Bringing Hard Radiation Back to the Lab

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Previously, on X-ray Analysis Methods...

X-ray radiation mostly used in lab instruments:

- **Cu** radiation
  - Cu Kα: \( \lambda = 0.15418 \text{ nm} \)
    - (8.05 keV, conventional resolution)
  - Cu Kα1: \( \lambda = 0.15056 \text{ nm} \) (high resolution)
Most laboratory diffractometers are dominated by Cu sources ... but why?

- Historically, Cu anode X-ray tubes were the cheapest and easiest to build.
- Because Cu sources dominate, advanced detectors and optics are often developed for Cu sources first.
  - It tends to be easier to build detector and optics for softer radiation.
  - Example: Silicon-based position sensitive detectors (PSD) provide fast XRPD data collection without a loss of resolution.
    - Si-based PSD’s are much more efficient with lower energy X-rays, such as Cu radiation, than they are with hard radiation such as Mo or Ag radiation.
New sensor materials for hybrid pixel detectors make hard radiation diffractometers faster and more versatile.

Detection Efficiency

<table>
<thead>
<tr>
<th></th>
<th>Mo radiation</th>
<th>Ag radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scintillation</td>
<td>~100%</td>
<td>~100%</td>
</tr>
<tr>
<td>Thin Si sensor (300 micron)</td>
<td>30%</td>
<td>20%</td>
</tr>
<tr>
<td>Thick Si sensor (750 micron)</td>
<td>65%</td>
<td>30%</td>
</tr>
<tr>
<td>CdTe sensor</td>
<td>~100%</td>
<td>~100%</td>
</tr>
</tbody>
</table>

- Thicker Si sensors provided some support for hard radiation, but only to a certain level.
- New CdTe-based hybrid pixel detectors are now available for laboratory diffractometers.
- Hybrid pixel detectors:
  - Function as position sensitive detectors for fast data collection
  - Offer 2D imaging capabilities
  - High dynamic range and small pixel size combine for versatile data collection

Ag radiation is 22.2 keV
Mo radiation is 17.5 keV
Opportunities for X-ray scattering research using hard radiation

Bulk analysis of metals and intermetallics

Transmission XRPD through highly absorbing materials or in-situ sample stages

Pair distribution function (PDF) measurements with higher intensity or shorter time

Computed tomography (CT) through more highly absorbing materials or thicker samples
Pair Distribution Function Analysis
Total scattering: Bragg peaks and diffuse scattering

- A perfect crystal creates sharp Bragg peaks that can be calculated and modeled purely as Bragg diffraction.
- Information about periodic structure
  - Average positions
  - Displacement parameters
  - Average occupancies
- An atom out of place or missing redistributes intensity from the Bragg peak to “diffuse scatter”, an oscillation throughout the pattern
- Information about local structure
  - Local distortions
  - Differences between different atoms on the same equivalent site
Pair Distribution Function Analysis is “Total X-ray Scattering” Analysis

COUNT EVERY X-RAY!!
EVERY X-RAY COUNTS!!
What is Pair Distribution Function (PDF) analysis?

- PDF analysis is a total scattering method

- PDF provides information about interatomic distances in materials
  - The PDF provides the probability of finding a distance R between two atoms in a material
  - Diffraction provides information about average structure
  - PDF analysis provides information about local structure

- PDF analysis can be applied to:
  - Amorphous phases (liquids, glasses)
  - Nanomaterials (nanoparticles, quantum dots, objects such as nanotubes or nanosheets)
  - Materials with disorder (semiconductors, relaxor ferroelectrics, perovskites)
What do you learn from PDF?

- Atomic distances
- Average coordination number
- Thermal/static disorder
- Particle size
Is this sample extremely nanocrystalline or amorphous?
- Both produce broadened, poorly defined scattering “humps”
- This is relevant for pharma, catalysts, nanochemistry, etc
Nanocrystals versus Amorphous

- Nanocrystalline materials have well-defined long-range order extending to the boundary of the crystallite size

- Amorphous materials have signal that slowly dampens (decays) as long-range order is lost between disordered molecules
The GaliPIX\textsuperscript{3D} can collect PDF data 10 times faster than other common detectors.

\( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3 \) data collected in **8 hours** with the GaliPIX\textsuperscript{3D}.

\( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3 \) data collected in **66 hours** with the X’Celerator.

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**Atomic PDF G(r) [Å\textsuperscript{2}]**

**Radial distance [Å]**

**Rw = 0.19**
Faster PDF data collection creates the opportunity for PDF at non-ambient conditions

- The GaliPIX\textsuperscript{3D} reduced data collection times to 4 hours per scan for C\textsubscript{60}
- Comparing room temperature to low temperature data shows the phase transition to ordered molecules at 100K

\begin{itemize}
  \item \textit{C\textsubscript{60} molecules arranged in an f.c.c. structure}
\end{itemize}
Amorphous K-based Geopolymers are produced from amorphous metakaolin, making production control difficult.

- Geopolymers are ceramic-like inorganic polymers produced at low temperature.
- Properties similar to cement without CO$_2$ emissions during production.
- The starting material (Metakaolin) and the final product (KGP) are BOTH amorphous.

J. L. Bell, J. Mater. Chem., 2008, 18, 5974–5981
PDF is one of the few techniques to distinguish between amorphous k-geopolymer and metakaolin.
Crystallization of Lactose

Counts

Spraydried 0 hours
Spraydried 24 hours
Spraydried 48 hours
Spraydried 96 hours

G(r)

Crystalline Lactose

Amorphous Lactose
Crystalline mixture: α- and β-Lactose

Multi-phase refinement (α/β) 56:44
Bulk Analysis of Metals and Intermetallics
Hybrid pixel detectors can be used for 2D diffraction measurements

- 2D diffraction is useful because XRPD is an inefficient measurement technique
  - Only a small fraction of the scattered X-rays are observed by the detector
  - A point detector scanning in an arc around the sample only observes one point on each Debye diffraction cone
  - You can increase the amount of scattered X-rays observed by using a 2D detector to image part of the Debye diffraction ring

2D diffraction patterns of sugar with varying granularity
X-ray wavelength greatly affects the X-ray penetration depth

Penetration Depth (microns) at $\omega=20^\circ$

<table>
<thead>
<tr>
<th>Material</th>
<th>Cr (2.29 Å)</th>
<th>Co (1.79 Å)</th>
<th>Cu (1.54 Å)</th>
<th>Mo (0.71 Å)</th>
<th>Ag (0.56 Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>19</td>
<td>39</td>
<td>60</td>
<td>572</td>
<td>1131</td>
</tr>
<tr>
<td>Cu</td>
<td>6</td>
<td>11</td>
<td>17</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>Steel</td>
<td>9</td>
<td>9</td>
<td>4</td>
<td>28</td>
<td>54</td>
</tr>
<tr>
<td>W</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Inconel</td>
<td>6</td>
<td>7</td>
<td>7</td>
<td>26</td>
<td>37</td>
</tr>
<tr>
<td>Ni-35Al</td>
<td>7</td>
<td>14</td>
<td>22</td>
<td>29</td>
<td>55</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>16</td>
<td>32</td>
<td>7</td>
<td>58</td>
<td>112</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>13</td>
<td>25</td>
<td>5</td>
<td>43</td>
<td>84</td>
</tr>
<tr>
<td>NdFeB</td>
<td>7</td>
<td>6</td>
<td>3</td>
<td>26</td>
<td>50</td>
</tr>
<tr>
<td>Si</td>
<td>18</td>
<td>36</td>
<td>54</td>
<td>527</td>
<td>1040</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>23</td>
<td>46</td>
<td>18</td>
<td>155</td>
<td>298</td>
</tr>
</tbody>
</table>
Greater penetration depth may improve grain statistics for bulk analysis of course grained materials

2D XRD from arc-melted Ti-Nb-Zr alloy

Co radiation

Mo radiation
Shorter wavelengths increase the number of peaks measured within a set scan range.

