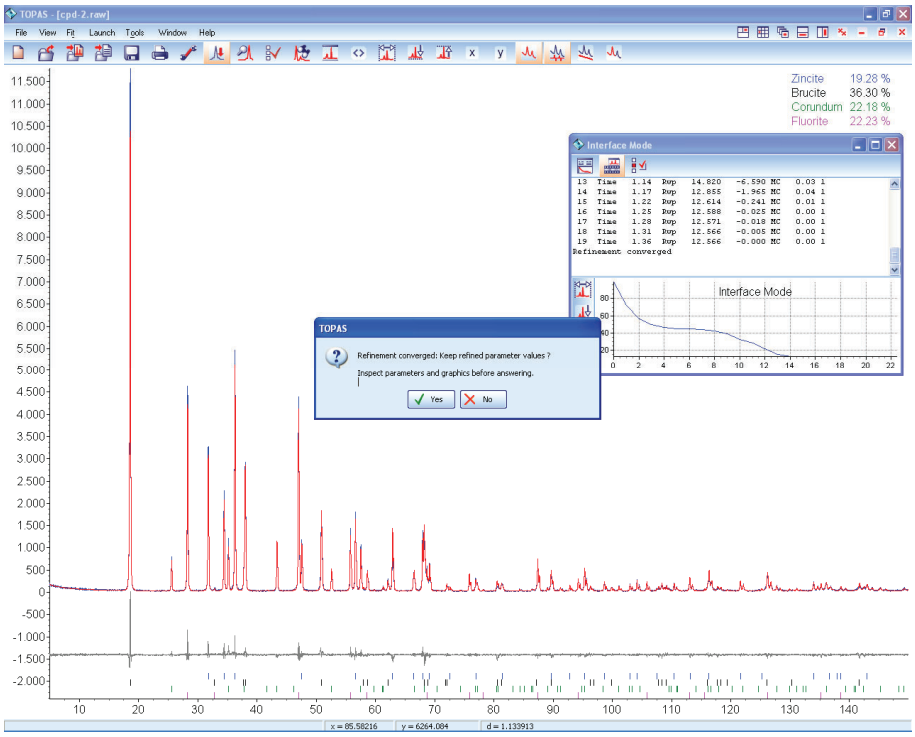


8. Inspect the quantification results. The accuracy obtained should be about ± 2 % in weight, which is worse compared to the previous refinement results in section 2.7.1.1.
As exactely the same background, instrument and microstructure models have been used, the reason for the worse results must be related to the crystal structure data used.
Inspect the CIF files (e.g. using a text editor). Note, that temperature factors are completely missing for all phases, forcing TOPAS to use default values (that is 1 $Å^2$).
Switch to the *Parameters Window* and select the *Sites* page for each phase. The temperature factors are located in the row headed with *Beq*. Adopt the temperature factors provided in the following list, which have been taken from the STR structure entries used in section 2.7.1.1

Brucite:	Mg:	0.43	O:	1.00	H:	1.00
Corundum:	Al:	0.32	O:	0.33		
Fluorite:	Ca:	0.41	F:	0.62		
Zincite:	Zn:	0.45	O:	0.73		



9. Restart the refinement and inspect the quantification results. Now the accuracy of your results should be about ± 1 % in weight.



Beside excellent quantification results also optimum structure data for each phase have been obtained. Of course these may be used to either modify / extent an existing TOPAS structure database or to create a new user structure database.

To save structure dependend refinement results as *.STR files proceed as follows:

10. Open the *Parameters Window*

11. Focus the *Structure* item you want to save as an *.STR file.

12. Select *Save Structure in STR format*

It is strongly recommended not to overwrite original structure entries coming with one of the TOPAS structure databases. Instead, always save your data in separate subdirectories, which can be freely named and located on any data carrier.

When keeping the following hints in mind, you will be able to build a structure database, which is unrivalled in performance and data quality:

- Whenever useful add meaningful parameter limits (*min* - *max* values) to each refineable parameter, in particular to lattice and microstructure parameters. Use your knowledge about your samples to ensure, that such limits are not too restrictive. Watch out for parameter values, which are coming close to or even clash with a limit (during and after refinement).
- Always set the refinement codes for lattice and microstructure parameters to "Refine", unless there is a clear reason not to do so.
- In contrast to this, for quantitative analysis, always set the refinement codes for atomic coordinates, occupancy and temperature factors to fix, unless there is a clear reason not to do so.
- In case of doubt the March-Dollase parameter and its refinement code should be set to 1 and "Fix", respectively, unless preferred orientation has always to be considered for the present phase.
  In general, needless refinement of preferred orientation may lead to strong parameter correllations (in particular with the scale factors of the other phases present in your sample), resulting in significant quantification errors.

If samples with similar phase abundances are to be evaluated frequently (e.g. for quality or process control), it should be considered to save a TOPAS project file (*.PRO) as well, and to include it into your structure database. Project files are ideal templates and allow very fast, easy, reliable and automatable quantifications. This is demonstrated for the OPC example in section 2.7.3.

2.7.2 Quantification of CPD-3

This excercise demonstrates how to quantify amorphous phase amounts using the spiking technique with Corundum as the spike phase (30.79%).

1. Start TOPAS
2. Load the raw data by importing the file CPD-3.RAW into your document. By default this file is located in C:\TOPAS4\TUTORIAL\QPARR.
3. Switch to the *Parameters Window*, expand the range item of CPD-3.RAW and perform the following tasks:
   - Focus the *Emission Profile* item and load the predefined emission profile CUKA5.LAM. By default this file is located in C:\TOPAS4\LAM.
   - Focus the *Background* item. Use a Chebychev polynomial of 5th order and the *1/X Bkg* function.
   - Focus the *Instrument* item and define the instrument settings according to the following two tables:

Equatorial Convolutions:		**Axial Convolutions:**	
Receiving Slit Width	☑	Full Axial Model	☑
FDS [1)] Shape, Angle	☑	Primary Soller	☑
		Secondary Soller	☑

Instrument Parameter:		**Value:**
Goniometer Radius	Primary:	173 mm
	Secondary:	173 mm
Receiving Slit Width	Width:	0.3 mm
FDS [1)] Shape, Angle	Angle:	1°
Soller Slits	Primary:	4.6°
	Secondary:	4.6°

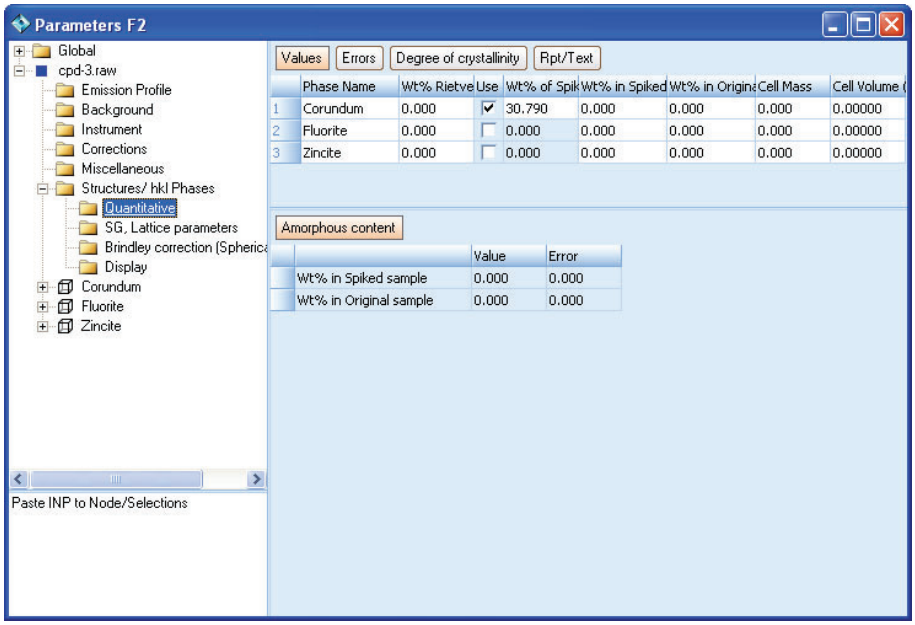
[1)] Fixed Divergence Slit

   - Focus the *Corrections* item. Check the *Zero error* and set its code to "Refine". In addition polarization effects coming from the secondary Graphite monochromator have to be accounted for. Therefore check *LP factor* as well and set the monochromator angle to 26.4° 2θ.
   - Focus the *Miscellaneous* item and set *Start X* to 24. This avoids the need to model the amorphous background bump.

- Focus the CPD-3.RAW range item and import the structure entries for the three phases Corundum, Fluorite, and Zincite (multi-selection is supported):

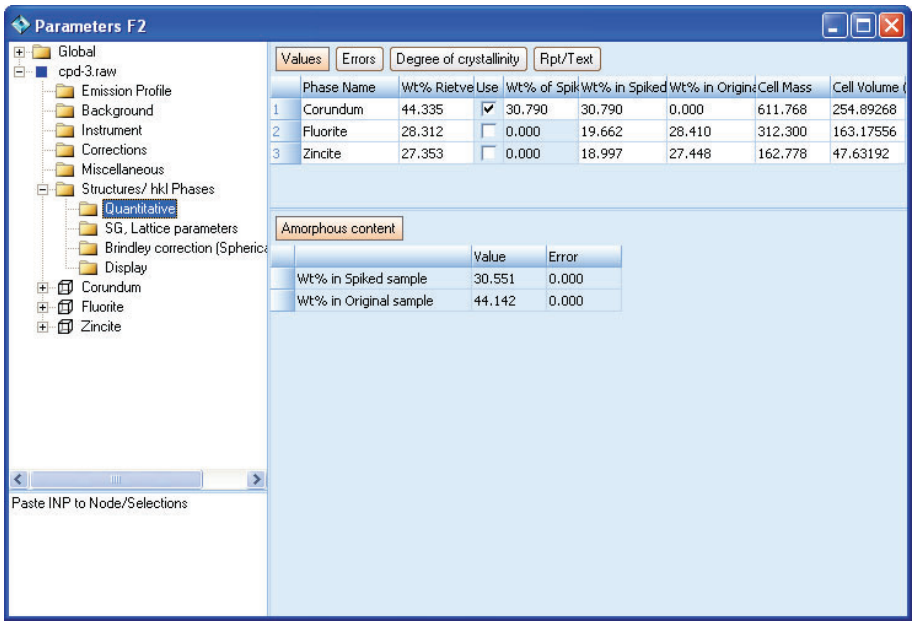
  1. CORUNDUM.STR
  2. FLUORITE.STR
  3. ZINCITE.STR

  By default these files are located in C:\TOPAS4\TUTORIAL\QPARR.
- Expand the *Structures/ hkl Phases* item and focus the *Quantitative* item. Define Corundum as a spike phase and enter its known phase amount (30,79%).



4. Run the refinement and inspect the quantification results. They are given as:

- *Wt% Rietveld* : Relative phase amounts of crystalline phases only
- *Wt% in Spiked sample* : Absolute phase amounts of all phases
- *Wt% in Original sample* : Absolute phase amounts of all phases in the original sample, i.e. without the spike phase



The expected ("true") values for the phase amounts in the spiked sample are given in the table below. The accuracy of your results should be about ± 1 % in weight.

CPD-2	Corundum [%]	Fluorite [%]	Zincite [%]	Glass [%]
Weighed	30,79	20,06	19,68	29,47
XRF	31,06	19,89	19,64	27,14

Note: Glass content underestimated by XRF due to presence of sodium (not measured) in glass.

