

Adsorption studies with various adsorptives from 77 K up to 323 K

Characterization of
particles · powders · pores

Introduction

Surfaces are formed by all solids as external interfaces and are present as micropores, mesopores, macropores or as external surfaces on non-porous particle areas. The results of gas adsorption measurements are the sum of particle surfaces including surface roughness and open pores. In principle, a complete isotherm or, for the determination of the BET surface area, only a part of an isotherm is measured. Figure 1 shows such sorption isotherms of nonporous carbon black, mesoporous glass and a microporous metal-organic framework, together with standard range to calculate BET surface areas.

Traditionally, nitrogen adsorption at the temperature of liquid nitrogen (77.4 K) is used as the standard procedure. From a scientific point of view, however, argon and krypton are more suitable adsorptives for the surface and pore analysis of many materials. When compared to the N₂ molecule, single atomic noble gases are spherically symmetrical. Consequently, the space requirement of adsorbed argon and krypton atoms is not influenced by the spatial orientation on the surface (see Figure 2). Interactions between argon or krypton atoms and the solid surface are also less affected by the surface polarity, since the noble gas atoms do not have an electric quadrupole moment.

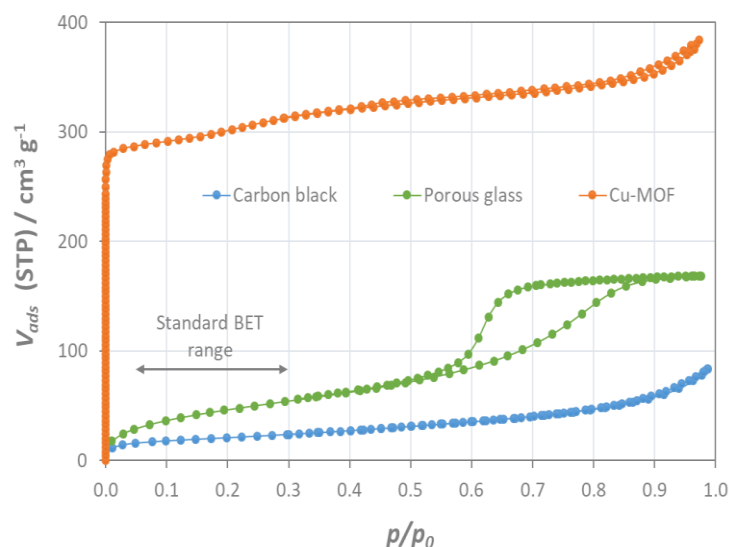


Figure 1 Adsorption and desorption isotherms of argon at 87 K of nonporous carbon black, mesoporous glass and a microporous Metal-Organic-Framework (Cu-MOF).

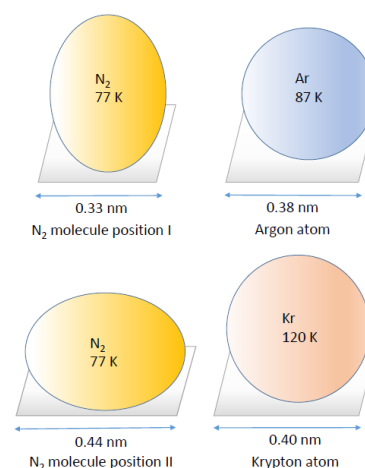


Figure 2 Schematic comparison of the nitrogen molecule at 77 K [1] with the noble gases argon 87 K and krypton 120 K. The nitrogen molecule can adsorb in different positions, whereas the spherical shape of the noble gas atoms allows only one position.

In addition to Ar and Kr, other nonpolar adsorptives such as Xe, CH₄ and SF₆ were used in this study. Furthermore, O₂, N₂ and CO₂ were used as adsorptive molecules with quadrupole moments as well as methane, ethane, propane and n-butane. Table 1 shows the mentioned adsorptives and measuring temperatures (boiling points) with the used cryoTune temperature controller for experimental setup (explained later) and some of the adsorptive parameters: density of liquid adsorptive ρ_{Liquid} , space requirement for one adsorbate atom or molecule a_m , saturation pressure p_0 and the non-ideality factor of the real gases F_{ni} .

