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BEYOND THE SURFACE

CUTTING-EDGE ADSORPTION APPROACHES FOR POROUS MATERIAL CHARACTERIZATION BY MICROTRAC

CONTENTS

GENERAL INTRODUCTION

The characterization of porous materials is essential in many scientific and industrial fields, including energy storage, catalysis, gas separation, pharmaceuticals, electronics, and advanced materials engineering. Many of these materials—such as carbons, catalysts, ceramics, adsorbents, and electrode materials used in batteries and fuel cells—possess complex porous structures and large internal surface areas that strongly influence performance. Reliable analytical methods are therefore required to quantify their structural properties.

Among available characterization techniques, gas **adsorption** analysis is one of the most widely used and powerful tools for investigating porous materials. This method is based on **adsorption**, in which gas molecules interact with and accumulate on the surface of a solid. By measuring the amount of gas adsorbed as a function of pressure at constant temperature, an **adsorption** isotherm is obtained. Analysis of these isotherms provides key information, including specific surface area, pore volume, pore-size distribution, and **adsorption** mechanisms.

Several analytical approaches have been developed to interpret **adsorption** isotherms and extract meaningful structural parameters. One of the most widely used is the Brunauer–Emmett–Teller (BET) theory, which determines specific surface area from gas **adsorption** data. The BET method is a standard technique in both research and industrial quality control due to its robustness and simplicity. However, accurate application requires careful evaluation of the isotherm and appropriate selection of the pressure range used for analysis.

In materials containing **micropores**, conventional BET analysis may yield inaccurate surface area values because **micropore** filling can occur in the same pressure range as monolayer formation. To address this limitation, validation approaches such as the Rouquerol criteria ensure that the selected BET fitting region produces physically meaningful results. These criteria are particularly important for Type I isotherms, characteristic of microporous materials.

Beyond isotherm interpretation, improvements in measurement techniques also play a crucial role in obtaining reliable and reproducible data. Advanced methodologies such as **Advanced Free Space Measurement** (**AFSM™**) enhance accuracy and reproducibility, particularly for pore size distribution and surface area determination. For materials with very low surface areas, krypton **adsorption** at 77 K provides improved sensitivity compared to conventional nitrogen **adsorption**.

This document presents an overview of key concepts and methodologies used in gas **adsorption** analysis for porous material characterization, including **adsorption** isotherms, the BET method, Rouquerol criteria, and advanced measurement techniques.

Following this overview, several case studies demonstrate the application of these techniques to materials such as zeolites, carbon nanotubes, mesoporous silica, and carbon fibers, illustrating how **adsorption** measurements can be used to investigate pore structure, surface properties, and **adsorption** behavior in practical scenarios.

1. ADSORPTION ISOTHERMS: DEFINITION AND OBTAINED INFORMATION

Adsorption is a ubiquitous but poorly understood natural phenomenon that has important industrial applications in separations, catalysis, and gas storage. Adsorption measurements are also widely used to characterize material properties for the development and manufacture of batteries, fuel cells, carbons, catalysts, pharmaceuticals, cosmetics, ceramics, semiconductors, adsorbents for separations, and other products containing porous solids.

Adsorbents are typically highly porous solids with surface areas of up to several thousand square meters (comparable to an international soccer field!) per gram of adsorbent. Adsorption occurs when **adsorbate** molecules coat the surfaces and fill the pores of an adsorbent. Adsorbate molecules move from a bulk gas or liquid phase (sometimes called an adsorptive phase, though we avoid this term because it can be mistaken for an adjective) into the adsorbed phase, i.e., the layer(s) of **adsorbate** molecules coating the adsorbent's surfaces and filling its pores.

