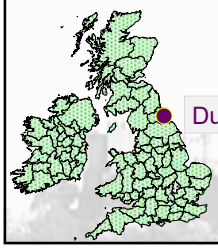
Structural Rietveld Refinements

Prof. John S.O. Evans, Durham Chemistry

Stuttgart School, 2025



Outline of session

- Fundamentals of structural Rietveld refinement
- Short recap of Robert's content we'll use in common refinements
- Intro to INP files (launch mode)
- Exercises (>30 minutes?)

Stuttgart page

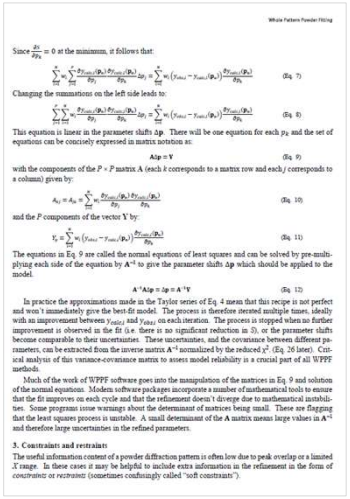
https://topas.webspace.durham.ac.uk/stuttgart-school-2025/

The notes – Whole Powder Pattern Fitting (WPPF)

1. Intro/overview
2. Least squares maths
3. Constraints and restraints
4. Quantities refined
5. Factors affecting intensities
6. Agreement factors
7. Multiple data sets
8. Refinement strategy

[Listen this morning, read at your leisure]

WPPF concise notes



Whole Pattern Powder Fitting

Since $\frac{\partial S}{\partial p_k} = 0$ at the minimum, it follows that:

$$\sum_{i=1}^{P}\sum_{i=1}^{n} w_i \frac{\partial y_{calc,i}(\mathbf{p}_k)}{\partial p_j}\frac{\partial y_{calc,i}(\mathbf{p}_k)}{\partial p_k}\Delta p_j = \sum_{i=1}^{n} w_i \left(y_{obs,i} - y_{calc,i}(\mathbf{p}_k)\right)\frac{\partial y_{calc,i}(\mathbf{p}_k)}{\partial p_k} \quad \text{(Eq. 7)}$$

Changing the summations on the left side leads to:

$$\sum_{j=1}^{P}\left[\sum_{i=1}^{n} w_i \frac{\partial y_{calc,i}(\mathbf{p}_k)}{\partial p_j}\frac{\partial y_{calc,i}(\mathbf{p}_k)}{\partial p_k}\right]\Delta p_j = \sum_{i=1}^{n} w_i \left(y_{obs,i} - y_{calc,i}(\mathbf{p}_k)\right)\frac{\partial y_{calc,i}(\mathbf{p}_k)}{\partial p_k} \quad \text{(Eq. 8)}$$

This equation is linear in the parameter shifts $\Delta\mathbf{p}$. There will be one equation for each p_k and the set of equations can be concisely expressed in matrix notation as:

$$\mathbf{A}\Delta\mathbf{p} = \mathbf{Y} \quad \text{(Eq. 9)}$$

with the components of the $P \times P$ matrix $\mathbf{A}$ (each k corresponds to a matrix row and each j corresponds to a column) given by:

$$A_{kj} = A_{jk} = \sum_{i=1}^{n} w_i \frac{\partial y_{calc,i}(\mathbf{p}_k)}{\partial p_j}\frac{\partial y_{calc,i}(\mathbf{p}_k)}{\partial p_k} \quad \text{(Eq. 10)}$$

and the P components of the vector $\mathbf{Y}$ by:

$$Y_k = \sum_{i=1}^{n} w_i \left(y_{obs,i} - y_{calc,i}(\mathbf{p}_k)\right)\frac{\partial y_{calc,i}(\mathbf{p}_k)}{\partial p_k} \quad \text{(Eq. 11)}$$

The equations in Eq. 9 are called the normal equations of least squares and can be solved by pre-multiplying each side of the equation by $\mathbf{A}^{-1}$ to give the parameter shifts $\Delta\mathbf{p}$ which should be applied to the model.

$$\mathbf{A}^{-1}\mathbf{A}\Delta\mathbf{p} = \Delta\mathbf{p} = \mathbf{A}^{-1}\mathbf{Y} \quad \text{(Eq. 12)}$$

In practice the approximations made in the Taylor series of Eq. 4 mean that this recipe is not perfect and won't immediately give the best-fit model. The process is therefore iterated multiple times, ideally with an improvement between $y_{calc,i}$ and $y_{obs,i}$ on each iteration. The process is stopped when no further improvement is observed in the fit (i.e. there is no significant reduction in S), or the parameter shifts become comparable to their uncertainties. These uncertainties, and the covariance between different parameters, can be extracted from the inverse matrix $\mathbf{A}^{-1}$ normalized by the reduced χ^2 (Eq. 26 later). Critical analysis of this variance-covariance matrix to assess model reliability is a crucial part of all WPPF methods.

