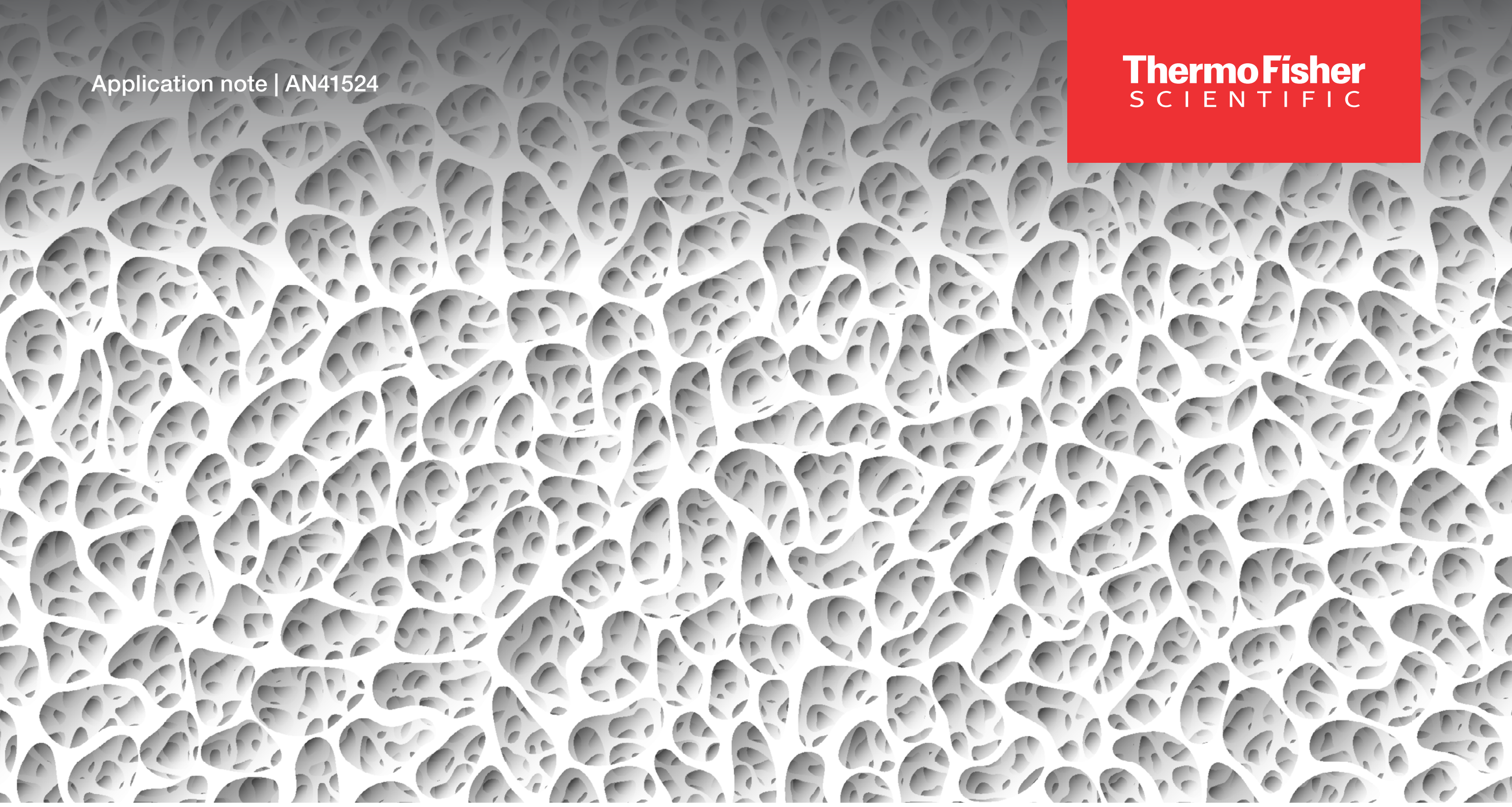
Application note | AN41524



Characterizing structural ordering in porous materials using the Thermo Scientific™ ARL™ X'TRA Companion X-Ray Diffractometer

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Introduction

Porous framework materials such as covalent organic frameworks (COFs), metal–organic frameworks (MOFs), and mesostructured oxides represent an important class of engineered solids for applications in adsorption, separation, and catalysis. These materials are defined by their high specific surface area and well-ordered pore architectures, which can be tuned across the micro- to mesoporous range. COFs provide lightweight, crystalline organic networks with layered structures and accessible pore channels, while MOFs such as NU-1000 combine inorganic nodes with organic linkers to form robust three-dimensional frameworks. Mesostructured alumina materials, analogous to SBA-type architectures, offer ordered pore systems embedded in an amorphous oxide matrix with good thermal and chemical stability. Together, these materials enable controlled transport and interaction of molecules, making them attractive for environmental, energy storage and chemical processing applications such as catalysis.

