

Introduction to TOPAS

Part 2

Structure solution methods and Quantitative Rietveld analysis

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Outline:

Part 2

Structure solution

- Simulated annealing
- Charge flipping
- Rigid bodies

Quantitative Rietveld analysis

- Sample preparation and data collection
- Corrections
- Treatment of disorder or missing phases

Documentation:

TOPAS Tutorial

TOPAS User manual

TOPAS Reference Manual

Tutorial example files

The Classic SDPD Process



- Peak Finding
- Indexing



- Intensity Extraction
 - Le Bail, Pawley
- Structure Determination using $F^2(\text{obs})$
- Structure Refinement using $y_i(\text{obs})$ or $F^2(\text{obs})$

$F^2(\text{obs})$: Observed structure factors

$y_i(\text{obs})$: Observed step intensity data

Structure Refinement using $F^2(\text{obs})$: Two-Stage Method (Will, 1979)

Structure Refinement using $y_i(\text{obs})$: Rietveld method (Rietveld, 1967, 1969)

The Classic SDPD Process



- Peak Finding
- Indexing



- Intensity Extraction
 - Le Bail, Pawley
- Structure Determination using $F^2(\text{obs})$
- Structure Refinement using $y_i(\text{obs})$ or $F^2(\text{obs})$

SDPD Processes in TOPAS

$F^2(\text{obs})$ or $y_i(\text{obs})$

- Peak Finding
- Indexing



- Intensity Extraction
 - Le Bail, Pawley
- Structure Determination using $F^2(\text{obs})$
- Structure Refinement using $y_i(\text{obs})$ or $F^2(\text{obs})$

Suited for

- Simulated annealing
- Charge Flipping

- "Profiling"
 - Le Bail, Pawley
- Structure Determination AND Refinement using $y_i(\text{obs})$

TOPAS Approach
Coelho (2000)

Suited for

- Simulated annealing

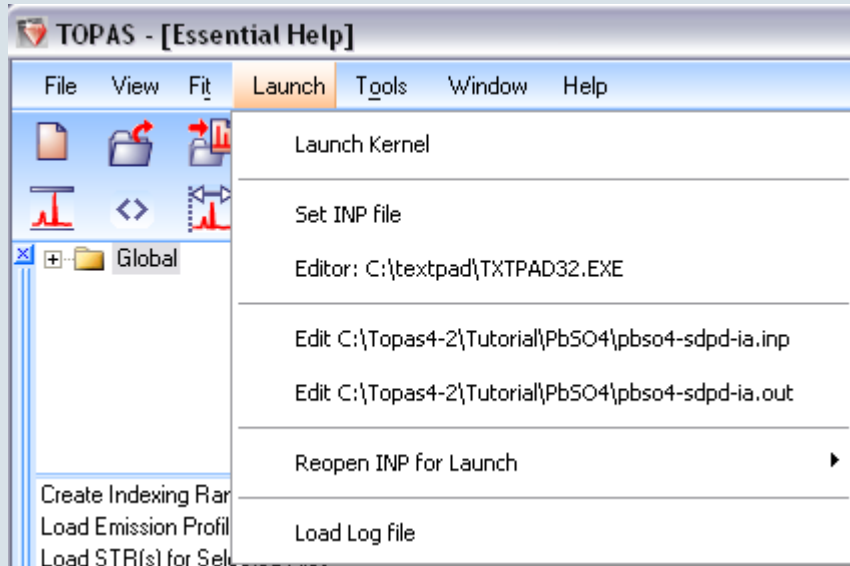
Structure Determination

Simulated Annealing

- Simulated annealing is a direct space approach where adjustable parameters lie in direct rather than reciprocal space
- Procedure:
 1. A trial crystal structure is constructed by randomly positioning and orienting individual atoms, molecular fragments or complete molecules (rigid bodies) taking into account (known or guessed) space group information
 2. After calculating diffraction data and comparing it against the measured diffraction data, the variable parameters of the model are adjusted in order to maximise the level of agreement between the observed and calculated data (i.e., minimize χ^2).
- This procedure is typically applied to single-crystal-type structure factors, but has been extended to step intensity data
⇒ TOPAS (Coelho, 2000)

Structure Determination

Simulated Annealing example: PBSO4

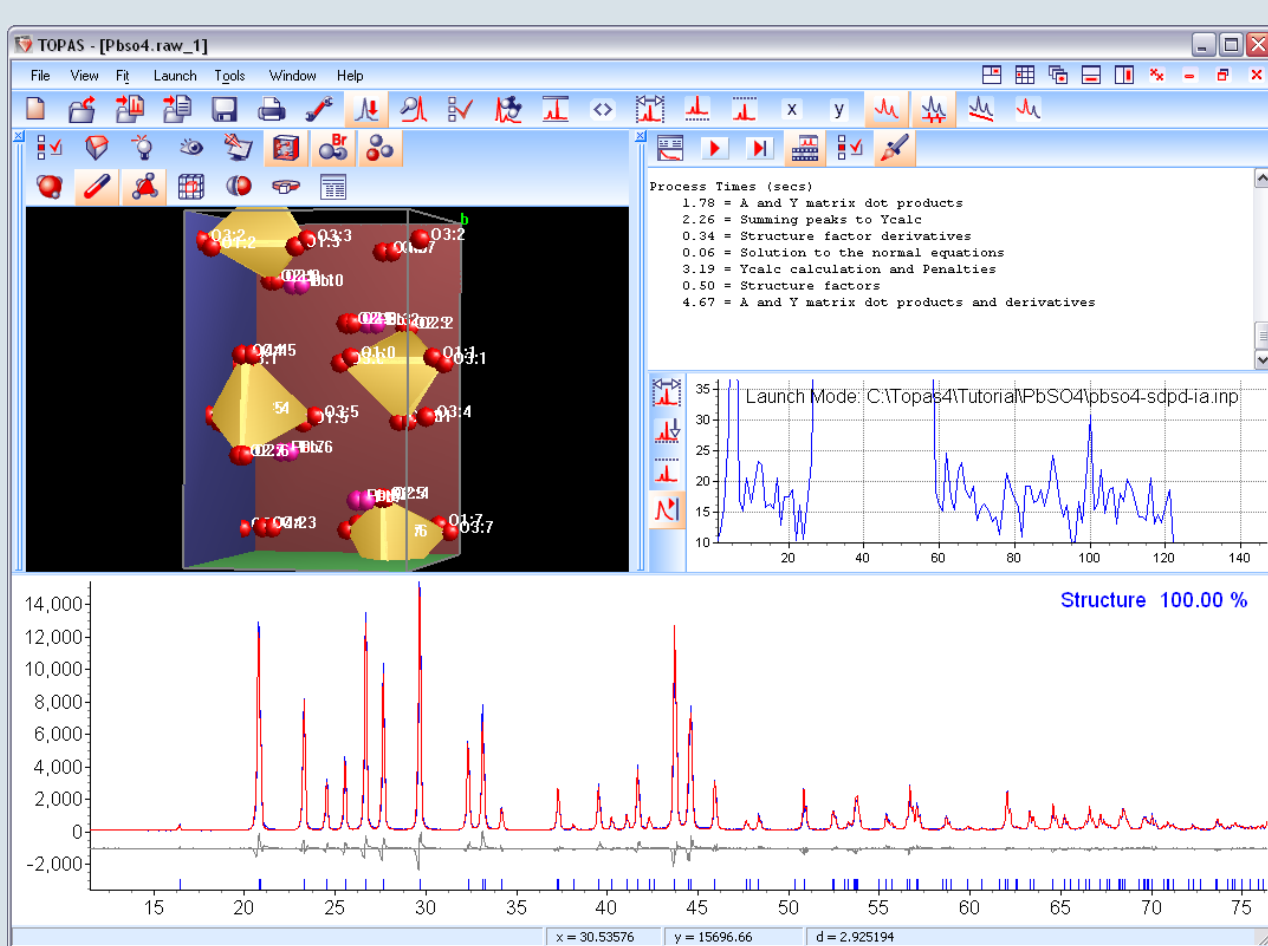


```
iters 10000
Auto_T(10)
RAW(Pbso4)
CuKα5(0.001)
LP_Factor(26.37)
Radius(173)
Full_Axial_Model(12, 15, 12, 5.1, 5.1)
Divergence(1)
Slit_Width(0.2)
bkg -129.186085 273.399239 -138.181022 72.48562 -26.4674473 17.2793392
One_on_X(, 8070.92751)
ZE(, 0.00280)
finish_X 100
Structure_Solution_Weighting
str
  space_group P_b_n_m
  a 6.96367
  b 8.48468
  c 5.40148
  scale @ 0.0003327635
  site Pb x @ 0.001 y @ 0.001 z @ 0.001 occ Pb+2 1 beq 1
  site S x @ 0.001 y @ 0.001 z @ 0.001 occ S 1 beq 1
  site O1 x @ 0.001 y @ 0.001 z @ 0.001 occ O-2 1 beq 1.5
  site O2 x @ 0.001 y @ 0.001 z @ 0.001 occ O-2 1 beq 1.5
  site O3 x @ 0.001 y @ 0.001 z @ 0.001 occ O-2 1 beq 1.5
  site O4 x @ 0.001 y @ 0.001 z @ 0.001 occ O-2 1 beq 1.5
CS_L(, 786.98060)
Strain_L(, 0.06718)
occ_merge S* occ_merge_radius .6
occ_merge O* occ_merge_radius .6
occ_merge Pb* occ_merge_radius .6
normalize_FCs
view_structure
append_fractional
append_bond_lengths
```

- Set input file to TOPAS tutorial example
- use your favorite text editor or notepad to edit and view the files

Structure Determination

Simulated Annealing example: PBSO4



- After refinement two oxygen atoms are „merged“ in the structure viewer

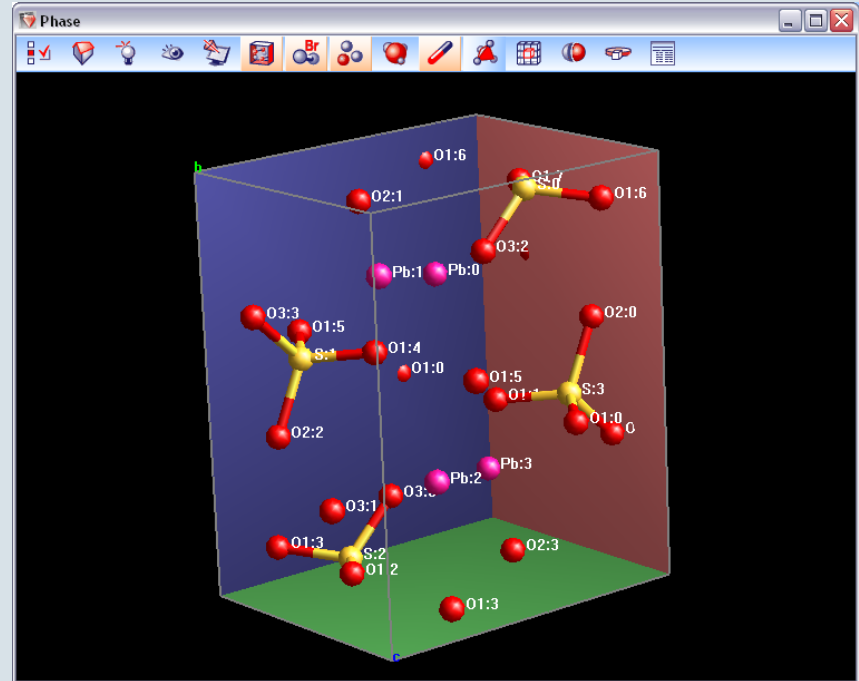
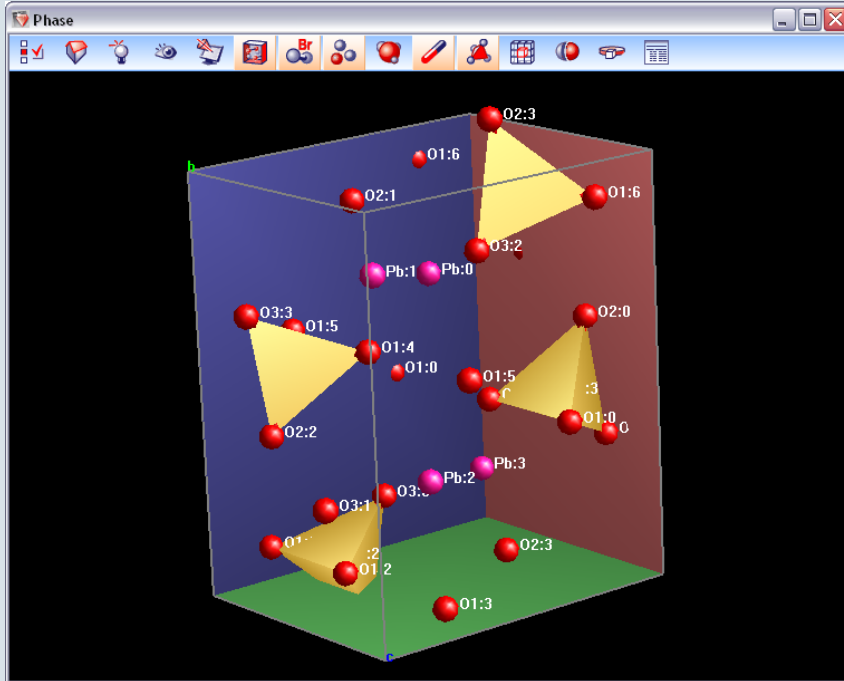
- Comment out one oxygen site, set the other occupancies to 1

- Comment out the occ_merge commands

Re-run the refinement

Structure Determination

Simulated Annealing example: PBSO4



- Structure viewer with numerous display options

Structure Determination

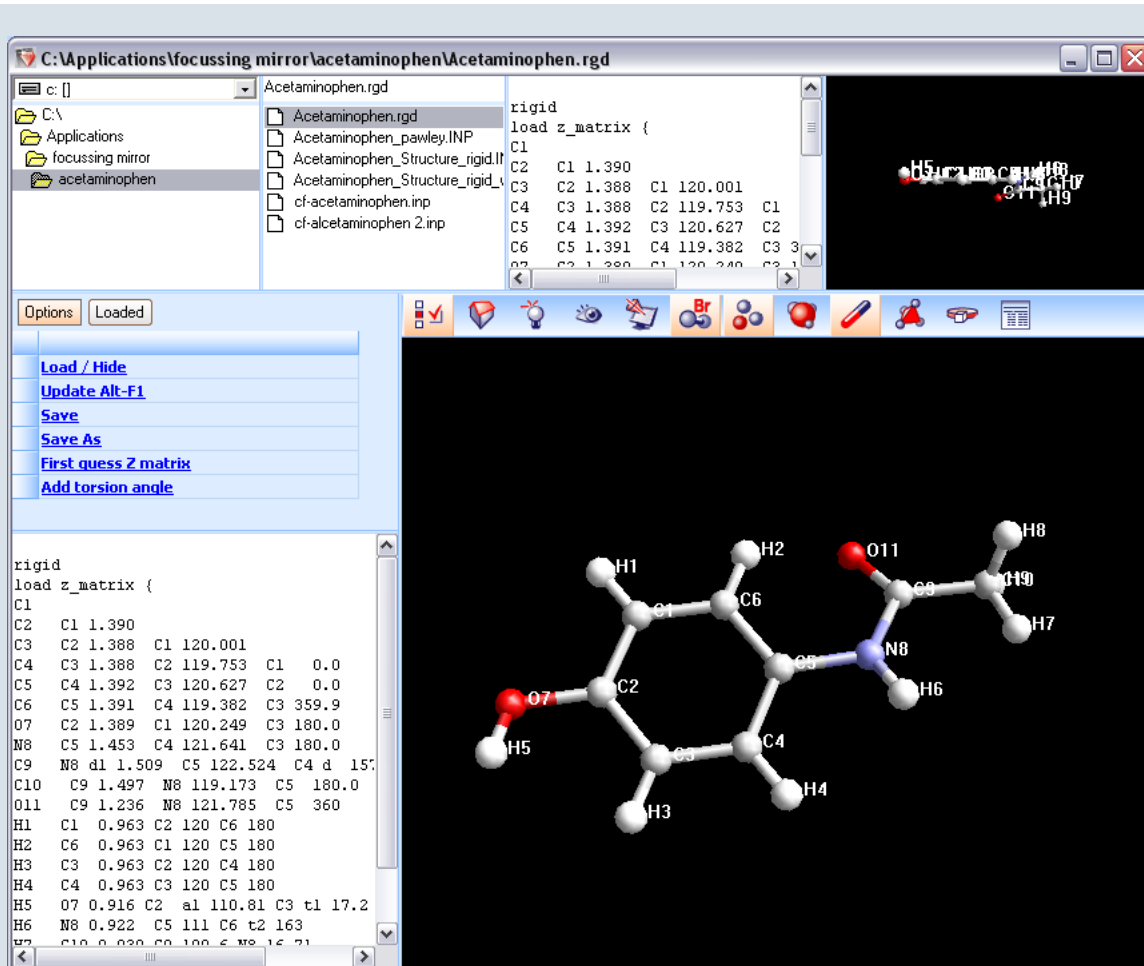
Penalty functions, Bond length restraints, atomic interactions



- Penalty Functions can only be used in Launch Mode
- Introduction of suitable penalty functions reduces the number of local minimums in χ^2 and increases chance for global minimum. Several penalty functions are implemented as macros.
- Anti-Bump (ton, s1,s2,r0,wby)
ton: sets_to_N of the box_interaction keyword
[s1,s2]: Sites
r0: distance
wby: weight given to the penalty function
Bond-length penalty function as a function of distance
- Coulomb-Interaction penalties (Born Mayer, Lennard-Jones Potential) suited for ionic atomic models. A general real space (GRS) series is used to calculate Coulomb terms for all space groups.
GRS_Interaction (s1,s2,wqi,wq2,c,ro,n)
s1,s2: sites
wqi,wq2: valence charges
c: name of the GRS series
ro: distance
n: exponent of the repulsion part of the Lennard-Jones potential
- GRS_BornMayer (S1,S2,Wqi,wqj,c,r0,b)
- Parabola_N(n1,n2,s1,s2,ro,wby)
Applies a penalty function of the distance between atoms. The closer the atoms are the higher the penalty is.

