Geometry, Polarization and Absorption Corrections for Two-dimensional X-ray Diffraction

Bob He  Bruker AXS, Inc.
**XRD²: What do we know about two-dimensional XRD?**

<table>
<thead>
<tr>
<th>Most recognized features of XRD² for pharmaceutical:</th>
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<tbody>
<tr>
<td>▪ High speed: $10^2$ higher than XRD with a point detector</td>
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<tr>
<td>▪ Reliable info: Integration in $\gamma$ (ring) direction</td>
</tr>
<tr>
<td>▪ Micro scale sample: Point beam and 2D pattern</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Most concerns with XRD²:</th>
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<tr>
<td>▪ Resolution and geometry defocusing</td>
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<tr>
<td>▪ Relative intensity is different from Bragg-Brentano</td>
</tr>
<tr>
<td>▪ Higher instrument cost (but much higher productivity)</td>
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This presentation interprets the differences and suggests the best use of XRD² systems.
# X-ray Applications for typical pharmaceutical samples

<table>
<thead>
<tr>
<th>XRD &amp; XRD$^2$</th>
<th>Single Crystal</th>
<th>Several Grains</th>
<th>Powder</th>
<th>Finished Product</th>
<th>Solutions</th>
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<tbody>
<tr>
<td>Qualitative Phase ID</td>
<td>✓⊗</td>
<td>✓⊗</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Quantitative Rietveld analysis</td>
<td></td>
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<td>✓</td>
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<tr>
<td>Quantitative analysis with standards</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>X-ray movie, Non-Ambient</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<td>✓</td>
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<tr>
<td>Structure solution, Indexing</td>
<td>✓</td>
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<tr>
<td>Microdiffraction/ Mapping</td>
<td>✓⊗</td>
<td>✓⊗</td>
<td>✓⊗</td>
<td>✓⊗</td>
<td>✓⊗</td>
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<td>Shape analysis</td>
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<td>✓⊗</td>
<td>✓⊗</td>
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<tr>
<td>Grain-Size det.</td>
<td>✓</td>
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<tr>
<td>%Crystallinity</td>
<td>✓⊗</td>
<td>✓⊗</td>
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<td>✓⊗</td>
<td>✓⊗</td>
</tr>
</tbody>
</table>

✓ - can be performed by either XRD or XRD$^2$

Φ – better with XRD$^2$

⊕ - accept performance and accurate results only with XRD$^2$
Bragg-Brentano-Geometry

Advantages

- Resolution
- Less expensive

Disadvantages

- Requires flat sample surface
- Requires bulky powder sample
- Slow
Soller slits are used to control axial divergence.

- In Bragg-Brentano geometry, the line focus beam can be considered as a superposition of point beams.
- All in parallel with the diffractometer plane and the same geometry condition separated by soller slit foils.
XRD²: Two-dimensional X-ray Diffraction

Advantages
- High speed
- Micro scale sample
- Virtual oscillation (large grain size & preferred orientation)

Disadvantages
- Resolution is limited by the detector PSF
- Defocusing at low angle in reflection
- Expensive
XRD²: Data Collection:

Acetaminophen powder

5 second data collection

30 second data collection
**XRD²: Diffraction vector approach**

<table>
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<th>Applications</th>
<th>Vector approaches</th>
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<td>Phase Identification:</td>
<td>Polarization and absorption correction</td>
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<td>Texture Analysis:</td>
<td>Orientation mapping angles; Data collection strategy (scheme)</td>
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<tr>
<td>Stress Measurement:</td>
<td>Fundamental equation derived by second order tensor transformation; Data collection strategy (scheme)</td>
</tr>
<tr>
<td>Crystal Size Analysis:</td>
<td>Equations for the effective volume calculation at both reflection and transmission modes.</td>
</tr>
</tbody>
</table>
Laue equation

\[ a \cdot (s - s_0) = h \lambda \]
\[ b \cdot (s - s_0) = k \lambda \]
\[ c \cdot (s - s_0) = l \lambda \]
XRD$^2$ & Powders

