New Possibilities for X-ray Diffractometry

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Abstract

During the last years the instrumentation for X-ray metrology has improved remarkably. There are numerous new solutions for all components such as sources, optics and detectors.

We will present a new development of X-ray sources which we deliver in custom-built modules: the IµS^{TM} – Incoatec Microfocus Source. The IµS^{TM} is a high-brilliance X-ray source incorporating a 30 W microfocus sealed tube together with an high-performance graded multilayer X-ray optics, named “Quazar”. The brilliance of IµS^{TM} is comparable to that of a traditional rotating anode system running at 4.0 to 5.4 kW. In addition to that, IµS^{TM} offers numerous benefits, such as no moving parts, a long lifetime without maintenance, and air-cooling. It can be integrated into all common X-ray analytical systems and is available for Cu or Mo radiation. The new Quazar optics deliver parallel or focused beams with different customized flux densities, divergencies and spot sizes. With IµS^{TM}, data quality and ease of operation are immensely improved in X-ray analytical applications, such as biological and chemical crystallography, microdiffraction, and small angle X-ray scattering (SAXS).

Introduction

X-ray diffraction (XRD) is a very popular non-destructive technique for analyzing a wide range of materials, including fluids, polymers, catalysts, pharmaceuticals, thin-film coatings, metals, minerals, ceramics and semiconductors. Throughout industry and research institutions, XRD has become an indispensable method for materials investigation and quality control. Applications include qualitative and quantitative phase analysis, structure and relaxation determination, texture and residual stress investigations, phase transitions and reactions under a controlled environment, micro-diffraction, size distributions in nano-materials, lab- and process automation, and high-throughput polymorph screening.

The main hardware components of laboratory X-ray diffractometers include an X-ray source, optics for monochromatization and shaping of the X-ray beam, a sample stage usually on a goniometer, and an appropriate detector. In this contribution, we will present a new set-up for the beam delivering system, the source plus the optics. The Incoatec Microfocus Source IµS^{TM} has a small spot of below 50 µm and a very high power load on the anode. The small size of the source is ideal for the use of 2-dim shaping X-ray optics. Laterally graded multilayer mirrors collimate the flux emitted from the source focus within a large solid angle and reflect a monochromatic beam onto the sample .

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Parallel beam geometries are always needed for measurements which cannot accept a large divergence. Typical applications for a parallel beam geometry are X-ray reflectometry, small angle scattering and high-resolution measurements of lattice constants, e.g. for stress measurements. Focused geometries are used when analyzing very small and weakly scattering samples where every photon is needed. This is the case in single crystal diffractometry with larger molecules and proteins. These samples usually contain only light elements such as C, O, P and S and are characterized by large lattice constants. The outer dimensions of the crystals typically range from 10 to 300 µm. Ideally, the X-ray beam is shaped to match the dimensions of the single crystal. If the beam is too small, only a small and - in the case of a sample rotation - alternating part of the crystal is focused on by the beam and contributes to the diffractogram. If the beam is larger than the crystal, the excess part of the beam contributes only to the background diminishing the quality of the measurement.

In the following section we will outline the basic physics behind the source and the optics. We will summarize how the main properties of the X-ray beam are affected by the optics. In the section ‘Incoatec Microfocus Source IµS’ we will present the common solutions for the X-ray generation in home-lab instruments. The second part will highlight the design, the production and the characteristics of the 2-dim shaping multilayer optics. We will conclude this section with a summary of the technical details of the IµS. The last section ‘Applications’ will show selected examples of the gain in performance with the new IµS$^{\mathrm{TM}}$ system. Selected data from single crystal diffraction on small molecules and proteins and from small angle scattering will outline the data quality that can now be obtained with just 0.03 kW.

The physics

Typical X-ray sources in lab instruments produce a broad spectrum of photon energies. The source spectrum consists of characteristic emission lines which are defined by the anode material, and of the continuous spectrum of the Bremsstrahlung which is dependent on the generator settings. In diffractometry only a small range of the characteristic radiation is usually used and the beam needs to be monochromatized. The most widespread photon energies are Cu Kα at 8.04 keV and Mo Kα at 17.45 keV.