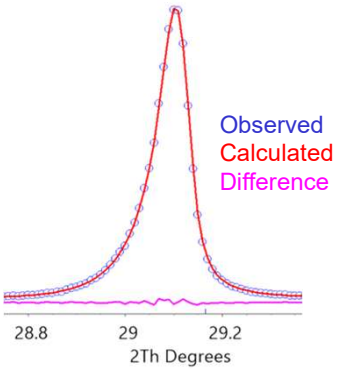
Much of the work of WPPF software goes into the manipulation of the matrices in Eq. 9 and solution of the normal equations. Modern software packages incorporate a number of mathematical tools to ensure that the fit improves on each cycle and that the refinement doesn't diverge due to mathematical instabilities. Some programs issue warnings about the determinant of matrices being small. These are flagging that the least squares process is unstable. A small determinant of the $\mathbf{A}$ matrix means large values in $\mathbf{A}^{-1}$ and therefore large uncertainties in the refined parameters.

3. Constraints and restraints

The useful information content of a powder diffraction pattern is often low due to peak overlap or a limited X range. In these cases it may be helpful to include extra information in the refinement in the form of *constraints* or *restraints* (sometimes confusingly called "soft constraints").

What is Rietveld refinement vs WPPF?

- Minimise the difference between an observed and a calculated powder diffraction pattern based on a (structural) model
- Model must contain all the relevant information
- Done by iterative non-linear least squares by calculating parameter shifts required to improve the fit of the starting model
- Maths in the notes
- Key difference to Pawley/Le Bail is that intensities are determined by a crystallographic model – so you can extract structural information

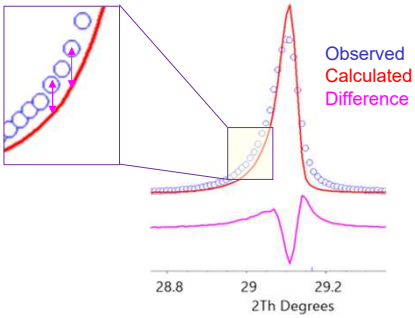


Minimisation, R-factors, etc

Minimise: $\sum_{i=1}^{N} w_i\left(y_{obs,i} - y_{calc,i}\right)^2$

Monitor: $\mathrm{R_{wp}} = \sqrt{\frac{\sum_{i=1}^{N} w_i\left(y_{obs,i} - y_{calc,i}\right)^2}{\sum_{i=1}^{N} w_i {y_{obs,i}}^2}}$

Monitor: $\mathrm{GoF} = \sqrt{\chi^2} = \frac{\mathrm{R_{wp}}}{\mathrm{R_{exp}}} = \sqrt{\frac{\sum_{i=1}^{N} w_i\left(y_{obs,i} - y_{calc,i}\right)^2}{N - P}}$



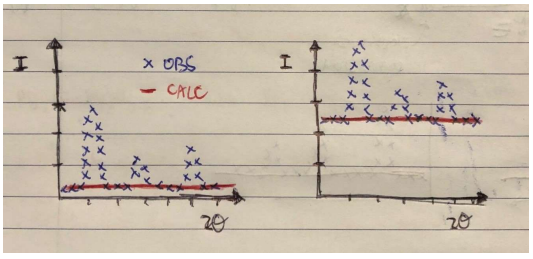
N is the number of data points and P the number of parameters. Least-squares uses a $1/\sigma(y_{obs,i})^2$ weighting, where $\sigma(y_{obs,i})$ is the experimental uncertainty in $y_{obs,i}$.

Other R-factors (e.g. background subtracted) in notes

Target R-factor for a good refinement?

- TOPAS forum question (× 100): how low should my R-factor be for a good refinement?

