

# IUPAC recommendation consequences for micropore adsorption studies

## Introduction

The IUPAC-report "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution" contains essential guidelines for obtaining and interpreting experimental data by means of gas adsorption [1]. This includes an extended classification of physisorption isotherms and hysteresis types. Furthermore, it takes account of scientific and technological progress made in the characterization of porous materials during the last 30 years.

A key topic within that report is the recommendation to employ argon at the boiling point temperature of liquid argon (87 K) for micropore analysis. Argon atoms provide distinct advantages over nitrogen molecules for gas sorption analyses, including the following:

- Unlike nitrogen, argon has no quadrupole moment. Thus, using argon as adsorbate eliminates specific chemical interactions with polar/ionic surface sites.
- As a result, argon physisorption isotherms provide much more reliable fingerprints of the interactions modeled by today's most advanced DFT-techniques for pore size characterization.
- Argon sorption analyses at its boiling point 87 K can be significantly faster than conventional N<sub>2</sub> 77 K experiments, because the filling of a pore size can occur much more readily at higher relative pressures (see Fig. 1).

Despite these tremendous advantages, the characterization of porous materials with argon is not yet commonly used since liquid argon can be relatively expensive or even unavailable in some regions. The 3P cryoTune-technology provides a compact and convenient accessory, which allows for IUPAC-recommended argon sorption analyses at 87.3 K without use of liquid argon. The unique sample holder concept provides a stable temperature control between 82 K and 135 K using liquid nitrogen. Thus, it represents, both, an adequate substitution for liquid argon and a powerful tool for adsorption studies within an extended temperature range.

In our study, we have explored differences in micropore filling between nitrogen and argon at temperatures of 77 K and 87 K on an active carbon and a zeolite. Fig. 1 shows Ar 87 K and N<sub>2</sub> 77 K isotherms to study the micropore filling of zeolite 13 X and active carbon D55, measured with 3P micro 300 and the cryoTune 87 to thermostate the temperature of 87 K without the use of liquid argon. Our results clearly demonstrate the uncertainty in texture analysis raised by the quadrupole moment of nitrogen molecules, not only for the micropore filling but also for other texture characteristics, e.g., for determination of the BET surface area.

With the development of the external cryoTune modules that fit to almost all state-of-the-art physisorption instruments it is now possible to implement the IUPAC recommendation regarding the characterization of micropores with argon at 87 K. This application note showcases the advantages of following these recommendations and highlights the differences which are to be expected in analytical data obtained by physisorption analysis with N<sub>2</sub> at 77K and Ar at 87 K.

# IUPAC recommendation consequences for micropore adsorption studies

## IUPAC recommendation for the characterization of micropores

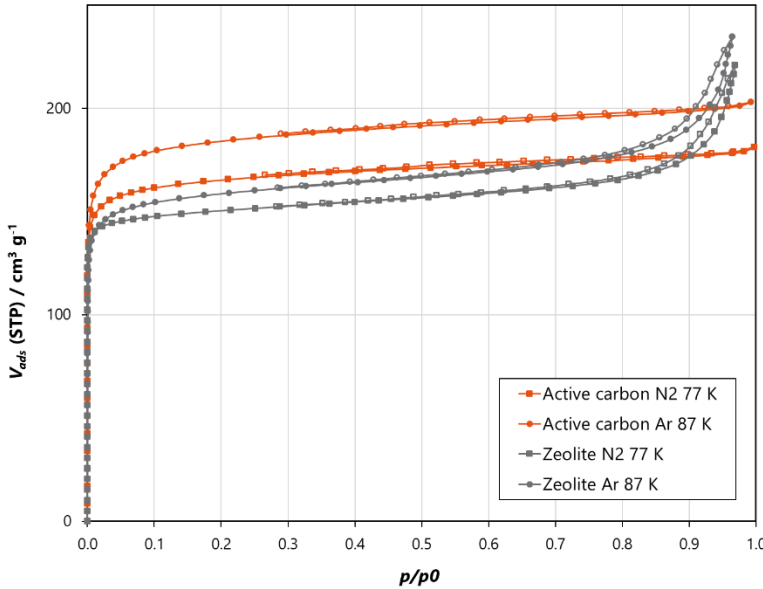
The IUPAC recommendation [1] addresses the following points in the application of N<sub>2</sub> for the characterization of micropores:

1. So-called ultramicropores (pore diameter < 0.7 nm) only possess a diameter roughly 2 to 3 times that of the molecular diameter and are filled with adsorbate atoms or molecules in a primary micropore filling process. Larger micropores are filled by a secondary micropore filling process, which occurs in a pressure range from  $p/p_0 = 0.01$  to 0.15 with N<sub>2</sub> at 77 K and Ar at 87 K.
2. The N<sub>2</sub> molecule possesses a quadrupole moment caused by the non-spherical symmetry of charge distribution from electrons around the nuclei in the N<sub>2</sub>-molecule. This quadrupole moment causes the nitrogen molecules to interact in very specific ways with different functional groups on surfaces, for example with cations in zeolites, and are responsible for a shift of the initial relative pressures in isotherms towards lower relative pressures. This shift is not caused by the pore structure which is supposed to be characterized. These undesired effects can lead to special interactions of nitrogen molecules on functional groups close to pore apertures and in turn block these pores by obstructing diffusion pathways for following molecules. Furthermore, the shift is also influenced by the electronic structure of the surface (differences in polarity, presence of cations, or dipole induction) and can change in magnitude depending on the sample type and its surface polarity.
3. Argon has no quadrupole moment and cannot cause the aforementioned problems, which has led to the idea to characterize micropores with Argon adsorption at 77 K. Unfortunately, this characterization would be carried out 6.5 K below the triple point temperature of Argon, which causes the description of the adsorbate phase to be indistinct since the phase diagram states that no liquid phase would be present. Additionally and conclusively, no complete sorption isotherms can be measured with Argon at 77 K since the  $p_0$  value of the undercooled liquid Argon is 30.66 kPa, but the dosed Argon would resublimates at 25.33 kPa and forms a solid in the measuring cell.
4. Argon at 87 K has none of these problems and thus offers the optimum conditions with regards to gas, temperature and pure dependence of the sorption equilibrium on pore size and shape.

## Measurements conducted with N<sub>2</sub> and Ar at 77K and 87 K

A Faujasite zeolite sample (2 mm spherical particles) and a narrow-pore activated carbon sample (granulate with grain size of 1 mm to 4 mm) were measured with N<sub>2</sub> and Ar at 77 K and 87 K over the complete relative pressures range on a 3P micro instrument equipped with 1000 Torr-, 10 Torr- and 0.1-Torr-transducers. For these experiments between 100 and 200 mg of sample were used. The zeolite sample was evacuated for 6 h at 350 °C, the activated carbon was evacuated for 6 h at 300 °C. Before the actual measurement, all samples together with the measuring system were degassed for 16 h in situ on the analysis station and the analysis was started immediately afterwards. Experimental conditions were the same for all measurements and we used the dosing amount routine for all isotherms with identical equilibrium criteria. Fig. 1 shows the corresponding results for zeolite and activated carbon. Due to the higher adsorbate density, the Ar 87 K isotherms show higher uptake than the N<sub>2</sub> 77 K isotherms as expected. All isotherms are of type I(a) according to the new IUPAC classification and typical for microporous materials with pore sizes below 1 nm. The isotherms of the zeolite show an increase towards the end of the relative pressure range indicating a secondary pore system, which comes from the binding agent between the zeolites particles. Comparing the two isotherms shows that the filling of this secondary pore system occurs both with N<sub>2</sub> at 77 K and with Ar at 87 K.

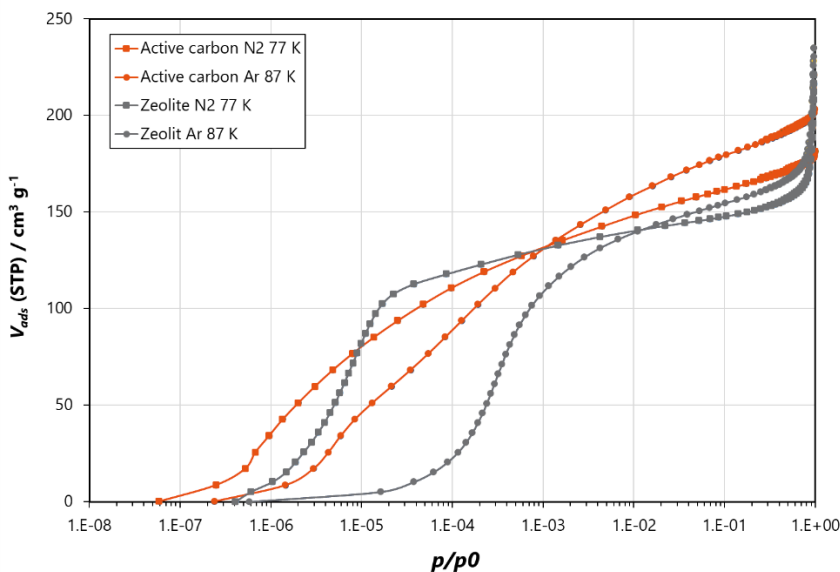
# IUPAC recommendation consequences for micropore adsorption studies



**Figure 1**  $N_2@77K$  and  $Ar@87K$  isotherms of activated carbon (orange) and zeolite (grey)

## Discussion of the sorption isotherms in the micropore region

The characterization of micropores requires a logarithmic representation as shown in Fig. 2. It shows that the zeolite isotherms exhibit a steeper slope than the isotherms of the activated carbon. This allows the conclusion, that the zeolite has a much narrower pore size distribution than the activated carbon. The adsorption of  $N_2$  and  $Ar$  on activated carbons occurs at smaller relative pressures than the respective zeolite isotherm, the activated carbon has a certain number of smaller pores than the zeolite. The image also shows a distinct shift of the zeolite isotherm compared to the isotherm of the activated carbon when measuring with  $Ar$  at 87 K.