The beam of an X-ray source is characterized by the flux density Φ (counts/s/mm^2) and the convergence angle Ω (mrad). The brilliance of an X-ray source is $B = \Phi / (\Omega_x \times \Omega_y)$, with x and y as the two axes perpendicular to the propagation direction of the X-ray beam. For a symmetrical spot the brilliance is

$$B = \Phi / \Omega^2 \quad [\mathrm{counts/s/mm^2/mrad^2}] \qquad (1)$$

which is flux density divided by the convergence/divergence. The Liouville theorem declares that B is a constant of the source and can not be increased without increasing the power load on the anode. If an optical element reflects the beam, the brilliance would only remain constant in the ideal case, that is when the reflectivity R of the optics is 100%. In reality, the brilliance is diminished by the true reflectivity R of the optics that is usually ≤ 90 %.

Therefore, the source is an important contributor to the performance quality of an X-ray instrument. The source should offer the best possible brilliance. The beam shaping optics should, then, perform without significant loss to preserve the source brilliance. As stated in the introduction, the beam cross-section should match the sample diameter. The best way to achieve this is to focus the beam onto the sample. Otherwise, the beam needs to be shaped by using slits or pinholes which diminish the total flux on the sample.

For a high performance optics the main requirements are best possible reflectivity and precise beam shaping to satisfy the requirements of the experiment on the spatial resolution and on the total flux density. Furthermore, most modern X-ray analytical methods need a monochromatic beam. Multilayer mirrors have prooved to be the best optical elements in fulfilling the above demands on monochromaticity as well as flux [1]. These mirrors consist of multilayer films which reflect X-rays by the effect of Bragg diffraction. The modified Bragg equation for multilayers is:

$$\lambda = 2d\sin\theta \cdot \left(1 - \frac{\delta}{\sin^2\theta}\right) \qquad (2)$$

with wavelength λ [nm], lattice constant d [nm], angle of incidence θ and the dispersion δ.

The single layers, each one only a few nanometers thick, are mostly amorphous. The multilayer may consist of up to several hundred layers. A high reflectivity is obtained when the multilayer materials have a high density difference and simultaneously a low absorption. When choosing multilayer materials, their optical constants δ and β are tuned to the application by the simulation of the optical properties of the multilayer thin film.

In addition, the optimum layer thickness profile and substrate shapes are determined. A parabolic mirror is required for obtaining a parallel beam, whereas elliptical mirrors are necessary for focusing optics (see fig. 1). In order to shape the X-ray beam in two dimensions, two parabolical or elliptical mirrors are arranged in a 90° side-by-side geometry. The beam is shaped by double reflection. At Incoatec, this type of optics is called Montel optics [2].

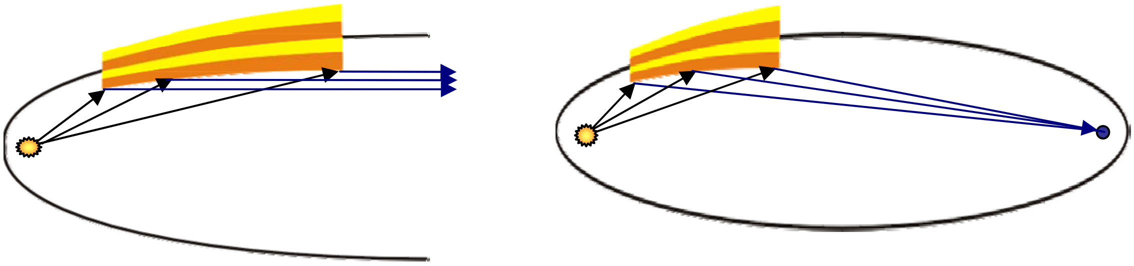


Figure 1: Principle of laterally graded multilayer optics - left a parabolic shape for a parallel beam, right an elliptical shape for focusing

At Incoatec we use ray tracing methods to calculate all beam properties along the beam propagation direction from the source to the sample [3]. This enables us to optimize the beam characteristics to match the requirements of the user and allows for the development of sophisticated multilayer optics. Ray tracing is a Monte-Carlo simulation method where statistically generated X-rays are transmitted through the virtual optical system. For realistic simulations, it is essential to take the properties of the source correctly into account. In particular, the extended source dimensions sometimes lead to results that differ significantly from performance estimations based on ideal point-source assumptions.