High $\mathrm{R_{wp}}$
High $\mathrm{R_{Bragg}}$



Low(er) $\mathrm{R_{wp}}$
High $\mathrm{R_{Bragg}}$

- Answer: useful summary in Brian Toby paper cited in the notes

***R* factors in Rietveld analysis: How good is good enough?**

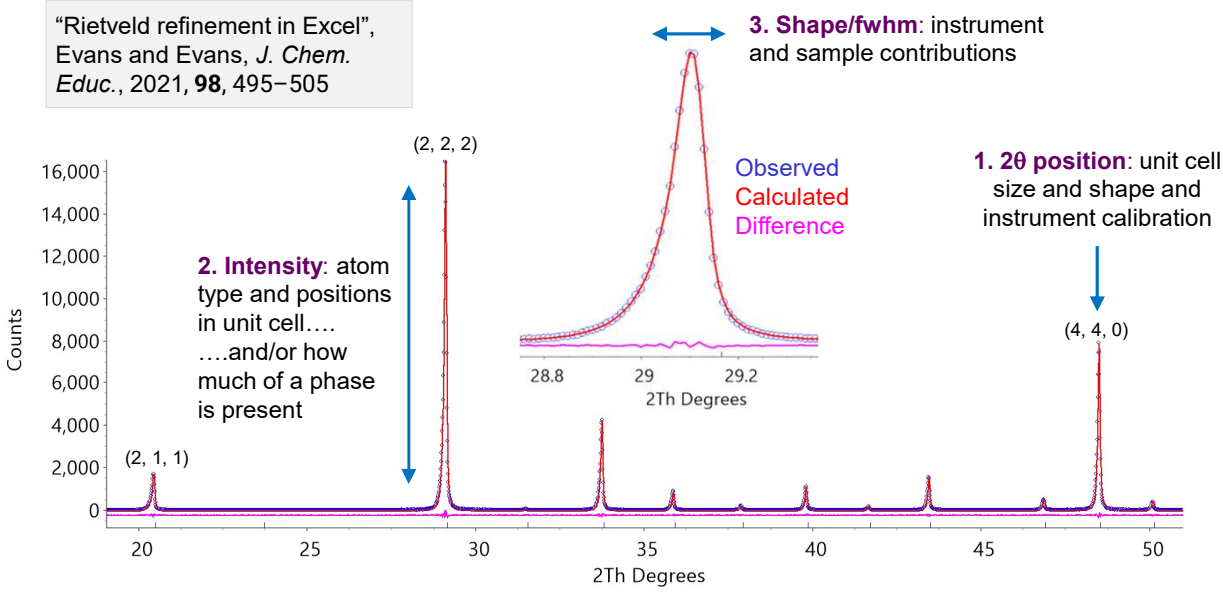
Brian H. Toby
BESSRC/XOR, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois

(Received 19 December 2005; accepted 27 January 2006)

The definitions for important Rietveld error indices are defined and discussed. It is shown that while smaller error index values indicate a better fit of a model to the data, wrong models with poor quality data may exhibit smaller values error index values than some superb models with very high quality data. © *2006 International Centre for Diffraction Data.* [DOI: 10.1154/1.2179804]

What do we have to think about in the Rietveld model?

"Rietveld refinement in Excel", Evans and Evans, *J. Chem. Educ.*, 2021, **98**, 495−505



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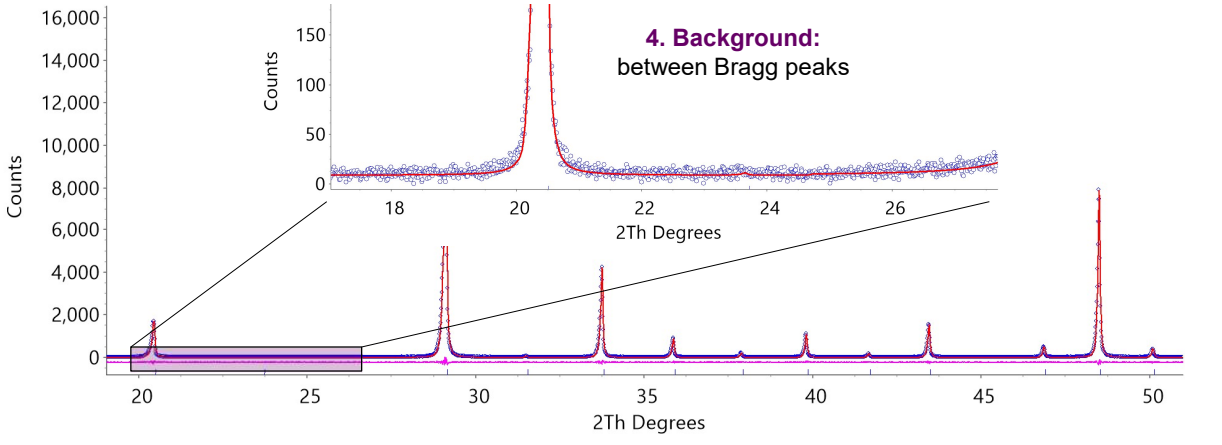
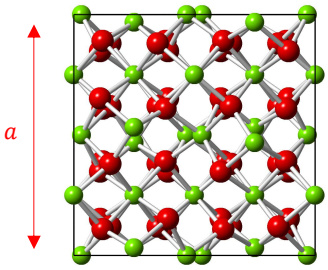