X-ray diffraction (XRD) plays a central role in the characterization and differentiation of these porous materials. Low-angle diffraction features reveal long-range pore ordering and allow estimation of characteristic pore spacings, while the presence or absence of higher-angle reflections provides insight into framework crystallinity and dimensionality. Layered COFs exhibit distinct low-angle reflection series associated with in-plane ordering, often accompanied by broader features related to interlayer stacking. In contrast, mesostructured alumina shows pronounced low-angle reflections from ordered pore arrays but lacks sharp wide-angle crystalline peaks due to its amorphous framework, whereas MOFs display multiple well-defined Bragg reflections indicative of periodic three-dimensional structures. By correlating diffraction patterns with structural organization, XRD enables rapid identification of material class, assessment of structural quality, and comparison of ordering across different porous systems.

Figure 1: ARL X'TRA Companion X-ray diffraction system.

Instrument & software

The ARL X'TRA Companion X-Ray Diffractometer (c.f. Figure 1) is a simple, easy-to-use benchtop instrument for routine phase analysis as well as more advanced applications. The ARL X'TRA Companion XRD uses a θ/θ goniometer (160 mm radius) in Bragg-Brentano geometry coupled with a 600 W X-ray source (Cu or Co). The radial and axial collimation of the beam is controlled by divergence and Soller slits, while air scattering is reduced by a variable beam knife. An integrated water chiller is available as an option. Thanks to the advanced solid state pixel detector (55 x 55 µm pitch), the ARL X'TRA Companion XRD provides very fast data collection and comes with single-click Rietveld quantification capabilities and automated result transmission to a LIMS (Laboratory Information Management System) seamless integrated into Thermo Scientific™ SolstiX™ Pronto instrument Control Software.

Experimental

A COF 2D layered material (Py MV DBA type), Nu1000 MOF and SBA-15 Alumina were prepared using top loading sample zero background cups and measured in reflection mode using Cu Kα (1.541874 Å) radiation for 30 minutes with sample spinning. (Figure 2). The data was analyzed and visualized using Profex software [1].

Results and discussion

From Le Bail refinements [2] of the porous materials, distinct structural motifs were identified for each sample, highlighting the capability of XRD to differentiate ordered frameworks across material classes (see Figures 2–4). The COF sample (Figure 2; Py MV DBA type) is well described by a hexagonal model [3] (space group P6/mmm) with refined lattice parameters a ≈ 4.227 nm and c ≈ 0.331 nm, consistent with a large pore layered 2D framework. The dominant low-angle reflection at ~2.41° 2θ (d ≈ 3.66 nm) and its higher-order reflections confirm long-range in-plane ordering, while the (001) reflection at ~26.9° 2θ corresponds to an interlayer stacking distance of ~3.31 Å. This combination of large in-plane periodicity and short stacking repeat is characteristic of crystalline layered COF architectures. Such large-pore COFs represent an important subclass of framework materials, as they combine high surface area with accessible mesopores, making them particularly relevant for adsorption, catalysis, and molecular transport applications.