Incoatec Microfocus Source IµS™

Generally, there exist three different types of X-ray sources for diffractometry: sealed tubes (ST), microfocus low-power tubes (µS) and rotating anode generators (RAG). In comparison, the water-cooled sealed tubes are inexpensive and need very low maintenance. The most brilliant sources with the best performance, but also with the highest price and significant maintenance are the latest generations of rotating-anode generators. They offer the highest brilliances. The performance of the newest microfocusing rotating anode generators which still run at about 2.7 kW is comparable with synchrotrons of the 2nd generation.

For IµS we decided to incorporate the newest type of microfocus low power sources, which offers a small source spot in the range of below 50 µm. The X-rays are produced very effectively with a high power load in that small spot. This low power tube needs a generator with only 30 W continuous maximum power. The complete source is, therefore, operating air-cooled by a small fan and does not require an additional cooling medium. Figure 2 shows a picture of the IµS system.

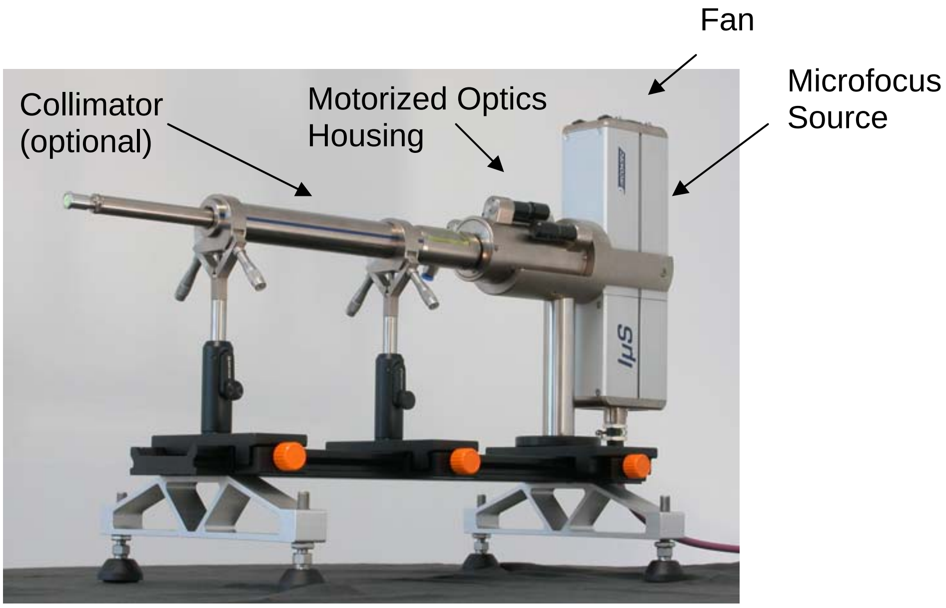


Figure 2: Incoatec Microfocus Source IµS™ – the optics are mounted in a housing which can be evacuated to prevent radiation damage of the multilayer and to minimize air scattering

The beam profile of the source is shaped in 2 dimensions by the newest types of Montel mirrors, the so-called Quazar optics. Using ray tracing calculations they are optimized with respect to the source profile and to the application of the users.

Basically, three types of Quazar Optics are offered for the following purposes: focusing-beam optics which deliver as much flux as possible in a small spot with a moderate divergence (a), parallel-beam optics with low divergence with a larger beam size (b), and hybride optics that focus in one dimension and that render a parallel beam perpendicular to it (c).

