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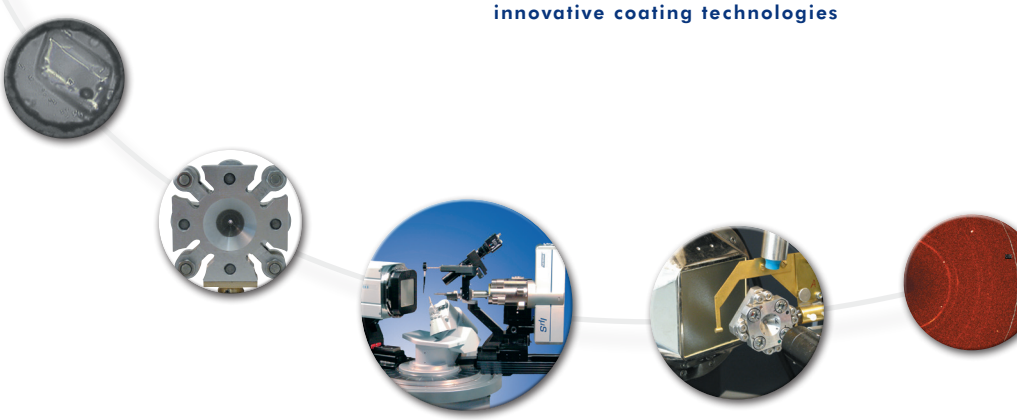

Application Note 5

High-Pressure Crystallography with Silver Radiation

Introduction

Diamond anvil cells (DAC's) are widely used for studying the properties of materials under high pressure. One of the most important applications of current high-pressure research is the study of the polymorphic behavior of molecular compounds, such as pharmaceuticals, using X-ray diffraction.
The area of reciprocal space that is accessible in a high-pressure X-ray diffraction experiment is primarily restricted by the geometry of the DAC. For a typical single crystal experiment using Mo radiation and a DAC with a half opening angle of 45°, only a small fraction of all reflections can be collected. This can be as low as 30 % for triclinic crystal structures. By using radiation with a shorter wavelength, such as Ag-K_α, a larger portion of the reciprocal space is accessible. However, because of the low intensity of conventional Ag sealed tubes, Mo sources are commonly used for high-pressure studies in the home lab.
Third generation microfocus sealed tube sources, such as the IμS (Incoatec Microfocus Source), deliver - in combination with 2D focusing multilayer mirrors - flux densities beyond that of traditional X-ray sources. With the Ag-IμS, the diffracted intensity is at least 3 times higher than that of a 1.5 kW Ag sealed tube with graphite monochromator. Therefore, the Ag-IμS is a promising alternative to classical sealed tube sources used in high-pressure crystallography.

Experimental Set-up

Comparative measurements have been performed on a Bruker AXS APEX II goniometer using the Ag-IμS and a 2 kW Mo sealed tube, which was equipped with a flat graphite monochromator and a modified 0.5 mm collimator. An APEX II detector optimized for Mo-K_α radiation was used for both experiments. The beam from the multilayer mirror of the Ag-IμS was focused on the sample position. A crystal of gabapentin heptahydrate in a Be-free DAC (half opening angle of 45°, 0.3 mm inconel gasket) was applied for both data collections using comparable data collection strategies. Both data sets were proces-

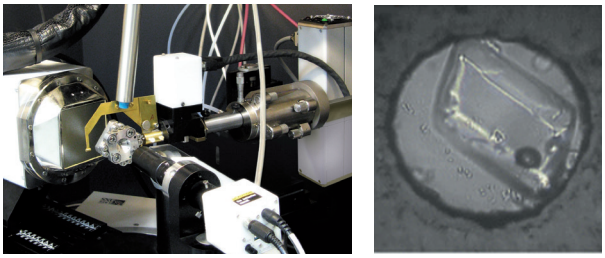

Figure 1: The Ag-IμS on a Bruker AXS APEX II QUAZAR goniometer with a Be-free DAC and modified collimator (left); gabapentin crystal (F. P. A. Fabbiani et al., CrystEngComm. 2010, 12, 2354) in a 0.3 mm inconel gasket, 0.8 GPa (right).

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sed using the Bruker AXS APEX2 software package in combination with dynamic masks generated by ECLIPSE (S. Parsons, Edinburgh).