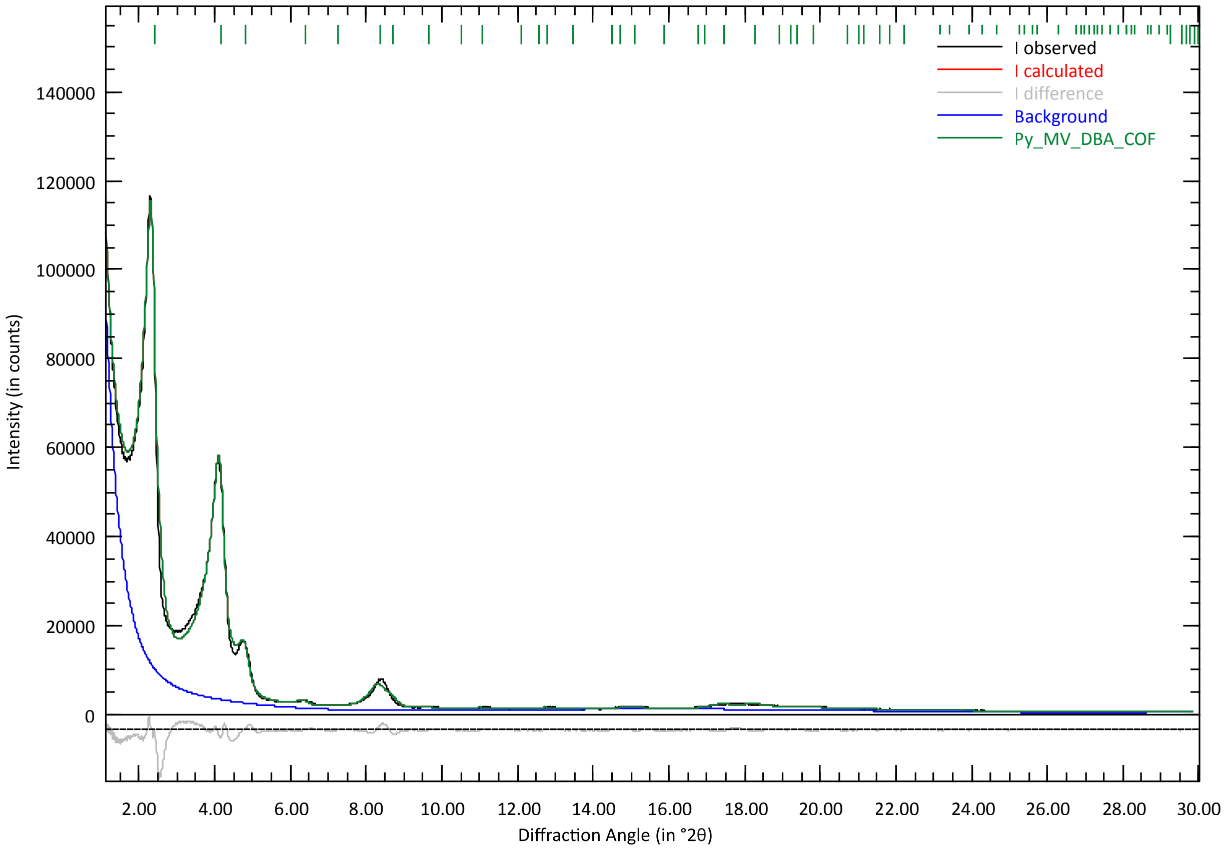

Figure 2: Le Bail fit (30 minutes) of a Py MV DBA type 2-D COF sample.

In contrast, the NU-1000 sample (Figure 3) is indexed using a hexagonal unit cell with a ≈ 3.954 nm and c ≈ 1.663 nm, reflecting a three-dimensional MOF framework with significantly larger periodicity along the c-axis [4]. The presence of multiple reflections across the measured angular range and the refined unit cell dimensions are consistent with a highly ordered crystalline framework rather than a layered structure. NU-1000 is a well-established zirconium-based MOF that is widely studied due to its high chemical stability and hierarchical pore system, making it a representative example of robust 3D porous frameworks used in catalysis and separation technologies.

The mesostructured alumina sample (SBA-15) [5] shows the expected low-angle reflection series corresponding to a hexagonally ordered pore system, with a primary (100) reflection at ~0.90° 2θ (d ≈ 9.85 nm), yielding a lattice parameter of ~11.4 nm. The absence of sharp wide-angle Bragg reflections confirms that the pore walls are amorphous, and that the observed ordering arises from mesoscale periodicity rather than atomic crystallinity. Materials of this type are widely used as model mesoporous systems due to their uniform pore size distribution and well-defined long-range order, making them ideal benchmarks for evaluating low-angle diffraction performance.

The refined structural parameters highlight the fundamental differences in ordering across the three material classes. The COF exhibits strong in-plane periodicity combined with short-range interlayer stacking, indicative of a layered architecture with accessible mesopores. NU-1000, by contrast, displays extended periodicity in all three dimensions, consistent with a rigid three-dimensional porous framework. The mesostructured alumina demonstrates long-range pore ordering without atomic-scale crystallinity, as evidenced by the absence of high-angle diffraction features. These materials were deliberately selected as representative systems for layered, three-dimensional, and mesostructured porous architectures, respectively, enabling a comprehensive comparison of diffraction signatures across different framework types. These differences are directly reflected in the diffraction patterns and provide a clear basis for distinguishing framework type, dimensionality, and pore organization using PXRD (powder X-ray diffraction) alone. The results demonstrate that even with benchtop instrumentation, XRD enables robust structural classification of porous materials and supports rapid assessment of ordering and framework characteristics relevant for applications in adsorption, catalysis, and separation.

