Microfocus X-ray Sources for Chemical and High-Pressure Crystallography

Jürgen Graf

Incoatec GmbH, Geesthacht
Incoatec GmbH: INnovative COAting TEChnologies

Incoatec GmbH @ GIZT: Geesthachter Innovation and Technology Center

History and Background

• Company founded in Jan 2002

• **Spin-off** of the Department of Thin Film Technology, **GKSS Research Center**, located in Geesthacht near Hamburg

• **Joint venture** together with **Bruker AXS**

• Development and manufacturing of **multilayer X-ray optics** by **thin film technology**

• Own **application lab** and **R&D activities**

Incoatec on the GKSS Research Center, 30 km South of Hamburg
Multilayer X-ray Optics

Capture angle $\alpha$

$$m \cdot \lambda = 2 \cdot d \cdot \sin \Theta$$

$d = 2 - 6$ nm

$\theta_m \approx 1.0^\circ$ (Cu-K$_\alpha$)

$\theta_m \approx 0.5^\circ$ (Mo-K$_\alpha$)

W/C Multilayer (TEM, Uni Kiel, Prof. Jäger)
Microfocus X-ray Sources

- Mirror should “see” the whole source:
  - Multilayer mirrors work best with microfocus X-ray sources

1.2 kW Microfocus Rotating Anode 30 W Microfocus Sealed Tube
Power loading of X-ray sources

Power loading in all solid-target X-ray sources is limited by heat dissipation.

- **Large spot**
  - Quasi-1D heat flow limits power density
  - ~0.5 kW/mm²
  - Rel. brightness: 1

- **Small spot**
  - 2D heat flow allows more efficient cooling
  - ~ 5 kW/mm²
  - Rel. brightness: <10X

- **Large or small spot**
  - Heat spread by rotation
  - >10 kW/mm²
  - Rel. brightness: <100X

Incoatec Microfocus Source – $\mu$S

- High-brilliance **microfocus sealed tube** X-ray source
- Spot size < 50 $\mu$m
- Low power: max. 30 W
- Air-cooled
- Family of 2D beam shaping Montel optics:
  - The Quazar Optics (focusing or parallel beam)
- Implemented in many new Bruker AXS instruments
- Upgrade on older diffractometers

- Cu, Cr, Mo and Ag radiation

> 100 sold worldwide

3 years warranty
$I\mu S$ for Mo-$K_\alpha$ Radiation

Beam Profile

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**Mo-$I\mu S$**

- Relative Flux: 1

**Mo-ST**

- Relative Flux: 3.0

*Beam profiles recorded with Mo-$I\mu S$ and 2 kW Mo sealed tube (graphite monochromator, 0.5 mm monocap)*
Mo-\(\mu\)S vs. 2 kW Mo-Sealed Tube

- Flux through pinholes with different diameter (calibrated PN diode)
Mo-\(\mu\)S vs. 2 kW Mo-Sealed Tube

\(P2_1, \: Z = 2, \: \mu = 0.10 \text{ mm}^{-1}\)

<table>
<thead>
<tr>
<th>Source</th>
<th>Mo-(\mu)S</th>
<th>Mo-ST</th>
<th>Mo-(\mu)S</th>
<th>Mo-ST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure [s/0.3°]</td>
<td>30</td>
<td>90</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>&lt; (I&gt;_{\text{norm}} # )</td>
<td>139</td>
<td>7.3</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>&lt; (I/\sigma &gt; )</td>
<td>15.3</td>
<td>10.7</td>
<td>37.6</td>
<td>30.4</td>
</tr>
<tr>
<td>(R_{\text{int}} )</td>
<td>0.039</td>
<td>0.062</td>
<td>0.021</td>
<td>0.023</td>
</tr>
<tr>
<td>(R_1 )</td>
<td>0.039</td>
<td>0.056</td>
<td>0.030</td>
<td>0.031</td>
</tr>
<tr>
<td>(wR2 )</td>
<td>0.092</td>
<td>0.105</td>
<td>0.082</td>
<td>0.082</td>
</tr>
<tr>
<td>N1-C9 dist. [Å]</td>
<td>1.325(3)</td>
<td>1.325(4)</td>
<td>1.323(2)</td>
<td>1.324(2)</td>
</tr>
</tbody>
</table>

\(C_{24}H_{21}N_3O_3\)

# Normalized to min/°
Conclusions:

• Mo-\(\mu\)S always superior for small crystals (< 0.15 mm)

• Comparable results for larger crystals (> 0.20 mm), often with shorter exposure times

