

## Application of Customized Optistat<sup>®</sup> DN Cryostat for Advanced Adsorption and Structural Characterization Studies

There is a growing need for advanced adsorption studies (on novel nanoporous materials), and *state-of-the-art* porous materials characterization, which requires to investigate the effect of temperature on adsorption, mainly because of the ongoing research efforts towards gas storage (hydrogen, methane and carbon dioxide) and separation applications.

An important quantity which can be derived from adsorption data obtained at various temperatures is the isosteric heat of adsorption, which has become a key quantity for characterizing the potential of metal-organic frameworks (MOFs) and other materials for gas storage (e.g. hydrogen, methane, CO<sub>2</sub>) applications. In order to address this need Quantachrome Instruments and OXFORD Instruments (Abingdon, U.K.) have collaborated in developing a new *cryostat* (a customized Optistat<sup>®</sup> DN cryostat) specially designed to provide the precise temperature control required for advanced gas sorption studies on the Autosorb-1. The new cryostat gives researchers the ability to easily perform gas sorption studies over a wide temperature range at any temperature between 77 K and 200 K using only liquid nitrogen as a cryogen. The use of only liquid nitrogen makes it also possible to perform state-of-the-art micropore analysis with argon at its boiling temperature (87.3 K) without the necessity of acquiring liquid argon, or even to apply other adsorptives at subcritical conditions (e.g. methane;  $T_{c,bulk} \approx 190$  K) for textural characterization applications at temperatures which cannot be achieved without a cryostat (because of the restriction of having only a limited number of specific temperatures using baths of different cryogenic liquids or melting solids). In the following sections we will discuss some aspects of selected applications which benefit from application of the new cryostat.

### (1) Aspects of the application of argon 87 K adsorption for state-of-the art micro/mesopore analysis

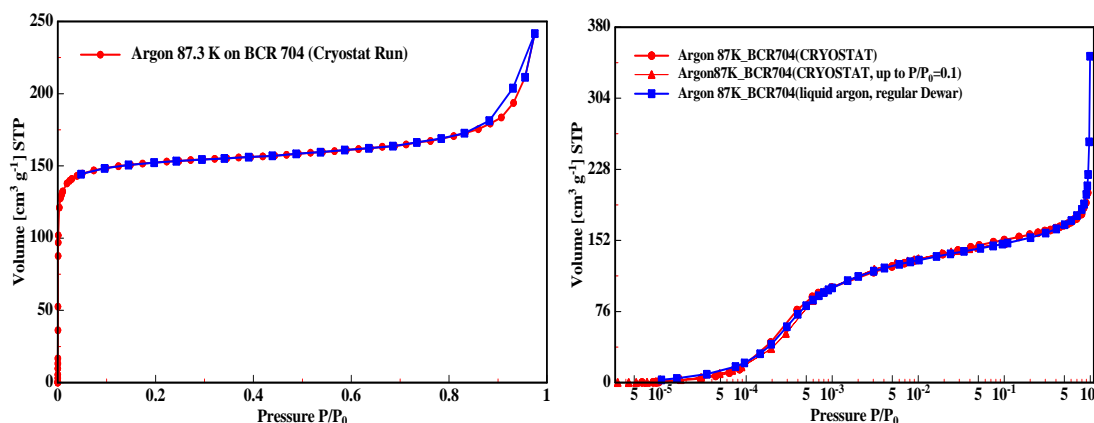
For a long time nitrogen adsorption at 77 K has been being considered to be the standard adsorptive for micro- and mesopore size analysis, but it is meanwhile generally accepted that nitrogen adsorption is not satisfactory with regard to a quantitative assessment of the microporosity, especially in the range of ultramicropores (pore widths < 0.7 nm) [e.g. 1- 3, and references therein]. Consequently, alternative probe molecules have been suggested, e.g. argon and carbon dioxide. Although the kinetic diameters of nitrogen (0.36nm), argon (0.34 nm) and carbon dioxide (0.33 nm) are similar, the adsorption behavior of these three adsorptives is quite different. For many microporous systems (zeolites in particular) the use of argon as adsorptive at its boiling temperature (87.3 K) appears to be very helpful [3, 4].

