Dealing with overlapped data

Bill David, ISIS Facility,
Rutherford Appleton Laboratory, UK

Powder diffraction: issues and algorithms

Bill David, ISIS Facility,
Rutherford Appleton Laboratory, UK

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WIFD - standard disclosure

- 1983-5 (Oxford to ISIS)
  - GENIE – data manipulation and analysis package
    - based on VMS command line interpreter – still in use
    - (I still have my VAX (called JARAK) in the basement)
- 1983-
  - CCSL – FORTRAN77 crystallographic subroutine library
  - (www.iill.fr/dif/ccsl/html/ccsldoc.html) Rubbia effect
  - basis of all Rietveld analysis at RAL until 1992
- 1997-
  - DASH - structure solution from powders
    - SA5TOR (VAX VMS) -2 weeks
    - GUI (Winteracter – all FORTRAN – 6 months)
    - CCDC – α and β testing – 18 months

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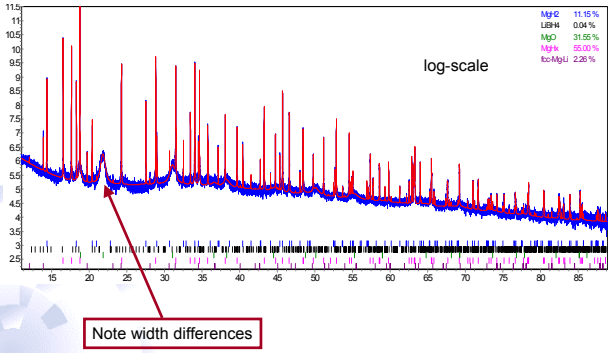
Major advances in instrumentation



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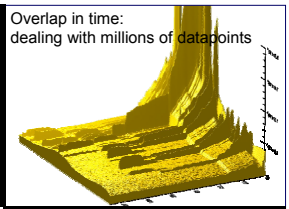
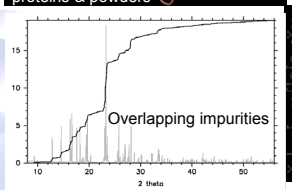
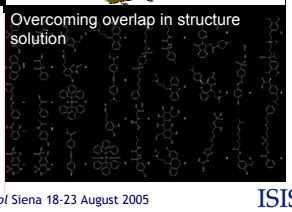
Outline







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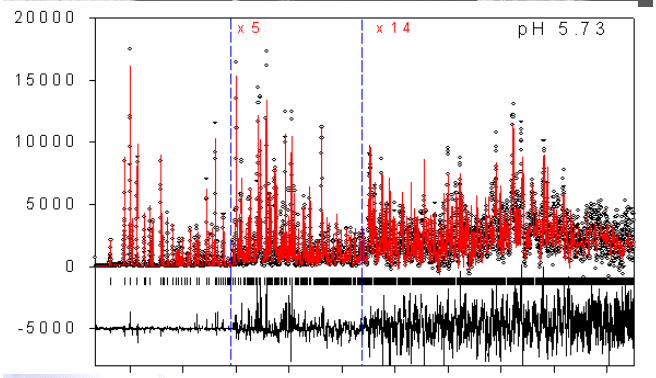
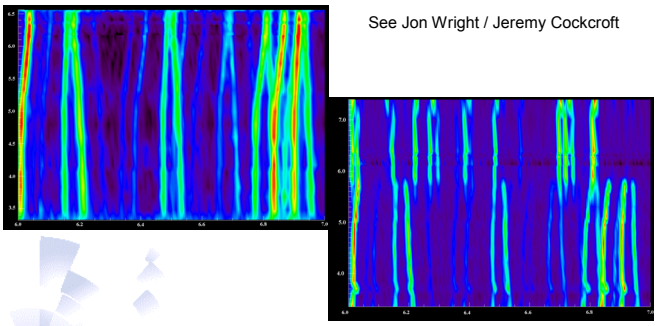
Proteins and powders