• Precise crystal centring and scaling are essential for data quality

### Got Small Crystals? – Inorganics

- Comparison **Mo-μS** vs. **4 kW Mo RAG #** plus flat graphite monochromator

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>CuSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Size [mm³]</strong></td>
<td>0.04 × 0.04 × 0.02</td>
<td>0.07 × 0.05 × 0.05</td>
</tr>
<tr>
<td><strong>Source</strong></td>
<td><strong>Mo-μS</strong></td>
<td><strong>FR 591</strong></td>
</tr>
<tr>
<td><strong>Power [kW]</strong></td>
<td>0.03</td>
<td>4.0</td>
</tr>
<tr>
<td><strong>Exposure time [s/°]</strong></td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td><strong>&lt; I &gt;</strong></td>
<td>17.1</td>
<td>2.9</td>
</tr>
<tr>
<td><strong>&lt; σ &gt;</strong></td>
<td>1.6</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>R1</strong></td>
<td>0.084</td>
<td>0.090</td>
</tr>
<tr>
<td><strong>wR2</strong></td>
<td>0.240</td>
<td>0.241</td>
</tr>
</tbody>
</table>

# FR591 plus flat graphite monochromator, 0.3 mm collimator
All data recorded with a Nonius Kappa CCD goniometer
* Approximation for 30 W: < I > = 263.4, < σ > = 6.4
Got Small Crystals? – MOF

\[
P4_2/n, \ Z = 8
\]

\[
a = b = 23.69 \text{ Å}, \ c = 14.99 \text{ Å}
\]

\[
\mu (\text{Mo}) = \sim 0.5 \text{ mm}^{-1}
\]

“C\text{40}_2\text{H}_{24}\text{N}_8\text{Zn}”

\[
\text{Mo-}\mu\text{S}
\]

120 s/0.5°, APEX II
DX = 41 mm, 2\theta = 11°
Got Small Crystals? – MOF

- Typical diffraction patterns recorded with Cu-\(\mu\)S MX (FWHM = 0.12 mm)

Cu-\(\mu\)S MX

60 s/0.5°, APEX II
DX = 51 mm, \(2\theta = -32°\)

120 s/0.5°, APEX II
DX = 51 mm, \(2\theta = -93°\)
Got Small Crystals? – MOF

\[ \text{Size [mm}^3\text{]} \quad 0.04 \times 0.03 \times 0.01 \]

<table>
<thead>
<tr>
<th>Source</th>
<th>Cu-(\mu)S MX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure time [s/0.5°]</td>
<td>60 - 120</td>
</tr>
<tr>
<td>Total time [d]</td>
<td>~ 2.5</td>
</tr>
<tr>
<td>Resolution [Å]</td>
<td>0.88 (0.98 – 0.88)</td>
</tr>
<tr>
<td>&lt; I/(\sigma) &gt;</td>
<td>16.2 (3.4)</td>
</tr>
<tr>
<td>&lt;Redundancy&gt;</td>
<td>6.5 (2.4)</td>
</tr>
<tr>
<td>(R_{\text{int}})</td>
<td>0.0545 (0.2330)</td>
</tr>
</tbody>
</table>

\[ \text{\(P4_2/n, \ Z = 8\)} \]
\[ a = b = 23.69 \text{ Å, } c = 14.99 \text{ Å} \]
\[ \mu \text{ (Cu)} = \sim 4 \text{ mm}^{-1} \]

\[ \text{\(C_{40}H_{24}N_8Zn\)} \]
I\(\mu\)S for Ag-K\(\alpha\) Radiation

- **Ag-I\(\mu\)S:**
  - Power Settings: 50 kV, 600 \(\mu\)A
  - FWHM = 0.09 mm\(^8\); FW0.1M = 0.23 mm
  - Divergence = 5 mrad
  - At least 3x \(< I >\) of 1.5 kW Ag ST

\& Beam profiles of attenuated primary beam have been recorded @ DX = 1 cm in 4 s exposures

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## Strong Absorber – Murdochite

**Fd-3m, Z = 4**

### Crystal Structure

- **Compound:** \( \text{Cu}_6\text{PbO}_{8-x}(\text{Cl, Br})_x \)

### Data Collection Details

<table>
<thead>
<tr>
<th>Source</th>
<th>Ag-(\mu S)</th>
<th>Mo-(\mu S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu) [mm(^{-1})]</td>
<td>20.6</td>
<td>38.4</td>
</tr>
<tr>
<td>Exposure [s/0.3°]</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Max. resolution [Å]</td>
<td>0.61 (0.71 – 0.61)</td>
<td>0.77 (0.87 – 0.77)</td>
</tr>
<tr>
<td>(&lt; I/\sigma &gt;)</td>
<td>186.8 (143.5)</td>
<td>187.7 (159.7)</td>
</tr>
<tr>
<td>(&lt; I/\sigma &gt; (0.77 \text{ Å}))</td>
<td>216.6 (192.7)</td>
<td>187.7 (159.7)</td>
</tr>
<tr>
<td>Unique data</td>
<td>127 (43)</td>
<td>69 (17)</td>
</tr>
<tr>
<td>(R1, wR2)</td>
<td>0.0176, 0.0450</td>
<td>0.0184, 0.0510</td>
</tr>
<tr>
<td>(U_{eq} \text{ (O1)})</td>
<td>0.0028(4)</td>
<td>0.0048(10)</td>
</tr>
<tr>
<td>(d(\text{Pb1-O1}) \text{ [Å]})</td>
<td>2.290(3)</td>
<td>2.296(6)</td>
</tr>
</tbody>
</table>

