BRUKER

# DIFFRAC.SUITE

## User Manual

TOPAS 5 Tutorial

XRD

Innovation with Integrity

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# 1 INTRODUCTION

TOPAS comes with a large number of selected examples demonstrating much of its functionality in both GUI and Launch Mode. It is assumed that TOPAS has been installed in the default location C:\TOPAS5.

Example files are found in the \TUTORIAL directory, the directory structure is shown in Table 1.1. Table 1.2 gives a detailed example listing including references. All 3rd party data are either publicly accessible or courtesy of the respective author(s).

For selected examples (see column "Exercise") step-by-step procedures are provided in this manual. These exercises build on each other and get increasingly complex, thereby assuming mastery of all previous exercises. For quantitative phase analysis, indexing as well as structure determination tutorials can be ignored.

**GUI versus Launch Mode operation:**

Graphical User-Interface examples are always provided in *.PRO format, while Launch Mode INP files are always in *.INP format. For launch mode users, all *.PRO files are also available in *.INP format. Launch Mode users may inspect these INP files in an editor to follow the tutorial.

Table 1.1: Tutorial files directory structure.

- 🗀 – Tutorial
  - 🗀 – Individual Line Fitting
  - 🗀 – Indexing
    - 🗀 – LP-Search
    - 🗀 – LSI
  - 🗀 – Whole Powder Pattern Decomposition
  - 🗀 – Structure Determination and Refinement
  - 🗀 – Quantitative Phase Analysis
    - 🗀 – Automatic Removal of Phases
    - 🗀 – Constrained elemental composition
    - 🗀 – Constrained phase composition
    - 🗀 – Degree of Crystallinity Method
    - 🗀 – External Standard Method
    - 🗀 – Internal Standard Method
    - 🗀 – Pattern Scaling Method
    - 🗀 – PONKCS Method
    - 🗀 – Rietveld Method
  - 🗀 – Size-Strain Analysis
    - 🗀 – Double-Voigt Approach
    - 🗀 – WPPM
  - 🗀 – Miscellaneous
    - 🗀 – Absorption Edges
    - 🗀 – Anisotropic Line Broadening
    - 🗀 – Chebychev Parameters
    - 🗀 – Conditional Preferred Orientation
    - 🗀 – EDXRD
    - 🗀 – Magnetic Refinements
    - 🗀 – Minimization
    - 🗀 – Rigid Body Editor
    - 🗀 – Stacking Faults
    - 🗀 – TOF neutron data
    - 🗀 – TOPAS Batch Operation
    - 🗀 – Tube Tails
    - 🗀 – User-defined Output

Table 1.2: Example listing. Data types include: a) laboratory X-ray data, b) synchrotron X-ray data, c) constant wavelength neutron data, d) time-of-flight neutron data, e) single crystal data.

| Example | Comment | Data type | Exercise | GUI |
|---|---|---|---|---|
| **\Individual Line Fitting** | | | | |
| Y2O3 | Single line up to whole powder pattern fitting | a | ✓ | ✓ |
| Quartz | Dealing with high degrees of peak overlap | a | ✓ | ✓ |
| 1976 | Simultaneous fitting of multiple datasets | a | ✓ | ✓ |
| **\Indexing** | | | | |
| LSI | For details refer to Table 2.2 | a, b, e | ✓ | ✓ |
| LP-Search | For details refer to Table 2.1 | a | ✓ | ✓ |
| **\Whole Powder Pattern Decomposition** | | | | |
| PbSO4 1) | Pawley and Le Bail fitting | a | ✓ | ✓ |
| Cime 2) | Pawley and Le Bail fitting | b | ✓ | ✓ |
| Protein 3) | Pawley and Le Bail fitting | b | | ✓ |
| **\Structure Determination and Refinement** | | | | |
| PbSO4 1) | Indexing, Pawley and Le Bail fitting, simulated annealing, charge flipping, difference Fourier analysis, combined X-ray - neutron refinement, rigid bodies, occupancy merging | a, c | ✓ | (✓) |
| Cime 2) | Indexing, Pawley and Le Bail fitting, simulated annealing, charge flipping, rigid bodies | b | ✓ | (✓) |
| AlVO4 4) | Pawley and Le Bail fitting, simulated annealing, charge flipping, rigid bodies, restraints, penalties | a | | (✓) |
| Ae 5) | Simulated annealing, charge flipping, anisotropic temperature factors | e | | (✓) |
| CF 6) | Charge flipping on difficult data: poor resolution data. preventing uranium atom solutions, origin finding, pseudo-symmetry | b, e | | ✓ |
| **\Quantitative Phase Analysis\Automatic Removal of Phases** | | | | |
| CPD-1 7) | Automatic removal of phases not present in a sample | a | | |
| **\Quantitative Phase Analysis\Constrained Elemental Composition** | | | | |
| CHEM | Constrained and restrained elemental composition | a | | |
| VEGARD | Application of Vegard's law | a | | |
| **\Quantitative Phase Analysis\Constrained Phase Composition** | | | | |
| ZrO2 | Constrained and restrained phase composition | a | | |
| **\Quantitative Phase Analysis\External Standard** | | | | |
| CPD-3 7) | External standard method, amorphous content | a | | ✓ |
| **\Quantitative Phase Analysis\Degree of Crystallinity Method** | | | | |
| M2A | Single line fitting | a | | ✓ |
| KCP 9) | Rietveld refinement | b | | ✓ |
| **\Quantitative Phase Analysis\Internal Standard** | | | | |
| CPD-3 7) | Internal standard method, amorphous content | a | ✓ | ✓ |

| Example | Comment | Data type | Exercise | GUI |
|---|---|---|---|---|
| **\Quantitative Phase Analysis\PONKCS Method** | | | | |
| CPD-1 7) | PONKCS method, all phases crystalline | a | ✓ | ✓ |
| NS 8) | PONKCS method, amorphous content | a | ✓ | ✓ |
| **\Quantitative Phase Analysis\Pattern Scaling Method** | | | | |
| CPD-1 7) | Pattern scaling method | a | | |
| **\Quantitative Phase Analysis\Rietveld Method** | | | | |
| CPD-1 7) | Rietveld analysis | a | ✓ | ✓ |
| CPD-2 7) | Rietveld analysis, preferred orientation | a | | ✓ |
| OPC | Rietveld analysis, ordinary Portland clinker | a | | ✓ |
| **\Size-Strain Analysis\Double-Voigt Approach** | | | | |
| SSRR 10) | Size-strain analysis using the Double-Voigt approach | a, b, c, d | ✓ | ✓ |
| **\Size-Strain Analysis\WPPM** | | | | |
| | Various examples for WPPM based size analysis using fit objects, user-defined convolutions and Fourier transforms | a | | |
| **\Miscellaneous\Absorption Edges** | | | | |
| | Various examples for fitting of absorption edges | a | | ✓ |
| **\Miscellaneous\Anisotropic Line Broadening** | | | | |
| | Various examples for fitting of microstructure induced anisotropic line width and line asymmetry 11) | a, b | | |
| **\Miscellaneous\Chebychev Parameters** | | | | |
| | Code snippet demonstrating access to individual Chebychev polynomial parameters | | | |
| **\Miscellaneous\Conditional Preferred Orientation** | | | | |
| | Code snippet demonstrating turning-off preferred orientation dependent of phase wt% | | | |
| **\Miscellaneous\EDXRD** | | | | |
| EDXRD 12) | Pawley and Rietveld refinement of energy dispersive X-ray data | b | | |
| **\Miscellaneous\Magnetic Refinements** | | | | |
| LaMnO3 13) | Magnetic structure refinement | c | | |
| **\Miscellaneous\Minimization** | | | | |
| Min | Various examples demonstrating several aspects of the TOPAS minimization capabilities | | | |
| **\Miscellaneous\Rigid Body Editor** | | | | |
| | Example rigid bodies used in the rigid body editor tutorial | | ✓ | |
| **\Miscellaneous\Stacking Faults** | | | | |
| KAOL 13) | Demonstrates layer randomization | | | |
| **\Miscellaneous\TOF Neutron Data** | | | | |
| TOF 14) | Rietveld refinement | d | | |

| Example | Comment | Data type | Exercise | GUI |
|---|---|---|---|---|
| **\Miscellaneous\TOPAS Batch Operation** | | | | |
| BATCH | Demonstrates batch operation of TOPAS | a | | |
| **\Miscellaneous\Tube Tails** | | | | |
| 660A53 [15)] | Demonstrates fitting of tube tails | a | | ✓ |
| **\Miscellaneous\User-defined Output** | | | | |
| OUT | Demonstrates user-defined output of refinement results | | | |

1) Hill (1992); 2) http://www.ccp14.ac.uk; 3) Von Dreele (2000); 4) Göbel (1999); 5) Jin et al. (2003), Karakurt et al. (2003), Li et al. (2003); 6) Schaefer et al. (1998), Lister et. al. (2004), Von Dreele (2007), Christensen & Thom (1971); 7) Madsen et al. (2001); 8) Madsen et al. (2011); 9) Dinnebier et al. (1997); 10) Balzar (2001); 11) Fitch & Jobic (1993), Dinnebier et al. (1999), Hillier (2003), Raudsepp (2004); 12) Evans (2006); 13) Madsen (2013); 14) Evans et al. (1999); 15) Cline (2003)

# 2 GENERAL PROFILE ANALYSIS TECHNIQUES

## 2.1 Individual line fitting

### 2.1.1 Single line fitting

#### 2.1.1.1 Single line fitting with a Split-PVII function

1. Load the raw data by importing the file Y2O3.RAW. By default this file is located in C:\Topas5\Tutorial\Individual Line Fitting\.

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

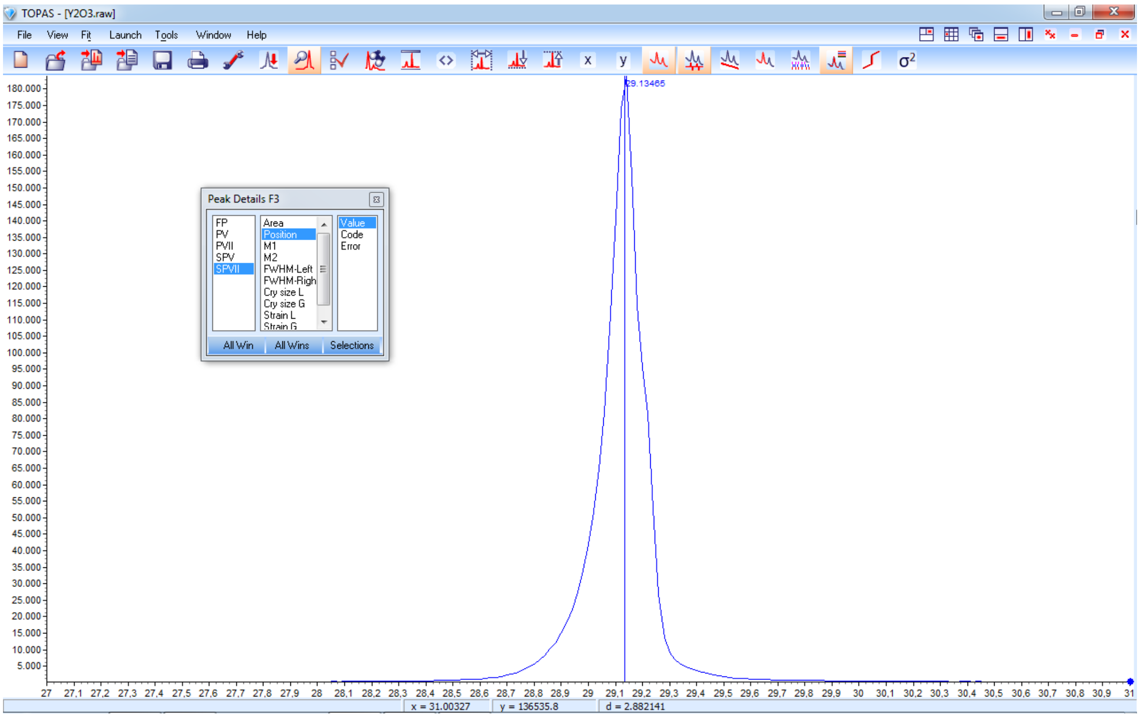
2. Zoom the first reflection in the region between 27° - 31° 2$\theta$.

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

3. Manually insert one peak at the desired 2$\theta$ position: Open the Peak Details Dialog, select the split-PVII function (SPVII), and insert one peak at the desired 2$\theta$ 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.

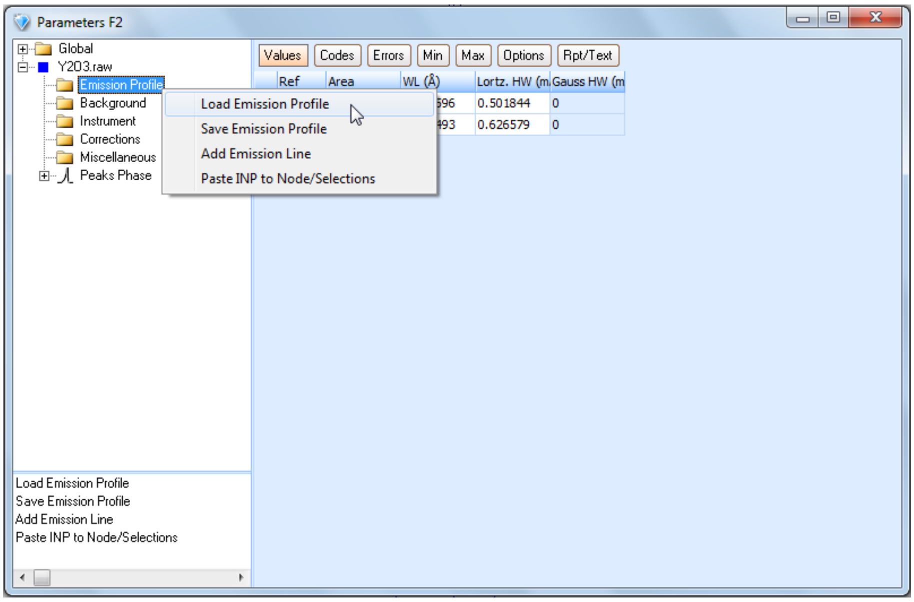
   If you incorrectly add a peak, press the "Ctrl" key and drag the mouse over the stick. Then press the "Del" key on your keyboard to delete the peak. You can also press F9 to delete the nearest peak to the mouse pointer or delete the peak in the *Parameters Window*.

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



**Hint!** The *Peak Search Dialog* provides convenient methods for automatic peak finding.

4. In the *Parameters Window* select the *Emission Profile* item and load the emission profile CuKa2_Analyt.lam. By default emission profiles are located in C:\Topas5\Lam.

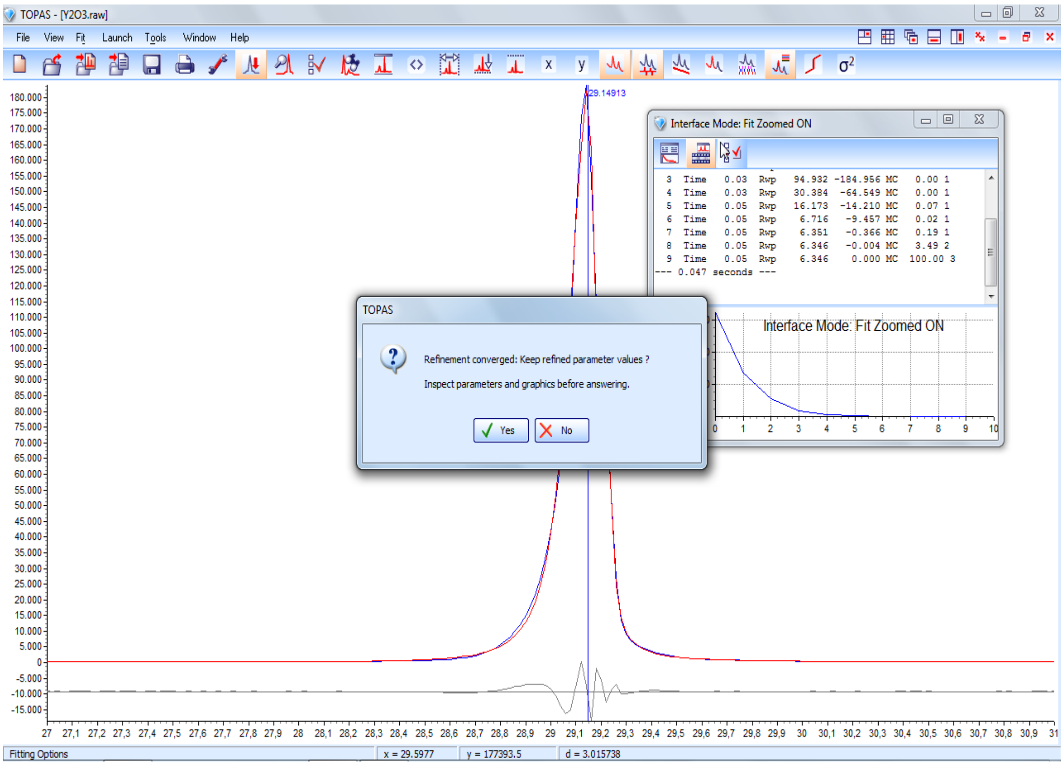


| Ref | Area | WL (Å) | Lortz. HW (m | Gauss HW (m |
|---|---|---|---|---|
| | | 596 | 0.501844 | 0 |
| | | 493 | 0.626579 | 0 |

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

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

| **Menu:** | **Icon:** | **Shortcut:** | **Result:** |
|---|---|---|---|
| *Fit –*<br>*Fit Window* | | F5 | Displays or hides the *Fit Window* |
| n.a. | ▶ | F6 | Runs the refinement |



```
  3  Time   0.03  Rwp   94.932 -184.956 MC   0.00 1
  4  Time   0.03  Rwp   30.384  -64.549 MC   0.00 1
  5  Time   0.05  Rwp   16.173  -14.210 MC   0.07 1
  6  Time   0.05  Rwp    6.716   -9.457 MC   0.02 1
  7  Time   0.05  Rwp    6.351   -0.366 MC   0.19 1
  8  Time   0.05  Rwp    6.346   -0.004 MC   3.49 2
  9  Time   0.05  Rwp    6.346    0.000 MC 100.00 3
--- 0.047 seconds ---
```

Refinement converged: Keep refined parameter values ?

Inspect parameters and graphics before answering.

x = 29.5977 y = 177393.5 d = 3.015738

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.

8. The refinement results can be inspected in the *Parameters Window* or using the *Peak Details Dialog*.
9. 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 any time 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 composite of several independent model functions. Therefore you have to state explicitly, if i) a model function is to be used, and ii) if the parameters of this function are to be refined or not. |
|---|---|

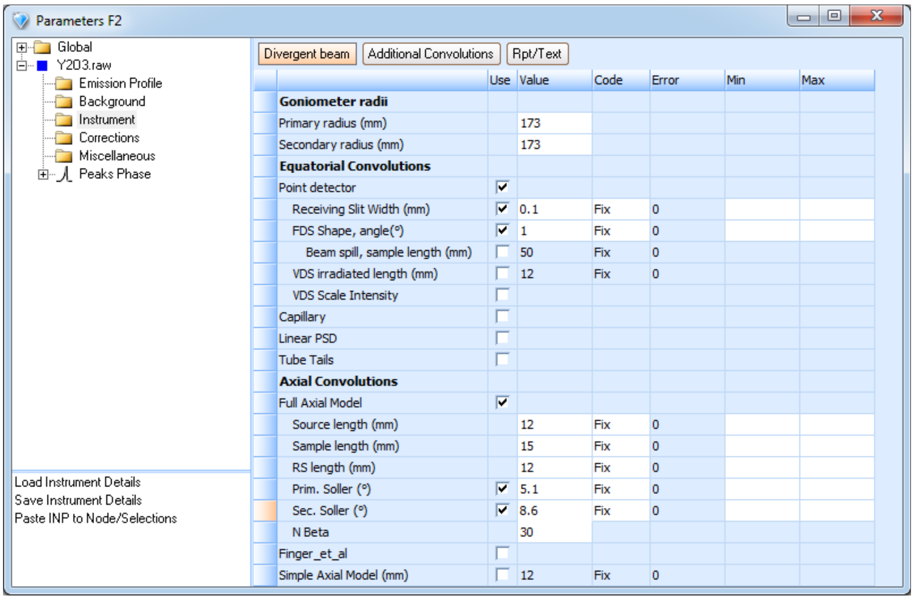
Repeat the previous exercise but apply the following changes:

1. Select FP (= First Principles) as profile function and insert one peak at the desired 2θ position.
2. Load the emission profile CuKa5_Berger.lam.
3. To use the FPA the instrument configuration has be to known. Select 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 | ☑ |

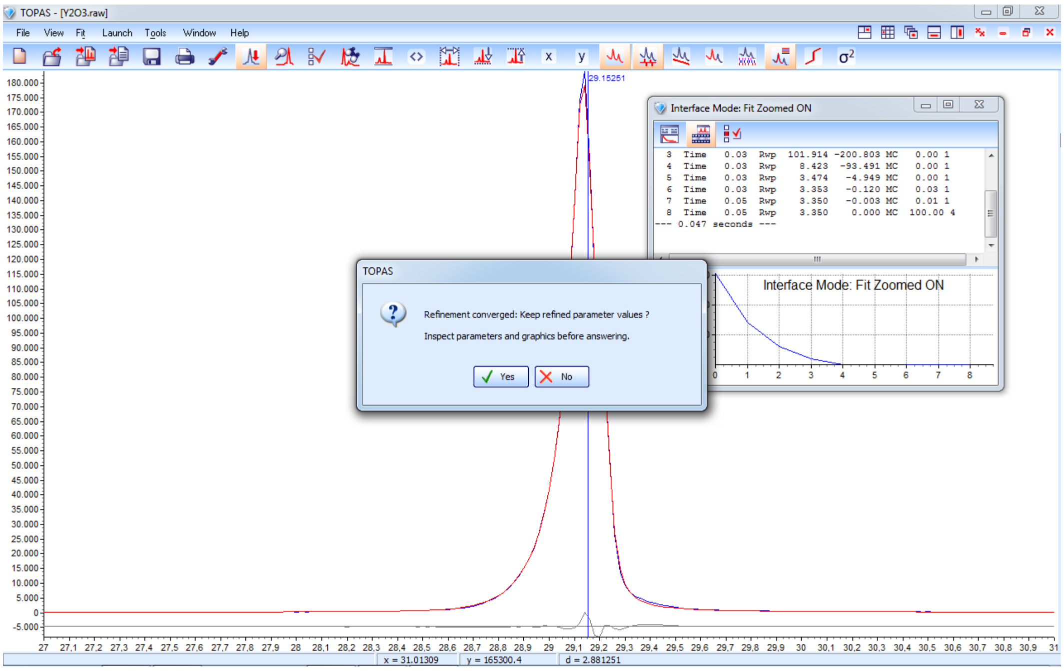
| **Instrument Parameter:** | | **Value:** |
|---|---|---|
| Goniometer Radius | Primary: | 173 mm |
| | Secondary: | 173 mm |
| Receiving Slit Width | Width: | 0.1 mm |
| FDS [1] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary: | 5.1° |
| | Secondary: | 8.6° |

[1] Fixed Divergence Slit



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| **Goniometer radii** | | | | | | |
| Primary radius (mm) | | 173 | | | | |
| Secondary radius (mm) | | 173 | | | | |
| **Equatorial Convolutions** | | | | | | |
| Point detector | ☑ | | | | | |
| Receiving Slit Width (mm) | ☑ | 0.1 | Fix | 0 | | |
| FDS Shape, angle(°) | ☑ | 1 | Fix | 0 | | |
| Beam spill, sample length (mm) | ☐ | 50 | Fix | 0 | | |
| VDS irradiated length (mm) | ☐ | 12 | Fix | 0 | | |
| VDS Scale Intensity | ☐ | | | | | |
| Capillary | ☐ | | | | | |
| Linear PSD | ☐ | | | | | |
| Tube Tails | ☐ | | | | | |
| **Axial Convolutions** | | | | | | |
| Full Axial Model | ☑ | | | | | |
| Source length (mm) | | 12 | Fix | 0 | | |
| Sample length (mm) | | 15 | Fix | 0 | | |
| RS length (mm) | | 12 | Fix | 0 | | |
| Prim. Soller (°) | ☑ | 5.1 | Fix | 0 | | |
| Sec. Soller (°) | ☑ | 8.6 | Fix | 0 | | |
| N Beta | | 30 | | | | |
| Finger_et_al | ☐ | | | | | |
| Simple Axial Model (mm) | ☐ | 12 | Fix | 0 | | |

4. Start the refinement.



Refinement converged: Keep refined parameter values ?

Inspect parameters and graphics before answering.

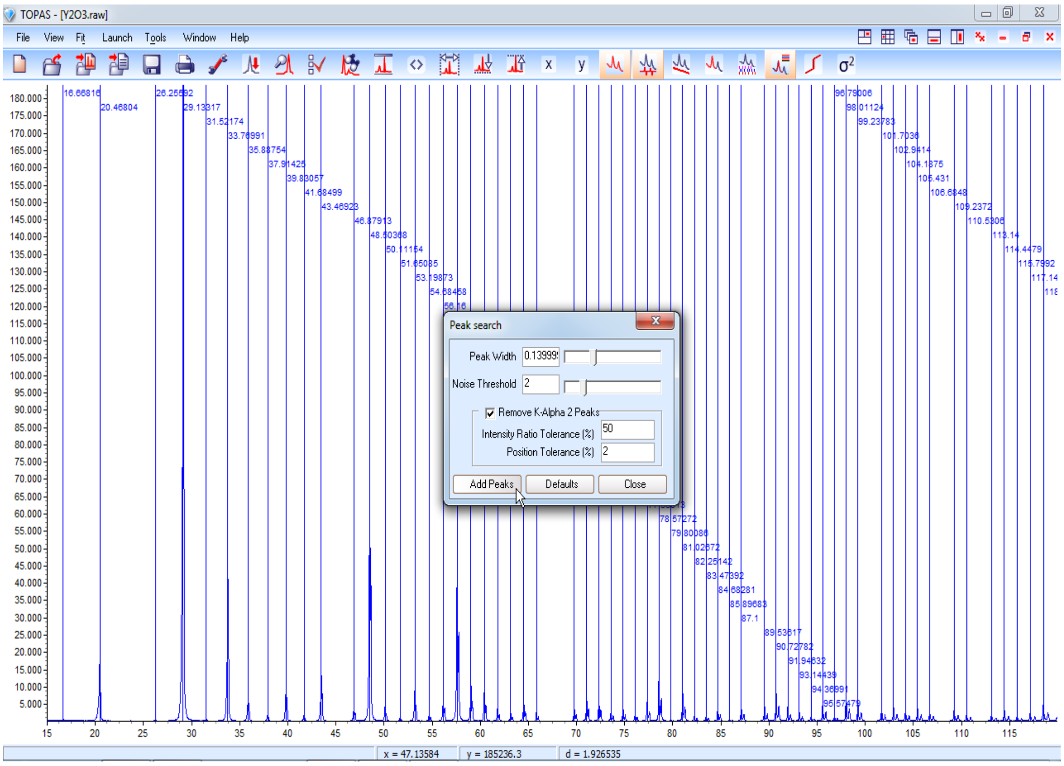
```
  3  Time   0.03  Rwp  101.914 -200.803 MC    0.00 1
  4  Time   0.03  Rwp    8.423  -93.491 MC    0.00 1
  5  Time   0.03  Rwp    3.474   -4.949 MC    0.00 1
  6  Time   0.03  Rwp    3.353   -0.120 MC    0.03 1
  7  Time   0.05  Rwp    3.350   -0.003 MC    0.01 1
  8  Time   0.05  Rwp    3.350    0.000 MC  100.00 4
--- 0.047 seconds ---
```

**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 generally do not coincide with the peak maximum.

## 2.1.2 Whole Powder Pattern Fitting

1. Import the file Y2O3A.RAW. By default this file is located in C:\Topas5\Tutorial\Individual Line Fitting\.
2. Select FP as profile function.
3. Perform a peak search using the *Peak Search Dialog*. Define a *Peak Width* of about 0.14 (this value should correspond approximately 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* |



Peak Width 0.13999

Noise Threshold 2

☑ Remove K-Alpha 2 Peaks

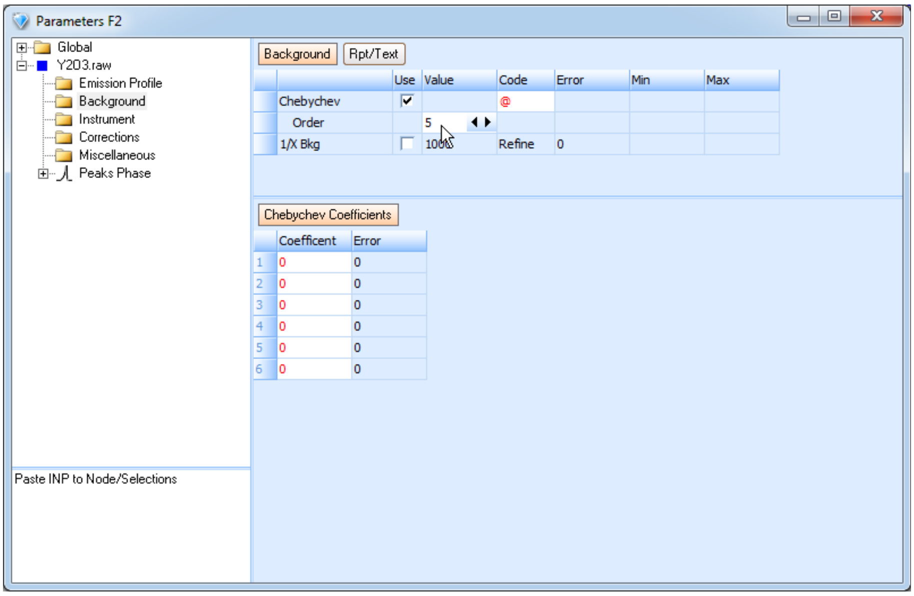
Intensity Ratio Tolerance (%) 50

Position Tolerance (%) 2

x = 47.13584 y = 185236.3 d = 1.926535

**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.EVA after a search/match operation.

4. Load the emission profile CuKa5_Berger.lam.
5. Select the *Background* item and use a Chebychev Polynomial of 5th order.



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Chebychev | ☑ | | @ | | | |
| Order | | 5 | | | | |
| 1/X Bkg | ☐ | 1000 | Refine | 0 | | |

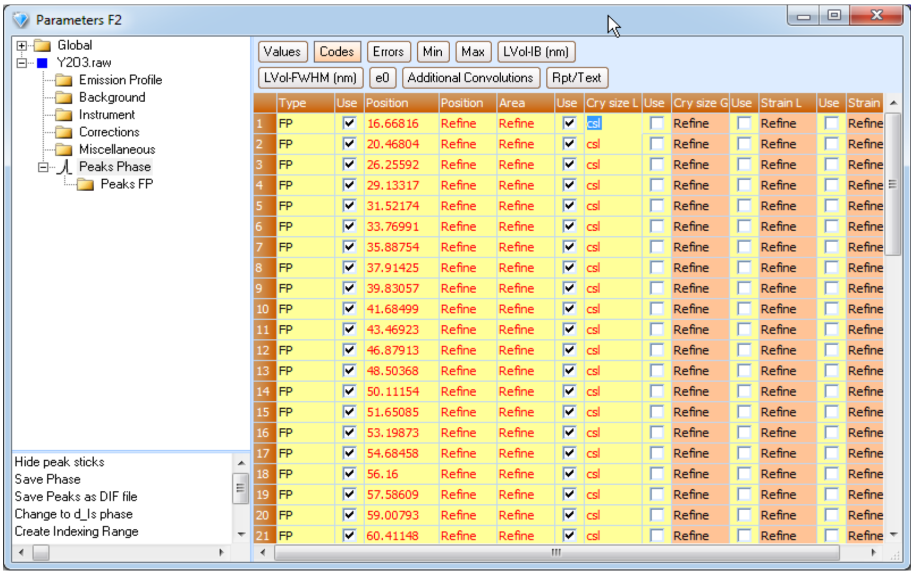
| | Coefficent | Error |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 0 | 0 |
| 3 | 0 | 0 |
| 4 | 0 | 0 |
| 5 | 0 | 0 |
| 6 | 0 | 0 |

6. Apply the following instrument settings:

| **Instrument Parameter:** | | **Value:** |
|---|---|---|
| Goniometer Radius | Primary:<br>Secondary: | 173 mm<br>173 mm |
| Receiving Slit Width | Width: | 0.1 mm |
| FDS [1] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary:<br>Secondary: | 5.1°<br>8.6° |

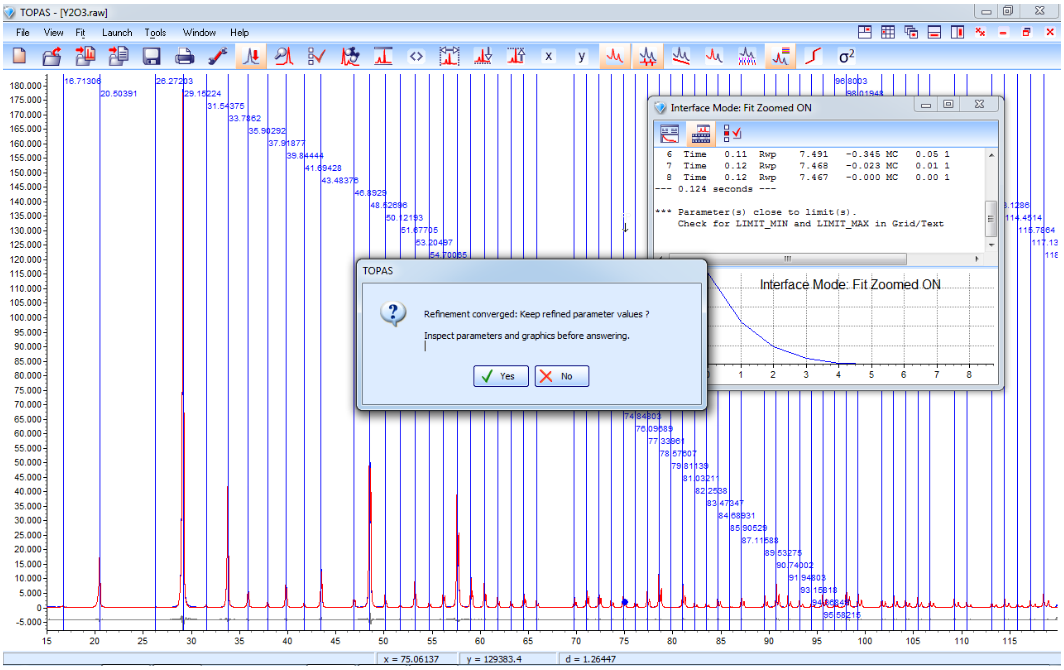
[1] Fixed Divergence Slit

7. Refine on an isotropic crystallite size parameter. Select 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.



| | Type | Use | Position | Position | Area | Use | Cry size L | Use | Cry size G | Use | Strain L | Use | Strain |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | FP | ☑ | 16.66816 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 2 | FP | ☑ | 20.46804 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 3 | FP | ☑ | 26.25592 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 4 | FP | ☑ | 29.13317 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 5 | FP | ☑ | 31.52174 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 6 | FP | ☑ | 33.76991 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 7 | FP | ☑ | 35.88754 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 8 | FP | ☑ | 37.91425 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 9 | FP | ☑ | 39.83057 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 10 | FP | ☑ | 41.68499 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 11 | FP | ☑ | 43.46923 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 12 | FP | ☑ | 46.87913 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 13 | FP | ☑ | 48.50368 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 14 | FP | ☑ | 50.11154 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 15 | FP | ☑ | 51.65085 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 16 | FP | ☑ | 53.19873 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 17 | FP | ☑ | 54.68458 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 18 | FP | ☑ | 56.16 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 19 | FP | ☑ | 57.58609 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 20 | FP | ☑ | 59.00793 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |
| 21 | FP | ☑ | 60.41148 | Refine | Refine | ☑ | csl | ☐ | Refine | ☐ | Refine | ☐ | Refine |

