X-RAY DIFFRACTION

Total Scattering Solutions PDF Analysis with the D8 Diffractometer Family

Defects and disorder within materials play an important role in determining their physical properties. Pair distribution function (PDF) analysis is an analytical technique that can provide local structural information from disordered materials. Such materials can be liquid, amorphous, nanocrystalline, or crystalline with local structural distortions or partially ordered regions. A PDF is obtained from a so-called "total scattering" measurement, which utilizes both Bragg diffraction and the underlying diffuse scattering signal. It is in this weak, broad diffuse scattering signal where the critical details of the local structure are encoded.

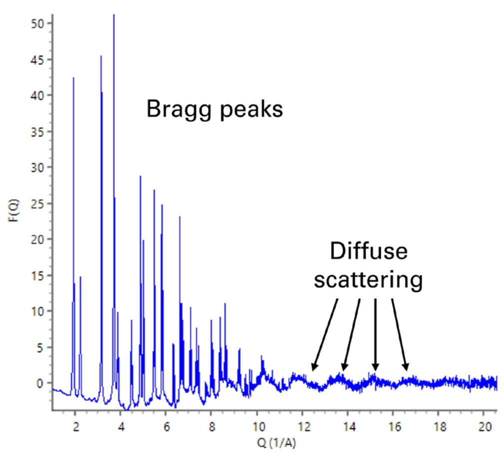
The D8 ADVANCE and D8 DISCOVER from Bruker AXS are ideal for the acquisition of high-quality total scattering data with unparalleled speed and accuracy. Combined with the powerful DIFFRAC.EVA and DIFFRAC.TOPAS software packages, Bruker offers complete analytical solutions for any total scattering application, from fingerprinting of amorphous phases to full structural characterization of intrinsically disordered materials.

What is PDF?
Learn more at Bruker YouTube channel

What is "Total Scattering"?

Traditional powder diffraction methods extract structural information about crystalline materials from the Bragg peaks. These peaks only provide information about the long-range order in a sample. Information on local structural features of the material (including defects or disorder) is encoded in the diffraction signal as diffuse scattering, which appears in the data as broad peaks, or wave-like signals between or underneath the Bragg peaks, extending to high scattering angle. In completely disordered materials, such as glasses and liquids, the diffuse scattering makes up the entire scattering signal.

Total scattering measurements record both the Bragg (long-range order), and diffuse (local structure) scattering signal. Such data can therefore contain a complete picture of the material's structure.

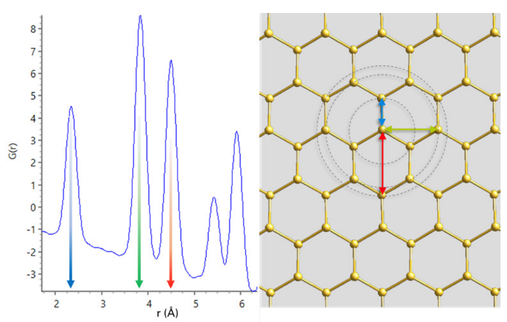


Reduced structure function, F(Q), of a sample containing both Bragg peaks and diffuse scattering.

What is the Pair Distribution Function (PDF)?

A Pair Distribution Function (PDF) is obtained from total scattering data, which must first be corrected and normalized to obtain the total structure function: F(Q). The F(Q) is then Fourier transformed to give the PDF, or G(r), which displays the data in real space. This complex data processing is easily done with just a few clicks in DIFFRAC.EVA.

The produced PDF consists of a series of peaks, representing the probability of finding two atoms separated by a distance, r, from one-another in the structure. The x-axis of the PDF is typically displayed in Ångstroms and is therefore a measure of real-space distances in the material, and structural information can be extracted from it directly.