Adsorption studies with various adsorptives from 77 K up to 323 K

Characterization of
particles · powders · pores

Table 1 The adsorptives used in this study, their boiling temperatures, adsorptive parameters, and the used cryoTune options.

Adsorptive	Boiling point T / K	$\rho^{Liquid} /$ $g\ cm^{-3}$	Critical diameter of atom/molecule / nm [2]	a_m for BET surface from ρ^{Liquid} / nm^2 ^{*4}	$p_0 /$ kPa	Non-ideality factor F_{ni} of the adsorptive ^{*3}	Type of cryoTune option used
Ar	87	1.39	0.34	0.143	101	$4.27 \cdot 10^{-5}$	cryoTune 87
Kr	120	2.41	0.36	0.163	101	$3.83 \cdot 10^{-5}$	cryoTune 120
Xe	165	2.94	0.41	0.192	101	$3.71 \cdot 10^{-5}$	cryoTune 120
SF ₆	209	1.91	0.67	0.276	101	$3.87 \cdot 10^{-5}$	cryoTune 195
CH ₄	112	0.42	0.40	0.174	101	$4.26 \cdot 10^{-5}$	cryoTune 87
Ethane	184	0.54	0.44	0.223	101	$3.86 \cdot 10^{-5}$	cryoTune 195
Propane	231	0.58	0.49	0.275	101	$3.93 \cdot 10^{-5}$	cryoTune 195
n-butane	273	0.60	0.49	0.322	101	$4.05 \cdot 10^{-5}$	cryoTune 195
O ₂	90	1.14	0.28	0.141	101	$4.09 \cdot 10^{-5}$	cryoTune 87
N ₂	77	0.81	0.30	0.162	101	$5.21 \cdot 10^{-5}$	cryoTune 77
CO ₂	195 ^{*1}	1.26	0.28	0.164 ^{*2}	188 ^{*2}	$2.09 \cdot 10^{-5}$	cryoTune 195
Ethene ^{*5}	169	0.58	0.39	0.203	101	$3.71 \cdot 10^{-5}$	cryoTune 120
CO ^{*5}	82	0.94	0.37	0.147	101	$5.11 \cdot 10^{-5}$	cryoTune 87
NH ₃ ^{*5}	240	0.70	0.29	0.128	101	$4.17 \cdot 10^{-5}$	cryoTune 195
iso- Butane ^{*5}	261	0.59	0.51	0.325	101	$1.71 \cdot 10^{-5}$	cryoTune 195

*1...sublimation point

*2...of the undercooled liquid

*3...mean value of van der Waals and Bethelot calculations

*4...calculated according $a_m = \left(\frac{M}{\rho_l \cdot N_A} \right)^{\left(\frac{2}{3} \right)}$

*5...These adsorptives were not used in this study, but can be used as alternative adsorptives.

Adsorption studies with various adsorptives from 77 K up to 323 K

The present study shows, in many points similar to the ISO 9277 [3] and IUPAC recommendation of 2015 [4]:

- a. From a scientific point of view, nitrogen is not a reasonable standard adsorptive for surface and pore analysis for many materials. This applies not only to micropore analysis, but also to the determination of specific surfaces, e.g. using the BET method. In particular, the sorption behavior of many other gases, vapors and liquids cannot, by definition, be correctly determined from the BET surface area obtained by nitrogen adsorption, since the result is strongly influenced by the quadrupole moment and an undefined space requirement of the non-spherical adsorptive molecule.
- b. A combined application of different adsorptives allows the characterization of specific surface and pore properties for certain groups of materials, e.g. by comparing the sorption results of adsorptives without or with quadrupole or dipole moment.
- c. The determination of micropore distributions and specific surface areas of porous and non-porous materials by Ar 87 K adsorption is scientifically necessary. The application of different adsorptives is useful for many groups of materials in order to evaluate specific surface properties. For comparison with results of the noble gases Ar, Kr and Xe, other adsorptives such as N₂ with a moderate and CO₂ with a large quadrupole moment are suitable.