Proteins and powders



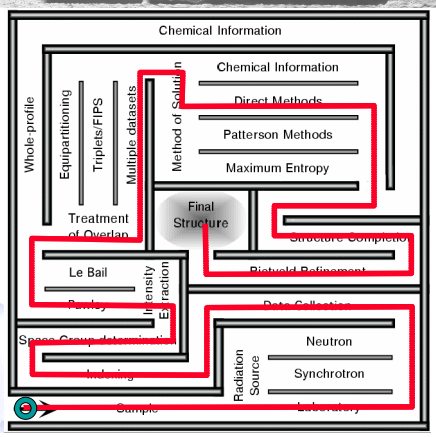
Proteins and powders



See Jon Wright / Jeremy Cockcroft

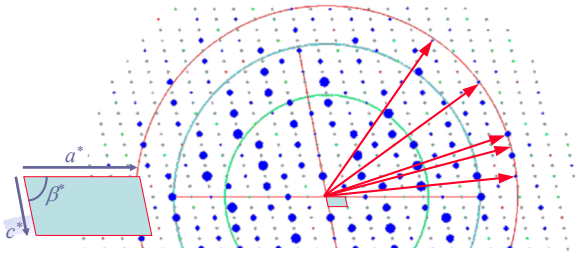
Colour representation of ID31 powder diffraction data from the pH variation experiment, from pH 6.56 – 3.33 of HEWL crystallised at (a) 4°C and (b) RT. At low temperature the tetragonal phase is favoured and a smooth anisotropic shift in the peak position is apparent.

powder diffraction - standard disclosure



after Baerlocher & McCusker

bottlenecks in the maze

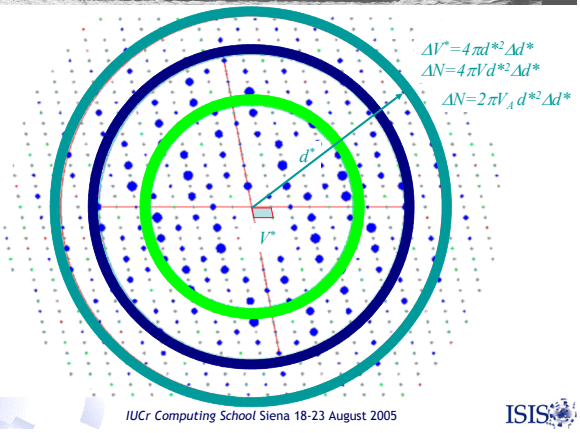


powder diffraction

radial reciprocal space distance only - *d*-spacing

$$Q_{hkl} = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^*\cos\alpha^* + 2hla^*c^*\cos\beta^* + 2hka^*b^*\cos\gamma^*$$

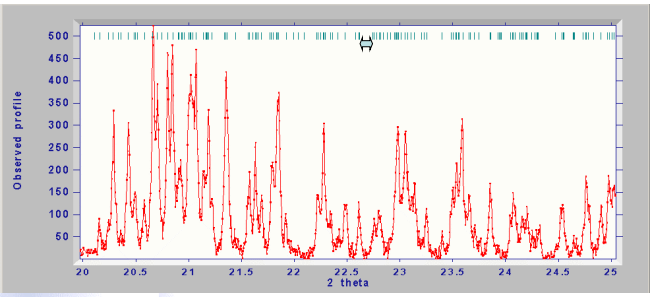
TRAFFIC JAM in the maze!



peak density - TRAFFIC JAM in the maze!

$$x = \Delta 2\theta / \langle \Delta 2\theta \rangle = \Delta N(2\theta) \times \Delta 2\theta$$

$$p_{NN}(x) \propto \exp(-x)$$



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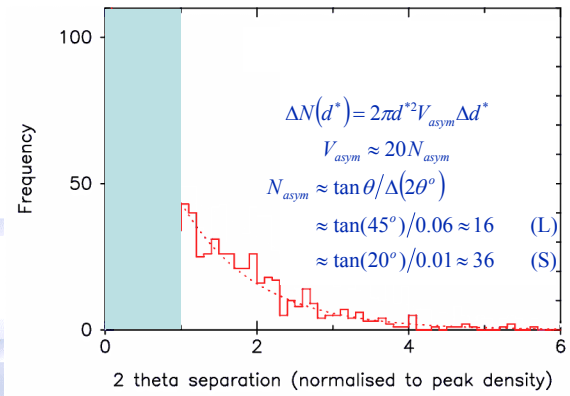
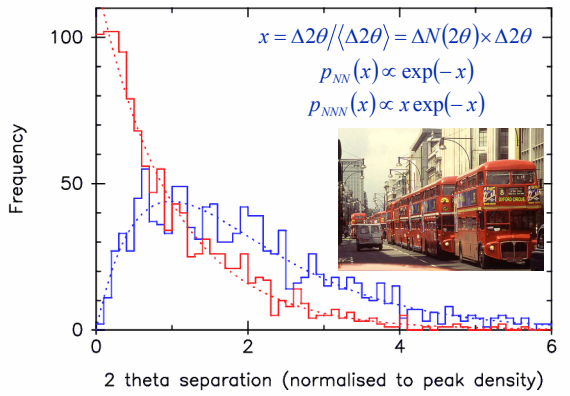
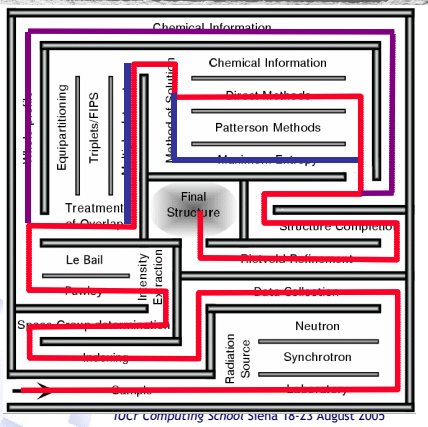


