

Small Molecule Analysis GeniX Cu High Flux

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Reflecting Future Technology

Application Note n° AN-G1

Abstract

Although Mo K α radiation is a kind of standard for small molecule analysis, a number of applications in chemical crystallography are best treated with Cu K α radiation.

This application note shows that accurate data can be collected on weakly diffracting and/or very small crystals from organic molecules and complicated inorganic structures with the combined GeniX- STOE IPDS2T.

This experiment was conducted on the GeniX CU High Flux beam delivery system which is installed at EPFL-Lausanne on a STOE IPDS2T diffractometer.

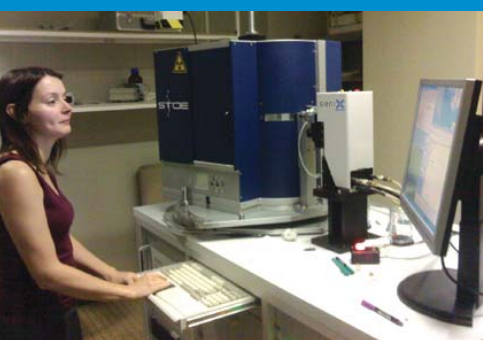


Fig. 1 : The combined GeniX-IPDS2T setup installed at EPFL-Lausanne.

Chemical crystallography with the GeniX Cu High Flux and the STOE-IPDS2T diffractometer

Data courtesy of K. Schenk, C. Besnard and M. Schiltz, Lab. de Cristallographie, EPFL, Switzerland.

Introduction

Although Mo K α radiation is widely used in routine small molecule structure determination, a number of applications in chemical crystallography are best treated with Cu K α radiation. These include studies on weakly diffracting and/or very small crystals, measurements on partially disordered or fibrous samples, absolute structure determination and others. To evaluate the suitability of the STOE image-plate system IPDS2T equipped with a GeniX CU High Flux x-ray generator manufactured by XENOCS for applications in chemical crystallography, we have carried out trial measurements on two samples that are commonly used for testing purposes.

1. Data collection on YLID (C₁₁H₁₀O₂S)

YLID is a small-molecule standard widely used in single-crystal diffraction. It belongs to the orthorhombic system so that the refinement of the cell angles provides a good check of the alignment, geometric accuracy and general performances of a laboratory diffractometer setup.

The GeniX microbeam system was operated at 50 kV, 1 mA. The circular image plate (scanned surface: 170 mm radius) was positioned at a distance of 40 mm from the sample with a 60° 2-theta offset, thus allowing data to be collected to minimum Bragg spacings of 0.83 Å. A highly redundant data set, consisting of three 0–180° omega-scans recorded at three different phi angles (0°, 45° and 90°) was collected. The data comprise a total of 540 frames, each corresponding to a 1° omega rotation and an exposure of 60 seconds. The frames were indexed and integrated with the XArea software from STOE. Data reduction (scaling and merging) was carried out with the program XRed from STOE. For comparison, reference data on the same sample were also collected on a sealed tube Mo K α source in our laboratory, using an IPDS2 diffractometer from STOE. Structure refinement was carried out with SHELXL.

Refined cell parameters are reported in Table I for both measurements, along with available reference data (G.L.Bryant¹). Data reduction and structure refinement statistics are reported in Table II. The data collected on the IPDS2T / GeniX system are slightly better than the literature values that were obtained from one of the best reputed Cu K α instruments on the market (Bryant¹). Most certainly, they would be even better had we been given a better mounted and shaped test-crystal. The comparison of the two measurements ascertains the superior intensity of the Xenocs/GeniX source. For roughly the same Rs value the exposure time with Mo radiation (53kV,43mA) had to be five times bigger than that with the microsource.

Table I : Cell parameter refinement of YLID.

nc: non-constrained refinement ; c: constrained refinement (i.e. cell angles are fixed at 90°)

	a / Å	b / Å	c / Å	$\tilde{\alpha}$	$\tilde{\beta}$	$\tilde{\gamma}$
IPDS2T + GeniX CU High Flux	nc 5.9603(5)	9.0354(5)	18.3859(12)	90.036(5)	90.033(6)	90.036(6)
	c 5.9677(4)	9.0336(5)	18.3883(11)			
IPDS2 + sealed tube Mo K α	nc 5.9606(5)	9.0337(7)	18.3818(15)	90.014(7)	90.010(6)	90.027(6)
	c 5.9606(3)	9.0338(5)	18.3796(15)			
Reference (Bryant) Cu K α	c 5.96260(10)	9.03940(10)	18.3890(2)			

2. Data collection on Zeolite LTA {Na₁₂[Al₁₂Si₁₂O₄₈] · 27 H₂O}₈

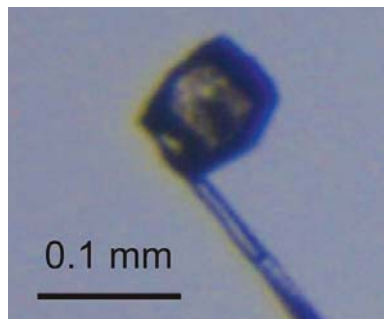


Fig. 2 : Picture of the small crystal of Zeolite A that was used to collect data.