2.7.3 Quantification of OPC

For this tutorial example the three ordinary portland clinkers RM 8486, RM 8487, and RM 8488 from NIST have been selected, as these reference materials are readily available and their phase composition is well known. Certified phase amounts have been determined by means of microscopic analysis. [1]

There are the following files at hand:

- Measurement data for all three clinkers: D8-8486.RAW, D8-8487.RAW, and D8-8488.RAW
- A predefined project file OPC.PRO containing all relevant structure entries for ordinary portland clinkers

The PRO file has been generated as described in section 2.7.1.1. It is assumed, that all structure entries have been optimized as demonstrated in section 2.7.1.2.

The qualitative phase composition of the clinkers is as follows:

RM	C3S	C2S	C3A	C4AF	MgO	Free Lime
8486	✓	✓	✓	✓	✓	
8487	✓	✓	✓	✓		✓
8488	✓	✓	✓	✓		

Perform a quantification of all clinkers.

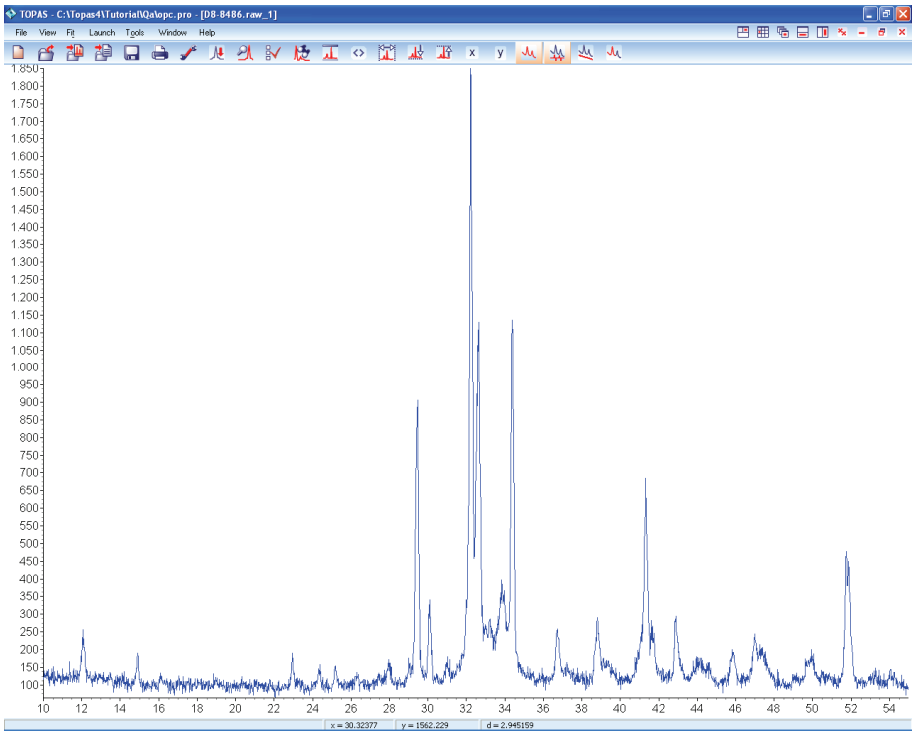
1. Start TOPAS and open the project file OPC.PRO. By default this file is located in C:\TOPAS4\TUTORIAL\QA.

Menu:	Icon:	Result:
File - *Open Project File...*		Opens a project file

In the *Scan Window* the measurement data for RM 8486 are displayed.

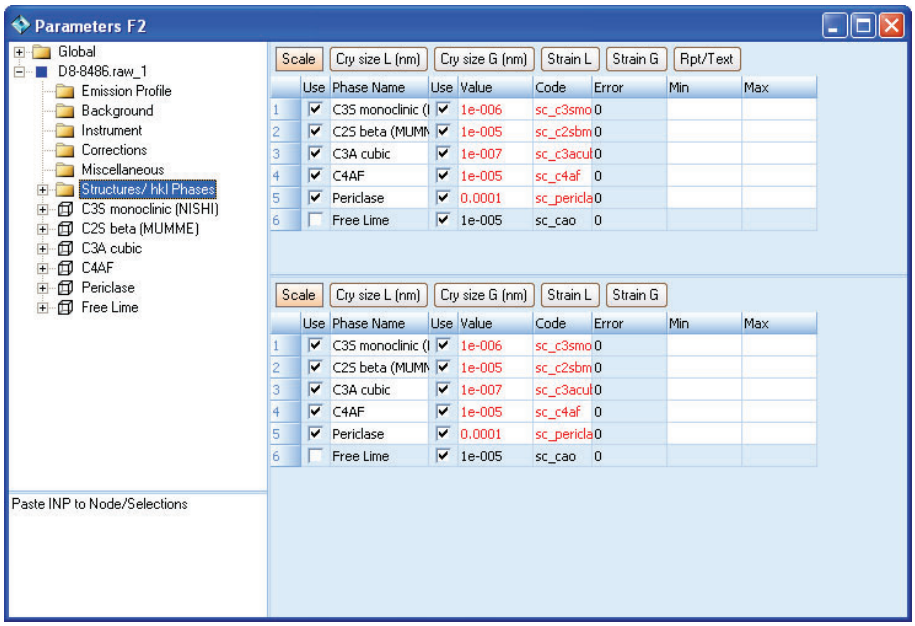
[1] More information about the NIST clinker (including on-line versions of the certificates) can be found in the internet using the following link:

http://www.nist.gov

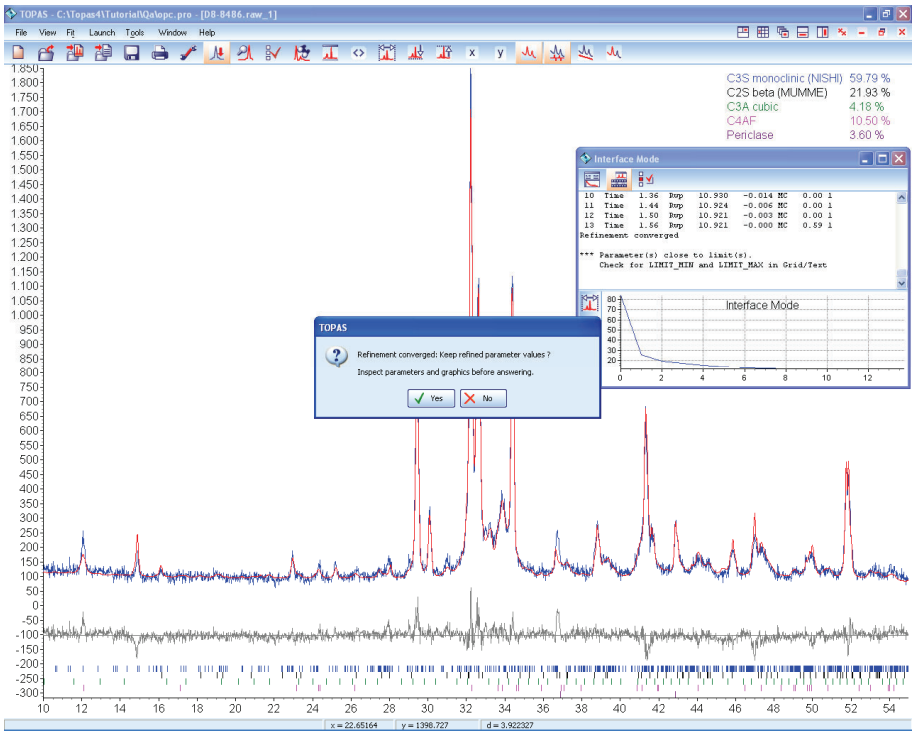


2. Switch to the Parameters Window and focus the *Structures/ hkl Phases* item.

Check the "Use" parameter for each phase to be quantified according to the qualitative phase composition as given above.

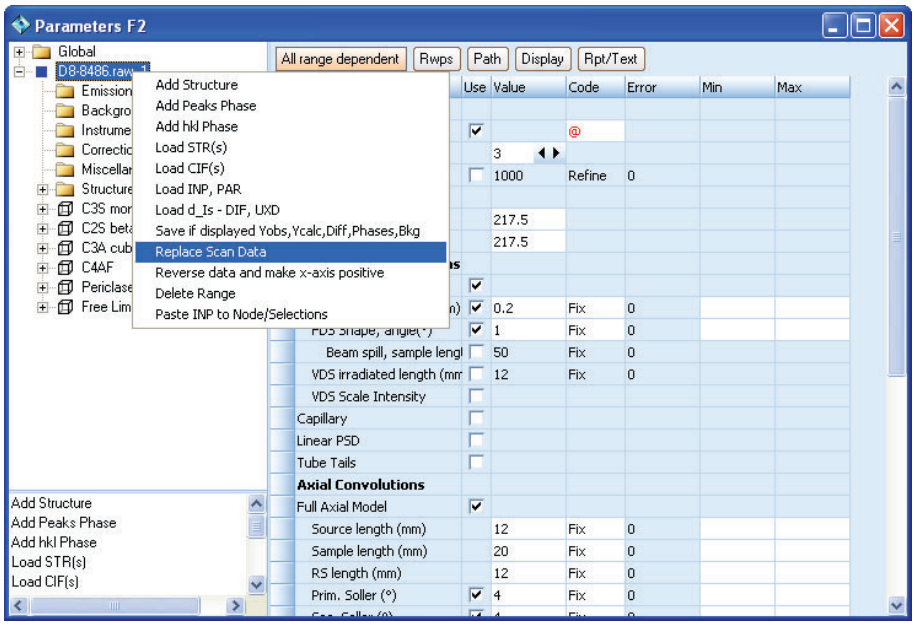


3. Start the refinement and note the refinement results.



4. Continue with the remaining clinker data from scratch.

- Select *File - New*
- Reload OPC.PRO
- Exchange the measurement data. Focus the range item of the current clinker data, select *Replace Scan Data* in the short cut menu, and load the next clinker data.
- proceed with steps 2 - 4.



Phase abundances as certified by NIST including estimated standard deviations σ (microscopical results) are given in the following three tables for all clinkers. Ideally your results should be within the ± 2σ range as provided in the last row of all tables.

RM 8486	NIST [%]	Error σ [%]	Range ± 2σ [%]
C3S	58,47	1,65	55,17 - 61,77
C2S	23,18	1,94	19,30 - 27,12
C3A	1,15	0,10	0,95 - 1,35
C4AF	13,68	0,63	12,42 - 14,94
MgO	3,21	0,72	0,49 - 5,93

RM 8487	NIST [%]	Error σ [%]	Range ± 2σ [%]
C3S	73,39	1,57	70,25 - 76,53
C2S	7,75	1,23	5,29 - 10,21
C3A	12,09	0,88	10,33 - 13,85
C4AF	3,27	0,70	1,87 - 4,67
Free Lime	2,45	0,48	1,49 - 3,41