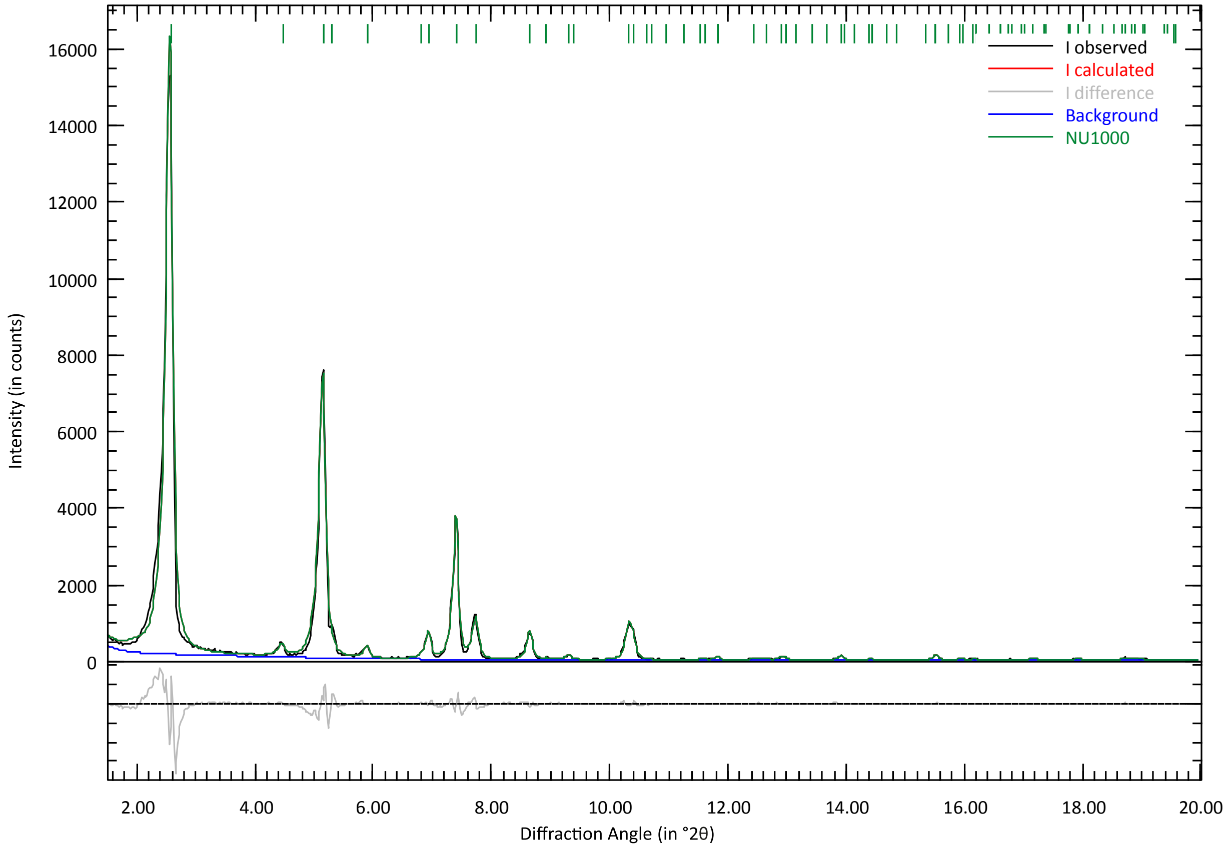

Figure 3: Le Bail fit (30 minutes) of a NU1000 MOF sample.

Your benefits

The ARL X'TRA Companion XRD system delivers high-quality diffraction data within minutes, enabling reliable identification and differentiation of porous material classes such as COFs, MOFs, and mesostructured oxides. Low-angle measurements provide direct insight into pore ordering and lattice parameters, while the accessible angular range allows assessment of framework dimensionality and crystallinity. Le Bail fitting supports extraction of unit-cell parameters for both layered and three-dimensional frameworks, enabling structural classification without requiring full structural models.