8. Start the refinement.



```
  6  Time   0.11  Rwp    7.491   -0.345 MC   0.05 1
  7  Time   0.12  Rwp    7.468   -0.023 MC   0.01 1
  8  Time   0.12  Rwp    7.467   -0.000 MC   0.00 1
--- 0.124 seconds ---

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

TOPAS

Refinement converged: Keep refined parameter values ?

Inspect parameters and graphics before answering.

Yes No

## 2.1.3 Dealing with high degrees of peak overlap

This lesson is divided into three parts:

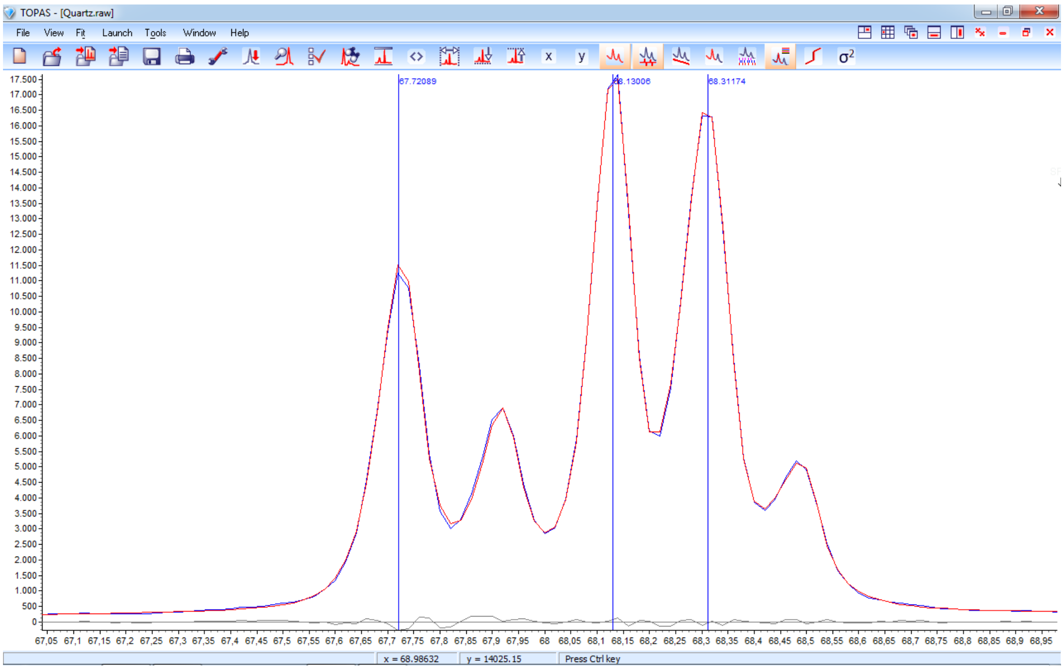
I. Unconstrained analytical profile fitting

II. Constrained analytical profile fitting

III. Use of Fundamental Parameters

### Part I: Unconstrained analytical profile fitting:

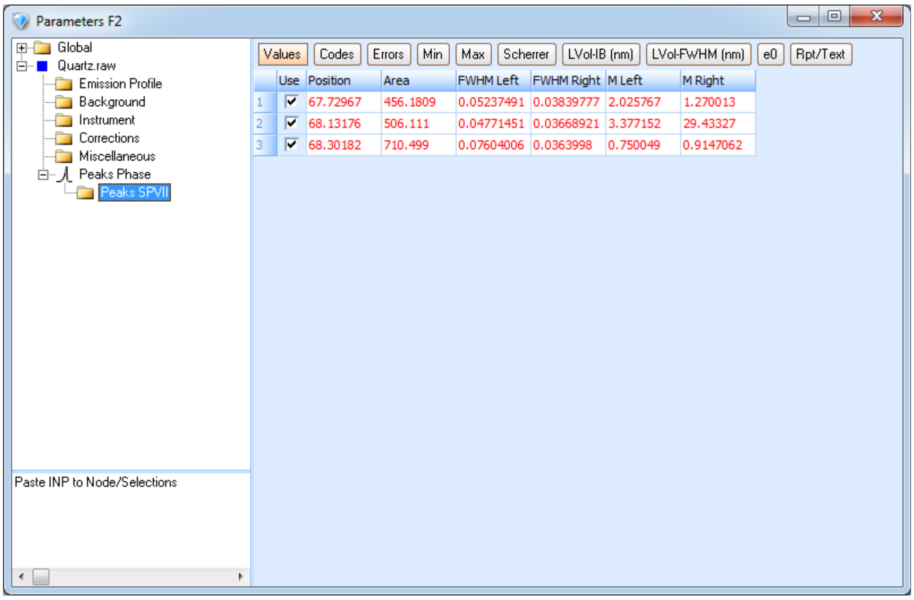
1. Import the file Quartz.raw. By default this file is located in C:\Topas5\Tutorial\Individual Line Fitting\.
2. Select SPVII as profile function and insert three peaks at the appropriate 2θ positions.
3. Load the emission profile CuKa2_Analyt.lam.
4. Fit the data. After refinement note the excellent 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.



x = 68.98632 y = 14025.15 Press Ctrl key

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

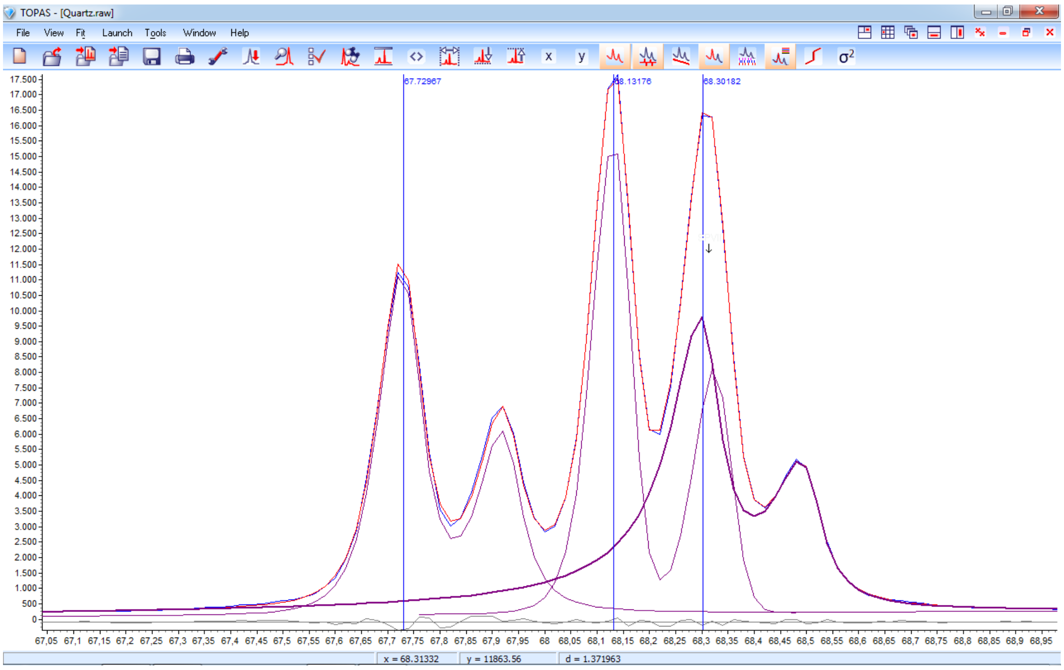
   Very inconsistent refinement results for half widths and PearsonVII exponents can be seen at the very first sight. A closer review of the refined integrated intensities shows up a severe refinement error: E.g. the area of the third peak is approximately 50% larger as the area of the second peak, although a visual inspection of the pattern would indicate a reversed ratio.



|  | Use | Position | Area | FWHM Left | FWHM Right | M Left | M Right |
|---|---|---|---|---|---|---|---|
| 1 | ☑ | 67.72967 | 456.1809 | 0.05237491 | 0.03839777 | 2.025767 | 1.270013 |
| 2 | ☑ | 68.13176 | 506.111 | 0.04771451 | 0.03668921 | 3.377152 | 29.43327 |
| 3 | ☑ | 68.30182 | 710.499 | 0.07604006 | 0.0363998 | 0.750049 | 0.9147062 |

6. 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 -*<br>*Curves - Calculated* |  | n.a. | Displays / hides calculated curves |
| *View -*<br>*Curves - Background* |  | n.a. | Displays / hides background curves |
| *View -*<br>*Curves - Difference* |  | n.a. | Displays / hides difference curves |
| *View -*<br>*Curves - Single Peaks* |  | n.a. | Displays / hides single peaks |



```
x = 68.31332   y = 11863.56   d = 1.371963
```

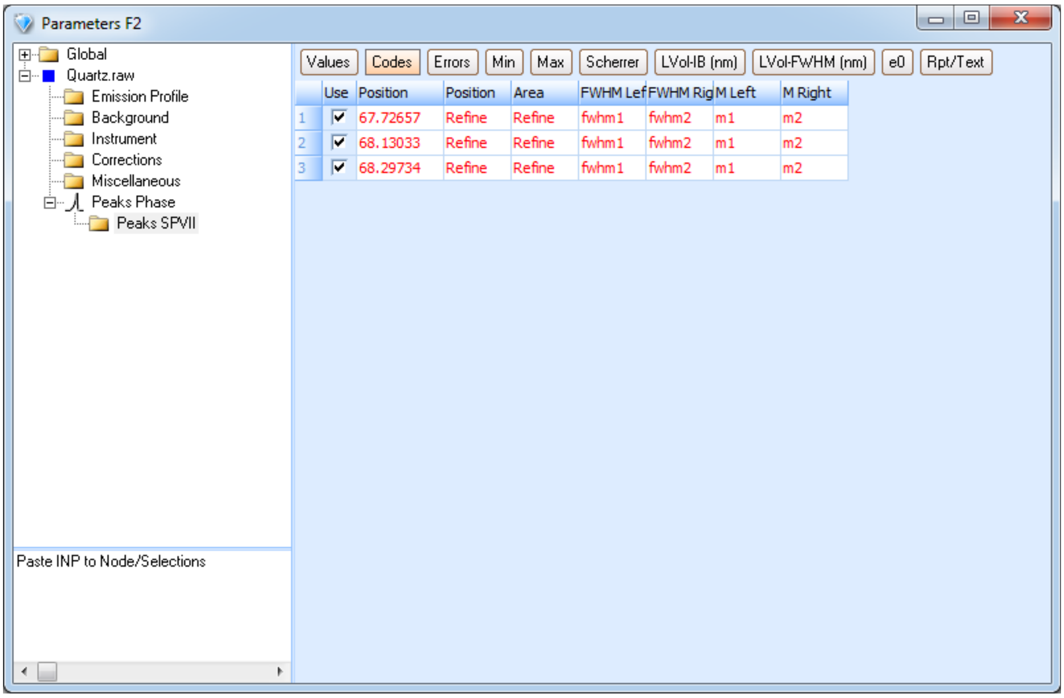
The reason for this misfit are strong correlations particularly between the parameters describing the right wing of the second and the left wing of the third peak. Intensity errors of a magnitude of several 100% are common in cases such as this. For this peak cluster a meaningful decomposition is not 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.

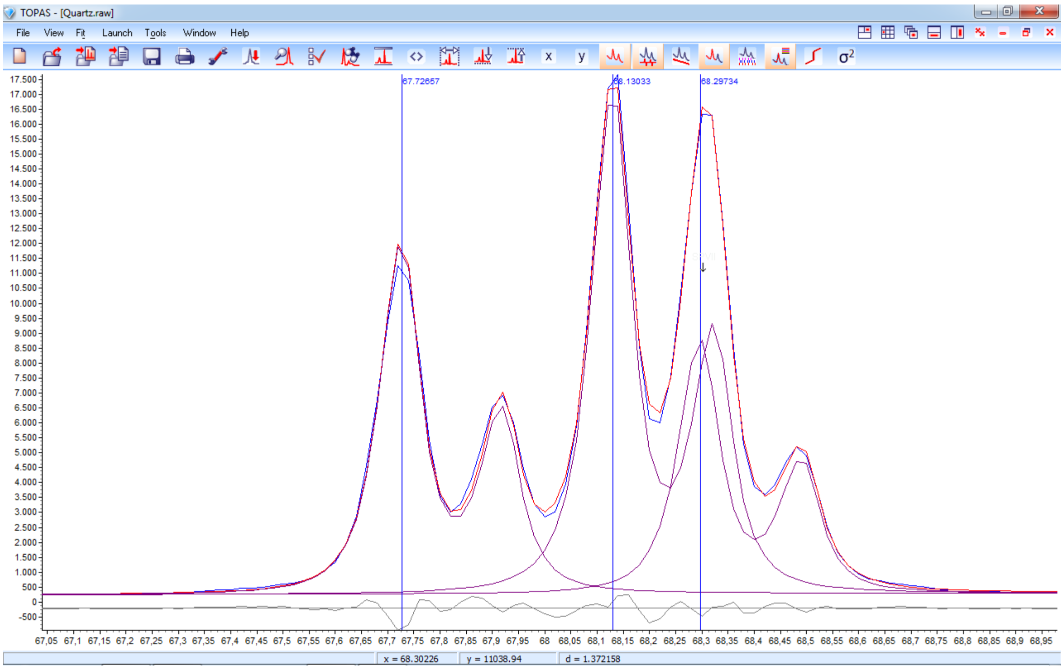
7. In the *Parameters Window* select the SPVII item and select the *Codes* page. To constrain a group of parameters replace their refinement flags by entering any arbitrary text (lower case only!), which must be the same for all parameters within a group. In this example there are 4 parameters groups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



| | Use | Position | Position | Area | FWHM Lef | FWHM Rig | M Left | M Right |
|---|---|---|---|---|---|---|---|---|
| 1 | ☑ | 67.72657 | Refine | Refine | fwhm1 | fwhm2 | m1 | m2 |
| 2 | ☑ | 68.13033 | Refine | Refine | fwhm1 | fwhm2 | m1 | m2 |
| 3 | ☑ | 68.29734 | Refine | Refine | fwhm1 | fwhm2 | m1 | m2 |

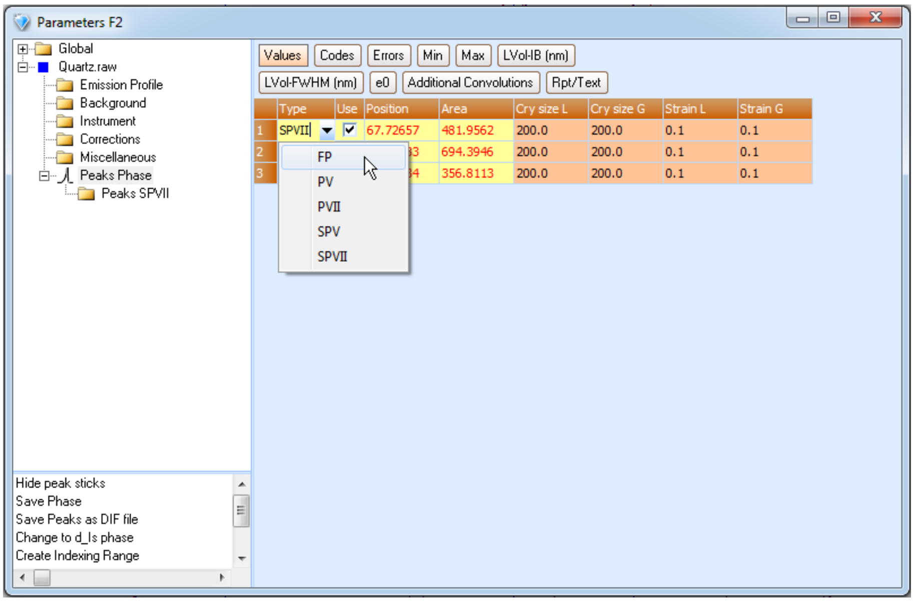
As an unconstrained refinement has been carried out before, the values of all parameters are different. Therefore switch to the *Values* page and define identical parameter values within a parameter group, e.g. 0.05 for all halfwidths and 1 for all exponents.

8. 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.



## Part III: Use of Fundamental Parameters:

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



| | Type | Use | Position | Area | Cry size L | Cry size G | Strain L | Strain G |
|---|---|---|---|---|---|---|---|---|
| 1 | SPVII | ☑ | 67.72657 | 481.9562 | 200.0 | 200.0 | 0.1 | 0.1 |
| 2 | | | 3 | 694.3946 | 200.0 | 200.0 | 0.1 | 0.1 |
| 3 | | | 4 | 356.8113 | 200.0 | 200.0 | 0.1 | 0.1 |

10. Load the emission profile CuKa5_Berger.lam.

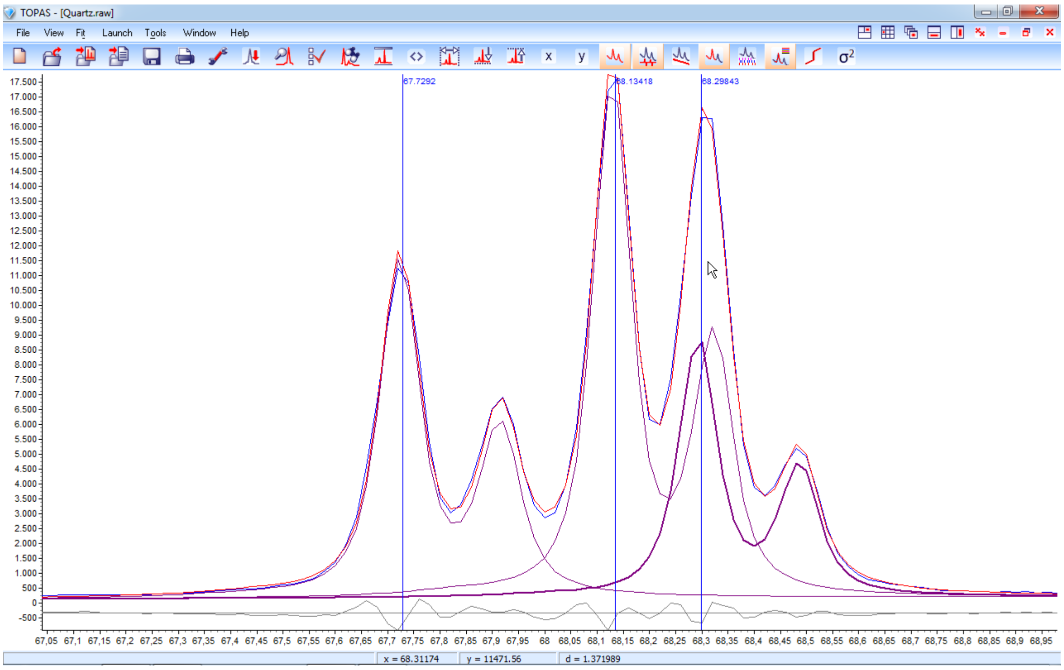
11. Apply the following instrument settings:

| **Instrument Parameter:** | | **Value:** |
|---|---|---|
| Goniometer Radius | Primary:<br>Secondary: | 217.5 mm<br>217.5 mm |
| Receiving Slit Width | Width: | 0.1 mm |
| FDS [1] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary:<br>Secondary: | 4°<br>4° |

[1] Fixed Divergence Slit

12. Select the *Peak Phase* item, select the *Codes* page and refine the *Cry Size L* parameter for all peaks.

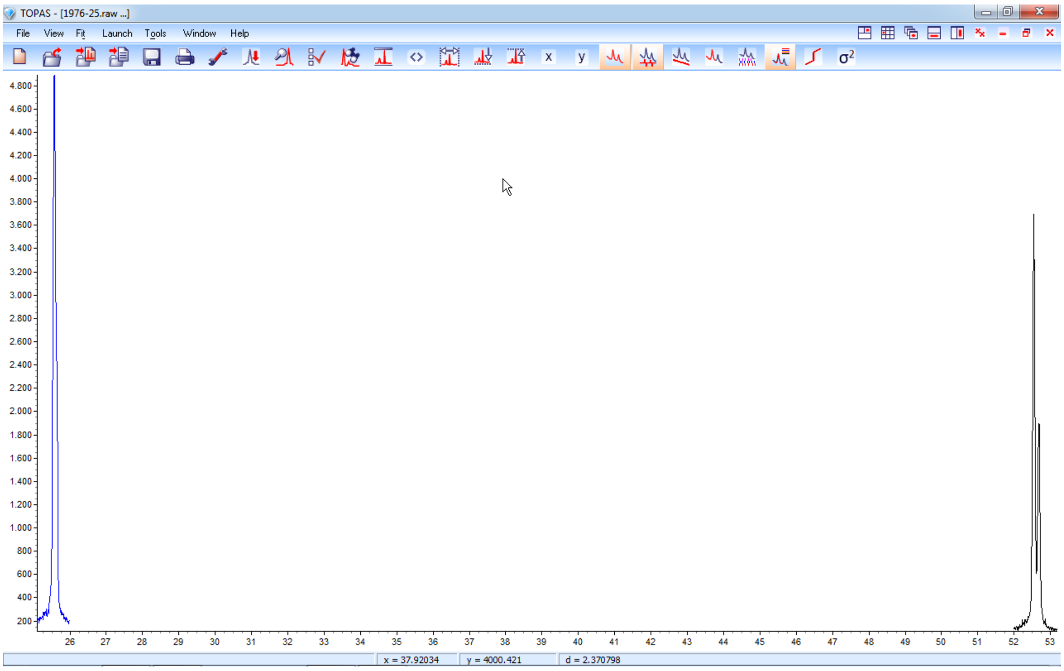
13. Fit the data. You will obtain an $R_{WP}$ of about 3.8%. Although higher than the unconstrained refinement using analytical profile functions, this time the best refinement results possible have been obtained!



**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.

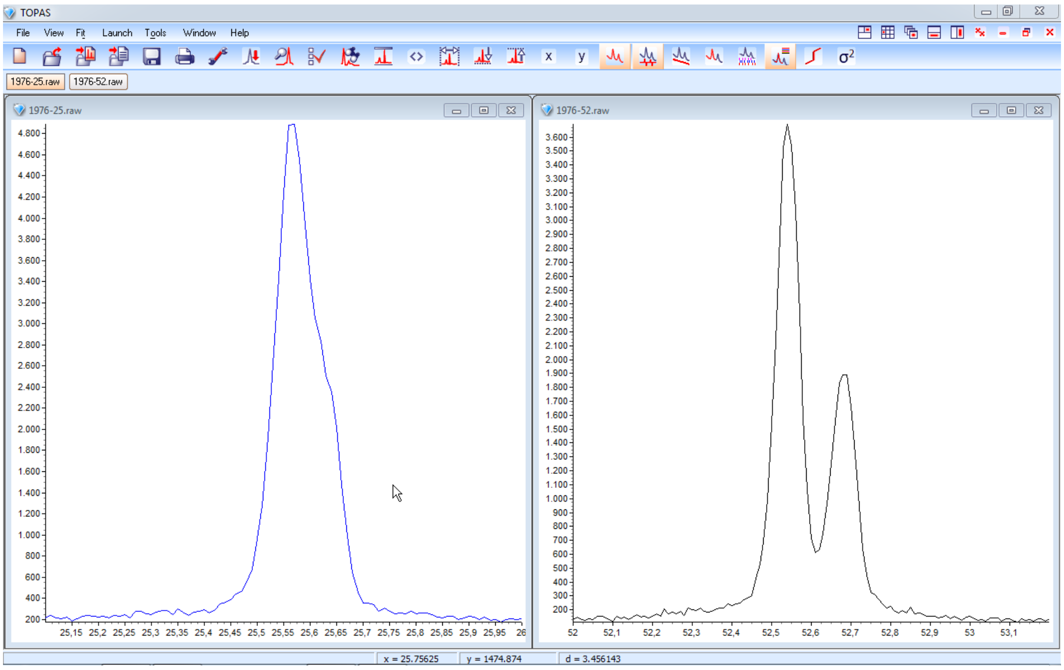
### 2.1.4 Simultaneous fitting of multiple datasets

1. Import the files 1976-25.RAW and 1976-52.RAW. By default both files are located in C:\Topas5\Tutorial\Individual Line Fitting\.
2. By default both ranges are displayed in one single *Scan Window*.



Display both ranges in separate *Scan Windows*.

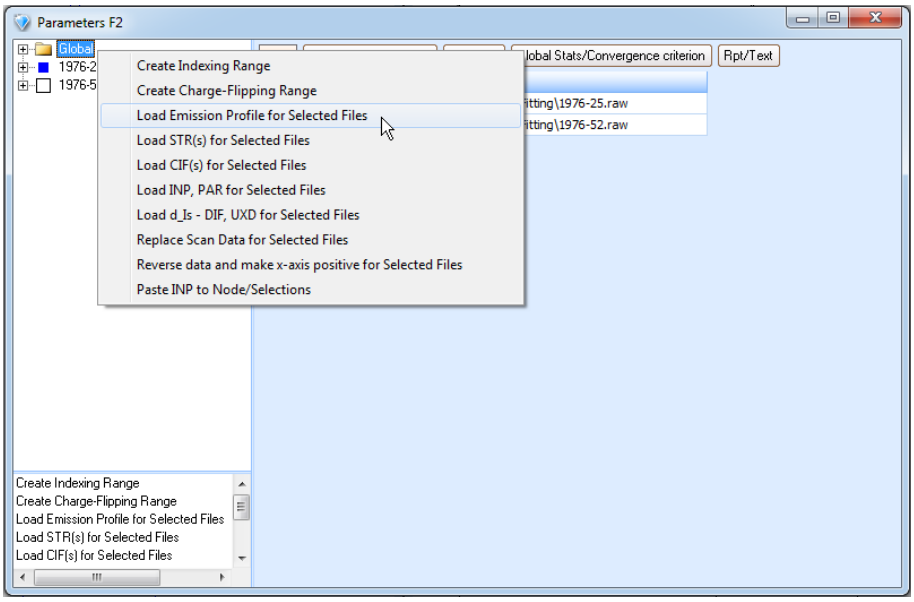
| Menu: | Icon: | Shortcut: | Result: |
|---|---|---|---|
| *Window -*<br>*One Scan per Window* | n.a. | n.a. | Displays each range in a different *Scan Window* |



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

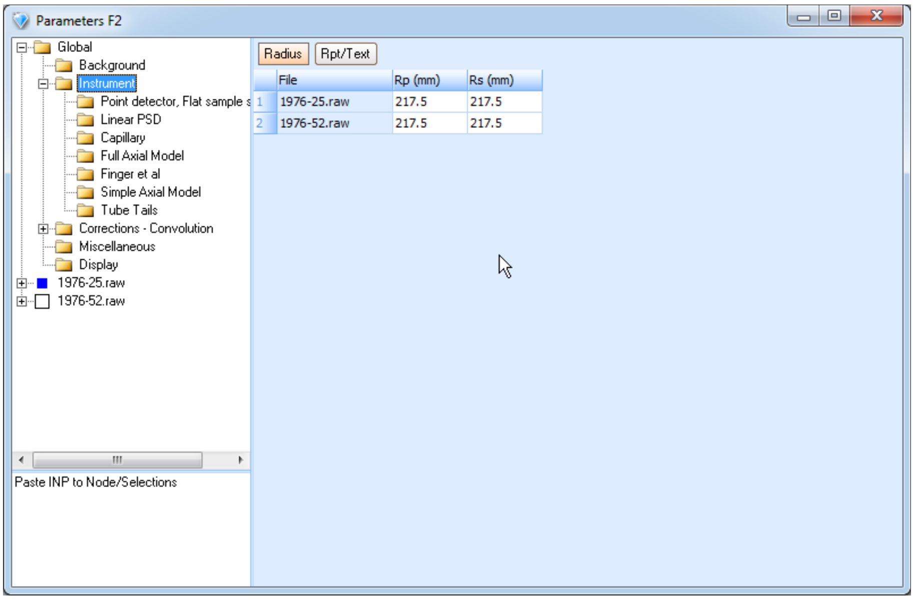
   - Select the *Global* item, select both data files in the *Path* page, and load the emission profile CuKa5_Berger.lam for all selected files.



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

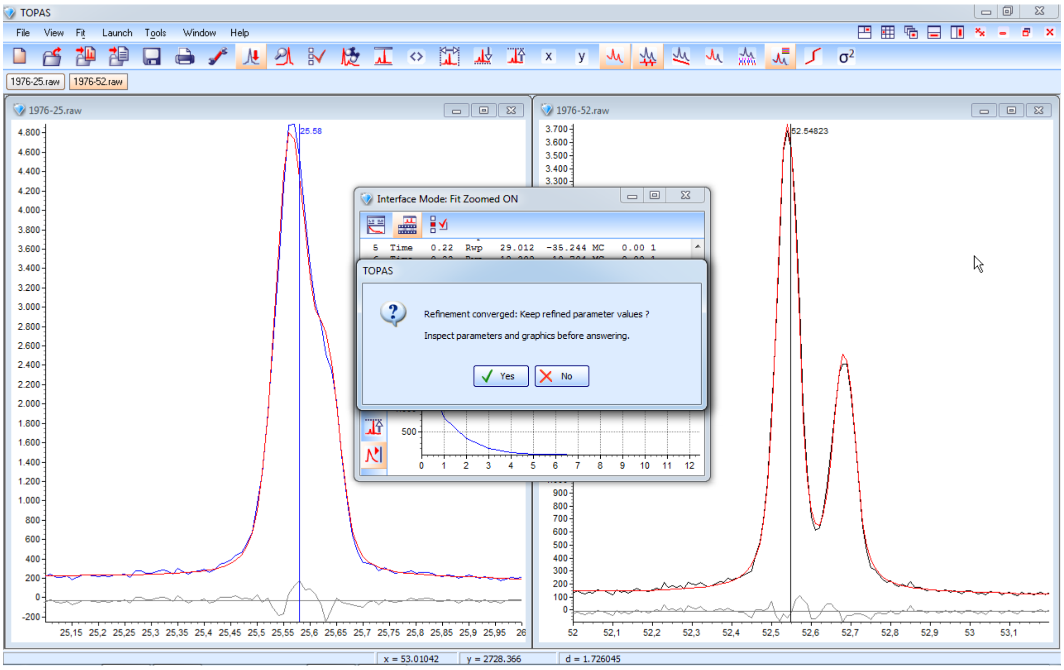
| **Instrument Parameter:** | | **Value:** |
|---|---|---|
| Goniometer Radius | Primary: | 217.5 mm |
| | Secondary: | 217.5 mm |
| Receiving Slit Width | Width: | 0.2 mm |
| FDS 1) Shape, Angle | Angle: | 1° |
| Soller Slits | Primary: | 2.3° |
| | Secondary: | 2.3° |

1) Fixed Divergence Slit



| | File | Rp (mm) | Rs (mm) |
|---|---|---|---|
| 1 | 1976-25.raw | 217.5 | 217.5 |
| 2 | 1976-52.raw | 217.5 | 217.5 |

5. Start the refinement.