Compared to nitrogen and carbon dioxide argon does not give rise to specific interactions with a variety of surface functional groups and exposed ions during adsorption. As a consequence, argon fills for instance zeolite micropores of dimensions 0.5 – 1 nm at much higher relative pressures (i.e.,  $10^{-5} < P/P_0 < 10^{-3}$ ) compared to nitrogen, which leads to accelerated diffusion and equilibration processes, and allows to obtain accurate high resolution adsorption isotherms within a reasonable time frame [1 - 4]. Similar observations have been made for argon and nitrogen adsorption on MOF materials [5].

Furthermore, in case of monatomic argon adsorption, the application of advanced theoretical approaches (based on statistical mechanics) is facilitated.

The use of argon as adsorptive has not only advantages for obtaining a reliable pore size analysis, but also for surface area analysis. It is known that the quadrupole moment of the N<sub>2</sub> molecule leads for instance to specific

interactions with polar hydroxyl surface groups, causing an orientating effect on the adsorbed nitrogen molecules. Consequently, on polar surfaces the effective cross-sectional area of adsorbed nitrogen is smaller than the customary value of  $0.162 \text{ nm}^2$ . For a completely hydroxylated surface cross-sectional area of  $0.135 \text{ nm}^2$  was proposed, based on measurements of the  $\text{N}_2$  volume adsorbed on silica spheres of known diameter [17]. Hence, since argon molecule is monatomic and much less reactive than the diatomic nitrogen molecule, argon adsorption (at 87 K) may seem to be an alternative adsorptive for surface area determination. Due to the absence of a quadrupole moment and the higher boiling temperature, the cross-sectional area of argon ( $0.142 \text{ nm}^2$  at 87.3 K) is less sensitive to differences in the structure of the adsorbent surface (Please see the review articles of Neimark *et al* [1] and Thommes [2] and the references therein for more information on this).



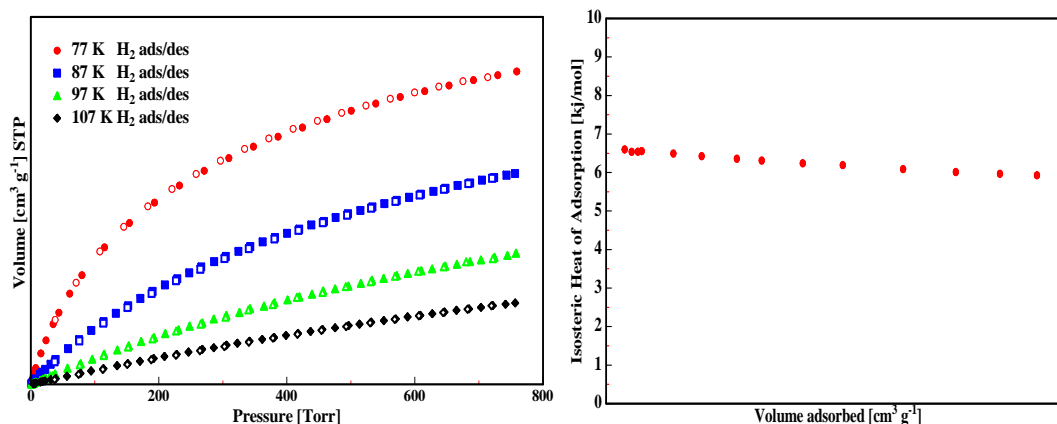
**Figure 1:** (a) Linear display of argon adsorption isotherm at 87.3 K on BCR 704. BCR 704 is a faujasite zeolite and microporous certified reference material (CRM) released by IRMM) obtained by using the Quantachrome cryostat. (b) Semi-logarithmic display of argon (87.3 K) adsorption isotherms; comparison of adsorption isotherms obtained with cryostat and liquid argon bath.

To demonstrate and validate the performance of the cryostat and also to highlight the importance of argon adsorption at 87.3 K for micropore analysis, we choose BCR 704 as a test material. BCR 704 is a faujasite zeolite and microporous certified reference material (CRM) released by IRMM) obtained by using the Quantachrome cryostat. Argon (87.3 K) isotherms obtained by using the new cryostat are shown in Figure 1. The results are in agreement with the specification for this CRM, and highly repeatable.

## (2) Aspects of the determination of the isosteric heat of adsorption

Studying the effect of temperature on adsorption does not only allow for studying fundamental adsorption phenomena, but also allows for an advanced characterization.