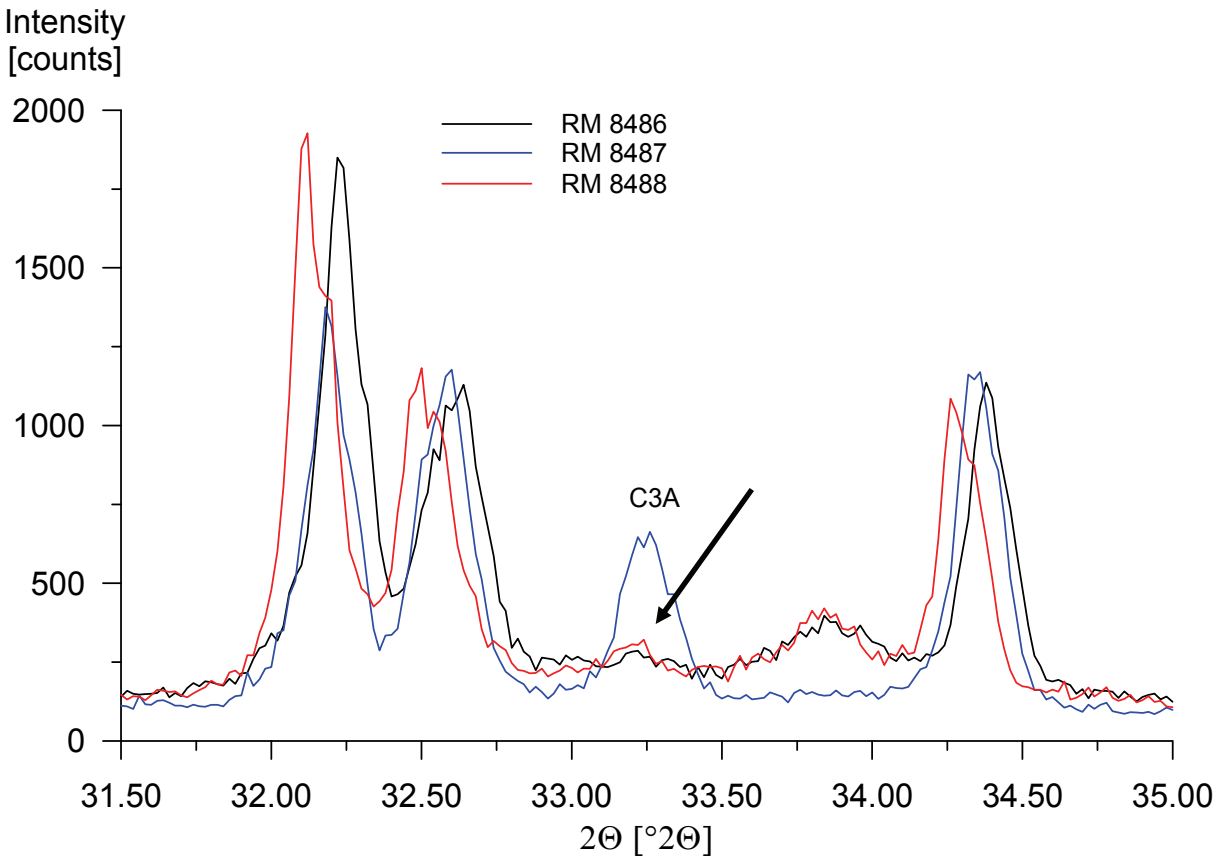
RM 8488	NIST [%]	Error σ [%]	Range ± 2σ [%]
C3S	64,97	0,56	63,85 - 66,09
C2S	18,51	0,58	17,35 - 19,67
C3A	4,23	1,35	1,53 - 6,93
C4AF	12,12	1,50	9,12 - 15,12

From your results the following should be seen:

- For all phases the accuracy of your results should be significantly better than +/- 3% with respect to the NIST certificate.
- For RM 8486 you should have obtained about 4.3 % C3A and 10.3 % C4AF. This significantly deviates from the certified NIST data.

Compare the C3A NIST data for all clinkers. Note the conspicuously low estimated standard deviation given for C3A in RM8486.

From a closer review of the XRD powder patterns in the figure below you should clearly see, that RM 8486 and RM 8488 must have a similar C3A content due to similar peak intensities (note the arrow pointing at the C3A peak). This is underlined by the high C3A peak intensity of RM 8487, which is consistent with the quantification results obtained by microscopy. Furthermore the sum of the interstitial phases for RM 8486 should be identical with your results, which also indicates, that your quantification results for C3A and C4AF are more reliable.

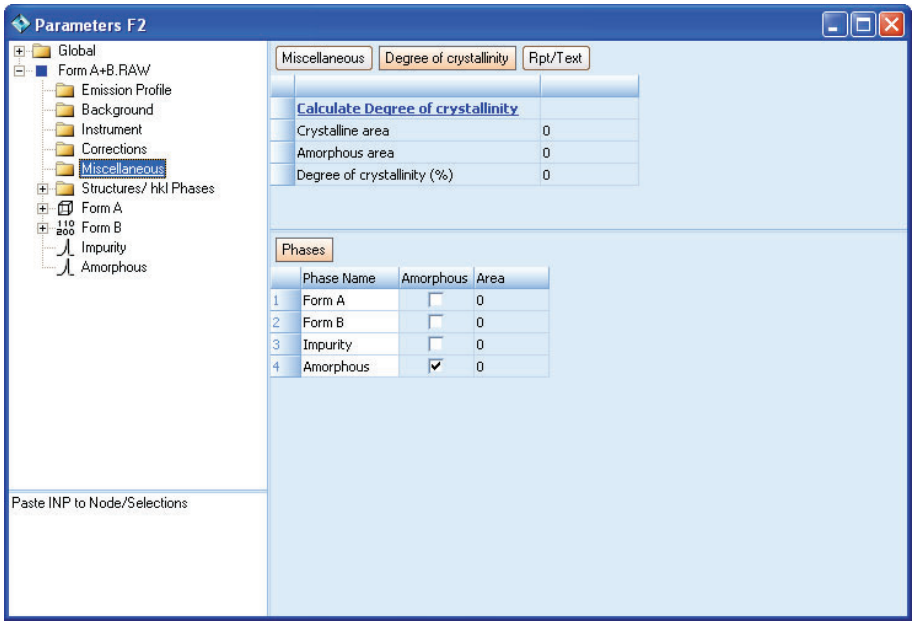


Comparison of C3A peak intensities for the NIST clinkers RM 8486, RM 8487, and RM 8488. Note the similar C3A intensities for RM 8486 and RM 8488.

3 MISCELLANEOUS

3.1 Degree of Crystallinity Determination

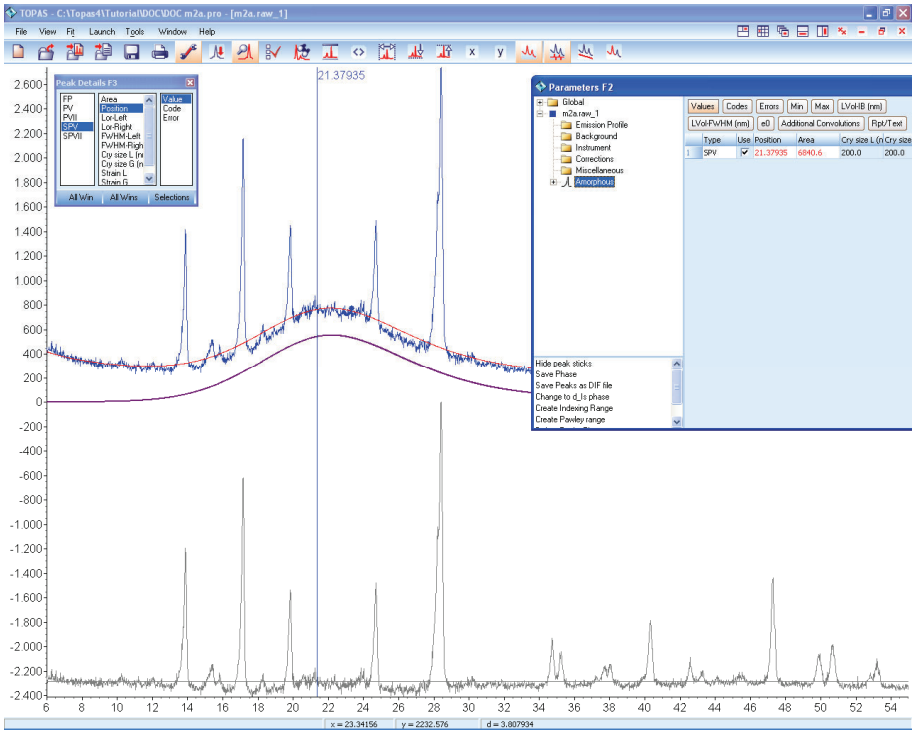
Degree of crystallinity calculations require the definition of at least two phases to describe the intensity contributions coming from the crystalline and the amorphous parts of the sample. *Peak Phases* (single line fitting), *hkl Phases* (Pawley and Le Bail fitting) and *Structures* (Rietveld refinement) can be used in any combination; the number of phases used for modeling both crystalline and amorphous contributions is not limited.



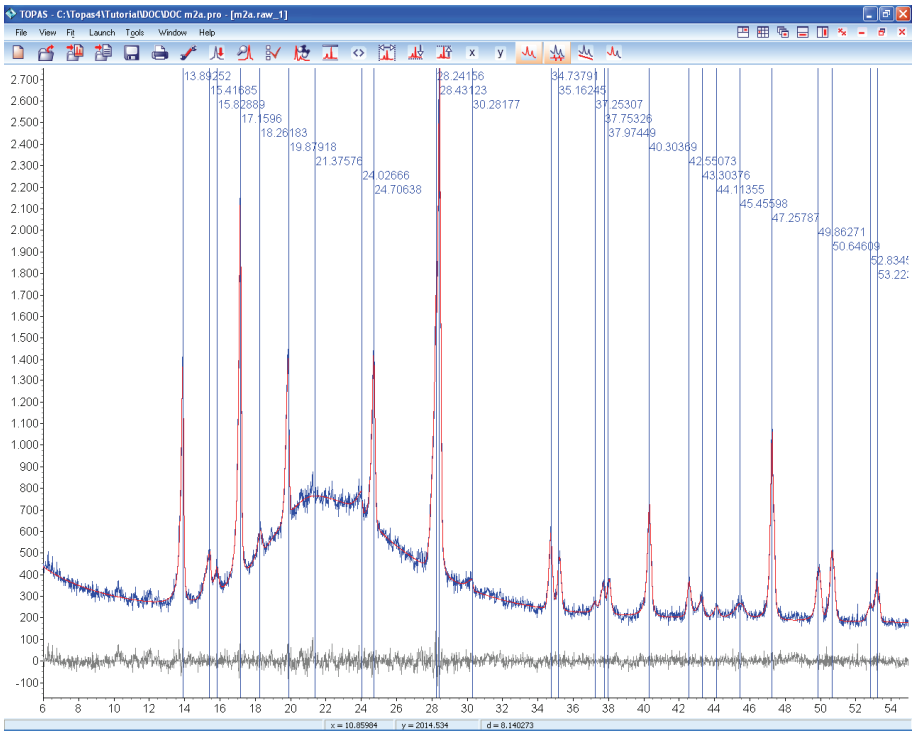
Hint!	Note, that degree of crystallinity calculations are only performed on demand; results are not automatically updated, if the refinement is continued!

3.1.1 Single line fitting of a polymer

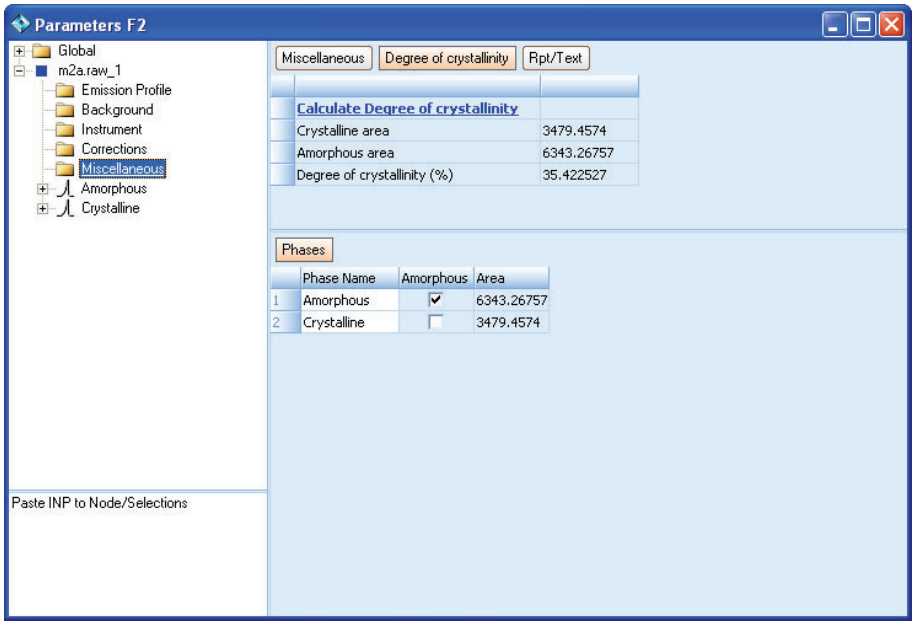
1. Start TOPAS
2. Load the raw data by importing the file M2A.RAW into your document. By default this file is located in C:\TOPAS4\TUTORIAL\DOC.
3. Focus the *Emission Profile* item and load the predefined emission profile CUKA2_ANALYT.LAM. By default this file is located in C:\TOPAS4\LAM.
4. Focus the *Background* item. Use a Chebychev polynomial of 1st order and the *1/X Bkg* function.
5. Firstly model the large amorphous bump. Insert a SPV peak at its peak maximum, rename the phase to "Amorphous" for more clarity, and start the refinement.