Diffraction from a textured Cu sample

- Co Radiation: 5 peaks
- Cu Radiation: 7 peaks
- Mo Radiation: 27 peaks
- Ag radiation: 32 peaks*
Case Study: Several research groups could not resolve the difference between W films because they only collected data to 90°

- The diffraction pattern for “ideal” tungsten is shown in black.
- For all films, the (220) peak at 87° 2theta was more intense than typical for W.
  - This correlates to [110] habit growth.
- The (222) peak at 115° 2theta varied significantly between films.
  - This correlates to [111] habit growth.
W films: Cu vs Ag radiation

- Ag radiation provides more peaks, including informative (222) peak, in a shorter scan range.
- Ag radiation penetrates completely through the W film, as indicated by the presence of the Si substrate peak.
Transmission through substrates for analysis of thick or highly absorbing films

- Penetration through W: 8 microns
- Penetration through Si: 1040 microns
Transmission Diffraction
Transmission and capillary geometry can be advantageous for some XRPD measurements.

- Capillary geometry reduces preferred orientation problems when dealing with samples with ‘difficult’ crystallite shapes (tiles, needles) like mica.
- Transmission geometry works well for small amounts of samples.
- Samples in capillaries can be sealed from air or humidity, or kept in a liquid.
- The X-ray beam cannot be overly absorbed by the sample for a transmission geometry.

\[
\begin{align*}
\text{d}^{\text{Quartz}}_{\text{[Cu]}} &= 2.0 \text{ mm } \tau = 0 \% \\
\text{d}^{\text{Quartz}}_{\text{[Mo]}} &= 2.0 \text{ mm } \tau = 17 \%
\end{align*}
\]
Reflection vs Transmission Texture Analysis

Texture Analysis of Cu foil with Ag radiation
Reflection or transmission geometry for in-situ battery research?

Reflection geometry (Cu radiation)
- Standard, well-known geometry
- Limited, angle-dependent penetration in layered materials
- Requires special cells (e.g. coin cell with Be window)

Transmission geometry (Mo radiation)
- Less well-known
- Always information from whole cell
- Standard pouch cells can be used

Transmission geometry is preferred!
In the transmission geometry, information from the whole cell is obtained! Mo radiation instead of Cu is required for good transmission through the cell.
Measurement examples

in operando cycling

3.0V

NMC 1 0 7

Cu 0 2 2

4.2V

NMC 1 0 -8

NMC 1 1 0

3.0V

NMC 1 1 3

charging

discharging

Scan number

Position [°2θ] (Molybdenum [Mo])

Counts

209.87
203.48
196.49
189.80
183.31
176.43
169.74
163.05
156.36
149.49
142.59
136.30
129.01
121.72
114.33
107.84
101.25
94.61
87.93
81.25
74.57
67.89
61.21
54.52
47.83
41.15
34.46
27.77
21.08
14.39
7.70

continuous charge/discharge C/10 rate
each line = 12min diffraction pattern
7- 55 °2θ}
XRPD analysis of materials inside a coin cell battery

- Data were collected from electrolyte and cathode while still in the coin cell battery.
- Most Lithium was in cubic form Im\(_3\)m (stable at RT).
- Li in cubic Fm\(_3\)m form was present in small amount.
  - This is not standard stable form at room temperature.
- Intermediate phases MnO\(_2\) and Li\(_{0.48}\)Mn\(_{0.89}\)O\(_2\) were visible.
- The Fe/Cr housing was only weakly observed.
CT through a coin cell battery would not be possible with Cu radiation

- CT with GaliPIX$^{3D}$ using Ag radiation

Disassembled CR2032 battery
Transmission Diffraction for In-situ Analysis in a Diamond Anvil Cell

- Diamond Anvil Cells are used to investigate matter under high pressure.
- The materials to be investigated can range from organic materials over superconducting materials to geological samples.
- The goal is to analyze either changes in chemical composition or phase transitions of the samples themselves.
- The pressure is applied by mechanical forces on the sample put between two diamonds.
In-situ High Pressure Analysis with Diamond Anvil Cell

- 2D scan with reflections from CsH$_2$PO$_4$ under high pressure together with strong reflections from diamond.
Summary

- Copper is NOT king
  - Other wavelengths of radiation are advantageous for diffraction analysis

- Traditional metallurgy analyses can use hard radiation with increased speed and versatility of hybrid pixel detector

- Hard radiation sources and detectors on laboratory instruments can duplicate many synchrotron experiments
  - Lab instruments will be slower than synchrotron
  - There are only 6 X-ray synchrotrons in the US with limited beam time

- Novel experiments can be designed with hard radiation sources and detectors
The PANalytical Award

• The PANalytical award recognizes and praises groundbreaking research that required the use of a laboratory X-ray diffraction, X-ray fluorescence or X-ray scattering instrument as the primary analytical technique.

