

# Pore Size and Pore Volume Measurement of Metal Organic Frameworks

Relevant for: MOFs, microporous adsorbents

Researchers involved in the field of functional solids need to understand the pore structure of the innovative class of solids called Metal Organic Frameworks (MOFs). Quantachrome's Autosorb iQ-MP and XR are the optimal precision gas sorption analyzers to investigate these otherwise challenging materials.

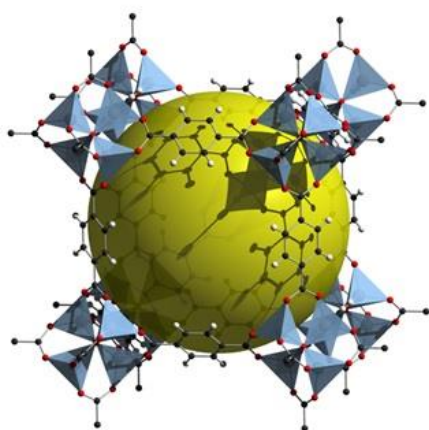


Figure 1: Example Metal Organic Framework (MOF). The yellow sphere represents the pore space within the crystal structure.

## 1 Why measure pore size in MOFs?

Metal-organic frameworks are crystalline solids with very high pore volumes and surface area, and as such, many are candidates for gas storage and gas separation. Theoretically the pore size can be calculated from X-ray diffraction and other scattering techniques.

However, gas sorption has the unique ability to directly probe the pore space thereby revealing additional information about the true nature of the material (is the porosity accessible?), and can additionally reveal structural changes in non-rigid materials. As such it can confirm the suitability, or not, of candidate materials for such gas storage applications.

## 2 Which instrument is used?

For this type of sample, the Autosorb iQ-MP and XR are normally used. These gas sorption analyzers feature both a fully integrated high vacuum system and very low pressure measuring capability required for measuring the adsorption process associated with micropore filling and can be used with a variety of suitable probe gases at a variety of temperatures.

These instruments are programmed to measure the gas adsorption isotherm from extremely low relative pressure ( $P/P_0$ ) up to near saturation ( $P/P_0 = 1$ ). In this way they automatically acquire the raw data from which the micropore distribution (size and volume) is calculated.

## 3 Which samples were analyzed?

As examples, a copper MOF and an indium soc-MOF with high adsorption capacity for hydrogen, carbon dioxide and methane were analyzed. The as-synthesized Cu-MOF had previously undergone methanol extraction and been evacuated to remove the solvent to reveal the thermally stable (up to 250°C), open pore structure.

## 4 How to measure the sample

### 4.1 Sample preparation

Prior to measuring the gas sorption isotherm, the sample must still be thoroughly degassed to remove any residual vapors. This particular Cu-MOF was prepared under high vacuum at 298 K (25°C) for 48 hours. Low temperature is important to minimize the risk of reducing the Cu II.

The soc-MOF was outgassed at room temperature for 6 hours, and then at 408 K (135°C) for 12 hours under high (turbomolecular pumped) vacuum. After degassing was finished, the sample was backfilled with nitrogen and cooled to room temperature. Helium should not be used to backfill due to buoyancy effects which will affect the accuracy of the sample mass determined by weighing.

### 4.2 Adsorptive and temperature choice

Argon gas is used to reduce any specific interactions with the functional groups in the MOF which might otherwise be encountered if using nitrogen. Argon's own boiling point, 87.3 K, is chosen for micropore measurements. A Dewar bath of liquid argon can be used, or the same temperature can be generated using the CryoSync cryogenic thermostat accessory; the means of cooling are equivalent in terms of the micropore analysis.