Recommendations of BET norm ISO 9277 and of IUPAC for characterization of surfaces and micropores materials

The ISO 9277 [3] mentions: "Very often, argon at liquid argon temperature [...] is a good alternative for specific surface determination [...] because it is chemically inert monoatomic gas with symmetrical electron shell configuration quite different from that of nitrogen." In addition, Annex A lists some recommended cross-sectional areas of adsorbate atoms and molecules with the following comments: "In the case of graphitized carbon and hydroxylated oxide surfaces, the orientation of the nitrogen quadrupole is dependent on the surface density of hydroxyl groups, because the nitrogen molecules tend to interact vertically with surface hydroxyl groups. This leads to a reduced value of cross-sectional area of nitrogen. It is recommended to use Ar at the temperature of liquid Ar (87.3 K) for the determination of the BET area of such surfaces." Furthermore, the ISO 9077 explains that Ar adsorption at liquid nitrogen temperature (77.3 K) is no suitable alternative to the Ar adsorption at 87.3 K.

The clear statement of the ISO norm 9277 [3] and the IUPAC recommendation from 2015 [4] has stipulated a fundamental goal for the scientific use of the gas adsorption technique to describe surface and pore phenomena: the use of Ar at 87 K for many materials. One can generalize this requirement as follows: many materials demand Ar 87 K measurement data, so the measurement of all materials by using Ar at 87 K should be considered scientifically as the most appropriate way.

The use of argon and nitrogen for micropore characterization

First of all, the differences between nitrogen and argon adsorption for microporous materials should be considered. Figure 3 shows that the nitrogen isotherms of a zeolite and an activated carbon is shifted to lower relative pressures, and the difference between Ar and N₂ is larger for the zeolite as compared to the activated carbon. The shift of the nitrogen isotherms to lower relative pressures causes a larger equilibration time (and measuring time respectively). In addition, this causes larger errors due to problems during the accurate measurement of the lowest relative pressures.

Adsorption studies with various adsorptives from 77 K up to 323 K

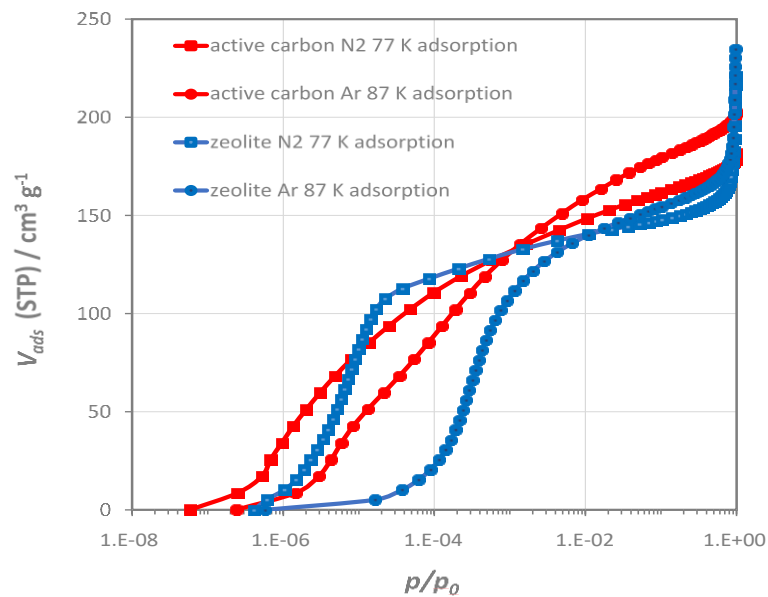
Characterization of
particles · powders · pores

The larger errors of the nitrogen isotherm are caused by the following points:

- The so-called thermal transpiration correction plays a role for very low pressures only.
- A possible helium entrapment of the material influences especially the relative pressures ($p/p_0 < 10^{-5}$).
- The so-called pressure table mode in the micropore range, which e.g. has been proposed by Quantachrome and is realized in older instrument versions as the micropore standard measuring mode [4], the number of gas doses in the low-pressure range can be extremely high. In practice, we found that such measurements with N_2 at 77 K in the micropore range can take > 70 hours. If the incremental dose mode is used, the measurement takes only 40 hours with nitrogen, but with argon at 87 K only 24 hours. Noble gases at higher temperatures (e.g. 87 K) and an intelligent incremental dose routine can reduce the measuring time. Hence, the sample throughput of a gas adsorption instrument can be increased and the temperature controllers of the cryoTune series offer a good configuration for that.

To sum up, Ar sorption measurements at 87 K are more accurate from scientific point of view because the Ar atom has no quadrupole moment. In addition, they are more precise because Ar measurements can be conducted in the optimal pressure range in a shorter analysis time.

Figure 3 N_2 77 K and Ar 87 K isotherms of a zeolite and an activated carbon: the N_2 77 K isotherms are shifted to the left (lower relative pressures) because of lower temperature, but also due to the specific quadrupole interactions between the N_2 molecule and the micropore surfaces.



Regarding micropore characterization, we can distinguish between three different scenarios:

- The micropores are large enough that the adsorption follows the mechanism based on the van der Waals interactions. Hence, we can use the sorption data to calculate micropore size distributions, BET surface areas and pore volumes. Such an example was investigated in the "Partikelwelt" article by the group of Prof. Fröba (University of Hamburg) [5]. A comparative study of BET surface areas of different Metal-Organic Frameworks (MOFs) was carried out with argon at 87 K and nitrogen at 77 K (see Table 2). It can be concluded that all BET surface values determined by nitrogen sorption are higher than those determined with argon. By comparing the difference in the BET values of the two adsorptives (Table 2, right column), it can be noted that there is no constant, certain factor between the values. To obtain scientifically accurate results, the measurement with the atomic adsorptive argon at 87 K is recommended for that type of materials.

Adsorption studies with various adsorptives from 77 K up to 323 K

Characterization of
particles • powders • pores

Table 2 BET surface areas of MOFs from Ar 87 K and N₂ 77 K isotherms. The structures of the MOFs are given in [5] and are based on functionalized benzene tricarboxylic acid (BTC).

	BET surface Ar 87 K / m ² g ⁻¹	BET surface N ₂ 77 K / m ² g ⁻¹	Comparison BET N ₂ 77 K vs. BET(Ar 87 K) / %
HKUST-1	1533	1674	+ 9.2
UHM-30	1648	1806	+ 9.6
UHM-31	1376	1808	+ 31.4
UHM-36	1223	1385	+ 13.2
UHM-37	1178	1305	+ 10.8
UHM-38	1198	1264	+ 5.5
UHM-39	1019	1213	+ 19.0

- b. Pore exclusion effects, where adsorptive molecules are larger than the micropores or the micropore entries, so that e.g. a 0.5 nm molecule cannot diffuse into a 0.4 nm ultramicropore. The questions for researchers may be: How can I recognize this effect? How can I prove whether my materials cause this pore exclusion effect? This question can be answered by measuring adsorption isotherms using different adsorptives with different critical diameters (see Table 1).
- c. Kinetic or blockage effects: as described in literature and in own investigations [6], nitrogen molecules do not diffuse into the inner pore space below 0.45 nm at 77 K, but adsorbs to 0.4 nm pores at room temperature. We studied and proved kinetic and blockage effects. Figure 4 shows the temperature dependency of the N₂ adsorption in Zeolite 4A at a constant pressure of 101 kPa (760 mmHg), using an equilibration time of 48 h for each point [7]. The adsorbed volume of N₂ is almost zero below a temperature of 100 K but increases with rising temperature. That means, that the first adsorbed N₂ molecules at 77 K or below 100 K only block the entries of the outer micropores but, e.g. at 120 K, many N₂ molecules are inside the microporous system after 48 h. However, these molecules have such a low diffusion rate and block the paths to the inner parts of the microporous materials. Hence, this can be called kinetic problem or blockage effect.