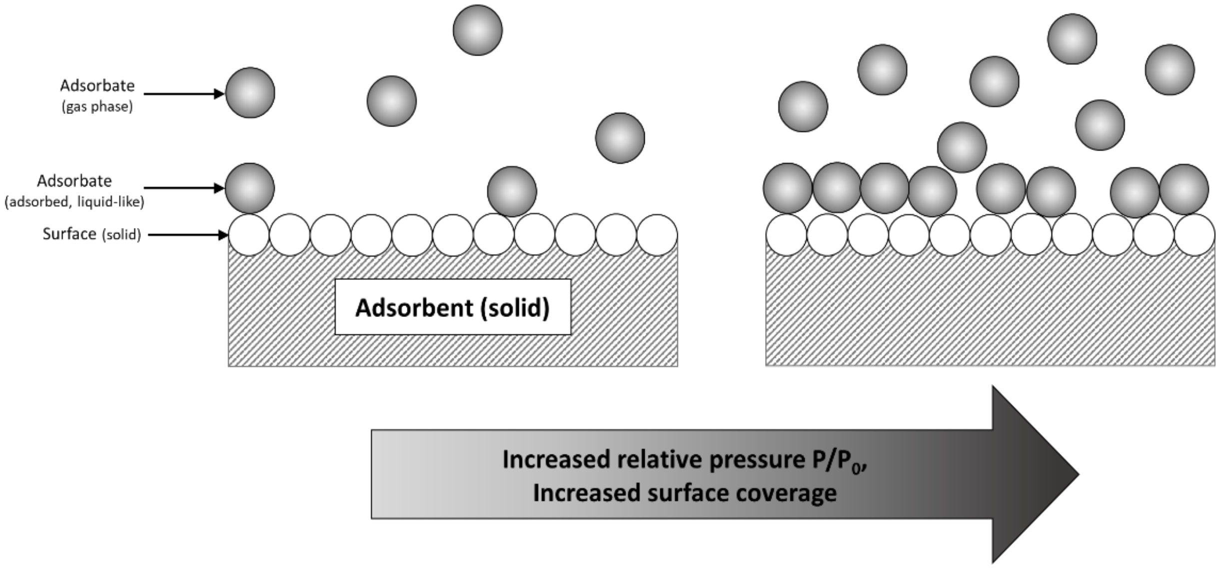


Figure 1 : Illustration depicting the different phases interacting with each other throughout the **adsorption** process.

Charcoal (carbon) is a widely known adsorbent that has been used for thousands of years to purify water by removing contaminants such as heavy metals and organic compounds, which are adsorbed into the pores of the charcoal. Zeolites are another common class of adsorbents used in separations (e.g., to dry gas streams by adsorbing water) and catalysis (in which **adsorbate** molecules react with ions or functional groups within the zeolite pores). Metal-organic frameworks (MOFs) are an exciting new class of adsorbents with structures that can be precisely optimized for individual applications. Because the variety of MOFs is practically infinite, high-throughput screening of MOFs has recently emerged as one of the most prominent applications of **adsorption** measurement.

The amount adsorbed depends on temperature and pressure (for gases) or concentration (for liquids) in the bulk phase. In practice, **adsorption** is usually measured by varying gas pressure at constant temperature. A small quantity of gas is injected into the sample, and the amount adsorbed is calculated from changes in the gas pressure. The resulting relationship between the adsorbed mass and gas-phase pressure at constant temperature is called the **adsorption** isotherm.

Adsorbate molecules are attracted from the gas phase to the atoms forming the surface of the solid adsorbent. Because of these attractive forces, **adsorbate** molecules first fill the smallest pores into which they can fit. As the gas-phase pressure increases, **adsorbate** molecules coat the surface and crowd into larger pores. If the pores are large enough, the **adsorbate** molecules can form a liquid within the pore (“capillary condensation”). The **adsorption** isotherm can therefore be used to characterize a solid’s surface area and pore-size distribution. This is most commonly done by measuring nitrogen **adsorption** isotherms at 77 K (the boiling temperature of liquid nitrogen at atmospheric pressure), but other gases such as argon, krypton, and carbon dioxide are sometimes used.

1a) How to Interpret an Isotherm?