Rigid body editor for molecules

Acetaminophen

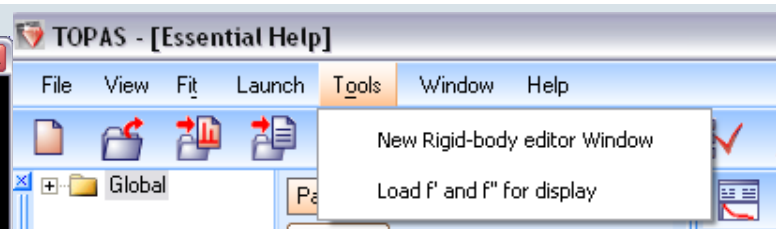


The screenshot shows the TOPAS Rigid Body Editor interface. The main window displays a 3D ball-and-stick model of an acetaminophen molecule with atoms labeled C1 through C9, H1 through H9, and O1 through O2. The interface includes a file explorer on the left, a command window at the top right, and a list of rigid body parameters at the bottom left.

```

rigid
load z_matrix (
C1
C2 C1 1.390
C3 C2 1.388 C1 120.001
C4 C3 1.388 C2 119.753 C1
C5 C4 1.392 C3 120.627 C2
C6 C5 1.391 C4 119.382 C3 3
C7 C2 1.389 C1 120.249 C3 180.0
N8 C5 1.453 C4 121.641 C3 180.0
C9 N8 d1 1.509 C5 122.524 C4 d 15;
C10 C9 1.497 N8 119.173 C5 180.0
O11 C9 1.236 N8 121.785 C5 360
H1 C1 0.963 C2 120 C6 180
H2 C6 0.963 C1 120 C5 180
H3 C3 0.963 C2 120 C4 180
H4 C4 0.963 C3 120 C5 180
H5 O7 0.916 C2 a1 110.81 C3 t1 17.2
H6 N8 0.922 C5 111 C6 t2 163
H7
H8
H9

```



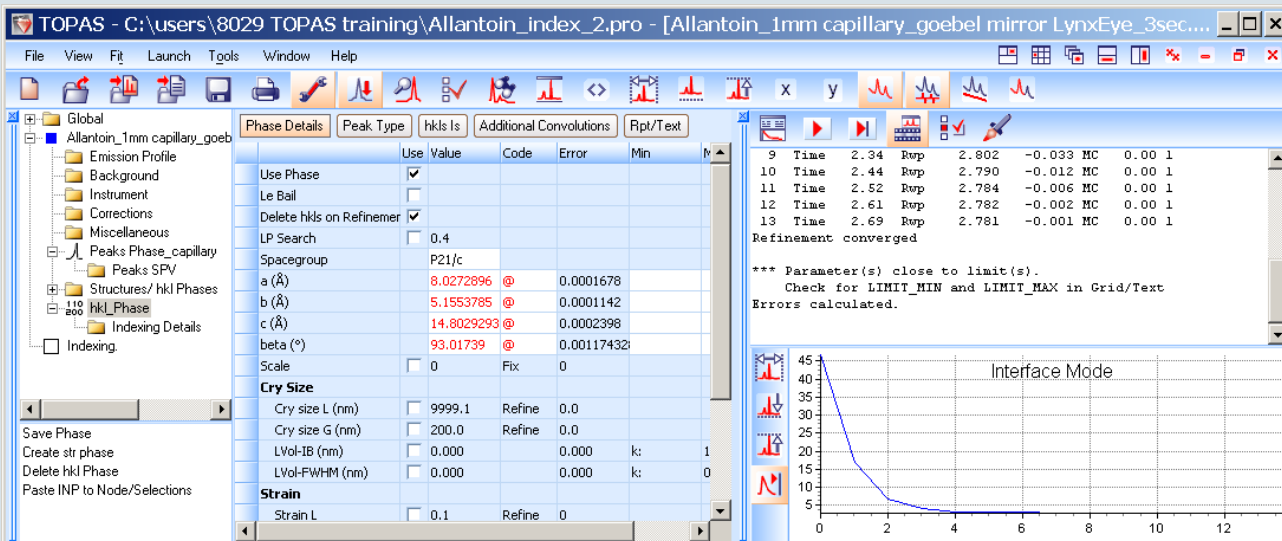
The screenshot shows the TOPAS menu bar and toolbar. The 'Tools' menu is open, showing options like 'New Rigid-body editor Window' and 'Load f' and f'' for display'.

Molecules can be entered as `z_matrix` or, if atomic coordinates are available, directly imported (point for site notation)

Bond lengths and angles can be defined as variables (with possible constraints)

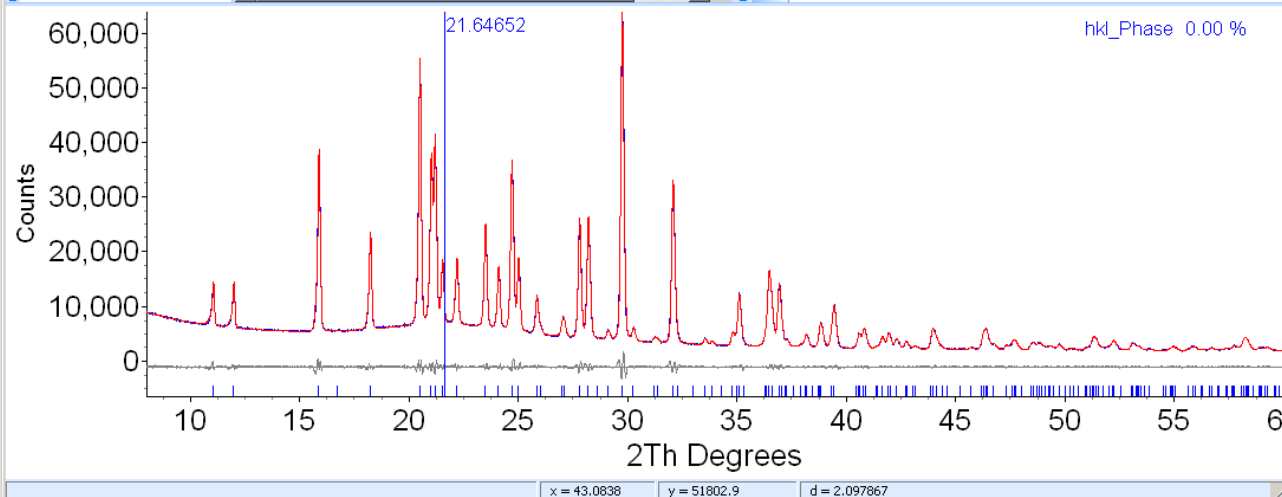
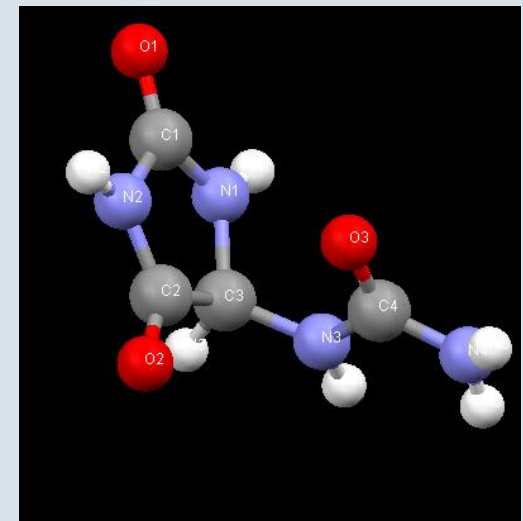
Example files are available in the `c:\topas\rigid` directory

Structure determination Indexing solution

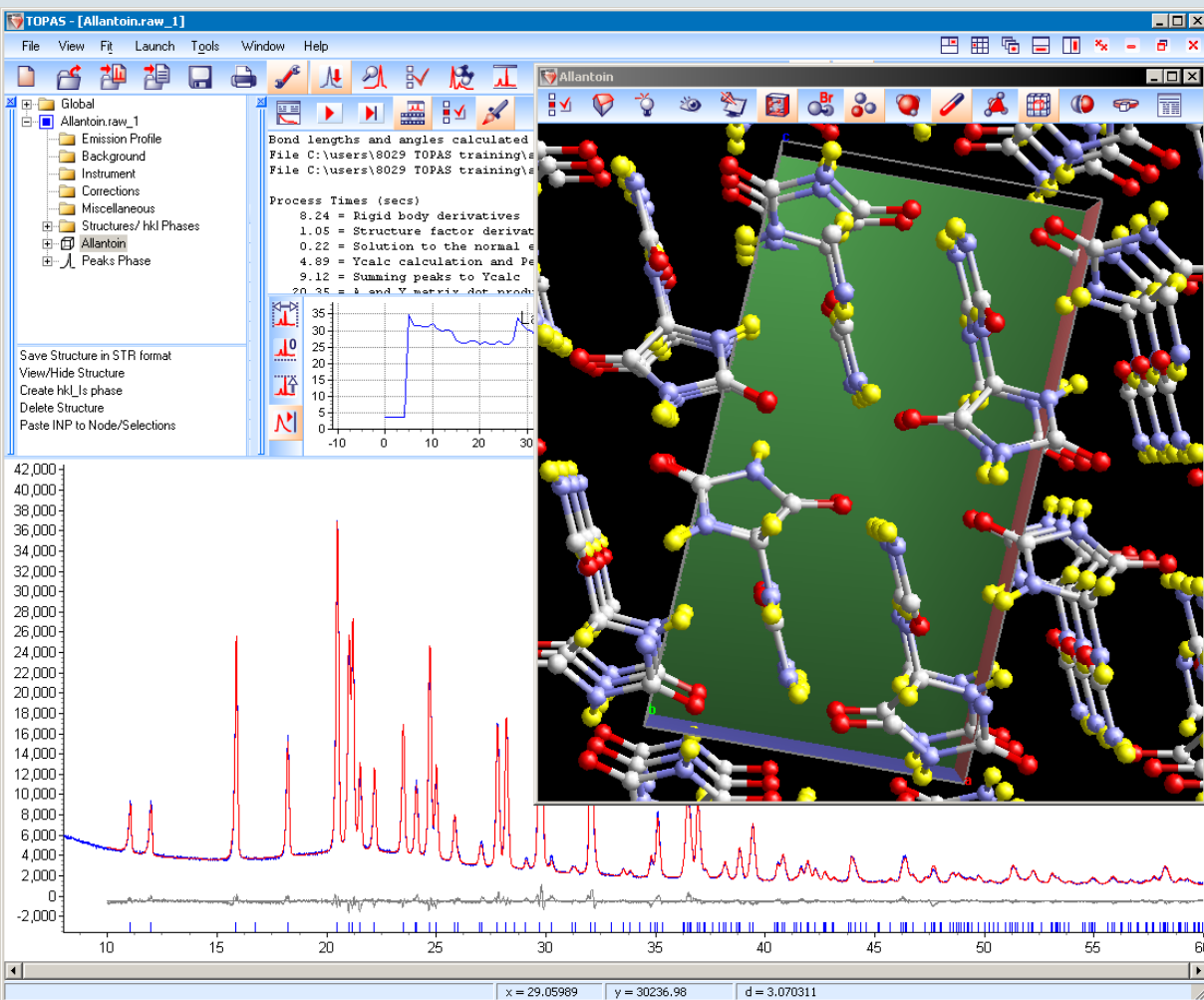


P21/c
A=8.02729
B=5.15538
C=14.8029
 $\beta = 93.017^\circ$

C₄H₆N₄O₃ molecule



Structure determination Allantoin Structure using a rigid body



R_WP: 3.6 GOF 2.23 R_Bragg: 1.9

Rigid Body definition with refinable parameters for certain bond lengths and angles

prm rCO 1.22844° min 1.1 max = 1.3;
Prm rCN 1.38049° min 1.2 max = 1.5;
Prm rCC 1.55547° min 1.3 max = 1.65;
prm rNH 0.94003° min 0.8 max = 1.1;
prm rCH 1.09498° min 0.8 max = 1.1;
prm t1 161.32814° min -180.0 max = 180.0;

rigid

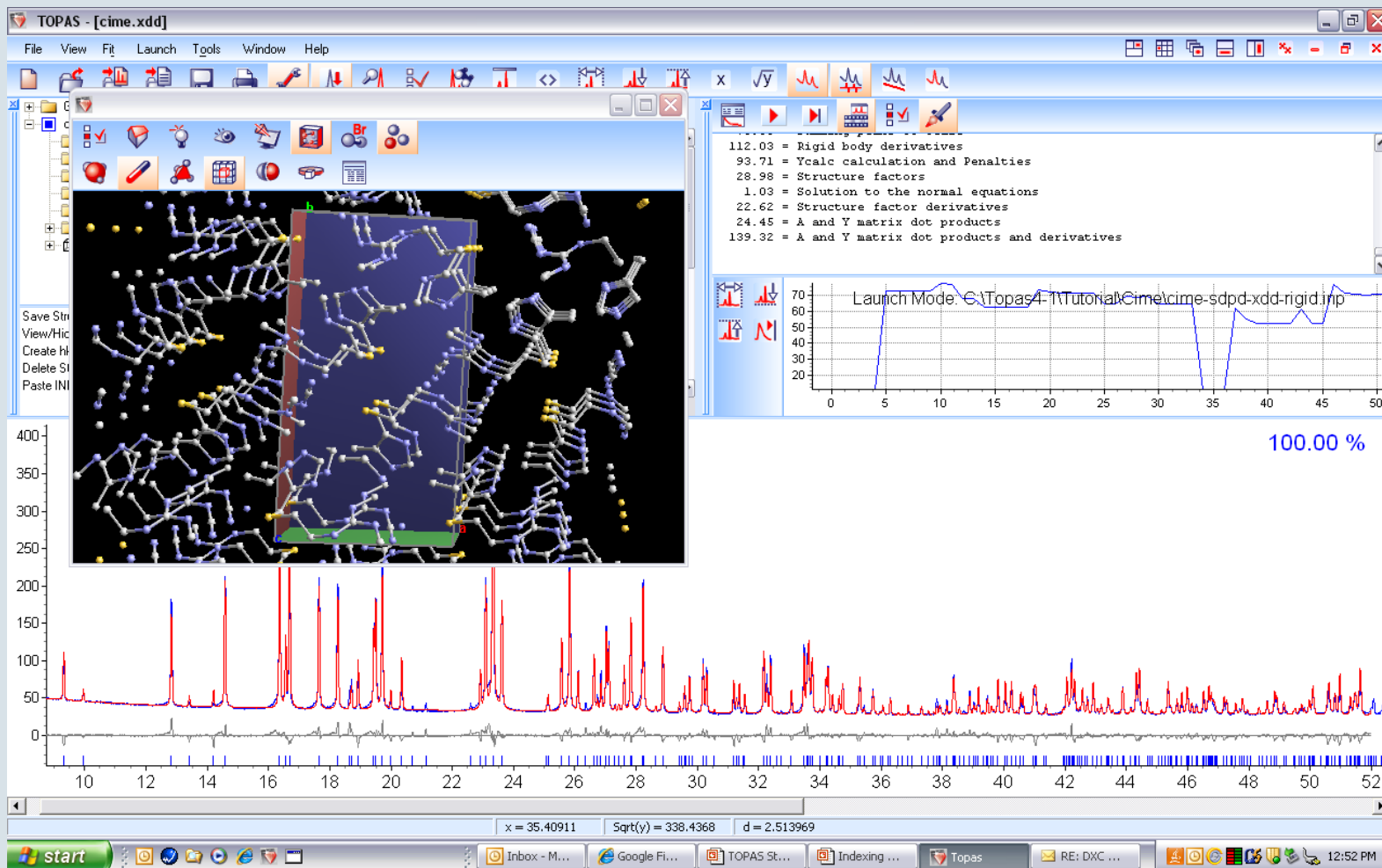
```
z_matrix C3
z_matrix C2 C3 = rCC;
z_matrix H3 C3 = rCH; C2 105.402
z_matrix N1 C3 = rCN; C2 100.717 H3 -118.051
z_matrix N3 C3 = rCN; C2 114.085 N1 -125.499
z_matrix N2 C2 = rCN; C3 106.935 N1 -5.652
z_matrix O2 C2 = rCO; C3 126.540 N2 -177.818
z_matrix C1 N1 = rCN; N2 37.005 C2 177.016
z_matrix H1 N1 = rNH; C1 122.928 C3 -178.264
z_matrix C4 N3 = rCN; C3 119.850 H3 = t1;
z_matrix H4 N3 = rNH; C3 113.023 C4 172.397
z_matrix H2 N2 = rNH; C1 119.991 C2 -165.935
z_matrix O1 C1 = rCO; N1 127.712 N2 177.677
z_matrix N4 C4 = rCN; N3 116.779 H4 10.982
z_matrix O3 C4 = rCO; N3 120.303 N4 -178.068
z_matrix H5 N4 = rNH; C4 112.943 O3 -20.399
z_matrix H6 N4 = rNH; C4 117.158 H5 -155.657
```

Rotate_about_axes(@ -217.23153°, @ -212.56492°, @ -292.67135°)

Translate(@ 6.21006°, @ -95.95035°, @ -5.15864°)

TOPAS Tutorial Cimetidine

Structure refinement using a rigid body model



Structure Solution with TOPAS

Charge flipping

- Included in TOPAS version 4 (A.A. Coelho, Acta Crystallographica A63 400-406(2007))
- Charge flipping algorithm (Ozlanyi, Sütó, 2004) aims to reconstruct directions of scattering vector by cycling between real space and reciprocal space

Works particularly well for high resolution data

Powder diffraction from Lab instruments are usually consider poor resolution data

Charge flipping combined with the tangent formula:

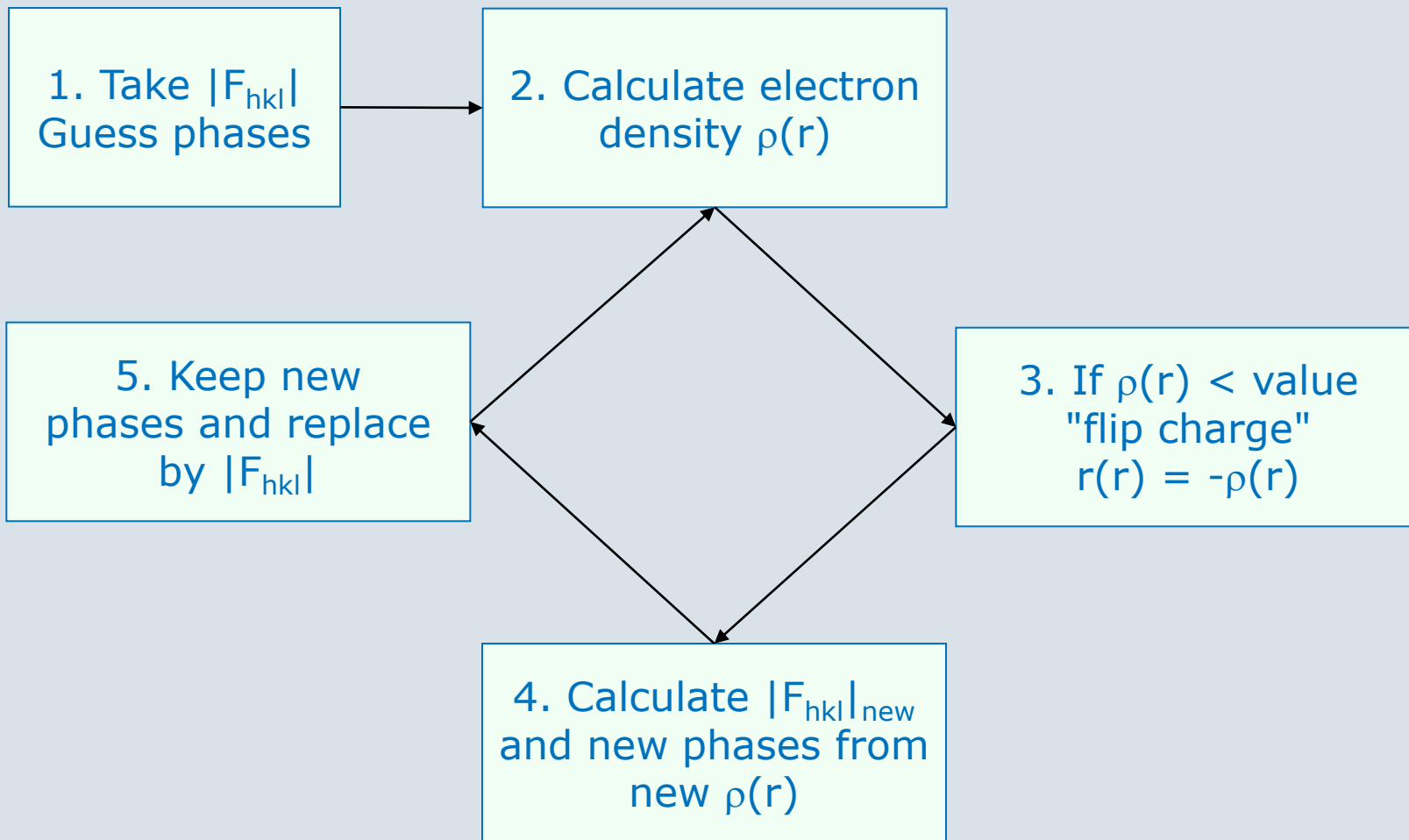
Coelho (2007), (A.A. Coelho, Acta Crystallographica A63 400-406(2007))

- **Allows solutions at poorer resolution**

- Automatic determination of the origin
- Symmetry consideration (symmetry_obey_0_to_1)
- Atom picking and assignment, Z_matrix guessing

Charge Flipping

Osztlányi and Sütő, 2004



Specific commands for charge flipping

First Step: Pawley fit in Launch mode

Save your Whole Powder Pattern fitting as an .inp file and add an
Out_cf_hkl(filename.hkl) or
Out_for_cf(filename.a)
command with your text editor (see cf-alvo4-pawley.inp example below)

```
xdd alvo4.xdd
CuKa1(0.001)
LP_Factor(27)
Radius(200.5)
Simple_Axial_Model(@, 1)
Zero_Error(@, 0)
bkg @ 0 0 0 0 0 0 0 0
hkl_Is
  space_group "p-1"
  a @ 6.54
  b @ 7.75
  c @ 9.12
  al @ 96.1
  be @ 107.2
  ga @ 101.4
  PV_Peak_Type(, 0, @, 0.05, @, 0.05, @, 0.05, @, 0.05, @, .05)
Out_for_cf(alvo4.a)           `Writes intensities into .a file
Out_cf_hkl(alvo4-pawley.hkl) ` writes intensities into .hkl file
```

Second Step: Set up input file for charge flipping

Example files in directory tutorial/cf/

e.g.: cf-ae5.inp

```
macro Nr { 100 }
```

```
verbose 0
```

```
charge_flipping
```

```
  cf_hkl_file ae5.hkl
```

```
  space_group C2/c
```

```
  a 28.850
```

```
  b 7.4438
```

```
  c 15.3364
```

```
  be 111.853
```



Reference to intensity file
Space group and lattice
parameters (fixed)

```
delete_observed_reflections = D_spacing < 1;
```

```
fraction_reflections_weak .4
```

```
add_to_phases_of_weak_reflections = 90 Ramp(1, 0, Nr);
```

```
symmetry_obey_0_to_1 = Ramp(0.5, 1, Nr);
```

```
flip_regime_2 = Ramp(2, 0, Nr);
```

```
Tangent(.3, 30)
```

```
Pick(10)
```

```
load f_atom_type f_atom_quantity
```

```
{
```

```
  O = 2 8;
```

```
  N = 4 8;
```

```
  C = 17 8;
```

```
}
```



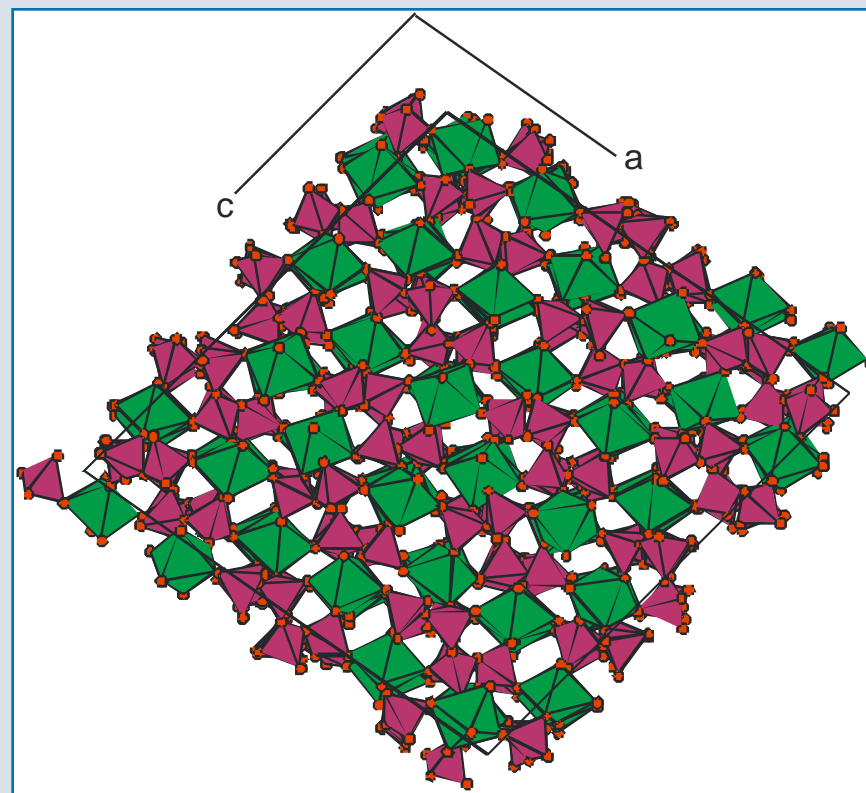
Use of Tangent formula
advisable for powder data

Load number of atoms in unit
cell

Example

Structure Determination of $\text{Mo}_2\text{P}_4\text{O}_{15}$

- One of the largest structures solved with TOPAS (simulated annealing)
- Single crystal data (Bruker AXS SMART 6000)
- SG: Pn (7)
- $a = 24.1134(6) \text{ \AA}$
- $b = 19.5324(5) \text{ \AA}$
- $c = 25.0854(6) \text{ \AA}$
- $\beta = 100.015(1)^\circ$
- $V = 4450.9 \text{ \AA}^3$
- 441 atoms in asymmetric unit



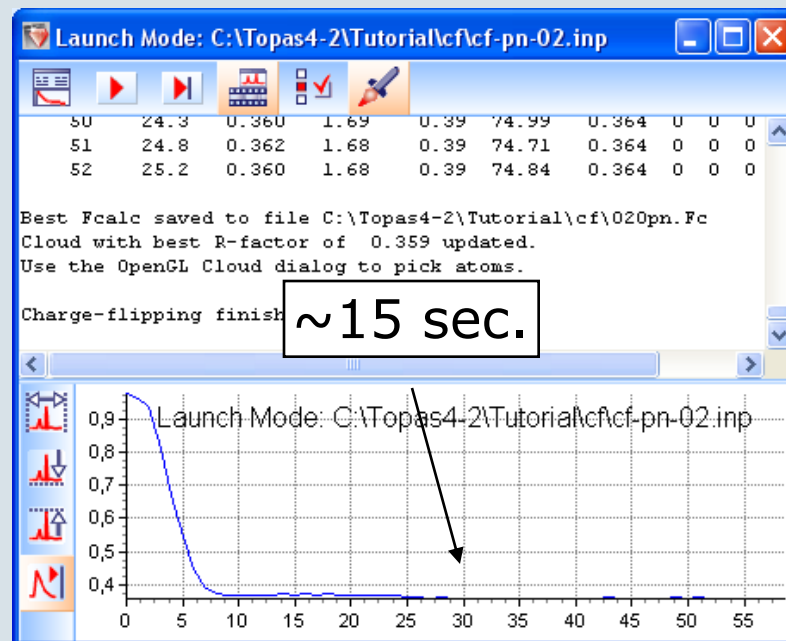
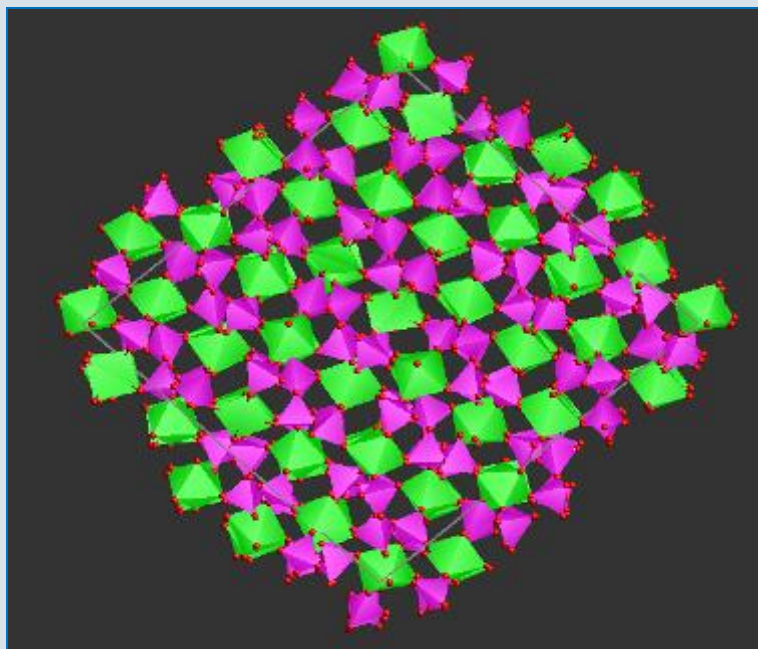
Lister et al., Chem. Commun., 2004, 2540

Example

Structure Determination of $\text{Mo}_2\text{P}_4\text{O}_{15}$

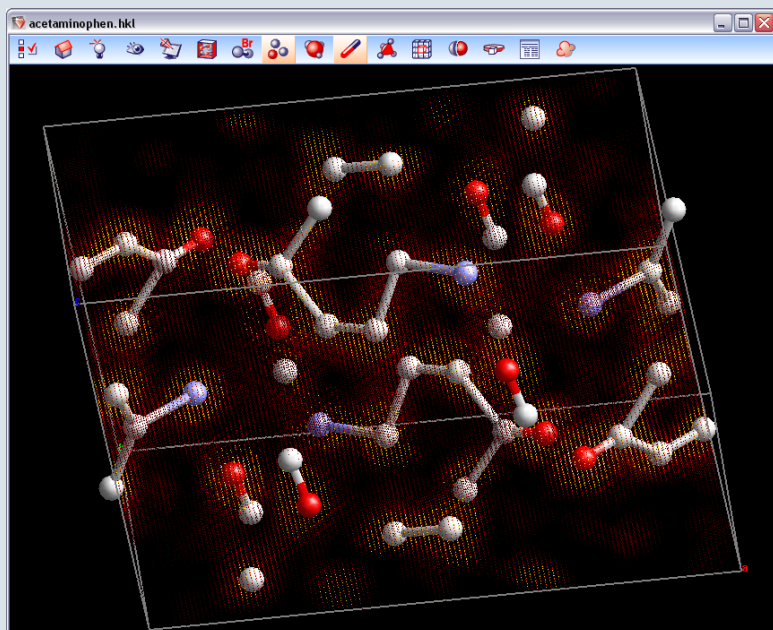
Charge Flipping

- "Default" run
- Typically very high proportion of 441 atoms correctly identified (>99%?)



Acetaminophen

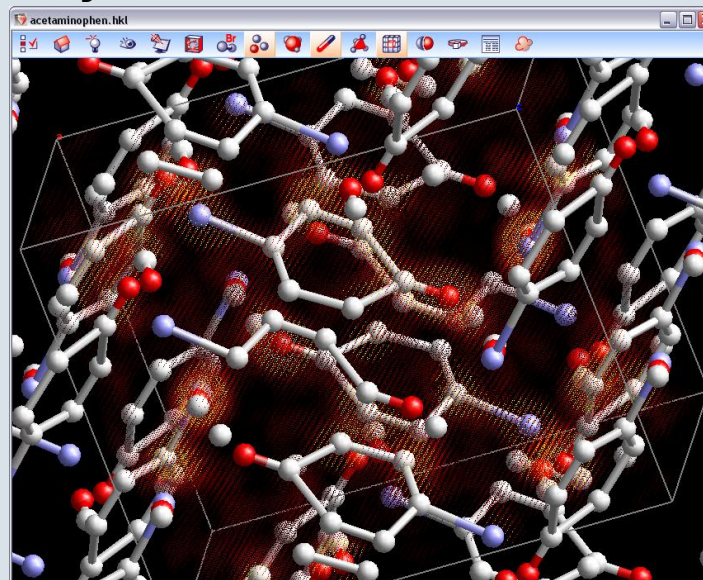
Trial run with Charge Flipping Method



Carbon rings with O and N are identified correctly from Electron cloud but not complete molecule

Required input: Peak intensities from Pawley fit (listed in hkl file)
 Number of atoms neglecting hydrogen
 load f_atom_type f_atom_quantity

```
{
N = 1 4;
C = 8 4;
O = 2 4;
}
```



Simulated Annealing vs. Charge Flipping

Conclusions



Simulated Annealing:

- Requires a trial structure model, which can be partial or random
- Performs better on poor quality data. Important advantage!
- Comparatively slow

Charge Flipping:

- No use of chemistry / trial structure models. Important advantage!
- Requires high quality data
- Even if the structure doesn't solve completely, heavy atoms and / or molecular fragments can often be found very quickly, which greatly assists subsequent simulated annealing structure determination
- Very fast; structures can be (partially) solved in seconds up to a few minutes, i.e. faster than one typically can create a start model / rigid body for simulated annealing

The Rietveld method

- is a standard-less full-profile approach to quantitative phase analysis
- uses every datapoint as a unique observation and least square methods to minimize the difference between calculated and measured intensities
- Residual of Least Square Refinement
$$R = \sum w_i(y_i - y_{c_i})^2$$

Rietveld Analysis requires:

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

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

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

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

Data collection

Measurement parameters:

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

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

Typical measurement parameters for analysis of mineral samples:

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

Data collection

General sample preparation requirements



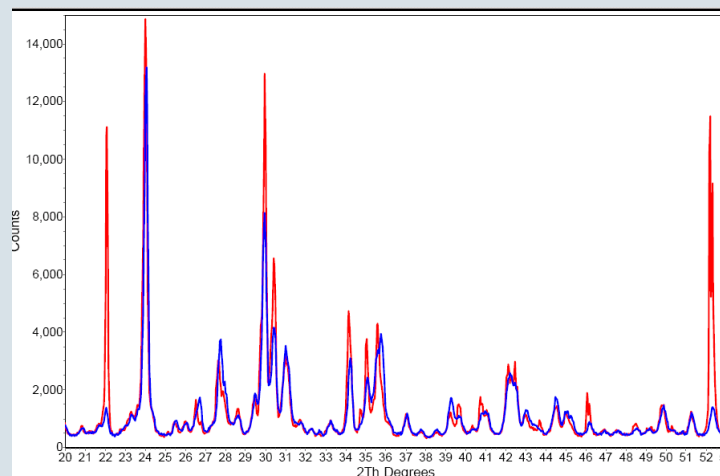
- Good mixing, powder sample should be representative for bulk sample (no segregation)
- Smooth flat surface
- Sufficient particles to cover the x-ray beam area
- Sample thickness should be sufficient for correct intensities (infinite thickness for correct intensities)
- For low density materials thin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

General Sample preparation requirements

Sufficient Grinding

■ Powder preparation

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



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

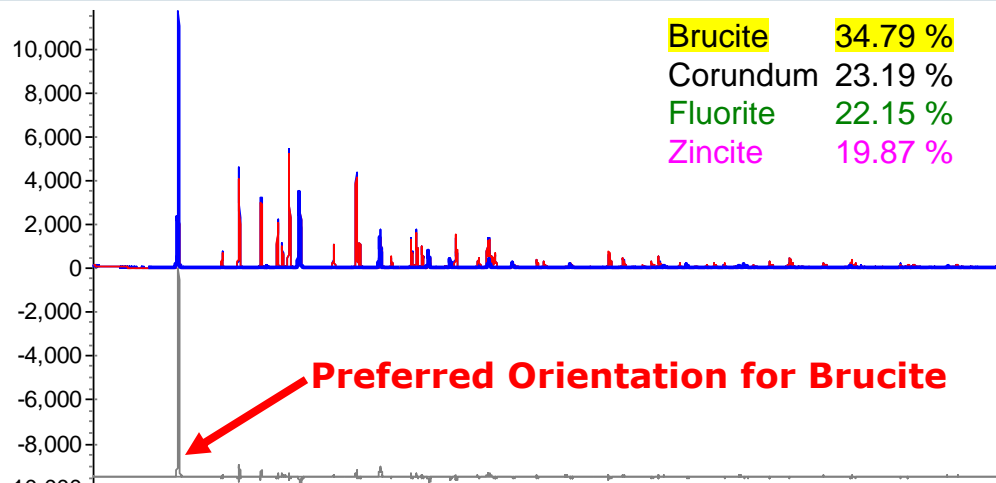
Quantitative Rietveld Analysis

Round-Robin example

File: C:\Topas 4.1\tutorial\qparr\cpd2.raw

Measurement circle radius: 173mm
 Emission profile: CuKα5.lam
 Background order 3, 1/x function
 Divergence: 1°, Receiving slit: 0.3mm
 Soller slits: prim. 4.6°, sec. 4.6°
 LP factor: 26.6 (graphite monochromator)