### Other Details

- **Size [mm\(^3\)]:** 0.11 \(\times\) 0.09 \(\times\) 0.06
- **Unique Data:**
  - Cu\(_6\)PbO\(_{8-x}\)(Cl, Br)\(_x\)
  - Fd-3m, \(Z = 4\)
  - Strong Absorber – Murdochite

- **Note:**
  - Source: Ag-\(\mu S\), Mo-\(\mu S\)
  - Exposure: 10 s/0.3°
  - Max. resolution: 0.61 Å
  - \(< I/\sigma >\): 186.8 Å
  - \(< I/\sigma > (0.77 \text{ Å})\): 216.6 Å
  - Unique data: \(R1, wR2\)
  - \(U_{eq} \text{ (O1)}\): 0.0028 Å
  - \(d(\text{Pb1-O1}) \text{ [Å]}\): 2.290 Å
Strong Absorber – Murdochite

- Calculated $0kl$ precession patterns

10 s/0.3°, APEX II

Ag-$\mu$S

Mo-$\mu$S

10 s/0.3°, APEX II
## High-Pressure Crystallography

Gabapentin Heptahydrate, $P-1, Z = 2$,

$\mu = 0.12 \text{ mm}^{-1}$

### Size [mm$^3$]

<table>
<thead>
<tr>
<th>Source</th>
<th>0.25 x 0.20 x 0.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-(\mu)S</td>
<td>2 kW Mo-ST</td>
</tr>
<tr>
<td>Exposure [s/0.3°]</td>
<td>20</td>
</tr>
<tr>
<td>Resolution [Å]</td>
<td>0.90 (1.00 – 0.90)</td>
</tr>
<tr>
<td>$&lt; I/\sigma &gt;$</td>
<td>19.6 (3.2)</td>
</tr>
<tr>
<td>Unique data</td>
<td>866 (170)</td>
</tr>
<tr>
<td>$&lt;\text{Redundancy}&gt;$</td>
<td>1.5 (0.9)</td>
</tr>
<tr>
<td>$&lt;\text{Completeness}&gt;$</td>
<td>40.6 (28.9)</td>
</tr>
<tr>
<td>$R_{\text{int}}$</td>
<td>0.0306 (0.1636)</td>
</tr>
</tbody>
</table>

C$_9$H$_{17}$NO$_2 \cdot 2$ H$_2$O

Gabapentin crystal in 300 \(\mu\)m gasket of Be-free DAC

Gabapentin

F. P. A. Fabbiani, Universität Göttingen

Jürgen Graf – Karlsruhe 2010
High-Pressure Crystallography

- Comparison of Ag-\(\mu\)S vs. 2 kW Mo-ST (graphite monochr.; 0.5 mm Collimator)

Gabapentin Heptahydrate, Be-free DAC (300 \(\mu\)m gasket, 0.8 GPa), Bruker AXS APEX II goniometer

Ag-\(\mu\)S

\[
\begin{align*}
&20 \text{ s/0.3°, APEX II} \\
&\text{DX} = 71 \text{ mm, } 2\theta = 0°, \omega = 0.5°, \phi = 0°
\end{align*}
\]

Mo-ST

\[
\begin{align*}
&20 \text{ s/0.3°, APEX II} \\
&\text{DX} = 71 \text{ mm, } 2\theta = 0°, \omega = 4°, \phi = 0°
\end{align*}
\]
High-Pressure Crystallography

- *Ag vs. Mo*: Gain in resolution by “Compression” of the Reciprocal Space

Gabapentin Heptahydrate, **Be-free DAC** (300 $\mu$m gasket, 0.8 GPa), Bruker AXS APEX II goniometer

\[
\text{Ag-I}\mu\text{S} \\
\begin{array}{c}
20 \text{s/0.3°, APEX II} \\
DX = 71 \text{ mm, } 2\theta = -15°, \omega = -160.1°, \varphi = 180°
\end{array}
\]
Summary

I\(\mu\)S for Mo and Ag – High flux density in small, convergent beam

• Ideal for small and medium sized crystals

• Ideal for high-pressure experiments

• Mo-I\(\mu\)S: at least 4-fold intensity gain compared to 2 kW Mo sealed tube
  - div = 5 mrad, FWHM = 0.12 mm; FW10%M = 0.30 mm

• Ag-I\(\mu\)S: at least 3-fold intensity gain compared to 1.5 kW Ag sealed tube
  - div = 5 mrad, FWHM = 0.09 mm; FW10%M = 0.23 mm
  - Ideal for crystals showing strong absorption or extinction
  - Ideal for high-resolution data sets and de-novo phase determination using high-pressure cells

• Cu-I\(\mu\)S powerful allrounder for Small Molecules, Proteins and Material Research
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