POWDER DIFFRACTION

Possibilities – Problems

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CONTENTS

• Information from a powder diffraction pattern
• Appearances
• Phase identification
• Indexing
• Stress/strain
• Rietveld refinements
• Background, counting statistics
• Preferred orientation
• Absorption
• Axial divergence
POSSIBILITIES

Information content of a powder pattern

- Background
  - Sample
    - Scattering from sample holder, air etc.
    - Compton scattering
  - Diffuse scattering:
    - Local structure
      - Amorphous fraction
      - Lattice dynamics
  - Lattice parameters:
    - Space group:
      - Macro-strain
      - Qualitative phase analysis
  - Crystal structure:
    - Atomic positions
    - Temperature factor
    - Occupancy
    - Texture
    - Quantitative phase analysis

- Reflections
  - Position
  - Intensity
  - Profile (FWHM, peak shape)
    - Instrument function
  - Sample broadening

Real structure:
- Micro-strain
- Domain size

POWDER DIFFRACTION

Graph showing intensity (a.u.) against 2 Theta (degrees).
POWDER DIFFRACTION

PHASE IDENTIFICATION
PHASE IDENTIFICATION

PATTERN CALCULATION
INDEXING

2θ  sin²θ  (h² + k² + l²)  h k l
25.96  0.05043
30.01  0.06704

Cubic:

(1 / d_{hal})² = (h² + k² + l²) / a²
2 d_{hal} sinθ_{hal} = λ
sin²θ_{hal} = (h² + k² + l²) λ² / (4a²)

62.54  0.26941
68.88  0.31984
70.97  0.33693
78.92  0.40391

\sin²\theta_{\text{hal}} = h^2 X_1 + k^2 X_2 + l^2 X_3 + hk X_4 + hl X_5 + kl X_6

PARTICLE SIZE - STRESS / STRAIN (DEFECTS)

Size (τ):

β = k λ / τ cos(θ) (Sherrer equation)
β^2 = FWHM_{obs}² - FWHM_{ref}² (rad)

Stress/strain (ε):

β = 4 ε tan(θ)

Williamson-Hall:

β = k λ / τ cos(θ) + 4 ε tan(θ)
β cos(θ) = k λ / τ + 4 ε sin(θ)
RIETVELD REFINEMENT

Least-squares: \[ D = \sum w_j (Y_{oi} - Y_{ci})^2 \]

\[ Y_{ci} = B_i + S \sum hkl A(2\theta) P_{hkl} Lp(2\theta) \Phi(2\theta-2\theta_{Bragg}) |F_{hkl}|^2 \]

- \( Y_{ci} \) = Calculated intensity
- \( B_i \) = Background intensity
- \( S \) = Scale factor
- \( A(2\theta) \) = Absorption correction
- \( P_{hkl} \) = Preferred orientation correction
- \( Lp(2\theta) \) = Lorentz and polarization correction
- \( \Phi(2\theta-2\theta_{Bragg}) \) = Profile function
- \( |F_{hkl}|^2 \) = Diffracted (single-crystal) intensity
RIETVELD REFINEMENT

Scolecite, Huber data

<table>
<thead>
<tr>
<th>Atom</th>
<th>Bond Length (Å)</th>
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<tr>
<td>Si(1)</td>
<td>O(1) 1.632(7)</td>
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<tr>
<td></td>
<td>O(2) 1.593(6)</td>
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<td>O(9) 1.597(6)</td>
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<td>Si(2)</td>
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<td>O(5) 1.621(8)</td>
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<td>O(8) 1.622(7)</td>
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<td>O(10) 1.641(8)</td>
</tr>
</tbody>
</table>

Al(1) - O(1) 1.694(8)
Al(2) - O(2) 1.775(8)
Al(2) - O(4) 1.768(8)
Al(2) - O(6) 1.739(7)
Al(2) - O(8) 1.730(8)

ANISOTROPIC SIZE EFFECTS

Fe$_2$O$_3$

\[ a = 5.0364(8), \ c = 13.750(2) \ \text{Å} \quad D(a) = 399(3) \ \text{Å}, \ D(c) = 87(2) \ \text{Å} \]
PROBLEMS - ERRORS

- Background
  - General
  - Fluorescence/incoherent scattering
  - Counting statistics
- Preferred orientation
  - Poor sample
  - Texture
- Systematic errors
  - Absorption – intensities
  - Absorption – peak positions
  - Axial divergence

BACKGROUND

- Read-out-noise
- Sample holder (transmission mode)
BACKGROUND

Reflection mode

Si single crystal (711 reflection tilted 5°)

BACKGROUND

Siderite, FeCO₃

Fluorescence scattering
BACKGROUND

\[ b(D) = 6.671 \text{ fm} \]
\[ Rp = 4.65 \% \]

\[ b(H) = -3.739 \text{ fm} \]
\[ Rp = 1.52 \% \]

Incoherent scattering!

COUNTING STATISTICS

Poisson statistics: \( \sigma^2(I) = I \)

\[ \sigma(I) / I = 1 / \sqrt{I} \]

Huber data on sugar. 10 / 60 / 480 min
COUNTING STATISTICS

Huber data on sugar. 10 / 60 / 480 min

COUNTING STATISTICS

1°= 50 steps, 530 s/step → 7 hours
POOR SAMPLE

PREFERRED ORIENTATION (TEXTURE)
POOR SAMPLE

Emery paper

POOR SAMPLE

Al₂O₃ powder

Emery paper
ABSORPTION EFFECTS

Transmission mode
Capillary sample

Reflection mode
Flat plate sample

AXIAL DIVERGENCE
AXIAL DIVERGENCE

Capillary sample: 1 mm beam height vs. 8 mm beam height

![Graph showing AXIAL DIVERGENCE with 1 mm beam height vs. 8 mm beam height comparison.](graph.png)