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



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

	hkl	Use	Value	Code
Direction 1	0 0 1	<input checked="" type="checkbox"/>	1	Refine
Direction 2		<input type="checkbox"/>	1	Refine
Fraction Dir. 1			0.5	Refine

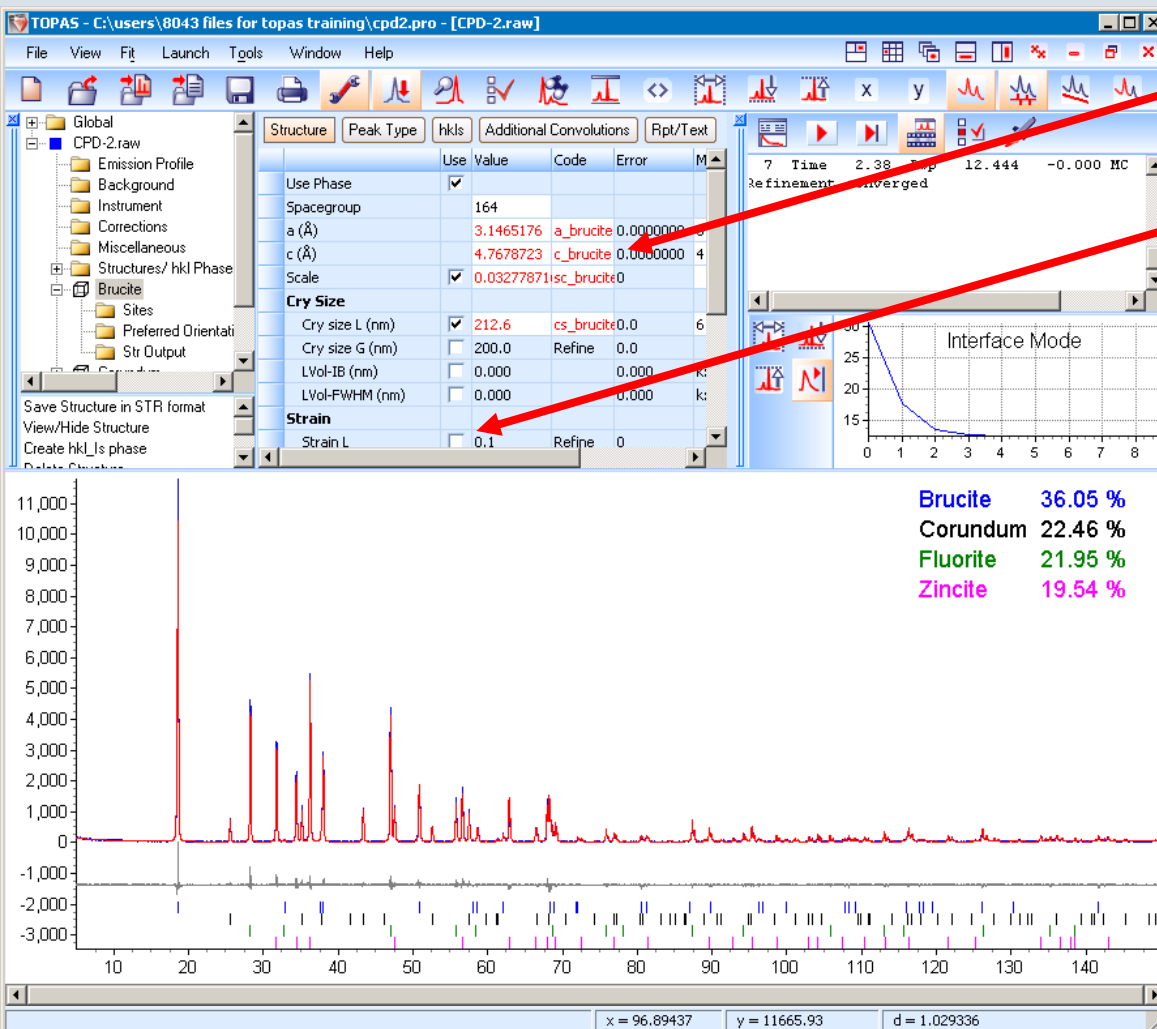
	Name	Use	Order
1	sh_48aee186_a3	<input type="checkbox"/>	4

Highlight Preferred Orientation in Brucite structure

Toggle Code column to Refine and Run Refinement again

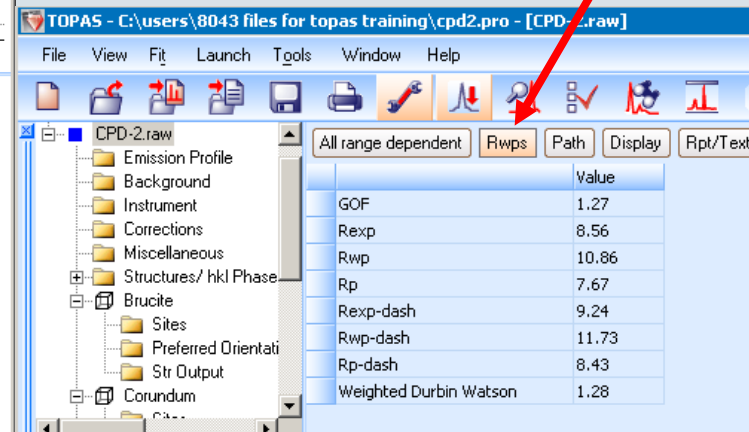
Quantitative Rietveld Analysis

Round-Robin example



Refined Lattice parameters and crystallite size for each phase

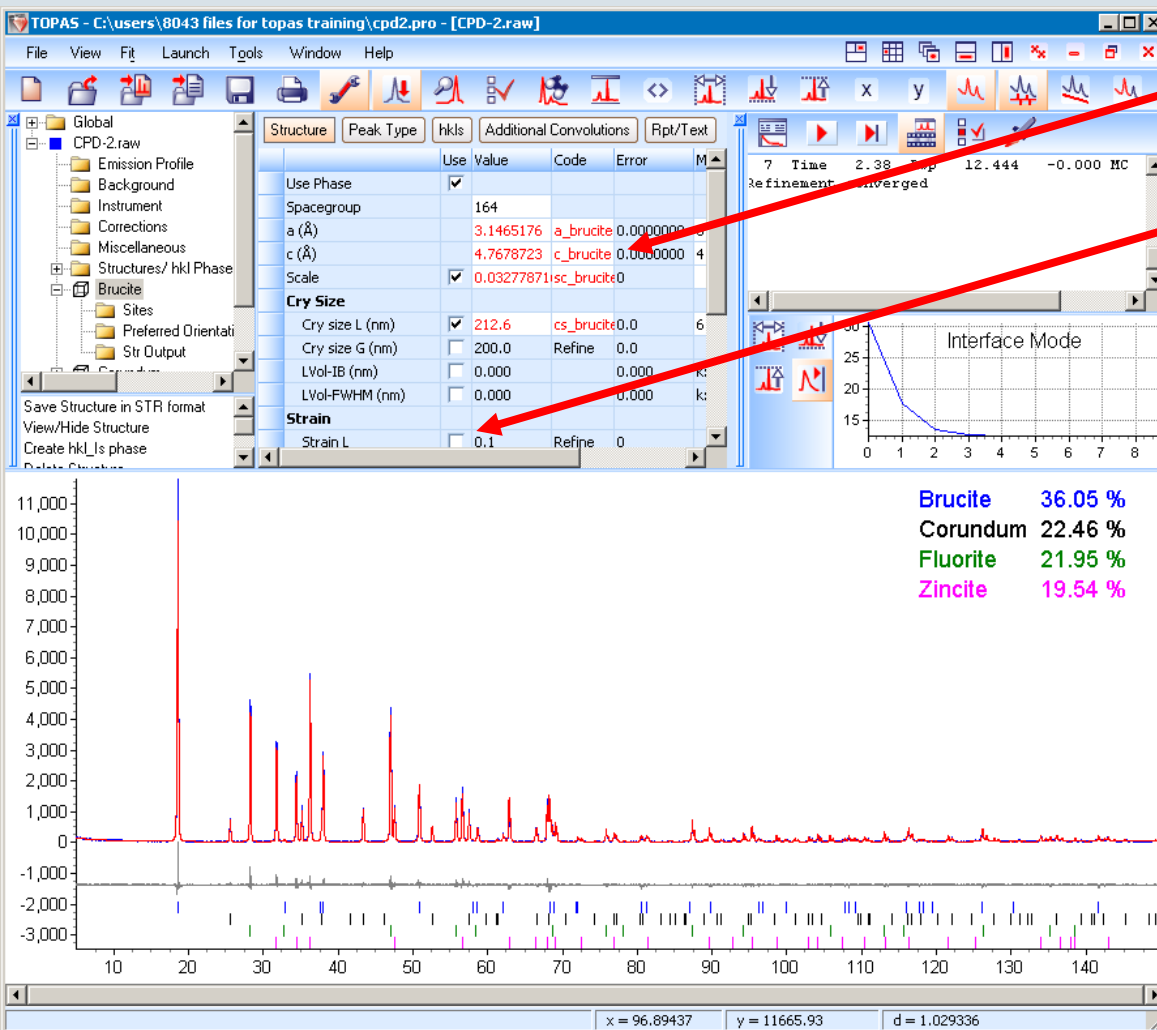
You may try to further improve the fit by introducing strain for Brucite
Residuals and Goodness of Fit



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

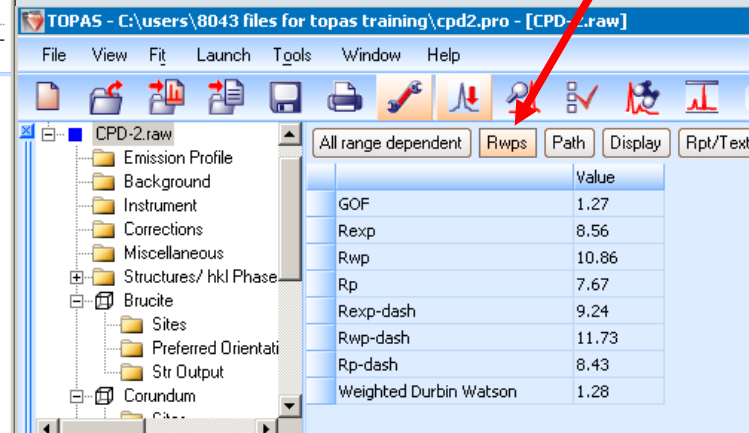
Quantitative Rietveld Analysis

Round-Robin example



Refined Lattice parameters and crystallite size for each phase

You may try to further improve the fit by introducing strain for Brucite
Residuals and Goodness of Fit

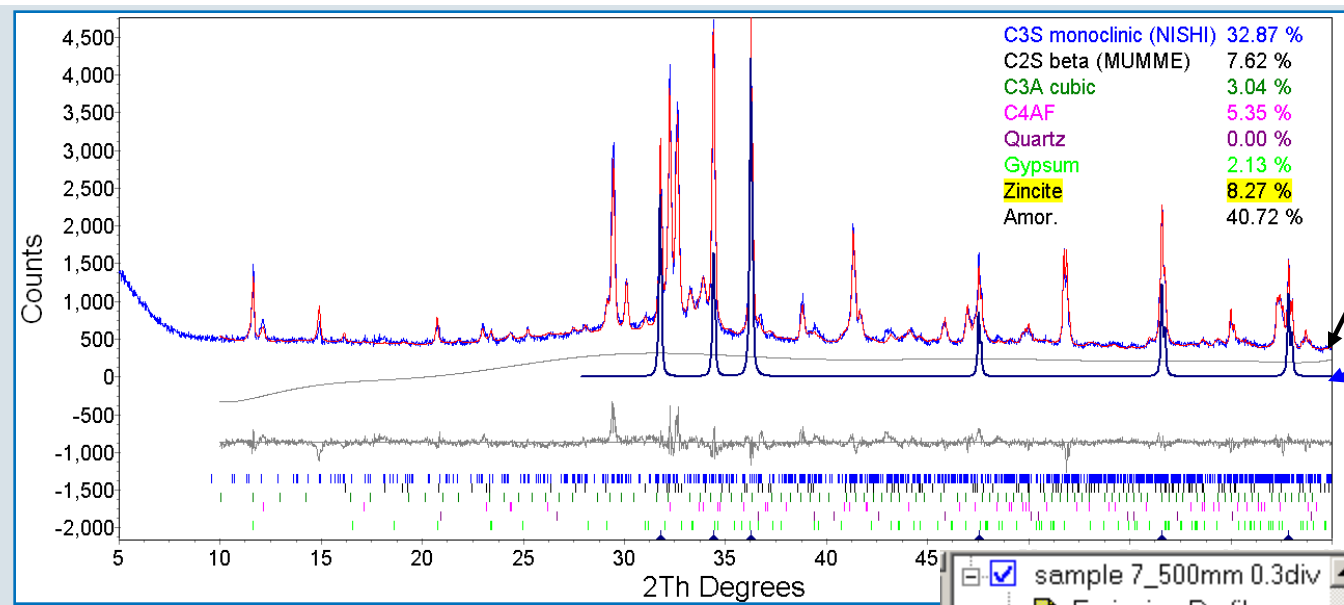


Save your results in a TOPAS project file (.pro)

Industrial application: Cement and flyash

Determination of amorphous component

Spiking the sample with an internal standard



Background was fitted with high-order polynomial function

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

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

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

sample 7_500mm 0.3div

- Emission Profile
- Background
- Instrument
- Corrections
- Miscellaneous
- Structures/ hkl Phases
 - C3S monoclinic (NISHI)
 - C2S beta (MUMME)
 - C3A cubic
 - C4AF
 - Quartz
 - Gypsum
 - Periclase
 - Zincite
- Sites
- Preferred Orientation

Structure	Peak Type	hkl	Additional Convolution
Use Phase	<input checked="" type="checkbox"/>		
Spacegroup		186	
a (Å)		3.2495907	a_zincite
c (Å)		5.2067137	c_zincite
Scale	<input checked="" type="checkbox"/>	0.00369548	sc_zincite
Cry Size			
Cry Size L(nm)	<input checked="" type="checkbox"/>	153.5	cs_zincite
Cry Size G(nm)	<input type="checkbox"/>	200.0	Refine
LVol-HB(nm)	<input type="checkbox"/>	0.000	
LVol-FWHM(nm)	<input type="checkbox"/>	0.000	
Strain			
Strain L	<input type="checkbox"/>	0.1	Refine
Strain G	<input type="checkbox"/>	0.1	Refine
a0	<input type="checkbox"/>	0.00000	
Wt% Rietveld		13.951	
Wt% of Spiked	<input checked="" type="checkbox"/>	8.270	

Industrial application: Cement + flyash

Determination of amorphous component

Spiking the sample with an internal standard



sample 7_500mm 0.3div

- Emission Profile
- Background
- Instrument
- Corrections
- Miscellaneous
- Structures/ hkl Phases
 - Quantitative**
 - SG-Lattice Paramete
 - Brindley Corrector
 - Display
- C3S monoclinic (NISH)
- C2S beta (MUMME)
- C3A cubic
- C4AF
- Quartz
- Gypsum
- Periclase

Paste INP to Node/Selections

Phase Name	Wt% Rietve	Use	Wt% of Spik	Wt% in Spiked	Wt% in Original	Cell Mass	Cell Vol (Å ³)
C3S monoclinic	55.459	<input type="checkbox"/>	0.000	32.875	35.839	8219.355	4307.46073
C2S beta (MUMME)	12.849	<input type="checkbox"/>	0.000	7.617	8.304	688.953	347.61380
C3A cubic	5.123	<input type="checkbox"/>	0.000	3.037	3.310	6484.622	3542.47539
C4AF	9.019	<input type="checkbox"/>	0.000	5.346	5.828	971.922	429.80950
Quartz	0.000	<input type="checkbox"/>	0.000	0.000	0.000	180.252	112.81456
Gypsum	3.599	<input type="checkbox"/>	0.000	2.134	2.326	672.560	495.62576
Periclase	0.292	<input type="checkbox"/>	0.000	0.000	0.000	161.217	74.79168
Zincite	13.951	<input checked="" type="checkbox"/>	8.270	8.270	0.000	162.778	47.61586

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

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

Rietveld Refinement Corrections



	Use	Value	Code
Peak shift			
Zero error	<input type="checkbox"/>	0	Refine
Sample displacement (mm)	<input checked="" type="checkbox"/>	-0.06369911	Refine
Intensity Corrections			
LP factor	<input checked="" type="checkbox"/>	26.6	Fix
Surface Rghnss Pitschke e	<input type="checkbox"/>		
Surface Rghnss Suortti	<input type="checkbox"/>		
Sample Convolutions			
Absorption (1/cm)	<input checked="" type="checkbox"/>	35.03862	Refine
Sample Thickness (mm)	<input type="checkbox"/>	10	Refine
Scale Intensity	<input type="checkbox"/>		
Sample Tilt (mm)	<input type="checkbox"/>	0	Refine

