

Analytical solutions for Metal Organic Framework materials

Grow your knowledge. Build robust structures.



The world of Metal Organic Frameworks

What are MOFs?

Metal Organic Frameworks (MOFs) are hybrid crystals created by selfassembling organic and inorganic molecules. MOFs contain nano-scale interconnected voids - giving them unrivaled potential for trapping, storing and catalyzing ions and molecules. Adjusting their local environment (such as the electric field, temperature, pressure or chemistry) can enable the adsorption or release of many molecules or ions.

What are they used for?

Thanks to their collection abilities, MOFs are ideal for several applications, including gas storage and separation, liquid separation and purification, electrochemical energy storage, catalysis, or drug delivery. They are also useful for gas sensor devices that measure and respond to this capture process.



The hybrid structure of MOFs

Organic molecules can form large, interpenetrating lattices made of a framework of large pores. But, on their own, they are relatively fragile. Reacting these molecules with metal ions creates MOFs: strong covalent structures that are more durable than organic crystals. These materials can be synthesized on surfaces as thin films, obtained from solution as dry powders, or used as nanoparticles in liquids.

Where materials analysis comes in

Crystal structures: Key to collection

What exactly makes MOFs so good at collection? Their complex crystal structures! These structures contain voids, and the interconnectivity between these voids makes MOFs nanoporous. The exact structure depends on the MOF's constituent molecules and how it is synthesized. By tailoring this, you can optimize size, connectivity and **binding affinity** to attract specific molecules or ions.

That means you need a deep understanding of the crystalline lattice structure and how it interacts with other molecular and ionic species. And for this, you need a strong understanding of the structural changes that result from variations in the host environment.

Particle morphology for maximum performance

How do you maximize the performance of a MOF powder to ensure robust, consistently processable products? By optimizing the physical properties of the particles!

Specifically, the particles' total surface area determines how effectively gas or liquid can flow through and how guickly the MOF can trap or release molecules or ions. So, for the best MOF product, particles must remain a **constant size, intact** and not agglomerated. The powder's flow and packing also have to be controlled. And for this, you need to understand the size and shape of your MOF particles.

How can we help?

At Malvern Panalytical, our global network of over 170 scientists is continuously working to support customers with advanced materials like MOFs.

Our solutions deliver in-depth materials insights, from nanoscale to macroscale. Whatever the project, product or process, we'll help you to optimize your material.

On the following pages, we hope you'll find solutions that could benefit you. If you want to dive deeper into their specific benefits, don't hesitate to get in touch!



Nanoparticles in liquid: hydrodynamic performance

One way to measure how effectively a MOF can harvest or release ions is to measure the elemental concentration of ions in residual concentrations in its carrier liquid.

When formulated as nanoparticles in suspension, MOFs can carry a whole range of active and targeted pharmaceutical drugs. That's because surface modification enables these nanoparticles to access cells. Understanding the hydrodynamic behavior of these surface-activated MOF nanoparticles is essential for all stages of the process.

"These are really exciting times - I have never seen such capabilities in a material. The selectivity, the robustness, the scale of response: it's mind-blowing."









Dr Ana Morfesis -Principal Scientist, Malvern Panalytical

Why is crystal structure analysis important?

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To understand your MOF structures in detail and check that your target MOF has been synthesized correctly, you need to be able to identify any changes to the crystal structure - quickly and easily.



What causes structural changes?

Structural variations can happen when raw materials are changed or if the material synthesis route is different. Long-term cycling or environmental conditions may also cause degradation in the lattice. Measurements can show whether your MOF's pores are empty or partially filled.

Empyrean: Structural solutions

The excellent fit of this high resolution and lowbackground transmission data demonstrates that great data quality leads to an accurately determined structural model. The result even locates the hydrogen atom of the MOF's phenolic group.





X-ray diffraction: A certified solution

X-ray powder diffraction is a well-established way to measure and verify crystal structure. Our Empyrean and Aeris X-ray diffractometers can provide the highest-quality powder diffraction data. Count on their resolution and sensitivity to pin down even the finest structural details.