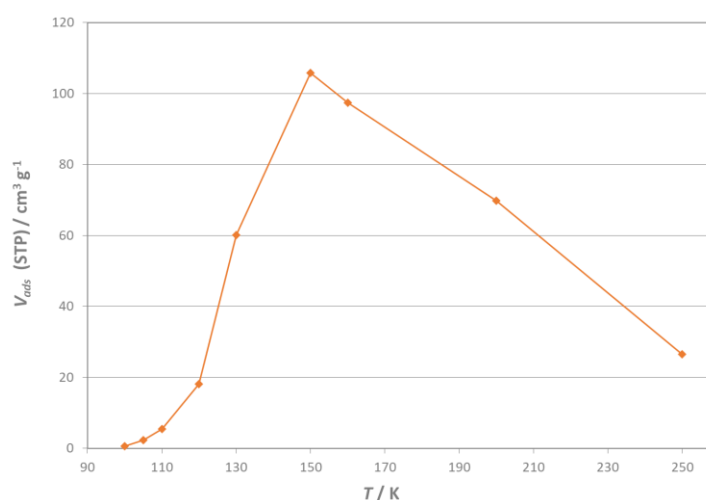


Figure 4 The temperature dependent N₂ adsorption on microporous Zeolite 4A (0.4 nm) shows a kinetic effect: N₂ does not fill the micropore system at low temperatures because of kinetic effects (respective pore blocking).

Adsorption studies with various adsorptives from 77 K up to 323 K

Characterization of
particles • powders • pores

The use of other adsorptives to study microporous materials

The adsorptives argon, krypton and methane (without quadrupole moment) as well as oxygen (little quadrupole moment) and nitrogen (higher quadrupole moment) were used to measure isotherms on a sample of activated carbon. As shown in Figure 5 and Table 3, the results using the first four adsorptives show an average BET surface area of $1365 \text{ m}^2 \text{ g}^{-1}$ with maximum deviation of 1.5 %, but the nitrogen result differs more than 5 % from the other data. This shows the clear influence of the quadrupole moment of the adsorptive on the results of the sorption measurements and underlines the necessity of using other adsorptives than nitrogen.

Figure 5 Adsorption isotherms using various adsorptives (at their boiling temperatures) on a sample of activated carbon.

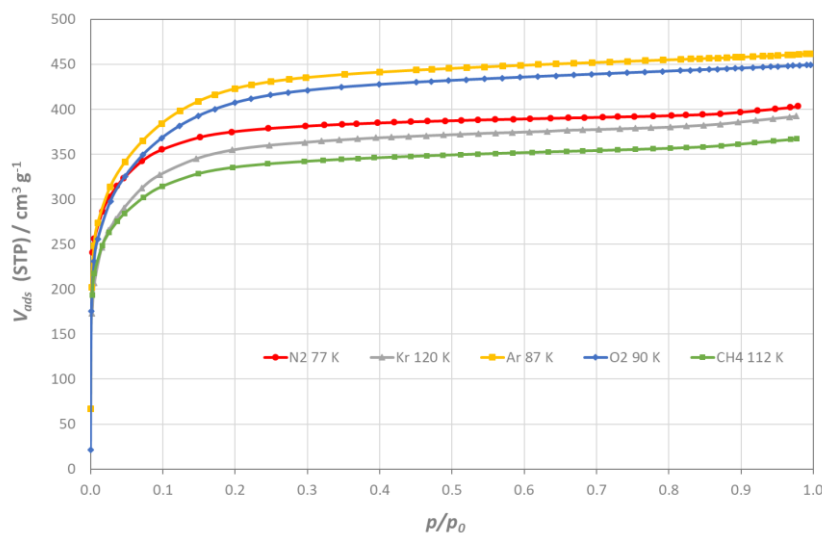


Table 3 BET surface areas calculated from sorption measurements using various adsorptives (at their boiling temperatures) on a sample of activated carbon. The results show the difference of the N_2 value in comparison to the group of nonpolar adsorptives.