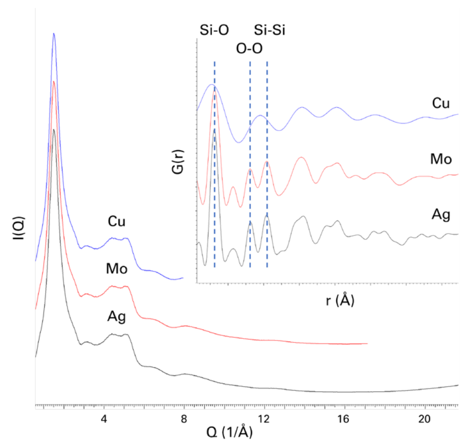
Schematic representation of a PDF (left) from a hexagonal array of atoms.

What are the instrument requirements for total scattering experiments?

There are three main requirements for the collection of total scattering data suitable for processing to a PDF:

1. **Measurements over a wide Q-range** (where $Q = 4\pi \sin(\theta) / \lambda$) to ensure good real-space resolution in PDF is achieved by using **shorter wavelength X-rays (Mo or Ag tube)** to expand measurable Q-range.
2. **Sufficient counting statistics and low background** ensuring accurate data and low noise in the PDF is accomplished using **anti-scatter accessories, dynamic measurement conditions, and low-noise, background-suppressing detectors with large field-of-view.**
3. **High instrument resolution** to reduce damping of the PDF (especially important for nanocrystalline sample) is achieved by using **dedicated focusing optics.**

The right combination of X-ray source, optics, beam-path accessories, and detector work together to reliably achieve superb data quality.

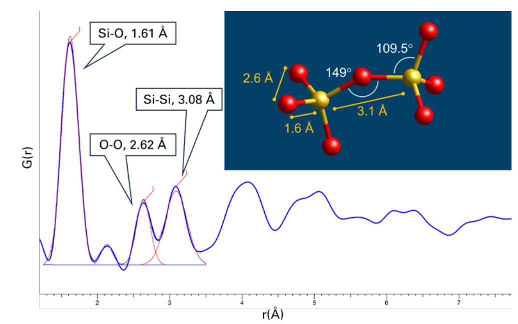


Accessible Q-range of amorphous silica data using X-rays from different anodes and corresponding PDFs (inset), highlighting importance of high energy X-rays.

Structure analysis of amorphous materials

The lack of characteristic crystalline peaks in the diffraction patterns of amorphous materials often prevents their clear identification. Using PDF analysis, the short-range order can serve as a fingerprint, and direct structural information can be extracted. The peak positions in the PDF give direct access to atom-pair distances, from which the local atomic arrangement of disordered materials, like glasses and liquids, can be inferred. Other analysis examples include:

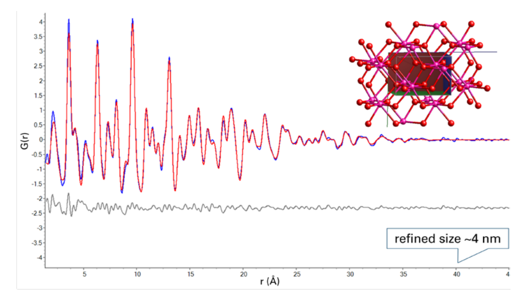
- Qualitative comparison of experimental PDFs of amorphous samples against known materials and polymorphs.
- Simple peak fits using DIFFRAC.EVA to identify the inclusion of a new atomic species or coordination environment in a complex mixture, such as a metallic glass.



Analysis of nanomaterials

Like amorphous materials, nanomaterials often show broad diffraction features which make them hard to analyze by traditional diffraction techniques. By contrast, the well-resolved peaks of a PDF contain a complete structural description of the material. Using small box modelling, analogous to profile fitting of the Rietveld method, it is possible to determine:

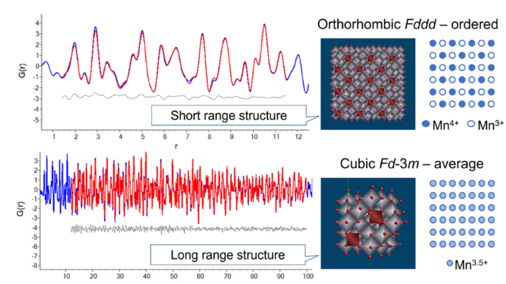
- Differences in atomic ordering of the nanoparticle compared to the bulk material.
- Nanoparticle size.
- Relative phase amounts (quantitative analysis).

