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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 IμS (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 or Ag-Kα radiation is much smaller than those for Cu radiation (θ_m: 1° (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 high-performance low-power X-ray sources with shorter wavelengths.

IμS for Mo-Kα radiation

The IμS for Mo radiation delivers a peak flux density of over $1*10^9$ photons/(s mm²) 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 with a 0.5 mm monocapillary or with a FR591 Mo rotating anode and a graphite monochromator. Table 1 summarizes details of two selected comparative measurements.

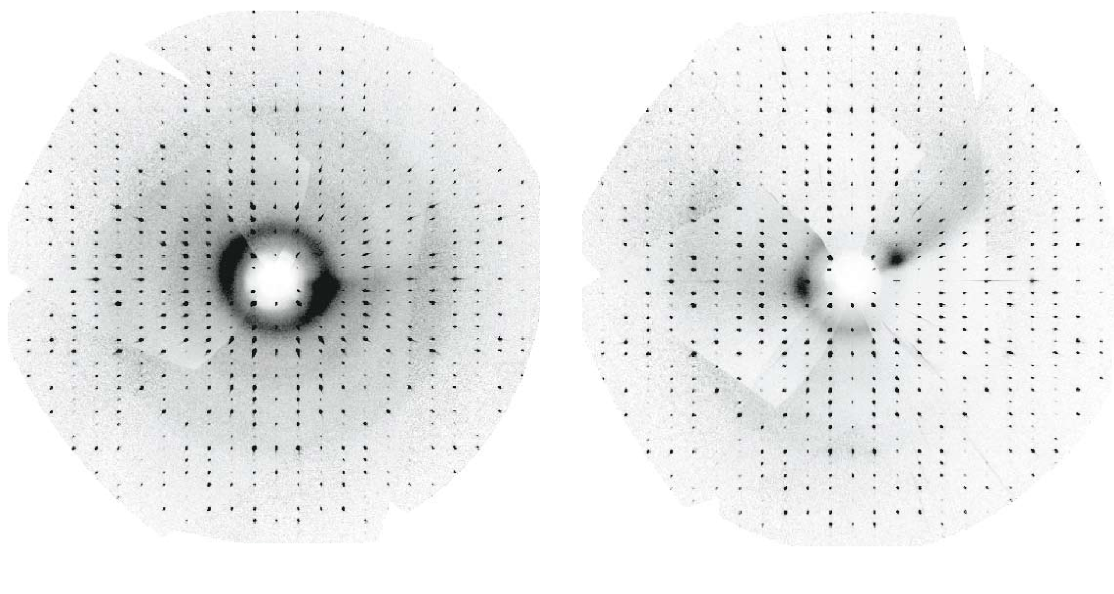

Figure 1: Calculated precession plots of the *hk*0 layer for an organic sample: Mo-Sealed Tube (67 s/°, left), Mo-IμS (16 s/°, right)

Source	IμS	Sealed Tube	IμS	FR591
Sample	$C_{24}H_{21}N_3O_3$		SiO_2	
Size [mm³]	0.10 x 0.05 x 0.05		0.02 x 0.04 x 0.04	
Detector	APEX II		KAPPA CCD	
Software	SAINT / SADABS		DENZO / SCALEPACK	
Power [kW]	0.03	2.0	0.03	4.0
Exposure time [s/°]	100	300	150	150
$<I>_{norm}$	139	19	17.1	5.9
$<I/\sigma>$*; $<\sigma>$**	15.3*	10.7*	1.6**	1.1**
*R*1 (all); *wR*2 (all)	0.039; 0.092	0.056; 0.105	0.084; 0.240	0.090; 0.241

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

IμS for Ag-Kα radiation

The IμS for Ag radiation delivers a peak flux density of about 1 x 10^9 photons/(s mm²) (@ 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-IμS and the Mo-IμS on organic and inorganic samples.