Adsorptive	T / K	BET / $\text{m}^2 \text{ g}^{-1}$	a_m from $\rho_{\text{liquid}} / \text{nm}^2$	cryoTune version
Ar	87	1384	0.143	cryoTune 87
Kr	120	1362	0.163	cryoTune 120
CH ₄	112	1371	0.174	cryoTune 87
O ₂	90	1345	0.141	cryoTune 87
N ₂	77	1438	0.162	cryoTune 77

The specific surface area (BET surface area) of non-microporous materials

We have investigated a set of numerous materials with only meso- or macropores as well as nonporous materials. They are referred to as non-microporous materials to show that no micropore effects (as mentioned in section 0c) play a role for the interpretation of the measurement data. Non-porous materials show an isotherm type II (nonporous or macroporous) or type IV (mesoporous) regarding IUPAC classification [4]. Both are typical isotherm types to apply the BET equation for the calculation of the specific surface area.

Table 4 shows the differences in the BET surface area of different non-microporous materials using nitrogen and argon as adsorptives. Especially deviations of 19 % or even 32 % between BET surface areas determined from N_2 77 K and Ar 87 K isotherms are a strong indication that the term "accuracy" could be doubtful concerning many traditionally determined BET surface areas by use of N_2 at 77 K.

Adsorption studies with various adsorptives from 77 K up to 323 K

Characterization of
particles · powders · pores

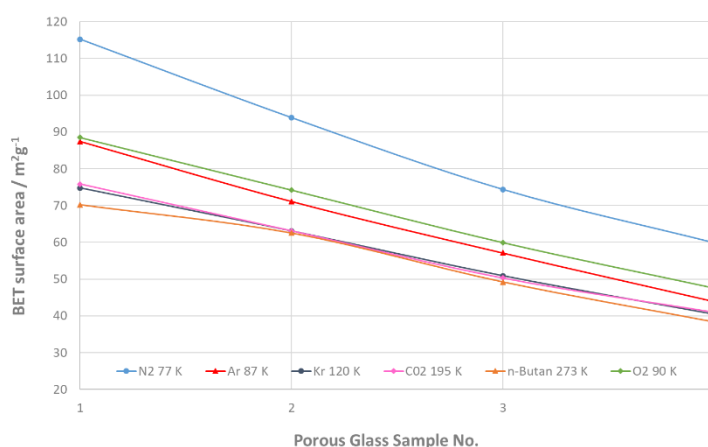
Table 4 BET surface areas of non-microporous materials determined by N₂ 77 K with Ar 87 K.

Material	Adsorptive	T / K	a _m / nm ²	BET / m ² g ⁻¹	Difference BET(N ₂)/BET(Ar)
Al ₂ O ₃ , macroporous	N ₂	77	0.162	5.42	+ 32 %
Al ₂ O ₃ , macroporous	Ar	87	0.143	4.11	
Silica, mesoporous	N ₂	77	0.162	194.9	+ 27 %
Silica, mesoporous	Ar	87	0.143	153.2	
Carbon black	N ₂	77	0.162	77.6	+ 19 %
Carbon black	Ar	87	0.143	65.1	
Tungsten carbide	N ₂	77	0.162	3.63	+ 12 %
Tungsten carbide	Ar	87	0.143	3.24	

In addition, we studied the BET surface area of mesoporous glasses using the adsorptives N₂, Ar, Kr, CO₂, n-butane and O₂ (see Figure 6). The results of the last mentioned five adsorptives are close together, especially Ar and O₂ results, but the BET surface area from N₂ 77 K measurements are 30 % higher compared to the Ar results. This leads to the following conclusions:

- N₂ at 77 K has a different adsorption behavior for the porous glasses in the relative pressure range of the first monolayer. The BET surface areas determined by Ar and O₂ (no and respectively small quadrupole moment) are about 30 % smaller compared to N₂ at 77 K with a larger quadrupole moment.
- The differences between the results of the other adsorptives need additional studies. Relevant questions could be if the parameters for CO₂ (where no liquid exists under normal conditions) are questionable, or if the used place for one n-butane adsorbate molecule is too low, because n-butane will adsorb to the surface in a flat and not a vertical position.
- The claim of accuracy of the measurement results should turn argon measurements at 87 K into the scientific standard or at least into the critical standard of comparison, especially where specific dissolution and exchange processes, aging rates, catalytic activities or other parameters are correlated with the specific surfaces of the investigated materials.