1. Peak position 2θ - Bragg's law

Positions: $\lambda = 2d_{hkl}sin\theta_{calc}$ $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2}$

$2\theta_{obs} = 2\theta_{calc} + \Delta 2\theta$

Depends on:
- zero point alignment error
- **sample displacement**
- sample transparency
- beam divergence
- peak asymmetry
- non-curved sample
- data reduction problems
- etc, etc



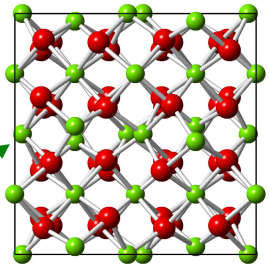
2. Intensity equations

Intensities: $I_{hkl} = scale \times m \times LP \times |F_{hkl}|^2 \times other\ corrections$

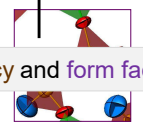
$LP = \frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}$ Relates experimental intensities to scattering from unit cell

Lorentz-polarisation instrument geometry

$F_{hkl} = \sum_j t_j \times occ_j \times f_j \times \exp[2\pi i(hx_j + ky_j + lz_j)]$ at (x_j, y_j, z_j)



$t_j = \exp\left(\frac{-B_j \sin^2\theta}{\lambda^2}\right)$ occupancy and form factor



$B_j = 8\pi^2 u^2$

rms displacement in Å

other corrections ?
- Preferred orientation
- Texture
- Absorption
- Extinction
- Beam decay or changes
- etc

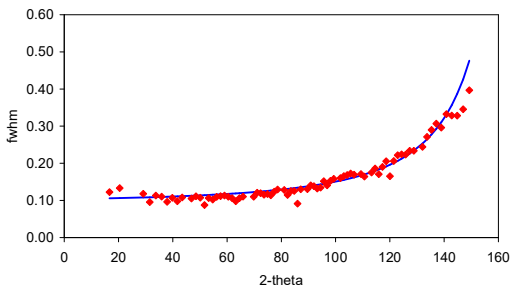
3. Peak shapes

- Peak shapes contain fascinating information – we'll learn about this tomorrow!
- We'll (mainly) take a simple empirical approach today
- If you're doing purely structural work (depends on relative intensities) minor misfits in peak shapes might not matter
- [Exercise tip: peak shapes can be anisotropic – different for different *hkl* reflections (or families of reflections)]

3. Empirical peak shapes in powder diffraction

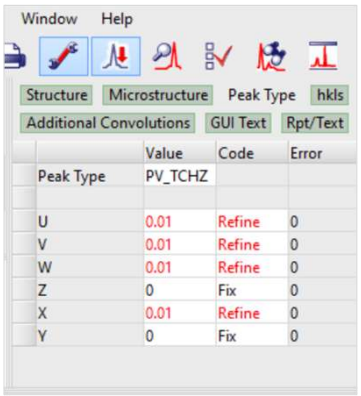
Gaussian: $fwhm = \left(U \tan^2\theta + V \tan\theta + W + \frac{Z}{\cos^2\theta} \right)^{1/2}$

Lorentzian: $fwhm = X \tan\theta + \frac{Y}{\cos\theta}$




```
TCHZ_Peak_Type(pku, 0.05`,pkv, -0.004`, pkw, 0.008`,
               pkz, 0.03`,pkx,  0.136`, pky, 0.04`)
```

U, V, W, X, Y (and *Z*) refineable parameters



Peaks can be anisotropic shape depends on *hkl*

4. Background description

- Smooth function in 2-theta (polynomial, Fourier series, etc)
- Perhaps broad peaks to describe “humps”
- Perhaps a function to describe e.g. capillary or short range order effects
- Perhaps fit an experimentally measured background during the Rietveld
- [Exercise tip: don’t forget point 2 on this slide!]