Bragg law

\[ n\lambda = 2d \sin \theta \]
XRD<sup>2</sup>: Diffraction pattern with both $\gamma$ and $2\theta$ information

\[
H = \frac{s - s_0}{\lambda} = \frac{1}{\lambda} \begin{bmatrix}
\cos 2\theta - 1 \\
- \sin 2\theta \sin \gamma \\
- \sin 2\theta \cos \gamma
\end{bmatrix}
\]
The incident beam is in the direction of the $X_L$ axis in the laboratory coordinates so that the unit vectors of the incident beam and diffracted beams are given respectively by:

$$s_0 = \begin{bmatrix} s_{0x} \\ s_{0y} \\ s_{0z} \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad s = \begin{bmatrix} s_x \\ s_y \\ s_z \end{bmatrix} = \begin{bmatrix} \cos 2\theta \\ -\sin 2\theta \sin \gamma \\ -\sin 2\theta \cos \gamma \end{bmatrix}$$
The diffraction vector is given in laboratory coordinates by

\[ H = \frac{s - s_0}{\lambda} = \frac{1}{\lambda} \begin{bmatrix} s_x - s_{0x} \\ s_y - s_{0y} \\ s_z - s_{0z} \end{bmatrix} = \frac{1}{\lambda} \begin{bmatrix} \cos 2\theta - 1 \\ -\sin 2\theta \sin \gamma \\ -\sin 2\theta \cos \gamma \end{bmatrix} \]

The direction of each diffraction vector can be represented by its unit vector given by:

\[ h_L = \frac{H}{|H|} = \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} = \begin{bmatrix} -\sin \theta \\ -\cos \theta \sin \gamma \\ -\cos \theta \cos \gamma \end{bmatrix} \]
The angular relationships between $X_L Y_L Z_L$ and $S_1 S_2 S_3$ are:

<table>
<thead>
<tr>
<th></th>
<th>$X_L$</th>
<th>$Y_L$</th>
<th>$Z_L$</th>
</tr>
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<tbody>
<tr>
<td>$S_1$</td>
<td>$a_{11}$</td>
<td>$a_{12}$</td>
<td>$a_{13}$</td>
</tr>
<tr>
<td>$S_2$</td>
<td>$a_{21}$</td>
<td>$a_{22}$</td>
<td>$a_{23}$</td>
</tr>
<tr>
<td>$S_3$</td>
<td>$a_{31}$</td>
<td>$a_{32}$</td>
<td>$a_{33}$</td>
</tr>
</tbody>
</table>

The transformation matrix from the diffraction space to the sample space is:

$$
\begin{bmatrix}
    a_{11} & a_{12} & a_{13} \\
    a_{21} & a_{22} & a_{23} \\
    a_{31} & a_{32} & a_{33}
\end{bmatrix}
\begin{bmatrix}
    -\sin \omega \sin \psi \sin \phi \\
    -\cos \omega \cos \phi \\
    -\cos \omega \sin \phi \\
\end{bmatrix}
\begin{bmatrix}
    \cos \omega \sin \psi \sin \phi \\
    \cos \omega \cos \phi \\
    \cos \omega \sin \phi \\
\end{bmatrix}
= \\
\begin{bmatrix}
    -\cos \psi \sin \phi \\
    -\sin \omega \cos \phi \\
    -\sin \omega \sin \phi \\
\end{bmatrix}
\begin{bmatrix}
    \cos \psi \cos \phi \\
    \cos \omega \cos \psi \\
    \sin \psi \\
\end{bmatrix}
The components of the unit vector $h_S$ in the sample coordinates $S_1S_2S_3$ is then given by

$$
\begin{bmatrix}
    h_1 \\
    h_2 \\
    h_3
\end{bmatrix}
= 
\begin{bmatrix}
    a_{11} & a_{12} & a_{13} \\
    a_{21} & a_{22} & a_{23} \\
    a_{31} & a_{32} & a_{33}
\end{bmatrix}
\begin{bmatrix}
    h_x \\
    h_y \\
    h_z
\end{bmatrix}
$$

Or in expanded form:

$$
\begin{align*}
    h_1 &= \sin\theta (\sin\phi\sin\psi\sin\omega + \cos\phi\cos\omega) + \cos\theta \cos\gamma \sin\phi \cos\psi \\
         &- \cos\theta \sin\gamma (\sin\phi\sin\psi \cos\omega - \cos\phi \sin\omega) \\
    h_2 &= -\sin\theta (\cos\phi\sin\psi \sin\omega - \sin\phi \cos\omega) - \cos\theta \cos\gamma \cos\phi \cos\psi \\
         &+ \cos\theta \sin\gamma (\cos\phi\sin\psi \cos\omega + \sin\phi \sin\omega) \\
    h_3 &= \sin\theta \cos\psi \sin\omega - \cos\theta \sin\gamma \cos\psi \cos\omega - \cos\theta \cos\gamma \sin\psi
\end{align*}
$$
XRD\(^2\): Fundamental Equation for Stress Measurement