6. Next model the peaks coming from the crystalline phase.
   - Focus the range item for m2a.raw, select *Add Peaks Phase*, and rename the phase to "Crystalline". Make sure that this range items keeps the focus.
   - Insert a peak for each reflection. It is recommended to fit reflections with high intensites first, and to include the smaller reflections step by step.



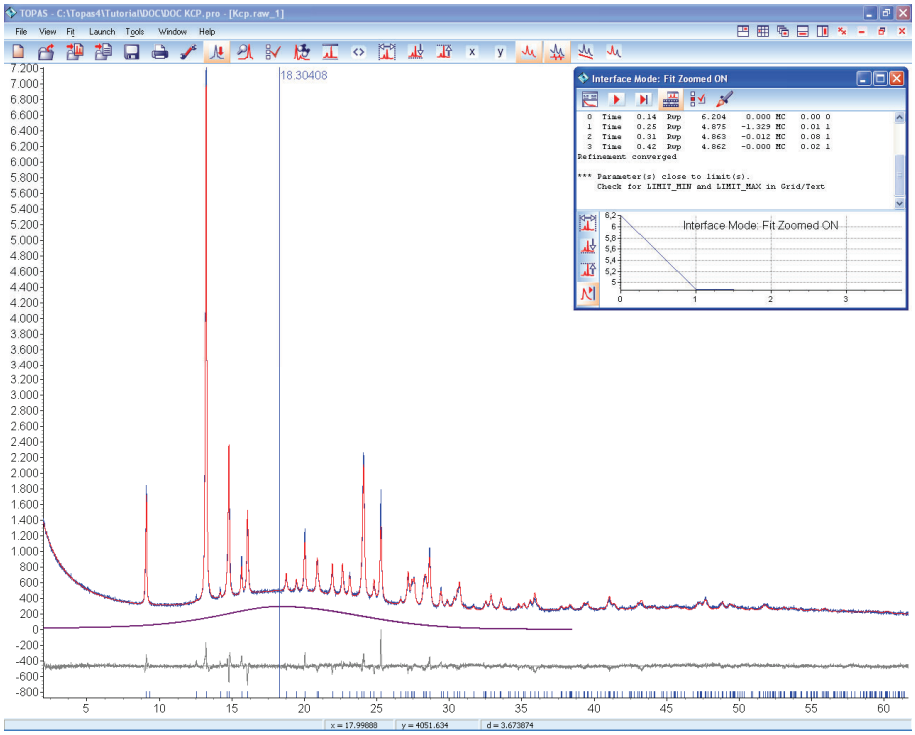
7. Focus the *Miscellaneous* item and select the *Degree of crystallinity* page. Define the amorphous phase and click on *Calculate Degree of crystallinity*.



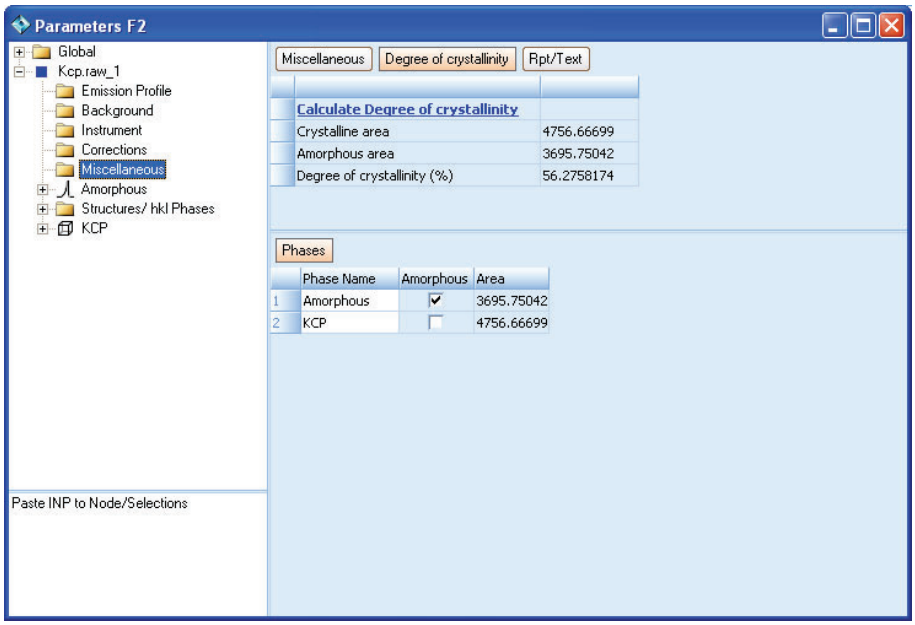
3.1.2 Combined Rietveld refinement / single line fitting of KCP

Not available in TOPAS P.

1. Start TOPAS and open the project file DOC KCP.PRO. By default this file is located in C:\TOPAS4\TUTORIAL\DOC.
2. Inspect the *Parameters Window*. It can be seen, that the crystalline phase KCP has been modelled using Rietveld structure refinement, while the amorphous background is described by a single SPV peak.



3. Focus the *Miscellaneous* item and select the *Degree of crystallinity* page. Define the amorphous phase and click on *Calculate Degree of crystallinity*.


Parameters F2
Global
Kcp.raw_1
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Amorphous
Structures/ hkl Phases
KCP
Paste INP to Node/Selections
Miscellaneous
Degree of crystallinity
Rpt/Text
Calculate Degree of crystallinity
Crystalline area 4756.66699
Amorphous area 3695.75042
Degree of crystallinity (%) 56.2758174
Phases
Phase Name Amorphous Area
1 Amorphous 3695.75042
2 KCP 4756.66699

3.2 Isotropic Size-Strain analysis

This lesson demonstrates the TOPAS convolution approach by accurately fitting all of the CeO_2 data made available as part of the size-strain round robin conducted by the IUCr CPD [1] (Balzar, 2001):

- laboratory X-ray data (D8 ADVANCE, Bruker AXS) [2]
- synchrotron X-ray data (NSLS X3B1, ESRF BM16)
- CW neutron data (ILL D1A, NCNR BT1)

A detailed description of the TOPAS convolution approach and its application to the round robin data is provided in the Users Manual, which should be read in conjunction with the present lesson.

Tutorial files (located in C:\TOPAS4\TUTORIAL\SIZESTRAIN by default) include two datasets from each instrument; one well crystallized specimen to determine the instrument functions ("sharp data") and one specimen exhibiting strong specimen broadening ("broad data"). Also provided are worked out PRO files for all datasets.

The following procedures will use the laboratory X-ray data as example adressing both, single line fitting as well as whole pattern fitting methods (WPPF, WPPD, and Rietveld refinement; the principles are always the same). All other datasets can be evaluated similarily. For peculiarities such as source emission profiles inspect the respective tutorial files.

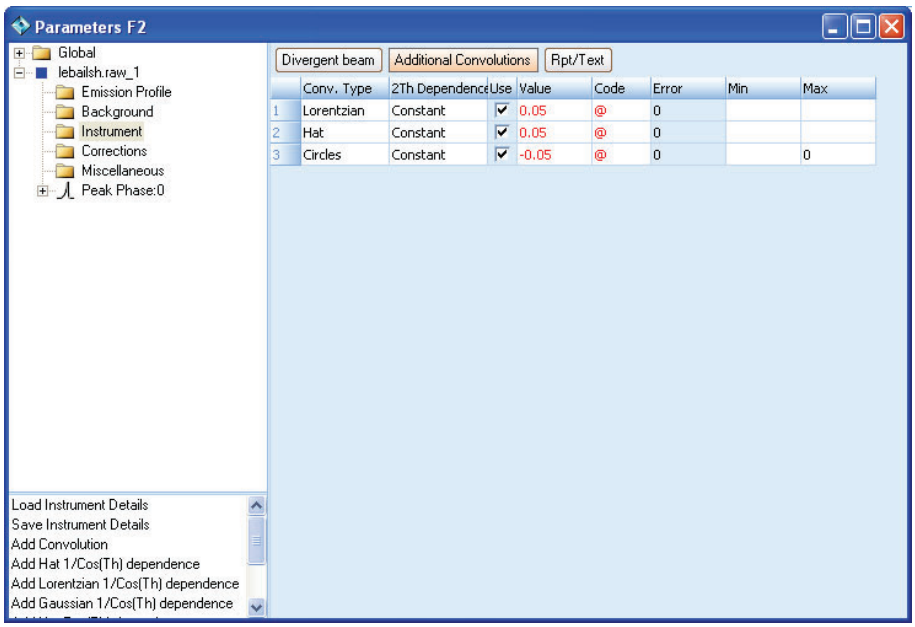
[1] International Union of Crystallography, Commission on Powder Diffraction

[2] As a result of sample displacement and a probably uneven sample surface (see Balzar, 2001), the data are affected by non-trivial 2θ and intensity deviations. The 2θ deviations are too complex to be treated by zero error or sample displacement corrections, but this can be ignored as far as the purpose of this tutorial is concerned. As the intensity errors dont allow for reliable Rietveld structure refinement, WPPD (Pawley fitting) is applied.
Also noted is a deviation of the $K\alpha_1/K\alpha_2$ ratio due to a slight miss-setting of the secondary monochromator, which is actually about 0.48 instead of about 0.51.

3.2.1 Empirical parameterisation of line profile shapes

Single line fitting:

1. Load the file LeBailSh.RAW and use the CuKa5 emission profile.
2. Zoom the first reflection in the region between 27.5° - 29.5° 2θ.
3. Insert a FP peak. Focus the *Peak Phase* item, select the *Code* page and disable *Cry Size L*; this parameter will not be used here as it does not have a (physical) meaning when fitting empirically.
4. Select the *Additional Convolutions* page.
   - As the line profile shape is obviously Lorentzian, add a *Lorentzian* type convolution and set its code to "Refine". Fit and inspect the data.
   - To broaden the calculated peak, add a *Hat* type convolution and set its code to "Refine". Fit and inspect the data.
   - To account for asymmetry, add a *Circles* type convolution and set its code to "Refine". As the asymmetry is towards low angles, set the value to -0.05, and constrain it to negative values by setting its maximum value to 0. Fit and inspect the data.

