Progress in Using Short Wavelength Radiation for Chemical Crystallography

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Introduction

Third generation microfocusing sealed tube sources with graded multilayer mirrors, such as the µS (Incoatec Microfocus Source), are now well established and give a performance beyond that of typical traditional X-ray sources, at power settings far below 1 kW. In contrast to multilayer mirrors for Cu sources, the maximum angles of incidence at which a multilayer mirror reflects Mo-Kα radiation is much smaller than those for Cu radiation (\(\theta_2 = 1.1^\circ\) (Cu); 0.5° (Mo); 0.4° (Ag)). Consequently, only a small fraction of the X-ray source can be captured. With today’s deposition technology, however, high quality multilayer mirrors can be produced not only with the required precision but also with a low interface roughness and small d-spacings that reflect higher energy radiation at larger angles of incidence. Together with the latest developments of microfocus sealed tubes, this makes way for new highperformance low-power X-ray sources with shorter wavelengths.

\(\mu\S for Mo-K_α radiation

The µS for Mo radiation delivers a peak flux density of over 1 \(\times 10^9\) photons/(s mm\(^2\)) in a 0.12 mm beam (FWHM). Comparative measurements were carried out on different samples of crystals varying in size under identical conditions using a Bruker Smart Apex II and a Nonius Kappa CCD diffractometer. For a proper comparison, reference data sets of the same crystals were also recorded with the same diffractometers equipped either with a 2 kW Mo sealed tube and a graphite monochromator or with a FR591 Mo rotating anode and a graphite monochromator. Table 1 summarizes details of two selected comparative measurements.

\(\mu\S for Ag-K_α radiation

The µS for Ag radiation delivers a peak flux density of about 1 \(\times 10^8\) photons/(s mm\(^2\)) (@ 30 W) in a beam with a FWHM of 0.09 mm, which is ideal for small crystals, especially for those of absorbing materials. The advantage of such short wavelength radiation is the reduced absorption and extinction, as well as the “compressed” reciprocal space thus gaining access to a larger range of d-spacings at a fixed 2θ setting. Table 2 shows the comparison of two single crystal diffraction experiments with the Ag-µS and the Mo-µS on organic and inorganic samples.

High-pressure crystallography

The larger reciprocal space that is accessible at a fixed 2θ setting and the small beam cross-section of the µS models for Mo and Ag radiation makes them an interesting alternative to sealed tube sources for diffraction studies on single crystals and powders using diamond anvil cells (DAC). The defined beam from the focusing optics reduces the background from the scattering at the gasket, as shown in Figure 3, thus improving the signal-to-noise ratio. Table 3 shows a comparison of two data sets measured with an Ag-µS and with a 2 kW Mo sealed tube. The sample used for this comparison was a single crystal of an organic compound grown in-situ in a Be-free DAC. The higher resolution and quantity of unique data, as well as the higher redundancy facilitate structure solution and refinement of high-pressure phases.

Table 1: Details of the comparative measurements on gabapentin heptahydrate in a DAC (* values for highest resolution shell 1.00 - 0.90 Å).

Table 2: Details of the comparative measurements with the Ag-µS and the Mo-µS.

Table 3: Details of the comparative measurements on gabapentin heptahydrate in a DAC (* values for highest resolution shell 1.00 - 0.90 Å). Pictures and data courtesy of Dr. F. P. A. Fabbiani, University of Göttingen, Germany.

Conclusion

The Ag-µS and the Mo-µS are powerful and cost-effective alternatives to classical sealed tube sources for diffraction studies at high resolution and, due to the small FWHM of the Ag-µS and the Mo-µS, they make them an interesting alternative to sealed tube sources for high-pressure and small-angle X-ray scattering studies.

Figure 1: Calculated precision plots of the NiO layer for an organic sample: Mo-Sealed Tube (67 s/°, left), Mo-µS (16 s/°, right).

Figure 2: Comparison of the residual density and the resolution limit (@ 2θ = 31°; ΔX = 51 mm) for C\(_6\)H\(_9\)N\(_3\)O\(_3\) SiO\(_2\): Ag-µS (200 s/°, left), Mo-µS (77 s/°, right).

Figure 3: Diffraction patterns of a gabapentin heptahydrate single crystal in a DAC: top: comparison of Ag-µS (20 s/°, left) against Mo-µS (20 s/°, right), below: diffraction patterns recorded with the Ag-µS illustrating the gain in resolution with Ag-radiation.

Figure 4: Comparison of the residual density and the resolution limit (at 2θ = 31°; ΔX = 51 mm) for C\(_6\)H\(_9\)N\(_3\)O\(_3\) SiO\(_2\): Ag-IµS (200 s/°, left), Mo-IµS (77 s/°, right).

Table 1: Selected details for the comparative measurements with the Mo-IµS.

Table 2: Details for the comparative measurements with the Ag-IµS and the Mo-IµS.

Table 3: Details of the comparative measurements with the Ag-IµS and the Mo-IµS.