The determination of the isosteric heat of adsorption has become an important aspect of characterizing the potential of metal-organic frameworks for hydrogen or other gas storage applications. The isosteric heat is a direct indicator of the strength and heterogeneity of the interaction between the adsorptive and the adsorbent. There are various methods available to obtain the isosteric heat of adsorption, but the application of the Clausius-Clapeyron expression [6, 7] is considered to be quite accurate and is frequently used. However, an accurate application of this method requires at least three closely spaced (in temperature) adsorption isotherms [7].



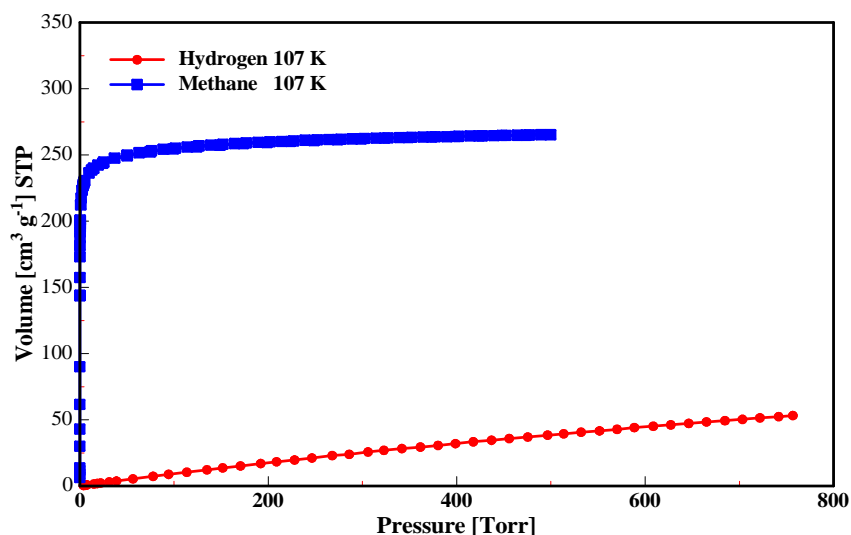
**Figure. 2:** (a) Hydrogen adsorption at (7 K – 107 K) on a MOF sample (b) Corresponding isosteric heat of adsorption.

Hence, it is therefore problematic that in many reports/publications the isosteric heat is often only derived from two experimental adsorption isotherms, which may lead to errors in the determination of the heat of adsorption.

An example of a hydrogen adsorption study on a MOF material covering a wider range of temperatures (from 77 K to 107 K) is shown in Figure 2. All hydrogen isotherms are reversible indicating that here the hydrogen isotherms were fully equilibrated and also that this particular MOF did not exhibit any framework changes during the adsorption process. Hence, useful isosteric heat of adsorption data could be obtained by applying the Clausius Clapeyron equation and are shown in Fig. 2b. The isosteric heat of adsorption at zero coverage is, at 6.5 kJ/mol, higher than for typical activated carbon materials [6]. The constancy of the heat of adsorption is indicative of the homogeneity of the H<sub>2</sub> adsorption sites, which is a desirable property for H<sub>2</sub> storage materials (a detailed discussion of low temperature H<sub>2</sub> data on a *sox*-MOF and corresponding isosteric heats obtained by using an Autosorb-1 MP coupled with the new Optistat cryostat is given in [5]).

### (3) Some aspects concerning the adsorption properties of nanoporous materials

As mentioned before, novel nanoporous materials, including MOF materials are considered as promising candidates for hydrogen and other gas storage (e.g. methane, carbon dioxide) applications. Within this context it is important to know the adsorption properties of a novel nanoporous material over a wide temperature and pressure range reflecting sub- and supercritical conditions (see for example [5, 6]).