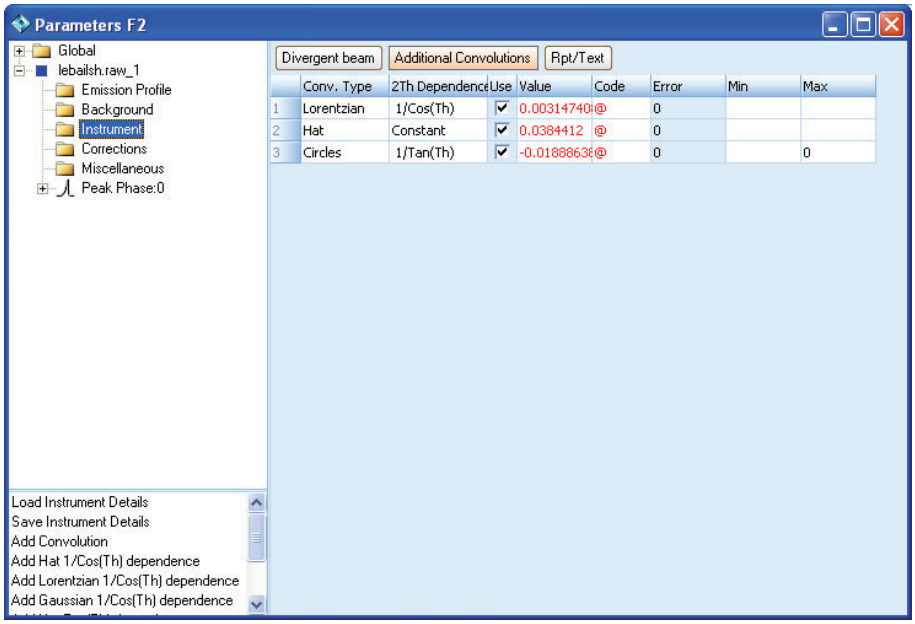


Whole powder pattern fitting:

To account for the angular dependence of peak shapes, the 2θ dependence of the different convolutions needs to be defined. Continue with the first example.

5. Use the entire pattern and insert a FP peak for each observed reflection.
6. Focus the *Background* item and select both a 2nd order polynomial and the *1/X Bkg* function.

7. Focus the *Peak Phase* item, select the *Code* page and disable *Cry Size L* for all peaks.
8. Fit the data.
9. Select the *Additional Convolutions* page.
   - For modelling crystallite size broadening towards high angles define the 2θ dependence of the *Lorentzian* convolution as 1/cos(Th). Fit and inspect the data.
   - To account for asymmetry, which is mainly due to axial divergence effects, define the 2θ dependence of the *Circles* convolution as 1/Tan(Th). Fit and inspect the data.



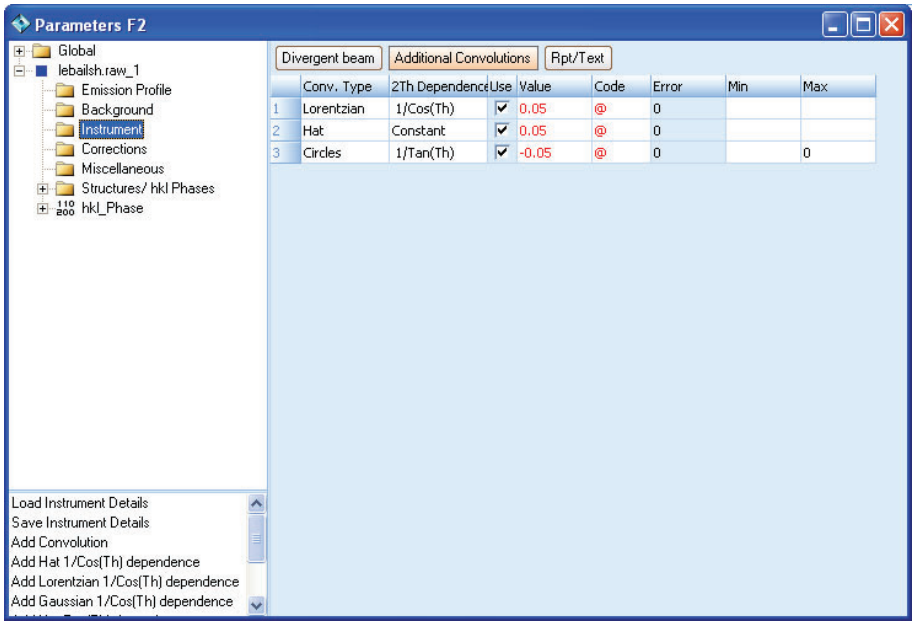
Whole powder pattern decomposition:

1. Load the file LeBailSh.RAW and use the CuKa5 emission profile.
2. Focus the *Background* item and select both a 2nd order polynomial and the *1/X Bkg* function.
3. Account for the 2θ deviations mentioned above.
   - Focus the *Corrections* page, select the sample displacement error and set its *Code* to "Refine".
   - Focus the *Miscellaneous* page and set *Finish_X* to about 100° 2θ.
4. Insert a hkl_I phase. Input the crystallographic data given below in the *Phase Details* page and refine on the lattice parameter. Disable *Cry Size L*; this parameter will not be used here as it does not have a (physical) meaning when fitting empirically.

Crystallographic Data for CeO_2:		
Space group		Fm3m
Cell parameter	a (Å)	5.41

5. Select the *Additional Convolutions* page.

- As the line profile shape is obviously Lorentzian, add a *Lorentzian* type convolution and set its code to "Refine". For modelling crystallite size broadening towards high angles, define the 2θ dependence of the *Lorentzian* convolution as 1/cos(Th). Fit and inspect the data.
- To broaden the calculated peak, add a *Hat* type convolution and set its code to "Refine". Fit and inspect the data.
- To account for asymmetry, add a *Circles* type convolution and set its code to "Refine". As the asymmetry is towards low angles, set the value to -0.05, and constrain it to negative values by setting its maximum value to 0. Fit and inspect the data.



3.2.2 Discrimination of instrument and specimen contributions

This lesson demonstrates size/strain analysis using both measured and calculated (FPA) instrument functions. The procedures are identical for single line fitting as well as for whole pattern fitting methods (WPPF, WPPD, and Rietveld refinement).

3.2.2.1 Measured instrument functions

The "sharp" data taken from the well crystallized specimen will be used to determine the measured instrument function.

1. Load the file LeBailSh.RAW.
2. Empirically parameterise the profile shapes as described in section 3.2.1, but use the *Additional Convolutions* page of the *Instrument* item to define the required convolutions. After refinement fix all convolution parameters, which are now representing the instrument function.
3. Focus the range item of LeBailSh.RAW, select *Replace Scan Data* in the short cut menu and load the file LeBailBr.RAW.
4. Refine on Cry Size L, Cry Size G, Strain L and Strain G (for single line fitting refine on isotropic parameters). Also calculate LVol-IB and e0, which should refine to about 23 ±1 nm and 0.007 ±0.003, respectively.

3.2.2.2 Fundamental parameters approach

With fundamental parameters the instrument function is calculated from first principles, therefore the "sharp" data are not needed.

1. Load the file LeBailBr.RAW.
2. Perform a single line or whole pattern fit using the following instrument settings:

Instrument Parameter:		**Value:**
Goniometer Radius	Primary:	217.5 mm
	Secondary:	217.5 mm
RS	Width:	0.1 mm
FDS	Angle:	1°
Soller Slits	Primary:	2.3°
	Secondary:	2.3°

Refine on Cry Size L, Cry Size G, Strain L and Strain G (for single line fitting refine on isotropic parameters). Also calculate LVol-IB and e0, which should refine to about 23 ±1 nm and 0.007 ±0.003, respectively.

3.3 Using the rigid body editor

Not available in TOPAS P.

The *Rigid Body Editor* provides for easy and intuitive creation and editing of rigid bodies, which are to be defined in INP format as described in the Technical Reference manual.

Rigid bodies comprise points in space defined using either the *point_for_site* or *z_matrix* keywords or both simultaneously. All or some of these points can then be operated on using the *rotate* and *translate* keywords.

The directory C:\TOPAS4\RIGID contains many rigid body examples in *.RGD files. These files can be viewed and modified using the *Rigid Body Editor*.

3.3.1 Creation of rigid bodies

3.3.1.1 Fractional or cartesian coordinates

The most basic means of setting up a rigid body is by means of fractional or Cartesian coordinates. To formulate e.g. a ZrO_6 octahedron enter the following keyword sequence in the *Editor*:

```
rigid
   point_for_site Zr
   point_for_site O1 ux =  2;
   point_for_site O2 ux = -2;
   point_for_site O3 uy =  2;
   point_for_site O4 uy = -2;
   point_for_site O5 uz =  2;
   point_for_site O6 uz = -2;
```

Update the *Main View* after each *point_for_site* statement to monitor the building of the rigid body.

This keyword sequence can be read in English, as follows:

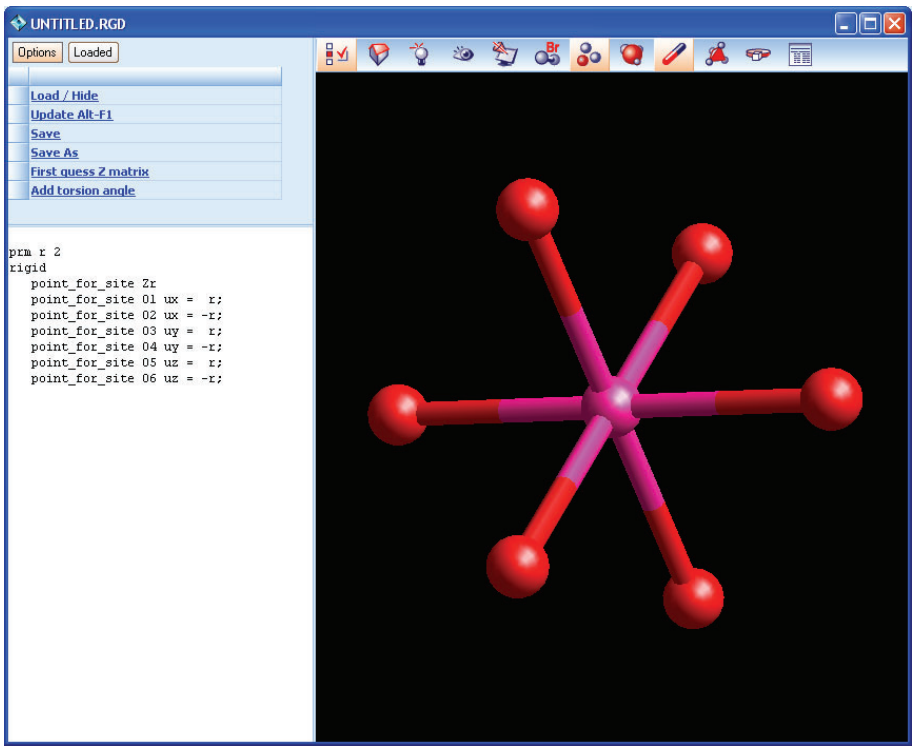
Define a rigid body
Place the Zr atom at 0, 0, 0
Place the O1 atom at 2, 0, 0
Place the O2 atom at -2, 0, 0
Place the O3 atom at 0, 2, 0
...

For a more general definition of this octahedron, which allows the easy refinement of the Zr-O distance, consider the following:

```
prm r 2
rigid
   point_for_site Zr
   point_for_site O1 ux =  r;
   point_for_site O2 ux = -r;
   point_for_site O3 uy =  r;
   point_for_site O4 uy = -r;
   point_for_site O5 uz =  r;
   point_for_site O6 uz = -r;
```

This keyword sequence can be read in English, as follows:

Define a distance parameter r with a value of 2
Define a rigid body
Place the Zr atom at 0, 0, 0
Place the O1 atom at r, 0, 0
...



3.3.1.2 Z-matrix representation

Rigid bodies can also be described using an internal coordinate description using a Z-matrix representation. Here a rigid body is built up atom-by-atom using a series of distance, angle, and torsion specifications.