As a second order tensor, the relationship between the measured strains and the strain tensor is given by:

\[ \varepsilon_{\{hkl\}} = \varepsilon_{ij} \cdot h_i \cdot h_j \]

the fundamental equation for stress measurement in XRD\(^2\):

\[
\begin{align*}
S_1 (\sigma_{11} + \sigma_{22} + \sigma_{33}) + \frac{1}{2} S_2 (\sigma_{11} h_1^2 + \sigma_{22} h_2^2 + \sigma_{33} h_3^2) \\
+ 2 \sigma_{12} h_1 h_2 + 2 \sigma_{13} h_1 h_3 + 2 \sigma_{23} h_2 h_3 &= \ln \left( \frac{\sin \theta_0}{\sin \theta} \right)
\end{align*}
\]
The pole figure angles \((\alpha, \beta)\) can be calculated from the unit vector components by the pole mapping equations:

\[
\alpha = \sin^{-1}|h_3| = \cos^{-1} \sqrt{h_1^2 + h_2^2}
\]

\[
\beta = \pm \cos^{-1} \frac{h_1}{\sqrt{h_1^2 + h_2^2}} \quad \begin{cases} 
\beta \geq 0^\circ & \text{if } h_2 \geq 0 \\
\beta < 0^\circ & \text{if } h_2 < 0
\end{cases}
\]
The integrated intensity diffracted from random polycrystalline materials is given by:

\[ I_{hkl} = k_I \frac{P_{hkl}}{v^2} (LPA) \lambda^3 F_{hkl}^2 \exp\left( -2M_t - 2M_s \right) \]

where:

- \( k_I \) - instrument constant;
- \( P_{hkl} \) - the multiplicity of the planes;
- \( v \) - the volume of the unit cell;
- \((LPA)\) - the Lorentz-polarization and absorption factors;
- \( F_{hkl}^2 \) - the structure factor of the crystal plane \((hkl)\) and \( \exp(-2M_t-2M_s) \) - the attenuation factor due to lattice thermal vibrations and weak static displacements.

Denotes the factors which are different between Bragg-Brentano geometry and XRD\(^2\) geometry. \( k_I \) is determined by the source, optics and detector (PPXRD-7) \((LPA)\) will be given in this presentation.
The polarization factor for Bragg-Brentano geometry with incident beam monochromator is:

\[ P_I = \frac{1 + \cos^2 2\theta_M \cos^2 2\theta}{1 + \cos^2 2\theta_M} \]

where \(2\theta_M\) is the Bragg angle of the monochromator.

The general polarization factor for the diffracted beam to point \(P\) is:

\[ P_G = \frac{(\cos^2 2\theta \cos^2 \rho + \sin^2 \rho)\cos^2 2\theta_M + \cos^2 2\theta \sin^2 \rho + \cos^2 \rho}{1 + \cos^2 2\theta_M} \]

Geometric relationship between the monochromator and detector in laboratory coordinates.
The unit vector of the diffraction vector $H_p$ and its projection on $Y_L-Z_L$ plane, $H'_p$, in the laboratory system are given respectively as:

$$H_L = \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} = \begin{bmatrix} -\sin \theta \\ -\cos \theta \sin \gamma \\ -\cos \theta \cos \gamma \end{bmatrix} \quad H'_L = \begin{bmatrix} 0 \\ h'_y \\ h'_z \end{bmatrix} = \begin{bmatrix} 0 \\ -\sin \gamma \\ -\cos \gamma \end{bmatrix}$$

The unit vector of $Y_L$ is $y_L=[0,1,0]$, then:

$$\cos \rho = \cos(h'_L \cdot y_L) = H_L \cdot y_L = -\sin \gamma$$

Therefore, $\cos^2 \rho = \sin^2 \gamma$ and $\sin^2 \rho = \cos^2 \gamma$

The polarization factor for XRD$^2$ can then be given as a function of both $\theta$ and $\gamma$:

$$P(\theta, \gamma) = \frac{(1 + \cos^2 2\theta_M \cos^2 2\theta) \sin^2 \gamma + (\cos^2 2\theta_M + \cos^2 2\theta) \cos^2 \gamma}{1 + \cos^2 2\theta_M}$$
**XRD$^2$: Sample Absorption Correction**