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

Using the correct structure file

Phase identification



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

Using the correct structure file

Structure databases

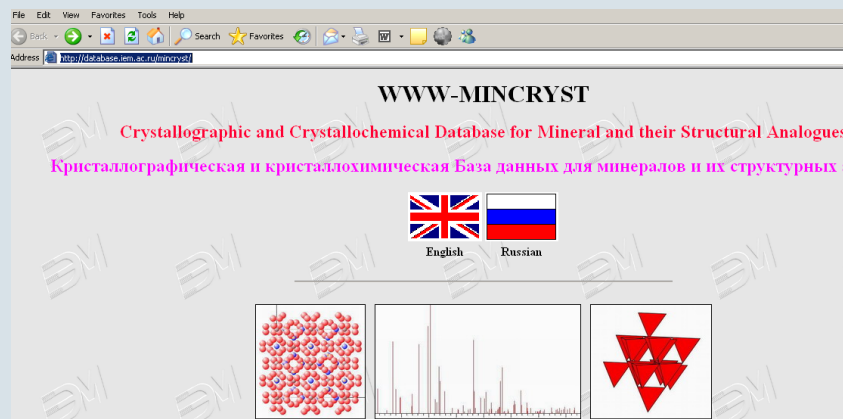
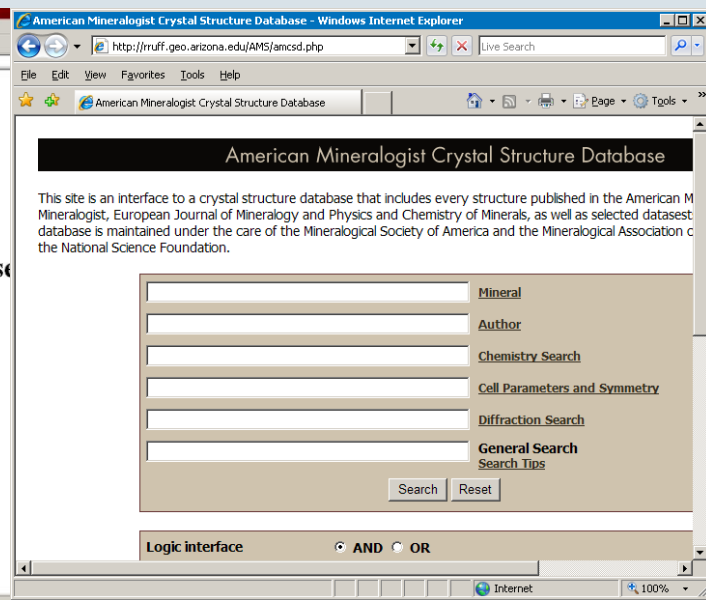
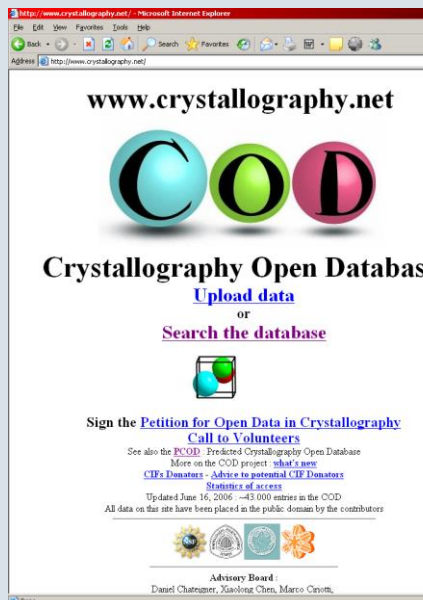


- Inorganic crystal structure database (ICSD) available at www.nist.gov or at <http://icsdweb.fiz-karlsruhe.de/index.php>
- Bruker-AXS structure database (a few hundred minerals)

Free databases:

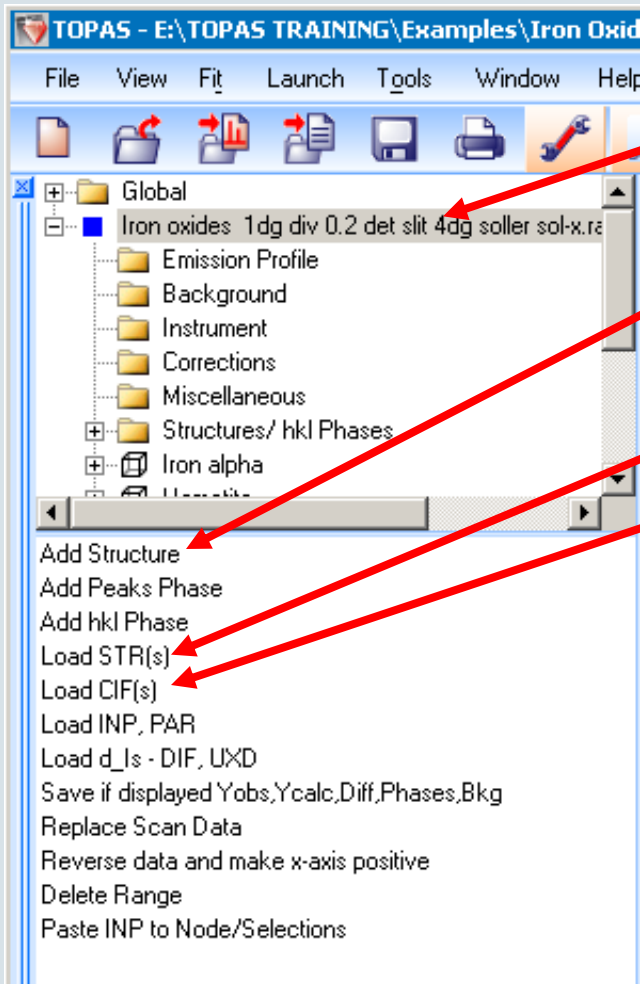
- www.crystallography.net
- American Mineralogist Crystal structure database
<http://rruff.geo.arizona.edu/AMS/amcsd.php>
- Min-Chryst
<http://database.iem.ac.ru/mincryst/>
- Search for the structure in Google

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



Structure files

Entering the structure into TOPAS



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

Structure files

Example: Chlorite

Unit cell parameters



TOPAS - C:\users\old data\6008 RC\RC3-3_co radiation_3.pro - [RC 3-3 co rad 35KV 40ma 0.7div 0.2det sol-x.raw_1]

File View Fit Launch Tools Window Help

Structure Peak Type hkl Additional Convolutions Rpt/Text

	Use	Value	Code	Error	Min	Max
Use Phase	<input checked="" type="checkbox"/>					
Spacegroup		12				
a (Å)		5.3442000	a_chlorite	0.0000000	5.1900	5.5100
b (Å)		9.2660321	b_chlorite	0.0000000	8.9890	9.5450
c (Å)		14.2592097	c_chlorite	0.0000000	13.8420	14.6980
beta (°)		97.04304	be_chlorite	0		
Scale	<input checked="" type="checkbox"/>	2.08979475	sc_chlorite	0		
Cry Size						
Cry size L (nm)	<input checked="" type="checkbox"/>	360.2	cs_chlorite	0.0	32	
Cry size G (nm)	<input type="checkbox"/>	200.0	Refine	0.0		
LVol-IB (nm)	<input type="checkbox"/>	0.000		0.000	k:	1
LVol-FWHM (nm)	<input type="checkbox"/>	0.000		0.000	k:	0.89
Strain						
Strain L	<input type="checkbox"/>	0.1	Refine	0		
Strain G	<input type="checkbox"/>	0.1	Refine	0		
e0	<input type="checkbox"/>	0.00000		0.00000		
Wt% Rietveld		4.883		0.000		
Wt% of Spiked	<input type="checkbox"/>	0.000				
Wt% in Spiked sample		2.361		0.000		
Wt% in Original sample		2.574		0.000		
Cell Mass		1191.935		0.000		
Cell Volume (Å ³)		700.78128		0.00000		
Cry LAC (1/cm)		140.716		0.000		
Cry Density (g/cm ³)		2.824		0.000		
R Bragg		4.985				

Save Structure in STR format
View/Hide Structure
Create hkl_Is phase
Delete Structure
Paste INP to Node/Selections

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

Structure files

Example: Chlorite

Atomic sites



TOPAS - C:\users\old data\6008 RC\RC3-3_co radiation_3.pro - [RC 3-3 co rad 35KV 40ma 0.7div 0.2det sol-]

File View Fit Launch Tools Window Help

Global
 RC 3-3 co rad 35KV 40ma 0.7c
 Emission Profile
 Background
 Instrument
 Corrections
 Miscellaneous
 Structures/ hkl Phases
 Zincite
 Quartz
 Hematite
 Magnetite
 Muscovite 2M1
 Chlorite 11b
 Sites
 Preferred Orientation
 Str Output

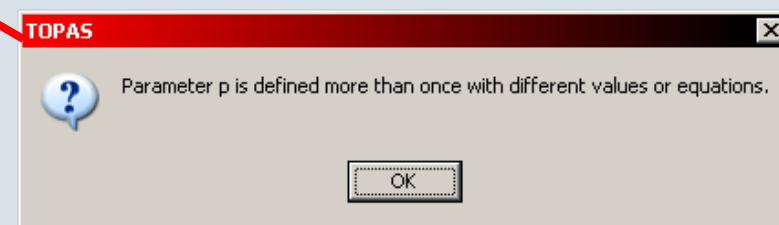
Site	Np	x	y	z	Atom	Occ.	Beq.
1	s1	2	0.00000	0.00000	0.00000	MG+2	0.3358
2					FE+2	0.6642	1
3	s2	4	0.00000	0.66780	0.00000	MG+2	0.9703
4					FE+2	0.0297	1
5	s3	4	0.31500	0.00000	0.92570	O-2	1
6	s4	8	0.18900	0.16670	0.07740	O-2	1
7	s5	8	0.22480	0.16690	0.19370	SI+4	0.66
8					AL+3	0.34	1
9	s6	4	0.80300	0.00000	0.76430	O-2	1
10	s7	8	0.51100	0.22800	0.23630	O-2	1
11	s8	4	0.82800	0.00000	0.57110	O-2	1
12	s9	8	0.13100	0.34630	0.42850	O-2	1
13	s10	4	0.00000	0.83360	0.50000	MG+2	0.7016

Values Codes Errors Min Max Rpt/Text

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

Add Site(s) before selected site(s)
 Add Site at bottom
 Add Atom at selected site(s)
 Paste INP to Node/Selections

- For quantitative analysis of phase mixtures the atomic sites (x,y,z) of the phases are never refined.
- In solution phases such as Chlorite the occupation factors for the Mg/Fe substitution may be refined.
- The x, y or z positions in blue color designate special positions for this unit cell.
- The atom or ion must be part of the drop down list in the atom column (with imported cif files this could lead to an error message)
- Parameter names like „p“ or „s“ have to be unique within a TOPAS project. If not, it will lead to this error message → rename parameters

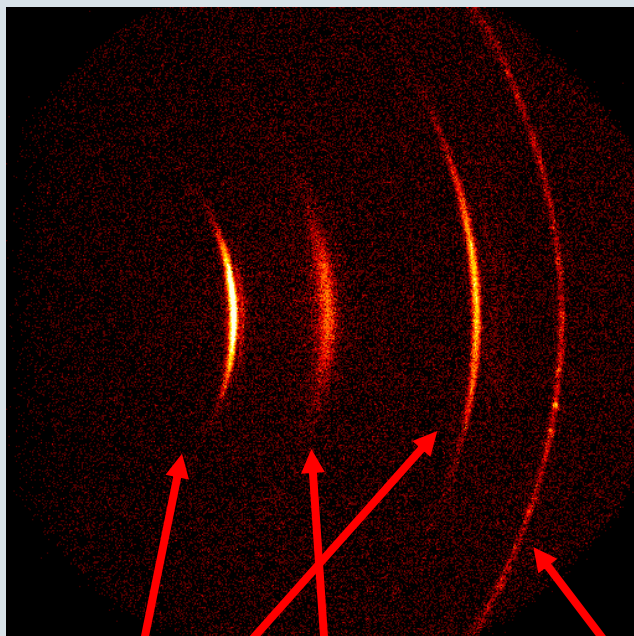


Corrections for non-ideal powder samples

Texture or preferred orientation



Slate Tile, as an example for strong texture

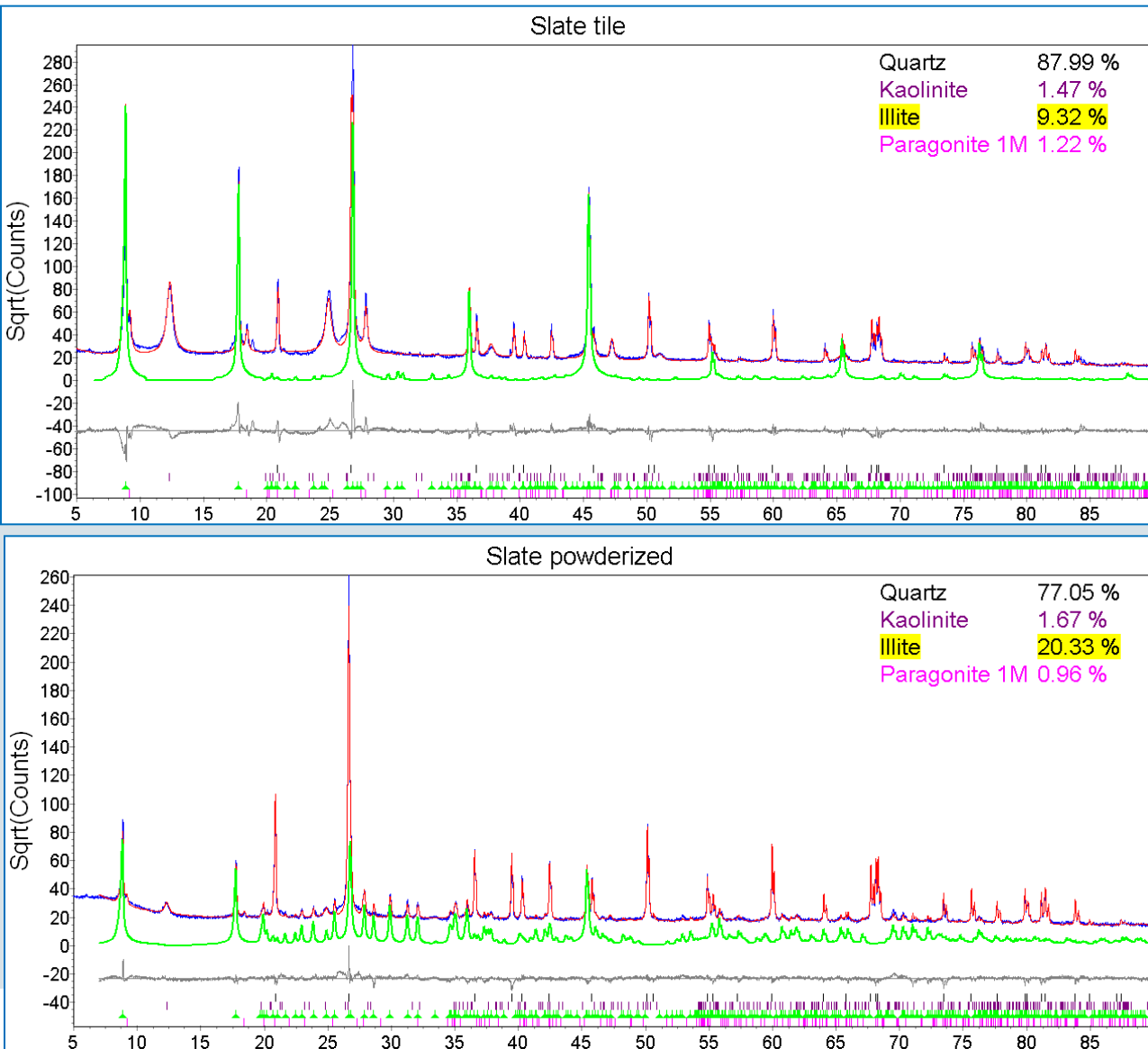


- Preferred orientation of needle or plate-like crystallites can often be corrected with the March-Dollase function
- For minerals with multiple cleavage directions a spherical harmonics correction can be applied.
- Acceptable limits of preferred orientation corrections should ideally be tested with a standard mixture

Illite, Kaolinite, Quartz

Correction for non-ideal powder samples

Texture or preferred orientation

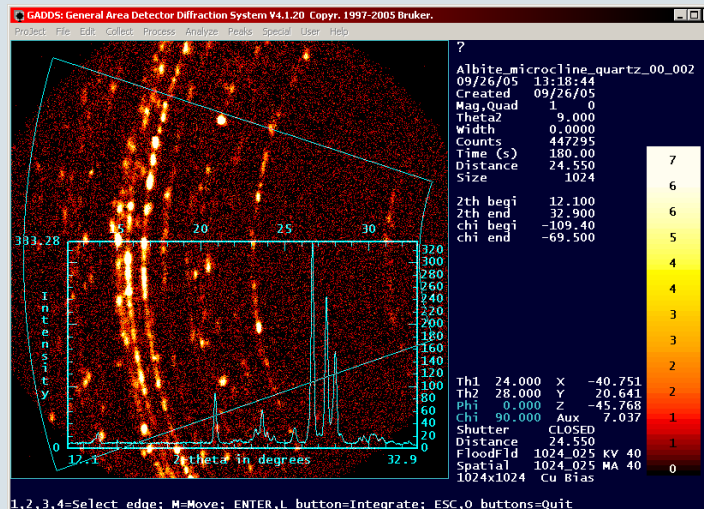
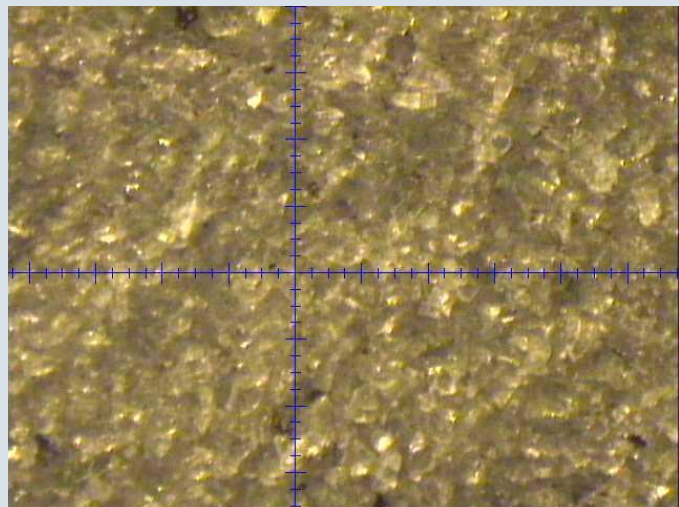


- ← Unground sample
- Comparison of slate tile and ground slate (Calculated Illite patterns are highlighted)
- The (001) directions of Illite, Kaolinite and Paragonite were corrected with the March-Dollase model for both sample
- Preferred Orientation is too severe to be corrected with March Dollase model
- Ground sample
- Samples measured with Vantec-1 detector
- 0.1sec/step