How much information is in a powder pattern, what can I refine?

- Rarely enough!
- See notes for a more mathematical answer
- Bring in restraints and constraints to help refinement as “extra information”
- [Tomorrow we will use symmetry mode ideas as a different flavour of “extra information”]

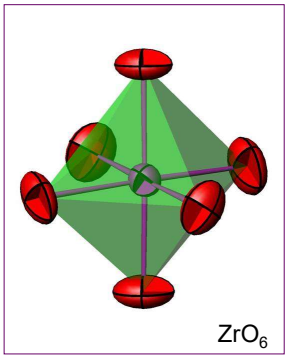
Restraints in Rietveld refinement

- You might know that a Zr-O bond in a ZrO_6 octahedron should be ~2.075 Å
- "extra information"
- Apply a "penalty" or "restraint" if it's different in the model

$$penalty = (model's\ ZrO_{dist} - 2.075)^2$$

$$\chi^2_{\text{restraints}} = f(all\ penalties)$$

$$\chi^2_{\text{total}} = \chi^2_{\text{data}} + weight \times \chi^2_{\text{restraints}}$$



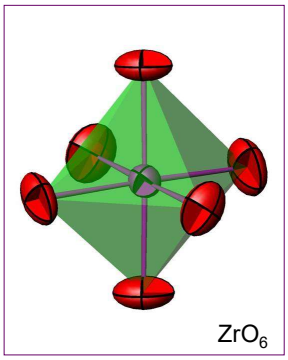
ZrO_6

- [What about standard uncertainties or esd's if you do this? What do they mean?]

Constraints in Rietveld refinement – e.g. rigid bodies

- You might want to force a ZrO_6 group to be a perfect octahedron
- Constraints change the least squares equations
- 21 *xyz* parameters become 3 positions and 3 rotations?

```
macro Octahedron(Zr1, o1, o2, o3, o4, o5, o6, 2.075)
{
   Point_for_site(s0,  0,  0,  0)
   Point_for_site(s1,  r,  0,  0)
   Point_for_site(s2, -r,  0,  0)
   Point_for_site(s3,  0,  r,  0)
   Point_for_site(s4,  0, -r,  0)
   Point_for_site(s5,  0,  0,  r)
   Point_for_site(s6,  0,  0, -r)
}
```

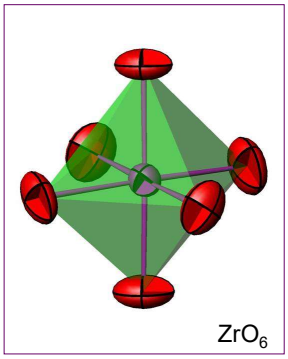


ZrO_6

- [More detail in Sebastian's lecture tomorrow]

Constraints in Rietveld refinement – e.g. TLS matrices

- In a rigid group atoms ought to vibrate in related ways
- 42 u_{ij} parameters become 2 TLS parameters?



How reliable is the model: variance covariance matrix

e.g. fit a straight line $y = mx + c$ to a set of n y_{obs} values to determine the gradient m and intercept c

1. Eq'ns in matrix form → 2. Solve to find unknowns $\mathbf{x}$ → 3. Calculate the matrix $\mathbf{M}$ with straight-forward maths → 4. $\mathbf{M}$ contains variances and covariances

$$\mathbf{Ax} = \mathbf{y}$$

observations
vector of unknowns
design matrix

$$\mathbf{x} = \left(\mathbf{A}^{\mathbf{T}}\mathbf{A}\right)^{-1}\mathbf{A}^{\mathbf{T}}\mathbf{y}$$

$$\mathbf{M} = \frac{n}{n-p}\frac{\sum_1^n w_i(obs-calc)^2}{\sum_1^n w_i}\left(\mathbf{A}^{\mathbf{T}}\mathbf{W}\mathbf{A}\right)^{-1}$$

observations
parameters

$$\mathbf{M} = \begin{pmatrix} \sigma_m^2 & \sigma_m\sigma_c\mu_{mc} \\ \sigma_m\sigma_c\mu_{mc} & \sigma_c^2 \end{pmatrix}$$