A Z-matrix representation of the ZrO_6 octahedron discussed in section 3.3.1.1 can be formulated, as follows:

```
prm r 2
rigid
   z_matrix Zr
   z_matrix O1    Zr =r;
   z_matrix O2    Zr =r;    O1 90
   z_matrix O3    Zr =r;    O1 90    O2 90
   z_matrix O4    Zr =r;    O1 90    O2 180
   z_matrix O5    Zr =r;    O1 90    O2 270
   z_matrix O6    Zr =r;    O1 180   O2 0
```

Update the *Main View* after each *z_matrix* statement to monitor the building of the rigid body.

This Z-matrix can be read in English, as follows:

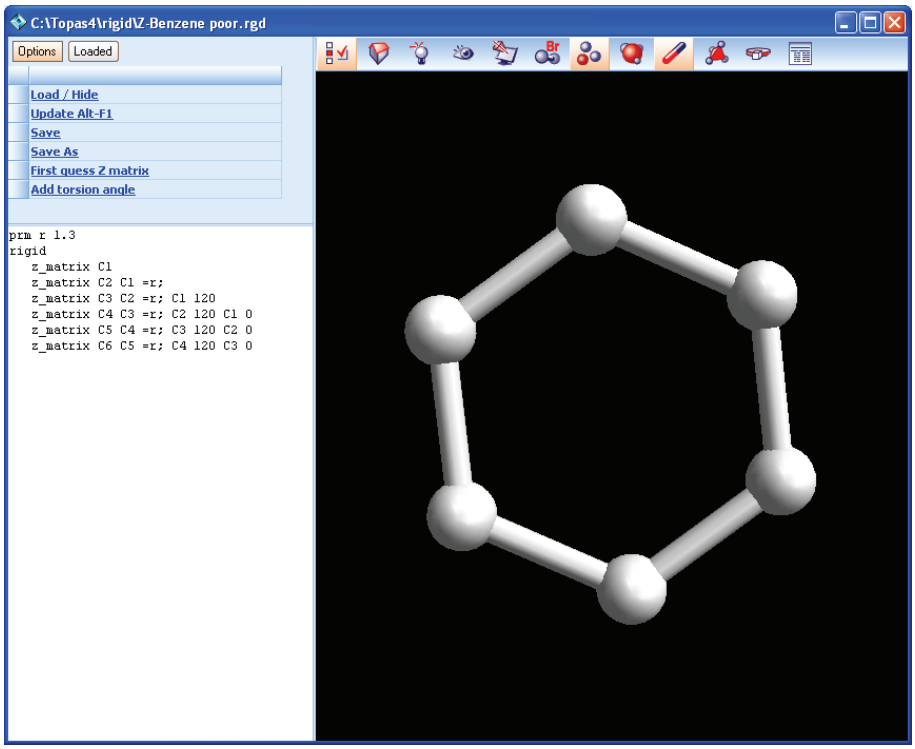
Define a distance parameter r with a value of 2
Define a rigid body
Place Zr at 0, 0, 0
Place O1, at a distance of r away from Zr
Place O2, at a distance of r away from Zr,
making an angle of 90 with Zr and O1
Place O3, at a distance of r away from Zr,
making an angle of 90° with Zr and O1,
and making a torsion of 90° with Zr, O1 and O2
...

It should be apparent from this example, that there are many different ways of defining a Z-matrix, e.g. by starting with a different atom at the origin.

The Z-matrix representation is of particular advantage for describing molecules, consider the following example constituting a Benzene ring:

```
prm r 1.3
rigid
   z_matrix C1
   z_matrix C2   C1 =r;
   z_matrix C3   C2 =r;   C1 120
   z_matrix C4   C3 =r;   C2 120  C1 0
   z_matrix C5   C4 =r;   C3 120  C1 0
   z_matrix C6   C5 =r;   C4 120  C1 0
```

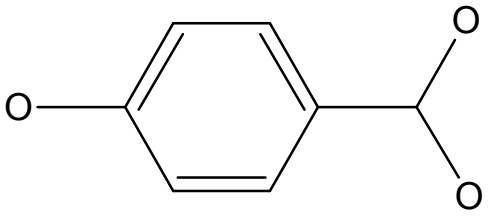
Update the *Main View* after each *z_matrix* statement to monitor the building of the rigid body.



3.3.2 Creation of rigid bodies from published crystal structures

A formulation of any complexity can be obtained from databases of existing structures by simply using fractional or Cartesian coordinates of structure fragments. This also includes output from sketch programs for drawing chemical structures, if fractional or Cartesian coordinates are provided.

Consider the following structure fragment (*para*-hydroxybenzoate), hydrogens will be ignored for simplicity:



A paper describing a structure with a *para*-hydroxybenzoate group is e.g. Dinnebier et al. (1999). The following fractional coordinates are given in this paper for the individual atoms forming the *para*-hydroxybenzoate group:

	x	y	z
O1	0.5255	0.243	0.871
C1	0.6106	0.256	0.842
C2	0.6458	0.463	0.681
C3	0.6613	0.063	0.973
C4	0.7317	0.477	0.652
C5	0.7472	0.077	0.943
C6	0.7824	0.284	0.783
C7	0.8741	0.298	0.752
O2	0.9091	0.511	0.692
O3	0.9179	0.104	0.83

As fractional coordinates are dependent on lattice parameters, it is necessary to convert them into Cartesian coordinates. It is suggested to perform this convertion before defining the rigid body, but it can also be done within TOPAS on the fly (as shown below).

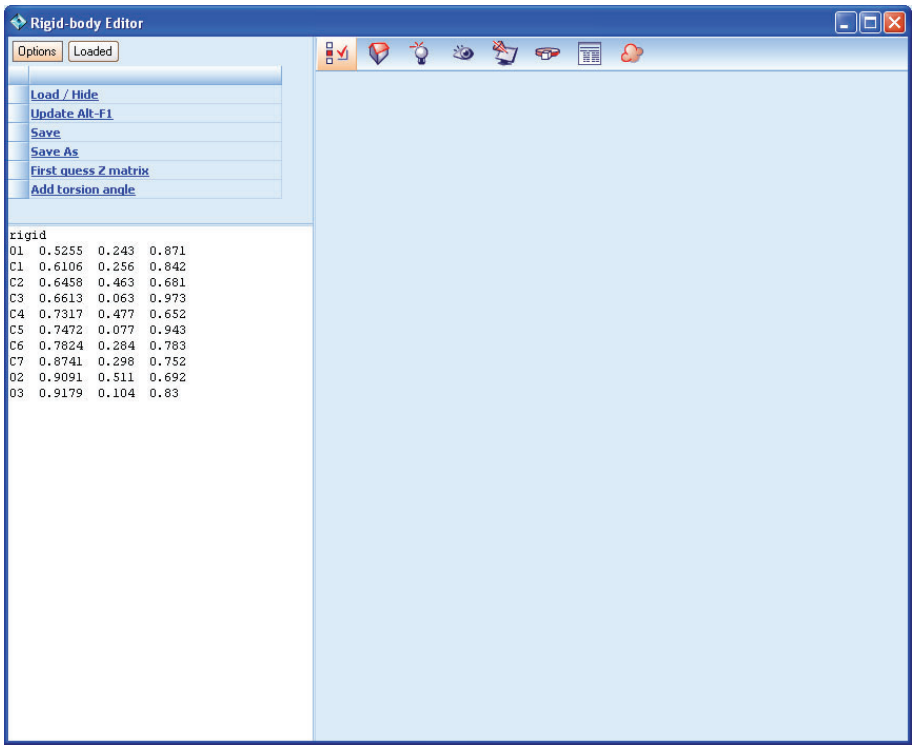
Lattice parameters a, b, c given by Dinnebier et al. (1999) are

```
a (Å) 16.0608
b (Å)  5.38291
c (Å)  3.63834
```

Cartesian coordinates are obtained from fractional coordinates x, y ,z by multiplying them with the respective lattice parameter a, b, c.

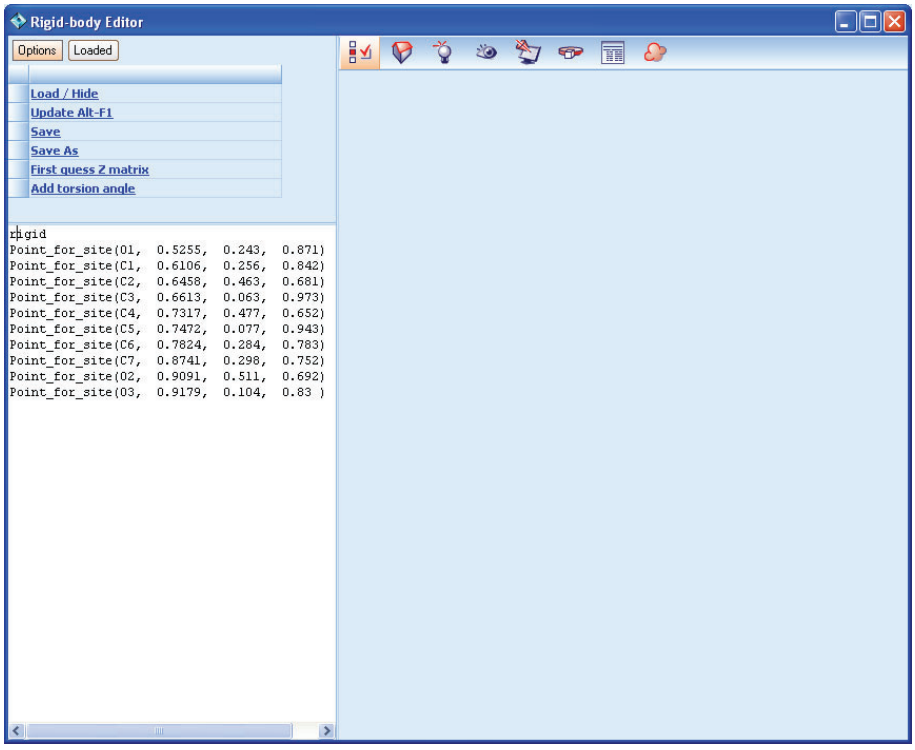
A rigid body for *para*-hydroxybenzoate can be defined in the *Rigid Body Editor* as follows:

1. In the *Editor* window define a rigid body using the *rigid* keyword and input the *para*-hydroxybenzoate structure details as listed above.