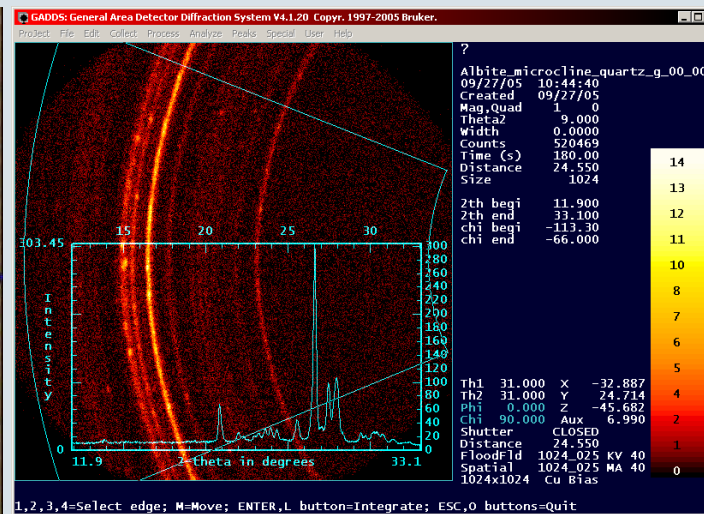
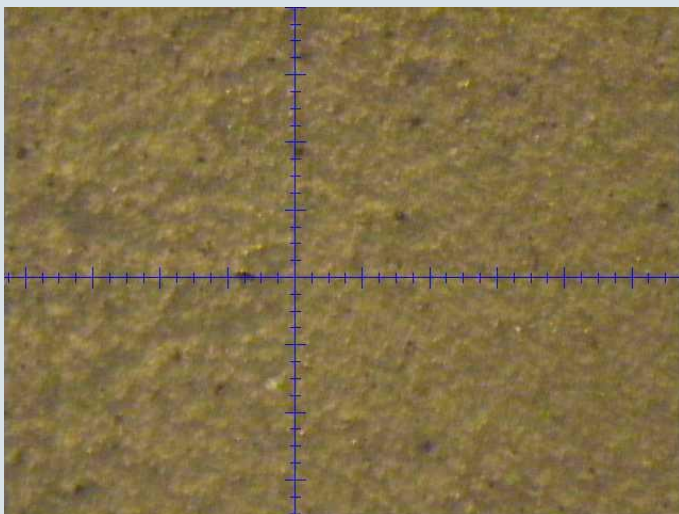


Corrections for non-ideal powder samples

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



- Coarse powder of Albite, Microcline and Quartz (some grains are larger than 50 μ m)

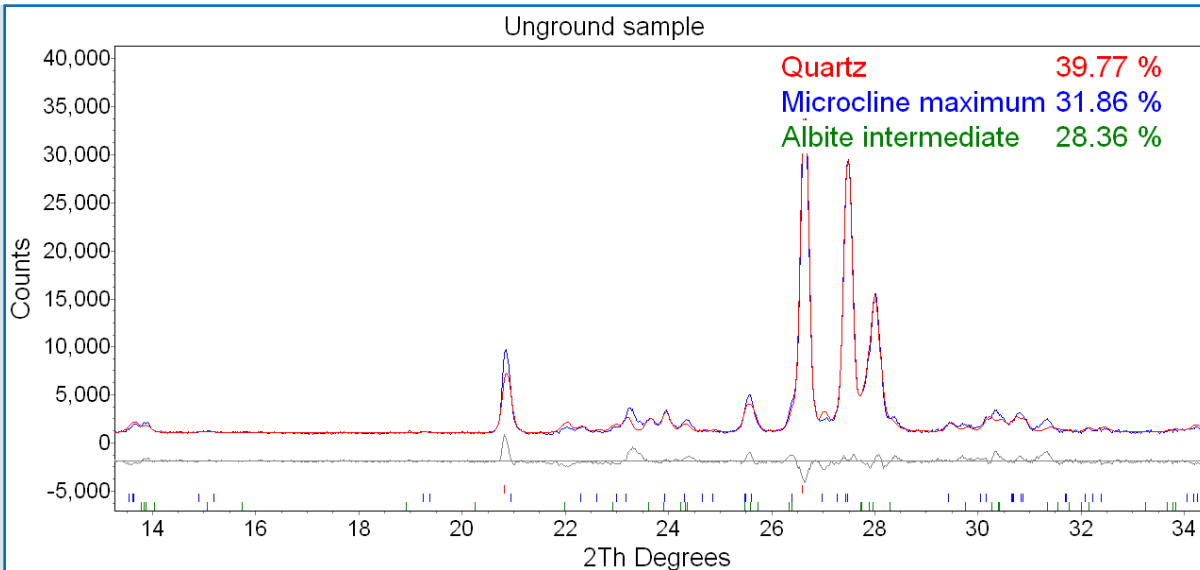


- Identical Powder, wet ground in Micronising Mill for 30 minutes

Gadds data at 25cm sample-detector distance

Corrections for non-ideal powder samples

Large grains, spottiness effect, Micro absorption

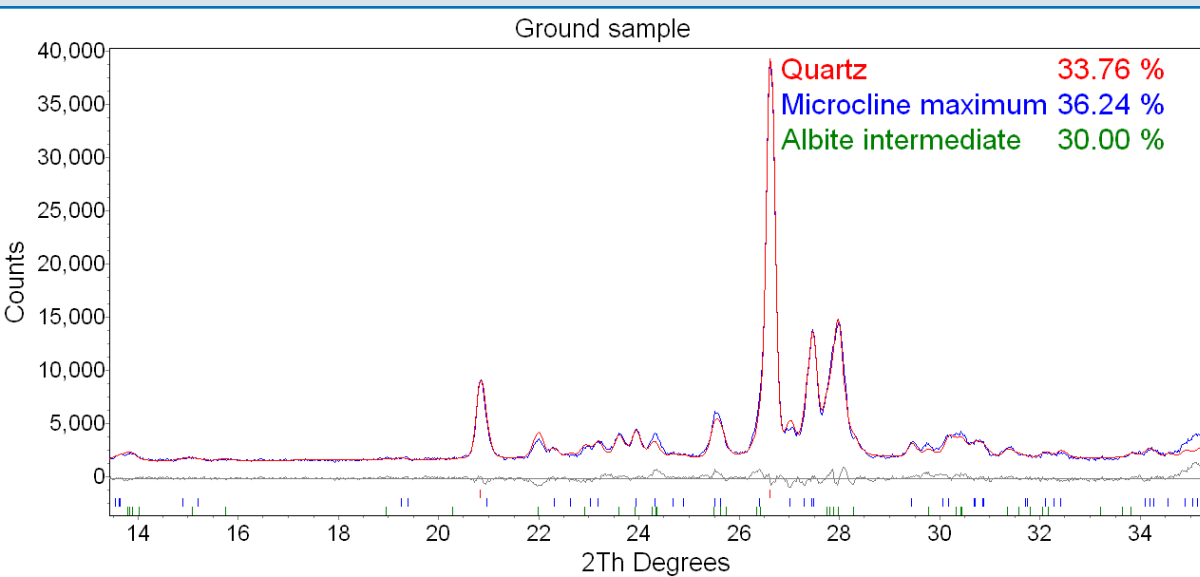


← **Unground sample**

Weighted compositions:

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

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



← **Ground sample**

Gadds data at 25cm sample-detector distance

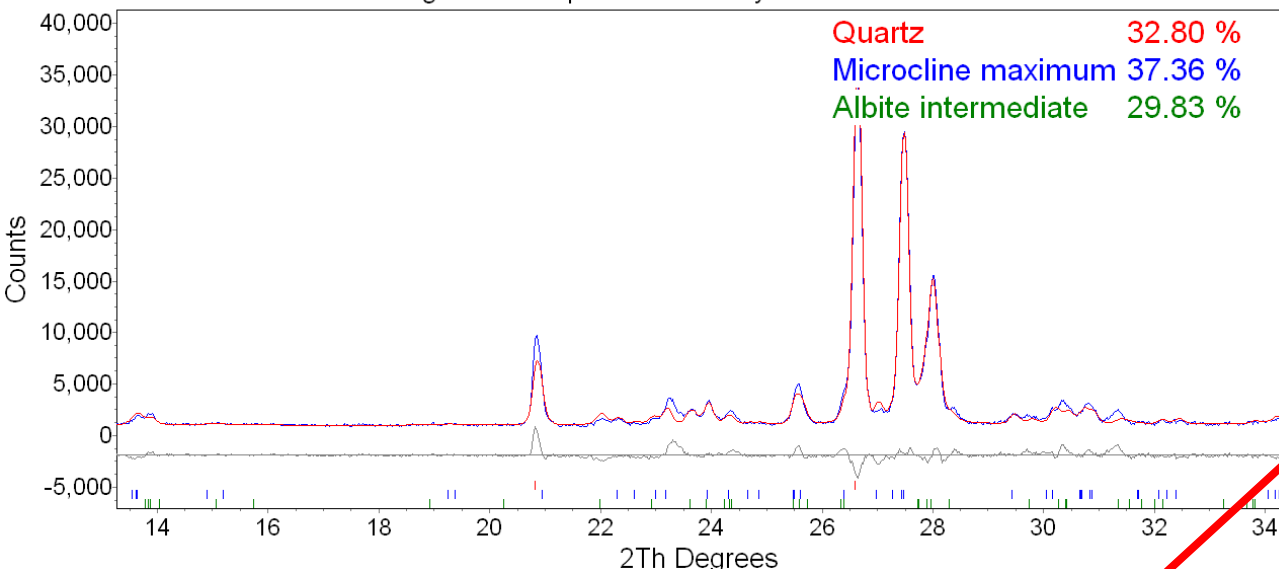
Corrections for non-ideal powder samples

Micro absorption

Brindley correction



Unground sample with Brindley correction



Weighted compositions:

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

- Larger Quartz grains of 50 μ m were assumed.

Brindley Correction (Spherical Particles)				
Phase Name	Use	Radius(cm)	Pk Den.	Mass Ab.Coeff(cm ² /g)
Quartz	<input checked="" type="checkbox"/>	0.05	0.4	36.01106
Microcline maximum	<input checked="" type="checkbox"/>	0.005	0.4	49.87407
Albite intermediate	<input checked="" type="checkbox"/>	0.005	0.4	33.9074

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

Corrections for non-ideal powder samples



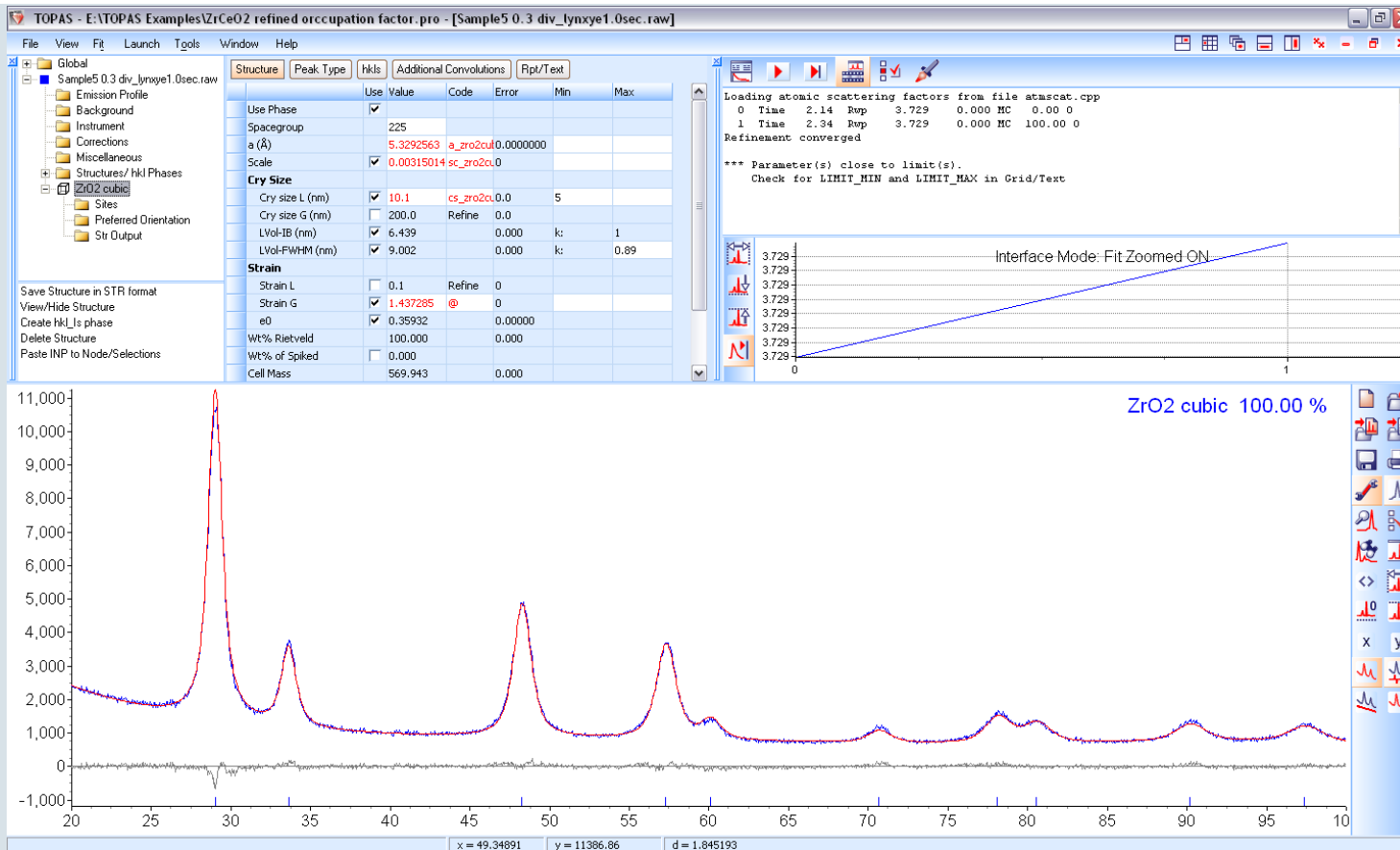
- Preferred orientation effects
 - March Dollase
 - Spherical harmonics
- Micro absorption
 - Brindley correction for spherical particles
- Surface roughness
 - Correction according to Pitschke or Suortti

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

- Flat samples with powder grain sizes below approx. $5\mu\text{m}$.
- If possible, minimize preferred orientation by using back or side loaded sample holders

Rietveld refinements:

Refining crystallite size, strain, and occupation factors on Zr(Ce)O₂



- Average crystallite refined using Scherrer equation
- Strain refined to fit additional broadening at higher angles
- Determination of crystallite size distribution with Double Voigt fitting possible in Launch mode

Rietveld refinements:

Refining crystallite size, strain, and occupation factors on Zr(Ce)O₂



TOPAS - E:\TOPAS Examples\ZrCeO2 refined orccupation factor.pro - [Sample5 0.3 div_lynxye1.0sec.raw]

File View Fit Launch Tools Window Help

Global
Sample5 0.3 div_lynxye1.0sec.raw
Emission Profile
Background
Instrument
Corrections
Miscellaneous
Structures/ hkl Phases
ZrO2 cubic
Sites
Preferred Orientation
Str Output

Add Site(s) before selected site(s)
Add Site at bottom
Add Atom at selected site(s)
Paste INP to Node/Selections

	Values	Codes	Errors	Min	Max	Rpt/Text		
Site	Np	x	y	z	Atom	Occ.	Beq.	
1	s1	4	0.00000	0.00000	0.00000	Zr+4	0.6546	1.3
2					Ce+4	0.3454	1	
3	s2	8	0.25000	0.25000	0.25000	O-2	1.06	7

	Values	Codes	Errors	Min	Max			
Site	Np	x	y	z	Atom	Occ.	Beq.	
1	s1	4	0.00000	0.00000	0.00000	Zr+4	0.6546	1.3
2					Ce+4	0.3454	1	
3	s2	8	0.25000	0.25000	0.25000	O-2	1.06	7

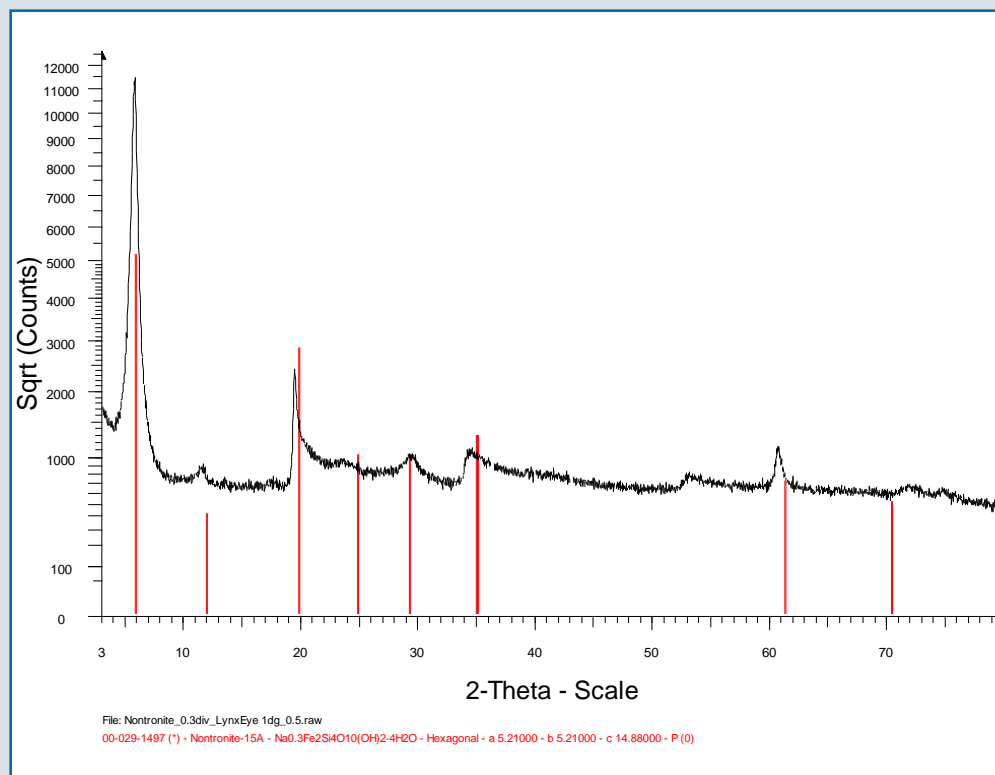
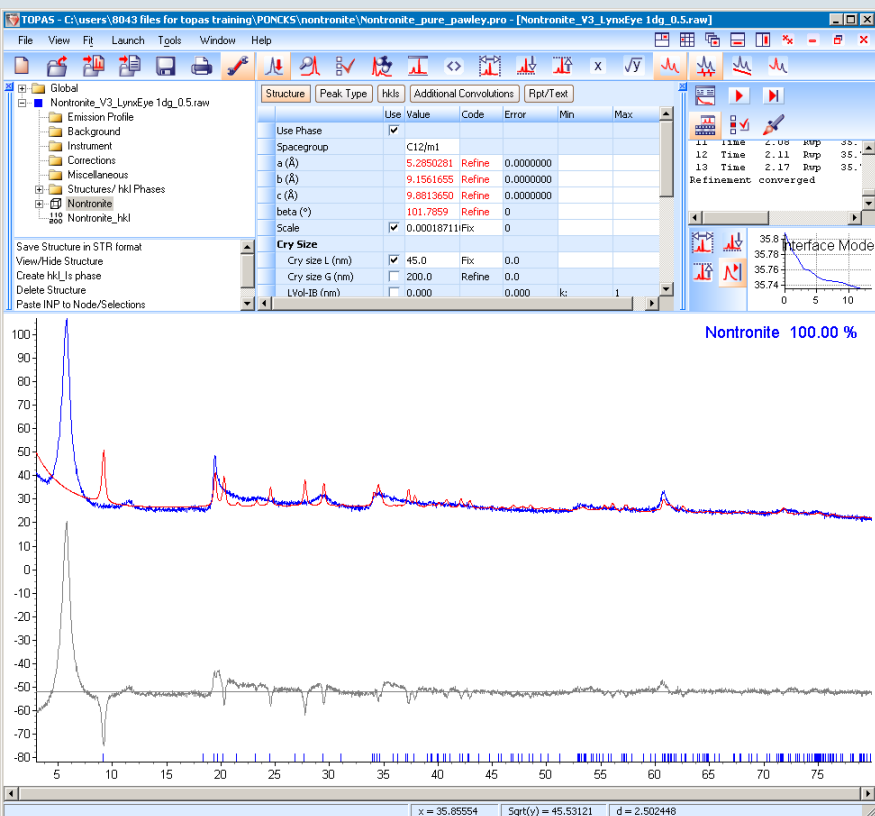
- Substitution of Zr with Ce
- Refinement of Occupation factor to determine concentration of Cerium