Figure 6 BET results of four different porous glasses (No. 1-4) determined with six different adsorptives at their boiling points (for CO₂ at its sublimation point).



Furthermore, studies on the BET surface area of cellular concrete using eight adsorptives were carried out. The results (see Table 5) of a completely different material group confirm the key messages of our study: The data for the first six adsorptives (Ar, n-butane, propane, ethane, CH₄ and O₂) show only slight differences.

Adsorption studies with various adsorptives from 77 K up to 323 K

Characterization of
particles • powders • pores

These differences should be further studied including the adsorbate parameters, the BET calculation model as well as the position of elongated but nonpolar molecules in the monolayer on the solid surface (e.g., for ethane, propane and n-butane). However, the N₂ results are 57 % higher compared to the Ar 87 K BET surface area – which is in accordance with the aforementioned results and is due to the high quadrupole moment of the N₂ molecule. In addition, the BET results for CO₂ sorption at 195 K are more than three times than the BET surface area calculated from Ar 87 K. This can be explained with a three times stronger quadrupole moment of CO₂ compared to N₂.

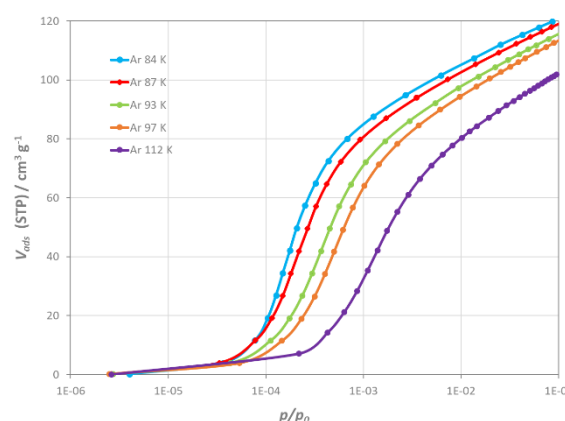
Table 5 BET results for cellular concrete using eight different adsorptives at their boiling points (for CO₂ at its sublimation point).

Adsorptive and temperature	BET surface area / m ² g ⁻¹	Shape/quadrupole of adsorptive molecule/atom	Comparison to BET(Ar 87 K) / %
Ar 87 K	42.0	Spherical	n. a.
n-Butane 273 K	30.9	Elongated	- 26
Propane 230 K	34.9	Elongated	- 17
Ethane 185 K	34.9	Elongated	- 17
CH ₄ 112 K	48.1	Spherical	+ 15
O ₂ 90 K	49.4	Ellipsoidal with small quadrupole moment	+ 18
N ₂ 77 K	65.9	Ellipsoidal medium quadrupole moment	+ 57
CO ₂ 195 K	111.1	Elongated with high quadrupole moment	+ 165

The use of the cryoTune series with different sorption analyzers

For measuring the sorption isotherms of many adsorptives, the availability of the corresponding liquid gas for cooling is usually a problem. The cryoTune series is a novel temperature control option for modern gas sorption devices, which only requires readily available, inexpensive liquid nitrogen for cooling. Additionally, a cryoTune allows the measurement of isotherms at different temperatures for thermodynamic calculations, e.g. for the calculation of the isosteric heat of adsorption (sorption enthalpies). An example for the sorption of Ar at different temperatures between 84 K and 112 K is given in Figure 7.

Figure 7 Ar isotherms of Zeolite 13X at different temperatures. Such isotherms, e.g. at 84, 87, 93, 97 and 112 K, can be used for thermodynamic calculations.