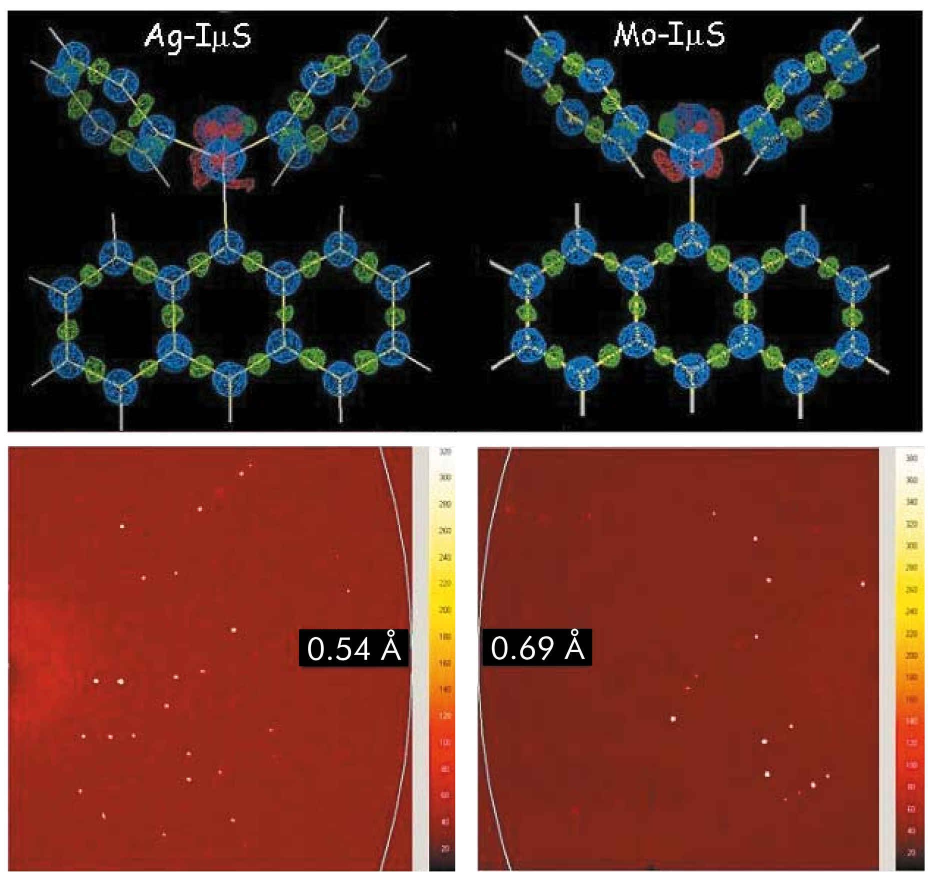

Figure 2: Comparison of the residual density and the resolution limit (at 2θ = 31°; DX = 51 mm) for $C_{26}H_{19}PS$: Ag-IμS (200 s/°, left), Mo-IμS (77 s/°, right)

Source	Ag-IμS	Mo-IμS	Ag-IμS	Mo-IμS
Sample	$C_{26}H_{19}PS$		$Cu_6PbO_{8-x}(Cl,Br)_{2x}$	
Size [mm³]	0.14 x 0.14 x 0.14		0.12 x 0.09 x 0.06	
μ [mm^{-1}]	0.14	0.25	20.6	38.4
Exposure time [s/0.3°]	60	6 / 40	10	10
Max. resolution [Å]	0.54	0.69 / 0.50	0.61	0.77
Unique data	25679	31921	127	69
$<I/\sigma>$	22.3	33.8	158.9	137.9
$<I/\sigma>$ (to 0.80 Å)	49.6	70.9	181.4	140.1
*R*1 (all); *wR*2 (all)	0.040; 0.115	0.034; 0.094	0.0196; 0.0525	0.0197; 0.0536

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

High-pressure crystallography

The larger reciprocal space that is accessible at a fixed 2θ setting and the small beam cross-section of the IμS 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 a Ag-IμS 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.