Treatment of disordered or missing phases

Nontronite

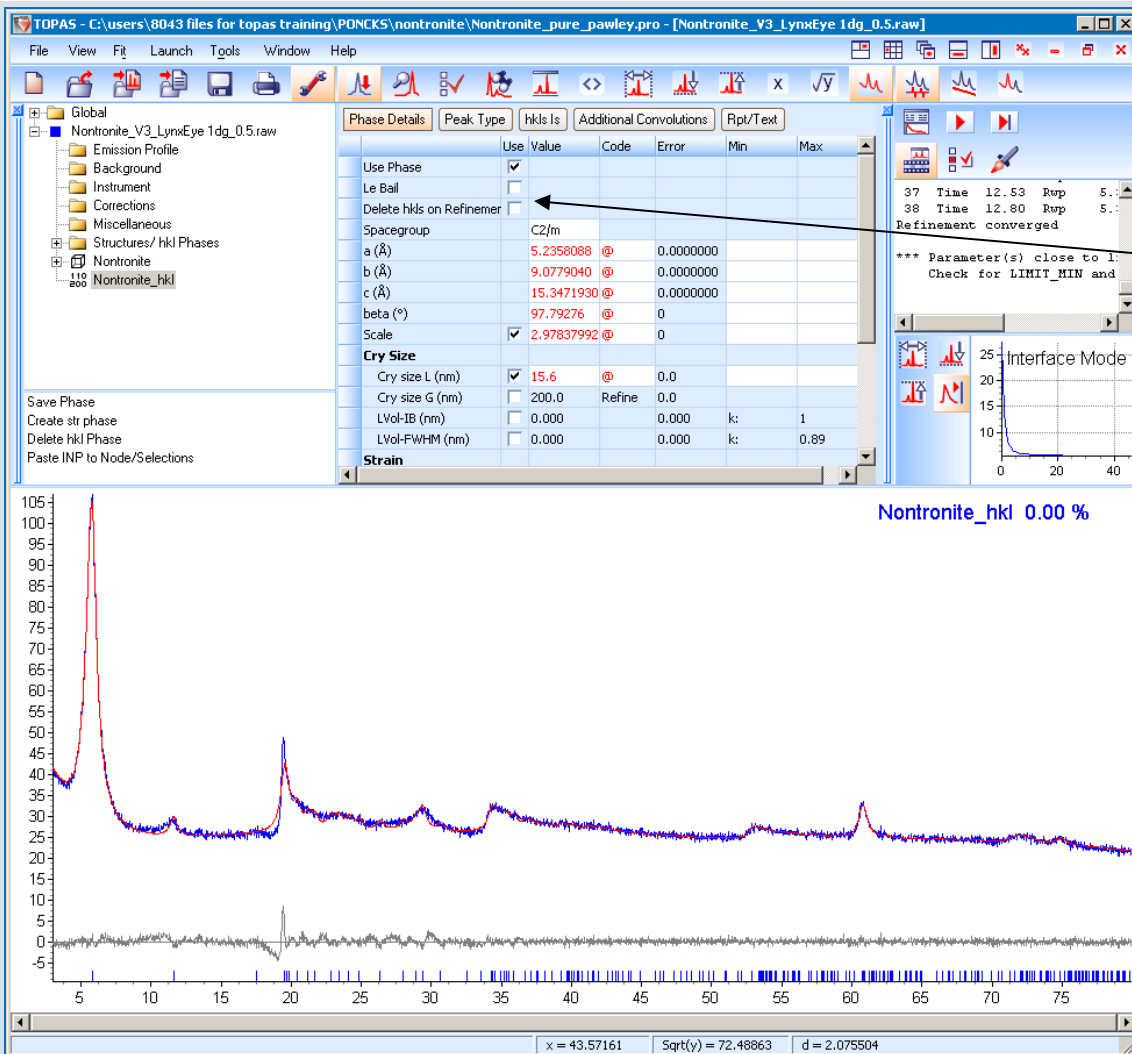
- Nontronite has only one published structure file, which does not match the observed pattern

- The published ICDD pattern matches better and has unit cell parameters

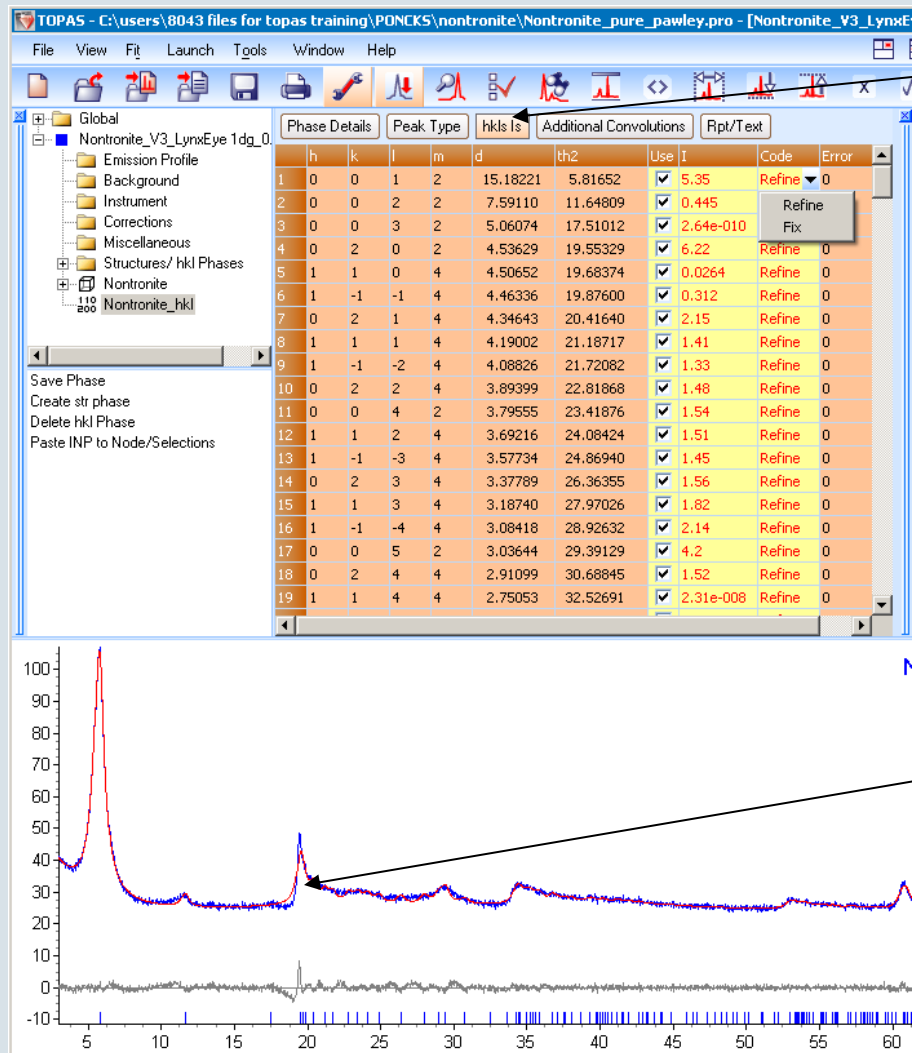


Pawley Fit of Nontronite pattern

- Create a hkl_IS phase to fit the Nontronite and refine intensities of all peaks individually
- Uncheck „delete hkl's on refinement“
- Uncheck Le Bail



Pawley Fit of Nontronite pattern



- After refinement go to the hkl_IS tab and set all Intensities to Fixed
- Select all peaks by clicking in the upper right corner of the grid and fix the intensities in the code column
- To be able to scale the whole Nontronite pattern and use it for quantification, the sample has to be calibrated with a known standard such as corundum

Note a misfit in this region may lead to correlations with other phases, if overlapping peaks are present.

Nontronite-Corundum mixture for Calibration

- Refine the Nontronite-Corundum mixture

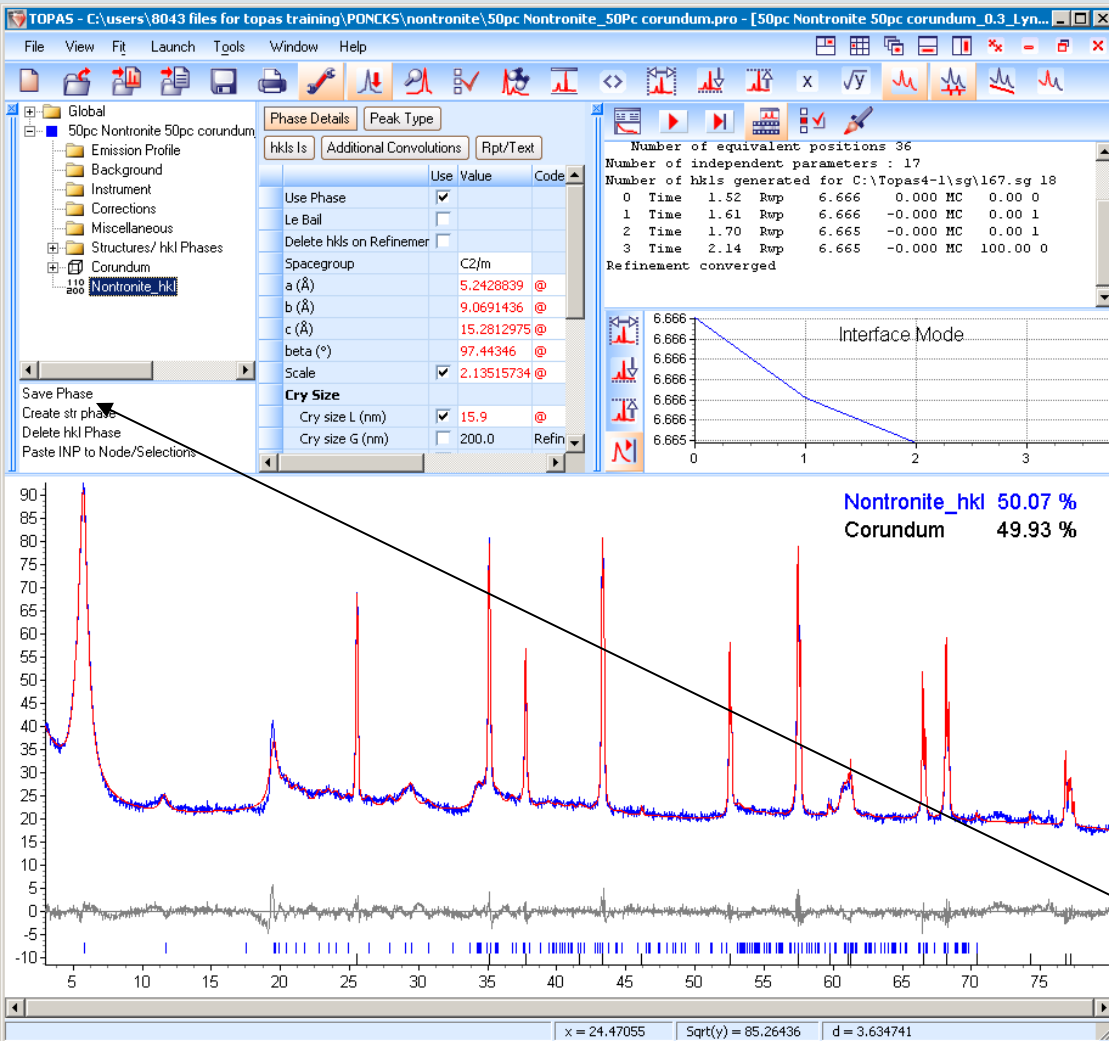
The mass M was modified in order to get the correct quantitative result
 MVW (0.14, 720.4781635, 0)

(This has to be done with a text editor in the project file)

```

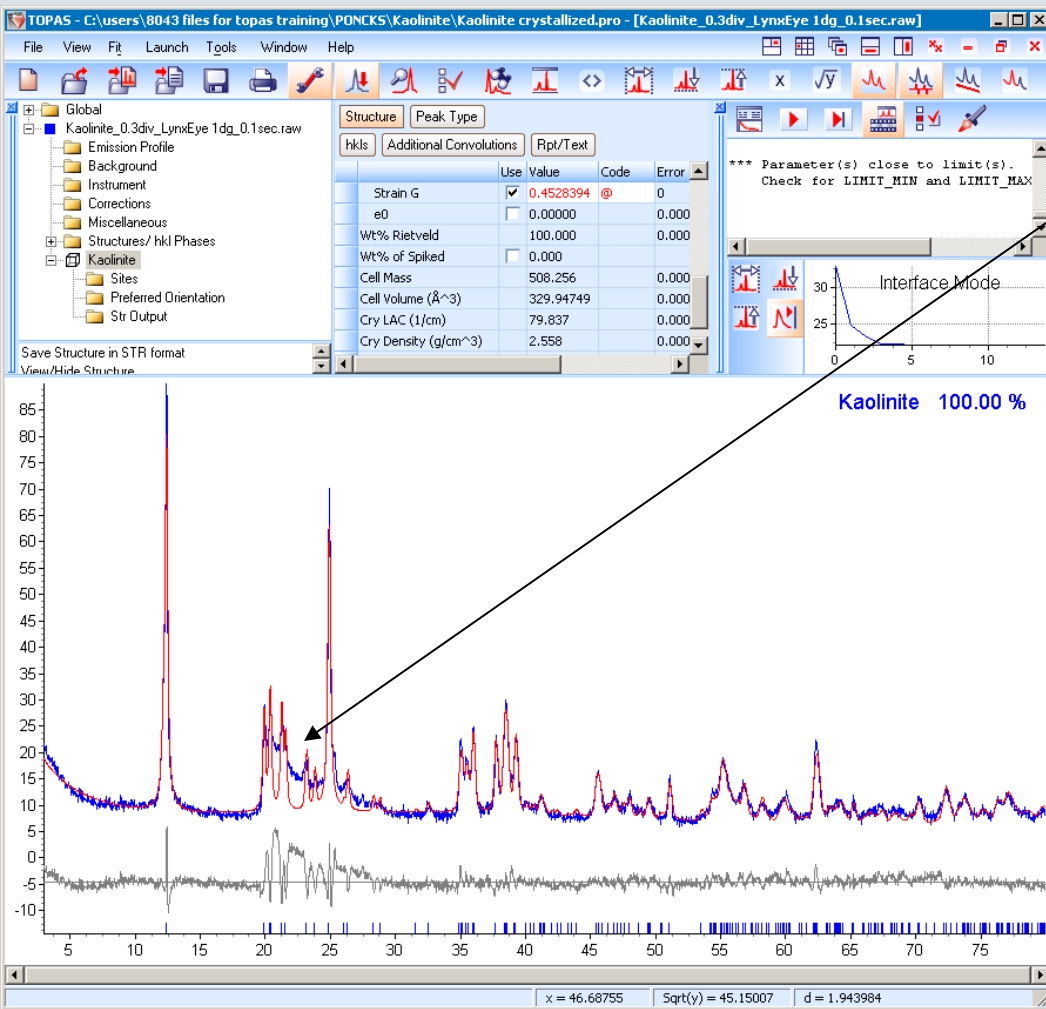
phase_name "Nontronite_hkl"
space_group C2/m
scale @ 2.135136883
MVW( 0.14,~ 720.4781635, 50.60176163)
be @ 97.44386175
a ~@ 5.242848071
b ~@ 9.069166117
c ~@ 15.28135335
  