Aeris: Rapid fingerprinting

The powder diffraction scan below was obtained in a 5-minute scan on the Aeris diffractometer. It shows two MOF samples with nominally the same constituents, synthesized by two different routes. The green arrows show extra reflections, indicating that Sample 2 is not pure enough.



Binding affinity

Why analyze crystal structure during occupancy cycling?

By studying the MOF's crystal structure during occupancy cycling, you can understand how morphology, packing, and use environment affect its performance - and design your use environment accordingly.



Integrated non-ambient measurements

Our X-ray diffractometers let you study the crystal structure changes in your MOFs - whatever the operating conditions. Choose from several integrated non-ambient chambers and reaction cells, and rapidly identify points of change with HighScore software, incorporating 2D and 3D graphics and cluster analysis.

Empyrean: Capture and release of water

Because the MOF CAU-10-H can store water molecules (H_2O) , it has potential applications in water harvesting.

These isoline plots show variable in situ relative humidity data collected at two temperatures, demonstrating the effect of temperature on the adsorption and desorption of water within the sample.





Binding affinity at different sites

What are the benefits of understanding binding affinity at specific binding sites in your MOF pores? Better MOF structures for specific adsorption species, and long-term robustness in various use environments.



A complete thermodynamic profile

By measuring heat transfer during binding, you can accurately determine binding constants (K_p) , reaction stoichiometry (N), enthalpy (ΔH), and entropy (ΔS). Our ultrasensitive Microcal PEAQ-ITC microcalorimeter makes measuring these thermodynamic changes easy – giving you a complete thermodynamic profile of adsorption and desorption.

Basics of ITC experiment

Universal technique based on heat detection



Integration of heats are used to extract affinity (KD), stoichiometry (N) and binding enthalpy (ΔH) using appropriate binding model

ITC: Example report

The MOF NU-1000 can effectively extract uremic toxins¹ - both when free in aqueous media and when bound to human serum albumin (HSA). These authors measured the interactions of the toxins at different binding sites in the MOF using ITC, revealing both entropically and enthalpically driven adsorption at two different pore sites.

Particle size

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More optimized product formulation

MOFs are often produced in powder form, as they precipitate from a reaction in a solvent. The physical form must remain reproducible and stable. This means the powder particles must stay a constant size, intact, and not agglomerated throughout their use. Fast particle size distribution measurements can help you quickly understand these process parameters to deliver optimum product size.

The right size for the right application

Each MOF has an optimum particle size - and size distribution - for its intended application:

- Bulk MOF powder particles designed to interact with gases can be 1 to 100s of microns large
- For batteries, smaller particles (20 nm to 1 micron) reduce ionic diffusion lengths. They must be distributed evenly in thin multi-layered structures.
- · For drug delivery in biological systems, MOF nanocrystals (<100nm) in suspension are used. They can be small enough even to penetrate the blood brain barrier.



Smarter particle sizing: What's the best option?

But which particle sizing method is right for you? Each instrument in the table has different benefits - and they can also measure additional attributes. Ultimately, your research, development, or production requirements will determine the best instrument and method. And with this many options, we're sure to find your match!

Mastersizer 3000: Particle size distribution

This figure shows the results of a laser diffraction measurement using the Mastersizer 3000. The sample data from 5 measurements reveal a narrow and reproducible particle size distribution peaking at 48µm.



Mastersizer 3000: Particle agglomeration

This figure shows the results of a laser diffraction measurement using the Mastersizer 3000. The sample was measured in a dispersion revealing a broad distribution of fine and agglomerated particles. The mean particle size reduces after sonication, showing a reduction in agglomeration.



Particle shape

The importance of particle shape

In powder, particle shape affects packing, flow, and the chance of agglomeration. In dispersion, particle shape can influence the stability of a formulation. Imaging is a great way to measure particle size and shape to understand or monitor performance.

Tracking particle degradation

Repeated cycling, along with the influx and outflux of ions and molecules, can cause particle degradation or incomplete emptying of the MOF, leaving a residual occupancy that increases over time.

