Introduction to TOPAS
Part 2
Structure solution methods and Quantitative Rietveld analysis

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Bruker-Axs
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 $F^2$(obs)

- Structure Refinement using $y_i$(obs) or $F^2$(obs)

$F^2$(obs): Observed structure factors
$y_i$(obs): Observed step intensity data
Structure Refinement using $F^2$(obs): Two-Stage Method (Will, 1979)
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 $y_i(\text{obs})$

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

**TOPAS Approach**
Coelho (2000)

Suited for
- Simulated annealing
- Charge Flipping

Suited for
- 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 $\chi^2$).

This procedure is typically applied to single-crystal-type structure factors, but has been extended to step intensity data $\Rightarrow$ TOPAS (Coelho, 2000).
Structure Determination
Simulated Annealing example: PBSO$_4$

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

```
ites 10000
Auto_T(10)
RAW(Pbso4)
CuKa5(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_FC
  view_structure
  append_fractional
  append_bond_lengths
```
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
Penalty Functions can only be used in Launch Mode

Introduction of suitable penalty functions reduces the number of local minimums in $\chi^2$ 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 calculated 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 Lenard-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

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
β=93.017°

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 \( r_{CO} \) 1.22844° min 1.1 max = 1.3;
Prm \( r_{CN} \) 1.38049° min 1.2 max = 1.5;
Prm \( r_{CC} \) 1.55547° min 1.3 max = 1.65;
prm \( r_{NH} \) 0.94003° min 0.8 max = 1.1;
prm \( r_{CH} \) 1.09498° min 0.8 max = 1.1;
prm \( t_1 \) 161.32814° min -180.0 max = 180.0;

rigid

z_matrix C3
z_matrix C2 C3 = \( r_{CC} \);
z_matrix H3 C3 = \( r_{CH} \); C2 105.402
z_matrix N1 C3 = \( r_{CN} \); C2 100.717 H3 -118.051
z_matrix N3 C3 = \( r_{CN} \); C2 114.085 N1 -125.499
z_matrix N2 C2 = \( r_{CN} \); C3 106.935 N1 -5.652
z_matrix O2 C2 = \( r_{CO} \); C3 126.540 N2 -177.818
z_matrix C1 N1 = \( r_{CN} \); N2 37.005 C2 177.016
z_matrix H1 N1 = \( r_{NH} \); C1 122.928 C3 -178.264
z_matrix C4 N3 = \( r_{CN} \); C3 119.850 H3 = t1;
z_matrix H4 N3 = \( r_{NH} \); C3 113.023 C4 172.397
z_matrix H2 N2 = \( r_{NH} \); C1 119.991 C2 -165.935
z_matrix O1 C1 = \( r_{CO} \); N1 127.712 N2 177.677
z_matrix N4 C4 = \( r_{CN} \); N3 116.779 H4 10.982
z_matrix O3 C4 = \( r_{CO} \); N3 120.303 N4 -178.068
z_matrix H5 N4 = \( r_{NH} \); C4 112.943 O3 -20.399
z_matrix H6 N4 = \( r_{NH} \); C4 117.158 H5 -155.657

Rotate_about_axes(@ -217.23153°, @ -212.56492°, @ -292.67135°)
Translate(@ 6.21006°, @ -95.95035°, @ -5.15864°)
TOPAS Tutorial Cimetedine
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


- **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
Oszlányi and Sütő, 2004

1. Take $|F_{hkl}|$
   Guess phases

2. Calculate electron density $\rho(r)$

3. If $\rho(r) <$ value "flip charge"
   $r(r) = -\rho(r)$

4. Calculate $|F_{hkl}|_{\text{new}}$
   and new phases from new $\rho(r)$

5. Keep new phases and replace by $|F_{hkl}|$
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, @, .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*

```plaintext
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

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;
}
```

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

Use of Tangent formula advisable for powder data
Load number of atoms in unit cell
Example
Structure Determination of Mo$_2$P$_4$O$_{15}$

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

Lister et al., Chem. Commun., 2004, 2540
Example
Structure Determination of Mo$_2$P$_4$O$_{15}$

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

~15 sec.
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;
}

Bruker AXS
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
  \[ R = \sum w_i (y_i - y_c) \]

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:

\[ \frac{W_r}{W} = \frac{S_r (ZMV)_r}{\sum S_t (ZMV)_t} \]

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

Measurement parameters:

Depend on sample properties: Determine peak width with a short test scan
- Adjust step size for sufficient amount of data points (6 data points above FWHM)
- Adjust time/step for sufficient counting statistics (at least a few thousand counts on the most intense peaks for basic quantitative analysis)

Typical measurement parameters for analysis of mineral samples:
- 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 (transparancy 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 μm to increase number of crystallites and avoid spotiness effect.
  - Wet grinding with alcohol in MrCrone Mill is ideal for many geological samples.
  - Too coarse grinding also affects preferred orientation.
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

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Brucite</td>
<td>34.79 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corundum</td>
<td>23.19 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorite</td>
<td>22.15 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zincite</td>
<td>19.87 %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Preferred Orientation for Brucite
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

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

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

8.27 wt% Zincite was added to the sample as an internal standard.
Industrial application: Cement + flyash

Determination of amorphous component
Spiking the sample with an internal standard

Phase amounts and amorphous content in original sample is calculated in the TOPAS software.
Rietveld Refinement Corrections

- 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

![TOPAS - [CPD-2.raw] menu with highlighted corrections and settings]
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


- 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 databases 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

- 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 1000 nm. Clays phases may require smaller crystallite sizes to fit broad peaks.
- Entering the weight of an internal standard in % allows quantification of amorphous materials.
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 50μm)
- Identical Powder, wet ground in Micronising Mill for 30 minutes

Gadds data at 25cm sample-detector distance
Corrections for non-ideal powder samples
Large grains, spottiness effect, Micro absorption

**Unground sample**

Weighted compositions:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>29.64</td>
</tr>
<tr>
<td>Microcline</td>
<td>36.63</td>
</tr>
<tr>
<td>Quartz</td>
<td>33.73</td>
</tr>
</tbody>
</table>

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

**Ground sample**

Gadds data at 25cm sample-detector distance
Corrections for non-ideal powder samples
Micro absorption
Brindley correction

Weighted compositions:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>29.64</td>
</tr>
<tr>
<td>Microcline</td>
<td>36.63</td>
</tr>
<tr>
<td>Quartz</td>
<td>33.73</td>
</tr>
</tbody>
</table>

Larger Quartz grains of 50 μm were assumed.

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\( \mu \)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)O$_2$

- Average crystallite refined using Scherrer equation
- Strain refined to fit additional broadening at higher angles
- Determination of crystallite size distribution with Double Voight fitting possible in Launch mode
Rietveld refinements:
Refining crystallite size, strain, and occupation factors on Zr(Ce)O2

- 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 hkls 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)

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

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
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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Use</th>
<th>Value</th>
<th>Code</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direction 1</td>
<td></td>
<td>0.1</td>
<td>@</td>
<td>0</td>
</tr>
<tr>
<td>Direction 2</td>
<td></td>
<td>1</td>
<td>@</td>
<td>0</td>
</tr>
<tr>
<td>Fraction Dr. 1</td>
<td></td>
<td>0.5</td>
<td>@</td>
<td>0</td>
</tr>
</tbody>
</table>

Bruker AXS
Even a Pawley fit cannot 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?

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