These structural insights are directly linked to functional properties such as pore size, accessibility, and framework organization, which are critical for applications in adsorption, catalysis, and separation. The ability to rapidly distinguish between ordered mesostructures, layered frameworks, and fully crystalline porous materials provides a robust basis for material selection, quality control, and optimization of performance in industrial and research environments.

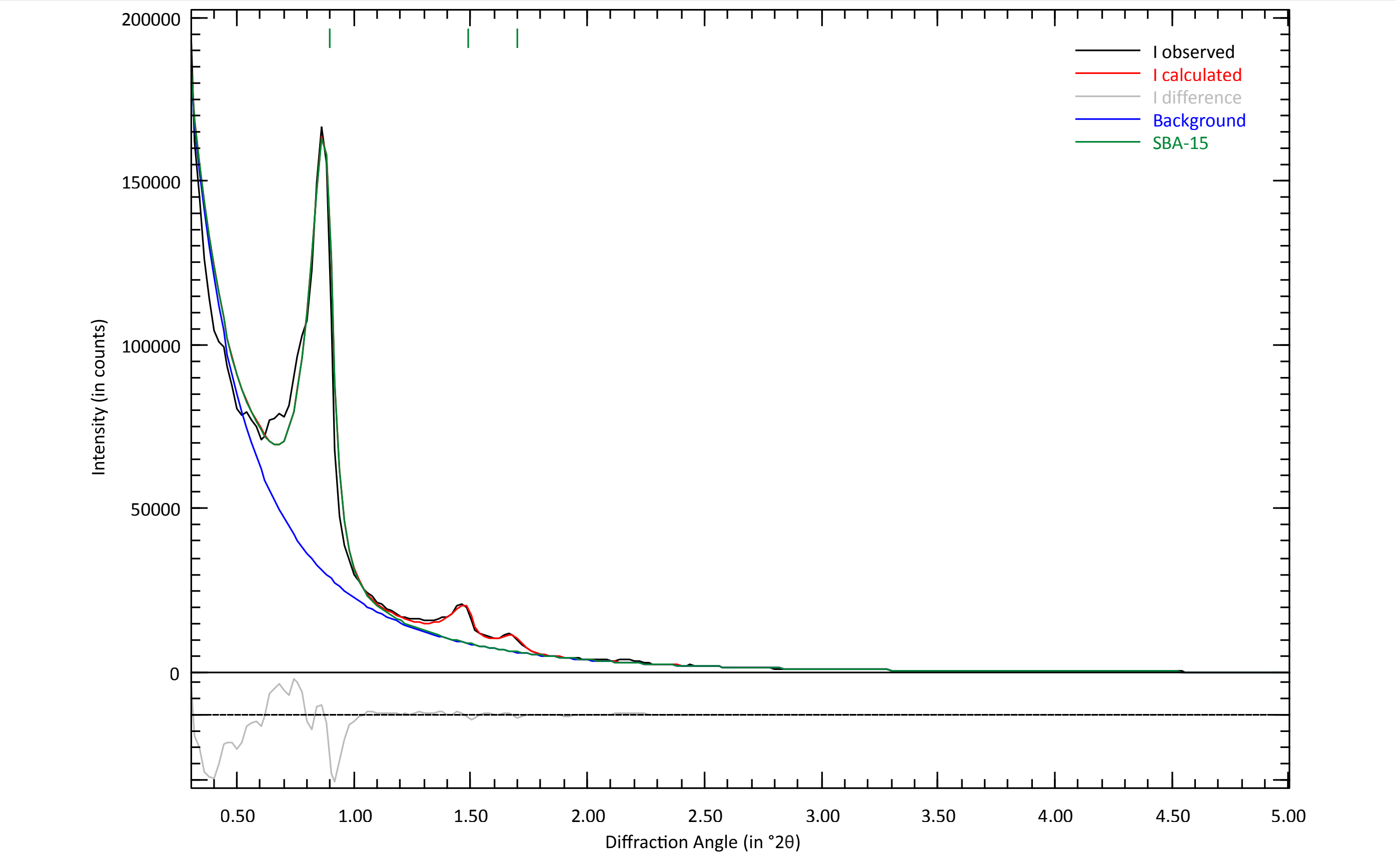

Figure 4: Le Bail fit of a (30 minutes) of an SBA-15 Al_2O_3 sample.

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