2. Use the *Point_for_site* macro to define points in space for each atom:

```
O1, 0.5255, 0.243, 0.871    ⇨   Point_for_site(O1, 0.5255, 0.243, 0.871)
C1, 0.6106, 0.256, 0.842    ⇨   Point_for_site(C1, 0.6106, 0.256, 0.842)
...
```



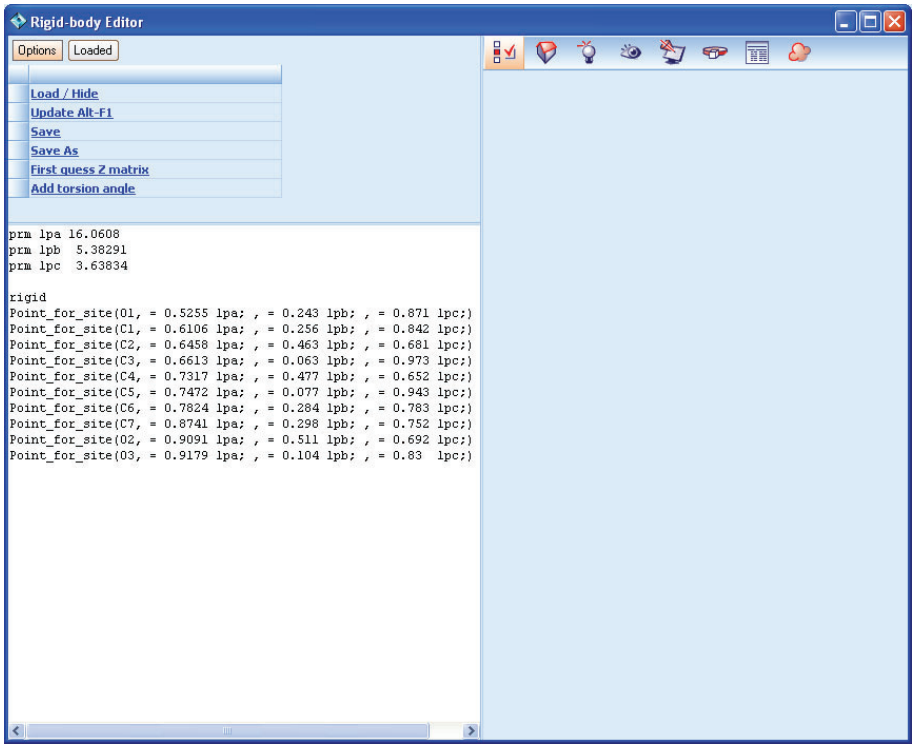
3. Convert the fractional coordinates into Cartesian coordinates:

- Define 3 parameters representing the lattice parameters:

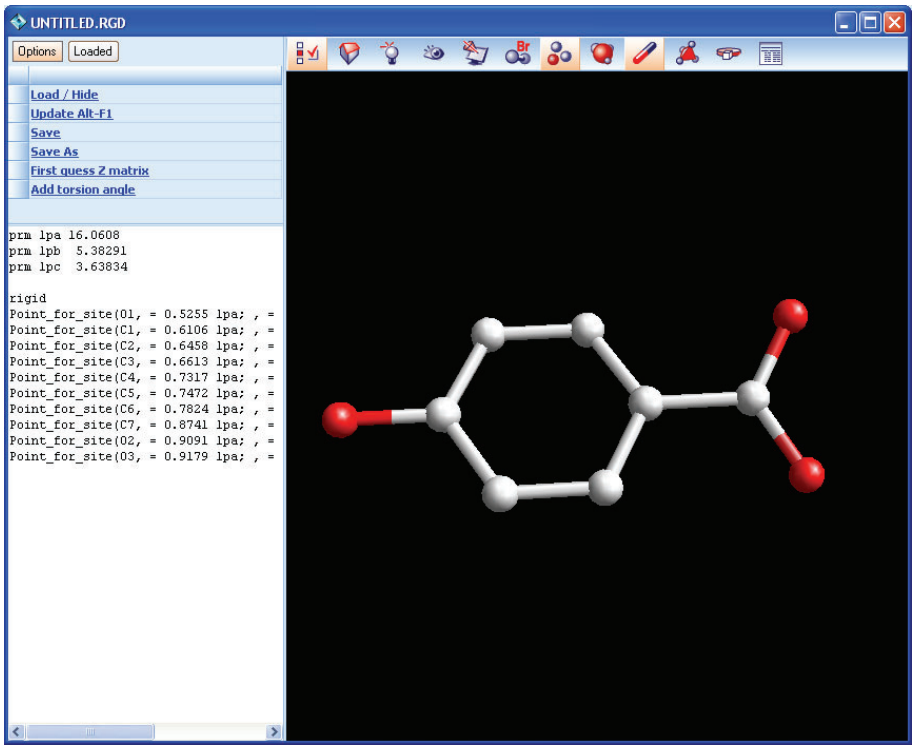
```
prm lpa 16.0608
prm lpb  5.38291
prm lpc  3.63834
```

- Multiply the fractional coordinates x, y , z with the respective lattice parameters a, b, c.

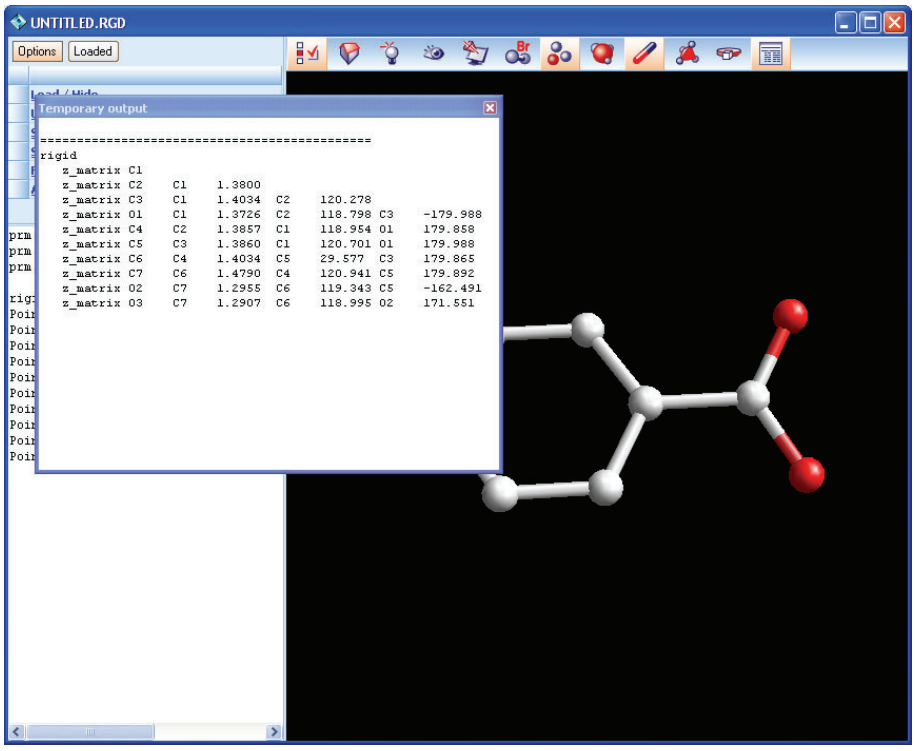
```
Point_for_site(O1, = 0.5255 lpa; , = 0.243 lpb; , = 0.871 lpc;)
Point_for_site(C1, = 0.6106 lpa; , = 0.256 lpb; , = 0.842 lpc;)
...
```



4. Update the *Main View* to view the rigid body.



5. To convert the present Cartesian rigid body definition into the more useful Z-matrix representation click on *First guess Z matrix*. A temporary output window will be opened with a Z-matrix proposal, which can be copied and pasted into the Editor window to replace the original Cartesian rigid body description.



An inspection of the temporary window output reveals slight distortions of bond distances and angles due to rounding errors (limited number of digits given for the fractional coordinates). This example highlights one important advantage in using a Z-matrix representation in TOPAS: both bond lengths and angles can be easily inspected and directly modified.

3.3.3 Torsions

In TOPAS there are numerous ways to introduce and refine torsions within rigid bodies, please refer to the Technical Reference manual. When using a Z-matrix representation it is particularly easy to refine on each individual bond length and angle defined in the Z-matrix description.

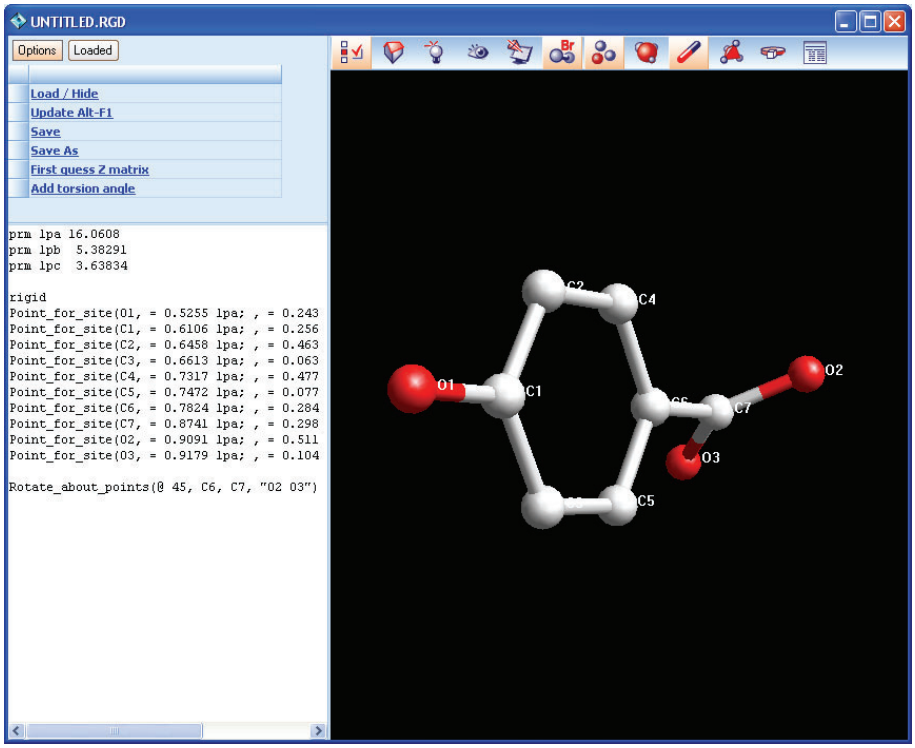
Probably the most straightforward possibility to introduce torsions is using the *Rotate_about_points* macro, which expects the following arguments:

- Amount the rigid body is rotated about the specified rotation vector in degrees
- Rotation vector defined by two selected sites
- A list of sites to be rotated about the specified rotation vector

Consider the para-hydroxybenzoate example discussed in section 3.3.2, where the carboxyl group can rotate out of the molecular plane. Using the *Rotate_about_points* macros this can be described as e.g.

```
Rotate_about_points(@ 45, C6, C7, "O2 O3")
```

where the sites O2 and O3 are rotated about a vector defined by the sites C6 and C7. The (refineable) torsion angle has been set arbitrarily to 45°.



3.4 TOF Neutron Data

The peak position for neutron time-of-flight data is typically calculated in time-of-flight space, tof, or:

$$tof = t0 + t1\ dhkl + t2\ dhkl2$$

The three parameters t0, t1 and t2 are characteristic of a given counter bank on a TOF powder diffractometer, the macro

```
TOF_x_axis_calibration(t0, t0v, t1, t1v, t2, t2v)
```

can be used for x-axis calibration.

Precise values for constants t0, t1 and t2 must be obtained by fitting to a powder diffraction pattern of a standard material. Typically instrument scientists will determine the instrument constants from a standard sample at the beginning of each run and tell users the values.

The following code example describes both a Pawley fit and a Rietveld refinement to ISIS TOF CeO_2 data found in C:\TOPAS4\TUTORIAL\CEO2; refer to the Technical Reference manual for a description of macros and keywords used:

```
TOF_XYE(sh1.xye, 50)
   bkg @ 0 0 0 0 0 0 0 0
   start_X 800000 finish_X 5000000
   TOF_LAM(0.001)
   TOF_x_axis_calibration(!t0,-473.01851,
                          !t1, 1545995.67071,
                          !t2, -223.64743)
   TOF_Exponential(@, 100, @, 15, 4, t1, +)
   TOF_Exponential(@, 100, @, 15, 4, t1, -)
' ------------------------------------------------   Pawley Refinement
   hkl_Is
      Cubic(lp 5.4103)
      TOF_PV(@, 100, @, 0.5, t1)
      default_I_attributes 100000000
      space_group "Fm-3m"
' ------------------------------------------------   Rietveld Refinement
    scale_pks = D_spacing^4;
    STR(Fm-3m)
      Cubic(lp 5.4103)
      site Ce1 x  0.00  y 0.00  z 0.00 occ Ce 1 beq @ 0.5
      site O1  x  0.25  y 0.25  z 0.25 occ O  1 beq @ 0.5
      TOF_PV(@, 100, @, 0.5, t1)
      scale @ 1
```

3.5 Fourier analysis

Not available in TOPAS P.

The keyword *fourier_map* allows to calculate a Fourier map on refinement termination, the map will be shown in the Structure Viewer window. Fourier maps can be calculated for x-ray or neutron single crystal or powder data.