Beam Characteristics of the Ag-IμS

The Ag-IμS delivers a focused and monochromatic beam with a FWHM of about 0.09 mm (FW0.1M = 0.23 mm) in the image focus and a divergence of 5 mrad. In contrast to the typical top-hat shaped beam profile that is produced by sources coupled to a flat graphite monochromator, the focused beam from the IμS has a Gaussian-like profile. Therefore, the maximum intensity is concentrated in the center of the beam.

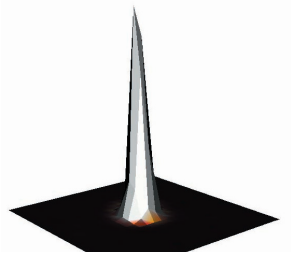

Figure2: Beam profile of the Ag-IμS

Results

The sharp beam profile from the Ag-IμS produces a high flux density at the sample position which leads to high diffracted intensities. The small beam cross-section and the short wavelength significantly reduce the background that results from scattering at the gasket of the DAC, as shown in the figure below.

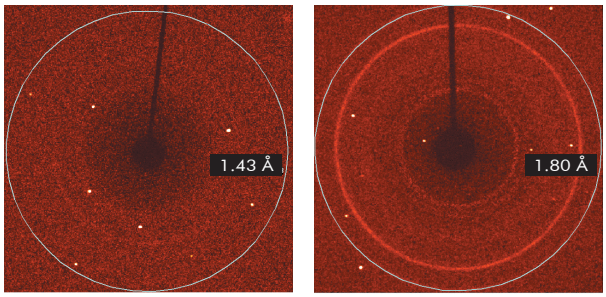

Figure 3: Diffraction patterns of the gabapentin heptahydrate crystal ($C_9H_{17}NO_2 \cdot 7H_20$; Ø ≈ 0.25 mm) grown in-situ in a Be-free DAC (2θ = 0°, ω = 0.5° (Ag) resp. 4° (Mo), φ = 0°): Ag-IμS (left), Mo sealed tube (right). Please note that the crystal moved slightly during data collection and, therefore, the two diffraction patterns do not show the same Bragg peaks.

Furthermore, a larger area of the reciprocal space is accessible with the Ag-IμS. The two diffraction patterns in Figure 4 demonstrate that a larger portion of the high resolution reflections would not be accessible in these orientations with Mo radiation, as they would be partially or completely shadowed by the exit cone of the DAC.

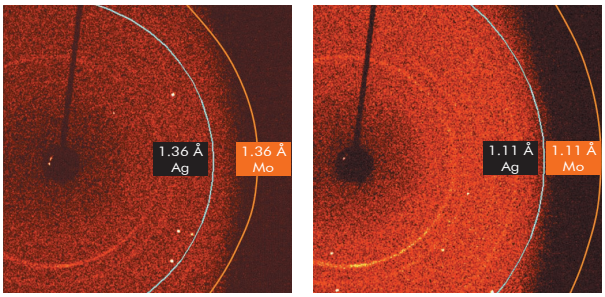

Figure 4: Diffraction patterns illustrating the gain in resolution with Ag radiation (2θ = -15°, ω = -160.1° (left) resp. -162.2° (right))

Table 1 shows the statistics for the two gabapentin data sets, which were integrated down to 0.90 Å.

Source	Ag-IμS	Mo-ST
Power [kW]	0.03	2.0
Exposure time [s/°]	20	20
<I>	368.8 (64.9)*	378.0 (61.0)*
<I/σ>	19.6 (3.2)*	18.3 (4.7)*
Unique data	866 (170)*	721 (135)*
<Multiplicity>	1.5 (0.9)*	1.1 (0.7)*
<Completeness> [%]	40.6 (28.9)*	33.7 (22.6)*
R_{int}	0.0306 (0.1636)*	0.0342 (0.1489)*
R1(I>2 σ(I))#	0.0487(630)#	0.0532 (523)#
wR2 (all)&	0.1025 (860)&	0.1232 (705)&

Table 1: Data statistics for the comparative measurement (resolution 0.90 Å (1.00 – 0.90); #, & number of reflections used).*

The Ag-IμS data set has a significantly higher completeness and contains about 20 % more unique reflections. The overall integrated intensity and the signal-to-noise ratio of the Ag-IμS data set are slightly higher compared to the Mo sealed tube data set. The results from the structure refinement (137 parameters, 100 restraints) clearly underline that the Ag-IμS prevails.

Conclusion

The Ag-IμS is a powerful X-ray source for high-pressure crystallography that outperforms classical sealed tube sources. The higher resolution and number of unique data, as well as the higher redundancy facilitate structure solution and refinement of high-pressure phases.

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