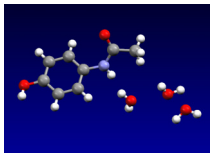
peak density - TRAFFIC JAM in the maze!



dealing with the TRAFFIC JAM of peak overlap

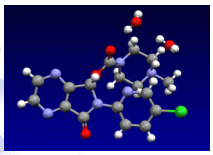


Dehydration of pharmaceutical compounds



Paracetamol hydrates

$C_8H_9NO_2.nH_2O$
pain-killer, analgesic, antipyretic
4'-hydroxyacetanilide,
acetaminophen, tylenol

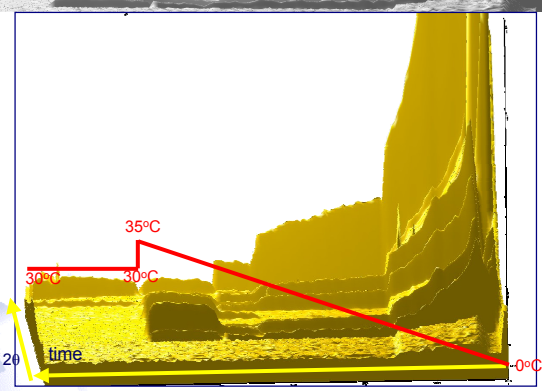


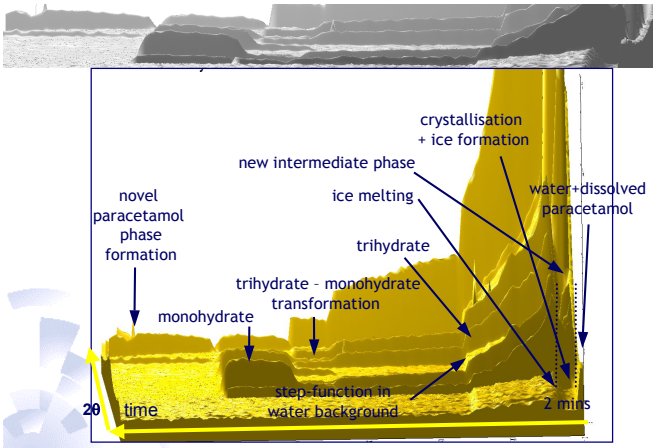
Zopiclone hydrates

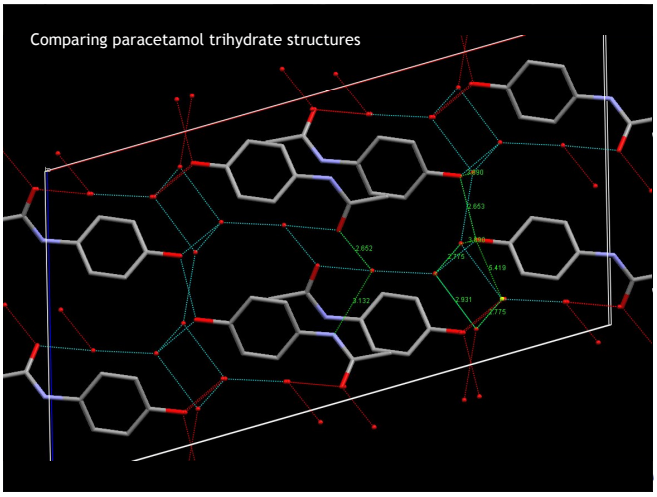
$C_{17}H_{17}ClN_5O_3.2H_2O$
hypnotic – insomnia
line phases: dihydrate - anhydrous