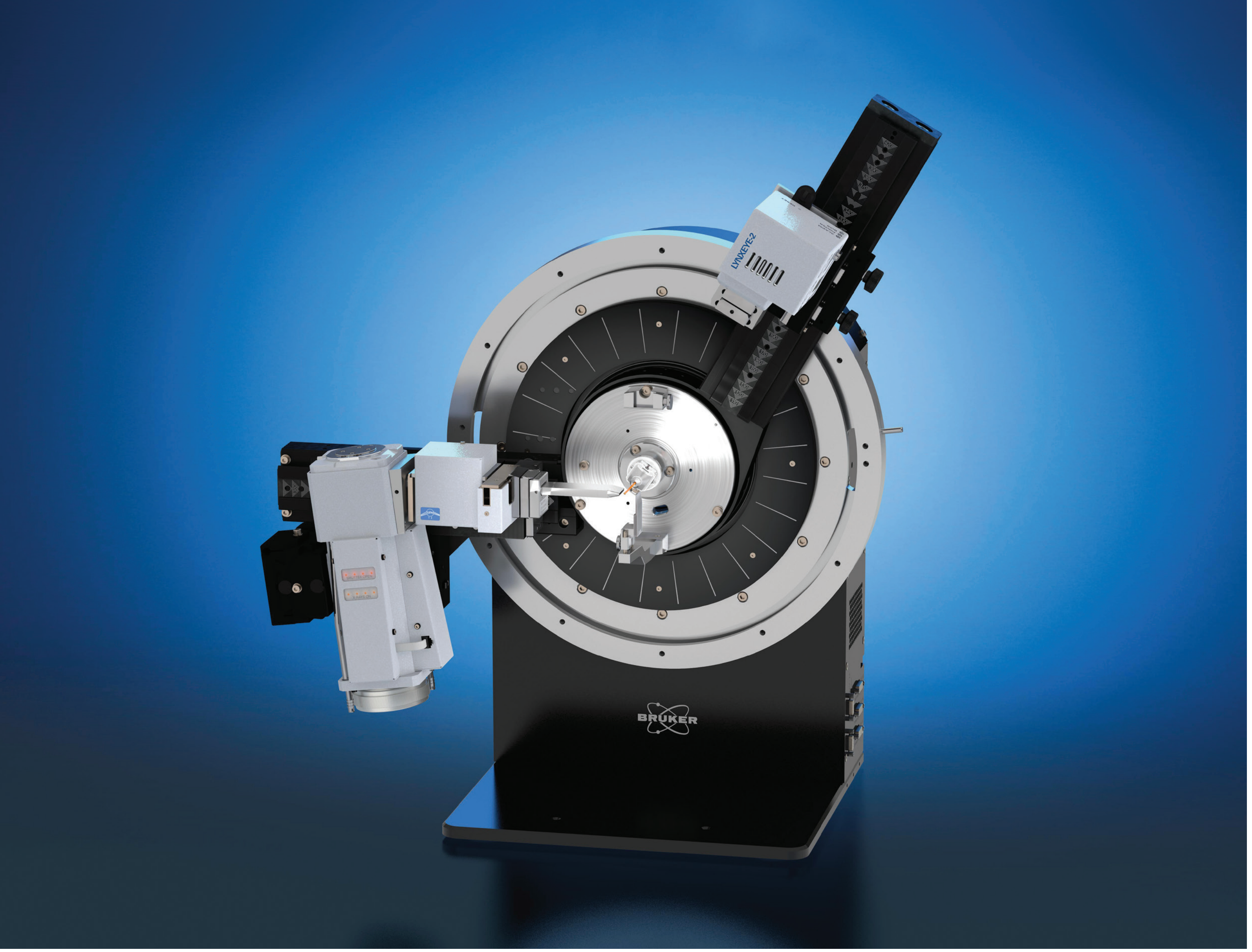


Local structure distortion in crystalline materials

Interesting material properties can manifest due to small distortions in the crystal structure, which are all but invisible in the diffraction data. PDF data is displayed in real space, which allows for evaluation over different length scales and provides a more complete picture of the overall structure. To investigate the intermediate range structure in the PDF, Johansson monochromators, which produce a monochromatic $K\alpha_1$ primary beam at the expense of intensity, have typically been used to observe these structural features without the interference of $K\alpha_2$. Alternatively, using the powerful deconvolution algorithms in TOPAS V7, $K\alpha_2$ can be cleanly removed from the experimental data when employing high-intensity optics like focusing Göbel mirrors. More complex modelling techniques include:

- Joint Rietveld-PDF refinements to study differences between local and average structure.
- Box-car refinements to investigate structural parameters over different length scales.





Total solutions for total scattering

Whether investigating the short-range atomic ordering in amorphous glasses or the local structural distortions of a promising cathode material, PDF analysis is the perfect tool to add to the toolbox. The D8 ADVANCE and D8 DISCOVER can be readily configured to collect high-quality total scattering data for PDF analysis, no matter the sample type. For example, a Mo sealed tube combined with a motorized divergence slit, capillary stage, and a LYNXEYE XE-T detector is a great routine solution, particularly for lighter, low-absorbing samples in large capillaries, as the beam size can be adjusted to match the sample size and bring more flux onto the sample.

Dedicated primary optics can be added, like a focusing Göbel mirror to boost flux density for small sample amounts or a Johansson monochromator to provide spectrally pure $K\alpha_1$ data. Upgrading the detection side with an EIGER2 R 500K improves the counting statistics and decreases measurement time using its large active area. The detector can be positioned close to the sample to further maximize intensity, far away when resolution is important, or anywhere in between to strike the perfect balance.

DIFFRAC.SUITE software completes the PDF analysis solution. In WIZARD, advanced measurement strategies capturing critical scattering features can be easily defined; DIFFRAC.EVA offers simple and reliable processing of total scattering data into a PDF; using DIFFRAC.TOPAS local structural features can be modelled and visualized.

Sources

Bruker offers the widest variety of x-ray sources for line and point-focus applications. High-energy Mo or Ag anodes deliver the short wavelengths required to achieve data with high Qmax for PDF analysis.

Ceramic sealed tubes
- Long life, low maintenance, and easy to exchange to suit different applications

TXS-HE*
- Highest available power density for maximum intensities and fastest measurement times

IµS*
- Air-cooled, high-brilliance point source providing maximum intensity, ideal for point-focus applications

* Only available on the D8 DISCOVER

Optics

Beam-path optics determine the instrument geometry and condition the beam for the best fit to the sample size.

Motorized Divergence Slits
- Straightforward solution for all wavelengths
- PDF data collection in reflection and transmission geometry

Focusing Göbel mirror
- Highest flux density
- Fastest data collection in transmission
- Ideal for small sample amounts

Johansson Monochromator
- Pure $K\alpha_1$ beam: no $K\alpha_2$ artifacts at higher r
- Best instrument resolution; minimal instrument damping

Detectors

Large, efficient detectors reduce measurement time, combined with excellent energy resolution for lowest background signal.

LYNXEYE Family of strip detectors
- 0D, 1D, and 2D data acquisition
- Not only suitable for hard X-rays but a great choice for all wavelengths from Cr – Ag
- Unmatched energy discrimination for best performance and up to 100% filtering of sample fluorescence

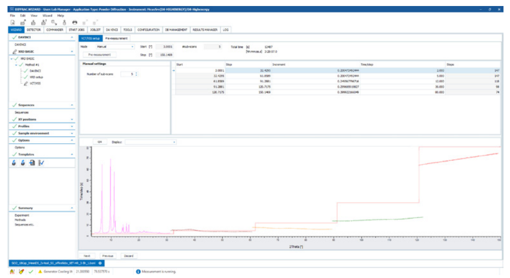
EIGER2 R 250/500K hybrid pixel detector
- Unrivaled 0D/1D/2D integration
- Suitable for all wavelengths: Cr, Co, Cu, Mo, and Ag
- Largest active area providing maximum intensity and fastest measurement times

DIFFRAC.SUITE – the intuitive guide

Experiment planning in WIZARD

The high Q range of a total scattering measurement is important as it contains the finest details of the structure. The scattering signals at high Q are particularly weak and can be often hidden in the noise. To counteract this, more time should be dedicated to the measurement of the high Q (i.e., high 2θ) range during data collection.