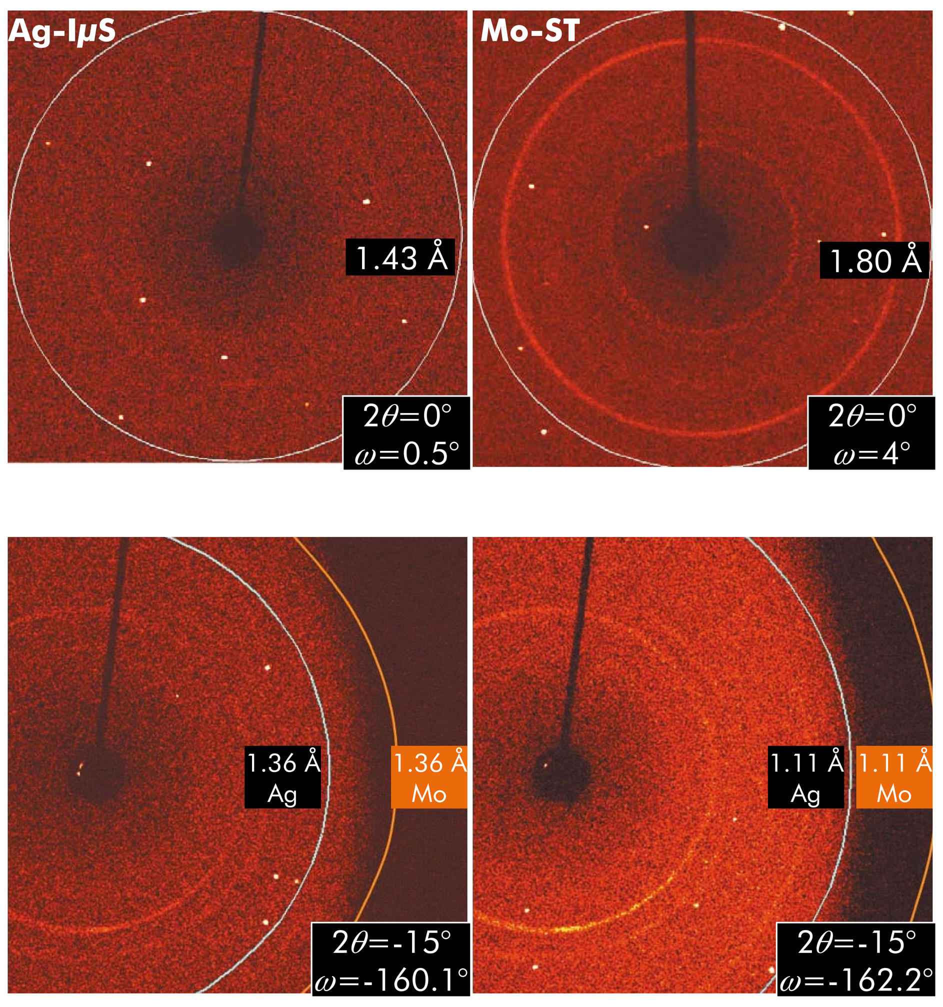

Figure 3: Diffraction patterns of a gabapentin heptahydrate single crystal in a DAC: top: comparison of Ag-IμS (20 s, left) against Mo sealed tube (20 s, right); below: diffraction patterns recorded with the Ag-IμS illustrating the gain in resolution with Ag-radiation.

Source	Ag-IμS	Mo-ST
Power [kW]	0.03	2.0
Exposure time [s/0.3°]	20	20
Unique data	866 (170)*	721 (135)*
Redundancy	1.5 (0.9)*	1.1 (0.7)*
Completeness	40.6 (28.9)*	33.7 (22.6)*
$<I>$	368.8 (64.9)*	378.0 (61.0)*
$<I/\sigma>$	19.6 (3.2)*	18.3 (4.7)*
R_{int}	0.0306 (0.1636)*	0.0342 (0.1489)*
*R*1, *wR*2	0.0487 (0.1025)	0.0532 (0.1232)

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-IμS and the Mo-IμS 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 focused beam, for high-pressure studies. The defined beam profile of the focusing optics reduces the background from the scattering at the gasket and, therefore, improves the signal-to-noise ratio. The Mo-IμS gives a performance comparable to a traditional 4 kW rotating anode with a graphite monochromator, while the diffracted intensity of the Ag-IμS is about 3 times higher than that of a 1.4 kW Ag sealed tube with a graphite monochromator.

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