```

- Save the Nontronite_hkl file as an inp file to use with other mixtures

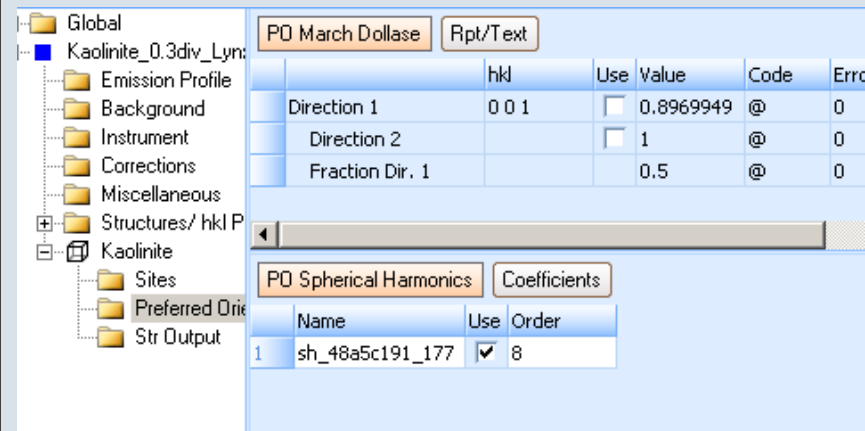


Rietveld refinement of Kaolinite

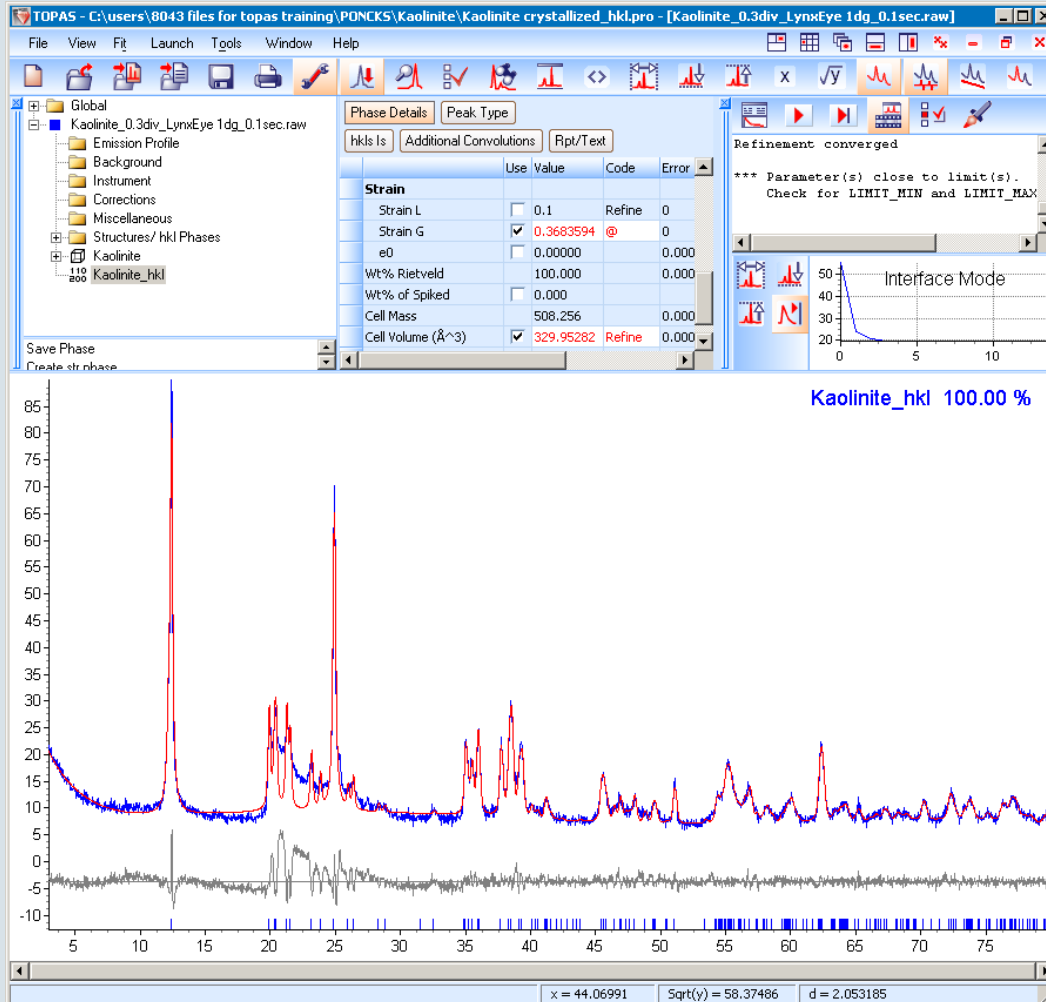
Treatment of disorder



- The published structure of Kaolinite does not fit for the disorder even for a relatively well crystallized Kaolinite sample and with introduction of strain
- Spherical harmonics correction for preferred orientation was applied but only improves some peak intensities and adds more parameters that may correlate with other phases

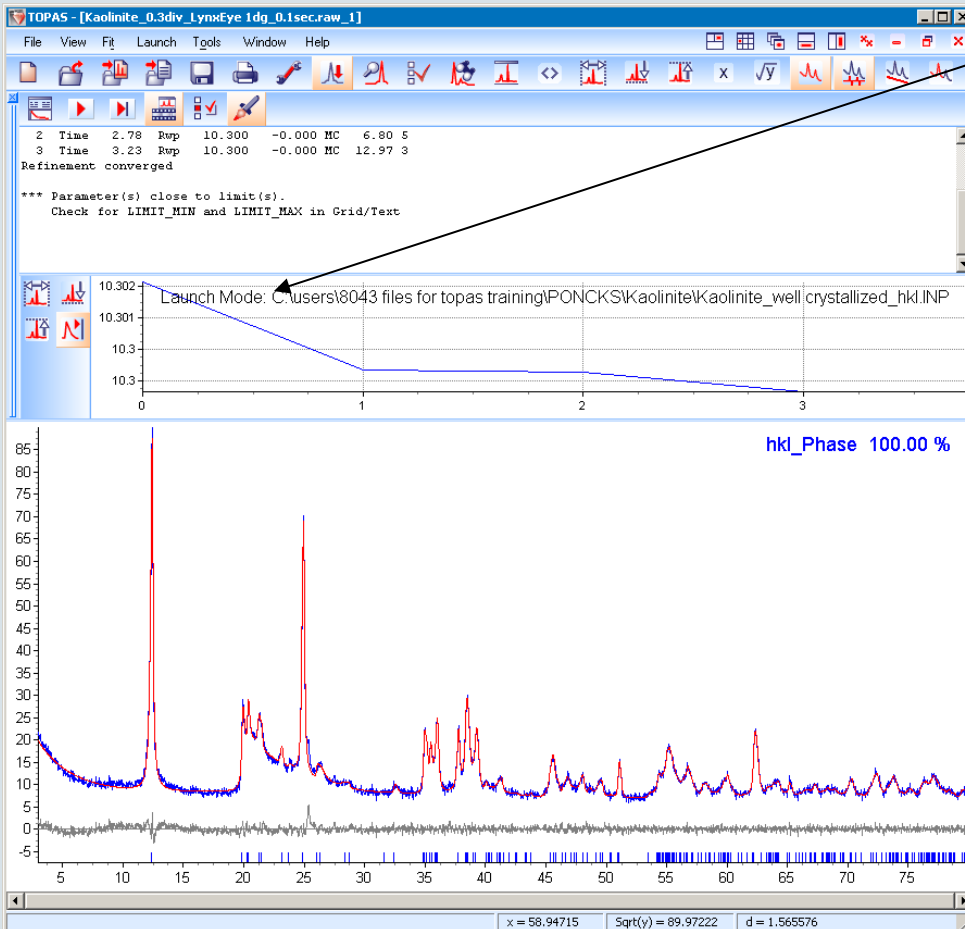


Pawley Fit of Kaolinite



- Even a Pawley fit can not fit the disorder
- → go to Launch mode and use anisotropic peak broadening

Pawley Fit of Kaolinite with anisotropic peak broadening



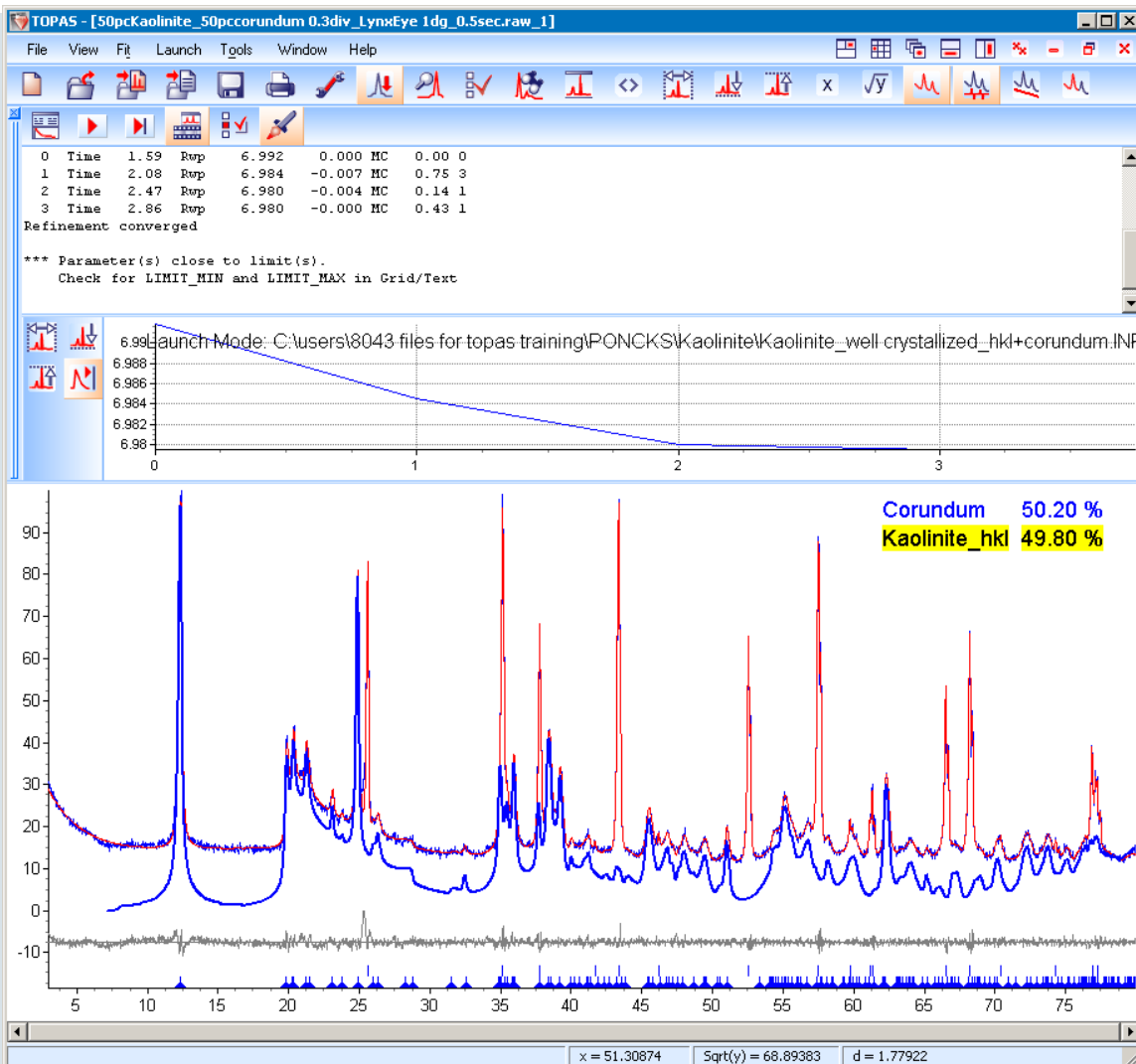
- Works only in Launch mode
→ File → Export to INP file → edit the file with a text editor
- Syntax: add the following line to the hkl phase in the input file

```
spherical_harmonics_hkl sh  
sh_order 8  
exp_conv_const = (sh-1) / Sin(Th);
```
- Other broadening functions are available, see TOPAS Technical Reference
- Close the project
- Launch → set Input file → Run refinement
- Fix all intensities and anisotropic parameters of the hkl phase in the input file
- This hkl file can be used for quantification in phase mixtures after determination of the MVW value with a standard mixture

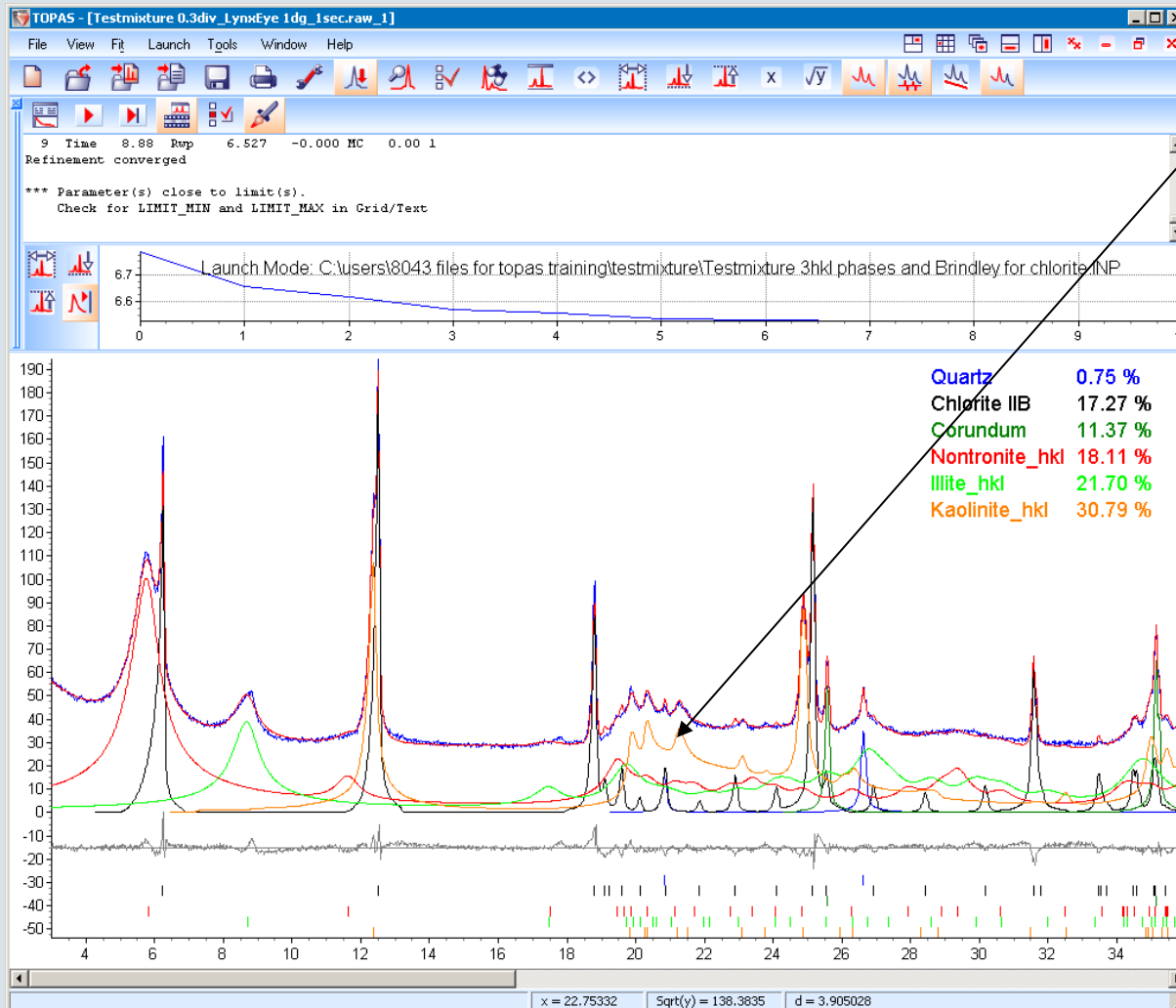
Calibration with a standard mixture of 50% Kaolinite and 50% corundum

- The 50% corundum 50% Kaolinite standard mixture was run for calibration
- The M value in the input file was empirically determined so that it results in the known concentration

phase_name "Kaolinite_hkl"
 MVW(0.930, 331.202155`,
 49.802`)



Testmixture quantified using 3 structures and 3 hkl phases



- Kaolinite disorder well described (within 2% of weighted mixture)
- Still some correlation between Illite and Kaolinite but all phases within 3% of the weighted phase mixture

What about preferred orientation effects?

```
phase_name "Illite_hkl"  
CS_L(@, 13.81035`)  
Strain_G(@, 1.63671`)  
r_bragg 2.10323796  
MVW( 0.232, 935.900508`, 21.085`)  
space_group "C12/c1"  
a @ 5.23726`  
b @ 8.80488`  
c @ 20.35754`  
be @ 94.47024`  
Preferred_Orientation(@, 0.90023` min =0.8; max =1,,, 0 0 1)
```

Using real samples we often have to take into account preferred orientation.

Most clays have preferred orientation effects that may depend on sample preparation

In TOPAS hkl_Phases can be combined with the Preferred_Orientation macro.

This is working in the Launch mode, as well as in the GUI. But **editing is not supported** in the GUI
(Modifications have to be done using a text editor)

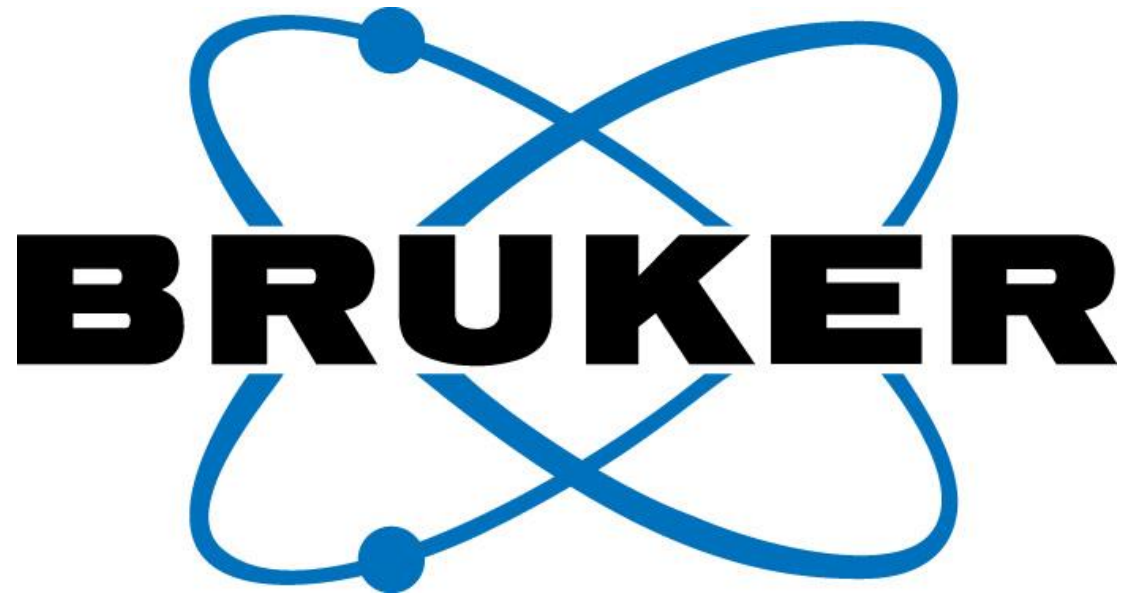
Practical TOPAS demonstrations and questions



As time allows:

- Rigid body examples
- Charge flipping example

- Quantitative Rietveld Analysis



www.bruker-axs.com