You can track this particle degradation using imaging with Raman spectroscopy chemical analysis, giving vital clues about your products' shelf-life. Raman can help you see what proportion of your particles have an adequate loading of, for instance, active pharmaceutical ingredient (API).

Automated imaging for advanced particle characterization

Automated imaging gives you both instant and long-term information on the physical robustness and performance of your individual MOF particles. With Morphologi 4, you can scan 10,000 - 500,000 particles and get a full set of size and shape results for each particle. All in just 30 minutes!

What's more, you can opt for your results to show only what's most relevant to you. And, with Morphologi 4-ID, you can return to any individual particle for more detailed analysis, including Raman chemical profiling.

Morphologi 4-ID: Raman spectroscopy

This figure shows a published result of some imaging and Raman results demonstrating the degradation of biocompatible MOF crystals in a biological medium. The MOF crystals are being studied for their potential in drug delivery applications. It is important that the particles are dissolved in the body during drug release. The authors studied new particles before degradation





- and then particles in biological medium (I) which, over time, developed denuded regions around the edges (II). Raman spectroscopy revealed that the degraded region was losing the organic ligand in the MOF².
- Further studies showed the eventual collapse of the inorganic matrix as it dissolved in the biological medium.

² Int. J. Pharm. 2017531(2): 424-432 <u>https://doi.org/10.1016/j.ijpharm.2017.05.056</u>

Nanoparticles in liquids

Why study nanoparticle stability?

Understanding the size and surface charge of MOF nanoparticles in solution is critical to controlling mobility and aggregation. Controlling particle size in bioactive drugs is particularly important, as it ensures that drug carriers can pass through biological barriers and reach their intended destination.



Modifying nanoparticle surfaces

Modifying the surface of MOF nanoparticles can help optimize their behavior in liquids. In drug delivery, for instance, the right surface enables access to cells. In water treatment, adjusting surface charge can optimize the absorption of toxic pollutants³.



Light scattering for in-depth nanoparticle analysis

You can measure the size of nanoparticles in liquids using Dynamic Light Scattering (DLS) on the Zetasizer Advance. Or, to analyze particle drift for Zeta potential, use Electrophoretic Light Scattering (ELS). And Nanosight NS300 complements these measurements, providing real-time imaging of particle movement, with tracking analysis for both sizing and concentration.

Nanoparticles in liquids

Know your purity levels

Knowing the purity of your starting materials and intermediate precursors can be important in developing your MOF synthesis and product processing.



Monitoring impurities from catalyst residuals

MOFs can be used as catalysts - for example, in the production of carbon nanotubes.⁷ Catalyst residues can cause unwanted impurities in nanomaterials, affecting their properties and the final application. XRF analysis can monitor these impurities.

Example applications

- For battery and electronic applications, MOF particles must remain structurally stable under environmental changes. Zeta potential is a useful measure of this stability^{4,5} when pH values change.
- MOFs can be used as catalysts to degrade pharmaceuticals and cosmetics and prevent them from contaminating waste. Dynamic light scattering can qualify and control the synthesis of suitable catalytic MOF particles⁶.





³ Journal of Environmental Sciences, Volume 80, June 2019, Pages 197-207: https://doi.org/10.1016/j.jes.2018.12.013

- ⁴ Front. Chem, 04 August 2020: <u>https://doi.org/10.3389/fchem.2020.00617</u>
- ⁵ Nano Energy, Volume 65, November 2019, 104032: <u>https://doi.org/10.1016/j.nanoen.2019.104032</u>
- ⁶ Chemosphere, Volume 196, April 2018, Pages 105-114: <u>hhttps://doi.org/10.1016/j.chemosphere.2017.12.164</u>

⁷ Reference: Inorg. Chem. 2019, 58, 5, 3227-3236 : <u>https://pubs.acs.org/doi/10.1021/acs.inorgchem.8b03318</u>

Assessing ionic uptake and expulsion

You can measure how effectively your MOF particles trap and release ions from solutions by measuring ion concentrations - for example in filtered solutions, or (for batteries) in separators and electrolytes.