The absorption can be measured by the transmission coefficient:

$$A = \frac{1}{V} \int_V e^{-\mu \tau} \, dV$$

where $\tau$ is the total beam path and $A$ is the average over all the element $dV$. For Bragg-Brentano geometry, we have:

$$A_{BB} = \frac{1}{2\mu}$$

Absorption correction of flat slab:

To make the relative intensity comparable to Bragg-Brentano geometry, we introduce a normalized transmission coefficient $T$:

$$T = A / A_{BB} = 2\mu A$$
D8 DISCOVER with GADDS HTS (IµS):
Reflection & Transmission (Pharmaceutical Delight)

- Reflection mode
- Transmission mode
### Comparison: Ibuprofen

**IµS & VÅNTEC-2000 vs. Classical set-up**

<table>
<thead>
<tr>
<th>Sealed Tube</th>
<th>IµS – XRD² – focus</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 0.3 mm collimator</td>
<td>• 2mmX2mm on sample, and 200um spot focused on detector</td>
</tr>
<tr>
<td>• Sample-Detector distance 29 cm</td>
<td>• small slice for integration to obtain better resolution</td>
</tr>
</tbody>
</table>

**120 sec collection time**

**15 sec collection time**

![IµS XRD² focus diagram](image-url)

![Sealed Tube XRD² focus diagram](image-url)
**XRD$^2$: Sample Absorption Correction**

For reflection mode diffraction with a thick plate:

\[
\begin{bmatrix}
1 \\
0 \\
0
\end{bmatrix}
\begin{bmatrix}
\cos 2\theta \\
-\sin 2\theta \sin \gamma \\
-\sin 2\theta \cos \gamma
\end{bmatrix}
\]

\[s_o = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad s = \begin{bmatrix} \cos 2\theta \\ -\sin 2\theta \sin \gamma \\ -\sin 2\theta \cos \gamma \end{bmatrix}\]

and

\[
\begin{bmatrix}
-\sin \omega \cos \psi \\
\cos \omega \cos \psi \\
\sin \psi
\end{bmatrix}
\]

\[n = \begin{bmatrix} -\sin \omega \cos \psi \\ \cos \omega \cos \psi \\ \sin \psi \end{bmatrix}\]

The normalized transmission coefficient:

\[
T = \frac{2 \cos \eta}{(\cos \eta + \cos \zeta)}
\]

\[
\cos \eta = -s_o \cdot n = \sin \omega \cos \psi
\]

with

\[
\cos \zeta = s \cdot n = -\cos 2\theta \sin \omega \cos \psi \\
-\sin 2\theta \sin \gamma \cos \omega \cos \psi - \sin 2\theta \cos \gamma \sin \psi
\]
**XRD²: Sample Absorption Correction**

For transmission mode:

\[
\mathbf{s}_o = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad \mathbf{s} = \begin{bmatrix} \cos 2\theta \\ -\sin 2\theta \sin \gamma \\ -\sin 2\theta \cos \gamma \end{bmatrix}
\]

and

\[
\mathbf{n} = \begin{bmatrix} \sin \omega \sin \psi \sin \phi + \cos \omega \cos \phi \\ -\cos \omega \sin \psi \sin \phi + \sin \omega \cos \phi \\ \cos \psi \sin \phi \end{bmatrix}
\]

The normalized transmission coefficient:

\[
T = \frac{2 \sec \eta [\exp(-\mu t \sec \eta) - \exp(-\mu t \sec \zeta)]}{\sec \zeta - \sec \eta}
\]

\[
\cos \eta = \mathbf{s}_o \cdot \mathbf{n} = \sin \omega \sin \psi \sin \phi + \cos \omega \cos \phi
\]

\[
\cos \zeta = \mathbf{s} \cdot \mathbf{n} = (\sin \omega \sin \psi \sin \phi + \cos \omega \cos \phi) \cos 2\theta \\
+ (\cos \omega \sin \psi \sin \phi - \sin \omega \cos \phi) \sin 2\theta \sin \gamma \\
- \cos \psi \sin \phi \sin 2\theta \cos \gamma
\]
The integrated intensity with texture is:

\[ I_{hkl} = k_l \frac{P_{hkl}}{v^2} (LPA) \lambda^3 F_{hkl}^2 g_{hkl}(\alpha, \beta) \exp(-2M_t - 2M_s) \]

where \( g() \) is the normalized pole density function.