### 4.3 Instrument settings and other parameters

- Sample mass used: 35 mg
- Void volume method: measured using helium
- Data point mode: Target  $P/P_0$  pressure table
- Micropore range points: 10 per decade
- Equilibration time settings 12 minutes until  $10^{-5} P/P_0$ , 7 minutes until  $10^{-2} P/P_0$ , 3 minutes above  $10^{-2} P/P_0$ .
- Mesopore points: 40 adsorption, 40 desorption
- Starting  $P/P_0$ :  $1 \times 10^{-7}$
- End  $P/P_0$ : 0.995
- $P_0$  mode: measure
- Sample cell type: 6 mm, large bulb

### 4.4 Procedure

Accurate sample mass is determined by weighing after the sample degassing to obtain the dry sample mass. The usual filler rod, which is used to reduce the void volume, is omitted when measuring micropores. Use of a filler rod can restrict the diffusion to the sample of the adsorptive at very low pressures.

The Dewar is filled to the base of the neck with freshly drawn liquid argon. The  $P_0$  cell and liquid argon level sensor must be installed according the instruction manual. As soon as the sample cell has been installed at the analysis station and the analytical parameters entered into the software, the analysis is started.

## 5 Results

### 5.1 Isotherms

#### 5.1.1 Cu-MOF

The isotherm (**Figure 3**) displayed a characteristic sigmoidal curve below  $P/P_0 = 0.01$ . This monotonic increase indicates the region of micropore filling and the  $P/P_0$  values over which it occurs reflect the pore size distribution. This pressure range is comparable to that of the well-known ZSM-5 zeolite having cylindrical pore channels.

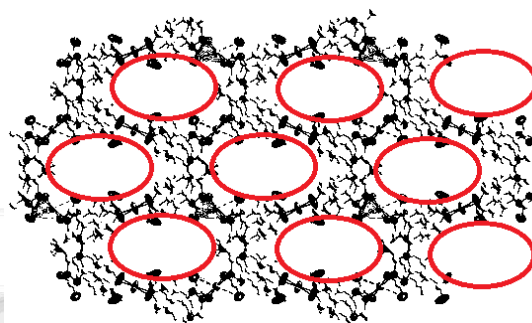


Figure 2: Ovoid cylindrical channels in the Cu-MOF crystal structure (after Ref 1).

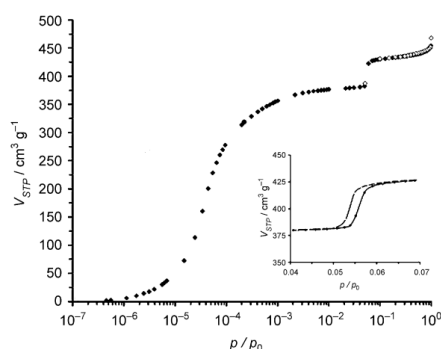


Figure 3: Argon isotherm for Cu-MOF displayed on semi-logarithmic scale. Inset shown on linear scale (after Ref 1).

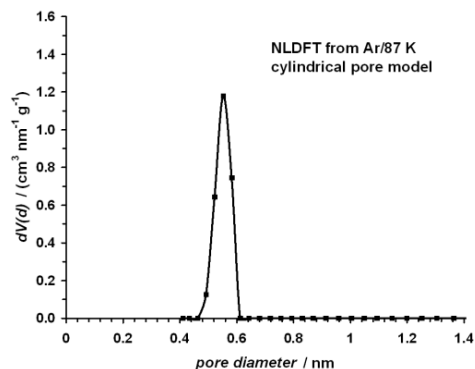


Figure 5: pore size distribution of Cu-MOF calculated by NLDFT (cylindrical zeolite pore model) (after Ref 1).

## 5.2 soc-MOF

This isotherm (Figure 4) displayed a similar, characteristic sigmoidal curve at somewhat higher relative pressures than the Cu-MOF. As before, this monotonic increase indicates the region of micropore filling and the  $P/P_0$  values over which it occurs reflect the pore size distribution. Soc-MOF does not display any second pore filling step/hysteresis above the micropore filling step indicating a rigid structure.

