Powder Diffraction

\[ n \cdot \lambda = 2 \cdot d \cdot \sin(\theta) \]
Digital Diffractometers

Transmission Geometry

- Glass Capillary
- Foil
- Fluid Cell

Capillaries are ideal for:
- Light atoms (Polymers, Pharmaceuticals)
- Small amounts
- Hazardous materials
- Air-sensitive materials

Use characteristic radiation with low absorption coefficient

Reflective Geometry

- Flat powder sample

Reflective Geometry is ideal for:
- Absorbing materials (Ceramics, Metals)
- Thin films
- Texture analysis

Use characteristic radiation with high absorption coefficient
Features:
Peak Positions (°2theta)
Peak Intensities (counts)
Peak Width (°2theta)

Phases are identified from peak positions only
Search-Match software:
- Extract peak positions
- Compare with database

Databases:
- PDF-2 (commercial)
- PDF-4+ (commercial)
- COD (free online resource)
Rietveld Refinement

For more than just identification:

Rietveld refinement

Extracts much more information from powder XRD data:

- Unit cell dimensions
- Phase quantities
- Crystallite sizes / shapes
- Atomic coordinates / Bond lengths
- Micro-strain in crystal lattice
- Texture effects
- Substitutions / Vacancies

Prof. Hugo Rietveld

No phase identification!

Identify your phases first
(unknown phase → no Rietveld refinement)

No structure solution
(just structure refinement)

Needs excellent data quality!
Rietveld Refinement

Known structure model

Calculate theoretical diffraction pattern

Compare with measured pattern

Optimize structure model, repeat calculation

Minimize differences between calculated and observed pattern by least-squares method
Beginning of the refinement:
- Phase was identified correctly (peaks at the right position)
- But differences exist:
  - Peak width
  - Peak positions slightly shifted
  - Intensities
After the refinement:
- Straight difference curve (only noise)
Mathematical model for peak shape required.
Modelling the Peak Profile

Traditional («Rietveld») Approach:
Pseudo Voigt curves for $K\alpha_1$, $K\alpha_2$ and $K\beta$

$$V_P(x) = n \cdot L(x) + (1-n) \cdot G(x)$$

Lorentzian curve
$$L(x) = \frac{1}{1 + \left(\frac{x-x_0}{\omega}\right)^2}$$

Gaussian curve
$$G(x) = \exp[-\ln(2) \cdot \left(\frac{x-x_0}{\omega}\right)^2]$$

Lorentzian ($\omega = 1.0$)  
Gaussian ($\omega = 1.0$)  
Pseudo-Voigt ($n = 0.5$)
Pseudo-Voigt Curves

$n = 0.0$
$n = 0.25$
$n = 0.5$
$n = 0.75$
$n = 1.0$

$\omega = 1.0$
$\omega = 0.5$
$\omega = 0.25$
Pseudo-Voigt Curves

Fitting $n$, $\omega$ to peaks of a reference material
Pseudo-Voigt: Problems

Peaks at low 2θ angles are asymmetric.
Pseudo-Voigt curves are symmetric.
Alternatives to PV function:

- Pearson VII
- Thompson-Cox-Hastings PV
- Split PV
- PV with axial divergence
  (Finger-Cox-Jephcoat PV)
Fundamental Parameters Approach FPA

Calculate the peak profile from the device configuration

Take into account the contributions of:

- Source emission profile (X-ray wavelength distribution from Tube)
- Every optical element in the beam path (position, size, etc.)
- Sample contributions (peak broadening due to crystallite size & strain)
Fundamental Parameters Approach
If done properly:

Very good description of the peak profile
Summary: Rietveld Basics

- Calculate XRD pattern from model structure
- Minimize differences between calculated and measured pattern
- Accurate mathematical description of peak profile required:
  - Classical Rietveld approach: Fit a peak shape function (PV or similar) to reference pattern
  - Fundamental Parameters Approach: Calculate peak profile from device configuration
Refinement Strategies