Type (a) is called SCD and is mainly used for single crystal diffraction. Type (b) is called LD and offers a beam with low divergence, for applications like small angle scattering. These low divergence models are available with three different divergences: 1.0 mrad, 0.5 mrad, and 0.35 mrad. Other models can be made upon request. Since brilliance is not a function of the optics, equation (1) can be used to calculate the flux density differences between the models with different divergences. With equation (1) it can be seen that the flux densities of the LD models are typically 1-2 orders of magnitude lower than the flux densities of the SCD models. The integral flux is then a function of the cross section of the beam. Since most low-divergence applications such as microdiffraction do not require large beam cross sections, the flux of the LD models is usually significantly smaller than the flux of the SCD models.

	Flux (counts/s)	Focal Spot Diameter (µm)	Divergence (mrad)	Distance between source and image focus (mm)
SCD Cu	> 3 *10^8	250	5	600
SCD Mo	> 1 *10^7	100	5	400
			Divergence (mrad)	Configuration
LD Cu - HR			0.35	High resolution
LD Cu - MR			0.5	Medium resolution
LD Cu - LR			1	Low resolution

Table 1: Technical details for different types of IµS

In tab. 1 the main technical details are summarized. IµS is currently available for Cu and Mo radiation. The high flux and the stable beam allow for high performance measurements for SCD or SAXS.

Applications

In this section we will present selected results that show the high performance of IµS^{TM} in comparison to conventional sources used in the home-lab.

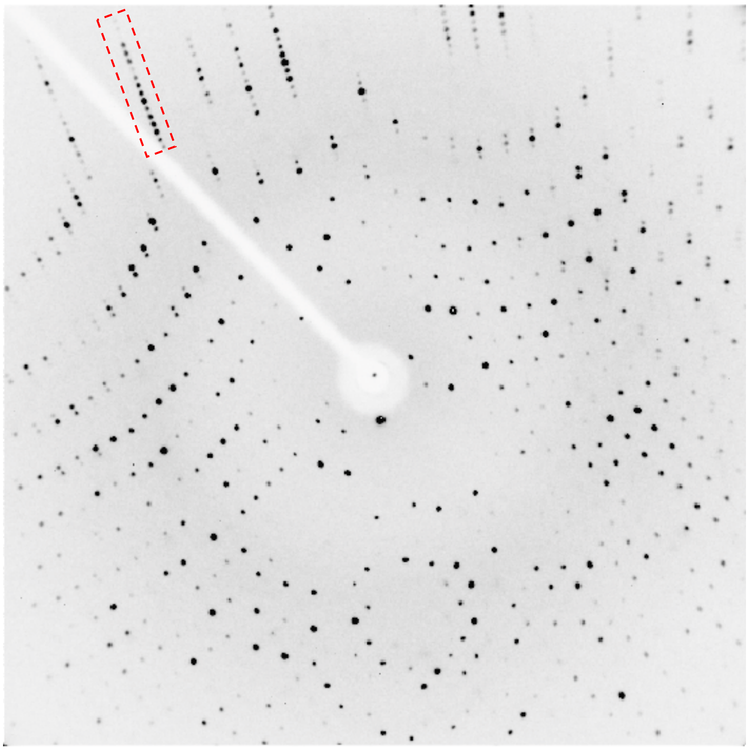
Structure determination on small and weakly scattering crystals requires a highly intense X-ray beam with a moderate divergence. These crystals consist of simple organic molecules and large macromolecules, such as proteins. In protein and small molecule crystallography, Cu-Kα is, usually, used for radiation. We have, therefore, tested IµS^{TM} in the SCD Cu configuration. This set-up delivers a total flux that is about 1.5 to 3 times higher than that of a traditional rotating anode generator combined with a first generation Montel multilayer mirror which is the commonly used source in home-lab protein crystallography experiments and five times higher than that of a sealed tube Montel multilayer combination. In our experimental set-up, the X-ray beam is focused onto the sample.