For the BB geometry, \( g_{hkl}(\frac{\pi}{2}, 0) \)

The texture effect for XRD\(^2\):

\[ I_{hkl}^c = \frac{I_{hkl}^m}{\langle g_{hkl}(\Delta \gamma) \rangle} \]

Correct to the B-B equivalent with a texture effect:

\[ I_{hkl}^{BB} = \frac{g_{hkl}(\frac{\pi}{2}, 0)I_{hkl}^m}{\langle g_{hkl}(\Delta \gamma) \rangle} \]

For fiber texture:

\[ \langle g_{hkl}(\Delta \gamma) \rangle = \frac{\int_{\gamma_1}^{\gamma_2} g_{hkl}[\chi(\gamma)]\gamma d\gamma}{\gamma_2 - \gamma_1} \]

and \( \chi = \cos^{-1} |h_3| \)
XRD$^2$: Summary and Suggestions

- Two-dimensional X-ray diffraction has many advantages over the conventional diffraction (speed, completeness and accuracy, micro-sample volume).
- The discrepancy between XRD$^2$ and Bragg-Brentano in geometry, polarization, absorption and preferred orientation can be interpreted and corrected.
- Fortunately, most of the discrepancies can be ignored without affecting the specific application.
- Or the corrections are already built in the software, so users do have to work on the correction details.
## XRD²: Theory, System and Applications

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<tr>
<th>X-ray Diffraction (XRD)</th>
<th>Small Angle X-ray Scattering</th>
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<td>Geometry Conventions</td>
<td>Micro Diffraction</td>
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<td>Thin Films</td>
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<td>Quantitative Analysis</td>
<td>High-Throughput Screening</td>
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<td>Texture</td>
<td>Forensics and Archaeology</td>
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<td>Stress</td>
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*Bruker AXS*
XRD²: Fundamentals, theory and applications

THE FUNDAMENTALS, THEORY, AND WIDE-RANGING APPLICATIONS OF TWO-DIMENSIONAL X-RAY DIFFRACTION

Two-Dimensional X-Ray Diffraction is proving itself as an ideal non-destructive, analytical method for measuring the atomic arrangement of materials and extracting an array of information beyond the limitations of conventional X-ray diffraction. Researchers in materials science, chemistry, physics, pharmaceuticals, and related fields will find this introductory reference invaluable in understanding and applying two-dimensional X-ray diffraction for examining a broad range of samples.

Two-Dimensional X-ray Diffraction shows how two-dimensional X-ray diffraction can be a useful tool for the examination of metals, polymers, ceramics, semiconductors, thin films, coatings, paints, biomaterials and composites for material science researches, molecular structure determination and polymorphism study for drug discovery and processing, and sample with micro volume or micro area for forensic analysis, and archeology analysis. To name just a few of the method’s applications.

The text covers:
- The fundamentals of X-ray diffraction and its extension to two-dimensional X-ray diffraction
- The geometry conventions and diffraction vector approach for diffraction data interpretation, data correction, and process algorithms for various applications
- Instrumentation technology, including the critical components, such as X-ray source and optics, two-dimensional detector, goniometer, and sample stages
- The configurations of the two-dimensional X-ray diffraction systems for various applications, such as phase identification, texture, stress, microstructure analysis, crystallinity, thin film analysis, and combinatorial screening
- Experimental examples in materials research, pharmaceuticals, materials processing, and quality control

Written by one of the pioneers in the field, Two-Dimensional X-Ray Diffraction brings readers up to speed on a fast-rising, state-of-the-art method for materials characterization.

BOB BAOPING HE is the Director of R&D and Engineering at Bruker AXS (formerly Siemens AXS). He holds a PhD in materials science from Virginia Tech and holds twelve U.S. patents.
Finalist of MRS “Science as Art” competition:
3D View of Corundum Powder Pattern
Thank You for Your Attention