```
 5  Time   0.22  Rwp   29.012  -35.244 MC   0.00 1
```

Refinement converged: Keep refined parameter values ?

Inspect parameters and graphics before answering.

# 2.2 Indexing

## 2.2.1 LSI Indexing

Example files are found in the C:\Topas\Tutorial\Indexing\LSI directory, Table 2.1 provides the crystallographic data. Step-by-step procedures are provided for $PbSO_4$ and Cimetidine. Protein is an example for indexing of a very large unit cell.

Table 2.1: Crystallographic data for the LSI-Index tutorial examples.

| Example | Symmetry | Lattice parameters (Å) / (°) | | | Vol (Å$^3$) |
|---|---|---|---|---|---|
| PbSO4 1) | Orthorhombic | a = 8.482 | b = 5.397 | c = 6.959 | 319 |
| Cime 2) | Monoclinic | a = 10.395 | b = 18.820<br>β = 106.4 | c = 6.826 | 1281 |
| Protein 3) | Rhombohedral | a = 81.306 | | c = 73.064 | 420727 |

1) Hill (1992); 2) Cernik et al. (1991); 3) Van Dreele et al. (2000)

### 2.2.1.1 Indexing of $PbSO_4$

1. Load the raw data by importing the file PbSO4.raw.
2. Insert about 20 peaks at the desired 2θ positions (up to about 43° 2θ). Use the FP peak type.
3. Open the *Parameters Window* and expand the "Pbso4.raw" range:
   - Select the *Emission Profile* item and load the emission profile CuKa5_Berger.lam.
   - Select the *Background* item. Use a Chebychev Polynomial of 5th order as well as the *1/X Bkg* function. The latter accounts for increasing background due to air-scattering when coming close to the primary beam and also allows to use a Chebychev polynomial with less coefficients.
   - Select the *Instrument* item and define the instrument settings according to the following two tables:

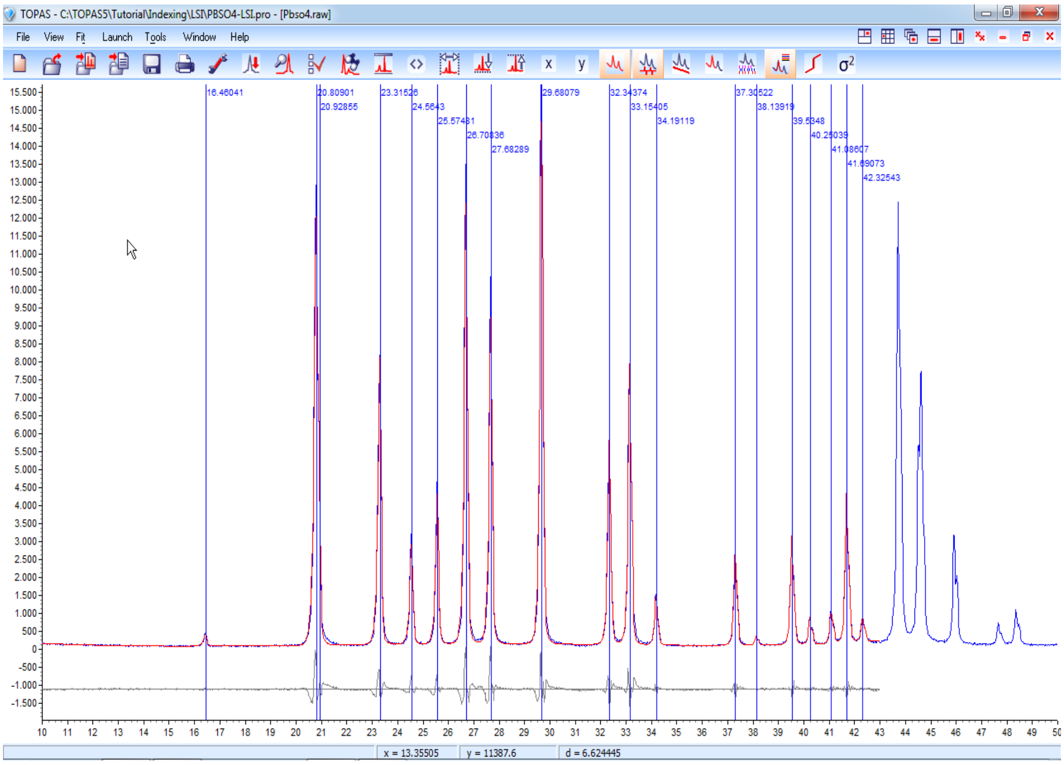
| • **Equatorial Convolutions:** | | • **Axial Convolutions:** | |
|---|---|---|---|
| • Receiving Slit Width | ☑ | • Full Axial Model | ☑ |
| FDS 1) Shape, Angle | ☑ | Primary Soller | ☑ |
| | | Secondary Soller | ☑ |

| **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° |

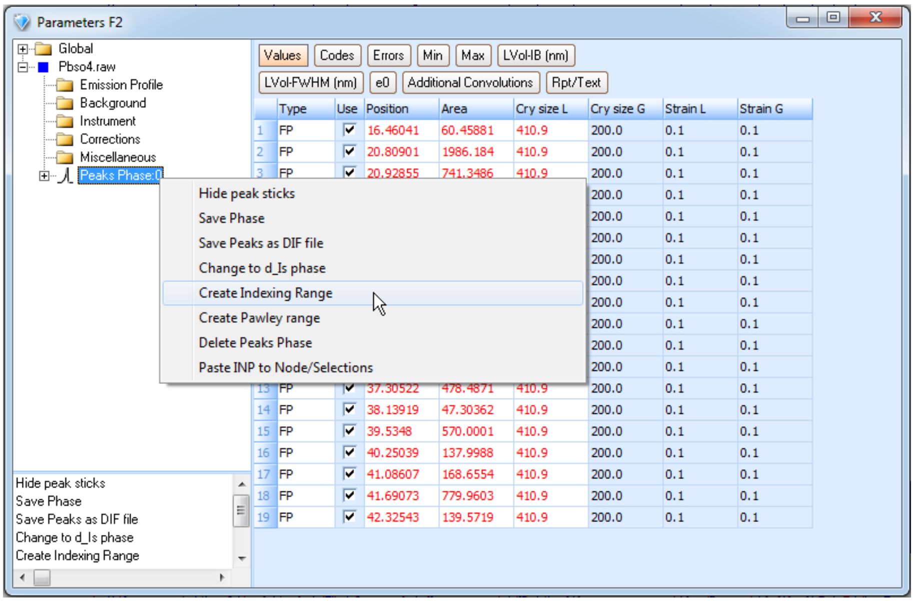
[1] Fixed Divergence Slit

- Select the *Miscellaneous* item. Set *Finish X* to about 43° 2θ to include all selected peaks.
- Refining on an isotropic crystallite size parameter will help to recognize strongly overlapping peaks. Select 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.

4. Run the refinement.



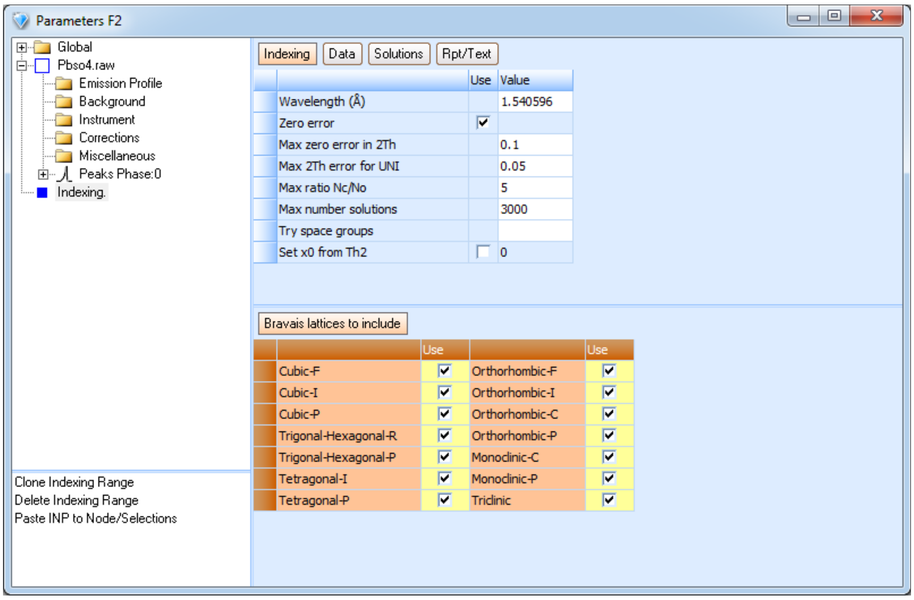
5. Select the peaks phase and create a new indexing range e.g. using the *Global* item shortcut menu. The wavelength as well as refined peak positions and intensities are automatically placed into the indexing range.



| | Type | Use | Position | Area | Cry size L | Cry size G | Strain L | Strain G |
|---|---|---|---|---|---|---|---|---|
| 1 | FP | ☑ | 16.46041 | 60.45881 | 410.9 | 200.0 | 0.1 | 0.1 |
| 2 | FP | ☑ | 20.80901 | 1986.184 | 410.9 | 200.0 | 0.1 | 0.1 |
| 3 | FP | ☑ | 20.92855 | 741.3486 | 410.9 | 200.0 | 0.1 | 0.1 |
| | | | | | | 200.0 | 0.1 | 0.1 |
| | | | | | | 200.0 | 0.1 | 0.1 |
| | | | | | | 200.0 | 0.1 | 0.1 |
| | | | | | | 200.0 | 0.1 | 0.1 |
| | | | | | | 200.0 | 0.1 | 0.1 |
| | | | | | | 200.0 | 0.1 | 0.1 |
| | | | | | | 200.0 | 0.1 | 0.1 |
| | | | | | | 200.0 | 0.1 | 0.1 |
| | | | | | | 200.0 | 0.1 | 0.1 |
| 13 | FP | ☑ | 37.30522 | 478.4871 | 410.9 | 200.0 | 0.1 | 0.1 |
| 14 | FP | ☑ | 38.13919 | 47.30362 | 410.9 | 200.0 | 0.1 | 0.1 |
| 15 | FP | ☑ | 39.5348 | 570.0001 | 410.9 | 200.0 | 0.1 | 0.1 |
| 16 | FP | ☑ | 40.25039 | 137.9988 | 410.9 | 200.0 | 0.1 | 0.1 |
| 17 | FP | ☑ | 41.08607 | 168.6554 | 410.9 | 200.0 | 0.1 | 0.1 |
| 18 | FP | ☑ | 41.69073 | 779.9603 | 410.9 | 200.0 | 0.1 | 0.1 |
| 19 | FP | ☑ | 42.32543 | 139.5719 | 410.9 | 200.0 | 0.1 | 0.1 |

6. Select the *Indexing* range and unselect the "Pbso4.raw" range. Optional: To remove clutter from the screen unselect all peaks or delete the *Peaks Phase*.

7. Select all Bravais lattice(s) to be included in the indexing run. Default indexing parameters are appropriate for this example.

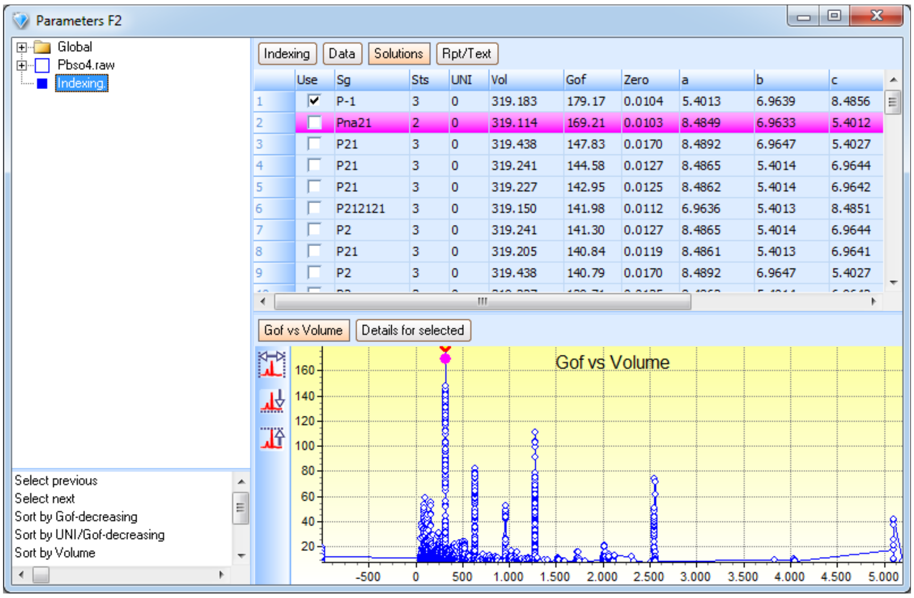


| | Use | Value |
|---|---|---|
| Wavelength (Å) | | 1.540596 |
| Zero error | ☑ | |
| Max zero error in 2Th | | 0.1 |
| Max 2Th error for UNI | | 0.05 |
| Max ratio Nc/No | | 5 |
| Max number solutions | | 3000 |
| Try space groups | | |
| Set x0 from Th2 | ☐ | 0 |

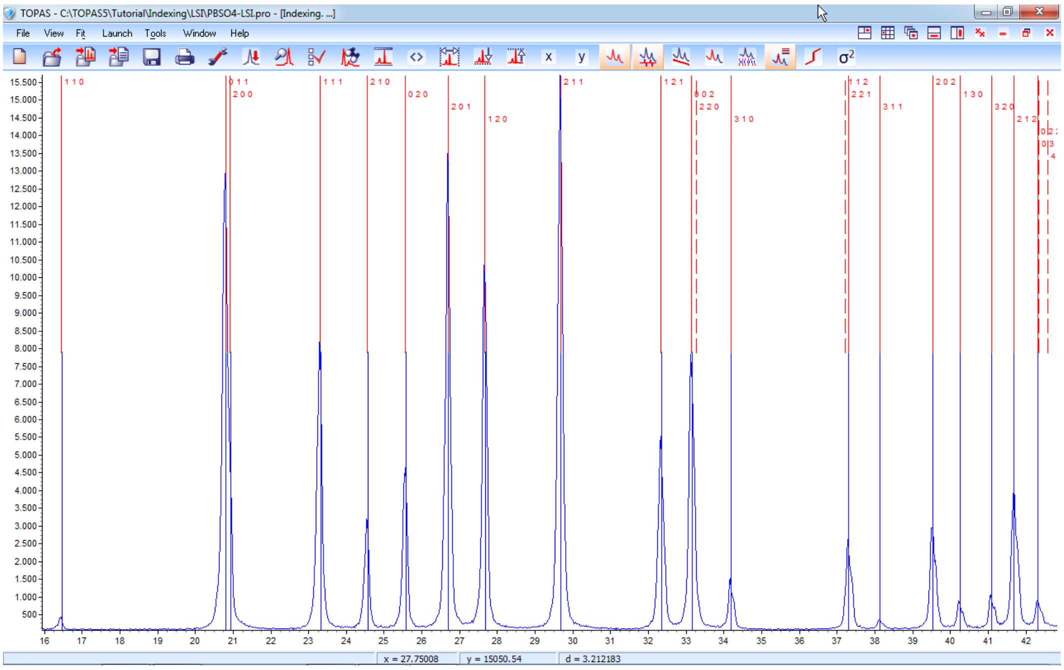
| | Use | | Use |
|---|---|---|---|
| Cubic-F | ☑ | Orthorhombic-F | ☑ |
| Cubic-I | ☑ | Orthorhombic-I | ☑ |
| Cubic-P | ☑ | Orthorhombic-C | ☑ |
| Trigonal-Hexagonal-R | ☑ | Orthorhombic-P | ☑ |
| Trigonal-Hexagonal-P | ☑ | Monoclinic-C | ☑ |
| Tetragonal-I | ☑ | Monoclinic-P | ☑ |
| Tetragonal-P | ☑ | Triclinic | ☑ |

8. Run the refinement.

9. Indexing details are provided in the *Solutions* page. For each selected solution observed and calculated peak positions are shown in the *Scan Window*. With the "Pbso4.raw" range selected as well, the raw data can be overlaid with or without the single peak fit results. It can be seen, that there are many triclinic and monoclinic top solutions with angles close to 90° obscuring a orthorhombic solution.



| | Use | Sg | Sts | UNI | Vol | Gof | Zero | a | b | c |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ☑ | P-1 | 3 | 0 | 319.183 | 179.17 | 0.0104 | 5.4013 | 6.9639 | 8.4856 |
| 2 | ☐ | Pna21 | 2 | 0 | 319.114 | 169.21 | 0.0103 | 8.4849 | 6.9633 | 5.4012 |
| 3 | ☐ | P21 | 3 | 0 | 319.438 | 147.83 | 0.0170 | 8.4892 | 6.9647 | 5.4027 |
| 4 | ☐ | P21 | 3 | 0 | 319.241 | 144.58 | 0.0127 | 8.4865 | 5.4014 | 6.9644 |
| 5 | ☐ | P21 | 3 | 0 | 319.227 | 142.95 | 0.0125 | 8.4862 | 5.4014 | 6.9642 |
| 6 | ☐ | P212121 | 3 | 0 | 319.150 | 141.98 | 0.0112 | 6.9636 | 5.4013 | 8.4851 |
| 7 | ☐ | P2 | 3 | 0 | 319.241 | 141.30 | 0.0127 | 8.4865 | 5.4014 | 6.9644 |
| 8 | ☐ | P21 | 3 | 0 | 319.205 | 140.84 | 0.0119 | 8.4861 | 5.4013 | 6.9641 |
| 9 | ☐ | P2 | 3 | 0 | 319.438 | 140.79 | 0.0170 | 8.4892 | 6.9647 | 5.4027 |



10. Repeat the indexing run with orthorhombic lattices only.

The best solution found is Pna21 (space group #33). Perform a Pawley or a Le Bail refinement to see if all solutions explain all observed peaks.

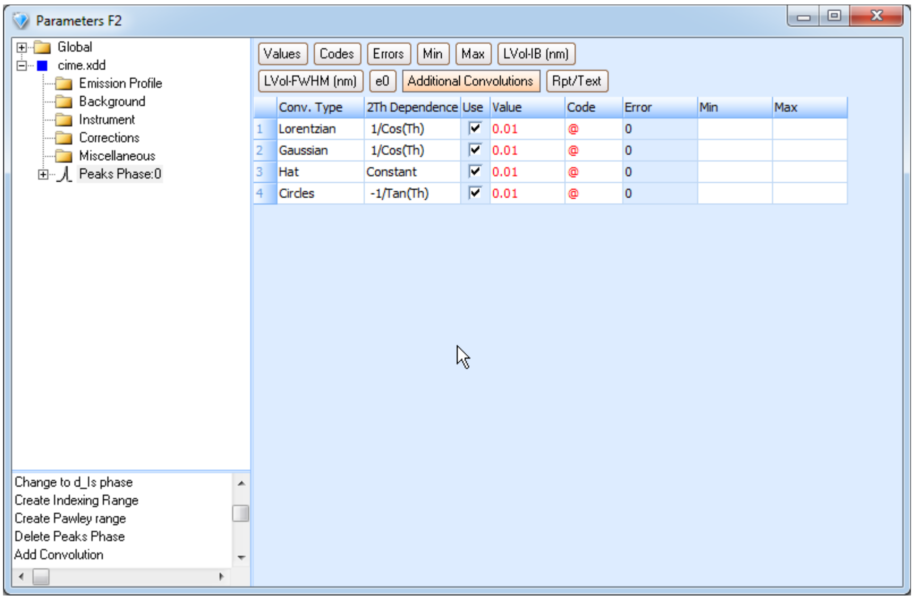
This solution is not unique, as both, Pna21 as well as Pnma (space group 62) corresponds to the same extinction symbol Pna-.

The correct solution is Pnma, a = 8.482 Å, b = 5.397 Å, c = 6.959 Å, volume = 319 Å$^3$.

### 2.2.1.2 Indexing of Cimetidine

1. Load the raw data by importing the file Cime.xdd.
2. Insert 20 - 25 peaks at the desired 2θ positions (up to about 24° 2θ). Use the FP peak type.
3. Open the *Parameters Window* and expand the "Cime.xdd" range:
    - Select the *Emission Profile*. Invoke the short cut menu of the *Emission Profile* item (right mouse button click) and insert an emission profile line using *Add Emission Line*. Define an emission profile with an area of 1, a wavelength of 1.529040 Å, as well as Lorentzian and Gaussian half-widths of the emission profile line of 0.0001 milli-Å.
    - Select the *Background* item. Use a Chebychev Polynomial of 5th order as well as the *1/X Bkg* function.
    - Select the *Miscellaneous* item. Set *Finish X* to about 24° 2θ to include all selected peaks.
    - Select the *Peak Phase* item, select the *Codes* page and uncheck the *Cry Size L* parameter for all peaks. Secondly switch to the *Additional Convolutions* page and add a *Lorentzian* convolution with 1/Cos(Th) dependence, a constant *Hat* convolution, and a *Circles* convolution with -1/Tan(Th) dependence. Set all values to 0.01 (very small as there is only little broadening) and parameter codes to "Refine".

Note: The source emission profile / instrument function of the present diffractometer is unknown, thus empirical profile fitting will be used. The emission profile used in the example is essentially a delta function, representing the actual wavelength used. Refinement of meaningful microstructure parameters is thus not possible.



| | Conv. Type | 2Th Dependence | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1/Cos(Th) | ☑ | 0.01 | @ | 0 | | |
| 2 | Gaussian | 1/Cos(Th) | ☑ | 0.01 | @ | 0 | | |
| 3 | Hat | Constant | ☑ | 0.01 | @ | 0 | | |
| 4 | Circles | -1/Tan(Th) | ☑ | 0.01 | @ | 0 | | |

4. Run the refinement. Refinement of overlapped and low intensity peaks will be difficult unless the background and the major peaks have been successfully fitted. Consider to exclude overlapped and low intensity peaks in the first refinement run(s) or fix their peak positions. Gradually include these peaks or their positions into the refinement. Refine on all peak positions once all calculated peaks "locked-in".
5. Select the peaks phase and 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.
6. Select the *Indexing* range and unselect the "Cime.xdd" range. Optional: To remove clutter from the screen unselect all peaks or delete the *Peaks Phase*.
7. Select all Bravais lattice(s) to be included in the indexing run. Default indexing parameters are appropriate for this example.
8. Run the refinement.
9. Indexing details are provided in the *Solutions* page. For each selected solution observed and calculated peak positions are shown in the *Scan Window*. Additionally, with the "cime.xdd" range selected as well, the raw data can be overlaid with or without the single peak fit results.

   It can be seen, that there are many triclinic top solutions with angles close to 90° obscuring a monoclinic solution. Repeat the indexing run with monoclinic lattices only.

The best solutions found usually include P2 (Vol = 1281 Å$^3$), P21 (Vol = 1281 Å$^3$), and P21/c (Vol = 2562 Å$^3$ $\Rightarrow$ doubled volume / doubled a lattice parameter). Perform Pawley or Le Bail refinements to see if all solutions explain all observed peaks.

P2 and P21 imply 2 (4, 6, …) copies of a molecule in a general position, while P21/c implies 4 (8, 12, …) copies of the molecule in a general position.

A typical organic molecule occupies ~17 Å$^3$. Cimetidine has 17 non-H atoms, thus 1281 Å$^3$ / (17*17 Å$^3$) fits 4 molecules, making this the highest probable trial cell. Perform another Pawley or Le Bail refinement to see if the P21/c cell with halved lattice parameter a explains all observed peaks. Perform analogous checks for other trial cells.

The correct solution is P21/c, a = 6.825 Å, b = 18.819, c = 10.394 Å, ß = 106.44°, volume = 1280 Å$^3$ (Cernik et al., 1991).

## 2.2.2 Tips and Tricks

Indexing of powder data is a complex problem, which does not permit solutions to be identified with certainty. Any indexing methods report 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.

### 2.2.2.1 TOPAS tweaks

- **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

- **Refine on isotropic line profile shapes**

  Refining on an isotropic line profile shape will help to recognize strongly overlapping peaks. For samples exhibiting anisotropic line broadening consider using the LP-Search method (section 2.2.3).

- **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.

- **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.

- **Play with the "Good" and "Max ratio 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 ratio 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. E.g., for triclinic cells, a large number of calculated lines that don’t correspond to observed lines is worrisome as triclinic space groups do not have systematic absences.

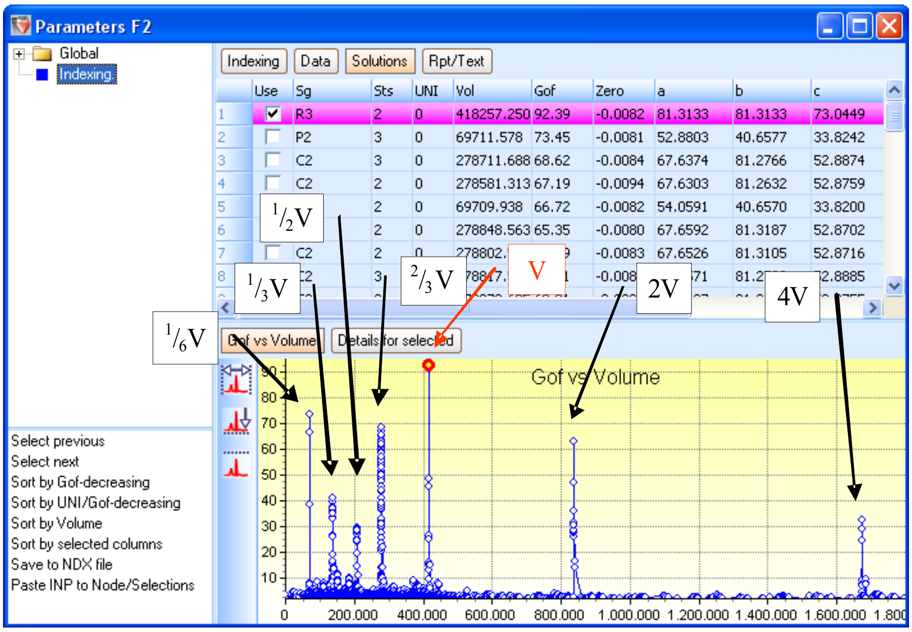
- **Use the "goodness-of-fit versus volume plot" to identify pseudo-solutions**

  Frequently solutions will be found with fractional or multiple volumes of the correct cell: 1/2V, 2/3V, V, 2V, 3V, 4V, ... Multiplied volumes are often the result of multiplied lattice parameters. Also, 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 cell can be indexed by an orthorhombic cell with 1/2 volume

  etc.

  Also, a/b, a/c, etc. ratios of $\sqrt{2} = 1.414$ or $\sqrt{3} = 1.732$ may indicate pseudo-solutions.

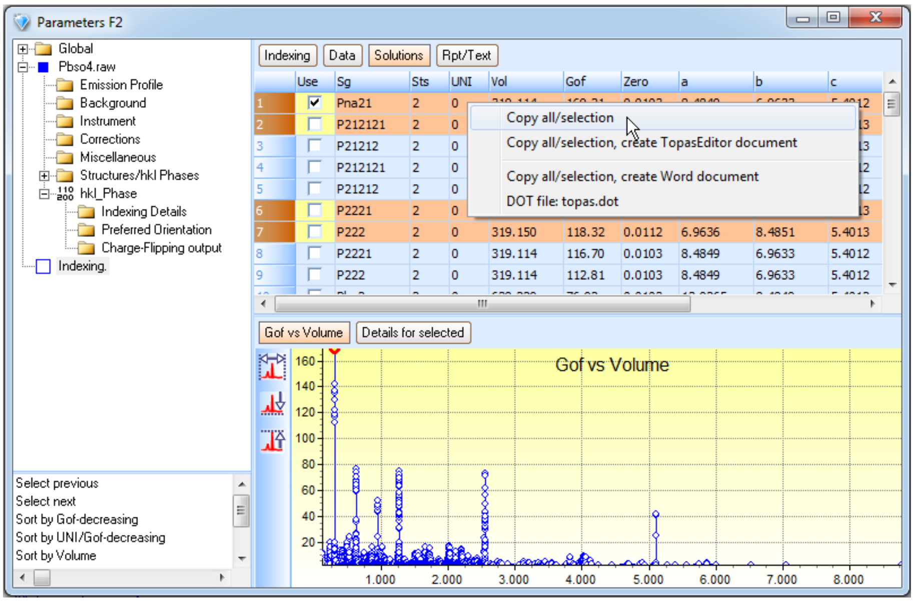


| | Use | Sg | Sts | UNI | Vol | Gof | Zero | a | b | c |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ☑ | R3 | 2 | 0 | 418257.250 | 92.39 | -0.0082 | 81.3133 | 81.3133 | 73.0449 |
| 2 | ☐ | P2 | 3 | 0 | 69711.578 | 73.45 | -0.0081 | 52.8803 | 40.6577 | 33.8242 |
| 3 | ☐ | C2 | 3 | 0 | 278711.688 | 68.62 | -0.0084 | 67.6374 | 81.2766 | 52.8874 |
| 4 | ☐ | C2 | 2 | 0 | 278581.313 | 67.19 | -0.0094 | 67.6303 | 81.2632 | 52.8759 |
| 5 | | | 2 | 0 | 69709.938 | 66.72 | -0.0082 | 54.0591 | 40.6570 | 33.8200 |
| 6 | | | 2 | 0 | 278848.563 | 65.35 | -0.0080 | 67.6592 | 81.3187 | 52.8702 |
| 7 | ☐ | C2 | 2 | 0 | 278802. | | -0.0083 | 67.6526 | 81.3105 | 52.8716 |
| 8 | | C2 | 3 | | 78817. | | -0.008 | | 81.2 | 2.8885 |

- **Always perform single or multiple Pawley / Le Bail refinements to see if trial cells explain all observed peaks**

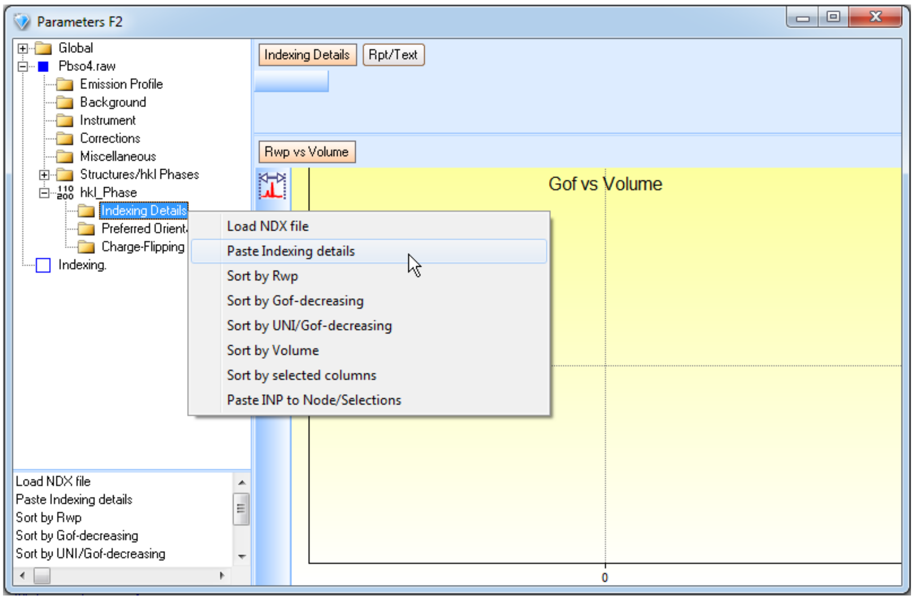
  TOPAS allows multiple, automatic Pawley / Le Bail refinements of selected trial cells:

  1. Switch to the *Solutions* page. Select and copy all trial cells you would like to refine.

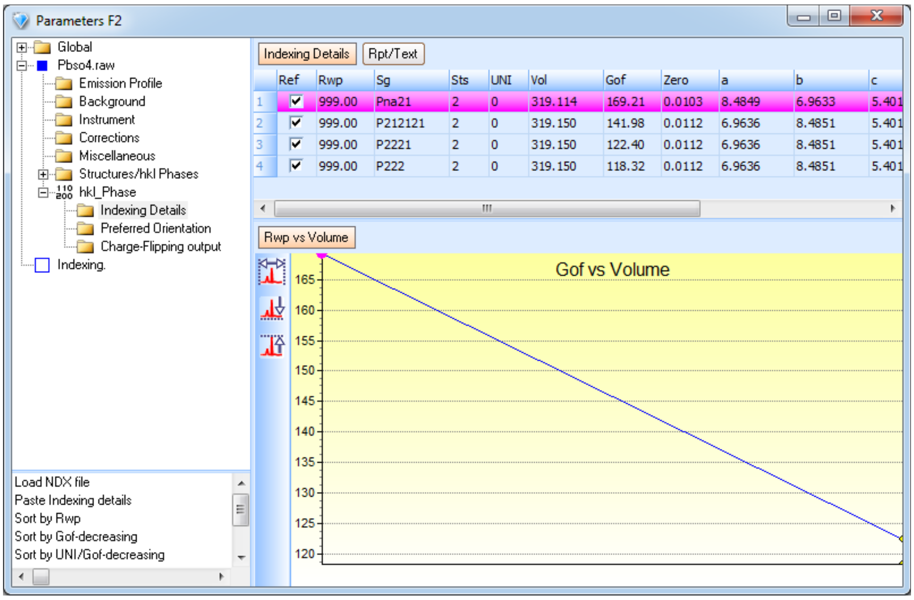


| | Use | Sg | Sts | UNI | Vol | Gof | Zero | a | b | c |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ☑ | Pna21 | 2 | 0 | | | | | | 12 |
| 2 | ☐ | P212121 | 2 | 0 | | | | | | 13 |
| 3 | ☐ | P21212 | 2 | 0 | | | | | | 13 |
| 4 | ☐ | P212121 | 2 | 0 | | | | | | 12 |
| 5 | ☐ | P21212 | 2 | 0 | | | | | | 12 |
| 6 | ☐ | P2221 | 2 | 0 | | | | | | 13 |
| 7 | ☐ | P222 | 2 | 0 | 319.150 | 118.32 | 0.0112 | 6.9636 | 8.4851 | 5.4013 |
| 8 | ☐ | P2221 | 2 | 0 | 319.114 | 116.70 | 0.0103 | 8.4849 | 6.9633 | 5.4012 |
| 9 | ☐ | P222 | 2 | 0 | 319.114 | 112.81 | 0.0103 | 8.4849 | 6.9633 | 5.4012 |

  2. Create and expand a *hkl_Phase* item and select the *Indexing Details* item. Insert the indexing details by selecting *Paste Indexing details* in the shortcut menu.



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



| | Ref | Rwp | Sg | Sts | UNI | Vol | Gof | Zero | a | b | c |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ☑ | 999.00 | Pna21 | 2 | 0 | 319.114 | 169.21 | 0.0103 | 8.4849 | 6.9633 | 5.401 |
| 2 | ☑ | 999.00 | P212121 | 2 | 0 | 319.150 | 141.98 | 0.0112 | 6.9636 | 8.4851 | 5.401 |
| 3 | ☑ | 999.00 | P2221 | 2 | 0 | 319.150 | 122.40 | 0.0112 | 6.9636 | 8.4851 | 5.401 |
| 4 | ☑ | 999.00 | P222 | 2 | 0 | 319.150 | 118.32 | 0.0112 | 6.9636 | 8.4851 | 5.401 |

#### 2.2.2.2 Use of specialized 3rd party helper software

The following software can greatly assist efforts in space-group determination:

1. **Chekcell / Truecell:**
   Checkcell is a powder indexing helper tool for unit cell and space-group assignment, while Truecell searches for more symmetric multiple cells from a given cell.

   Both software packages can be obtained here:
   http://www.ccp14.ac.uk/ccp/web-mirrors/lmgp-laugier-bochu/
2. **ExtSym:**
   ExtSym (Markvardsen at al., 2001, 2008) helps to determine the extinction symbol of a crystalline material from powder diffraction data. It returns a ranked list of the probabilities of the extinction symbols belonging to a crystal system The top ranked symbols from a ExtSym output table is very likely to include the correct extinction symbol. Structure determination should be attempted in the sequence suggested by the ranked list.

   Most significantly, ExtSym interfaces TOPAS and can be easily used in connection with Pawley refinements.

   ExtSym can be obtained here:
   http://www.markvardsen.net/projects/ExtSym/main.html
3. **Computational Crystallography Toolbox**

   Excellent tools to put lattices in standard form (and more) can be found in the Computational Crystallography Toolbox, http://cci.lbl.gov/cctbx/index.html, (Grosse-Kunstleve et al., 2002).

## 2.2.3 LP-Search

Example files are found in the C:\Topas\Tutorial\Indexing\LP-Search directory, Table 2.2 provides the crystallographic data.

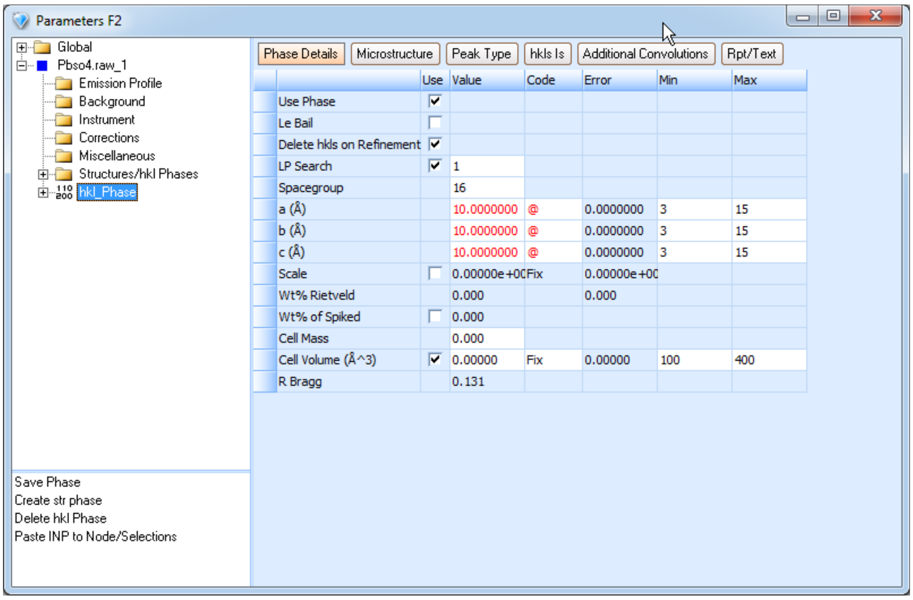
Table 2.2: Crystallographic data for the LP-Search tutorial examples.

| **Example** | **Symmetry** | **Lattice parameters (Å) / (°)** | | | **Vol (Å$^3$)** |
|---|---|---|---|---|---|
| PbSO4 (1) | Orthorhombic | a = 8.482 | b = 5.397 | c = 6.959 | 319 |
| Cime (2) | Monoclinic | a = 10.395 | b = 18.820<br>β = 106.4 | c = 6.826 | 1281 |
| Captopril (3) | Orthorhombic | a = 8.811 | b = 17.984 | c = 6.837 | 1082 |
| Zopiclone Dihydrate (3) | Monoclinic | a = 16.374 | b = 7.030<br>β = 108.6 | c = 17.185 | 1926 |
| ZrMo2O8 (4) | Orthorhombic | a = 5.879 | b = 7.329 | c = 9.130 | 393 |

(1) Hill (1992); (2) Cernik et al. (1991); (3) Florence (2002); (4) Allen at al. (2003)

### 2.2.3.1 General guidelines

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



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Use Phase | ☑ | | | | | |
| Le Bail | ☐ | | | | | |
| Delete hkls on Refinement | ☑ | | | | | |
| LP Search | ☑ | 1 | | | | |
| Spacegroup | | 16 | | | | |
| a (Å) | | 10.0000000 | @ | 0.0000000 | 3 | 15 |
| b (Å) | | 10.0000000 | @ | 0.0000000 | 3 | 15 |
| c (Å) | | 10.0000000 | @ | 0.0000000 | 3 | 15 |
| Scale | ☐ | 0.00000e+0( | Fix | 0.00000e+0( | | |
| Wt% Rietveld | | 0.000 | | 0.000 | | |
| Wt% of Spiked | ☐ | 0.000 | | | | |
| Cell Mass | | 0.000 | | | | |
| Cell Volume (Å^3) | ☑ | 0.00000 | Fix | 0.00000 | 100 | 400 |
| R Bragg | | 0.131 | | | | |

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 parameter correlation.

**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.

#### 2.2.3.2 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 2.2.3.1.
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* check box
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 and Le Bail fitting

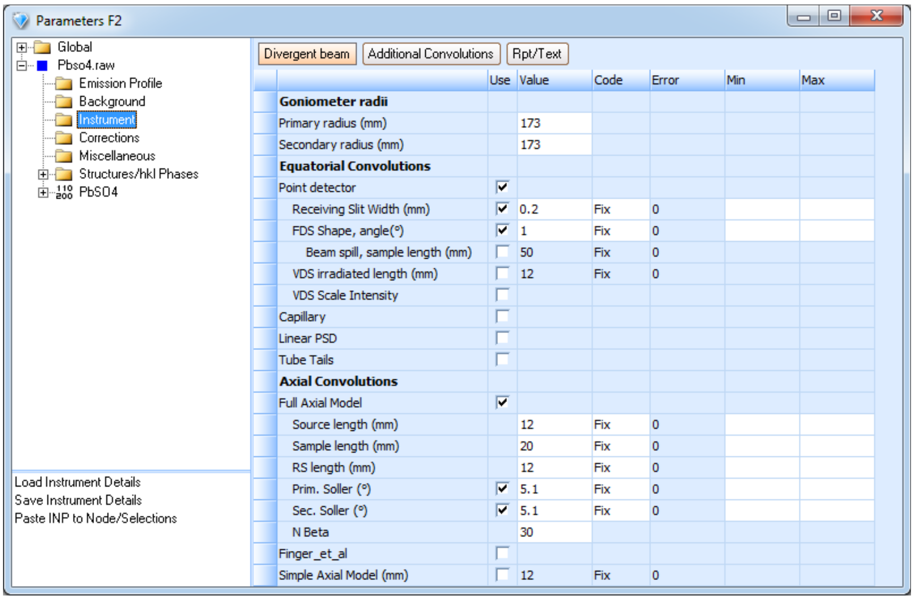
### 2.3.1.1 Pawley and Le Bail fitting of $PbSO_4$

1. Load the raw data by importing the file PbSO4.RAW into your document. By default this file is located in C:\Topas5\Tutorial\Whole Powder Pattern Decomposition\PbSO4\.
2. Open the parameters window and define the refinement model.
    - Select the *Emission Profile* item and load the emission profile CuKa5_Berger.lam.
    - Select the *Background* item. Use a Chebychev Polynomial of 5th order as well as the *1/X Bkg* function. The latter accounts for increasing background due to air-scattering when coming close to the primary beam and also allows to use a Chebychev polynomial with less coefficients.
    - Select 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:<br>Secondary: | 173 mm<br>173 mm |
| Receiving Slit Width | Width: | 0.2 mm |
| FDS [1] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary:<br>Secondary: | 5.1°<br>5.1° |

[1] Fixed Divergence Slit

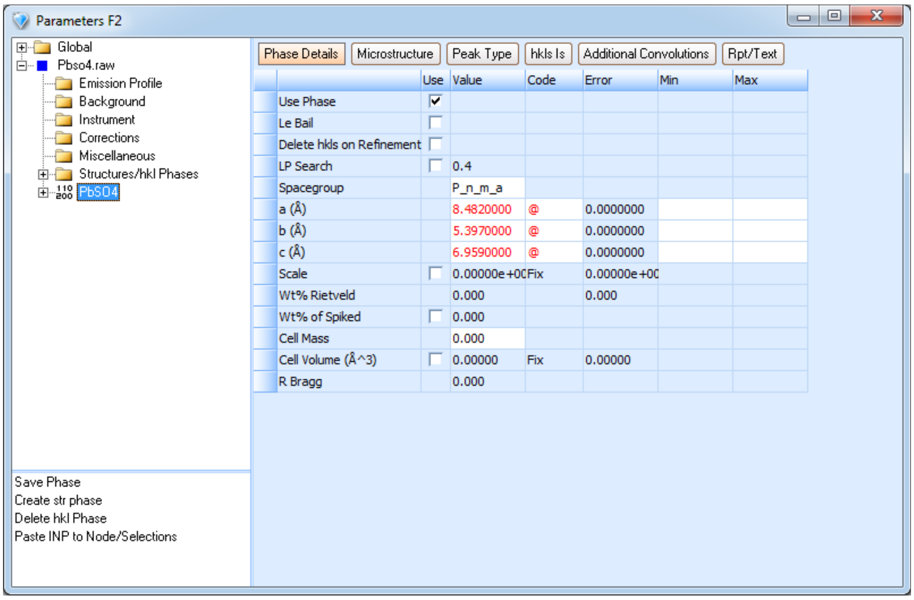


| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| **Goniometer radii** | | | | | | |
| Primary radius (mm) | | 173 | | | | |
| Secondary radius (mm) | | 173 | | | | |
| **Equatorial Convolutions** | | | | | | |
| Point detector | ☑ | | | | | |
| Receiving Slit Width (mm) | ☑ | 0.2 | Fix | 0 | | |
| FDS Shape, angle(°) | ☑ | 1 | Fix | 0 | | |
| Beam spill, sample length (mm) | ☐ | 50 | Fix | 0 | | |
| VDS irradiated length (mm) | ☐ | 12 | Fix | 0 | | |
| VDS Scale Intensity | ☐ | | | | | |
| Capillary | ☐ | | | | | |
| Linear PSD | ☐ | | | | | |
| Tube Tails | ☐ | | | | | |
| **Axial Convolutions** | | | | | | |
| Full Axial Model | ☑ | | | | | |
| Source length (mm) | | 12 | Fix | 0 | | |
| Sample length (mm) | | 20 | Fix | 0 | | |
| RS length (mm) | | 12 | Fix | 0 | | |
| Prim. Soller (°) | ☑ | 5.1 | Fix | 0 | | |
| Sec. Soller (°) | ☑ | 5.1 | Fix | 0 | | |
| N Beta | | 30 | | | | |
| Finger_et_al | ☐ | | | | | |
| Simple Axial Model (mm) | ☐ | 12 | Fix | 0 | | |

- Select 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.
- Select 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*.
- Select the *hkl_Phase* item. 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".
- Optional: To perform a Le Bail refinement check the Le Bail checkbox.

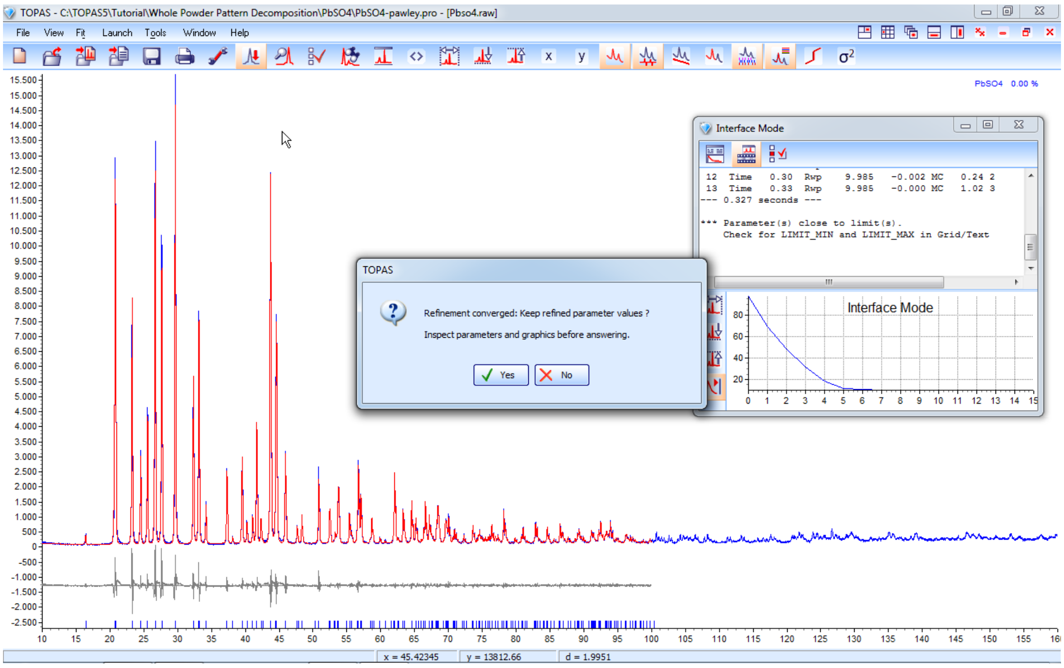
**Crystallographic Data for $PbSO_4$:**

| | | |
|---|---|---|
| Space group | | : Pnma |
| Cell parameters | a (Å) | : 8.482 |
| | b (Å) | : 5.397 |
| | c (Å) | : 6.959 |



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Use Phase | ☑ | | | | | |
| Le Bail | ☐ | | | | | |
| Delete hkls on Refinement | ☐ | | | | | |
| LP Search | ☐ | 0.4 | | | | |
| Spacegroup | | P_n_m_a | | | | |
| a (Å) | | 8.4820000 | @ | 0.0000000 | | |
| b (Å) | | 5.3970000 | @ | 0.0000000 | | |
| c (Å) | | 6.9590000 | @ | 0.0000000 | | |
| Scale | ☐ | 0.00000e+0 | Fix | 0.00000e+00 | | |
| Wt% Rietveld | | 0.000 | | 0.000 | | |
| Wt% of Spiked | ☐ | 0.000 | | | | |
| Cell Mass | | 0.000 | | | | |
| Cell Volume (Å^3) | ☐ | 0.00000 | Fix | 0.00000 | | |
| R Bragg | | 0.000 | | | | |

3. Run the refinement.