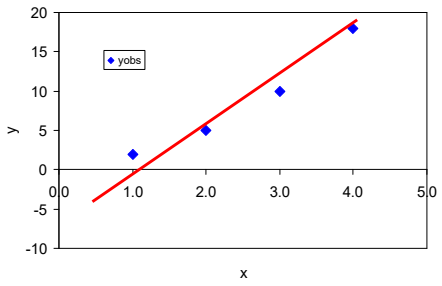
covariance
variance

μ_{mc} = correlation coefficient

Correlation matrix from software →

There's an example in the on-line notes of how to do this by hand – tedious but good to do once in your life!

Correlated parameters e.g. online by-hand problem



$$y = mx + c$$

$m = 5.3(8)$
$c = -4.5(20)$

$\sigma_m = 0.79$
$\sigma_c = 2.17$
$\mu_{mc} = -0.91$

gradient and intercept anti-correlated

Rietveld refinement correlations

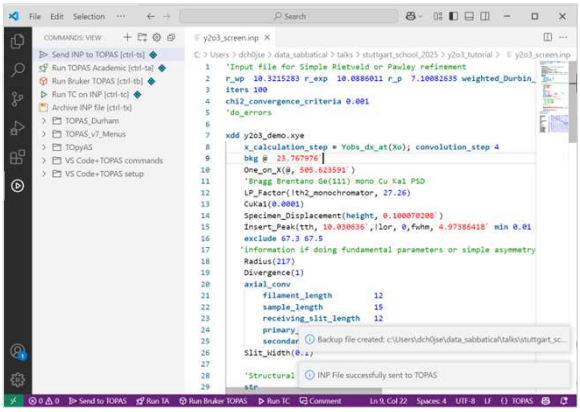
- Zero point, sample displacement, unit cell
- Wavelength, unit cell
- Occupancy, scale factor, temperature factor
- Peak shape coefficients, size, strain
- Phase fractions, temperature factors, occupancies

Topas simplest launch mode INP file

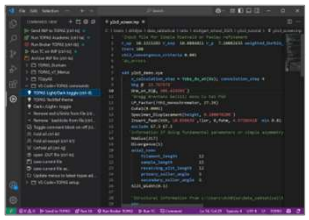
```
'Input file for Simple Rietveld
r_wp  10.3215283 r_exp  10.0886011 r_p  7.10082635 weighted_Durbin_Watson  1.98433763
gof  1.02308815
iters 100
chi2_convergence_criteria 0.001

xdd y2o3_demo.xye
    x_calculation_step = Yobs_dx_at(Xo); convolution_step 4
    bkg @  0 0 0
    LP_Factor(!th2_monochromator, 27.26)
    CuKa1(0.0001)
    str
        space_group "Ia-3"
        site Y1     x 0.25  y 0.25  z 0.25  occ Y+3  1  beq 0.25
        site Y2     x 0.97  y 0.00  z 0.25  occ Y+3  1  beq 0.25
        site O1     x 0.39  y 0.15  z 0.38  occ O-2  1  beq 0.25
        TCHZ_Peak_Type(pku, 0.039,pkv, -0.02,pkw, -0.001,!pkz, 0.00,pkx, 0.009, pky, 0.001)
```

New for Stuttgart 2025: TOPAS + VS Code topas-editor



- Easier to install
- Menus simplified
- Light and dark schemes
- Easier to customise
- New commands/ways of working
- Ctrl-t keys: ta, tc, ts
- Pop up help menus
- Will have bugs!



Controlling parameters in INP files

```
'parameters are turned on and off with a ! Symbol or using @

a   10.156 'fixed cell parameter with no name
a @ 10.156 'refined cell parameter with automatic name

a !lpa 10.156  'fixed cell parameter a with a name
a  lpa 10.156` 'refined cell parameter a with a name

prm !prm_name 10.156  'a fixed parameter with a name
prm  prm_name 10.156` 'a refined parameter with a name
```

Quiz: TOPAS crimes/pitfalls

```
str
    space_group "Ia-3"
    a @  10.598107`
    b @  10.498107`
    c @  10.698107`
    al @ 90
    be @ 90
    ga @ 90
    volume  1190.378`
```

```
str
    space_group "Ia-3"
    a lpa  10.598107`
    b lpa  10.598107`
    c lpa  10.598107`
    al !alpha 90
    be !beta  90
    ga !gamma 90
    volume  1190.378`
```

```
str
    space_group "Ia-3"
    a lpa 10.598107`
    b = Get(a);
    c = Get(a);
```

```
str
    space_group "Ia-3"
    Cubic(@ 10.598107`)
```