The WIZARD plug-in of DIFFRAC.SUITE allows the user to easily configure a Variable Counting Time (VCT) strategy. With VCT the measurement range in 2θ is divided into sections, each with its own defined time per step. In this way more measurement time can be devoted to high 2θ angles, improving counting statistics and increasing sensitivity. This allows the user to optimize the time available for the experiment and ensures the best data quality.



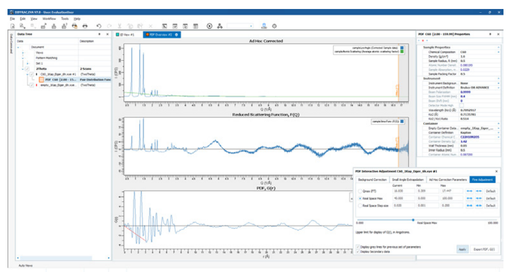
Experiment planning in WIZARD

Variable Counting Time (VCT) ensures the best data quality for PDF Analysis!

Effortless PDF generation in DIFFRAC.EVA

One of the biggest barriers to entry into PDF analysis has traditionally been processing of the raw total scattering data into the PDF. With DIFFRAC.EVA starting from version 7, PDF generation from raw data is simple and intuitive: with just a few clicks, users can create high-quality, physically accurate PDFs with easy-to-understand visual feedback. The PDF processing tool in DIFFRAC.EVA automatically corrects for background and Compton scattering, absorption, polarization, and X-ray fluorescence, then normalizes and Fourier transforms the data, all within seconds!

For further quantitative analysis, the experimental PDF can be exported into DIFFRAC.TOPAS for exploring new horizons in evaluation and understanding of amorphous materials, nanostructures, or local effects in disordered structures.



The PDF processing window in DIFFRAC.EVA

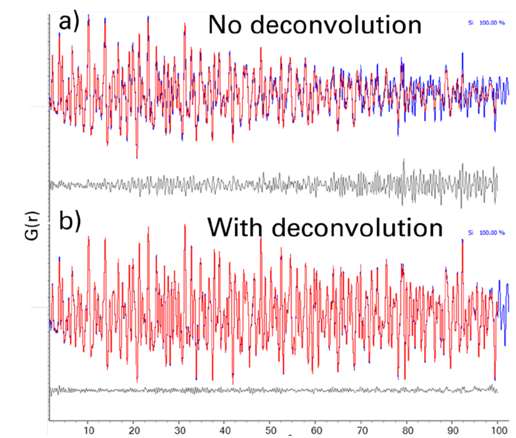
With DIFFRAC.EVA, entry into PDF analysis has never been easier!

PDF Data Analysis with DIFFRAC.TOPAS

The real-space nature of the PDF provides direct access to structural information. For example, the average bond length between atom pairs can be determined from the PDF peak position. However, this basic analysis quickly reaches a limit when looking beyond the first few pairs of atoms, or when analyzing more complex structures, due to the shear wealth of information available in the PDF. With DIFFRAC.TOPAS, more advanced and quantitative analysis of PDF data becomes possible. TOPAS is the leading profile fitting based software for evaluation of quantitative phase analysis, microstructure analysis and crystal structure analysis for both classic Bragg-diffraction and total scattering PDF data.

PDF Generation with deconvolution

More complex applications can benefit from the PDF generation method available in DIFFRAC.TOPAS, which includes a unique deconvolution process that can remove instrument and emission profile contributions like peak asymmetry, Kα_2, and Bremsstrahlung from the raw data. These effects, while unapparent in the low-r region of the PDF, become more evident when the intermediate structural range (above ~25 Å) is of interest. The resulting PDF is sharper after the deconvolution process, particularly in this intermediate structural range, making it easier to identify structural features.