```
 12  Time   0.30  Rwp    9.985   -0.002 MC   0.24 2
 13  Time   0.33  Rwp    9.985   -0.000 MC   1.02 3
--- 0.327 seconds ---

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

Refinement converged: Keep refined parameter values ?

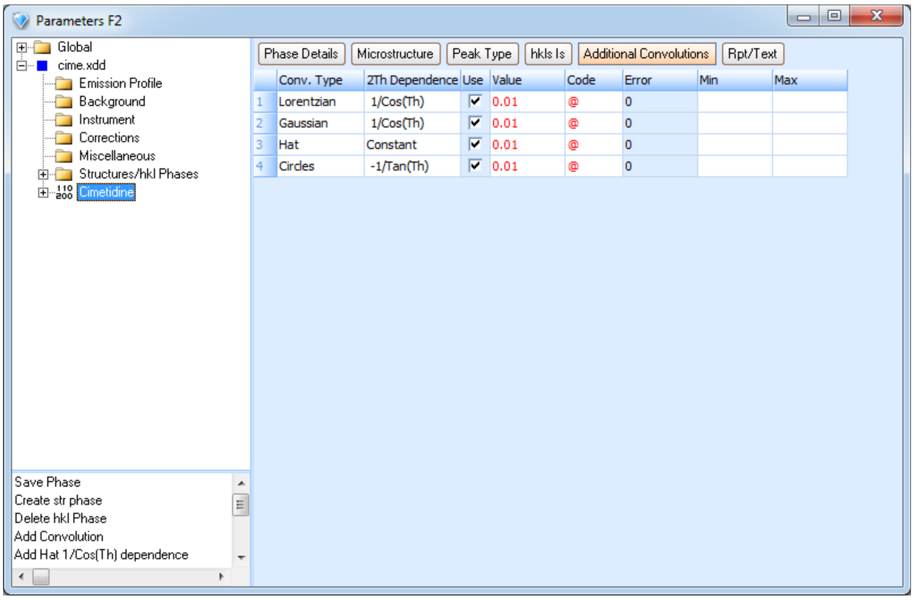
Inspect parameters and graphics before answering.

### 2.3.1.2 Pawley and Le Bail fitting of Cimetidine

1. Load the raw data by importing the file CIME.XDD into your document. By default this file is located in C:\Topas5\Tutorial\Whole Powder Pattern Decomposition\Cime\.
2. Open the parameters window and define the refinement model.
   - Select the *Emission Profile* item and define a emission profile with a wavelength of 1.529040 Å as well as Lorentzian and Gaussian half-widths of the emission profile line of 0.0001 milli-Å.
   - Select the *Background* item. Use a Chebychev Polynomial of 5th order as well as the *1/X Bkg* function.
   - Select the *Corrections* item. Check the zero point error and set its code to "Refine". Check the LP factor and set the monochromator angle to 90° 2θ.
   - Select the *Miscellaneous* item and set *Finish X* to about 52° 2θ.
   - Insert a new hkl_I phase. Invoke the short cut menu of the range entry for Cime.xdd and select *Add hkl phase*.
   - Select the *hkl_Phase* item. Input the crystallographic data given below in the *Phase Details* page and change all lattice parameter codes to "Refine".

| **Crystallographic Data for Cimetidine** | | |
|---|---|---|
| Space group | | : P21/c |
| Cell parameters | a (Å) | : 6.8256 |
| | b (Å) | : 18.8200 |
| | c (Å) | : 10.3950 |
| | ß (°) | : 106.4 |

   - Switch to the *Additional Convolutions* page and add a *Lorentzian* convolution with 1/Cos(Th) dependence, a constant *Hat* convolution, and a *Circles* convolution with -1/Tan(Th) dependence and set their respective parameter codes to "Refine".



| | Conv. Type | 2Th Dependence | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1/Cos(Th) | ☑ | 0.01 | @ | 0 | | |
| 2 | Gaussian | 1/Cos(Th) | ☑ | 0.01 | @ | 0 | | |
| 3 | Hat | Constant | ☑ | 0.01 | @ | 0 | | |
| 4 | Circles | -1/Tan(Th) | ☑ | 0.01 | @ | 0 | | |

- Optional: To perform a Le Bail refinement check the *Le Bail* checkbox.

3. Run the refinement.

## 2.3.2 Tips and tricks

In TOPAS the default is Pawley refinement, the flag *lebail* triggers a Le Bail refinement. The ability to easily switch between Pawley and Le Bail fitting back and forth, while maintaining all previously refined parameters as needed / feasible, allows maximum exploitation of both methods.

Important application areas for both methods are:

- Parallel Pawley and Rietveld refinements can help to distinguish misfits due to inadequate structure and profile shape models
    - As a consequence, the best achievable profile reliability factors by Rietveld refinement can be estimated by a Pawley refinement
- Modelling of complex profile shapes, e.g. profile shape anisotropy, can more easily be performed by a Pawley fit before introducing / refining structure information for Rietveld structure refinement
- Switching between Pawley and Le Bail fitting allows validation of refined structure factors

By default hkls are automatically deleted when the refinement is started (*Delete hkls on Refinement* checkbox). This avoids ambiguities when changing the space group or the 2θ range.

When switching between Pawley and Le Bail refinement it is mandatory to consider the following 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.

## 2.4 Structure determination

The principles of structure determination using TOPAS are discussed in the Technical Reference manual in detail. The following methods are covered by step by step exercises below:

1. Global optimization - Monte-Carlo
   - Step intensities
2. Global optimization - Simulated Annealing (only available in Launch Mode!)
   - Step intensities
   - Peak maximum intensities
   - Structure factors
3. Charge Flipping
4. Difference Fourier Analysis (only available in Launch Mode!)

### 2.4.1 Global Optimization - Monte-Carlo

Small structures can be solved using a basic Monte-Carlo type approach in both GUI as well as Launch Mode and if data quality is good. The examples discussed are particularily educational as they nicely demonstrate the underlying principle of TOPAS's Global Optimization approach and its relationship to the classic Rietveld method of structure refinement when using step intensity data, and can be operated in GUI mode.

Note, that this Monte-Carlo approach is generally not recommended for practical work because search of parameter space is inferior, and so is the structure determination success rate. Simulated Annealing is the method of choice.

Also note that in GUI mode there is no possibility to define any user-defined refinement parameters / models such as chemical or geometric constraints / restraints / penalties, weighthing schemes etc. Serious structure analysis work using Simulated Annealing requires TOPAS operation in Launch Mode and is discussed in section 2.4.2.

#### 2.4.1.1 Structure determination of $PbSO_4$

1. Perform a Pawley fit as described in section 2.3.1.1.
2. After refinement all refined parameters (background, corrections, lattice parameters, profile parameters, ...) must be fixed.
3. Select the *hkl_Phase* item for $PbSO_4$. Invoke its short cut menu and select *Create str phase*. Disable the hkl_Phase item by clearing the *Use Phase* checkbox.

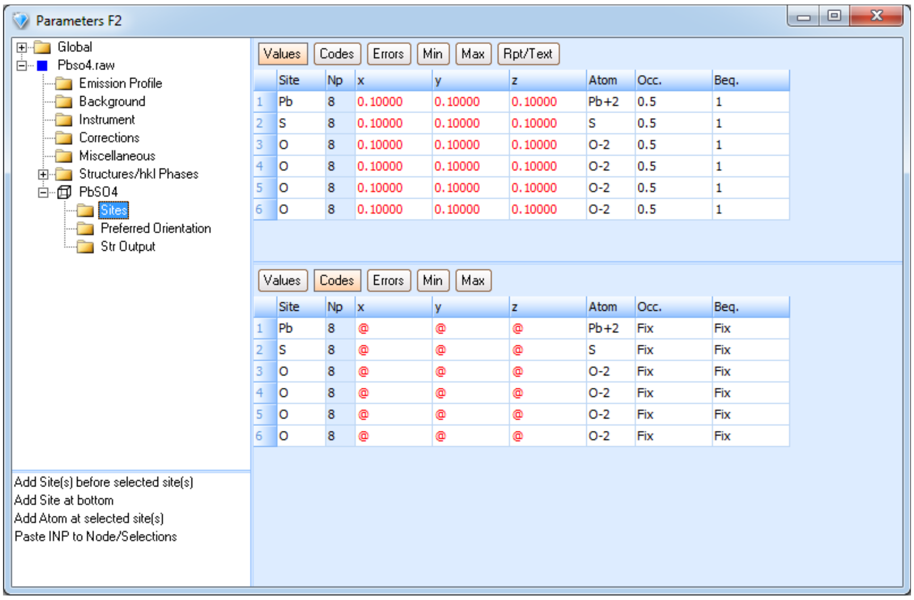
4. Construct a trial structure for $PbSO_4$. Expand the *Structure* item and select the *Site* item. Insert 6 sites by selecting *Add site at bottom* in the short cut menu and input the structure data provided in the table below.

   This trial structure is based on the following considerations:

   - According to the chemical formula the trial crystal structure is defined using 6 individual atoms on <u>general</u> positions arbitrarily set to e.g. x = y = z = 0.001.
   - Space group Pnma (#62) will generate 8 equivalent positions per general position, that is 8 Pb, 8 S, and 32 O atoms. 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. Therefore, as long as special positions haven't been identified, the occupancies for all sites have to be set to 0.5.

**Atom coordinates and isotropic thermal parameters for $PbSO_4$:**

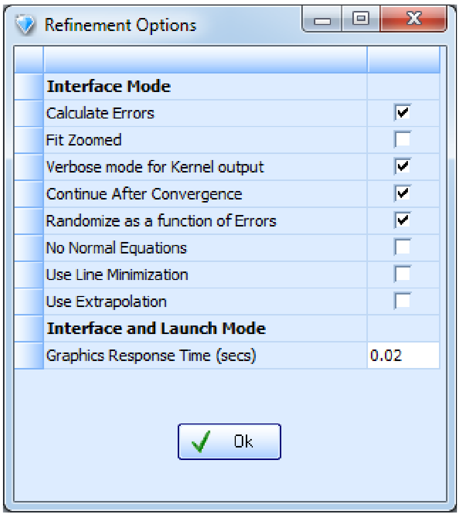
| **Site:** | **x** | **y** | **z** | **Atom** | **Occ** | **B[$A^2$]** |
|---|---|---|---|---|---|---|
| Pb | 0.001 | 0.001 | 0.001 | Pb+2 | 0.5 | 1 |
| S | 0.001 | 0.001 | 0.001 | S | 0.5 | 1 |
| O1 | 0.001 | 0.001 | 0.001 | O-2 | 0.5 | 1 |
| O2 | 0.001 | 0.001 | 0.001 | O-2 | 0.5 | 1 |
| O3 | 0.001 | 0.001 | 0.001 | O-2 | 0.5 | 1 |
| O4 | 0.001 | 0.001 | 0.001 | O-2 | 0.5 | 1 |



| | Site | Np | x | y | z | Atom | Occ. | Beq. |
|---|---|---|---|---|---|---|---|---|
| 1 | Pb | 8 | 0.10000 | 0.10000 | 0.10000 | Pb+2 | 0.5 | 1 |
| 2 | S | 8 | 0.10000 | 0.10000 | 0.10000 | S | 0.5 | 1 |
| 3 | O | 8 | 0.10000 | 0.10000 | 0.10000 | O-2 | 0.5 | 1 |
| 4 | O | 8 | 0.10000 | 0.10000 | 0.10000 | O-2 | 0.5 | 1 |
| 5 | O | 8 | 0.10000 | 0.10000 | 0.10000 | O-2 | 0.5 | 1 |
| 6 | O | 8 | 0.10000 | 0.10000 | 0.10000 | O-2 | 0.5 | 1 |

| | Site | Np | x | y | z | Atom | Occ. | Beq. |
|---|---|---|---|---|---|---|---|---|
| 1 | Pb | 8 | @ | @ | @ | Pb+2 | Fix | Fix |
| 2 | S | 8 | @ | @ | @ | S | Fix | Fix |
| 3 | O | 8 | @ | @ | @ | O-2 | Fix | Fix |
| 4 | O | 8 | @ | @ | @ | O-2 | Fix | Fix |
| 5 | O | 8 | @ | @ | @ | O-2 | Fix | Fix |
| 6 | O | 8 | @ | @ | @ | O-2 | Fix | Fix |

5. Switch to the *Codes* page and change the code for all coordinates to "Refine".
6. Switch to the *Min* page and change the lower limit for all coordinates to -1.
7. Switch to the *Max* page and change the upper limit for all coordinates to 1.
8. To speed up calculations select the *Global* item, switch to the *Global Stats/Convergence Criterion*, and set *Chi2 convergence criterion* to 0.01.
9. Select the *Structure* item and open the *Structure Viewer* by selecting *Hide/View Structure*.
10. To initiate the Monte-Carlo process, open the *Fit Window* and its *Refinement Options Dialog*. Check the following three items: *Calculate Errors*, *Randomize as a Function of Errors*, and *Continue After Convergence*.



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

11. Start the refinement and monitor both the atom movements in the *Structure Viewer* as well as $R_{WP}$ in the *Fit 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.
12. Once $R_{WP}$ drops down to ~10.5% the structure is solved. Stop the refinement.
13. Examine the structure in the Structure Viewer. Note the sets of two overlapping Pb, S and O atoms, respectively, where each atom represents an occupancy factor of 0.5. These overlaps indicate special positions.

14. Select the *Structure - Site* item and inspect the refined coordinates.
    - For Pb, S and two O atoms it will be seen that the respective z-coordinates are close to 0.25 and / or 0.75, and thus the special position for these sites have been identified. 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 0.25 and / or 0.75, as applicable, change the occupancy factors to 1, and stop refining the z-coordinates.
    - Check the coordinates of the remaining two O atoms. It can be seen, that these two 0 atoms sit on equivalent positions, thus one of the two atoms is redundant and must be deleted. Change the occupancy factors of the remaining O atom to 1.
15. Perform a final Rietveld refinement.
    - Open the *Fit Window* and its *Refinement Options Dialog*. Clear the *Randomize as a Function of Errors* and *Continue After Convergence* checkboxes.
    - Refine all temperature factors
    - Include all previously fixed parameters (background, corrections, lattice parameters, profile parameters, ...) into the refinement.
    - Reset *Chi2 convergence criterion* to a value that ensures convergence. The default 0.001 works well in most cases.
    - Start the refinement.

### 2.4.1.2 Structure determination of Cimetidine

1. Perform a Pawley fit as described in section 2.3.1.2.
2. After refinement all refined parameters (background, corrections, lattice parameters, profile parameters, ...) must be fixed.
3. Select the *hkl_Phase* item for Cimetidine. Invoke its short cut menu and select *Create str phase*. Disable the hkl_Phase item by clearing the *Use Phase* checkbox.
4. Construct a trial structure for Cimetidine. Expand the *Structure* item and select the *Site* item. Insert 17 sites by selecting *Add site at bottom* in the short cut menu and input the structure data provided in the table below.

   This trial structure is based on the following considerations:

   - According to the chemical formula the trial crystal structure is defined using 17 individual atoms on general positions arbitrarily set to e.g. x = y = z = 0.001.
   - Space group P21/c (#14) will generate 4 equivalent positions per general position. This is consistent 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.

**Atom coordinates and isotropic thermal parameters for Cimetidine:**

| Site: | x | y | z | Atom | Occ | B[A$^2$] |
|---|---|---|---|---|---|---|
| S1 | 0.001 | 0.001 | 0.001 | S | 1 | 1 |
| N1 | 0.001 | 0.001 | 0.001 | N | 1 | 1 |
| N2 | 0.001 | 0.001 | 0.001 | N | 1 | 1 |
| N3 | 0.001 | 0.001 | 0.001 | N | 1 | 1 |
| N4 | 0.001 | 0.001 | 0.001 | N | 1 | 1 |
| N5 | 0.001 | 0.001 | 0.001 | N | 1 | 1 |
| N6 | 0.001 | 0.001 | 0.001 | N | 1 | 1 |
| O01 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |
| O02 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |
| O03 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |
| O04 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |
| O05 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |
| O06 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |
| O07 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |
| O08 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |
| O09 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |
| O10 | 0.001 | 0.001 | 0.001 | O | 1 | 1 |

5. Switch to the Codes page and change the code for all coordinates to "Refine".
6. Switch to the Min page and change the lower limit for all coordinates to -1.
7. Switch to the Max page and change the upper limit for all coordinates to 1.
8. To speed up calculations select the *Global* item, switch to the *Global Stats/Convergence Criterion*, and set *Chi2 convergence criterion* to 0.01.
9. Select the *Structure* item and open the *Structure Viewer* by selecting *Hide/View Structure*.
10. To initiate the Monte-Carlo process, open the *Fit Window* and its *Refinement Options Dialog*. Check the following three items: *Calculate Errors*, *Randomize as a Function of Errors*, and *Continue After Convergence*.
11. Start the refinement and monitor both the atom movements in the *Structure Viewer* as well as $R_{WP}$ in the *Fit Window*.
12. Once $R_{WP}$ drops down to ~12.8% the structure is solved. Stop the refinement.
13. Check connectivity and correct atom types (O, N) where necessary
14. Perform a final Rietveld refinement.
    - Open the *Fit Window* and its *Refinement Options Dialog*. Clear the *Randomize as a Function of Errors* and *Continue After Convergence* checkboxes.
    - To calculate bond lengths and angles expand the *Structure* item, select the *Str Output* item and check the *Generate Bond-lengths/errors* checkbox.
    - Include all previously fixed parameters (background, corrections, lattice parameters, profile parameters, ...) into the refinement.
    - Reset *Chi2 convergence criterion* to a value that ensures convergence. The default 0.001 works well in most cases.
    - Start the refinement

From the results (bond lengths and angles) and the graphical structure display two issues should be clearly apparent:

1. Incorrect connectivity. Powder X-ray diffraction data quality does not allow to distinguish between carbon and nitrogen atoms
2. Refined bond lengths and angles significantly deviate from expected values

An appropriate structure refinement will require some sort of suited geometric constraints, restraints, or penalties. This requires TOPAS operation in Launch Mode, see section 2.4.2.

## 2.4.2 Global optimization - Simulated Annealing

**Launch Mode only!**

TOPAS operation in Launch Mode requires knowledge of the TOPAS macro language and editing of an INP file. An easy way to learn the macro language is to perform the Pawley refinements in the following step-by-step exercises in GUI Mode, as described in sections 2.3.1.1 and 2.3.1.2, and to switch between the "Grid" and the "Text" views after each step to monitor the build-up of an INP file. The resulting INP file can be either saved using the command *File - Export to INP file* or copied into a text editor.

Table 2.3: Comparison of input files for Pawley refinement, structure determination (simulated annealing, SA), and final Rietveld structure refinement of PbSO$_4$ using step intensity data (Coelho, 2000).

| Pawley refinement ("profiling") | Structure determination (SA) | Final structure refinement (Rietveld) |
|---|---|---|
| | **`Auto_T(10)`** | |
| `xdd Pbso4.raw` | `xdd Pbso4.raw` | `xdd Pbso4.raw` |
| `... ' instrument parameters` | `... ' instrument parameters` | `... ' instrument parameters` |
| `bkg @ 0 0 0 ...`<br>`One_on_X(@, 0)` | `bkg   -129.19 273.40 -138.18 ...`<br>`One_on_X( , 8070.93)` | `bkg @ -129.19 273.40 -138.18 ...`<br>`One_on_X(@, 8070.93)` |
| `ZE(@, 0.0)` | `ZE(, 0.003)` | `ZE(@, 0.003)` |
| `LP_factor (26.37)` | `LP_factor (26.37)` | `LP_factor (26.37)` |
| `hkl_I`<br>`  space_group P_n_m_a`<br>`  a @ 8.47`<br>`  b @ 5.39`<br>`  c @ 6.95` | **`str`**<br>`  space_group P_n_m_a`<br>`  a    8.48468`<br>`  b    5.40148`<br>`  c    6.96367` | `str`<br>`  space_group P_n_m_a`<br>`  a    8.48468`<br>`  b    5.40148`<br>`  c    6.96367` |
| | **`scale @ 0.00001`** | `scale @ 0.00001` |
| | **`site Pb x @ 0.001 y @ 0.001`** `...`<br>**`site S  x @ 0.001 y @ 0.001`** `...`<br>**`site O1 x @ 0.001 y @ 0.001`** `...`<br>**`...`** | `site Pb x @ 0.188 y   0.25  ...`<br>`site S  x @ 0.427 y   0.75  ...`<br>`site O1 x @ 0.592 y   0.75  ...`<br>`...` |
| `CS_L(@, 1000)`<br>`Strain_L(@, 0.01)` | `CS_L(, 786.981)`<br>`Strain_L(, 0.067)` | `CS_L(@, 786.981)`<br>`Strain_L(@, 0.067)` |
| Note:<br>• Fix all parameters after refinement | Note:<br>• Invoke simulated annealing (Auto_T)<br>• Add a trial structure model | Note:<br>• Stop simulated annealing<br>• Refine all appropriate parameters |

Table 2.4: Comparison of input files for Pawley refinement, structure determination (simulated annealing, SA), and final structure refinement of PbSO$_4$ using structure factors.

| Pawley refinement | Structure determination (SA) | Final structure refinement |
|---|---|---|
| | **`Auto_T(10)`** | |
| `xdd Pbso4.raw` | **`xdd Pbso4.scr`** | **`xdd Pbso4.scr`** |
| `... ' instrument parameters` | | |
| `  bkg @ 0 0 0 ...`<br>`  One_on_X(@, 0)` | | |
| `  ZE(@, 0.0)` | | |
| `  LP_factor (26.37)` | | |
| `  hkl_I`<br>`    space_group P_n_m_a`<br>`    a @ 8.47`<br>`    b @ 5.39`<br>`    c @ 6.95` | **`  str`**<br>`    space_group P_n_m_a`<br>`    a    8.48468`<br>`    b    5.40148`<br>`    c    6.96367` | `  str`<br>`    space_group P_n_m_a`<br>`    a    8.48468`<br>`    b    5.40148`<br>`    c    6.96367` |
| | **`    scale @ 0.00001`** | `    scale @ 0.00001` |
| | **`    site Pb x @ 0.001 y @ 0.001 ...`**<br>**`    site S  x @ 0.001 y @ 0.001 ...`**<br>**`    site O1 x @ 0.001 y @ 0.001 ...`**<br>**`    ...`** | `    site Pb x @ 0.188 y   0.25  ...`<br>`    site S  x @ 0.427 y   0.75  ...`<br>`    site O1 x @ 0.592 y   0.75  ...`<br>`    ...` |
| `    CS_L(@, 1000)`<br>`    Strain_L(@, 0.01)` | | |
| **`  Create_hklm_d_Th2_Ip_file(Pbso4.scr)`** | | |

#### 2.4.2.1 Structure determination of $PbSO_4$

Example files are found in C:\Topas5\Tutorial\Whole Powder Pattern Decomposition\PbSO4\.

**Whole Powder Pattern Decomposition**

1. Perform a Pawley refinement.

   You may perform the Pawley refinement either

   - in GUI Mode, as described in section 2.3.1.1, and export an input file once the refinement is finished (command *File - Export to INP file*), or
   - in Launch Mode by setting the predefined input file: PbSO4-Pawley.inp (command *Launch - Set INP file*). Inspect the file and run it (command *Launch - Launch Kernel*)

2. Fix all parameters after refinement

Relevant sections of the input file are shown in the 1st column of Table 2.3. Remember to fix all parameters before proceeding with the structure determination step.

**Structure determination**

3. Modify your input file as follows and as shown in the 2nd column of Table 2.3. Alternatively inspect and run the predefined input file PbSO4-SDPD-IA.INP.
   - Invoke simulated annealing by adding the macro Auto_T(10). The temperature regime as defined in the macro Auto_T and the value 10 is sufficient for most cases. For details refer to the Technical Reference manual.
   - Replace the "hkl_I phase" by a "str phase" and construct a trial structure for $PbSO_4$ using the same considerations as in section 2.4.1.1. Insert 6 sites (1 Pb, 1 S, and 4 O sites), for example,

     ```
     site Pb x @ 0.001 y @ 0.001 z @ 0.001 occ Pb+2 0.5 beq 1
     ```

     and so on. Remember to set the occupancies for all sites to 0.5.

4. Optionally add the following keyword within the *str* block (e.g. below the *site* keywords):
   - *append_fractional* and *calculate_bondlengths* is used to calculate equivalent positions as well as bond lengths and angles respectively; this assists in structure validation and can help to identify special positions.
   - *normalize_FC* normalizes fractional site coordinates.
   - *view_structure* is used to display the structure in the Structure Viewer window.

5. Set the appropriate input file and launch the kernel. Monitor both the atom movements in the *Structure Viewer* window and $R_{WP}$ in the *Fit 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.

6. Once $R_{WP}$ drops down to ~9.9% the structure is solved. Stop the refinement.

7. Examine the structure in the Structure Viewer. Note the sets of two overlapping Pb, S and O atoms, respectively, where each atom represents an occupancy factor of 0.5. These overlaps indicate special positions.
8. Inspect the refined coordinates. Identify the special positions and fix their coordinates as described in section 2.4.2.1. Note that *append_fractional* greatly facilitates the identification of the redundant O atom. Fix the occupancy factors for all sites.

**Structure refinement (Rietveld method)**

9. Modify your input file as follows and as shown in the 3rd column of Table 2.3. Alternatively inspect and run the predefined input file PbSO4-Rietveld.INP.
   - Stop simulated annealing by disabling or deleting the Auto_T macro
   - Refine on all appropriate model parameters

Comments and ideas for further working:

- **Structure determination - identification of special sites**

  In this example the occupancies for all sites had been manually set to 0.5 to maintain the expected scattering power, based on knowledge of both the number of formula units present in the unit cell as well as space group site symmetry considerations. A more straightforward way is to use the *occ_merge* keyword 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. Add the following lines within the *str* block (e.g. below the *site* keywords):

  ```
  occ_merge S*  occ_merge_radius .6
  occ_merge O*  occ_merge_radius .6
  occ_merge Pb* occ_merge_radius .6
  ```

  When two atoms approach within a distance less than the sum of their respective *occ_merge_radius*'s then the spheres intersect and occupancies will be merged as outlined in the Technical Reference manual. In the present example occupancy factor of about 0.5 will be found for atoms sitting (more or less) on top of each other and thus indicating the special positions.

- **Structure determination - "heavy atom method":**

  Constraining or restraining known heavy atom positions can greatly facilitate the structure determination process. In this example, the correct Pb position is normally found after a few refinement cycles. There are many possibilities to constrain or restrain the Pb position. The most rigid of which is to simply fix the Pb position found and to continue the refinement. A higher sophisticated and more recommended way is to constrain the Pb 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. Add the following line right after the Pb site:

  ```
  Keep_Atom_Within_Box(.25)
  ```

  Keep_Atom_Within_Box applies constraints such that the present site cannot more outside of a box with a length of 2 * 0.25Å. The advantage of doing so is that the position of the Pb atom can still be improved within user-defined limits while locating the remaining atoms.

- **Structure determination - usage of a rigid body for $SO_4$:**

  Add the following lines within the *str* block to define a rigid body for $SO_4$ using the z-matrix notation (for a tutorial on how to create rigid bodies refer to section 3.2):

  ```
  rigid
     z_matrix S
     z_matrix O1 S 1.48
     z_matrix O3 S 1.48 O1 109.471
     z_matrix O4 S 1.48 O1 109.471  O3 -120
     z_matrix O2 S 1.48 O1 109.471  O4 -120

     Rotate_about_axies(@ 0, @ 0, @ 0)

     Translate(@ 0, @ 0, @ 0)
  ```

  Do not refine any sulphur and oxygen coordinates as these will be calculated from the translation and rotation applied to the rigid body.

- **Structure determination - usage of peak maximum intensities:**

  Add the Decompose macro within the *xdd* block in your input file. Note the significantly increased calculation speed. For good quality powder data Decompose can greatly increase the structure determination success rate.

- **Structure determination and refinement - usage of structure factors:**

  A comparison of Table 2.3 with Table 2.4 shows the differences in refinements using step intensity data or structure factors, respectively. Repeat the exercise from the beginning but apply the following changes as indicated in Table 2.4.

  - Pawley refinement: Add the macro Create_hklm_d_Th2_Ip_file(Pbso4.scr) to write refined structure factors to the file Pbso4.scr
  - Structure determination: Load the structure factor data (*xdd* Pbso4.scr). Disable or delete all background / instrument / line profile parameters.
  - Structure refinement: Stop simulated annealing by disabling or deleting the Auto_T macro

  Note:

  - The methodology used here for structure determination and refinement can be also used for single crystal diffraction data.
  - For powder diffraction data, the combination of Pawley refinement and structure refinement using structure factors is known as the so-called Two-Stage Method (Will, 1979; Will, 2006).

### 2.4.2.2 Structure determination of Cimetidine

Small crystal structures can be solved using individual atoms when data quality is sufficiently high and has been demonstrated in section 2.4.1. This is normally not the case for larger, more complex structures and / or when data quality is low, requiring a reduction of the degrees of freedom in the trial structure. In the following the more common case of structure determination using a rigid body will be demonstrated.

Example files are found in C:\Topas5\Tutorial\Whole Powder Pattern Decomposition\Cime\.

**Whole Powder Pattern Decomposition**

1. Perform a Pawley refinement.

   You may perform the Pawley refinement either

   - in GUI Mode, as described in section 2.3.1.2, and export an input file once the refinement is finished (command *File - Export to INP file*), or
   - in Launch Mode by setting the predefined input file: Cime-Pawley.INP (command *Launch - Set INP file*). Inspect the file and run it (command *Launch - Launch Kernel*)

2. Fix all parameters after refinement

Relevant sections of the input file are shown in the 1st column of . Remember to fix all parameters before proceeding with the structure determination step.

**Structure determination**

3. Modify your input file as follows and as shown in the 2nd column of Table 2.5. Alternatively inspect and run the predefined input file Cime-SDPD-XDD-IA1.INP.

   - Invoke simulated annealing by adding the macro Auto_T(10). The temperature regime as defined in the macro Auto_T and the value 10 is sufficient for most cases. For details refer to the Technical Reference manual.
   - Replace the "hkl_I phase" by a "str phase" and construct a trial structure for Cimetidine using the same considerations as in section 2.4.1.2. Insert 17 sites (1 S, 1 6, and 10 C sites), for example,

     ```
     site S  x 0.001  y 0.001  z 0.001  occ S 1  beq 1
     ```

     and so on.

     Additionally construct a rigid body representing the Cimetidine molecule and enable both translation and rotation (for a tutorial on how to create a Cimetidine rigid body refer to section 3.2).

     Do not refine any coordinates as these will be calculated from the translation and rotation applied to the rigid body.

Table 2.5: Comparison of input files for Pawley refinement, structure determination (simulated annealing, SA), and final Rietveld structure refinement of Cimetidine using step intensity data (Coelho, 2000).

| **Pawley refinement ("profiling")** | **Structure determination (SA)** | **Final structure refinement (Rietveld)** |
|---|---|---|
|  | `Auto_T(10)` |  |
| `xdd Cime.xdd` | `xdd Cime.xdd` | `xdd Cime.xdd` |
| `...` | `...` | `...` |
| `bkg @ 0 0 0 ...`<br>`One_on_X(@, 0)` | `bkg   230.13 186.98 -32.10 ...`<br>`One_on_X( , 20324.33)` | `bkg @ 230.13 186.98 -32.10 ...`<br>`One_on_X(@, 20324.33)` |
| `ZE(@, 0.0)` | `ZE(, 0.010)` | `ZE(@, 0.010)` |
| `LP_factor (0)` | `LP_factor (0)` | `LP_factor (0)` |
| `hkl_I`<br>`space_group P21/C`<br>`a  @ 6.8256`<br>`b  @ 18.820`<br>`c  @ 10.395`<br>`be @ 106.4` | `str`<br>`space_group P21/C`<br>`a     6.82553`<br>`b     18.82094`<br>`c     10.39509`<br>`be    106.44` | `str`<br>`space_group P21/C`<br>`a  @ 6.82553`<br>`b  @ 18.82094`<br>`c  @ 10.39509`<br>`be @ 106.44` |
|  | `scale @ 0.00001` | `scale @ 0.00001` |
|  | `site S  x @ 0.001 y @ 0.001 ...`<br>`site N1 x @ 0.001 y @ 0.001 ...`<br>`...`<br>`... ' any constraints/restraints` | `site S  x @ 0.007 y @ 0.090 ...`<br>`site N1 x @ 0.994 y @ 0.091 ...`<br>`...`<br>`... ' any constraints/restraints` |
| `... ' profile parameters` | `... ' profile parameters` | `... ' profile parameters` |
| Note:<br>• Fix all parameters after refinement | Note:<br>• Invoke simulated annealing (Auto_T)<br>• Add a trial structure model | Note:<br>• Stop simulated annealing<br>• Refine all appropriate parameters |

Table 2.6: Comparison of input files for Pawley refinement, structure determination (simulated annealing, SA), and final structure refinement of Cimetidine using structure factors.

| Pawley refinement | Structure determination (SA) | Final structure refinement |
|---|---|---|
| | **Auto_T(10)** | |
| xdd Cime.xdd | **xdd cime.scr** | **xdd cime.scr** |
| ... | ... | ... |
| bkg @ 0 0 0 ...<br>One_on_X(@, 0) | | |
| ZE(@, 0.0) | | |
| LP_factor (0) | | |
| hkl_I<br>space_group P21/C<br>a **@** 6.8256<br>b **@** 18.820<br>c **@** 10.395<br>be **@** 106.4 | **str**<br>space_group P21/C<br>a 6.82553<br>b 18.82094<br>c 10.39509<br>be 106.44 | str<br>space_group P21/C<br>a 6.82553<br>b 18.82094<br>c 10.39509<br>be 106.44 |
| | **scale @ 0.00001** | scale @ 0.00001 |
| | **site S x @ 0.001 y @ 0.001** ...<br>**site N1 x @ 0.001 y @ 0.001** ...<br>**...**<br>**...** ' any constraints/restraints | site S x @ 0.007 y @ 0.090 ...<br>site N1 x @ 0.994 y @ 0.091 ...<br>...<br>... ' any constraints/restraints |
| ... ' profile parameters | | |
| **Create_hklm_d_Th2_Ip_file(cime.scr)** | | |

4. Optionally add the following keyword within the *str* block (e.g. below the *site* keywords):
    - *append_fractional* and *calculate_bondlengths* is used to calculate equivalent positions as well as bond lengths and angles respectively; this assists in structure validation and can help to identify special positions.
    - *normalize_FC* normalizes fractional site coordinates.
    - *view_structure* is used to display the structure in the Structure Viewer window.
5. Set the appropriate input file and launch the kernel. Once $R_{WP}$ drops down to ~9.2% the structure is solved. Stop the refinement.

**Structure refinement (Rietveld method)**

6. Modify your input file as follows and as shown in the 3rd column of Table 2.5. Alternatively inspect and run the predefined input file Cime-Rietveld.inp.
    - Stop simulated annealing by disabling or deleting the Auto_T macro
    - Refine on all appropriate model parameters

Note:

For the final structure refinement it is necessary to consider refinement of bond lengths and bond angles as well - only torsion angles have been refined at this point. The largest part of the remaining misfit, however, is due to the lack of hydrogen atoms, which should be included for final refinement (see also Cernik, 1991).

Comments and ideas for further working:

- **Structure determination - usage of peak maximum intensities:**
  Add the Decompose macro within the *xdd* block in your input file. Note the significantly increased calculation speed. For good quality powder data Decompose can greatly increase the structure determination success rate.
- **Structure determination and refinement - usage of structure factors:**
  A comparison of Table 2.5 with Table 2.6 shows the differences in refinements using step intensity data or structure factors, respectively. Repeat the exercise from the beginning but apply the following changes as indicated in Table 2.6.
    - Pawley refinement: Add the macro Create_hklm_d_Th2_Ip_file(cime.scr) to write refined structure factors to the file cime.scr
    - Structure determination: Load the structure factor data (*xdd* cime.scr). Disable or delete all background / instrument / line profile parameters.
    - Structure refinement: Stop simulated annealing by disabling or deleting the Auto_T macro

  Note:

    - The methodology used here for structure determination and refinement can be also used for single crystal diffraction data.
    - For powder diffraction data, the combination of Pawley refinement and structure refinement using structure factors is known as the so-called Two-Stage Method (Will, 1979; Will, 2006).

## 2.4.3 Charge Flipping

The Charge Flipping method only requires cell parameters, reflection indices and intensities as input and works particularily well on high quality data (for a definition of "high quality data" refer to the section "Structure determination" in the Technical Reference manual).

Powder diffraction data usually fall under the poor data quality category and require particular considerations. In the following several possibilities will be discussed to sharpen electron densities and to introduce the necessary perturbations in the Charge Flipping process to facilitate solution. For details refer to the Technical Reference manual.

### 2.4.3.1 Structure determination of $PbSO_4$

Example files are found in C:\Topas5\Tutorial\Structure Determination and Refinement\PbSO4\.

**Whole Powder Pattern Decomposition**

1. Perform a Pawley refinement.

   You may perform the Pawley refinement either

   - in GUI Mode, as described in section 2.3.1.1, or
   - in Launch Mode by setting the predefined input file: CF-PbSO4-Pawley.INP (command *Launch - Set INP file*). Inspect the file and run it (command *Launch - Launch Kernel*)

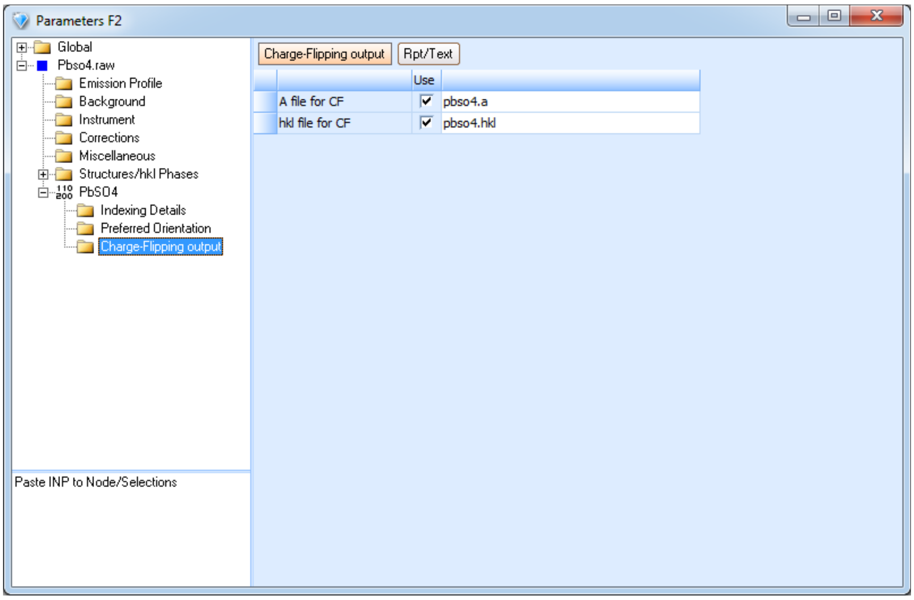
   Note: Limit the refinement to about 100° 2θ (for Cu radiation this is equivalent to a resolution of 1Å). At higher angles strong peak shifts can be seen, probably caused by a worn out goniometer, which will make the determation of the light atom (oxygen) positions difficult if not impossible.