Key points

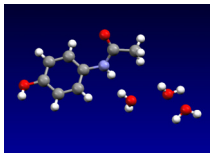
- Analysing all the data as fully as possible
  - Managing a million data-points
    - 130 patterns
    - 8520 points per pattern
    - 1,107,600 points
- Identifying change
  - Principal component analysis / clustering
- Quantitative phase analysis
- Structure determination
- Rietveld refinement
  - Structure, microstructure & inhomogeneity





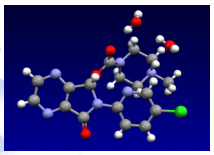


Dehydration of pharmaceutical compounds



Paracetamol hydrates

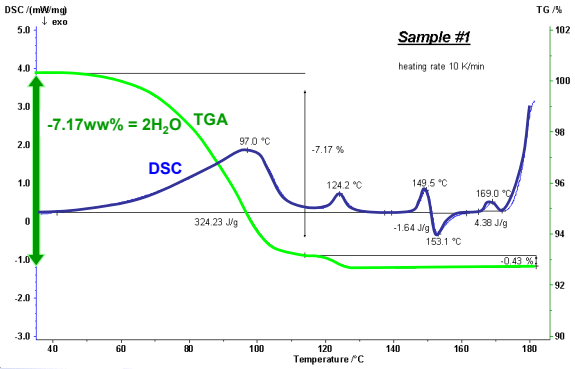
$C_8H_9NO_2.nH_20$
pain-killer, analgesic, antipyretic
4'-hydroxyacetanilide,
acetaminophen, tylenol

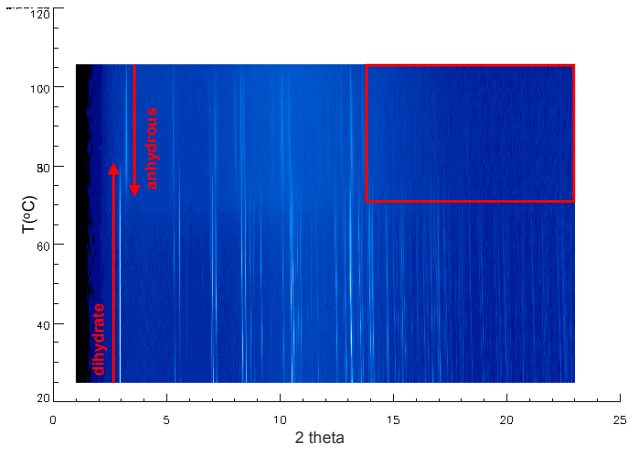


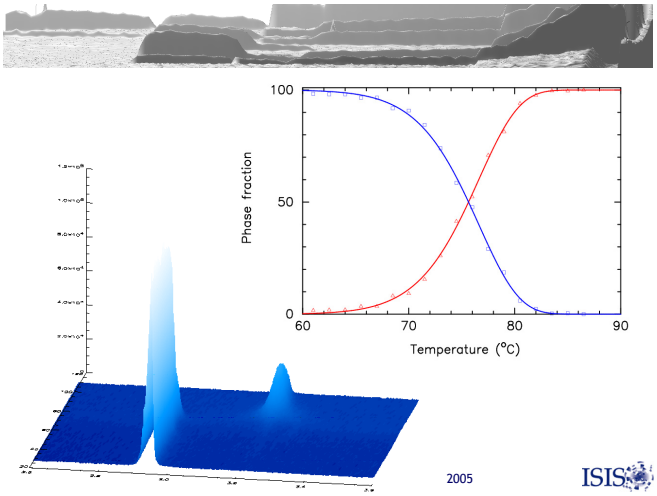
Zopiclone hydrates

$C_{17}H_{17}ClN_5O_3.2H_2O$
hypnotic - insomnia
line phases: dihydrate - anhydrous

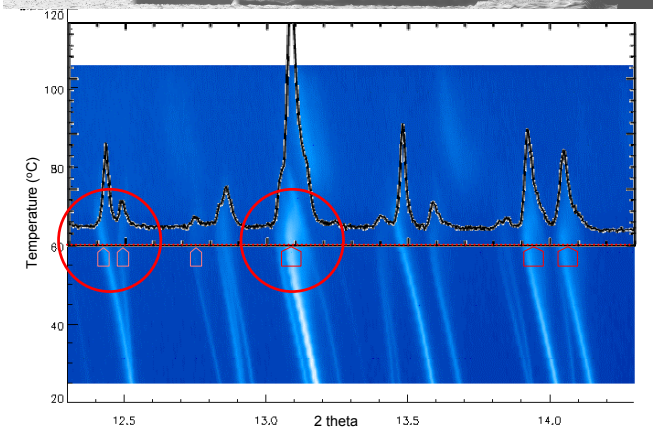
Zopiclone dehydration and phase transformations