• As such, recipients will not be limited to any brand of instrument, but rather to research that utilised an X-ray source to reach their conclusions.

• The annual award consists of a € 5 000 cash prize, a trophy and a certificate.

• http://www.panalytical.com/Events-overview/The-PANalytical-Award.htm

• Submissions for the PANalytical Award will be accepted until and including 1 December 2016. The full application form is to be completed by the first author of the journal article. Questions may be directed to award@panalytical.com
Computed Tomography (CT)
Supplemental Examples of CT analysis on a laboratory diffractometer
The GaliPIX3D expands the possibilities for CT on a multipurpose diffractometer

- Computed tomography measurements
  - A series of radiographs are collected while rotating the sample
  - The 2D detector serves as “digital film” for the radiograph
  - The 3D volume is reconstructed using a computer, revealing:
    - Exterior and interior dimensions
    - Variation in density due to phases or porosity
  - X-rays must be able to penetrate the sample with at least 5% transmission for CT measurements

X-rays must be able to penetrate the sample with at least 5% transmission for CT measurements.
Analytical examples

Cu-radiation
- CT on coal, coke and charcoal

Mo-radiation
- CT on sandstone
- CT on a Pb-glass doped mortar

Ag-radiation
- CT on a meteorite
- CT on a capacitor
- CT on a quartz glass lamp
CT from sandstone was collected using Mo radiation and the GaliPIX\textsuperscript{3D}

Radiograph with inclusions

CT-Reconstruction YZ-X
Sandstone CT revealed quartz and porosity distribution

Volume-Surface YZ-X  Quartz crystal matrix  Void distribution=3.75%
CT analysis of a quartz lamp could reveal the fractured tungsten wire

- Undestroyed W wire
- W wire only and metal parts
- Destroyed W wire
CT of Imilac Pallasite Meteorites using Ag radiation and the GaliPIX$^{3D}$

Dark blue: Fe-Ni metal matrix

Light blue/orange: Olivine single crystal
CT of Imilac Pallasite Meteorites using Ag radiation and the GaliPIX$^{3D}$

CT reconstruction of metal matrix, YZ at X=13.25
Conclusions

- Modern hard-radiation components (optics, detectors) allow for fast data collection

- The new GaliPIX^{3D} detector improves powder diffraction >10x and opens the road to entirely new applications
  - The problem of preferred orientation of mineralogical powder samples can be effectively solved by switching from Cu to “hard” (Mo, Ag) radiation
  - Computed Tomography (CT) can be collected from inorganic materials, such as geological specimens or engineered devices
  - Pair Distribution Function (PDF) data can be collected fast enough at sufficient quality to make laboratory PDF a realistic proposition

- Especially for geological or materials engineering samples, hard radiation provide new insights into materials
About PANalytical

- PANalytical is the world’s leading supplier of analytical instrumentation, software, and solutions for X-ray diffractometry and X-ray fluorescence.
- PANalytical is part of Spectris PLC, a company that develops and markets productivity-enhancing instrumentation and controls.
- PANalytical was founded as Philips Analytical in 1948 as part of Philips.
- PANalytical has over a century of experience in analytical X-rays, dating back to the Carl Müller tube factory founded in 1896.
- PANalytical pioneered the first commercial powder diffractometer in 1948.
- PANalytical has offices in more than 25 countries that cover a well-established service and sales network in more than 60 countries.
- PANalytical headquarters are situated in the Netherlands, where the production facility, main Application Competence Center, and X-ray tube factory are located.
- The North American Application Competence Center is located in Westborough, MA.

Disclaimer: PANalytical has performed this application feasibility study to the best of its ability, without giving any guarantee about the results obtained. It has been performed with the objective to illustrate, to the addressee of the report or prospective company, the potential performance and application solution that PANalytical proposes. PANalytical does not, under any circumstances, accept any liability for, or claims for damages, caused by the information that is contained in this report.
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