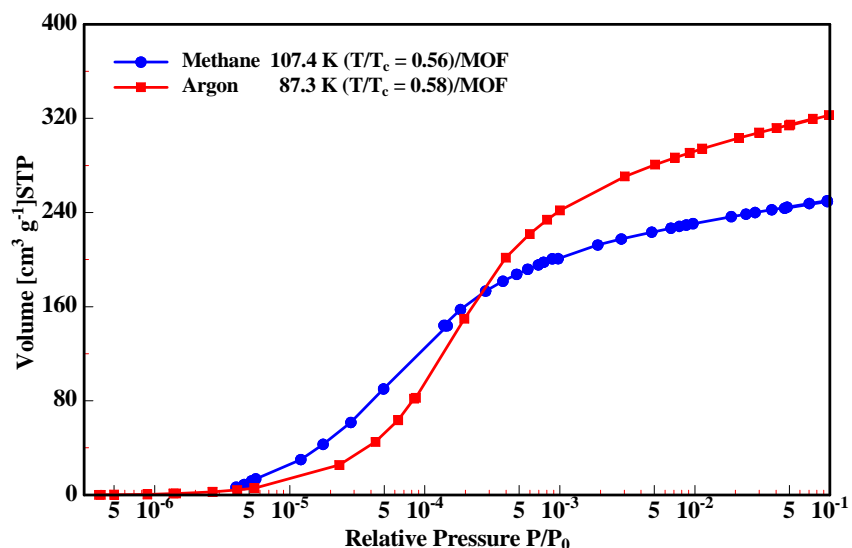


**Figure 3:** Adsorption of methane and hydrogen at 107 K on a MOF sample. At this temperature methane is subcritical ( $T/T_c = 0.56$ ), whereas hydrogen is supercritical ( $T/T_c = 3.23$ ).

An interesting example which demonstrates how the shape of an adsorption isotherm can be affected by different thermodynamic states of pore and bulk fluid phases is shown in Figure 3, in which the adsorption isotherms of hydrogen and methane at 107.4 K in a MOF sample are compared. The adsorption isotherms exhibit totally different shapes, which indeed is mainly due to the fact that at this temperature methane is subcritical ( $T/T_c = 0.56$ ), whereas hydrogen is supercritical ( $T/T_c = 3.23$ ). Hence, contrary to hydrogen, methane completely fills the pore space of this MOF with a liquid-like state, indicated by the observed plateau in the adsorption isotherm (i.e. a perfect type I adsorption isotherm is observed; the accessible pore diameter of this MOF sample corresponds to ca. 6.2 Å).

These results clearly reveal that the shape of the adsorption isotherms reflects details of the pore structure and surface chemistry, but is also strongly affected by the thermodynamic states of pore and bulk fluid phases. This has to be taken into account in particular if one compares differences in adsorption behavior and adsorption capacity of fluids in nanoporous materials; which also of importance for separation problems such as the  $\text{CO}_2/\text{CH}_4$  separation problem (see for instance ref. [5] for a detailed discussion concerning the effect of thermodynamic state of the bulk/pore fluid for differences in  $\text{CO}_2/\text{CH}_4$  adsorption capacity in soc-MOF).

Furthermore, methane (similar to argon) has no dipole or quadrupole moment, and it is interesting to check whether it is possible to use subcritical methane adsorption as a probe molecule for porosity analysis serve as reliable probe molecule textural characterization. In particular with regard to assessing the  $\text{CH}_4$  or  $\text{CO}_2$  gas storage capacities of this soc-MOF it is of interest to determine whether there is any advantage to determine the pore volume by using methane (below the critical temperature,  $T_c$ ) instead of using pore space/volumes obtained from other probe molecules (e.g. such as argon and nitrogen).



**Figure 4:** Semilogarithmic display of argon (87.3 K) and methane (107.4 K) adsorption in a MOF sample.

Adsorption isotherms of argon 87.3 K and methane at (107.4 K) on a MOF material displayed in the relative pressure range where pore filling occurs is shown in Figure 4.

Although argon and methane adsorption isotherms were measured at significantly different absolute temperature, the reduced temperatures ( $T/T_c = 0.58$  and  $0.56$ , respectively) are very similar. This also contributes to the fact that argon (87 K) and methane (107 K) fill the MOF micropores in comparable relative pressure range. Also, the pore volume obtained from the methane and argon adsorption data by applying the Gurvich rule are in very good agreement (the pore volumes were obtained after the pore filling was completed, i.e. at a rel. pressure of ca. 0.1 and a value of  $0.416 \text{ cm}^3/\text{g}$  was obtained from the methane adsorption isotherm; the pore volume obtained from argon adsorption is, with  $0.4116 \text{ cm}^3/\text{g}$ , almost identical). This good agreement in the pore volumes obtained from subcritical  $\text{CH}_4$  and Ar adsorption also indicates that using argon adsorption is sufficient for obtaining meaningful pore volume/porosity information also in the context of discussing  $\text{CH}_4$  adsorption/storage potential of the adsorbent material.

## References

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