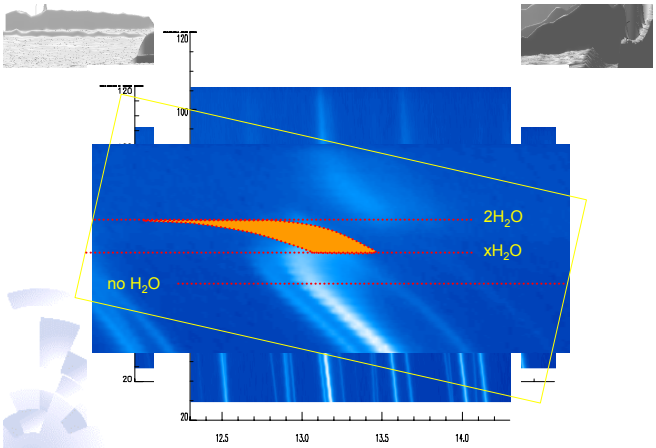




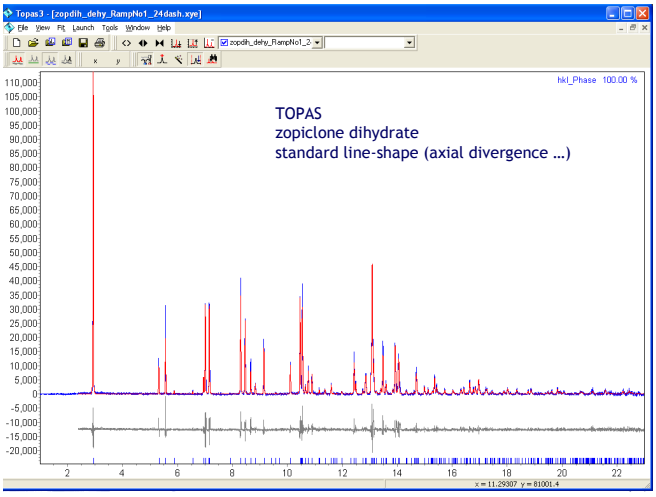


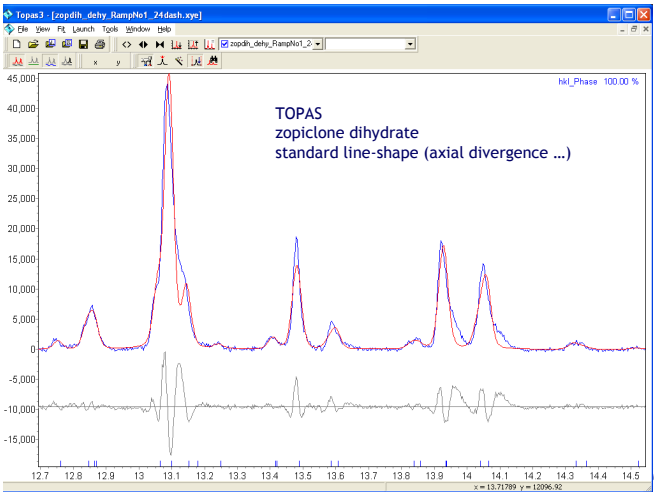
Complex anisotropic sample line-shape





ISIS





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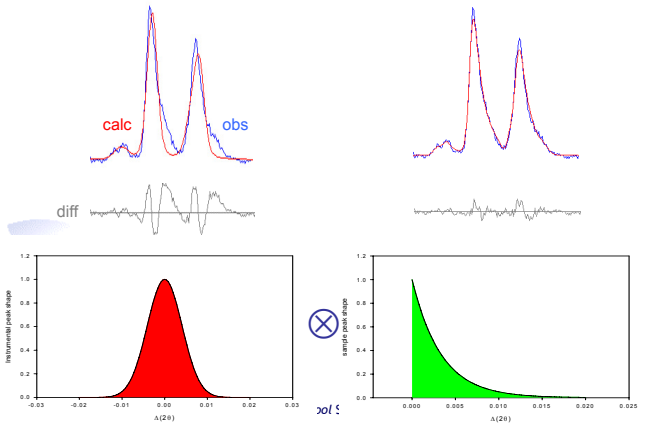