Elemental insights with X-ray fluorescence

Our X-ray fluorescence (XRF) instruments can help determine your sample's chemical composition whether it's solid, liquid, slurry, or loose powder. You can also use our sample preparation equipment to make peroxide solutions for ICP elemental analysis.



XRF spectrum of carbon nanotube sample showing residual impurities

Crystal structure



Research

You need a MOF crystal that fulfils your application requirements – without fail:

- A robust crystal structure that adsorbs the correct molecules or ions
- The right adsorption capacity obtained through the right physical morphology
- Understanding of the process, with matching fluid flow and composition (liquid or gas)
- Characterization and fine-tuning of adsorption and release parameters



Development

You need an upscaled process that achieves:

- The correct crystal structure
- The required physical morphology
- A robustly contained material
- Reproducible adsorption and release parameters

Our solutions

Crystal structure

Let our **Empyrean** and **Aeris** X-ray diffractometers take your crystal structure analysis to the next level.

Binding affinity

The ultrasensitive microcalorimetry of our **Microcal PEAQ-ITC** gives you direct measurements of binding affinity (K_D), stoichiometry (n), enthalpy (Δ H), and entropy (Δ S).

Particle size and shape

Use our **Mastersizer 3000** for particle size distribution with laser diffraction, **Morphologi 4** for particle size and shape analysis, and **Morphologi 4-ID** to analyze particulate chemistry with automated imaging and morphologically directed Raman spectroscopy (MDRS).

Elemental analysis

The X-ray fluorescence (XRF) spectroscopy of **Epsilon** and **Zetium** makes elemental analysis of MOFs and their fluid environments easier than ever.

Nanoparticles

Need to analyze MOF nanoparticles in suspension? **Zetasizer Advance** has you covered with dynamic light scattering (DLS) and electrophoretic light scattering (ELS). For particle size and concentration analysis, try **NanoSight NS300** using Nano Tracking Analysis (NTA).

Production

And you need product quality, every time:

- Testing for chemical impurities
- Fast quality assurance of crystal structure
- Fast quality assurance of sample morphology
- Effective in-line measurements
- Automated measurement and analysis

Let us help you























Empyrean

Empyrean is for you if you want:

- The world's most accurate **high-resolution goniometer** for state-of-the-art diffraction and scattering experiments.
- A full choice of Universal PreFIX optics and stages for fast, accurate component exchange.
- iCore and dCore optics for multiple measurements with batch automation.
- 0D, 1D and 2D **solid-state detectors** fully integrated, low-noise, and high-resolution.
- Advanced configurations for specialized measurements (capillary transmission, SAXS, GISAXS, HR-XRD, PDF and CT).

- The widest range of sample holders and sample stages for manual and automated sample exchange.
- Fully integrated non-ambient sample chambers.
- Bespoke **design and integration** for sample mounting and *in situ* experiments.
- HighScore and HighScore Plus: user-friendly software for phase analysis, Rietveld refinement, fingerprinting, cluster analysis, non-ambient studies – and more!
- Fully automated analysis routines for individual measurements or large data sets.

Aeris

Aeris is for you if you want:

- An easy-to-operate instrument combining **one-step** sample loading with simple push-button operation.
- The quality of a floor-standing diffractometer in compact form.
- Unrivaled low detection limits for small powder diffraction peaks and material variations.
- High-resolution 1D and 2D solid-state detectors.
- **Powder diffraction** measurements in reflection, transmission and grazing incidence.
- Safe, precise **external sample loading** anytime. No need to disturb ongoing measurements!

And for MOFS take a look at:







Automation streamlines your processes and cuts your production overheads. No more unnecessary expenses!

And for MOFS take a look at:



Low-background, high-resolution **iCore and dCore** detectors reveal even the smallest peaks in automated measurements.



Your choice of **optics and configurations** to minimize texture – and the best low-angle peak shapes for Rietveld fitting.



Integrated **non-ambient stages** for controlled, synchronized measurements – every time.