**Figure 2** Logarithmic adsorption isotherms of  $N_2@77K$  and  $Ar@87K$  of activated carbon and zeolite

# IUPAC recommendation consequences for micropore adsorption studies

Taking the IUPAC elaborations into account, Fig. 2 allows for the following conclusions:

- a. Argon isotherms at 87 K are shifted to higher relative pressures and thus easier to obtain from an operative point of view than nitrogen isotherms at 77 K.
- b. At the elevated measurement temperature of 87 K, the kinetic issues are less severe with regards to molecular diffusion at pore apertures.
- c. The steep initial slope of the micropore filling is identical in both N<sub>2</sub>- and Ar isotherms and in the case of the zeolite it is especially visible that the argon isotherm at 87 K is basically just a shift of the nitrogen isotherm at 77 K to higher relative pressures. Conclusively, the shape of the isotherm during micropore filling is only dependent on the adsorbent but not the adsorptive.
- d. Quadrupole effects from the N<sub>2</sub> molecule on the solids surface should mainly occur during monolayer assembling, if the resulting adsorbate-adsorbate interactions are considered negligible. This means, mainly parameters required for calculations within the monolayer should be dependent on the quadrupole moment of N<sub>2</sub>. In case of microporous structures this affects the primary micropore filling with steep isotherm slopes in the ranges of low relative pressures.
- e. If the shift in isotherms between a N<sub>2</sub> isotherm at 77 K and an Ar isotherm at 87 K is only dependent on temperature effects, this term would need to be equal for activated carbons and zeolites. However, Tab. 1 shows an example with a constant loading of 35 cm<sup>3</sup> g<sup>-1</sup> that the corresponding  $p/p_0$  of Ar at 87 K and N<sub>2</sub> at 77 K divert by a factor of 6 for activated carbons but a factor of 50 for zeolites.
- f. Based on the assumption, that pore characterizations with Argon at 87 K and Ar isotherms are not falsified by specific quadrupole interactions, the shift of N<sub>2</sub> isotherms for activated carbons and zeolites in comparison to the Ar-isotherms shows, that they are influenced not only by a temperature term. Therefore, we should introduce additionally a specific interactions term, which incorporates both the quadrupole moment of nitrogen molecules but also the polarity of the surface. This can be schematically written as

$$L = T + A + W$$

with

L...Shift of the N<sub>2</sub> isotherm at 77 K to the Ar isotherm at 87 K at low relative pressures (determined experimentally)

T...Temperature-term of the shift from 87 K to 77 K (determined experimentally)

A...unspecific adsorbate-solid-term, containing among others atomic or molecular size and allowing base of calculations for determining pore structures based on unspecific interactions such as van-der-Waals-interactions

W...specific adsorbate-solid interaction term, containing possible dipolar and quadrupolar interactions between adsorbate and solid (can be evaded by argon measurements at 87 K)

**Table 1** Relative pressure  $p/p_0$  and ratio of N<sub>2</sub> to Ar in the initial region of the adsorption isotherm (adsorbed amounts are 35 cm<sup>3</sup>/g respectively)

	$p/p_0$	Ratio of $p/p_0$ Ar@87K to $p/p_0$ N <sub>2</sub> @77K for volume adsorbed 35 cm <sup>3</sup> g <sup>-1</sup>
Zeolite N <sub>2</sub> at 77 K	0.000003	-
Zeolite Ar at 87 K	0.000150	50
Act. carbon N <sub>2</sub> at 77 K	0.000001	-
Act. carbon Ar at 87 K	0.000006	6

# IUPAC recommendation consequences for micropore adsorption studies

Materials with a known pore size distribution can be used to determine the specific interaction term  $W$ . This can be accomplished by using a material specific NLDFT kernel for analysis. Unfortunately, in practical use this is more often impossible as the majority of porous solids do not have a corresponding kernel. This means the  $W$ -term is undetermined for most materials. The term is therefore approximated by mean values – in the case of zeolites for example, this is done by using a unified interaction parameter or in the case of NLDFT-analysis by using a single kernel for all zeolites. This does not take into account, that zeolites may be quite different in their compositions and their exchangeable cations. This is why the strong variation in the left-shift of nitrogen isotherms to argon isotherms (see fig. 2) has prompted the IUPAC to recommend argon measurements at 87 K. This eliminates the specific interaction term  $W$  from the problem. This means in general, that if the specific interactions of the  $N_2$ -quadrupole moment cannot be prevented or cannot be taken into consideration for the analysis, the measurement should be conducted with Argon at 87 K.

## Literature

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