APPNOTE 2-05

Argon for surface and pore characterization

3P INSTRUMENTS

Characterization of
particles · powders · pores

Introduction

The critically reviewed IUPAC report "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution" was published in 2015 and is an up-to-date compendium for the characterization of porous materials using gas sorption [1]. Besides an extended isotherm classification, this updated release includes numerous recommendations for the measurement and interpretation of isotherm data. "New recommendations" that have been the basis of applying our measurement methods since many years. A fact that becomes obvious in this central topic is that the characterization of micropores using physisorption of should be carried out with argon at a temperature of 87 K (boiling temperature of argon). We have identified this advantage more than 20 years ago and its practical realization to achieve 87 K was by use of liquid argon for a long time.
More recently, we started to equip our instruments with so-called cryoTune modules, an option that was specifically designed for achieving an 82 – 135 K temperature range. In this way, not only the boiling point of the noble gas argon at 87 K, but also the boiling point of the noble gas krypton at 120 K becomes viable for isotherm analysis. This article describes these additional research options with a critical discussion of the nitrogen-based results as traditional basis not only for pore size but also for surface area determination.

The advantages of argon isotherms at 87 K in micropore analysis

For the sake of completeness, the main advantages of argon adsorption at 87 K compared to N_2 isotherm measurements at 77 K are as follows:

- Unlike nitrogen, argon has no quadrupole moment which is the reason that no specific interaction between adsorptive and polar or ionic surface areas is to be expected.
- Accordingly, argon isotherms produce much more reliable texture data regardless of the solid surface's chemical properties.
- Compared to nitrogen sorption at 77 K, argon adsorption analysis at 87 K is considerably less time-consuming, because the filling of similar pores can occur much more readily at much higher relative pressures (see Fig. 1).

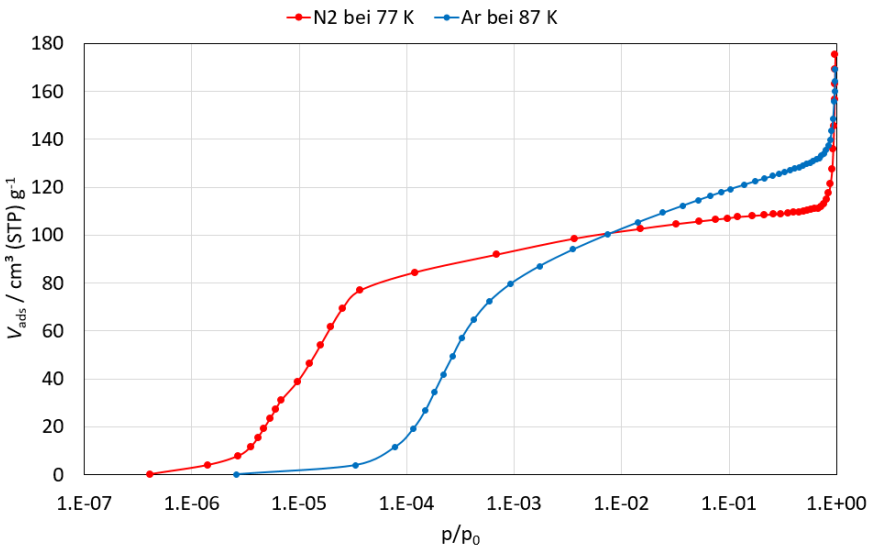

Figure 1 Ar@87K and N_2@77K isotherms in zeolite 13 X

The general idea for the development of the cryoTune modules was to make these advantages available to studies that have no liquid argon available. Furthermore, the acquisition of a so-called cryostat is associated with further considerable costs and is therefore not economical. The following section explains possibilities for additional measurements arising from the use of cryoTune modules, as the temperature range is not limited to 87 K. When filling the module with liquid nitrogen, a temperature range between 82 K and 135 K was achievable for our studies.

Determination of BET surface areas with alternative adsorptives and the question for correct cross-sectional areas of adsorbate molecules

The determination of specific surface areas A_S is almost exclusively done with BET evaluation of nitrogen isotherms at 77 K. In general, it determines the number of adsorbate molecules forming a monolayer n_M on the solid surface, which is then multiplied by the average cross-sectional area a_m of the adsorbate molecules:

$$A_S = a_m n_M N_A \qquad \text{Eq. 1}$$

A value for the cross-sectional area a_m can be calculated using the molar mass M and the density of the liquefied adsorptive p_L at the corresponding measuring temperature:

$$a_m = 1.091 \left(\frac{M}{\rho_L N_A} \right)^{2/3} \qquad \text{Eq. 2}$$

In case of nitrogen at 77 K, the cross-sectional area is assumed with $a_m(N_2)$ = 0.162 nm^2. There are very pragmatic reasons for the fact that nitrogen has become the adsorptive for the determination of specific surface areas. This is mainly attributable to the cost-efficient availability of this chemical material as high-purity inert gas on the one hand and in liquid state for the cooling of samples, which was obviously the only choice in the 1930s and 1940s on the other hand. Knowing that noble gases have more favorable adsorption properties because of their spherical symmetry, scientists soon started using alternative gases such as argon, krypton and xenon as adsorptives for the determination of specific surface areas. However, in most cases and due to a lack of economically viable alternatives, a measurement temperature of 77 K was used. For all of the above-mentioned noble gases, 77 K is below the triple point temperature. For the determination of BET surface areas, the saturated vapor pressure of the undercooled liquid is to be used instead the saturated vapor pressure of the re-sublimated gas. That means for krypton at 77 K that re-sublimates at 1.6 Torr (0.21 kPa), but for the BET calculation the p_0-value of 2.63 Torr (0.35 kPa) for the undercooled krypton liquid is to be used.

To overcome differences in the calculated surfaces, cross-sectional areas for noble gases were postulated there and then, which reproduced the values obtained with nitrogen using equation 1. Depending on the chemical properties of the evaluated surface, different values were constructed [2, 3, 4]. The argon example furthermore indicates that different cross-sectional area values for adsorbed argon atoms were calculated even with the same measurement temperature and the same surface conditions, depending on whether the calculation of the BET surface area refers to the saturated vapor pressure of the cooled liquid or the solid argon (see table 2). Table 1 compiles the cross-sectional areas of nitrogen, argon and krypton at a temperature of 77 K resulting from calculations based on equation 2 (from [2]). In case of argon and krypton, calculations were based on the density of undercooled liquids at 77 K. The standard cross-sectional area is indicated for comparative reasons. It becomes obvious that the calculated cross-sectional areas of argon and nitrogen has prevailed. In contrast, there is a considerable difference

between the calculated and the commonly used cross-sectional area requirement for krypton; a deviation caused by the alignment with the surface obtained with nitrogen, and which does not have a scientific explanation. Table 2 is even clearer about this issue.

Table 1 Cross-sectional areas of N_2, Ar and Kr at 77 K (from [2])

Adsorptive	cross-sectional area/ nm^2	
	Calculated with eq. 2 from liquid density	Commonly used value
Nitrogen	0.162	0.162
Argon	0.138	0.138
Krypton	0.152	0.202

Table 2 cross-sectional areas of an argon atom [nm^2] at 77 K (from [4])

Calculated with graphitized carbon black using p_0 (undercooled liquid)	Calculated with oxides using p_0 (undercooled liquid)	Calculated with oxides using p_0 (solid material)
13.8	16.3	18.2
14.3	17.7	158.5
13.7	16.1	17.9
15.1	16.7	18.2
13.7	16.6	18.1
14.3	15.3	17.9
12.9	16.6	17.4
13.0	17.6	17.8
Average value: 13.85 ± 0.7	Average value: 16.65 ± 0.7	Average value: 18.0 ± 0.7

Argon for surface and pore characterization

It summarizes three different average cross-sectional area for argon at 77 K obtained for surface areas determined with nitrogen and subsequent averaging. In this context, it is beyond comprehension why argon atoms specifically should require 20 – 30% more area occupancy in non-polar carbon surfaces, while the dumbbell-shaped nitrogen molecule with its additional quadrupole moment is allocated a universal area. This arrangement that can only be explained with lacking technical alternatives back at that time. From a scientific perspective, the question remains why the use of different adsorptives usually leads to different BET surface areas in solid materials and which adsorptive is the most suitable for coming closest to the actual geometric surface area. As these questions are still not fully answered, there is still a lot of uncertainty about the BET method, especially among critical users of it. It seems questionable to us that deviating results with other adsorptives compared to N_2 77 K BET calculations can be aligned simply by altering the cross-sectional area. Recent studies clearly confirm the doubts expressed quite some time ago already [3]. The fact that the N_2 molecule is indeed a somewhat special and certainly not the ideal probe, as it does not occur as a singular atom (spherical symmetry) and has an interfering quadrupole moment. Time may have come to turn the scientific discussion upside down, as from scientific perspective our following postulate seems to be worth a more profound research:

All texture-determining sorption measurements based on molecular cross-sectional area, in which the direct interaction between adsorptive atoms and the solid surface play a significant role should be carried out with noble gas adsorption at the noble gases boiling temperature, or it should at least be verified with such measurements.

Of course, one cross-sectional area value is unable to consider the various positions of a nitrogen molecule in a solid surface area - the contrary is the case. Based on the BET calculations from noble gas isotherms, we critically evaluate the question whether the BET surface area determined with nitrogen is scientifically plausible.