All the **sample holder types** you could want – and up to 48 samples loaded for automated batch analysis.

- The widest range of **sample holders** and **sample stages** with various options for manual and automated sample exchange.
- An uncoupled **theta-2theta goniometer** to keep your samples safe and your instrument clean.
- Rapid instant results with **RoboRiet automated analysis**. Wave goodbye to waiting times!
- Integrated non-ambient temperature chamber.
- Full integration into an automated lab or processing plant.



Grazing-incidence diffraction improves detection limits: Get ready to analyze even thinner films and coatings!



2D capability lets you check your crystallites' processing quality – large or small, random or preferred orientation.

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MicroCal PEAQ-ITC

MicroCal PEAQ-ITC is for you if you want:

- An easy-to-operate, ergonomically designed instrument. Say hello to a smoother experience!
- High-quality, reproducible results with minimal experimental artifacts.
- High signal-to-noise for greater confidence in your data's quality and relevance.
- An integrated washing module with quick disconnect fittings and liquid sensors.
- Full cleaning of both sample cell and titration syringe - even at elevated temperatures.
- Robust injection syringe filling and cleaning system.

- Hastelloy® sample cell: suitable for a wide range of compounds.
- · Instrument control software with guided workflows, step-by-step tutorials, and maintenance alerts.
- Analysis software with experimental design simulation, batch evaluation of large data sets, automated assessment of data quality, and a streamlined user interface.
- Presentation-quality graphics: sharing your findings just got easier.

Mastersizer 3000

Mastersizer 3000 is for you if you want:

- Robust, rapid particle size measurements spanning 10nm - 3500µm in a single optical path.
- Intuitive software with built-in expertise for faster analysis than ever!
- Measurement of dry powders, suspensions and emulsions, with multiple plug-and-play dispersion units.
- Easy, reproducible operating procedures via the Measurement Manager interface.

And for MOFS take a look at:



Robust injection syringe filling and cleaning system.







Integrated washing module with liquid sensors.



MicroCal PEAQ-ITC Automated.

And for MOFS take a look at:





Aero funnel sample feeder for Aero dry powder dispersion units. Enjoy rapid quality control for your bulk powder samples!

laboratory glassware for a

wide range of dispersant

volumes.

The Mastersizer 3000's versatility means you can create the ideal setup for consistent results - again and again.

- Live feedback on dispersion and sonication, for optimum particle conditions.
- A full real-time view of instrument controls, live data, and trends.
- Automatic cleaning and easy switching from liquid to dry dispersions. No additional stress necessary!
- Flexible dry dispersion for robust or fragile materials, and whatever the sample volume.
- Fully editable reporting so the benefits continue after analysis.



Hydro Insight - real-time images of liquid particle dispersions and individual particles, with quantitative data on particle shape.



Ask us about in-line and at-line particle sizers and bespoke auto- sampling solutions!



Morphologi 4-ID

Morphologi 4 and Morphologi 4-ID are for you if you want:

- To scan 10,000 500,000 particles from **0.5 to 1300µm** – with full results of up to 20 parameters in 30 minutes.
- Results that present only what's relevant to you.
- To analyze individual particles in more detail with Raman chemical profiling.
- A high-resolution microscope for the highest-quality particle images.
- Automated 'sharp-edge' analysis to detect low-contrast particles.
- An integrated dry powder dispersion unit for reproducible sample dispersion.
- Advanced data exploration tools for maximum sample knowledge.

Zetasizer Advance

Zetasizer Advance is for you if you want:

- A wider range of sample concentration and particle sizes - thanks to Non-Invasive Back Scatter (NIBS) technology.
- The highest-resolution sizing data from combined Multi-Angle Dynamic Light Scattering (MADLS®) technology.
- Accurate size measurements of 1nm-10µm particles.
- A confident understanding of your sample's stability and aggregation potential.

And for MOFS take a look at:



Integrated dry powder dispersion unit, making reproducible sample preparation easy.



Wet dispersion cell - so you can analyze 2-6 mL of your sample.



Imaging workflow and SOP control - from sample dispersion to data analysis.