Adsorption studies with various adsorptives from 77 K up to 323 K

Characterization of
particles • powders • pores

All these options of the cryoTune series, including the flexibility regarding adsorptives and temperatures, are available for almost all gas sorption instruments. We have good experiences with the use of 3P cryoTune upgrades for 3Flex or ASAP instruments from Micromeritics and Autosorb-iQ-versions from the former Quantachrome, but also for older instrument types like Autosorb-1 or NOVAe from the former Quantachrome. Independent of the instrument type, the handling of a cryoTune is very easy, and the cryoTune controller software is user-friendly and written in various languages. The fact that a cryoTune works absolutely noiseless and with very low energy consumption makes it applicable in all labs and without special requirements. The required space is minimized (see Figure 8) and the handling is user-friendly, too. Figure 9 shows the use of a cryoTune in connection with a gas adsorption instrument: The device is placed in the Dewar on the right and the small controller can be placed on top of the instrument. The sample cell is connected with one measuring port. The Dewar can be placed together with cryoTune next to or inside the cabinet of the analytical instrument. This offers the opportunity to use the cryoTune together with various instruments. The 3P micro 200 instrument offers another useful way for adsorption studies: Figure 9 shows the implemented two degassing ports on the left, a cold trap in the middle and two ports on the right. The cryoTune is connected to port 2 on the right, but a large Dewar on port 1. As this sorption instrument has separate gas lines, it is possible to measure, e.g. different samples in parallel, e.g. N₂ at 77 K on port 1 and Ar at 87 K on port 2, or Ar 87 K on port 1 but CO₂ with a second cryoTune on port 2 etc.

Figure 8 The use of a cryoTune: the cryoTune is placed inside the Dewar (1). The sample cell is then placed into the cryoTune (2). Finally, the Dewar is closed with the special isolation cover (3). The little hole in the cover on the right enables refilling of liquid nitrogen during a long-term measurement (normally not necessary). The hole is covered during the measurement to optimize the Dewar holding time.



Figure 9 The use of a cryoTune in connection with a 3P micro 200 instrument. The cryoTune is placed in the Dewar on the right and the small controller is positioned on the top of the instrument, the sample cell is connected with the measuring port.





Adsorption studies with various adsorptives from 77 K up to 323 K

The cryoTune facilitates the exact determination of BET surface areas and micropores. Furthermore, investigations of the adsorption of real gases are possible. In future publications, we will present the following:

- Results from additional adsorptives using a 3P cryoCooler (instead a cryoTune) to realize temperatures below 77 K, mainly for measurements of hydrogen and neon at their boiling points at 20 K and 27 K, respectively.
- Adsorption measurements with calculations of isosteric heat of adsorption, e.g. for hydrogen adsorption at 77 K, 87 K, 97 K and 107 K.
- The use of the 3P Sim software for the Simulation of mixed gas isotherms from pure gas isotherms.

As the cryoTune only needs liquid nitrogen for the tempering, these measurement and evaluation possibilities are now available to a broad community.

References

- [1] Hoffmann, J.: Dissertation, Uni Konstanz, 2002, p. 12 (only available in German)
- [2] Kast, W.: Adsorption aus der Gasphase, Verlag Chemie, Weinheim, 1988
- [3] ISO 9277:2010: Determination of the specific surface area of solids by gas adsorption – BET method
- [4] IUPAC recommendation, Pure Appl. Chem. 87(9-10), 2015, 1051-1069
- [5] Fröba, M.: Partikelwelt 17, p. 17 ff. (only available in German)
- [6] Lowell, S. et.al.: Characterization of Porous Solids and Powders, Kluwer 2004, p. 152
- [7] Reichenbach, C., Klank, D.: Partikelwelt 15, Quantachrome Germany, p. 19 (only available in German)

3P Instruments
Rudolf-Diesel-Str. 12
85235 Odelzhausen
Germany

www.3P-Instruments.com
info@3p-instruments.com
+49-8134 93240