2. After refinement save a ".a" (recommended) or ".hkl" file.

   - In GUI Mode expand the *hkl* item of $PbSO_4$, select the *Charge Flipping output* item, select the desired file type(s), and provide a filename, respectively
   - In Launch Mode add one of the following (or both) line(s) within the *hkl* block, e.g.,

     ```
     Out_for_cf(PbSO4.a)
     Out_cf_hkl(PbSO4.hkl)
     ```

   - Run one more refinement cycle



|  | Use |  |
|---|---|---|
| A file for CF | ☑ | pbso4.a |
| hkl file for CF | ☑ | pbso4.hkl |

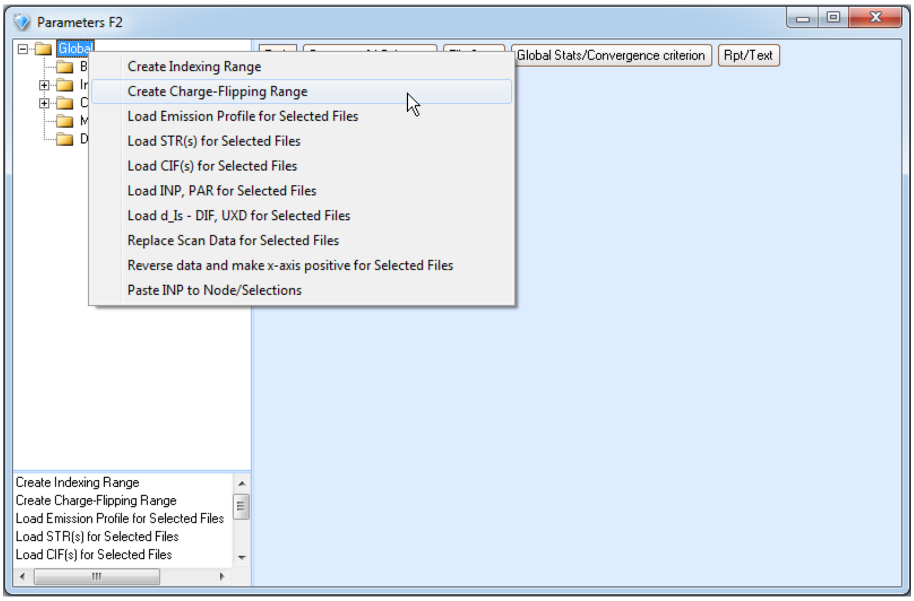
## Charge Flipping

Charge Flipping may be performed either

- in GUI Mode, as described below, or
- in Launch Mode by setting the predefined input file: CF-PbSO4.inp (command *Launch - Set INP file*). Inspect the file and run it (command *Launch - Launch Kernel*)

In GUI mode,

3. Create a new Charge Flipping range e.g. using the *Global* item shortcut menu.

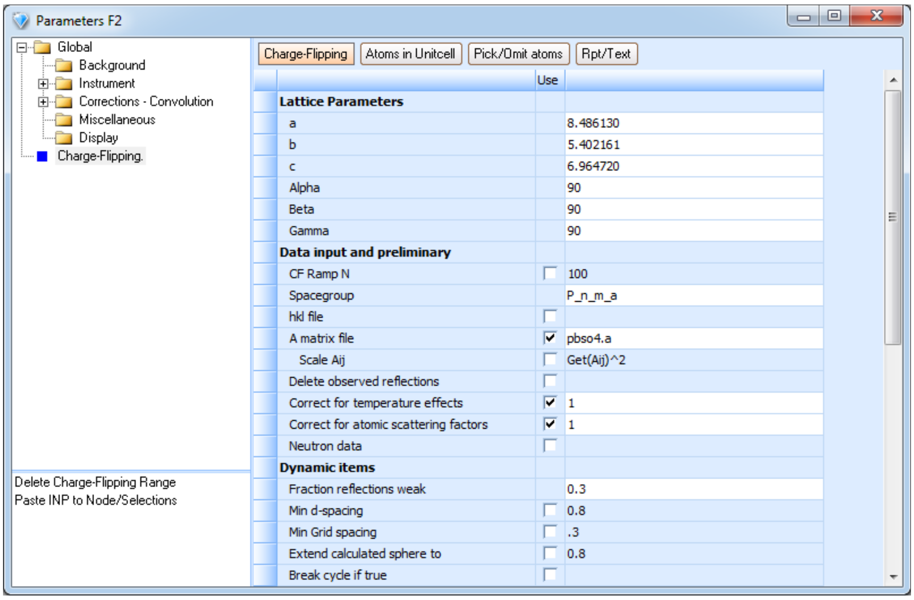


4. Input space group and lattice parameters as given below:

**Crystallographic Data for $PbSO_4$:**

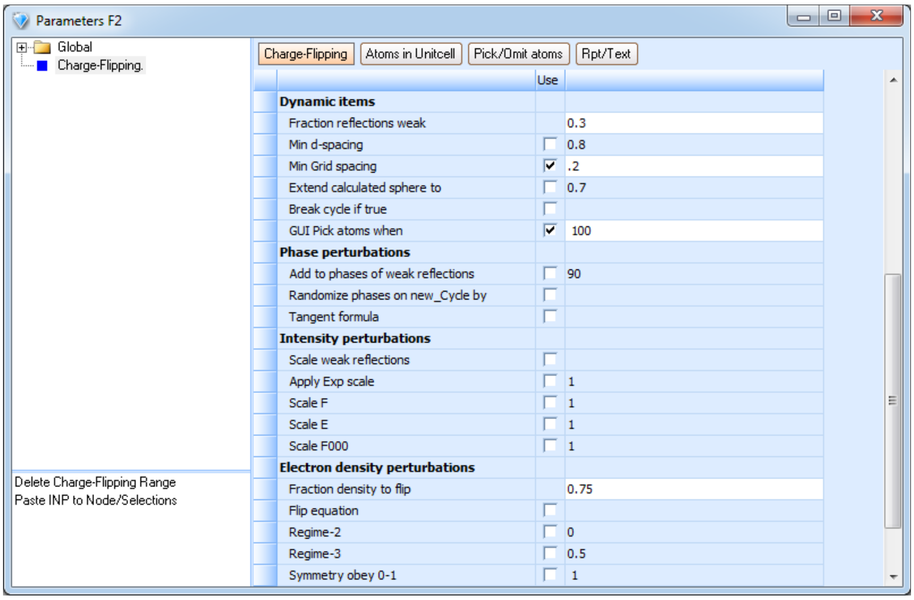
| | | |
|---|---|---|
| Space group | | : Pnma |
| Cell parameters | a (Å) | : 8.486136 |
| | b (Å) | : 5.402167 |
| | c (Å) | : 6.964702 |
| | al (°) | : 90° |
| | be (°) | : 90° |
| | ga (°) | : 90° |

5. Define an *A matrix file* (".a", recommended) or *hkl file* (".hkl") as obtained from Pawley fitting.

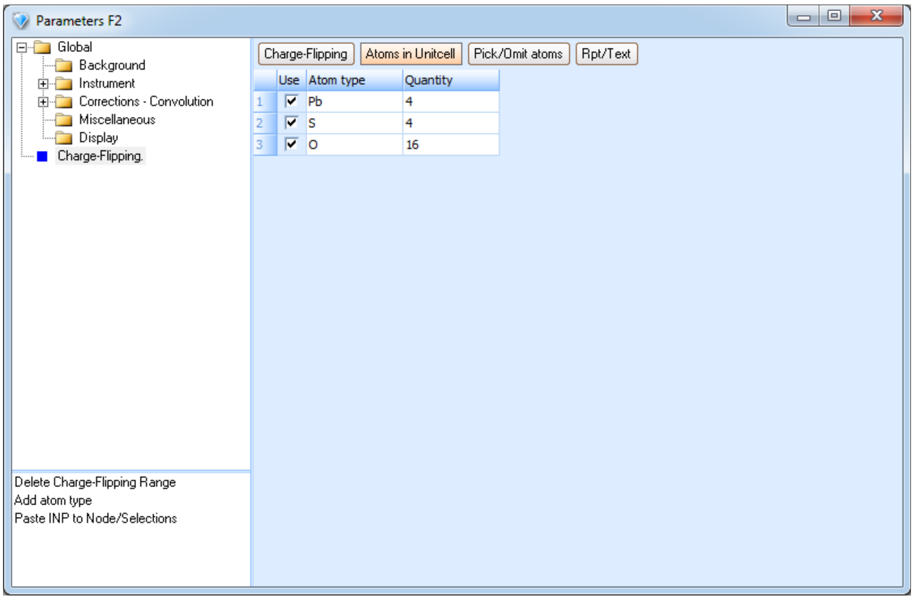


| | Use | |
|---|---|---|
| **Lattice Parameters** | | |
| a | | 8.486130 |
| b | | 5.402161 |
| c | | 6.964720 |
| Alpha | | 90 |
| Beta | | 90 |
| Gamma | | 90 |
| **Data input and preliminary** | | |
| CF Ramp N | ☐ | 100 |
| Spacegroup | | P_n_m_a |
| hkl file | ☐ | |
| A matrix file | ☑ | pbso4.a |
| Scale Aij | ☐ | Get(Aij)^2 |
| Delete observed reflections | ☐ | |
| Correct for temperature effects | ☑ | 1 |
| Correct for atomic scattering factors | ☑ | 1 |
| Neutron data | ☐ | |
| **Dynamic items** | | |
| Fraction reflections weak | | 0.3 |
| Min d-spacing | ☐ | 0.8 |
| Min Grid spacing | ☐ | .3 |
| Extend calculated sphere to | ☐ | 0.8 |
| Break cycle if true | ☐ | |

6. Optionally:
   - Reduce *Min Grid spacing* to e.g. 0.2 to increase the number of grid points. This will improve the graphical electron density display while increasing computing time
   - Perform automatic picking and assignment of atoms based on the known chemistry. Enable *GUI Pick atoms when* and set it's value to 100. This will initiate atom picking and assignment every 100 cycles. Switch to the *Atoms in Unitcell* page and define the contents of the unit cell in terms of atom types and their quantities as given by the chemical formula ($PbSO_4$) and the number of formula units in the unit cell (Z=4).



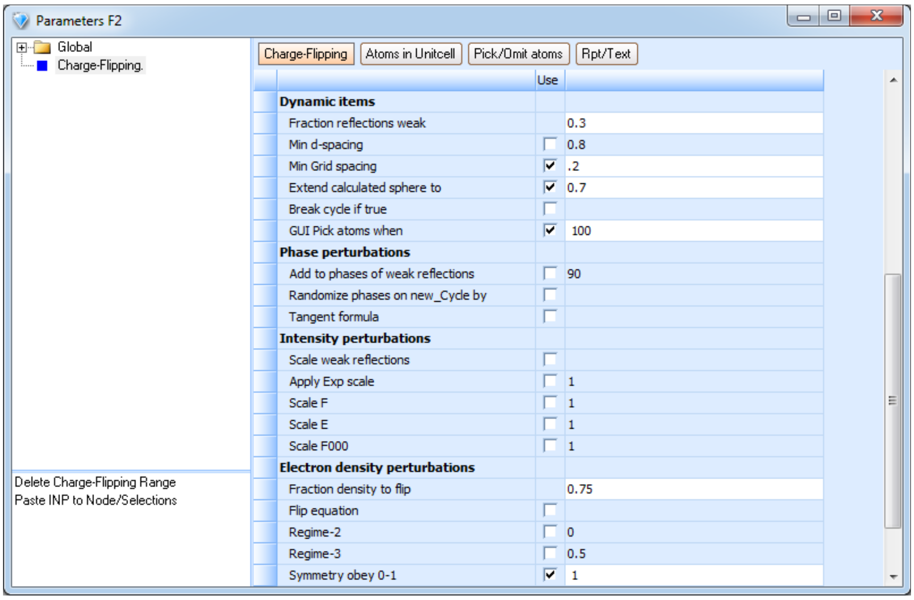
| | Use | |
|---|---|---|
| **Dynamic items** | | |
| Fraction reflections weak | | 0.3 |
| Min d-spacing | ☐ | 0.8 |
| Min Grid spacing | ☑ | .2 |
| Extend calculated sphere to | ☐ | 0.7 |
| Break cycle if true | ☐ | |
| GUI Pick atoms when | ☑ | 100 |
| **Phase perturbations** | | |
| Add to phases of weak reflections | ☐ | 90 |
| Randomize phases on new_Cycle by | ☐ | |
| Tangent formula | ☐ | |
| **Intensity perturbations** | | |
| Scale weak reflections | ☐ | |
| Apply Exp scale | ☐ | 1 |
| Scale F | ☐ | 1 |
| Scale E | ☐ | 1 |
| Scale F000 | ☐ | 1 |
| **Electron density perturbations** | | |
| Fraction density to flip | | 0.75 |
| Flip equation | ☐ | |
| Regime-2 | ☐ | 0 |
| Regime-3 | ☐ | 0.5 |
| Symmetry obey 0-1 | ☐ | 1 |



| | Use | Atom type | Quantity |
|---|---|---|---|
| 1 | ☑ | Pb | 4 |
| 2 | ☑ | S | 4 |
| 3 | ☑ | O | 16 |

7. Start the refinement. While the Pb and S positions will be found instantly, this is usually only true for 2-3 out of the 4 oxygens. Note the floating origin while the refinement is running.

8. To sharpen electron densities try the following
   - Use *Extend calculated sphere* to extending the Ewald sphere to e.g. 0.7Å.
   - Introduce symmetry constraints using *Symmetry obey 0-1.* This will also determine and fix the origin. Set the *Symmetry obey 0-1* parameter to 1.



| | Use | |
|---|---|---|
| **Dynamic items** | | |
| Fraction reflections weak | | 0.3 |
| Min d-spacing | ☐ | 0.8 |
| Min Grid spacing | ☑ | .2 |
| Extend calculated sphere to | ☑ | 0.7 |
| Break cycle if true | ☐ | |
| GUI Pick atoms when | ☑ | 100 |
| **Phase perturbations** | | |
| Add to phases of weak reflections | ☐ | 90 |
| Randomize phases on new_Cycle by | ☐ | |
| Tangent formula | ☐ | |
| **Intensity perturbations** | | |
| Scale weak reflections | ☐ | |
| Apply Exp scale | ☐ | 1 |
| Scale F | ☐ | 1 |
| Scale E | ☐ | 1 |
| Scale F000 | ☐ | 1 |
| **Electron density perturbations** | | |
| Fraction density to flip | | 0.75 |
| Flip equation | ☐ | |
| Regime-2 | ☐ | 0 |
| Regime-3 | ☐ | 0.5 |
| Symmetry obey 0-1 | ☑ | 1 |

9. Restart the refinement. The $PbSO_4$ structure will be solved instantly.

### 2.4.3.2 Structure determination of Cimetidine

Example files are found in C:\Topas5\Tutorial\Structure Determination and Refinement\Cime\.

**Whole Powder Pattern Decomposition**

1. Perform a Pawley refinement.

   You may perform the Pawley refinement either

   - in GUI Mode, as described in section 2.3.1.2, or
   - in Launch Mode by setting the predefined input file: CF-Cime-Pawley.inp (command *Launch - Set INP file*). Inspect the file and run it (command *Launch - Launch Kernel*)

2. Visually check the refinement quality. Calculated intensities at the low d-spacing edge of the pattern (d <1.135 Å, i.e. >84.7° 2θ) are probably in error to a large extent due to cut-off effects. It is therefore best to remove these reflections from further analysis as demonstrated below.

3. After refinement save a ".a" (recommended) or ".hkl" file.

   - In GUI Mode expand the *hkl* item of Cimetidine, select the *Charge Flipping output* item, select the desired file type(s), and provide a filename, respectively
   - In Launch Mode add one of the following (or both) line(s) within the *hkl* block, e.g.,

     ```
     Out_for_cf(Cime.a)
     Out_cf_hkl(Cime.hkl)
     ```

   - Run one more refinement cycle

**Charge Flipping**

Charge Flipping may be performed either

- in GUI Mode, as described below, or
- in Launch Mode by setting the predefined input file: CF-Cime.INP (command *Launch - Set INP file*). Inspect the file and run it (command *Launch - Launch Kernel*)

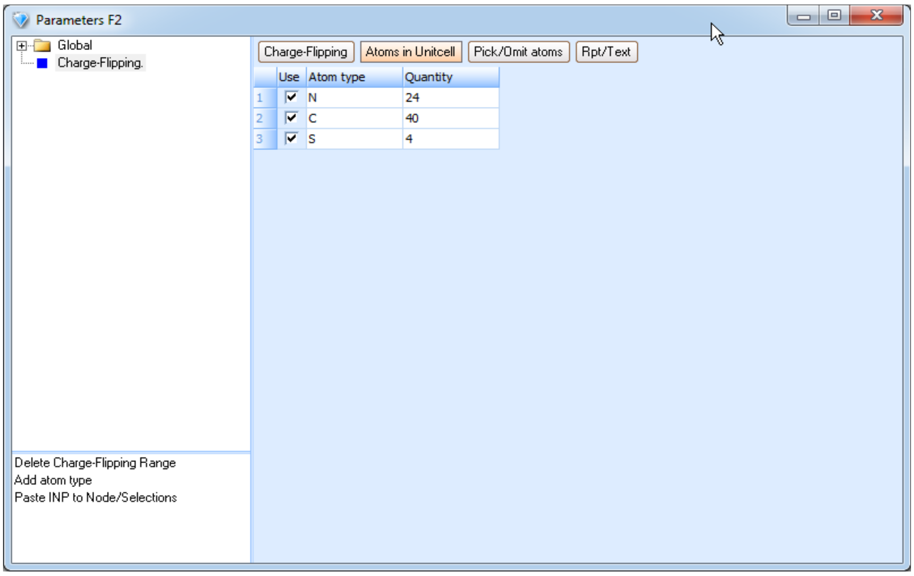
In GUI mode,

4. Create a new Charge Flipping range e.g. using the *Global* item shortcut menu.

5. Input lattice parameters as given below:

| **Crystallographic Data for Cimetidine:** | | |
|---|---|---|
| Space group | | : P21/c |
| Cell parameters | a (Å) | : 6.8256 |
| | b (Å) | : 18.8200 |
| | c (Å) | : 10.3950 |
| | al (°) | : 90° |
| | be (°) | : 106.4° |
| | ga (°) | : 90° |

6. Define an *A matrix file* (".a", recommended) or *hkl file* (".hkl") as obtained from Pawley fitting.
7. As the calculated intensities at the low d-spacing edge of the pattern are probably in error to a large extent it is best to remove these reflections. Check *Delete observed reflections* and define the lower d-spacing limit using the equation to at least "D_spacing < 1.135", but better to 1.1366.
8. To sharpen electron densities
   - use *Extend calculated sphere* to extending the Ewald sphere to e.g. 0.8Å.
   - Introduce symmetry constraints using *Symmetry obey 0-1.* This will also determine and fix the origin. Set the *Symmetry obey 0-1* parameter to 1.
9. Optionally reduce *Min Grid spacing* to e.g. 0.2 to increase the number of grid points. This will improve the graphical electron density display while increasing computing time
10. Optionally perform automatic picking and assignment of atoms based on the known chemistry. Switch to the *Atoms in Unitcell* page and define the contents of the unit cell in terms of atom types and their quantities as given by the chemical formula ($C_{10}H_{16}N_6S$, hydrogens will be ignored) and the number of formula units in the unit cell (Z=4).

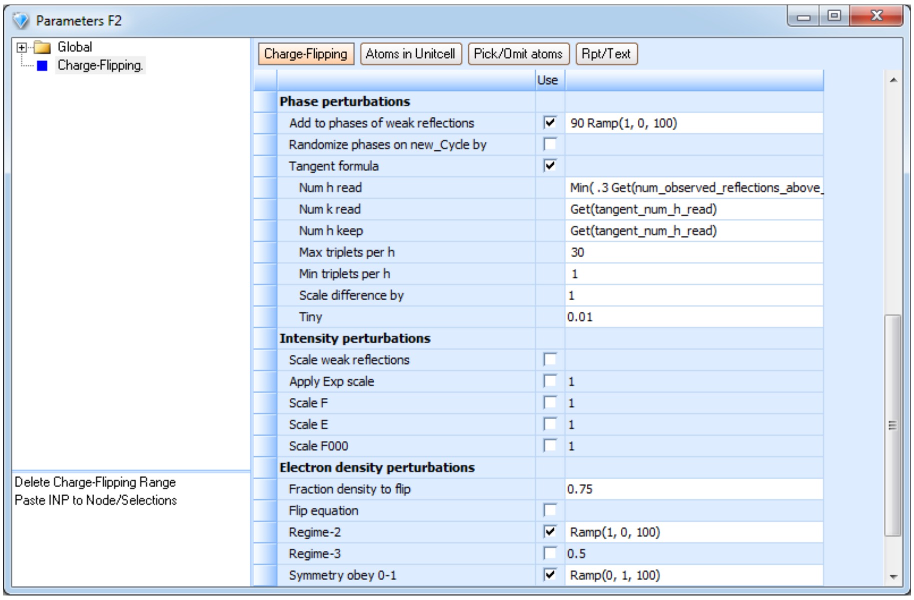


| | Use | Atom type | Quantity |
|---|---|---|---|
| 1 | ☑ | N | 24 |
| 2 | ☑ | C | 40 |
| 3 | ☑ | S | 4 |

11. Start the refinement. The system will be usually trapped within local parameter space, at R-factors of about 0.7 - 0.8. Cancel and repeat the refinement several times. The correct solution will be occasionally found at an R-factor of <0.55, this may require a few 1000 up to many 10000 cycles.

When using Charge Flipping the choice and amount of phase, electron density, and intensity perturbation necessary for finding a solution are important considerations; for details refer to the Technical reference. Not enough perturbation leads to the system being trapped while too much perturbation may lead to a solution not being found. The Ramp macro can be used to gradually vary control parameters in order to decrease perturbation; this is similar to a simulated annealing process where temperatures start at high values and then progressively lowered. Ramp control parameters comprise a start value, a final value, and the number of cycles used within a Ramp iteration.

12. Use the following perturbations and - where applicable - use the Ramp macro to gradually vary control parameters:
    - *Tangent formula*: Keep the default parameters.
    - *Add to phases of weak reflections*: 90 Ramp(1, 0, 100)
    - *Flip_regime_2*: Ramp (1, 0, 100)
    - *Symmetry_obey_0_1*: Ramp (0, 1, 100). Also try 0.5 as start value.



| | Use | |
|---|---|---|
| **Phase perturbations** | | |
| Add to phases of weak reflections | ☑ | 90 Ramp(1, 0, 100) |
| Randomize phases on new_Cycle by | ☐ | |
| Tangent formula | ☑ | |
| Num h read | | Min( .3 Get(num_observed_reflections_above_ |
| Num k read | | Get(tangent_num_h_read) |
| Num h keep | | Get(tangent_num_h_read) |
| Max triplets per h | | 30 |
| Min triplets per h | | 1 |
| Scale difference by | | 1 |
| Tiny | | 0.01 |
| **Intensity perturbations** | | |
| Scale weak reflections | ☐ | |
| Apply Exp scale | ☐ | 1 |
| Scale F | ☐ | 1 |
| Scale E | ☐ | 1 |
| Scale F000 | ☐ | 1 |
| **Electron density perturbations** | | |
| Fraction density to flip | | 0.75 |
| Flip equation | ☐ | |
| Regime-2 | ☑ | Ramp(1, 0, 100) |
| Regime-3 | ☐ | 0.5 |
| Symmetry obey 0-1 | ☑ | Ramp(0, 1, 100) |

13. Restart the refinement. The Cimetidine structure will be solved within a few 100 cycles.

### 2.4.3.3 Tips and tricks

- **The Tangent Formula on powder diffraction data**

  The benefit of using the tangent formula to sharpen electron densities can be seen in the CF-ALVO4 example, found in C:\Topas5\Tutorial\Structure Determination and Refinement\AlVO4\.

  - In GUI mode load and inspect CF-AlVO4.inp. Reduce *Min Grid spacing* to 0.2 or less to improve the graphical display of the electron densities and do not use the Tangent formula.
  - In Launch mode load and inspect CF-AlVO4.inp. Set *min_grid_spacing* to .2 or less and disable the Tangent macro:

  ```
  min_grid_spacing .2
  'Tangent(.3, 30)
  ```

  Run the refinement and view the Charge Flipping progress in the structure viewer. Optionally turn on "Display polygons". Electron densities will be quite diffuse resulting in difficulties to correctly pick lighter atoms.

  Rerun Charge Flipping using the Tangent formula. Electron densities are considerably sharper and a well defined solution at R<0.5 will be found quickly.

  Example CF-PbSO4 is similar.

  Use of the tangent formula should be generally considered for powder diffraction data.

- **Preventing uranium atom solutions using *pick_atoms***

  Randomly omitting a few of the highest intensity atoms using *pick_atoms* is an extremely effective means of preventing the occurance of uranium atom solutions ("random omit maps", Schneider and Sheldrick, 2002).

  The effect of *pick_atoms* can be seen in the CF-1A7Y-Omit example, found in C:\Topas5\Tutorial\Structure Determination and Refinement\CF\.

  - In GUI mode load and inspect CF-1A7Y-Omit.inp.
  - In Launch mode load and inspect CF-1A7Y-Omit.inp.

  When running the example without *pick_atoms* only uranium atom solutions will be found. Using *pick_atoms* the structure solves within a few 100 iterations and with a large contrast in R-factors before and at convergence.

  For details on *pick_atoms* and some more alternatives to avoid uranium atom solutions refer to the Technical Reference manual.

- **Origin finding and *symmetry_obey_0_to_1* on poor resolution data**

  When *symmetry_obey_0_to_1* is defined origin finding is performed each iteration of charge flipping. Symmetry elements of the space group are used in finding an origin. On finding an origin the electron density is shifted to a position that best matches the symmetry of the space group. Additionally a restraint is placed on the electron density pixels forcing symmetry to be obeyed. As a result *symmetry_obey_0_to_1* can assist in solving poor resolution data.

Consider the example CF-AlVO4 (AlVO$_4$ crystallizes in spacegroup P-1), found in C:\Topas5\Tutorial\Structure Determination and Refinement\ALVO4\.

- In GUI mode load and inspect CF-AlVO4.inp.
- In Launch mode load and inspect CF-AlVO4.inp.

Remove *symmetry_obey_0_to_1*. Run Charge Flipping and note the floating background. A complete solution of the structure is usually not found even after several 10.000 iterations.

Add *symmetry_obey_0_to_1* and run Charge Flipping; the origin is now fixed. The correct solution is found after a few 100 iterations.

- **Pseudo symmetry**

Charge Flipping works particularly well on pseudo symmetric structures (Oszlányi et al., 2006). Example CF-PN-02 is an oxide structure that contains 441 atom in the asymmetric unit (Lister et al., 2004), found in C:\Topas5\Tutorial\Structure Determination and Refinement\CF\

- In GUI mode load and inspect CF-PN-02.inp.
- In Launch mode load and inspect CF-PN-02.inp.

Run Charge Flipping to convergence. Pick atoms and turn on Octahedra viewing; all polyhedra should be well formed.

The tangent formula is used to assist *symmetry_obey_0_to_1* and to assist in finding the solution faster but is not required.

- ***symmetry_obey_0_to_1* versus the Oszlányi & Süto (2005) algorithm**

The Oszlányi & Süto (2005) algorithm can be used by replacing *symmetry_obey_0_to_1* and the Tangent macro with the following:

```
scale_F000 1
fraction_reflections_weak .4
add_to_phases_of_weak_reflections 90
user_threshold = 0.15 Get(max_density_at_cycle_iter_0);
```

Example files are found in C:\Topas5\Tutorial\Structure Determination and Refinement\CF\.

- In GUI mode load and inspect CF-PN-02-Gabor.inp.
- In Launch mode load and inspect CF-PN-02-Gabor.inp.

Slow convergence is observed and the reason is the use of F000 (finding the correct solution may take several 1000 iterations). Setting scale_F000 to zero greatly increases the rate of convergence.

This is opposite to the case of 1a7y where F000 is necessary.

- In GUI mode load and inspect CF-1A7Y-Gabor.inp.
- In Launch mode load and inspect CF-1A7Y-Gabor.inp.

Compare Charge Flipping runs with scale_F000 set to zero and to 1.

- **A difficult powder, CF-Sucrose**

Example CF-Sucrose, found in C:\Topas5\Tutorial\Structure Determination and Refinement\CF\, exhibits large oscillations in R-factors resulting in difficult to identify solutions; this can be prevented by increasing the amount of charge flipped and including *scale_density_below_threshold*=0, for example

```
fraction_density_to_flip 0.83
scale_density_below_threshold 0
```

- In GUI mode load and inspect CF-SUCROSE.INP.
- In Launch mode load and inspect CF-SUCROSE.INP.

When *scale_density_below_threshold*=0 is used the percentage of charge that is less than the threshold before the application of *scale_density_below_threshold* is reported; the difference between this reported value and (1-*fraction_density_to_flip*) gives the amount of flipped pixels that survived *scale_density_below_threshold*. At *fraction_density_to_flip* of 0.83 approximately 23% of pixels survives *scale_density_below_threshold*=0 which in effect means that only 23% of pixels are actually flipped out of the original 83%.

*picked_atom*s is used as a perturbation where 30% of atoms are omitted using:

```
pick_atoms *
   activate = Cycle_Iter == 0;
   insert = If(Rand(0, 1) > 0.3, 10, 0);
```

Note that atoms are inserted at an intensity that is 10 times the average intensity. This increases the weight of inserted atoms relative to electron density noise. It also initially gives more weight to weak reflections.

Use of *scale_density_below_threshold* often results in CF requiring more interations to solution; the correct solution is usually found within several 1000 iterations at an R-value of about 0.45.

## 2.4.4 (Difference) Fourier Analysis

**Launch Mode only!**

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 practice, performing a (difference) Fourier analysis is identical to performing a Rietveld refinement with the keywords *fourier_map* and *fourier_map_formula* included.

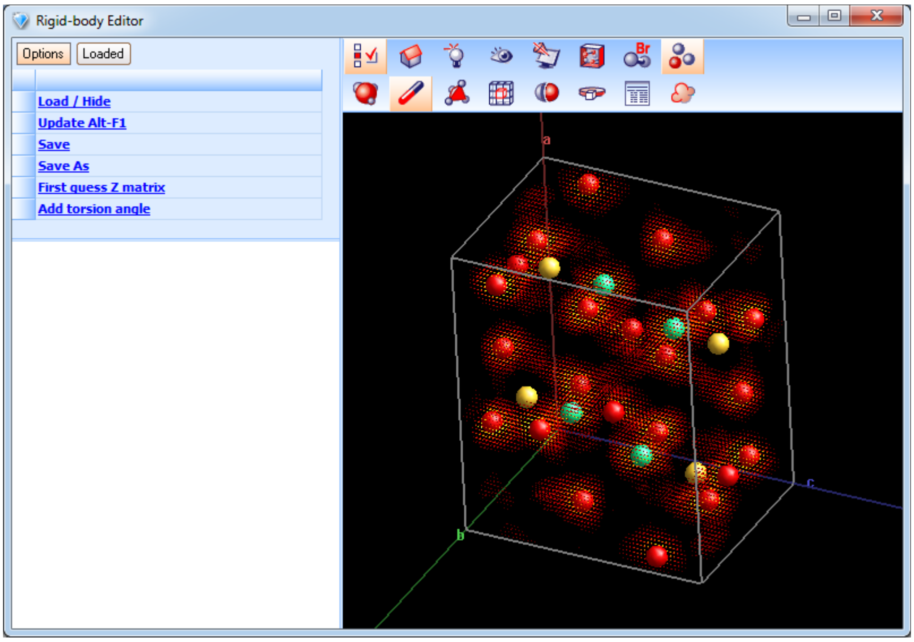
In the following example, found in C:\Topas5\Tutorial\Structure Determination and Refinement\PBSO4\, the generation of a difference Fourier map will be described to locate the oxygen positions in $PbSO_4$.

1. Load and inspect PbSO4-Fourier.inp.
2. To generate a Difference Map the following 2 lines are used:

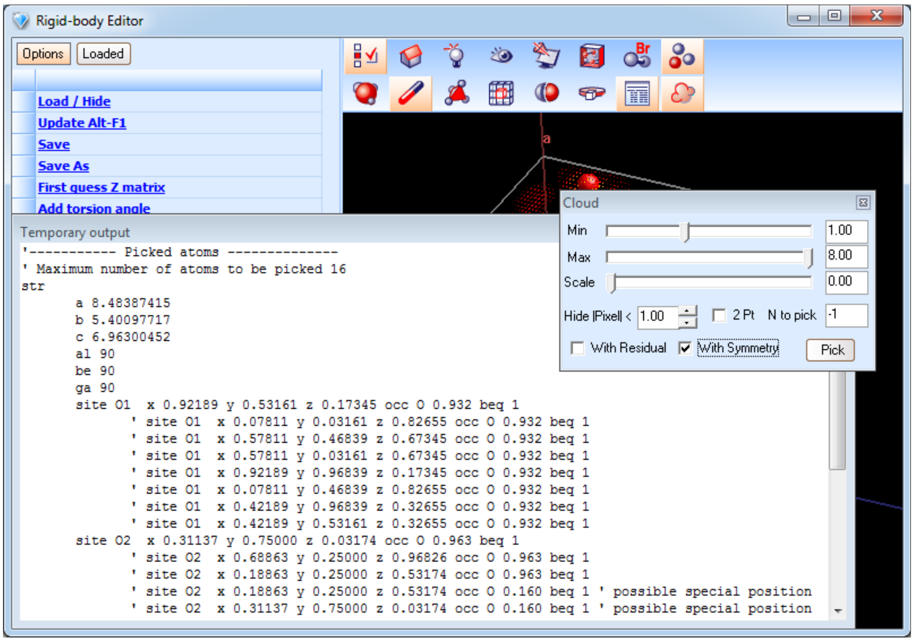
   ```
   fourier_map 1
      fourier_map_formula = Fobs - Fcalc;
   ```

3. 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.
4. 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
         {
            O  = 16;
         }
   ```



5. Open the *Temporary Output* window and the *Cloud Options Dialog*. In the latter check *With Symmetry* and click the *Pick* button. The positions of the picked oxygen atoms are displayed in the *Temporary Output* window with indication of possible special positions.



Min 1.00
Max 8.00
Scale 0.00
Hide |Pixel| < 1.00
☐ 2 Pt
N to pick -1
☐ With Residual
☑ With Symmetry

Temporary output