A great choice of sample holders, including slide holders for traditional microscopy.

And for MOFS take a look at:





The ZSU1002 cell for sample volumes as low as 3µL and particles up to 10µm. Say hello to a wider dynamic concentration range!

Our completely disposable cell - no more cross- contamination between measurements!

- Constant current mode say goodbye to data errors from electrode polarization.
- Repeatability with minimal sample preparation, thanks to the Adaptive Correlation algorithm.
- A sample-centric workflow to automate even the most complex analyses.
- · Instant automatic feedback and actionable advice.



The MPT-3 titrator automates your titrations for Zeta or size vs. pH.



Our dip cell lets you measure zeta potential in both aqueous and nonaqueous dispersants.

With Nanosight NS300, you can understand your nanoparticle suspensions in more depth than ever.

NanoSight

NanoSight NS300 is for you if you want:

- Particle size images and measurements from 10-1µm, at up to 1 × 10⁹ particles/mL.
- Particle-by-particle, high-resolution particle size data, plus concentration measurements for colloidal suspensions or nanoparticle solutions.
- Quantification of primary sample components, aggregates, and fluorescently tagged particles.
- High-resolution information on monomodal and polydisperse systems - across all kinds of materials.

Epsilon range

Epsilon 1 or Epsilon 4 is for you if you want:

- · Non-destructive detection of elements from C-Am, with detection limits from 1 ppm - 100%.
- A unique dynamic range and high elemental resolution - whatever the sample matrix.
- · Easy management of powders, solids, films, filters, and solutions.
- · Fast, accurate analysis, at-line or in-line.
- · Advanced data treatment algorithms.

And for MOFS take a look at:



Comprehensive realtime data viewing and analysis.



NanoSight syringe pump lets new particles flow continuously into the sample chamber.



NanoSight Sample Assistant: enjoy precise, reproducible, automated sample loading from a 96well plate.



Low-volume flow cell delivering data from as little as 250µL.

And for MOFS take a look at:



Epsilon 4's 10-position

changer, and unlimited

possibilities are endless!

belt automation. The

carousel, 50-100

position sample



Xflow automated elemental analysis of liquids - whether it's online or at-line.

Whatever your requirements, Epsilon has something for you – from the simplest monitoring to the most demanding measurements.

- Optional standardless analysis with Omnian software.
- A pass-fail fingerprint program for quick quality control.
- A full workflow package: from auto-sampling and sample preparation to measurement and analysis.
- Automation options.



Fusion sample preparation for XRF and ICP analysis.



Choose from a wide range of our certified reference materials (CRMs). We'll even create bespoke CRMs for your unique applications.



Why choose us?

When you make the invisible visible, the impossible is possible.

Our analytical systems and services help our customers to create a better world. Through chemical, physical and structural analysis of materials, they improve everything from the energies that power us and the materials we build with, to the medicines that cure us and the foods we enjoy.

We partner with many of the world's biggest companies, universities and research organizations. They value us not only for the power of our solutions, but also for the depth of our expertise, collaboration and integrity.

With over 2200 employees, we serve the world, and we are part of Spectris plc, the worldleading precision measurements group.

Malvern Panalytical. We're BIG on small™

Service & Support

Malvern Panalytical provides the global training, service and support you need to continuously drive your analytical processes at the highest level. We help you increase the return on your investment with us, and ensure that as your laboratory and analytical needs grow, we are there to support you.

Our worldwide team of specialists adds value to your business processes by ensuring applications expertise, rapid response and maximum instrument uptime.

- Local and remote support
- Full and flexible range of support agreements
- Compliance and validation support
- Onsite or classroom-based training courses
- e-Learning training courses and web seminars
- Sample and application consultancy



Malvern Panalytical

Grovewood Road, Malvern, Worcestershire, WR14 1XZ, United Kingdom

Tel. +44 1684 892456 Fax. +44 1684 892789 Lelyweg 1, 7602 EA Almelo, The Netherlands

Tel. +31 546 534 444 Fax. +31 546 534 598

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