Quiz: TOPAS crimes/pitfalls

```
str
    space_group "P-3m1“
    phase_name “SnS2“
    a 3.6999
    b 3.6999
    c 6.9779
    al 90
    be 90
    ga 120
    site Sn0             x 0.0000  y 0.0000  z 0.0000  occ Sn  1.0
    site S1              x 0.3333  y 0.6666  z 0.2117  occ S   1.0

    site Sn0 num_posns 1 x 0.0000  y 0.0000  z 0.0000  occ Sn  1.0
    site S1  num_posns 2 x =1/3;   y =2/3;   z 0.2117  occ S   1.0
```

Quiz: TOPAS crimes/pitfalls

```
str
    a 4.594
    b 4.594
    c 2.959
    al 90.
    be 90.
    ga 90.
    space_group "P42/mnm"
    site Ti1 x   0.000    y   0.000     z 0.000  occ Ti  1.0  beq 0.70000
    site O1  x @ 0.306    y @ 0.306     z 0.000  occ O   1.0  beq 0.70000

    site Ti1 x 0.000      y     0.000   z 0.000  occ Ti  1.0  beq 0.70000
    site O1  x o1x 0.306  y o1x 0.306   z 0.000  occ O   1.0  beq 0.70000

    site Ti1 x 0.000      y      0.000  z 0.000  occ Ti  1.0  beq 0.70000
    site O1  x o1x 0.306  y =Get(x);:0  z 0.000  occ O   1.0  beq 0.70000
```


Quiz: TOPAS crimes/pitfalls

```
TCHZ_Peak_Type(pku, 0.05`,pkv, -0.004`,pkw, 0.0008`, pkz, 0.003`,pkx, 0.136`, pky, 0.04`)


TCHZ_Peak_Type(pku, 0.05`,pkv, -0.004`,pkw, 0.0008`,!pkz, 0.00  ,pkx, 0.136`, pky, 0.04`)
```

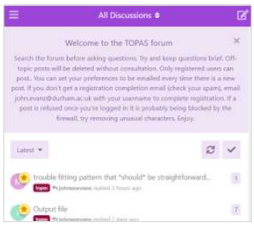
Quiz: TOPAS crimes/pitfalls

```
xdd y2o3_demo.xye
    x_calculation_step = Yobs_dx_at(Xo); convolution_step 4
    bkg @  0 0 0
    'Bragg Brentano Ge(111) mono Cu Ka1 PSD
    LP_Factor(!th2_monochromator, 27.26)
    CuKa1(0.0001)
    Specimen_Displacement(height, 0.068`)
    Zero_Error(@, -0.017)
    …
    …
```


Resources?

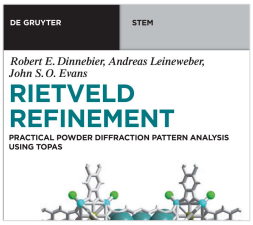
wiki site

forum

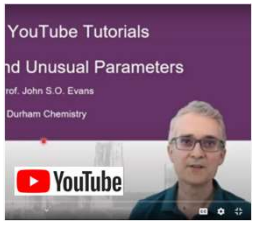


web tutorials

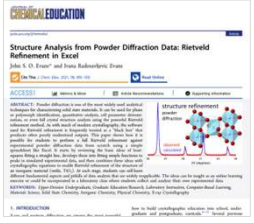
book



YouTube



Rietveld in excel



School breaks

School page

Exercises: individual or as a group?

- If you've never done a jEdit/VS Code TOPAS refinement before:
  - https://topas.webspace.durham.ac.uk/vscode_riet_pawley/
  - https://topas.webspace.durham.ac.uk/tutorial_tio2riet/
- If you've some experience with jEdit/VS Code:
  - https://topas.webspace.durham.ac.uk/tutorial_y2o3riet/
- If you don't have jEdit/VS Code template INP files online
- If you finish these try anything that interests you from:
  - https://topas.webspace.durham.ac.uk/topas_user_menu/
- Or try the Y_2O_3 tutorial in GSAS if you're really brave
- We will come round and help you

Stuttgart page