The type of the map is determined by the keyword *fourier_map_formula*, it can be a function of the reserved parameter names Fcalc, Fobs, and D_spacing. The most commonly used map types are "Fobs Maps" and "Difference Maps", they are generated as follows:

```
fourier_map_formula = Fobs;                ' The default
fourier_map_formula = Fobs - Fcalc;        ' Difference Fourier map
```

Fobs corresponds to the observed structure moduli; in the powder data case Fobs is calculated from the Rietveld decomposition formula. Phases are determined from Fcalc.

In the following example the generation of a difference Fourier map will be described to locate the oxygen positions in $PbSO_4$.

1. Start TOPAS.
2. In the Launch menu define the following predefined input file: PBSO4-FOURIER.INP. By default this file is located in C:\TOPAS4\TUTORIAL\DOC. Open the file for editing.
3. To generate a Difference Map insert the following 2 lines within the STR block:

   ```
   fourier_map 1
      fourier_map_formula = Fobs - Fcalc;
   ```

   Optionally *add the min_grid_spacing* keyword to modify the number of grid points for graphical purposes. Play with values between 0.1 and 0.4, a higher number of grid points will improve the graphics but slow down the calculation speed:

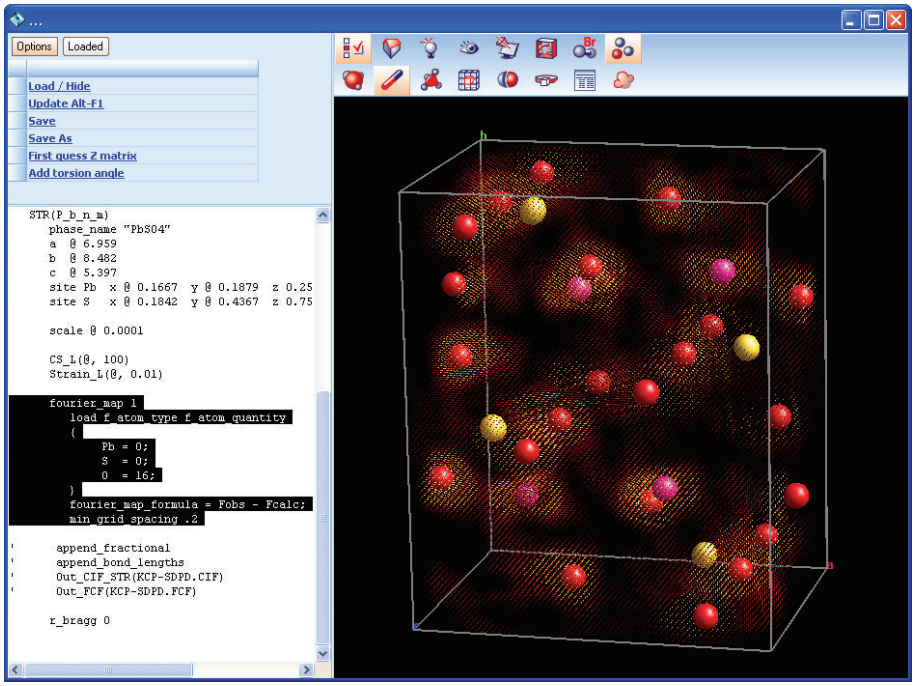
   ```
   min_grid_spacing .2
   ```

4. Start the refinement. After refinement a Rigid Body Editor window will be opened displaying the difference map. Peaks in the difference map are indicated by white balls, the missing oxygens forming SO_4 tetrahedra can be easily identified.
5. Alternatively, the oxygens can be found directly using the *f_atom_type* keyword. *f_atom_type* allows to define atom types and the number of atoms within the unit cell. Add the following lines withing the *fourier_map* block:

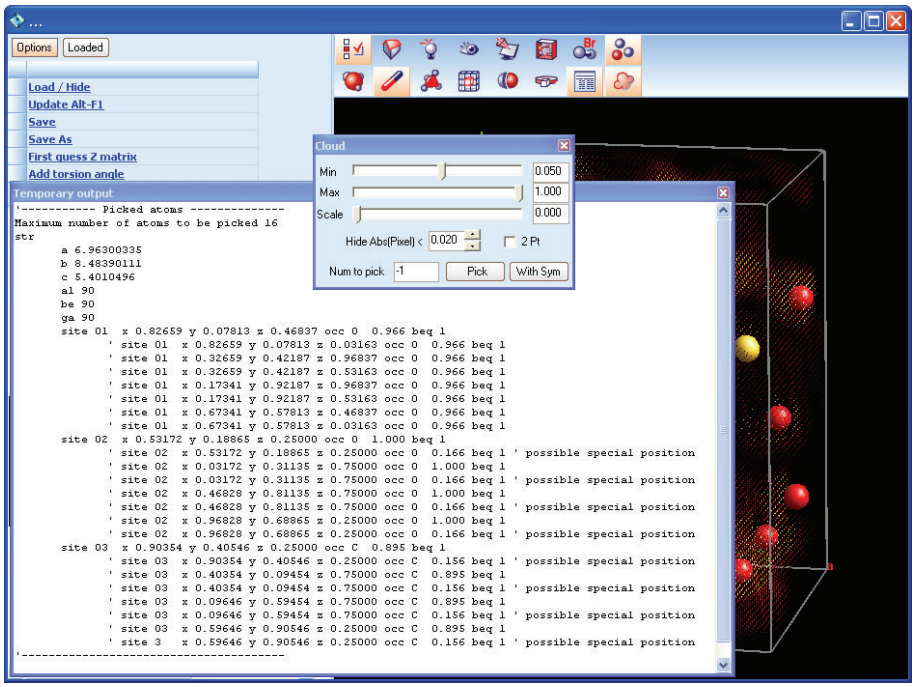
   ```
   load f_atom_type f_atom_quantity
   {
      Pb = 0;
      S  = 0;
      O  = 16;
   }
   ```

   Note, that *f_atom_quantity* for Pb and S has been set to 0; these two atom types are already defined by the structural model. The number of oxygens can be easily

derived from the chemical formula and from symmetry considerations, see section 2.4.3.



6. Open the Temporay Output window and the Cloud Options Dialog, and select "Num to pick" - "With Sym". The positions of the picked oxygen atoms are displayed in the Temporay Output window, furthermore special positions have been successfully identified.



4 REFERENCES

Balzar, D., Audebrand, N., Daymond, M.R., Fitch, A., Hewat, A., Langford, J.I., Le Bail, A., Louer, D., Masson, O., McCowan, C.N., Popa, N.C., Stephens, P.W. & Toby, B. H. (2004): *Size–strain line-broadening analysis of the ceria round-robin sample.* - J. Appl. Cryst., 37, 911–924

Cernik, R.J., Cheetham, A.K., Prout, C.K., Watkin, D.J., Wilkinson, A.P. & Willis, B.T.M. (1991): *The structure of cimetidine (C10H16N6S) solved from synchrotron-radiation X-ray powder diffraction.* - J. Appl. Cryst., **24**, 222-226.

Christensen, A. T. & Thom, E. (1971): *The crystal structure of 2-dimethylsulfuranylidene-1, 3-indanedione.* - Acta Cryst., **B27**, 581-586.

Dinnebier, R.E., Behrens, U. & Olbrich, F. (1997): *Solid state structures cyclopentadienyllithium, -sodium, and -potassium. Determination by high-resolution powder diffraction*. - Organometallics, **16 (17)**, 3855-3858.

Dinnebier, R. E. Von Dreele, R., Stephens, P. W., Jelonek, S. & Sieler, J. (1999): *Structure of Sodium-para-hydroxybenzoate NaO2C-C6H4OH by Powder Diffraction: Application of an Phenomenological Model of Anisotropic Peak Width*. - J. Appl. Cryst., **32**, 761–769.

Dinnebier, R. E., Bernatowicz, P., Helluy, X., Sebald, A., Wunschel, M., Fitch, A. & van Smaalen, S. (2002): *Redetermination of tetrakis(trimethylstannyl)germane.* - Acta Cryst., **B58**, 52-61.

Evans, J.S.O., David, W.I.F. & Sleight, A.W. (1999): *Structural investigation of the negative-thermal-expansion material ZrW2O8.* - Acta Cryst., **B55**, 333-340.

Fitch, A.N. & Jobic, H. (1993): *The Crystal Structure of Norbornane.* - J. Chem. Soc. Chem. Commun., **19**, 1516-1517.

Florence, A. (2002): Personal communication.

Fukuoka, H., Iwai, K., Yamanaka, S., Abe, H., Yoza, K. & Häming, L. (2000): *Preparation and Structure of a New Germanium Clathrate, $Ba_{24}Ge_{100}$.* - J. Solid State Chem., **151**, 117–121.

Göbel, H. (1999): Personal communication.

Hernandez, O., Hédoux, A., Lefebvre, J., Guinet, Y., Descamps, M., Papoular R. & Masson, O. (2002): *Ab initio structure determination of triphenyl phosphite by powder synchrotron X-ray diffraction.* - J. Appl. Cryst. , **35**, 212-219.

Hill, R.J. (1992): *Rietveld refinement round robin. I. Analysis of standard X-ray and neutron data for $PbSO_4$.* - J. Appl. Cryst., **25**, 589-610.

Hillier, S. (2003): Personal communication.

Jin, Z.M., He, L., Shen, L., Li, M. C. & Hu, M. L. (2003). Acta Cryst., **E59**, m1053-m1055.

Karakurt, T., Dinçer, M., Kahveci, B., Agar, E., Agar, A. & Sasmaz, S. (2003). Acta Cryst., **E59**, o1616-o1617

Langevelde, A. van, Peschar, R. & Schenk, H. (2001). Acta Cryst., **B57**, 372-377.

Li, X.-F., Feng, Y.-Q., Gao, B. & Li, N. (2003). Acta Cryst., **E59**, o1638-o1639.

S.E. Lister, I.R. Evans, J.A.K. Howard, A.Coelho & J.S.O. Evans (2004). Chem. Commun, **22**, 2540-2541.

Madsen, I.C. et al. (2001): *Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: samples 1a to 1h.* - J. Appl. Cryst., **34**, 409-426.

Morris, M. C., McMurdie, H. F., Evans, E. H., Paretzkin, B., deGroot, J. H., Hubbard, C. R. & Carmel, S. J. (1979). Natl. Bur. Stand. (US), Monogr. No. 25, §16.

Morris, M. C., McMurdie, H. F., Evans, E. H., Paretzkin, B., Hubbard, C. R. & Carmel, S. J. (1980). Natl. Bur. Stand. (US) Monogr. No. 25, §17.

Oszlányi, G. & Süto A. (2004): *Ab initio structure solution by charge flipping*. - Acta Cryst., **A60**, 134-141.

Raudsepp, M. (2004): Personal communication.

Scarlett, N.V.Y. et al. (2002): *Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: samples 2, 3, 4, synthetic bauxite, natural granodiorite and pharmaceuticals.* - J. Appl. Cryst., **35**, 383-400.

Schaefer, M., Sheldrick, G. M., Bahner, I. & Lackner, H. (1998). Angew. Chem. Int. Ed. Engl., **37**, 2381–2384.

Swanson, H. E., Morris, M. C., Stinchfield, R. P. & Evans, E. H. (1963). Natl Bur. Stand. (US) Monogr. No. 25, §2.

Toraya, H. & Yamazaki, S. (2002). Acta Cryst., **B58**, 613-621.

Von Dreele, R. B. (2007): Personal communication.

Von Dreele, R. B., Stephens, P. W., Smith, G. D. & Blessing, R. H. (2000): *The first protein crystal structure determined from high-resolution X-ray powder diffraction data: a variant of T3R3 human insulin-zinc complex produced by grinding.* - Acta Cryst., **D56**, 1549-1553