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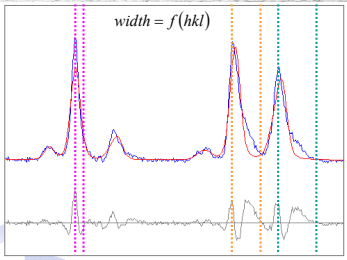


There is a distribution of water content leading to a distribution of lattice constants

$$d_0^{*2} = h^2 a_0^{*2} + k^2 b_0^{*2} + l^2 c_0^{*2} + 2hla_0^* c_0^* \cos\beta_0^*$$
$$= h^2 A_0^* + k^2 B_0^* + l^2 C_0^* + 2hlE_0^*$$
$$d_1^{*2} = h^2 A_1^* + k^2 B_1^* + l^2 C_1^* + 2hlE_1^*$$

$d_0^*(hkl)$ $d_1^*(hkl)$

$$\Delta(d^{*2})_{max} = h^2\Delta A^* + k^2\Delta B^* + l^2\Delta C^* + 2hl\Delta E^*$$

$$\Delta(2\theta^{\square})_{max} = (180/\pi)d^2(h^2\square + k^2\square + l^2\square + 2h\square)\tan\theta$$

ISIS

Complex anisotropic sample line-shape

$$\Delta(2\theta^{\square})_{max} = (180/\pi)d^2(h^2\square + k^2\square + l^2\square + 2hk\square)\tan\theta$$

we have defined the limits of the sample line-shape

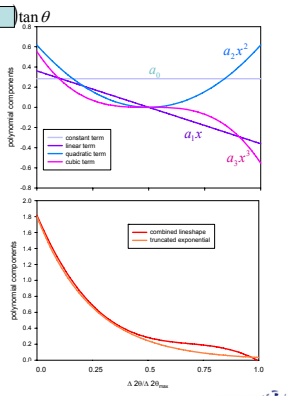
but we don't know the lineshape

construct a generalised lineshape using polynomials / orthogonal polynomials

cubic polynomial

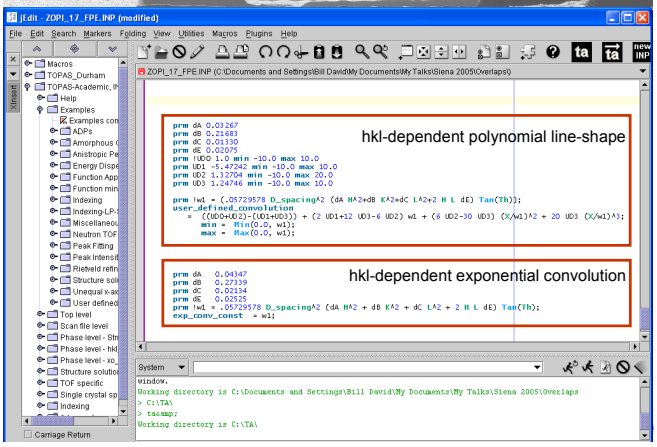
$$\Delta(2\theta^{\square}) = a_0 + a_1x + a_2x^2 + a_3x^3$$

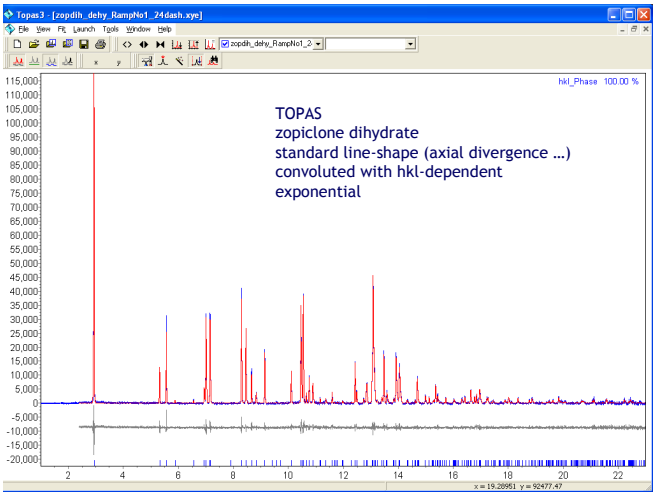
$$(2x-1) = \Delta(2\theta^{\square})/\Delta(2\theta^{\square})_{max}$$



ISIS

TOPAS screenshot





TOPAS
zopiclone dihydrate
standard line-shape (axial divergence ...)
convoluted with hkl-dependent exponential