```
'----------- Picked atoms --------------
' Maximum number of atoms to be picked 16
str
      a 8.48387415
      b 5.40097717
      c 6.96300452
      al 90
      be 90
      ga 90
      site O1  x 0.92189 y 0.53161 z 0.17345 occ O 0.932 beq 1
            ' site O1  x 0.07811 y 0.03161 z 0.82655 occ O 0.932 beq 1
            ' site O1  x 0.57811 y 0.46839 z 0.67345 occ O 0.932 beq 1
            ' site O1  x 0.57811 y 0.03161 z 0.67345 occ O 0.932 beq 1
            ' site O1  x 0.92189 y 0.96839 z 0.17345 occ O 0.932 beq 1
            ' site O1  x 0.07811 y 0.46839 z 0.82655 occ O 0.932 beq 1
            ' site O1  x 0.42189 y 0.96839 z 0.32655 occ O 0.932 beq 1
            ' site O1  x 0.42189 y 0.53161 z 0.32655 occ O 0.932 beq 1
      site O2  x 0.31137 y 0.75000 z 0.03174 occ O 0.963 beq 1
            ' site O2  x 0.68863 y 0.25000 z 0.96826 occ O 0.963 beq 1
            ' site O2  x 0.18863 y 0.25000 z 0.53174 occ O 0.963 beq 1
            ' site O2  x 0.18863 y 0.25000 z 0.53174 occ O 0.160 beq 1 ' possible special position
            ' site O2  x 0.31137 y 0.75000 z 0.03174 occ O 0.160 beq 1 ' possible special position
```

## 2.5 Structure refinement

In the following 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), located in C:\Topas5\Tutorial\Structure Determination and Refinement\PbSO4\.

### 2.5.1 Laboratory X-ray data

1. Load the raw data by importing the file PbSO4.raw into your document.

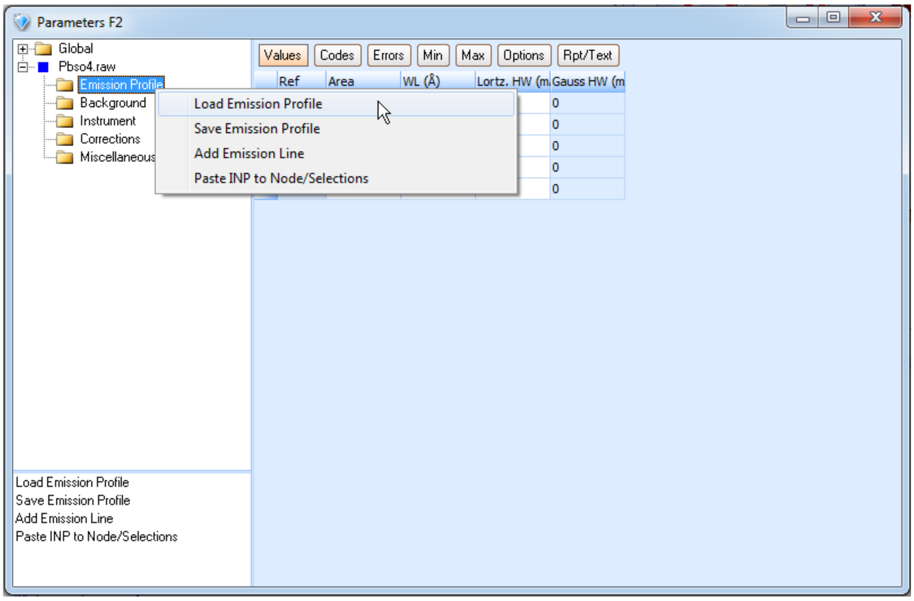
| **Menu:** | **Icon:** | **Shortcut:** | **Result:** |
|---|---|---|---|
| *File -<br>Import Data File(s)...* | 📊 | n.a. | Imports measurement data |

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

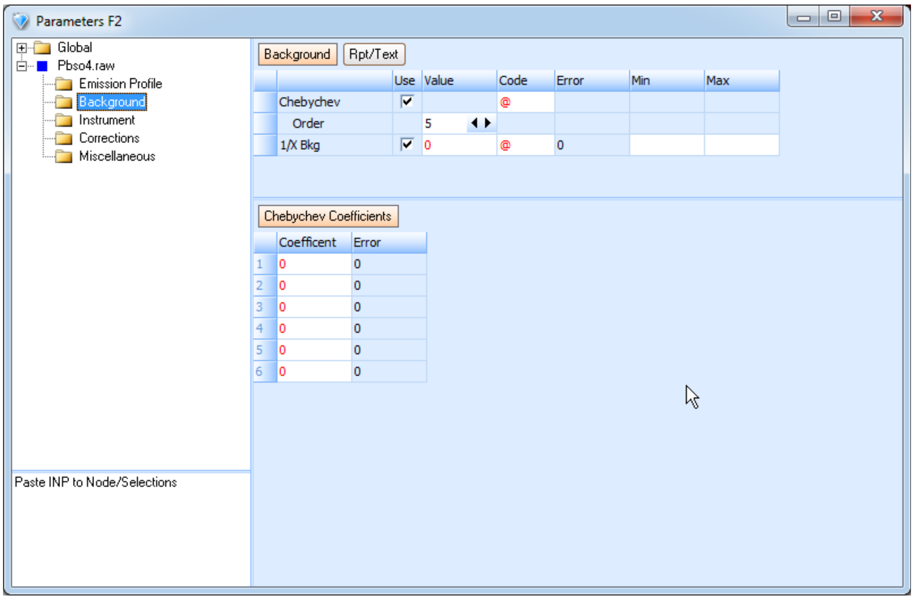
| **Menu:** | **Icon:** | **Shortcut:** | **Result:** |
|---|---|---|---|
| *View -<br>Parameters Window* | 🔧 | F2 | Displays or hides the *Parameters Window* |

In the *Parameters Window* expand the range item of PbSO4.RAW and perform the following tasks:

- Select the *Emission Profile* item and load the emission profile CuKa5_Berger.lam. By default this file is located in C:\Topas5\Lam.



- Select 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.



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Chebychev | ☑ | | @ | | | |
| Order | | 5 | | | | |
| 1/X Bkg | ☑ | 0 | @ | 0 | | |

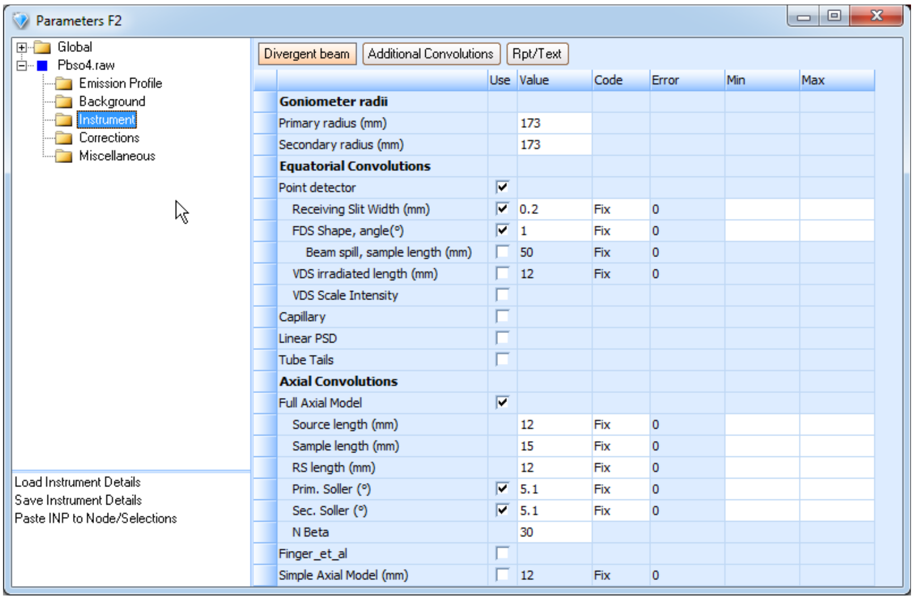
| | Coefficent | Error |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 0 | 0 |
| 3 | 0 | 0 |
| 4 | 0 | 0 |
| 5 | 0 | 0 |
| 6 | 0 | 0 |

- Select 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 | ☑ |

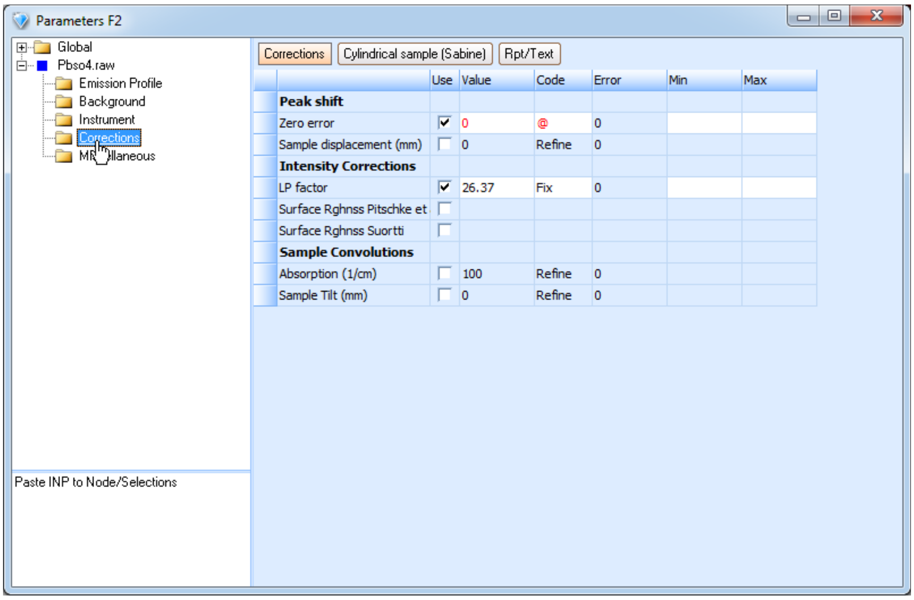
| **Instrument Parameter:** | | **Value:** |
|---|---|---|
| Goniometer Radius | Primary: | 173 mm |
| | Secondary: | 173 mm |
| Receiving Slit Width | Width: | 0.2 mm |
| FDS [1)] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary: | 5.1° |
| | Secondary: | 5.1° |

[1)] Fixed Divergence Slit



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| **Goniometer radii** | | | | | | |
| Primary radius (mm) | | 173 | | | | |
| Secondary radius (mm) | | 173 | | | | |
| **Equatorial Convolutions** | | | | | | |
| Point detector | ☑ | | | | | |
| Receiving Slit Width (mm) | ☑ | 0.2 | Fix | 0 | | |
| FDS Shape, angle(°) | ☑ | 1 | Fix | 0 | | |
| Beam spill, sample length (mm) | ☐ | 50 | Fix | 0 | | |
| VDS irradiated length (mm) | ☐ | 12 | Fix | 0 | | |
| VDS Scale Intensity | ☐ | | | | | |
| Capillary | ☐ | | | | | |
| Linear PSD | ☐ | | | | | |
| Tube Tails | ☐ | | | | | |
| **Axial Convolutions** | | | | | | |
| Full Axial Model | ☑ | | | | | |
| Source length (mm) | | 12 | Fix | 0 | | |
| Sample length (mm) | | 15 | Fix | 0 | | |
| RS length (mm) | | 12 | Fix | 0 | | |
| Prim. Soller (°) | ☑ | 5.1 | Fix | 0 | | |
| Sec. Soller (°) | ☑ | 5.1 | Fix | 0 | | |
| N Beta | | 30 | | | | |
| Finger_et_al | ☐ | | | | | |
| Simple Axial Model (mm) | ☐ | 12 | Fix | 0 | | |

- Select 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.



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| **Peak shift** | | | | | | |
| Zero error | ☑ | 0 | @ | 0 | | |
| Sample displacement (mm) | ☐ | 0 | Refine | 0 | | |
| **Intensity Corrections** | | | | | | |
| LP factor | ☑ | 26.37 | Fix | 0 | | |
| Surface Rghnss Pitschke et | ☐ | | | | | |
| Surface Rghnss Suortti | ☐ | | | | | |
| **Sample Convolutions** | | | | | | |
| Absorption (1/cm) | ☐ | 100 | Refine | 0 | | |
| Sample Tilt (mm) | ☐ | 0 | Refine | 0 | | |

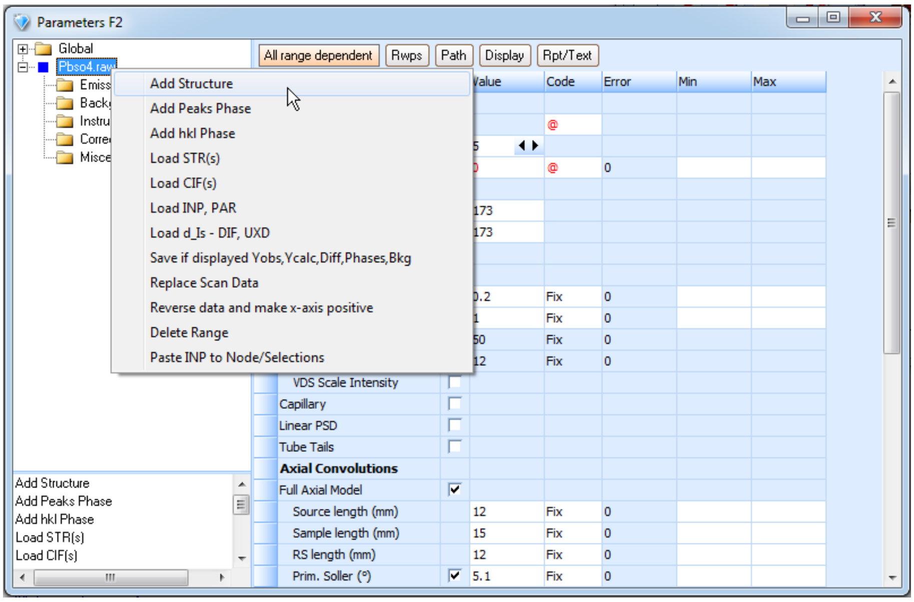
Paste INP to Node/Selections

3. 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 via *Add Structure*
   2. Import of TOPAS STR files via *Load STR(s)*
   3. Import of CIF files via *Load CIF(s)*

   In the following the manual input will be described.

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



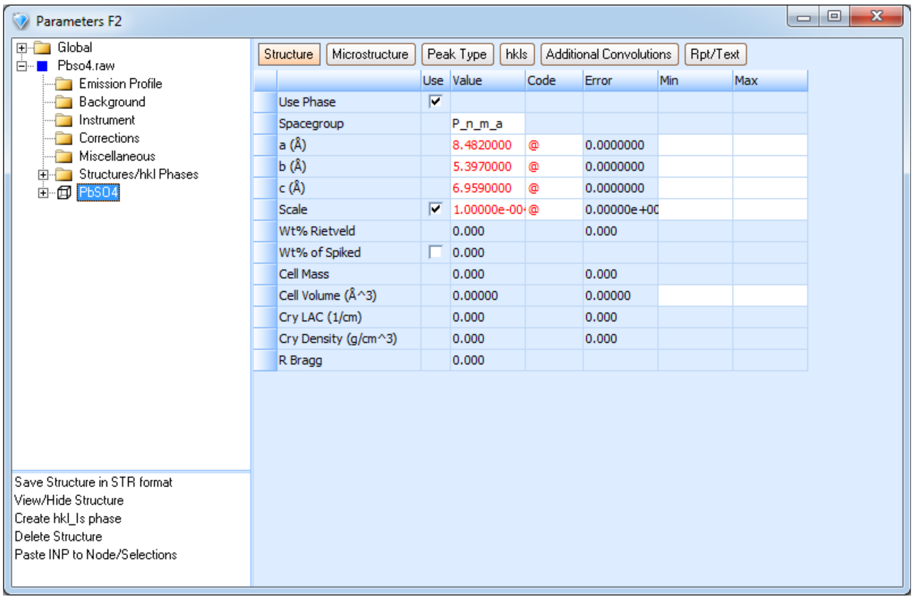
Full Axial Model ☑

| | Value | Code | Error |
|---|---|---|---|
| Source length (mm) | 12 | Fix | 0 |
| Sample length (mm) | 15 | Fix | 0 |
| RS length (mm) | 12 | Fix | 0 |
| Prim. Soller (°) ☑ | 5.1 | Fix | 0 |

- Select 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.

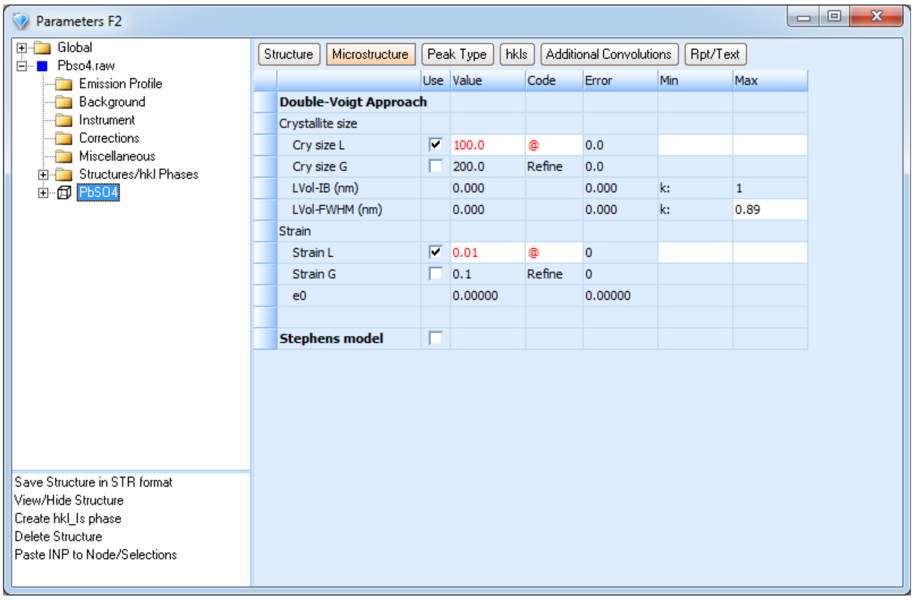
## Crystallographic Data for $PbSO_4$:

| | | |
|---|---|---|
| Space group | | : Pnma |
| Cell parameters | a (Å) | : 8.482 |
| | b (Å) | : 5.397 |
| | c (Å) | : 6.959 |



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Use Phase | ☑ | | | | | |
| Spacegroup | | P_n_m_a | | | | |
| a (Å) | | 8.4820000 | @ | 0.0000000 | | |
| b (Å) | | 5.3970000 | @ | 0.0000000 | | |
| c (Å) | | 6.9590000 | @ | 0.0000000 | | |
| Scale | ☑ | 1.00000e-00 | @ | 0.00000e+00 | | |
| Wt% Rietveld | | 0.000 | | 0.000 | | |
| Wt% of Spiked | ☐ | 0.000 | | | | |
| Cell Mass | | 0.000 | | 0.000 | | |
| Cell Volume (Å^3) | | 0.00000 | | 0.00000 | | |
| Cry LAC (1/cm) | | 0.000 | | 0.000 | | |
| Cry Density (g/cm^3) | | 0.000 | | 0.000 | | |
| R Bragg | | 0.000 | | | | |

- Switch to the *Microstructure* page. 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".

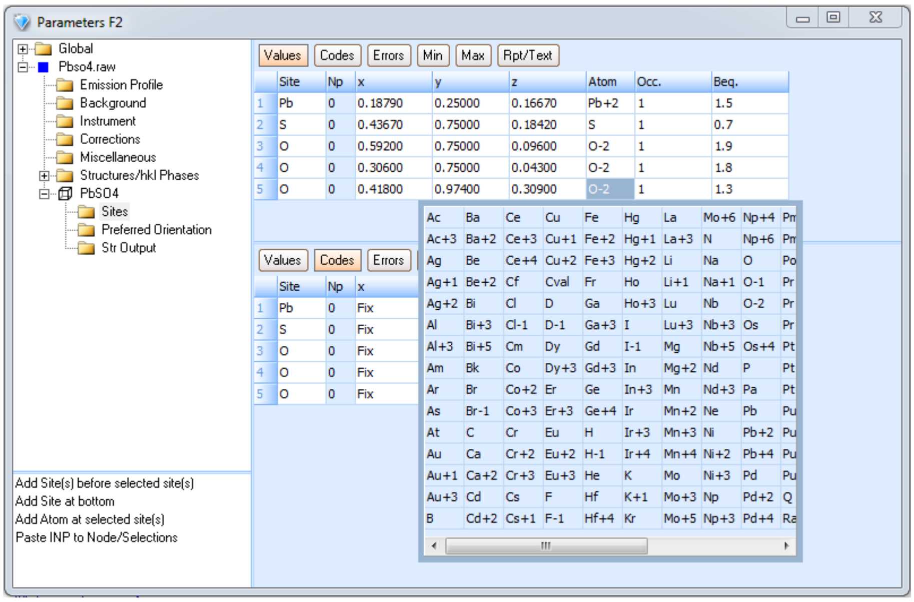


| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| **Double-Voigt Approach** | | | | | | |
| Crystallite size | | | | | | |
| Cry size L | ☑ | 100.0 | @ | 0.0 | | |
| Cry size G | ☐ | 200.0 | Refine | 0.0 | | |
| LVol-IB (nm) | | 0.000 | | 0.000 | k: | 1 |
| LVol-FWHM (nm) | | 0.000 | | 0.000 | k: | 0.89 |
| Strain | | | | | | |
| Strain L | ☑ | 0.01 | @ | 0 | | |
| Strain G | ☐ | 0.1 | Refine | 0 | | |
| e0 | | 0.00000 | | 0.00000 | | |
| | | | | | | |
| **Stephens model** | ☐ | | | | | |

- Expand the *Structure* item and select 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 | 0.1879 | 0.2500 | 0.1667 | Pb+2 | 1 | 1.5 |
| S | 0.4367 | 0.7500 | 0.1842 | S | 1 | 0.7 |
| O1 | 0.5920 | 0.7500 | 0.0960 | O-2 | 1 | 1.9 |
| O2 | 0.3060 | 0.7500 | 0.0430 | O-2 | 1 | 1.8 |
| O3 | 0.4180 | 0.9740 | 0.3090 | O-2 | 1 | 1.3 |

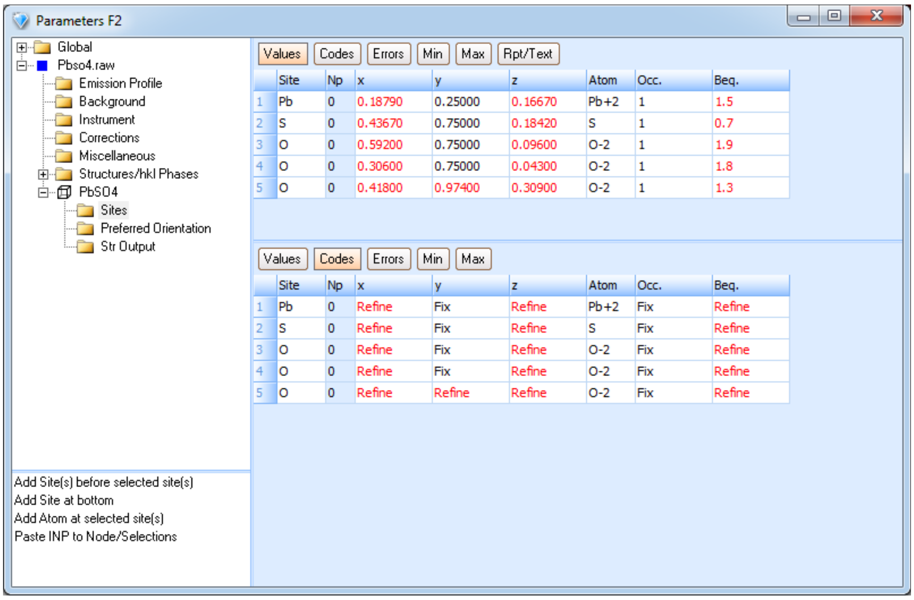


| | Site | Np | x | y | z | Atom | Occ. | Beq. |
|---|---|---|---|---|---|---|---|---|
| 1 | Pb | 0 | 0.18790 | 0.25000 | 0.16670 | Pb+2 | 1 | 1.5 |
| 2 | S | 0 | 0.43670 | 0.75000 | 0.18420 | S | 1 | 0.7 |
| 3 | O | 0 | 0.59200 | 0.75000 | 0.09600 | O-2 | 1 | 1.9 |
| 4 | O | 0 | 0.30600 | 0.75000 | 0.04300 | O-2 | 1 | 1.8 |
| 5 | O | 0 | 0.41800 | 0.97400 | 0.30900 | O-2 | 1 | 1.3 |

| | Site | Np | x |
|---|---|---|---|
| 1 | Pb | 0 | Fix |
| 2 | S | 0 | Fix |
| 3 | O | 0 | Fix |
| 4 | O | 0 | Fix |
| 5 | O | 0 | Fix |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ac | Ba | Ce | Cu | Fe | Hg | La | Mo+6 | Np+4 | Pm |
| Ac+3 | Ba+2 | Ce+3 | Cu+1 | Fe+2 | Hg+1 | La+3 | N | Np+6 | Pm |
| Ag | Be | Ce+4 | Cu+2 | Fe+3 | Hg+2 | Li | Na | O | Po |
| Ag+1 | Be+2 | Cf | Cval | Fr | Ho | Li+1 | Na+1 | O-1 | Pr |
| Ag+2 | Bi | Cl | D | Ga | Ho+3 | Lu | Nb | O-2 | Pr |
| Al | Bi+3 | Cl-1 | D-1 | Ga+3 | I | Lu+3 | Nb+3 | Os | Pr |
| Al+3 | Bi+5 | Cm | Dy | Gd | I-1 | Mg | Nb+5 | Os+4 | Pt |
| Am | Bk | Co | Dy+3 | Gd+3 | In | Mg+2 | Nd | P | Pt |
| Ar | Br | Co+2 | Er | Ge | In+3 | Mn | Nd+3 | Pa | Pt |
| As | Br-1 | Co+3 | Er+3 | Ge+4 | Ir | Mn+2 | Ne | Pb | Pu |
| At | C | Cr | Eu | H | Ir+3 | Mn+3 | Ni | Pb+2 | Pu |
| Au | Ca | Cr+2 | Eu+2 | H-1 | Ir+4 | Mn+4 | Ni+2 | Pb+4 | Pu |
| Au+1 | Ca+2 | Cr+3 | Eu+3 | He | K | Mo | Ni+3 | Pd | Pu |
| Au+3 | Cd | Cs | F | Hf | K+1 | Mo+3 | Np | Pd+2 | Q |
| B | Cd+2 | Cs+1 | F-1 | Hf+4 | Kr | Mo+5 | Np+3 | Pd+4 | Ra |

- 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!



| | Site | Np | x | y | z | Atom | Occ. | Beq. |
|---|---|---|---|---|---|---|---|---|
| 1 | Pb | 0 | 0.18790 | 0.25000 | 0.16670 | Pb+2 | 1 | 1.5 |
| 2 | S | 0 | 0.43670 | 0.75000 | 0.18420 | S | 1 | 0.7 |
| 3 | O | 0 | 0.59200 | 0.75000 | 0.09600 | O-2 | 1 | 1.9 |
| 4 | O | 0 | 0.30600 | 0.75000 | 0.04300 | O-2 | 1 | 1.8 |
| 5 | O | 0 | 0.41800 | 0.97400 | 0.30900 | O-2 | 1 | 1.3 |

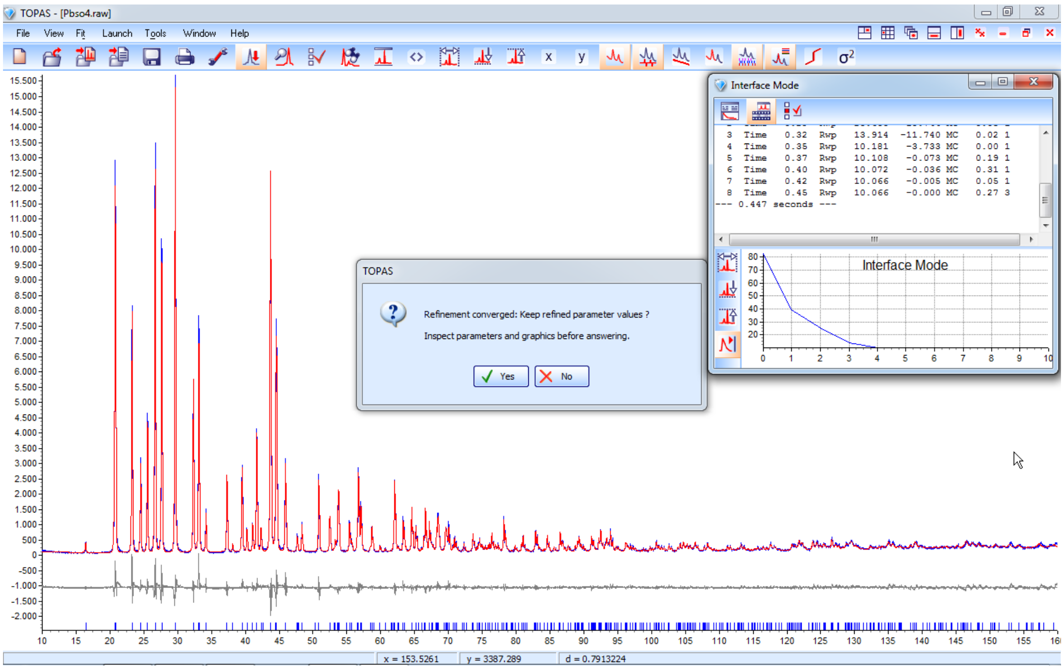
| | Site | Np | x | y | z | Atom | Occ. | Beq. |
|---|---|---|---|---|---|---|---|---|
| 1 | Pb | 0 | Refine | Fix | Refine | Pb+2 | Fix | Refine |
| 2 | S | 0 | Refine | Fix | Refine | S | Fix | Refine |
| 3 | O | 0 | Refine | Fix | Refine | O-2 | Fix | Refine |
| 4 | O | 0 | Refine | Fix | Refine | O-2 | Fix | Refine |
| 5 | O | 0 | Refine | Refine | Refine | O-2 | Fix | Refine |

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 –*<br>*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.



```
  3  Time   0.32  Rwp   13.914  -11.740 MC   0.02 1
  4  Time   0.35  Rwp   10.181   -3.733 MC   0.00 1
  5  Time   0.37  Rwp   10.108   -0.073 MC   0.19 1
  6  Time   0.40  Rwp   10.072   -0.036 MC   0.31 1
  7  Time   0.42  Rwp   10.066   -0.005 MC   0.05 1
  8  Time   0.45  Rwp   10.066   -0.000 MC   0.27 3
--- 0.447 seconds ---
```

TOPAS

Refinement converged: Keep refined parameter values ?

Inspect parameters and graphics before answering.

✓ Yes ✗ No

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.

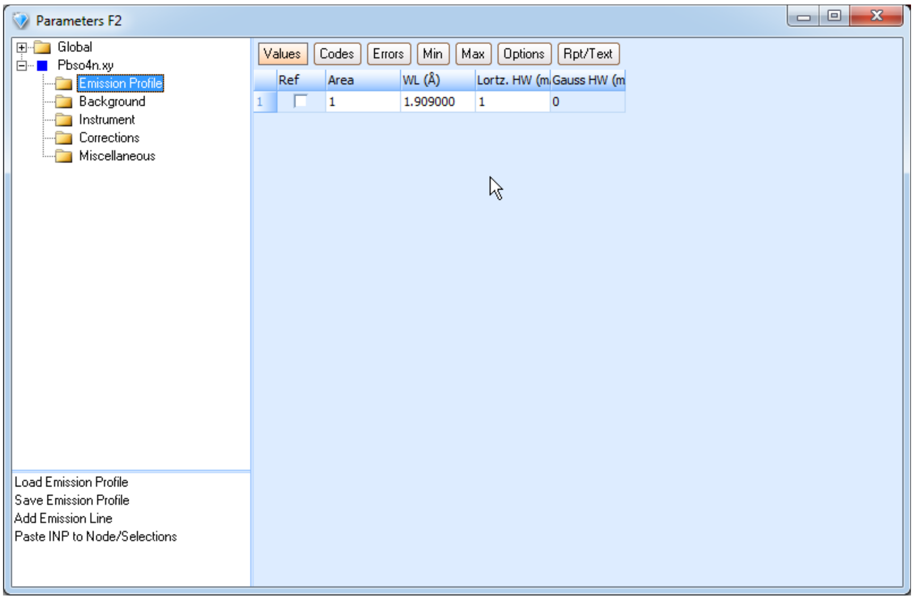
**Hint!** Fractional coordinates for special positions such as 1/3, 1/6, etc. are expected in the form of an equation such as
= 1/3, =1/6, etc. in the Codes page,
instead of values with re-occuring digits such as
0.3333..., 0.1666..., etc. in the Values page.
The correct parameter value will be calculated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

## 2.5.2 Constant wavelength neutron data

1. Load the raw data by importing the file PBSO4N.XY into your document. By default this file is located in C:\Topas5\Tutorial\Structure Determination and Refinement\PbSO4.
2. 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:

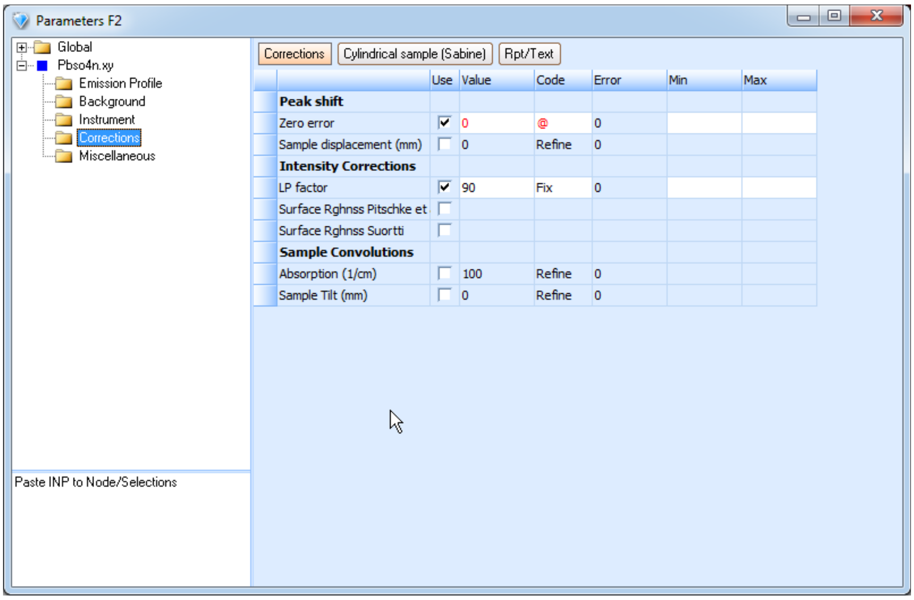
   - Select the *Emission Profile* item and define a source emission profile using λ = 1.909Å. Setting *Area* and *Lortz. HW* to 1 will do it for this example. For details about emission profiles refer to the Technical Reference manual.



|  | Ref | Area | WL (Å) | Lortz. HW (m | Gauss HW (m |
|---|---|---|---|---|---|
| 1 | ☐ | 1 | 1.909000 | 1 | 0 |

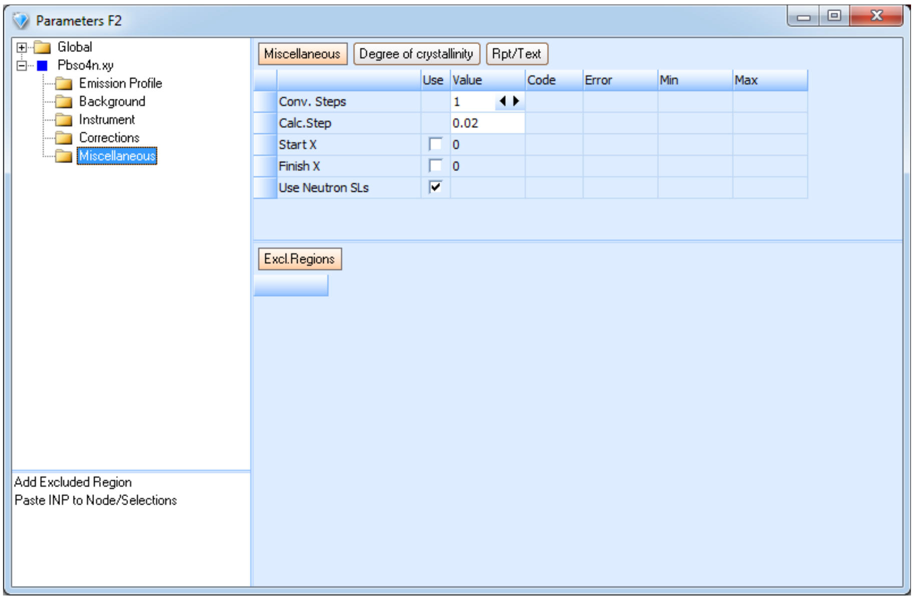
   - Select the *Background* item. Use a Chebychev polynomial of 3rd order and the *1/X Bkg* function.
   - Select the *Instrument* item. To describe peak asymmetry, select either the *Finger_et_al* or the *Simple Axial Model* and set the asymmetry parameter codes to "Refine". The instrument radii are of no importance for this example.

- Select 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.



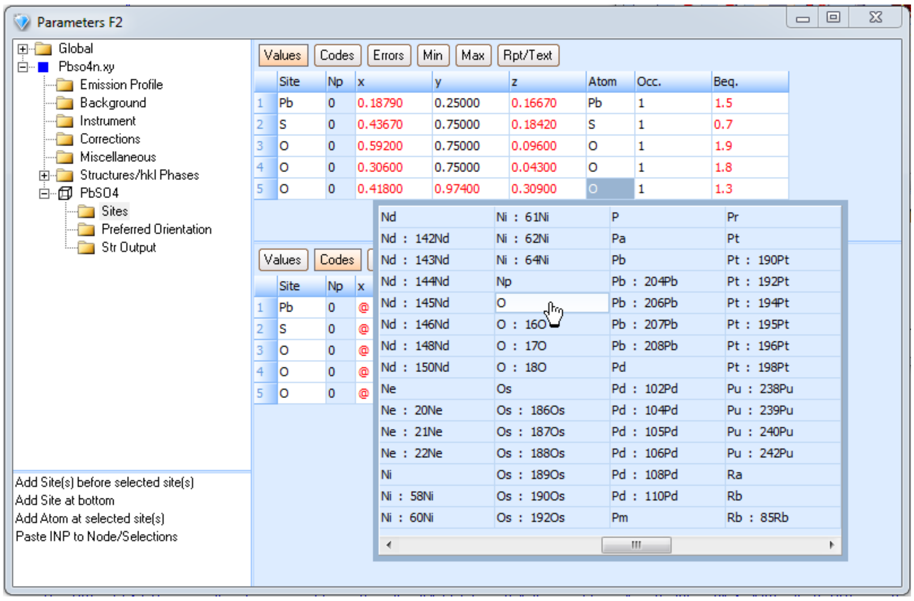
| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| **Peak shift** | | | | | | |
| Zero error | ☑ | 0 | @ | 0 | | |
| Sample displacement (mm) | ☐ | 0 | Refine | 0 | | |
| **Intensity Corrections** | | | | | | |
| LP factor | ☑ | 90 | Fix | 0 | | |
| Surface Rghnss Pitschke et | ☐ | | | | | |
| Surface Rghnss Suortti | ☐ | | | | | |
| **Sample Convolutions** | | | | | | |
| Absorption (1/cm) | ☐ | 100 | Refine | 0 | | |
| Sample Tilt (mm) | ☐ | 0 | Refine | 0 | | |

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



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Conv. Steps | | 1 | | | | |
| Calc.Step | | 0.02 | | | | |
| Start X | ☐ | 0 | | | | |
| Finish X | ☐ | 0 | | | | |
| Use Neutron SLs | ☑ | | | | | |

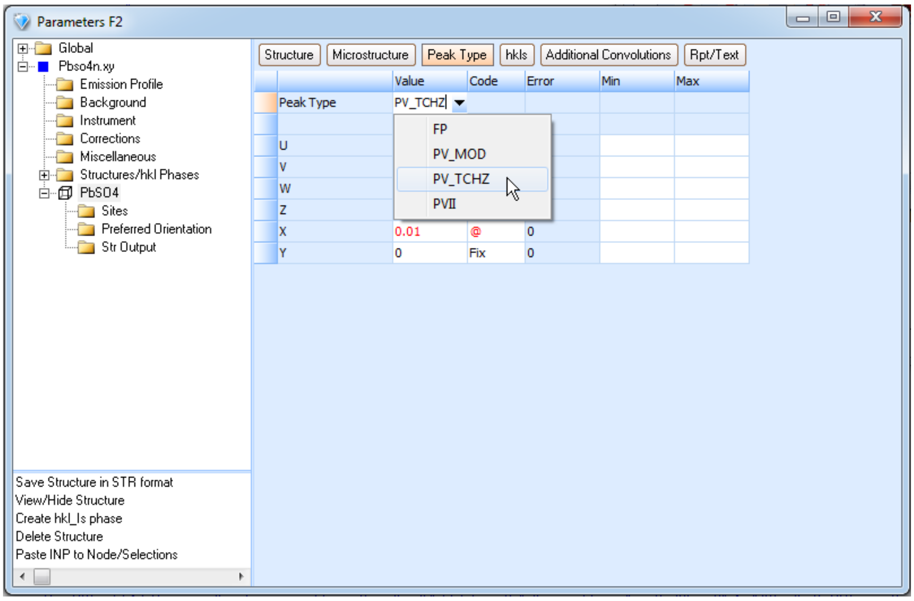
3. In the next step the crystal structure data for $PbSO_4$ has to be provided.
   - Create the structure model analogous to section 2.5.1. Note, that scattering lengths will be provided in the *Atom* drop down list, as *Fixed WL Neutron* has been checked in the *Miscellaneous* page.



| | Site | Np | x | y | z | Atom | Occ. | Beq. |
|---|---|---|---|---|---|---|---|---|
| 1 | Pb | 0 | 0.18790 | 0.25000 | 0.16670 | Pb | 1 | 1.5 |
| 2 | S | 0 | 0.43670 | 0.75000 | 0.18420 | S | 1 | 0.7 |
| 3 | O | 0 | 0.59200 | 0.75000 | 0.09600 | O | 1 | 1.9 |
| 4 | O | 0 | 0.30600 | 0.75000 | 0.04300 | O | 1 | 1.8 |
| 5 | O | 0 | 0.41800 | 0.97400 | 0.30900 | O | 1 | 1.3 |

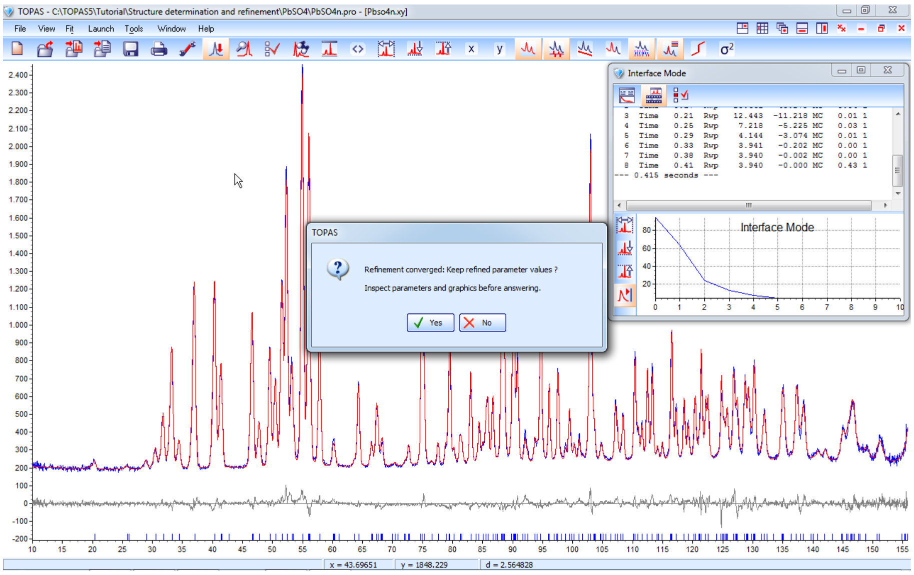
| | Site | Np | x |
|---|---|---|---|
| 1 | Pb | 0 | @ |
| 2 | S | 0 | @ |
| 3 | O | 0 | @ |
| 4 | O | 0 | @ |
| 5 | O | 0 | @ |

   - In the *Structure* page set the *Scale* factor to about 0.1.
   - Switch to the *Microstructure* page and 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.



| | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|
| Peak Type | PV_TCHZ | | | | |
| | | | | | |
| U | | | | | |
| V | | | | | |
| W | | | | | |
| Z | | | | | |
| X | 0.01 | @ | 0 | | |
| Y | 0 | Fix | 0 | | |

4. Start the refinement.