The sweet protein thaumatin is a standard reference sample in protein crystallography. We have investigated two thaumatin crystals with different dimensions. The basic statistical quantities of the two data sets are shown in table 2.

crystal size [μm]	400×250×100	150×100×80
resolution ($I > 2\ \sigma(I)$) [Å]	1.41	1.59
Limit of anomalous signal [Å]	2.3	2.8
$<I/\sigma>$	43.4 (4.1)	22.9 (2.8)
Mean redundancy	26.8 (11.4)	27.0 (11.9)
R (int)	0.0418	0.1009
R (p.i.m.)	0.0068	0.0180
exposure time per frame	10 s	50 s

Table 2: Basic crystallographic data of the two thaumatin data sets (crystal P41212, a = b = 57.9 Å, c = 149.6 Å)

A typical diffraction pattern of thaumatin is shown in figure 3. The high effective resolution of both data sets compares well with published measurements on similar thaumatin crystals performed with traditional rotating anode systems (effective resolution on thaumatin around 1.55 Å).



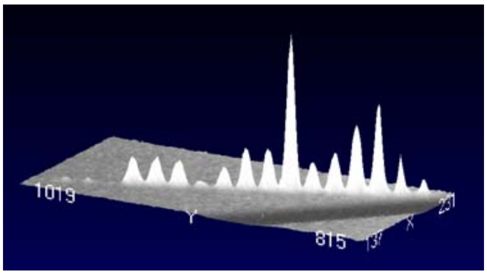


Figure 3: A typical diffraction pattern of a thaumatin crystal recorded with a Bruker AXS Smart 6000 goniometer equipped with IμS-SCD-Cu (approx. crystal size: 400 x 250 x 100 μm^3; 10 s/frames exposure time; 0.5° step size; 71 mm crystal-to-detector distance); left: a graphical representation of the distribution of intensity in the highlighted area showing the separation of the reflections along the c axis

A major challenge in drug design in crystallography / structure determination on small molecules is the structure determination on very small and poorly scattering crystals, for example pharmaceuticals. The most common sources are sealed tubes and rotating anodes. We, therefore, compared the diffraction of a $125\times20\times2\ \mu m^3$ crystal of small organic molecule on a sealed tube system coupled to a first generation Montel multilayer mirror with that of IµS. Both measurements were carried out with a Bruker AXS three-circle goniometers taking similar measurement strategies into account. The complete measurement with IµS was about 13 times faster. The results are shown in table 3.

	ST + Montel 200	I*µ*S
Power [kW]	1.2	0.03
Exposure Time [s/°]	200	15
resolution Limit [Å]	1.31	1.05
Independent Reflections	2621 (1274)*	5168 (2389)*

*number in brackets: reflections fulfilling $I > 2\sigma(I)$, σ: standard deviation of the intensity

Table 3: Comparison between sealed tube system and Incoatec Microfocus Source system

The effective resolution achieved with IµS is about 0.3 Å better than with the sealed tube system. The increase in effective resolution results in a doubling of the number of observed reflections, i.e. in the number of observations against which the structure model is fitted and refined.

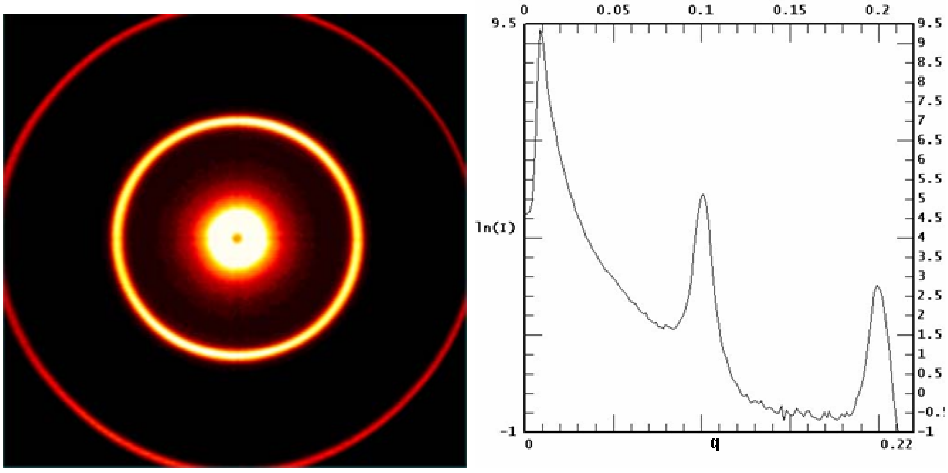


Figure 4: Typical scattering pattern together with the horizontal integration of a silver behenate standard sample