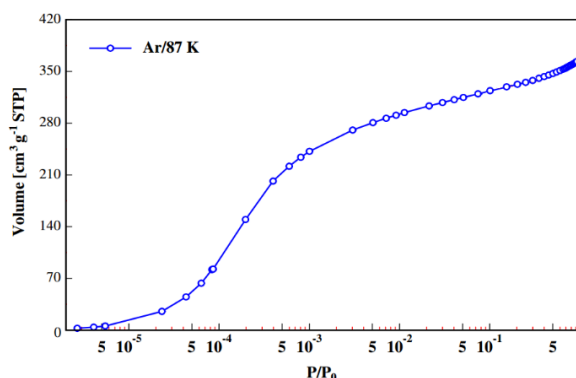


Figure 4: Argon isotherm for soc-MOF displayed on semi-logarithmic scale. (after Ref 2).

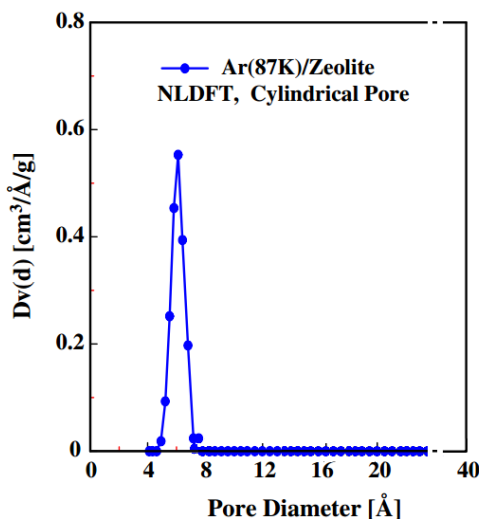


Figure 6: pore size distribution of soc-MOF calculated by NLDFT (cylindrical zeolite pore model) (after Ref 2).

## 5.3 Micropore size distributions

In order to determine the micropore size distribution, the NLDFT method was applied using a kernel (based on cylindrical zeolite pores to which MOF pores approximate) appropriate for argon at its own boiling point (~87K). The resulting distributions are shown in figures 5 and 6 for Cu-MOF and soc-MOF respectively. As suggested by the higher pore filling  $P/P_0$  of soc-MOF, its pore diameter is measurably, albeit only slightly, larger than that of Cu-MOF.

## 5.4 Total pore volume

The pore volume is calculated by applying the Gurvich rule [3] at  $P/P_0 = 0.95$ . The results for the two MOFs are shown in table 1.

Sample	Pore volume (cm <sup>3</sup> /g)
Cu-MOF	0.574
soc-MOF	0.47

Table 1: Total pore volumes.

## 6 Conclusions

The Autosorb iQ-MP and XR have the capability to automatically measure the argon adsorption isotherms at 87 K using either liquid argon or other cryostatic means, such as the Quantachrome CryoSync or CryoCooler.

Their high precision enables them to differentiate between two MOF's whose modal pore diameters differ by just 0.1 nm (1Å). Furthermore, the data quality is such that a structural change in non-rigid Cu-MOF can be precisely located with such resolution as to observe a subtle hysteresis effect associated with that particular structure-related phenomenon.



## 7 References

[1] D. Lässig, J. Lincke, J. Moellmer, C. Reichenbach, A. Moeller, R. Gläser, G. Kalies, K.A. Cychosz, M. Thommes, R. Staudt, H. Krautscheid, "A microporous copper metal-organic framework with high H<sub>2</sub> and CO<sub>2</sub> adsorption capacity at ambient pressure", *Angew. Chem. Int. Ed.* **2011**, 50(44), 10344-10348.

[2] J. Moellmer, E. B. Celer, R. Luebke, A. J. Cairns, R. Staudt, M. Eddaoudi, M. Thommes, "Insights on adsorption characterization of metal-organic frameworks: a benchmark study on the novel soc MOF", *Microporous Mesoporous Mater.* **2010** 129(3), 345-353.

[3] L.G. Gurvich, "Physicochemical attractive force", *J Phys Chem Soc Russ*, **1915**, 47, 805-827.

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