```
  3  Time   0.21  Rwp   12.443  -11.218 MC   0.01 1
  4  Time   0.25  Rwp    7.218   -5.225 MC   0.03 1
  5  Time   0.29  Rwp    4.144   -3.074 MC   0.01 1
  6  Time   0.33  Rwp    3.941   -0.202 MC   0.00 1
  7  Time   0.38  Rwp    3.940   -0.002 MC   0.00 1
  8  Time   0.41  Rwp    3.940   -0.000 MC   0.43 1
--- 0.415 seconds ---
```

Refinement converged: Keep refined parameter values ?

Inspect parameters and graphics before answering.

## 2.6 Quantitative phase analysis

The principles of quantitative phase analysis and the methodologies implemented in TOPAS are discussed in the Technical Reference manual in detail. The following selected methods are covered by step by step exercises below:

1. Quantitative phase analysis of crystalline materials
   - The traditional Rietveld method
   - The PONKCS method
2. Quantitative phase analysis of crystalline and amorphous materials
   - The internal standard method
   - The PONKCS method

### 2.6.1 Quantitative phase analysis of crystalline materials

This tutorial uses the CPD-1 data from the IUCr CPD Round-Robin on quantitative phase analysis (QPARR) conducted by the International Union of Crystallography IUCR (Madsen et al., 2001). CPD-1 comprises three-phase mixtures of Corundum, Zincite, and Fluorite, samples CPD-1a to CPD-1h, known compositions are provided in Table 2.7.

Table 2.7: Phase compositions for CPD-1.

| **Data** | **Corundum [%]** | **Fluorite [%]** | **Zincite [%]** |
|---|---|---|---|
| CPD-1a | 1.36 | 94.87 | 3.77 |
| CPD-1b | 94.31 | 4.33 | 1.36 |
| CPD-1c | 5.04 | 1.36 | 93.59 |
| CPD-1d | 13.53 | 53.58 | 32.89 |
| CPD-1e | 55.12 | 29.62 | 15.25 |
| CPD-1f | 27.06 | 17.72 | 55.22 |
| CPD-1g | 31.37 | 34.42 | 34.21 |
| CPD-1h | 35.12 | 34.69 | 30.19 |

All required diffraction data and crystal structure files are located in C:\Topas5\Tutorial\Quantitative Phase Analysis\Rietveld Method\CPD\.

#### 2.6.1.1 The traditional Rietveld method

1. Load any of the CPD-1 datasets (CPD-1A.RAW - CPD-1H.RAW) into your document.

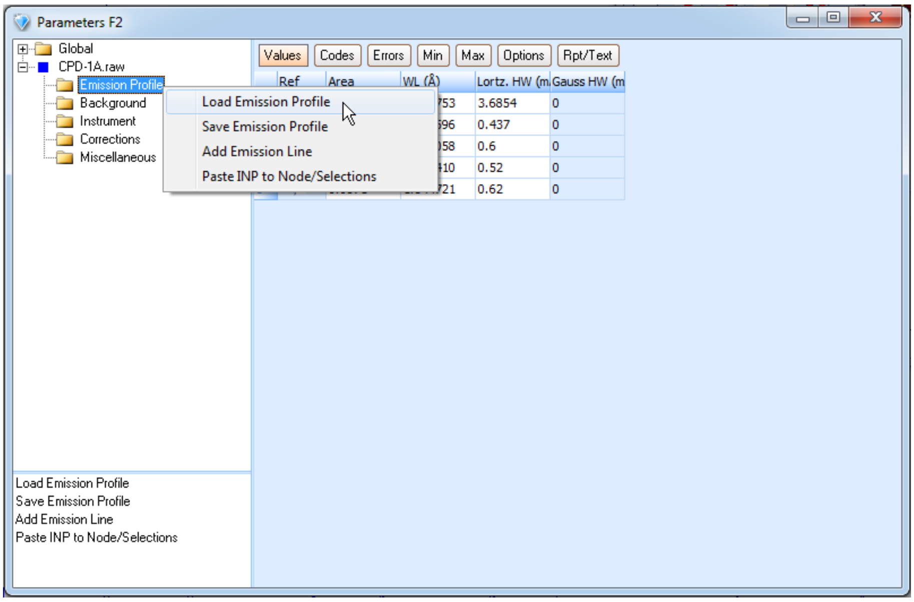
| Menu: | Icon: | Shortcut: | Result: |
|---|---|---|---|
| *File -*<br>*Import Data File(s)...* | | n.a. | Imports measurement data |

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

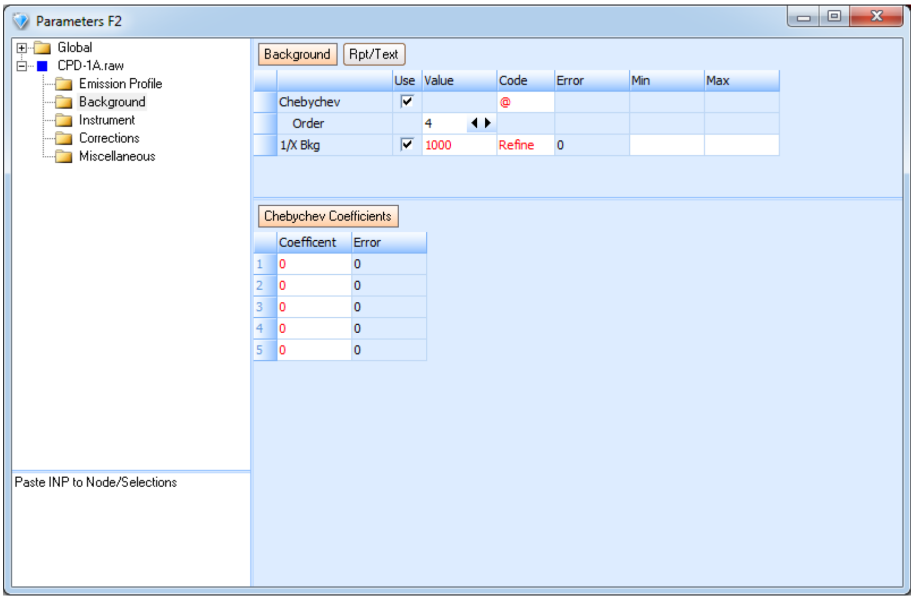
| Menu: | Icon: | Shortcut: | Result: |
|---|---|---|---|
| *View -*<br>*Parameters Window* | | F2 | Displays or hides the *Parameters Window* |

In the *Parameters Window* expand the data range item (*.RAW) and perform the following tasks:

- Select the *Emission Profile* item and load the emission profile CuKa5_Berger.lam. By default this file is located in C:\Topas5\Lam.



- Select 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.



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Chebychev | ☑ | | @ | | | |
| Order | | 4 | | | | |
| 1/X Bkg | ☑ | 1000 | Refine | 0 | | |

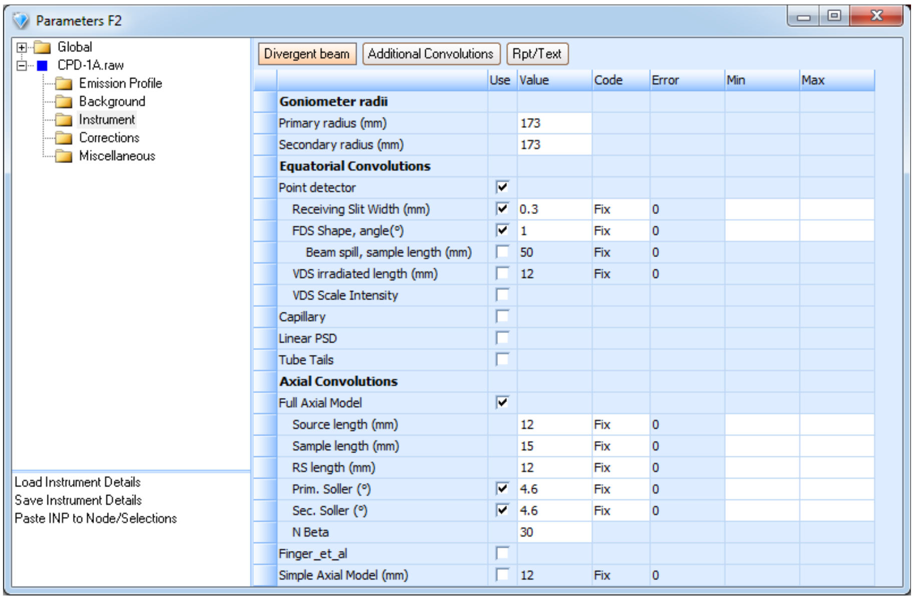
| | Coefficent | Error |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 0 | 0 |
| 3 | 0 | 0 |
| 4 | 0 | 0 |
| 5 | 0 | 0 |

- Select 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° |

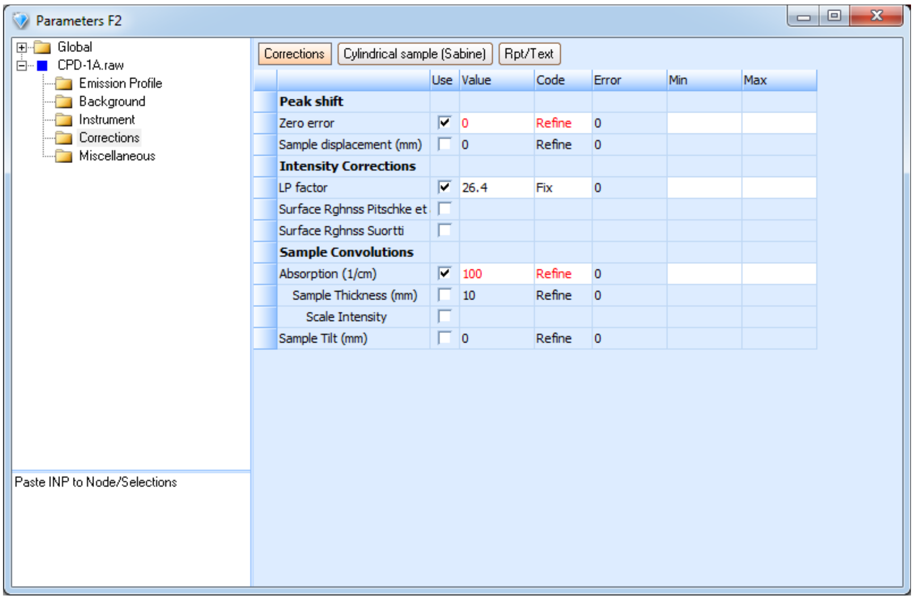
[1] Fixed Divergence Slit



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| **Goniometer radii** | | | | | | |
| Primary radius (mm) | | 173 | | | | |
| Secondary radius (mm) | | 173 | | | | |
| **Equatorial Convolutions** | | | | | | |
| Point detector | ☑ | | | | | |
| Receiving Slit Width (mm) | ☑ | 0.3 | Fix | 0 | | |
| FDS Shape, angle(°) | ☑ | 1 | Fix | 0 | | |
| Beam spill, sample length (mm) | ☐ | 50 | Fix | 0 | | |
| VDS irradiated length (mm) | ☐ | 12 | Fix | 0 | | |
| VDS Scale Intensity | ☐ | | | | | |
| Capillary | ☐ | | | | | |
| Linear PSD | ☐ | | | | | |
| Tube Tails | ☐ | | | | | |
| **Axial Convolutions** | | | | | | |
| Full Axial Model | ☑ | | | | | |
| Source length (mm) | | 12 | Fix | 0 | | |
| Sample length (mm) | | 15 | Fix | 0 | | |
| RS length (mm) | | 12 | Fix | 0 | | |
| Prim. Soller (°) | ☑ | 4.6 | Fix | 0 | | |
| Sec. Soller (°) | ☑ | 4.6 | Fix | 0 | | |
| N Beta | | 30 | | | | |
| Finger_et_al | ☐ | | | | | |
| Simple Axial Model (mm) | ☐ | 12 | Fix | 0 | | |

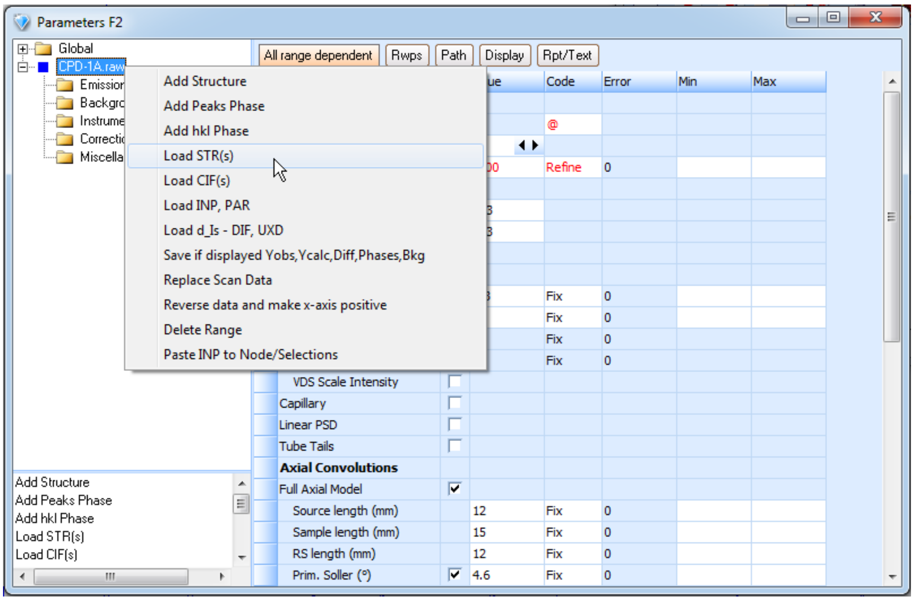
- Select the *Corrections* item. Check the *Zero error* and set its code to "Refine". In addition polarization effects coming from the secondary Graphite monochromator have to be accounted for. Therefore check *LP factor* as well and set the monochromator angle to 26.4° 2θ. Finally check *Absorption*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



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| **Peak shift** | | | | | | |
| Zero error | ☑ | 0 | Refine | 0 | | |
| Sample displacement (mm) | ☐ | 0 | Refine | 0 | | |
| **Intensity Corrections** | | | | | | |
| LP factor | ☑ | 26.4 | Fix | 0 | | |
| Surface Rghnss Pitschke et | ☐ | | | | | |
| Surface Rghnss Suortti | ☐ | | | | | |
| **Sample Convolutions** | | | | | | |
| Absorption (1/cm) | ☑ | 100 | Refine | 0 | | |
| Sample Thickness (mm) | ☐ | 10 | Refine | 0 | | |
| Scale Intensity | ☐ | | | | | |
| Sample Tilt (mm) | ☐ | 0 | Refine | 0 | | |

- Select the data range item (*.RAW) 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



Source length (mm) 12 Fix 0
Sample length (mm) 15 Fix 0
RS length (mm) 12 Fix 0
Prim. Soller (°) ☑ 4.6 Fix 0

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

| **Menu:** | **Icon:** | **Shortcut:** | **Result:** |
|---|---|---|---|
| *Fit –*<br>*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.

5. 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 Table 2.7. The accuracy of your results should be within ± 2 % in weight.
6. The elemental composition of the sample is automatically calculated. To view the results expand the *Structures/ hkl Phases* item, select the *Internal Standard Method* item, and switch to the *Elemental Composition* page.

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.

### 2.6.1.2 The PONKCS method

This example considers the three-phase mixtures of Corundum, Zincite, and Fluorite, samples CPD-1A to CPD-1H, as follows:

- Corundum is designated as the unknown about which there is only space group and lattice parameters information
- Crystal structures for Fluorite and Zincite are known
- Sample CPD-1E will be used to establish the calibration constant where Zincite is the standard material added at a known weight fraction (15.25%).
- Weight fractions of Corundum are 55.12% and of Fluorite 29.62%.

For defining a "PONKCS phase" for Corundum we will distinguish two cases:

1. Pure specimen available
2. Pure specimen unavailable

All required diffraction data and crystal structure files are located in C:\Topas5\Tutorial\Quantitative Phase Analysis\PONKCS Method\CPD\CPD-1\.

#### 2.6.1.2.1 Defining a "PONKCS phase" - pure specimen available

**Step 1: Perform a Pawley refinement on the Corundum data.**

1. Start TOPAS and load Corundum.raw.
2. Switch to the Parameters Window and define the refinement model. Expand the range item of Corundum.raw and perform the following tasks:
   - Select the *Emission Profile* item and load the emission profile CuKa5_Berger.lam. By default this file is located in C:\Topas5\Lam.
   - Select the *Background* item and use a Chebychev Polynomial of 5th order.
   - Select 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:<br>Secondary: | 173 mm<br>173 mm |
| Receiving Slit Width | Width: | 0.3 mm |
| FDS [1] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary:<br>Secondary: | 4.6°<br>4.6° |

[1] Fixed Divergence Slit

- Select the *Corrections* item. Check *Zero error* and *Sample Displacement* and set their codes to "Refine".
- We have to account for the polarization effects coming from the secondary Graphite monochromator. Therefore check *LP factor* as well and set the monochromator angle to 26.4° $2\theta$. Finally check *Absorption* and set its code to "Refine" in order to account for the significant profile shape distortion caused by the low mass absorption of the sample.
- Select *Miscellaneous*. *Check Start X* and set its value to 22. *Check Finish X* and set its value to 150
- Insert a new hkl_I phase. Select the range item for Corundum.raw and select *Add hkl phase*.
- Select the hkl_Phase item. Rename the item to "Corundum". Input the crystallographic data given below in the *Phase Details* page. Switch to the *Microstructure* page and make sure to refine on lattice parameters, *Cry Size L* and *Strain L*.

| **Crystallographic Data for Corundum:** | | |
|---|---|---|
| Space group | | : Trigonal R_-3_C (167) |
| Cell parameters | a (Å)<br>c (Å) | : 4.7592<br>: 12.992 |

3. Start the refinement

### Step 2: Determination of the calibration constant

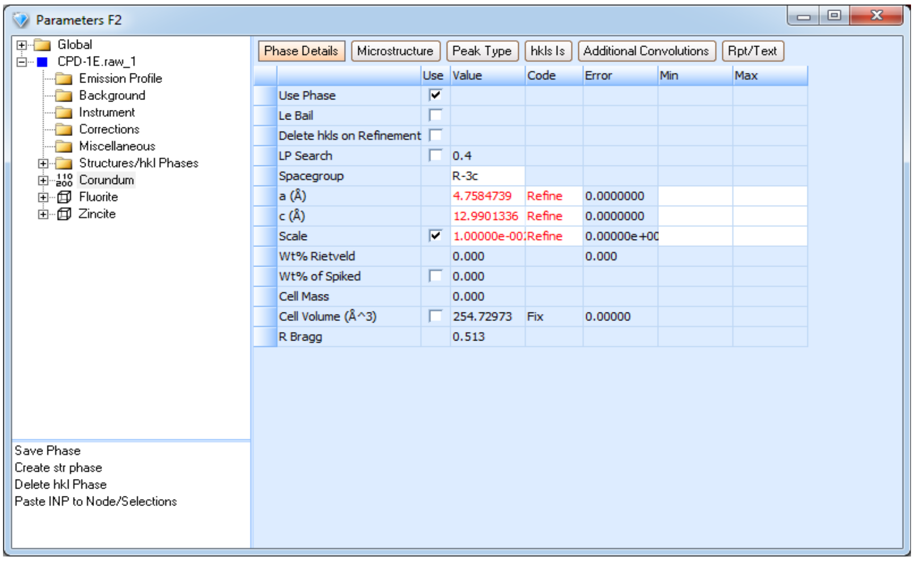
4. Both the mixture and the pure phase have been measured using identical instrument settings. It is thus most convenient to simply exchange the measurement data rather than restarting from scratch.

   Switch back to the *Parameters Window*. Select the Corundum.raw range item, select *Replace Scan Data* in the short cut menu, and load CPD-1E.raw.

5. Select the CPD-1E.raw range item and import the crystal structure data for Fluorite and Zincite:
    1. Fluorite.str
    2. Zincite.str

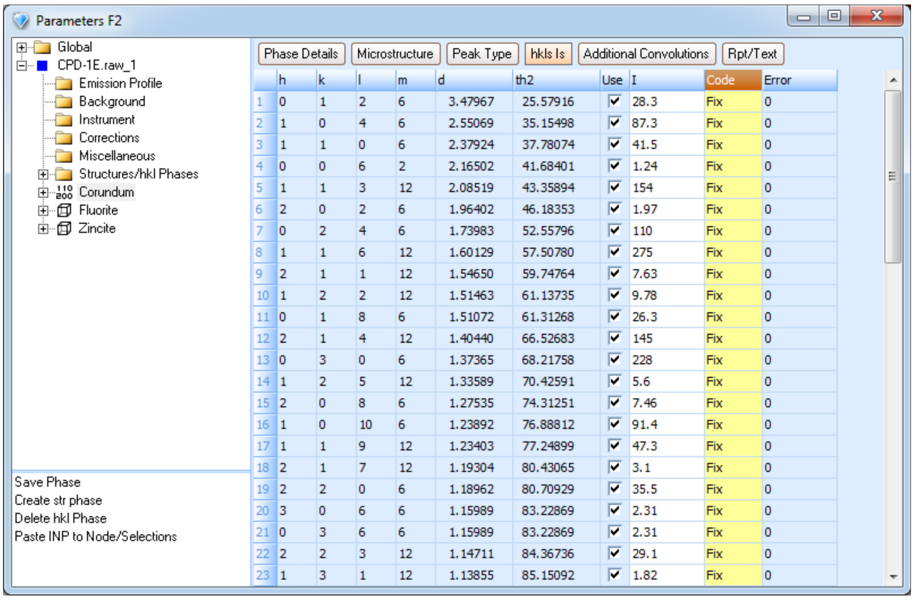
   DO NOT refine yet.

6. Select the Corundum range item
    - Uncheck *Delete hkls on Refinement* and refine the *Scale* factor



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Use Phase | ☑ | | | | | |
| Le Bail | ☐ | | | | | |
| Delete hkls on Refinement | ☐ | | | | | |
| LP Search | ☐ | 0.4 | | | | |
| Spacegroup | | R-3c | | | | |
| a (Å) | | 4.7584739 | Refine | 0.0000000 | | |
| c (Å) | | 12.9901336 | Refine | 0.0000000 | | |
| Scale | ☑ | 1.00000e-00 | Refine | 0.00000e+00 | | |
| Wt% Rietveld | | 0.000 | | 0.000 | | |
| Wt% of Spiked | ☐ | 0.000 | | | | |
| Cell Mass | | 0.000 | | | | |
| Cell Volume (Å^3) | ☐ | 254.72973 | Fix | 0.00000 | | |
| R Bragg | | 0.513 | | | | |

- Switch to the *hkl Is* page and fix all intensities



| | h | k | l | m | d | th2 | Use | I | Code | Error |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 1 | 2 | 6 | 3.47967 | 25.57916 | ☑ | 28.3 | Fix | 0 |
| 2 | 1 | 0 | 4 | 6 | 2.55069 | 35.15498 | ☑ | 87.3 | Fix | 0 |
| 3 | 1 | 1 | 0 | 6 | 2.37924 | 37.78074 | ☑ | 41.5 | Fix | 0 |
| 4 | 0 | 0 | 6 | 2 | 2.16502 | 41.68401 | ☑ | 1.24 | Fix | 0 |
| 5 | 1 | 1 | 3 | 12 | 2.08519 | 43.35894 | ☑ | 154 | Fix | 0 |
| 6 | 2 | 0 | 2 | 6 | 1.96402 | 46.18353 | ☑ | 1.97 | Fix | 0 |
| 7 | 0 | 2 | 4 | 6 | 1.73983 | 52.55796 | ☑ | 110 | Fix | 0 |
| 8 | 1 | 1 | 6 | 12 | 1.60129 | 57.50780 | ☑ | 275 | Fix | 0 |
| 9 | 2 | 1 | 1 | 12 | 1.54650 | 59.74764 | ☑ | 7.63 | Fix | 0 |
| 10 | 1 | 2 | 2 | 12 | 1.51463 | 61.13735 | ☑ | 9.78 | Fix | 0 |
| 11 | 0 | 1 | 8 | 6 | 1.51072 | 61.31268 | ☑ | 26.3 | Fix | 0 |
| 12 | 2 | 1 | 4 | 12 | 1.40440 | 66.52683 | ☑ | 145 | Fix | 0 |
| 13 | 0 | 3 | 0 | 6 | 1.37365 | 68.21758 | ☑ | 228 | Fix | 0 |
| 14 | 1 | 2 | 5 | 12 | 1.33589 | 70.42591 | ☑ | 5.6 | Fix | 0 |
| 15 | 2 | 0 | 8 | 6 | 1.27535 | 74.31251 | ☑ | 7.46 | Fix | 0 |
| 16 | 1 | 0 | 10 | 6 | 1.23892 | 76.88812 | ☑ | 91.4 | Fix | 0 |
| 17 | 1 | 1 | 9 | 12 | 1.23403 | 77.24899 | ☑ | 47.3 | Fix | 0 |
| 18 | 2 | 1 | 7 | 12 | 1.19304 | 80.43065 | ☑ | 3.1 | Fix | 0 |
| 19 | 2 | 2 | 0 | 6 | 1.18962 | 80.70929 | ☑ | 35.5 | Fix | 0 |
| 20 | 3 | 0 | 6 | 6 | 1.15989 | 83.22869 | ☑ | 2.31 | Fix | 0 |
| 21 | 0 | 3 | 6 | 6 | 1.15989 | 83.22869 | ☑ | 2.31 | Fix | 0 |
| 22 | 2 | 2 | 3 | 12 | 1.14711 | 84.36736 | ☑ | 29.1 | Fix | 0 |
| 23 | 1 | 3 | 1 | 12 | 1.13855 | 85.15092 | ☑ | 1.82 | Fix | 0 |

7. Make sure to refine on lattice parameters, *Cry Size L* and *Strain L* for Fluorite and Zincite
8. Start the refinement
9. Calculate the Corundum calibration constant $(ZM)_{corundum}$:

$$(ZM)_{corundum} = \frac{W_{corundum}}{W_{zincite}} \, \frac{S_{zincite}}{S_{corundum}} \, \frac{(ZM)_{zincite} V_{zincite}}{V_{corundum}}$$

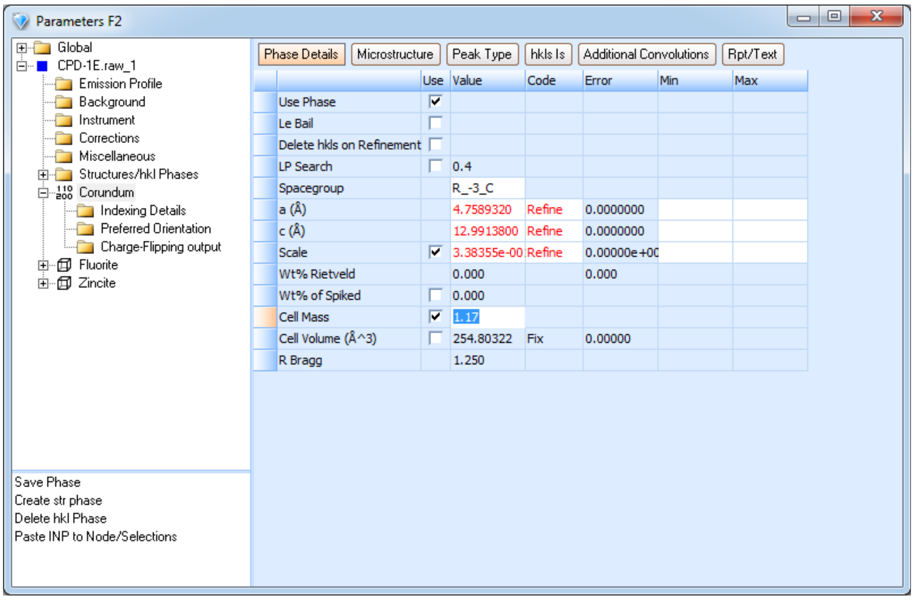
where

- $W_{corundum}$ and $W_{zincite}$ are the known weights (in %) for Corundum and Zincite, respectively,
- $S_{corundum}$ and $S_{zincite}$ are the refined *Scale* factors for Corundum and Zincite, respectively,
- $(ZM)_{zincite}$ is the *Cell Mass* of Zincite, and
- $V_{corundum}$ and $V_{zincite}$ are the refined *Cell Volumes* for Corundum and Zincite, respectively.

Your refinement should yield the following calibration constant within reasonable errors:

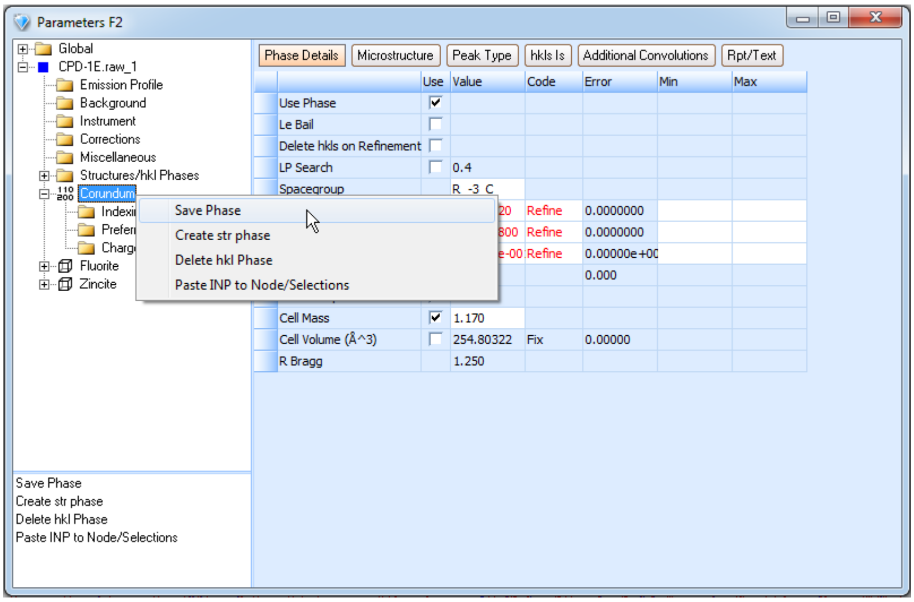
$$(ZM)_{corundum} = \frac{55.12}{15.25} \, \frac{0.0036}{0.338} \, \frac{162.8 \;\; 47.6}{254.8} \approx 1.17$$

10. Expand the *Structures/ hkl Phases* item, select the *Internal Standard Method* item, and enter the calibration constant of Corundum in the *Cell Mass* cell.



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Use Phase | ☑ | | | | | |
| Le Bail | ☐ | | | | | |
| Delete hkls on Refinement | ☐ | | | | | |
| LP Search | ☐ | 0.4 | | | | |
| Spacegroup | | R_-3_C | | | | |
| a (Å) | | 4.7589320 | Refine | 0.0000000 | | |
| c (Å) | | 12.9913800 | Refine | 0.0000000 | | |
| Scale | ☑ | 3.38355e-00 | Refine | 0.00000e+00 | | |
| Wt% Rietveld | | 0.000 | | 0.000 | | |
| Wt% of Spiked | ☐ | 0.000 | | | | |
| Cell Mass | ☑ | 1.17 | | | | |
| Cell Volume (Å^3) | ☐ | 254.80322 | Fix | 0.00000 | | |
| R Bragg | | 1.250 | | | | |

11. Select Corundum, then select *Save Phase*. Save the Corundum hkl phase as a PONKCS phase for re-use. It is suggested to use the *STR extension, this allows easy re-loading together with crystal structure data.



| | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|
| Use Phase | ☑ | | | | | |
| Le Bail | ☐ | | | | | |
| Delete hkls on Refinement | ☐ | | | | | |
| LP Search | ☐ | 0.4 | | | | |
| Spacegroup | | R -3 C | | | | |
| | | 20 | Refine | 0.0000000 | | |
| | | 800 | Refine | 0.0000000 | | |
| | | e-00 | Refine | 0.00000e+0 | | |
| | | | | 0.000 | | |
| | | | | | | |
| Cell Mass | ☑ | 1.170 | | | | |
| Cell Volume (Å^3) | ☐ | 254.80322 | Fix | 0.00000 | | |
| R Bragg | | 1.250 | | | | |

Save Phase
Create str phase
Delete hkl Phase
Paste INP to Node/Selections

### 2.6.1.2.2 Defining a "PONKCS phase" - pure specimen unavailable

The procedure is mostly identical to that described in section 2.6.1.2.1. In this example the intensities of the unknown, Corundum, need to be determined from a mixture, not from a pure specimen. This requires very careful modelling of the unknown to avoid erroneous accounting for some of the intensity of the other phases (specifically misfits). The calibration constant will be obtained from the same mixture / refinement.

1. Start from a new document (menu File - Close All) and load CPD-1E.raw.
2. Switch to the Parameters Window and define the refinement model. Expand the range item of CPD-1E.raw and perform the following tasks:
   - Select the *Emission Profile* item and load the emission profile CuKa5_Berger.lam. By default this file is located in C:\Topas5\Lam.
   - Select the *Background* item and use a Chebychev Polynomial of 5th order.
   - Select 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:<br>Secondary: | 173 mm<br>173 mm |
| Receiving Slit Width | Width: | 0.3 mm |
| FDS [1] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary:<br>Secondary: | 4.6°<br>4.6° |

[1] Fixed Divergence Slit

- Select the *Corrections* item. Check the zero point error and set its code to "Refine". Check the *Sample Displacement* and set its code to "Refine".
- We have to account for the polarization effects coming from the secondary Graphite monochromator. Therefore check *LP factor* as well and set the monochromator angle to 26.4° 2ح. Finally check *Absorption* and set its code to "Refine" in order to account for the significant profile shape distortion caused by the low mass absorption of the sample.
- Select *Miscellaneous*. Check *Start X* and set its value to 22. Check *Finish X* and set its value to 150.
- Select the CPD-1E.raw range item and import the crystal structure data for Fluorite and Zincite:

  1. Fluorite.str
  2. Zincite.str

  Make sure to refine on lattice parameters, *Cry Size L* and *Strain L*
- Insert a new hkl_I phase by selecting *Add hkl phase* and rename the item to "Corundum". Input the crystallographic data given below in the *Phase Details* page and make sure to refine on lattice parameters, *Cry Size L* and *Strain L*.

| Crystallographic Data for Corundum: | | |
|---|---|---|
| Space group | | : Trigonal R_-3_C (167) |
| Cell parameters | a (Å)<br>c (Å) | : 4.7592<br>: 12.992 |

3. Start the refinement
4. Select the Corundum range item
   - Uncheck *Delete hkls on Refinement* and refine the *Scale factor*
   - Switch to the *hkl Is* page and fix all intensities
5. Perform another the refinement to obtain scale factors for all three phases

6. Calculate the Corundum calibration constant (ZM)corundum. Your refinement should yield the following calibration constant within reasonable errors:

$$(ZM)_{corundum} = \frac{55.12}{15.25}\,\frac{0.0036}{1}\,\frac{162.8\;\;47.6}{254.8} \approx 0.395$$

7. Expand the *Structures/ hkl Phases item*, select the *Quantitative* item, and enter the calibration constant of Corundum.
8. Save the Corundum hkl phase as a PONKCS phase for re-use.

### 2.6.1.2.3 Quantitative analysis using PONKCS phases

Refine the remaining CPD-1 patterns using Corundum as a PONKCS phase.

1. Start from a new document and load CPD-1A.raw. Perform a refinement as described in section 2.6.1.1. DO NOT use crystal structure data for Corundum but load your PONKCS phase for Corundum as defined in the previous two sections (2.6.1.2.1 or 2.6.1.2.2).
2. Avoid frequent user-errors related to working with PONKCS phases:
   - *Delete hkls on Refinement* must be unchecked
   - The *Scale* factor must be refined
   - All intensities must be fixed (switch to the *hkl Is* page)
3. Start the refinement and note the results
4. Continue the analysis of all remaining sample data by using the *Replace Scan Data* feature rather than to restart from scratch:
   - Focus the data range item of the present refinement
   - Select *Replace Scan Data* in the short cut menu, and load the next data file
   - Start the refinement and note the results

   Repeat this step for all remaining sample data.

The accuracy of your results should be about ± 1 % in weight.

**Ideas for further working:**

- Repeat the same exercise designating Fluorite or Zincite as unknowns
- Repeat the same exercise designating all three phases as unknowns

## 2.6.2 Quantitative phase analysis of crystalline and amorphous materials

Quantitative analysis of crystalline and amorphous phases is an application area, which is particularily characterized by peak overlap problems. For well-crystalline phases providing sharp diffraction peaks, the degree of overlap largely depends on the number and structural complexity of the phases present. Additional overlap problems occur in the presence of poorly crystalline and amorphous phases, characterized by strong (microstructural) peak broadening and "amorphous bands", respectively. Discrimination of (instrument) background, crystalline and amorphous phase intensities is usually very difficult if not impossible unless additional information can be utilized, for example measurements / estimates of the instrument background and individual amorphous / crystalline phase intensities.

All required diffraction data and crystal structure files are located in C:\Topas5\Tutorial\Quantitative Phase Analysis\Internal Standard Rietveld Method\

### 2.6.2.1 The internal standard method

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

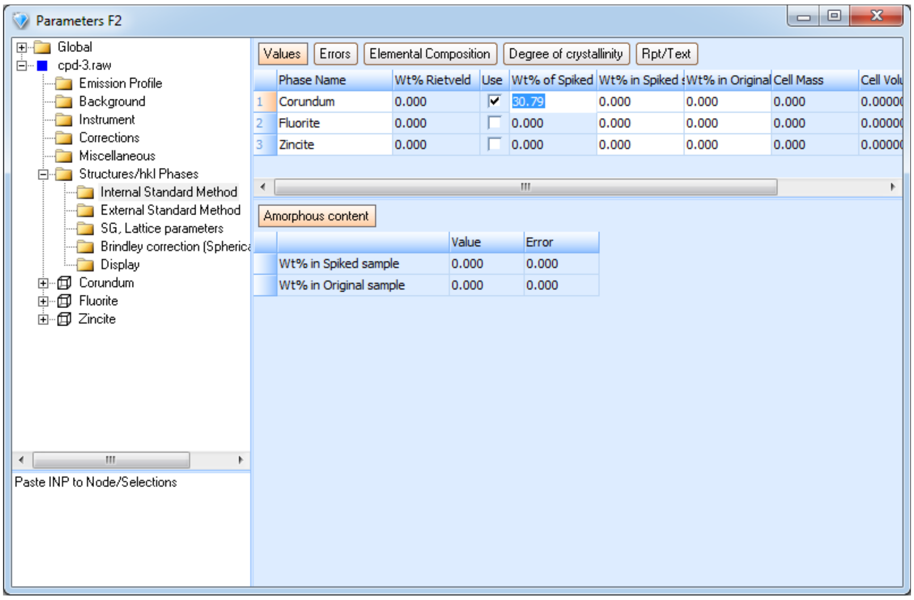
1. Start TOPAS and load CPD-3.raw.
2. Insert a single peak at about 22.5° 2θ to model the amorphous band.
3. Switch to the *Parameters Window*, expand the range item of CPD-3.RAW and perform the following tasks:
    - Select the *Emission Profile* item and load the emission profile CuKa5_Berger.lam. By default this file is located in C:\Topas5\Lam.
    - Select the *Background* item. Use a Chebychev polynomial of 5th order and the *1/X Bkg* function.
    - Select 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:<br>Secondary: | 173 mm<br>173 mm |
| Receiving Slit Width | Width: | 0.3 mm |
| FDS [1] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary:<br>Secondary: | 4.6°<br>4.6° |

[1] Fixed Divergence Slit

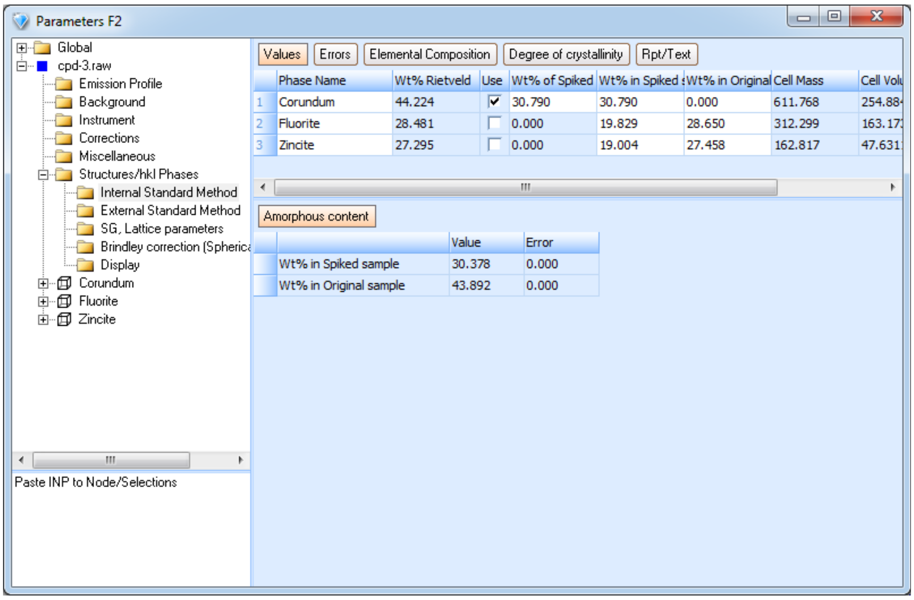
- Select the *Corrections* item. Check the *Zero error* and set its code to "Refine". In addition polarization effects coming from the secondary Graphite monochromator have to be accounted for. Therefore check *LP factor* as well and set the monochromator angle to 26.4° 2θ.
- Select the CPD-3.raw range item and import the structure entries for the three phases Corundum, Fluorite, and Zincite (multi-selection is supported):
    Corundum.str
    Fluorite.str
    Zincite.str
- Expand the *Structures/ hkl Phases* item and select the *Internal Standard Method* item. Define Corundum as a spike phase and enter its known phase amount (30,79%).



| | Phase Name | Wt% Rietveld | Use | Wt% of Spiked | Wt% in Spiked | Wt% in Original | Cell Mass | Cell Vol |
|---|---|---|---|---|---|---|---|---|
| 1 | Corundum | 0.000 | ☑ | 30.79 | 0.000 | 0.000 | 0.000 | 0.0000 |
| 2 | Fluorite | 0.000 | ☐ | 0.000 | 0.000 | 0.000 | 0.000 | 0.0000 |
| 3 | Zincite | 0.000 | ☐ | 0.000 | 0.000 | 0.000 | 0.000 | 0.0000 |

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

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



| | Phase Name | Wt% Rietveld | Use | Wt% of Spiked | Wt% in Spiked s | Wt% in Original | Cell Mass | Cell Volu |
|---|---|---|---|---|---|---|---|---|
| 1 | Corundum | 44.224 | ☑ | 30.790 | 30.790 | 0.000 | 611.768 | 254.88 |
| 2 | Fluorite | 28.481 | ☐ | 0.000 | 19.829 | 28.650 | 312.299 | 163.17 |
| 3 | Zincite | 27.295 | ☐ | 0.000 | 19.004 | 27.458 | 162.817 | 47.631 |

| | Value | Error |
|---|---|---|
| Wt% in Spiked sample | 30.378 | 0.000 |
| Wt% in Original sample | 43.892 | 0.000 |

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 ± 2 % in weight.

| CPD-3 | Corundum [%] | Fluorite [%] | Zincite [%] | Glass [%] |
|---|---|---|---|---|
| Weighed | 30,79 | 20,06 | 19,68 | 29,47 |

### 2.6.2.2 The PONKCS method

This tutorial uses the data from the Madsen et al. (2011) and Kern et al. (2012) papers on a survey of methodologies for the determination of amorphous content. The samples comprise three-phase mixtures of Corundum, Quartz, and amorphous Silica, samples NS-A to NS-I, known compositions are provided in Table 2.8.

By default all files are located in C:\Topas5\Tutorial\Quantitative Phase Analysis\PONKCS Method\Ns\.

Emphasis is placed on an accurate discrimination of instrument background and amorphous band intensities, as discussed below. The PONKCS procedure is mostly identical to that described in section 2.6.1.2.

Table 2.8: Phase compositions for NS-A to NS-I.

| Data | Corundum [%] | Quartz [%] | Glass [%] |
|---|---|---|---|
| NS-A | 50.01 | 0 | 49.99 |
| NS-B | 49.98 | 15.03 | 34.99 |
| NS-C | 49.99 | 30 | 20 |
| NS-D | 50 | 40 | 10 |
| NS-E | 50 | 45 | 5 |
| NS-F | 50.01 | 48 | 1.99 |
| NS-G | 50 | 49 | 1 |
| NS-H | 50.02 | 49.48 | 0.5 |
| NS-I | 49.87 | 50.13 | 0 |

Methods for direct modeling of amorphous bands, such as the PONKCS method, require the reliable and accurate discrimination between the actual amorphous bands and the instrument background, which is generally impossible (but at any rate highly prone to errors), unless additional information can be utilized.

Such information can be derived from a highly symmetric standard material, where the Bragg peaks can be adequately distinguished from the instrument background. This requires the standard material to be crystalline and to not contribute any fluorescence. If the standard and the sample were measured under identical conditions, the instrument background will be the same for both datasets. Including the standard data into the refinement will thus allow to derive the intensity contribution coming from the amorphous phase.

There are many ways to model amorphous bands, the following three alternatives have been shown to work very well:

1. Pawley fitting using an arbitrary unit cell to generate a sufficient number of peaks. This procedure is easiest to use and most flexible as it allows incorporation of concentration-dependent small angle X-ray scattering (SAXS) signals and fluorescense into the model, and will be therefore applied in the tutorial below.

2. Pawley fitting using a unit cell of the corresponding crystalline material, provided it adequately models the positions of the observable bands. Allowance for extreme peak broadening provides peak widths and shapes which represent those of the amorphous bands in the observed data. This often works for poorly or disordered phases, but will usually fails for glasses. SAXS signals and fluorescence need separate treatment, for example by refining one or more background functions.
3. Single line fitting using an arbitrary number of individual peaks. This approach is similarily flexible as the first one, but requires operation in LAUNCH mode. For a tutorial see Scarlett & Madsen (2006).

### 2.6.2.2.1 Defining a PONKCS phase for Silica

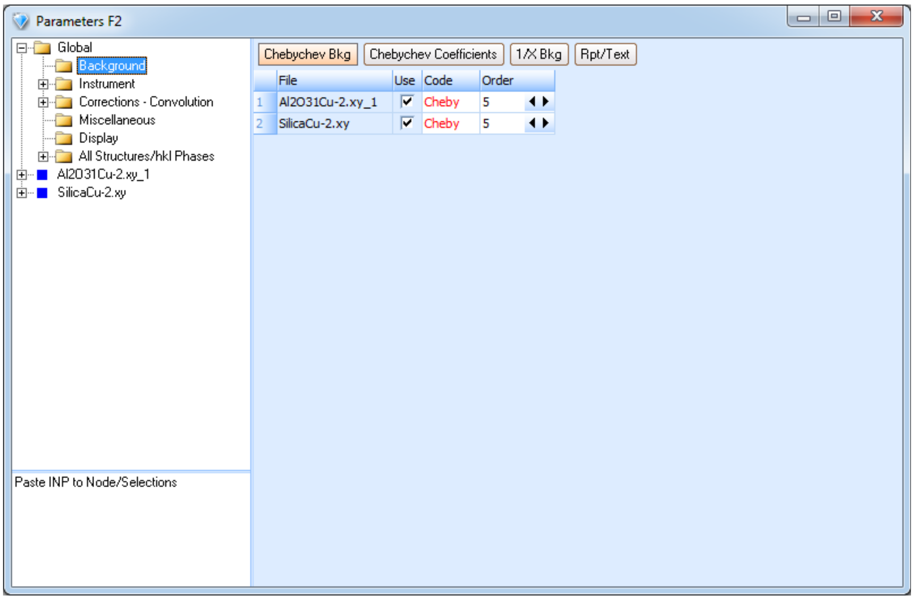
#### Step 1: Perform a Pawley refinement on the Silica data.

Perform the following steps or load and inspect the file "Silica - Bkg from Cor.pro"

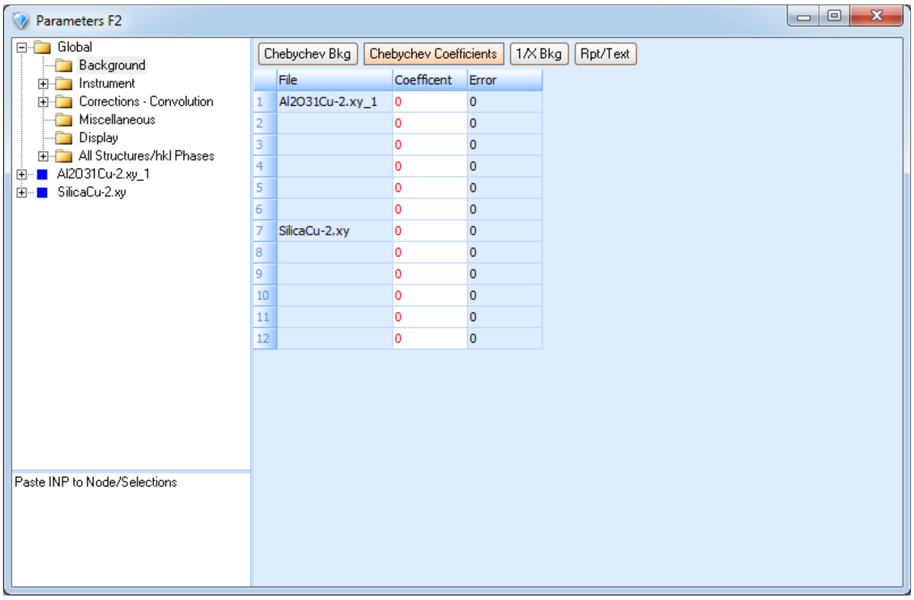
1. Load both the Silica and the Corundum data by importing the files Corundum.xy and Silica.xy into your document.

   Note the SAXS signal by the Silica at angles <10° 2θ, which is not to be confused with instrument background. This signal is concentration dependent and will be included into the Silica intensity model.

2. Switch to the *Parameters Window* and perform the following tasks for both the Silica and the Corundum ranges:
   - Select the *Emission Profile* item and load the emission profile CuKa5_Berger.lam. By default this file is located in C:\Topas5\Lam.
   - Select the *Background* item. Use a Chebychev polynomial of 5th order and the *1/X Bkg* function. As the instrument background is deemed to be the same for both ranges, provide identical parameter codes to both the Chebychev polynomial and the *1/X Bkg* function.



| | File | Use | Code | Order |
|---|---|---|---|---|
| 1 | Al2O31Cu-2.xy_1 | ☑ | Cheby | 5 |
| 2 | SilicaCu-2.xy | ☑ | Cheby | 5 |



| | File | Coefficent | Error |
|---|---|---|---|
| 1 | Al2O31Cu-2.xy_1 | 0 | 0 |
| 2 | | 0 | 0 |
| 3 | | 0 | 0 |
| 4 | | 0 | 0 |
| 5 | | 0 | 0 |
| 6 | | 0 | 0 |
| 7 | SilicaCu-2.xy | 0 | 0 |
| 8 | | 0 | 0 |
| 9 | | 0 | 0 |
| 10 | | 0 | 0 |
| 11 | | 0 | 0 |
| 12 | | 0 | 0 |

- Select 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:<br>Secondary: | 173 mm<br>173 mm |
| Receiving Slit Width | Width: | 0.3 mm |
| FDS [1] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary:<br>Secondary: | 4.6°<br>9.25° |

[1] Fixed Divergence Slit

Note: Soller slits were fitted to the incident beam, but not in the diffracted beam in order to maximise the observed intensities. The value 9.25° for the diffracted beam Soller slits sufficiently describes axial divergence of the diffracted beam and was obtained from refinements of the present tutorial data.

- Select the *Corrections* item. Check the *Zero error* and set its code to "Refine". To account for polarization effects coming from the secondary Graphite monochromator 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 account for the significant profile shape distortion caused by the low mass absorption of the sample.

3. Select the Corundum.xy range item and import the crystal structure for corundum:

   Corundum.str

4. Select the Silica.xy range item. Insert a new hkl_I phase by selecting *Add hkl phase* and rename the item to "Silica". Input the arbitrary unit cell data given below in the *Phase Details* page and make sure to refine on lattice parameters and *Cry Size L*.

| **Arbitrary unit cell data for Silica:** | | |
|---|---|---|
| Space group | | : Orthorhombic P222 (16) |
| Cell parameters | a (Å) | : 40 |
| | c (Å) | : 0.8 |

5. Run the refinement

**Step 2: Determination of the calibration constant**

Perform the following steps or load and inspect the file NS_A1 - Det of Silica Cal Factor.pro.

6. For determination of the calibration constant, a 50/50 mixture of Silica and Corundum will be used. Both the mixture and the pure phase have been measured using identical instrument settings. It is thus most convenient to simply exchange the measurement data rather than restarting from scratch.

   Switch back to the *Parameters Window*.

   - Delete the Corundum range item
   - Select the Silica range item, then select *Replace Scan Data* in the short cut menu, and load NS_A1.xy.

7. Select the NS_A1.xy range item and import the crystal structure data for Corundum:

   Corundum.str

   DO NOT refine yet.

8. Select the Silica phase item:

   - Uncheck *Delete hkls on Refinement*.
   - Set the *Scale* factor to e.g. 1 and refine it.
   - Fix the lattice parameters
   - Switch to the *Microstructure* page and fix *Cry Size L*.
   - Switch to the *hkl Is* page and fix all intensities

9. Start the refinement

10. Calculate the Silica calibration constant $(ZM)_{Silica}$:

$$(ZM)_{silica} = \frac{W_{silica}}{W_{corundum}} \frac{S_{corundum}}{S_{silica}} \frac{(ZM)_{corundum} V_{corundum}}{V_{silica}}$$

where

- $W_{silica}$ and $W_{corundum}$ are the known weights (in %) for Silica and Corundum, respectively,
- $S_{silica}$ and $S_{corundum}$ are the refined *Scale* factors for Silica and Corundum, respectively,
- $(ZM)_{corundum}$ is the *Cell Mass* of Corundum, and
- $V_{silica}$ and $V_{corundum}$ are the refined *Cell Volumes* for Silica and Corundum, respectively.

Your refinement should yield the following calibration constant within reasonable errors:

$$(ZM)_{corundum} = \frac{49.99}{50.01} \frac{0.00767}{0.506} \frac{611.768 \ 254.73}{89.65326} \approx 26.3409$$

11. Expand the *Structures/ hkl Phases* item, select the *Quantitative* item, and enter the calibration constant of Silica in the *Cell Mass* cell.

12. Select the Silica phase, then select *Save Phase*. Save the Silica hkl phase as a PONKCS phase for re-use. It is suggested to use the *STR extension, this allows easy re-loading together with crystal structure data.

#### 2.6.2.2.2 Quantitative analysis using a PONKCS phase for Silica

13. Select the NS_A1.xy range item and import the crystal structure data for Quartz:

    Quartz.str

14. Continue the analysis of all remaining sample data by using the *Replace Scan Data* feature rather than to restart from scratch:
    - Focus the data range item of the present refinement
    - Select *Replace Scan Data* in the short cut menu, and load the next data file
    - Start the refinement and note the results

The accuracy of your results should be about ± 1 % in weight.

# 3 MISCELLANOUS

## 3.1 Instrument function and size-strain determination

This lesson demonstrates how to determine instrument functions and isotropic size-strain via the so-called Double-Voigt Approach (e.g. Balzar, 1999) 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)
- TOF neutron data (ISIS)

Tutorial files 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"), and are found in C:\Topas5\Tutorial\Size-Strain Analysis\DoubleVoigt Approach\.

In the following, the determination of instrument functions and isotropic size-strain analysis is outlined for the laboratory X-ray data. The procedures described are equally applicable to all profile fitting methods supported by TOPAS (single line fitting, whole powder pattern fitting, Pawley and Le Bail fitting, Rietveld method).

#### 3.1.1.1 Measured instrument function

Size-strain analysis using measured instrument functions is a two-step approach requiring the determination of the instrument function in step 1, based on a reference material.

Note:
For accurate microstructure analysis a complication arises from the fact, that in practice measured instrument functions inevitably contain specimen contributions coming from the reference material. Even an ideally crystalline reference material will always contribute crystallite-size broadening at minimum. In addition, for divergent beam diffractometers, specimen transparency is another potential source of specimen broadening, whereby the instrument function is linked to specimen preparation (packing density). As a result, the broadening by the actual sample tends to be underestimated. This can get significant at smaller levels of micro-structural

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

[2] As a result of sample displacement and a probably uneven sample surface, the laboratory round robin data are affected by non-trivial $2\theta$ and intensity deviations (see Balzar, 2001). The $2\theta$ 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 single line fitting will be used. 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.

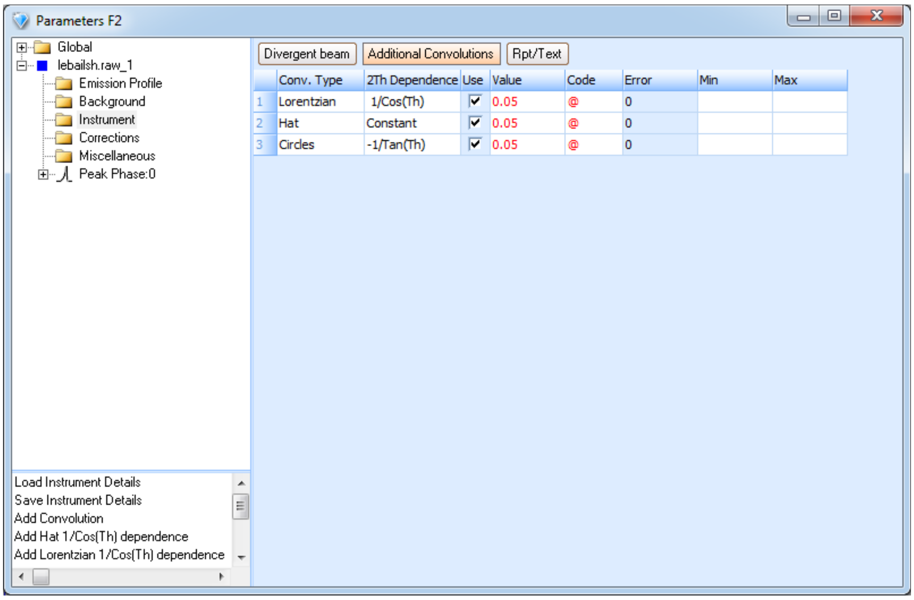
broadening, leading to overestimated micro-structure parameters (see e.g. Kern, 2008).

**Step 1:**

1. Load the file LeBailSh.raw and use the emission profile CuKa5_Berger.lam.
2. Insert a FP peak for each observed reflection.
3. Select the *Background* item and select both a 2nd order polynomial and the *1/X Bkg* function.
4. Select the *Peak Phase* item, select the *Code* page and disable *Cry Size L* for all peaks. This step is necessary to determine the instrument function as it is assumed that there are no specimen contributions coming from the standard material.
5. Select the *Additional Convolutions* page. Try various convolutions and angular dependencies and keep those resulting in a best fit. The principles of determining an instrument fucntion are described in the Technical Reference manual.

   The following three convolutions will yield good results:

   - As the line profile shape is obviously Lorentzian-type, add a Lorentzian convolution, and set its code to "Refine". Due to inherent size broadening of the standard material, define the 2θ dependence of the Lorentzian convolution as 1/Cos(Th), this is equivalent to the Scherrer equation. Fit and inspect the data.
   - To broaden the calculated peak, add a Hat type convolution and set its code to "Refine". This accounts for detector slit broadening, which is constant over 2θ. Fit and inspect the data.
   - To account for asymmetry, mostly due to axial and horizontal divergence, add a Circles type convolution, set its code to "Refine", and define the 2θ dependence of the Circles convolution as -1/Tan(Th). Fit and inspect the data.



| | Conv. Type | 2Th Dependence | Use | Value | Code | Error | Min | Max |
|---|---|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1/Cos(Th) | ☑ | 0.05 | @ | 0 | | |
| 2 | Hat | Constant | ☑ | 0.05 | @ | 0 | | |
| 3 | Circles | -1/Tan(Th) | ☑ | 0.05 | @ | 0 | | |

6. To save an instrument function use the *Instrument* item shortcut menu and select *Save Instrument Details*.

**Step 2:**

7. Select the range item of LeBailSh.raw, select *Replace Scan Data* in the short cut menu and load the file LeBailBr.raw.
8. Refine on *Cry Size L*, *Cry Size G*, *Strain L* and *Strain G*. Constrain these parameters to the same value for all peaks, respectively. Results for *LVol-IB* and *e0* should be within 23 ±1 nm and 0.0005 ±0.001, respectively.

#### 3.1.1.2 Calculated instrument function (fundamental parameters approach)

1. Load the file LeBailSh.raw and use the emission profile CuKa5_Berger.lam.
2. Insert a FP peak for each observed reflection.
3. Select the *Background* item and select both a 2nd order polynomial and the *1/X Bkg* function.
4. Select the instrument item and use the following instrument settings:

| **Instrument Parameter:** | | **Value:** |
|---|---|---|
| Goniometer Radius | Primary:<br>Secondary: | 217.5 mm<br>217.5 mm |
| Receiving Slit Width | Width: | 0.1 mm |
| FDS [1] Shape, Angle | Angle: | 1° |
| Soller Slits | Primary:<br>Secondary: | 2.3°<br>2.3° |

[1] Fixed Divergence Slit

5. Refine on *Cry Size L*, *Cry Size G*, *Strain L* and *Strain G*. Constrain these parameters to the same value for all peaks, respectively. Results for *LVol-IB* and *e0* should be within 23 ±1 nm and 0.0005 ±0.001, respectively.

## 3.2 Using the Rigid Body Editor

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:\Topas5\Rigid contains many rigid body examples in *.RGD files. These files can be viewed and modified using the *Rigid Body Editor*.

## 3.2.1 Creation of rigid bodies

### 3.2.1.1 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:

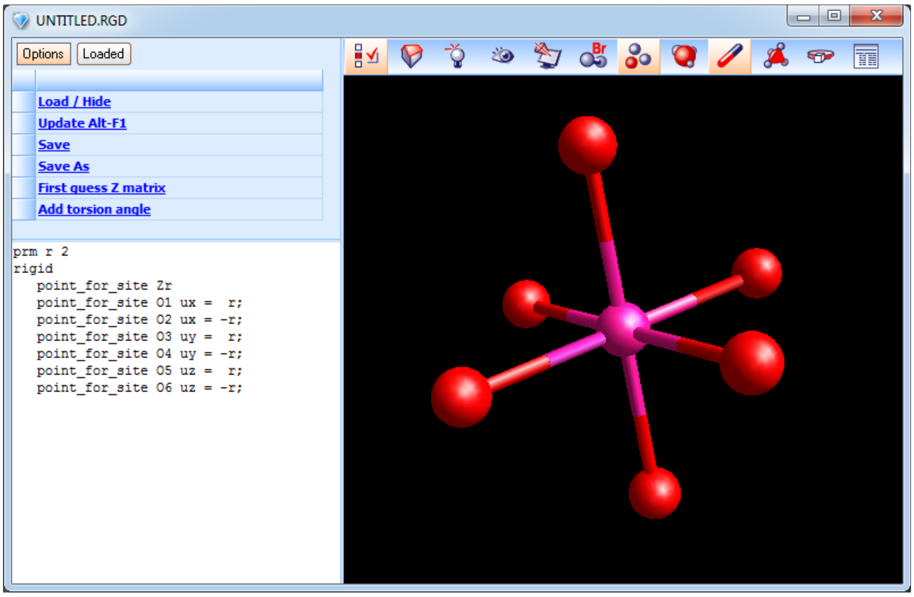
*Define a rigid body*
*Place the Zr atom at 0, 0, 0*
*Place the O1 atom at 2, 0, 0*
*Place the O2 atom at -2, 0, 0*
*Place the O3 atom at 0, 2, 0*
*...*

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*
*...*