Determination of the specific surface area of a macroporous alumina with selected adsorptives

Using the example of macroporous alumina (N5), BET surface areas determined for different adsorptives and measurement temperatures are to be compared. The specimen is a granulate with a grain diameter between 1 and 2 mm. The BET surface area (N_2 at 77 K) is approx. 5 $m^2\ g^{-1}$. As to see as example from the krypton isotherm at the boiling temperature 120 K, the adsorption follows the classical Typ II isotherm shape because of the absence of micropores. Therefore, this material is perfectly suitable for our purposes, as multilayer adsorption on the solid surface area is the only sorption mechanism suitable and meeting the requirements for the correct implementation of the BET method. When using the adapted cross-sectional areas for krypton and argon for our alumina, following BET surface areas (see table 3) are the result of using the adsorptives at 77 K.

Argon for surface and pore characterization

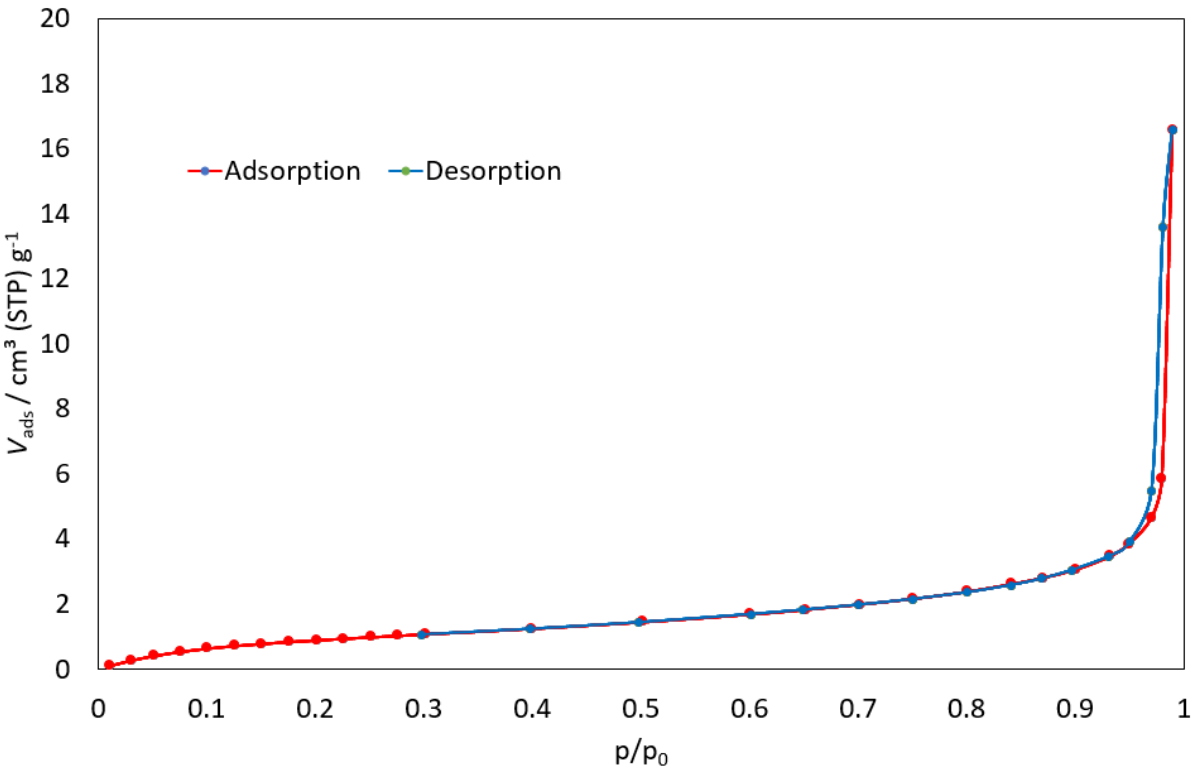

Figure 2 Typ II Kr 120 K isotherm for non-microporous N5 alumina

Table 3 Calculated BET surface area of alumina N5

Adsorptive	T / K	cross-sectional area calculated from	cross-sectional area/ nm^2	Surface Area (BET) / $m^2\ g^{-1}$
N_2	77	p_0 (liquid)	0.162	5.42
Kr	77	adjusted to $a_m(N_2)$	0.202	5.01
Ar	77	adjusted to $a_m(N_2)$ with p_0 (liquid)	0.166	5.22
Ar	77	adjusted to $a_m(N_2)$ with p_0 (solid)	0.180	5.24

The results are an impressive proof of the fact that rather similar surface areas can be calculated for different adsorptives, if you adhere to certain conventions and use "adapted" cross-sectional areas of noble gasses. If you remember the origin of the "adapted" cross-sectional area, matching values are no surprise, while the deviations occurring with different oxides become clear when reviewing the values of columns 2 and 3 of table 2. The results for alumina N5 differ substantially, if the cross-sectional area calculated from the liquid densities is used for the BET surface area calculations. These results are summarized in table 4.

