Dealing with overlapped data

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Powder diffraction: issues and algorithms

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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
      – basis of all Rietveld analysis at RAL until 1992
  • 1997-
    – DASH - structure solution from powders
      • SASTOR (VAX VMS) -2 weeks
      • GUI (Winteracter – all FORTRAN – 6 months)
      • CCDC – α and β testing – 18 months

Major advances in instrumentation

Major advances in instrumentation

Outline

Proteins and powders
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.
peak density - TRAFFIC JAM in the maze!

\[ \Delta N(\theta) = 2 \pi V_{\text{peak}} \Delta \theta \]
\[ V_{\text{peak}} = 20N_{\text{mon}} \]
\[ N_{\text{mon}} = \tan(\theta) / \Delta(\theta) \]
\[ = \tan(45^\circ) / 0.06 = 16 \quad (L) \]
\[ = \tan(20^\circ) / 0.01 = 36 \quad (S) \]

2 theta separation (normalised to peak density)

Dehydration of pharmaceutical compounds

**Paracetamol hydrates**
\[ \text{C}_9\text{H}_9\text{NO}_2 \cdot n\text{H}_2\text{O} \]
pain-killer, analgesic, antipyretic
4'-hydroxyacetanilide, acetaminophen, tylenol

**Zopiclone hydrates**
\[ \text{C}_{17}\text{H}_{17}\text{ClN}_5\text{O}_3 \cdot 2\text{H}_2\text{O} \]
hypnotic - insomnia
line phases: dihydrate - anhydrous

Key points

- Analysing all the data as fully as possible
  - Managing a million data-points
    \[ 130 \text{ patterns} \]
    \[ 8520 \text{ points per pattern} \]
    \[ 1,107,600 \text{ points} \]
- Identifying change
  - Principal component analysis / clustering
- Quantitative phase analysis
- Structure determination
- Rietveld refinement
  - Structure, microstructure & inhomogeneity
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Water + dissolved paracetamol crystallisation + ice formation

Ice melting

Trehydrate

Monohydrate - monohydrate transformation

Trehydrate – monohydrate transformation

New intermediate phase

Monohydrate

Crystallisation + ice formation

Time

Dehydration of pharmaceutical compounds

Paracetamol hydrates

C₈H₉NO₂·nH₂O

Pain-killer, analgesic, antipyretic

4’-hydroxyacetanilide, acetaminophen, tylenol

Zopiclone hydrates

C₁₇H₁₇ClN₅O₃·2H₂O

Hypnotic – insomnia

Line phases: dihydrate - anhydrous

Paracetamol trihydrate structures

Comparing paracetamol trihydrate structures

Zopiclone dehydration and phase transformations

DSC

TGA

-7.17%w/w = 2H₂O

Paracetamol trihydrate

T(oC)

Dihydrate

Anhydrous

Phase fraction

Temperature (°C)

2 theta

0 5 10 15 20 25

0 10 20 30 40 50 60 70 80 90

2005
There is a distribution of water content leading to a distribution of lattice constants:

\[
\Delta d_i(kk) = -k_i' \Delta A + k_i' \Delta B' + l_i' \Delta C' + 2k_{kk} \cos \beta'
\]

\[
\Delta d_i'(kk) = k_i' \Delta A' + k_i' \Delta B' + l_i' \Delta C' + 2k_{kk} \cos \beta'
\]

\[
\Delta \Delta d_{kk} = (1.00) \sigma_i \Delta (k) \Delta k_k
\]
Complex anisotropic sample line-shape

\[ \Delta (2\theta)^2 \theta_{\max} = \left\{ \begin{array}{ll}
0 & \text{if } 2\theta < \theta_{\max} \\
\frac{1}{2} & \text{if } 2\theta = \theta_{\max} \\
1 & \text{if } 2\theta > \theta_{\max}
\end{array} \right. \]

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
\[ \Delta (2\theta)^2 \theta_{\max} = a_0 + a_1 x + a_2 x^2 + a_3 x^3 \]
\[ (2\theta - 1) = \Delta (2\theta)^2 \theta_{\max} \]

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TOPAS screenshot

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

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