Relation

Pattern Features – Structural Features
Refinement Strategy: Mismatches

- Peak Position
- Absolute Intensities
- Relative Intensities
- Peak Width

How to fix this?
Wrong peak positions:

- Unit cell dimensions
- Sample height displacement
- Zero-shift (instrument misalignment)
Refined unit cell dimensions:

Peak positions matched!
Wrong absolute intensities:

- Weight fraction (scaling)
Refined scale factor:

Intensities improved (but not fixed)!
Wrong relative intensities:

Let's try this first

- Preferred orientation
- Graininess
- Atomic species
- Atomic coordinates
- Site occupancies
- Thermal displacement parameters
Refinement Strategies

Refined texture:
Intensities fixed!
Wrong peak width:

- Crystallite size
- Micro-strain in crystal structure
- Surface roughness
Refined crystallite sizes and micro-strain:
Peak shape fixed!
Phase composition: 100% Al₂O₃ Corundum

### Starting Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell $a$</td>
<td>0.4775 nm</td>
</tr>
<tr>
<td>Unit cell $c$</td>
<td>1.2993 nm</td>
</tr>
<tr>
<td>Crystallite Size</td>
<td>Inf.</td>
</tr>
<tr>
<td>Atomic Coordinates Al</td>
<td>0.0 / 0.0 / 0.3522</td>
</tr>
<tr>
<td>Atomic Coordinates O</td>
<td>0.3062 / 0.0 / 0.25</td>
</tr>
</tbody>
</table>

### Refined

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell $a$</td>
<td>0.4760127 +- 0.0000028 nm</td>
</tr>
<tr>
<td>Unit cell $c$</td>
<td>1.2995974 +- 0.0000077 nm</td>
</tr>
<tr>
<td>Crystallite Size</td>
<td>1267 + 138 nm</td>
</tr>
<tr>
<td>Atomic Coordinates Al</td>
<td>0.0 / 0.0 / 0.3522</td>
</tr>
<tr>
<td>Atomic Coordinates O</td>
<td>0.3062 / 0.0 / 0.25</td>
</tr>
</tbody>
</table>
## Summary: Refinement Strategy

<table>
<thead>
<tr>
<th>Effect in diffraction pattern</th>
<th>Origin in crystal structure model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrong peak positions</td>
<td>Unit cell dimensions</td>
</tr>
<tr>
<td></td>
<td>Sample height displacement</td>
</tr>
<tr>
<td></td>
<td>Zero-shift</td>
</tr>
<tr>
<td>Wrong absolute intensities</td>
<td>Weight fraction (scaling)</td>
</tr>
<tr>
<td>Wrong relative intensities</td>
<td>Preferred orientation</td>
</tr>
<tr>
<td></td>
<td>Grainy sample</td>
</tr>
<tr>
<td></td>
<td>Atomic species / Substitutions / Vacancies</td>
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<tr>
<td></td>
<td>Atomic coordinates</td>
</tr>
<tr>
<td></td>
<td>Site occupancies</td>
</tr>
<tr>
<td></td>
<td>Thermal displacement parameters</td>
</tr>
<tr>
<td>Wrong peak width</td>
<td>Crystallite size</td>
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<tr>
<td></td>
<td>Micro-strain</td>
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<tr>
<td></td>
<td>Surface roughness</td>
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<tr>
<td></td>
<td>Transparency</td>
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</table>
Rietveld Refinement

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Rietveld Software Packages

Academic Software:
- Fullprof
- GSAS
- BGMN
- Maud
- Brass
- … many more¹)

Commercial Software:
- HighScore+ (PANalytical)
- Topas (Bruker)
- Autoquan (GE)
- PDXL (Rigaku)
- Jade (MDI)
- WinX^{POW} (Stoe)

Lesson 2: BGMN and Profex

¹) http://www.ccp14.ac.uk/solution/rietveld_software/index.html