Table 4 BET surface areas of alumina N5 with cross-sectional areas of adsorbate molecules calculated from liquid densities

Adsorptive	T / K	Calculated cross-sectional area/ nm^2 from liquid densities	Surface Area (BET) / $m^2\ g^{-1}$
Kr	77	0.152	3.84
Kr	120	0.163	3.70
Ar p_0 (liquid)	77	0.138	4.35
Ar p_0 (solid)	77	0.138	4.03
Ar	87	0.143	4.11
N_2	77	0.162	5.42

Further, this table includes results from argon and krypton isotherms that could be measured at their boiling temperatures (87 K (Fig. 1) and 120 K (Fig. 2)). Thus, concerns resulting from the questionable nature of the adsorbate phase below the triple point temperature can be removed.

If using the cross-sectional areas calculated with equation 2 from liquid density, the BET surface area value determined from nitrogen now deviates considerably. If - regardless of minor deviations - the surface area values based on spherical adsorptives argon and krypton are rather similar at about 4 $m^2\ g^{-1}$, the calculation with nitrogen produces a substantially higher value of more than 5 $m^2\ g^{-1}$– a considerable deviation by more than 25%. This result lets us assume that the nitrogen molecules adsorbed in the monolayer can be oriented in close arrangement at a polar surface and that nitrogen molecules are oriented rather in upright position on the solid surface, and closer than at random orientation in liquid nitrogen. In this case, it would only be consequent for the evaluation of oxidic surface areas to use a modified, reduced cross-sectional area for nitrogen.

Summary

1. The BET surface area quotient of argon and nitrogen used from Tab. 4 leads to a cross-sectional area of nitrogen at alumina of 0.123 nm^2. This value corresponds to the outcome of other studies [2] and suggest a reduction of the nitrogen cross-sectional area to 0.13 nm^2.

2. The possibility of measuring krypton isotherms at 120 K opens innovative approaches for questioning considerably larger N_2 BET surface areas of oxidic materials.

3. Further investigations seem necessary to evaluate the relatively small difference in material parameters, e.g. between krypton measurements of 77 K and 120 K. In nonporous, macroporous and mesoporous materials, the corresponding specific surface area generally have a fixed value, i.e. one adsorptive should produce the same specific surface are even with different measuring temperatures. Options such as the cryoTune now offer a simple approach for measuring an entire isotherm family and interpreting the results for BET surface area, adsorbate density and cross-sectional areas between 87 K (p_0 of krypton approx. 12 Torr (1.6 kPa)) and 120 K (p_0 of krypton approx. 760 Torr (101.3 kPa)).

4. Our LabSPA (Lab for Scientific Particle Analysis) has such options available to run measurements of following adsorptives at their corresponding boiling temperatures:

- Argon at 87 K
- Carbon dioxide at sublimation temperature 195 K
- Ethane at 184 K and other hydrocarbons at their boiling temperatures
- Krypton at 120 K
- Methane at 112 K
- Nitrogen at 77 K
- Oxygen at 90 K
- Xenon at 160 K

Argon, krypton, and xenon are mono-atomic adsorptives without permanent electrical dipole or quadrupole moments. Due to its tetrahedral shape, the methane molecule is also of interest as a symmetrical adsorptive molecule without permanent electrical dipole or quadrupole moment [5]. Further measurement programs will evaluate, which deviations occur between the nitrogen, the argon, krypton, and xenon BET-results in various organic/inorganic hybrid materials (MOFs) and other meso and microporous pore systems. If you are interested obtaining a cryoTune, please contact us directly. These modules can not only be used with the adsorption instruments of 3P Instruments but with other gas adsorption instruments as well and we can help you to find the right procedure.

References

[1] IUPAC recommendation, Pure Appl. Chem. 87(9-10), 1051-1069 (2015)

[2] F. Rouquerol, J. Roquerol, K. Sing, Adsorption by powders & porous solids, p. 171 ff.

[3] A. L. McClellan, H. F. Harnsberger; Cross-sectional Areas of Molecules Adsorbed on Solid Surfaces; Journal of Colloid and Interface Science, 1967, 23, p. 577 – 599

[4] S. J. Gregg, K. S. W. Sing; Adsorption, Surface Area and Porosity; Academic Press, London and New York, 1967; p. 75 – 93

[5] C. Graham, J. Pierrus, R. E. Raab, Mol. Phys. 67 (1989) 929 – 955.

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

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