```
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;
```

### 3.2.1.2 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 3.2.1.1 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:

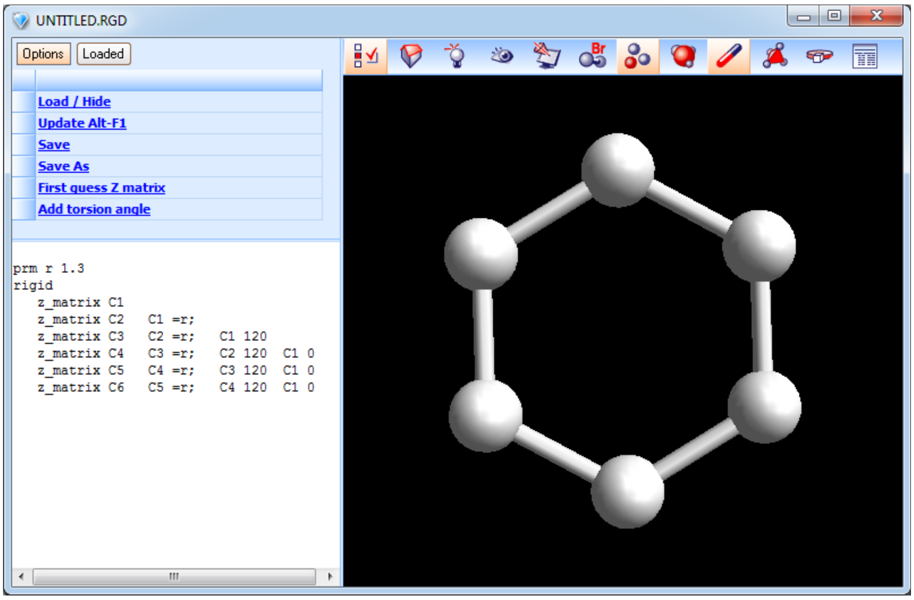
*Define a distance parameter r with a value of 2*
*Define a rigid body*
*Place Zr at 0, 0, 0*
*Place O1, at a distance of r away from Zr*
*Place O2, at a distance of r away from Zr,*
      *making an angle of 90 with Zr and O1*
*Place O3, at a distance of r away from Zr,*
      *making an angle of 90°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

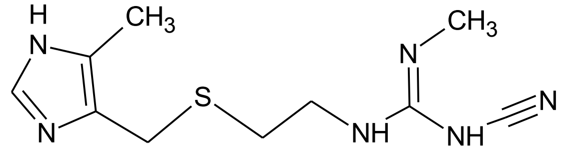
Update the *Main View* after each *z_matrix* statement to monitor the building of the rigid body.



```
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
```

### 3.2.2 Creation of a rigid body for Cimetidine using a z-matrix representation

Consider the following sketch of Cimetidine, $C_{10}H_{16}N_6S$, hydrogens will be ignored for simplicity:



1. Open a Rigid Body Editor window and create a rigid body for Cimetidine as follows. Alternatively load and inspect the predefined file Cimetidine.rgd
2. Using the sulphur atom as a start point, the rigid body definition may look as follows based on typical / guessed bond lengths and angles:

```
rigid
   z_matrix S1
   z_matrix C5  S1  1.85
   z_matrix C6  C5  1.45 S1 110
   z_matrix C1  C6  1.45 C5 126 S1 0
   z_matrix N2  C1  1.35 C6 108 C5 180
   z_matrix C10 N2  1.45 C1 108 C6 0
   z_matrix N4  C10 1.35 N2 108 C1 0
   z_matrix C8  C1  1.45 N2 126 C6 180
   z_matrix C3  S1  1.85 C5 120 C6 180
   z_matrix C7  C3  1.45 S1 120 C5 180
   z_matrix N3  C7  1.35 C3 120 S1 180
   z_matrix C4  N3  1.35 C7 120 C3 180
   z_matrix N1  C4  1.35 N3 120 C7 0
   z_matrix C9  N1  1.35 C4 120 N3 180
   z_matrix N5  C4  1.35 N3 120 C7 180
   z_matrix C2  N5  1.35 C4 120 N3 180
   z_matrix N6  C2  1.10 N5 180 C4 180
```

3. The cimetidine molecule has 9 torsion angles, which need to be refined. One possibility is the definition of a simple helper macro to turn refinement of all angles on and off at once:

```
macro RTA { @ }
```

Bounds to torsion angle space can be defined using the following helper macro, where the parameters v1 and v2 represent the maximum and minimum torsion angles:

```
macro TAB(v1, v2)
{
   min = v1; max = v2;
}
```

Suggested changes are highlighted in bold characters:

```
rigid
   z_matrix S1
   z_matrix C5  S1  1.85
   z_matrix C6  C5  1.45 S1 RTA 110 TAB(90, 120)
   z_matrix C1  C6  1.45 C5 126 S1 RTA 0
   z_matrix N2  C1  1.35 C6 108 C5 180
   z_matrix C10 N2  1.45 C1 108 C6 0
   z_matrix N4  C10 1.35 N2 108 C1 0
   z_matrix C8  C1  1.45 N2 126 C6 180
   z_matrix C3  S1  1.85 C5 120 C6 RTA 180
   z_matrix C7  C3  1.45 S1 120 C5 RTA 180
   z_matrix N3  C7  1.35 C3 120 S1 RTA 180
   z_matrix C4  N3  1.35 C7 120 C3 RTA 180
   z_matrix N1  C4  1.35 N3 120 C7 0
   z_matrix C9  N1  1.35 C4 120 N3 RTA 180
   z_matrix N5  C4  1.35 N3 120 C7 180
   z_matrix C2  N5  1.35 C4 120 N3 RTA 180
   z_matrix N6  C2  1.10 N5 180 C4 RTA 180
```

4. To refine bond distances, the following helper macros may be used. The macro RBD allows to turn refinement of all distances on and off at once, while the macro BDB allows to define bounds to expected bond distances:

```
macro RBD { }

macro BDB(v)
{
   min = v - .1; max = v + .1;
}
```

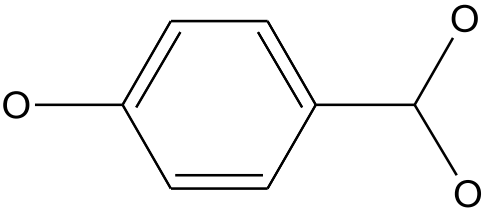
Suggested changes are highlighted in bold characters:

```
rigid
   z_matrix S1
   z_matrix C5  S1  RBD 1.85 BDB(1.85)
   z_matrix C6  C5  RBD 1.45 BDB(1.55) S1 RTA 110 TAB(90, 120)
   z_matrix C1  C6  RBD 1.45 BDB(1.45) C5 126 S1 RTA 0
   z_matrix N2  C1  RBD 1.35 BDB(1.35) C6 108 C5 180
   z_matrix C10 N2  RBD 1.45 BDB(1.45) C1 108 C6 0
   z_matrix N4  C10 RBD 1.35 BDB(1.35) N2 108 C1 0
   z_matrix C8  C1  RBD 1.45 BDB(1.45) N2 126 C6 180
   z_matrix C3  S1  RBD 1.85 BDB(1.85) C5 120 C6 RTA 180
   z_matrix C7  C3  RBD 1.45 BDB(1.45) S1 120 C5 RTA 180
   z_matrix N3  C7  RBD 1.35 BDB(1.35) C3 120 S1 RTA 180
   z_matrix C4  N3  RBD 1.35 BDB(1.35) C7 120 C3 RTA 180
   z_matrix N1  C4  RBD 1.35 BDB(1.35) N3 120 C7 0
   z_matrix C9  N1  RBD 1.35 BDB(1.35) C4 120 N3 RTA 180
   z_matrix N5  C4  RBD 1.35 BDB(1.35) N3 120 C7 180
   z_matrix C2  N5  RBD 1.35 BDB(1.35) C4 120 N3 RTA 180
   z_matrix N6  C2  RBD 1.10 BDB(1.10) N5 180 C4 RTA 180
```

### 3.2.3 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. An elegant option to perform this conversion is the calulation of the Cartesian coordinates on the fly by means of a couple of macros.

Lattice parameters for para-hydroxybenzoate given by Dinnebier et al. (1999) are

a (Å) = 16.0608
b (Å) = 5.38291
c (Å) = 3.63834
ß (°) = 92.8692

If the fractional coordinate system has the same origin as the cartesian coordinate system, the a-axis is collinear with the x-axis, and the b-axis lies in the xy-plane, fractional coordinates x, y, z can be converted to cartesian coordinates x_c, y_c, z_c through the following transformation matrix:

$$\begin{bmatrix} x\_c \\ y\_c \\ z\_c \end{bmatrix} = \begin{bmatrix} a & b\cos(\gamma) & c\cos(\beta) \\ 0 & b\sin(\gamma) & c\dfrac{\cos(\alpha)-\cos(\beta)\cos(\gamma)}{\sin(\gamma)} \\ 0 & 0 & c\dfrac{\upsilon}{\sin(\gamma)} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \tag{3.1}$$

where $\upsilon = \sqrt{1-\cos^2(\alpha)-\cos^2(\beta)-\cos^2(\gamma)+2\cos(\alpha)\cos(\beta)\cos(\gamma)}$

According to Eq. (3.1) Cartesian coordinates can be obtained from fractional coordinates using the following macros:

```
prm o_a 16.0608
prm o_b 5.38291
prm o_c 3.63834
prm o_alpha = 90 Deg;
prm o_beta  = 92.8692 Deg;
prm o_gamma = 90 Deg;

macro x_c(x,y,z)
{
= x*o_a + y*o_b*Cos(o_gamma) + z*o_c*Cos(o_beta);
}

macro y_c(x,y,z)
{
= y*o_b*Sin(o_gamma) + z*o_c*(Cos(o_alpha)
  Cos(o_beta)Cos(o_gamma))/Sin(o_gamma);
}

macro z_c(x,y,z)
{
= z*o_c*(Sqrt(1 - Cos(o_alpha)^2 - Cos(o_beta)^2
  Cos(o_gamma)^2 + 2*Cos(o_alpha)*Cos(o_beta)*
  Cos(o_gamma)))/Sin(o_gamma);
}

macro Cartesians(x,y,z)
{
x_c(x,y,z), y_c(x,y,z), z_c(x,y,z)
}
```

The actual conversion can then be performed by using the Point_for_site macro to define points in space for each atom and applying the Cartesians macro:

```
      x           y           z
O1    0.5255      0.243       0.871
C1    0.6106      0.256       0.842
...
```

⇨

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

The complete code is found in the file para-hydroxybenzoate.rgd.

To rotate the carboxyl group out of the molecular plane the *Rotate_about_points* macro can be used, 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°.

To convert the present Cartesian rigid body definition into the more useful Z-matrix representation open the file para-hydroxybenzoate.rgd in the Rigid Body Editor and 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 Dealing with time-of-flight (TOF) neutron data

**Launch Mode only**

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.

Accurate values for constants t0, t1 and t2 must be obtained by fitting to a powder diffraction pattern of a standard material and are typically provided by the instrument scientist.

The following code example describes both a Pawley fit and a Rietveld refinement to ISIS TOF $CeO_2$ data. 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 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
```

An example file is found in the C:\Topas5\Tutorial\Miscellaneous\TOF Neutron Data\ directory.

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