Fits to the G(r) of silicon powder measured on a D8 ADVANCE with Mo-radiation and a focusing mirror, generated a) without deconvolution and b) with deconvolution.

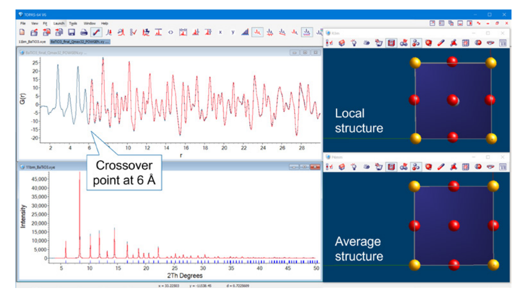
PDF Refinement

TOPAS is built around a general non-linear least-squares system written specifically to integrate various types of Bragg diffraction and PDF data. The result is speed – 3-6 orders of magnitude faster than alternative software – which is critical when thousands or even millions of atom pair correlations need to be calculated.

An additional benefit of the seamless integration of PDF refinements into TOPAS: all functionality for Bragg refinements is also available for PDF refinements, including

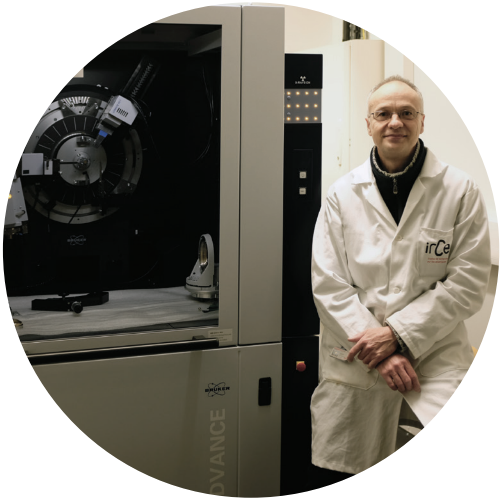
- Restraints and constraints
- Rigid bodies
- Simulated annealing
- Joint Bragg-PDF refinements
- And more!

Combined with the software's inherent speed means the options for modelling PDF data are virtually limitless.



Joint Bragg-PDF refinement on $BaTiO_3$ using distortion modes. Synchrotron Bragg and TOF neutron PDF data.

PDFs near synchrotron level quality



"As a major actor in research on advanced ceramics, the Institute of Research for Ceramics (IRCER) makes use of a wide range of equipment to characterize the materials at different scales. Among them, X-ray powder diffraction setups play a key role in gaining insight on the structural and physical properties of solids. The implementation of the Bruker D8 ADVANCE™ equipped with a silver X-ray tube together with a focusing Goebel mirror and the fast and energy-discriminating LYNXEYE XE-T detector allows us to obtain the atomic pair distribution function (PDF) of many oxides and non-oxides materials, be they crystalline or amorphous. Working in capillary mode, a tiny amount of powder is enough to obtain PDF in a quasi-routine fashion, with quality level near that of synchrotron instruments. By integrating this D8 ADVANCE equipment, the IRCER contributes to improve ceramics for energy, health, communication technologies, automotive and aerospace, for answering the future challenges of industry and society."

Olivier Masson, Professor in Material Science at the University of Limoges and IRCER (UMR 7315 CNRS), specialist in PDF analysis.

Configuration Examples

Source/Wavelength	Mo sealed tube	Mo sealed tube	Ag sealed tube
Primary Optic	Divergence slit	Focusing Göbel mirror	Focusing Göbel mirror
Stage	Rotation stage (reflection) Capillary stage (transmission)	Capillary stage	Capillary stage
Detector	LYNXEYE XE-T	EIGER2 R 250K	EIGER2 R 500K
Key Benefits	Economical Fast and alignment-free switching of tubes and stages Easily combined with Cu tube applications	Dedicated optic for high flux density Rapid data acquisition with large detector Also ideal for Rietveld structure analysis	Highest accessible Q-range for best PDF resolution Rapid data acquisition with large detector

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