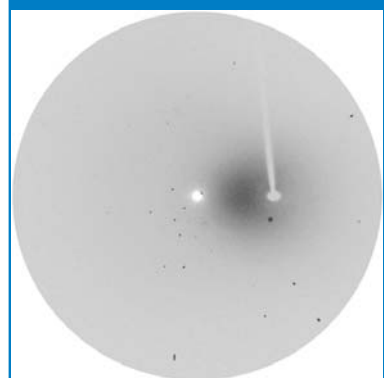


Fig. 3 : Diffraction frame recorded on a crystal of Zeolite A. Scan width : 1° (omega), exposure time : 90 sec, Crystal-detector distance : 70 mm, 2-theta offset : 45°.

Zeolites are aluminosilicate minerals. Their porous molecular structures have made them very attractive materials for a wide range of industrial applications including molecular sieves, catalysts and detergents.

Zeolite A exhibits the LTA (Linde Type A) structure. The topological unit cell of symmetry is doubled by the chemical partition between Al and Si, giving rise to a supercell with unit-cell parameters of 24.572 Å. The doubling of the unit-cell generates very weak superlattice reflections.

The STOE image plate system IPDS2T, equipped with a GeniX microbeam system from XENOCs was used to collect diffraction data on a small crystal (Fig. 2) of Zeolite A. The GeniX was operated at 50kV, 1mA and an exposure time of 90 seconds per 1° omega-rotation allowed to record data with good statistics (Fig. 3). The image plate was positioned at a distance of 70 mm from the sample and was offset in 2-theta by 45°. Three omega scans were collected at different phi angles producing highly redundant data. Data collection parameters and data reduction statistics are reported in Tables III and IV. In a reciprocal lattice reconstruction from the experimental data (Fig. 4), The superlattice reflections are clearly visible, thus substantiating the quality of the data. The framework structure (Fig. 5) could be solved using SHELXS with default parameters.

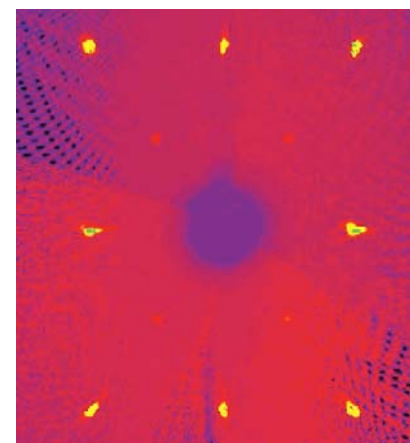


Fig. 4: Reciprocal lattice reconstruction of the (1, 1 0) plane from experimental data. The weak superlattice reflections are clearly visible.

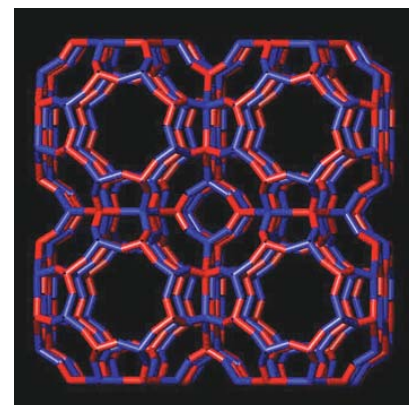


Fig. 5 : The framework structure of Zeolite A with Si-O And Al-O bonds colored respectively in blue and red.

Table II : Data reduction and structure refinement statistics for YLID.
SAV: Systematic absence violations, IEq: Inconsistent Equivalents.

	d _{min} / Å	R _{int}	R _s	SAV	IEq	R _i	Flack par.
IPDS2 + sealed tube Mo Kα	0.5717	0.0255	0.0242	0	3	0.0363	-0.005(61)
IPDS2T + GeniX CU High Flux	0.8354	0.0629	0.0362	0	291	0.0292	-0.019(21)
Reference (Bryant et al.) Cu Kα	0.9020	0.0627	0.0353	0	285	0.0240	-0.011(18)
Reference (Bryant et al.) Cu Kα	0.9020	0.0644	0.0343	13	218	0.0277	-0.022(19)

Table III : Data collection and reduction statistics for Zeolite A.

Refined unit cell Parameter: a / Å	24.5719 (0.0009)
Space group	Fm -3 c
Number of measured reflections	16249
Number of unique reflections	881
R _{int}	0.0575
Absorption correction transmission factors	Face-indexed 0.41 0.51
R _{int} after absorption correction	0.0545

Table IV : Data quality indicators for Zeolite A.

d _{min} / Å	14.19	2.60	1.90	1.62	1.42	1.31	1.21	1.13	1.06	0.99	0.93
Mean I/sd(I)	28.12	12.48	16.43	18.12	15.40	15.01	7.11	5.34	5.76	3.25	
R _{int}	0.048	0.076	0.068	0.054	0.043	0.040	0.050	0.054	0.072	0.152	
Completeness / %	98	100	100	100	100	100	100	100	100	100	

Conclusion

Accurate data were collected on samples from organic molecules and complicated inorganic structures with the combined GeniX-IPDS2T setup installed at EPFL-Lausanne.

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