First tests of the small angle scattering module performed with the low resolution Quazar mirror provided a divergence of 1 mrad. The scattering patterns were recorded with a Bruker AXS NanoSTAR using a three pinhole system (750 µm, 400 µm, 1000 µm). The HiSTAR detector was placed 1050 mm behind the sample stage. The figures 4 and 5 show two typical scattering plots. In the three-pinhole SAXS set-up, IµS-SAXS-LD shows a five fold intensity gain over the conventional home-lab set-up with a 1.4 kW fine focus sealed tube and cross-coupled Göbel mirrors. This gain in performance is the optimum achievable value as predicted by ray tracing calculations.

The resolution of the SAXS measurements can be increased with the high resolution types of IµS. Simultaneously the intensity will of course be lower.

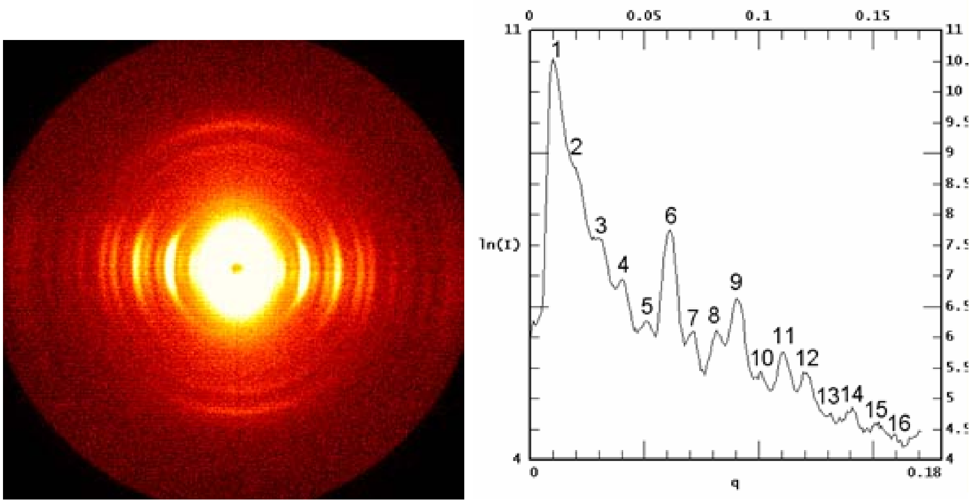


Figure 5: Scattering pattern together with the horizontal integration of a duck tail tendon.

Summary

The new Incoatec Microfocus Source IµS incorporates an optimized combination of an extremely bright and very durable stationary 30 W microfocus source and the newest type of Montels, the Quazar multilayer optics. IµS has all the advantages of a sealed tube system, and a performance exceeding combinations of traditional rotating anodes with multilayer optics. With IµS we have collected data of outstanding quality in single-crystal diffraction and small-angle scattering.

The applications demonstrate that we achieve very high fluxes of > $3*10^8$ cps for Cu-Kα with a focused geometry. For SAXS with parallel geometry we achieve a five fold intensity gain over conventional home-lab set-ups with 1.4 kW fine focus sealed tubes.

IµS is geared up as an upgrade for all existing diffractometers and is an affordable replacement for older high-power rotating anode sources, offering high performance together with customer convenience and low operating costs.

References

[1] M. Bargheer , N. Zhavoronkov, R. Bruch, H. Legall, H. Stiel, M. Woerner and T. Elsaesser, “Comparison of focusing optics for femtosecond X-ray diffraction”, Appl. Phys. B, 80 (6), pp. 715 – 719, 2005
[2] C. Michaelsen, J. Wiesmann, C. Hoffmann, A. Oehr, A. B. Storm, L. J. Seijbel, “Optimized performance of graded multilayer optics for X-ray single crystal diffraction“, Proc. SPIE 5193, pp. 211 – 219, 2004.
[3] D.L. Windt , “Simulation: IMD-Software for modeling the optical properties of multilayer films”, Computer in Physics, 12 (4), 1998.