Adsorption isotherms always provide the quantity adsorbed versus pressure. However, depending on the analysis conditions and the application, two isotherms can have different axes. The most common isotherm you’re likely to encounter will be a N_2 isotherm at 77 K. These isotherms typically display the ‘pressure’ axis in terms of relative pressure (P/P_0; P = equilibrium pressure and P_0 = saturation vapor pressure). This provides a dimensionless unit along the bottom where ‘0’ represents a complete vacuum and ‘1’ represents the saturation pressure of the **adsorbate** at the **adsorption** temperature. An example of this can be seen in **Figure 2**. However, in other studies, it is common for the ‘pressure’ axis to be in terms of absolute pressure, such as when determining the storage capacity for CH_4 or CO_2 in a material.

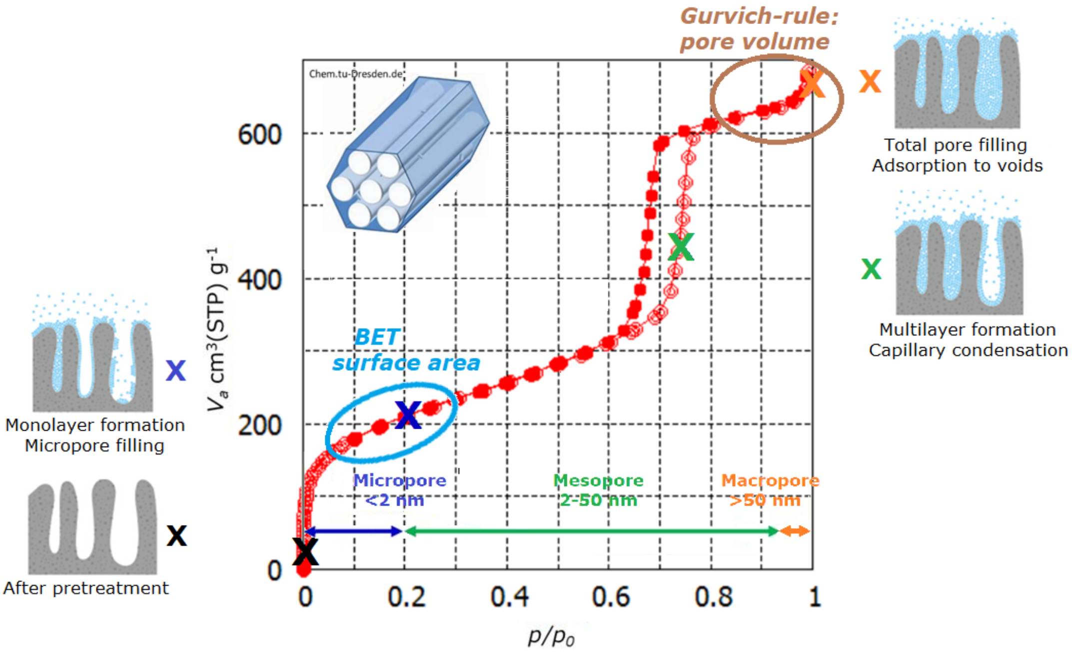


Figure 2 : Nitrogen sorption of mesoporous silica SBA-15 at 77 K with notations depicting the various stages of the **adsorption** process.

Much like the pressure axis, the quantity adsorbed axis can be expressed in several ways, but is typically expressed in either $cm^3\ g^{-1}$ or $mmol\ g^{-1}$. The former is common for specific surface area determinations, whereas the latter is more prevalent when determining the total storage capacity of an adsorbent, such as in carbon capture literature.

The data of an isotherm can take several shapes, depending on the nature of the adsorbent, **adsorbate**, and analysis conditions. As mentioned above, the most common isotherm uses the **adsorbate** N_2 and does the analysis at its boiling point, 77 K. These isotherms start near a pressure of '0'. As you approach relative pressures in the range of 0.05 to 0.3, a curve in the isotherm can typically be seen. **Figure 2**. This is due to the formation of a monolayer on the surface of the adsorbent and the completion of **micropore** filling (pores of 2 nm width or less). From here, multilayer **adsorption** occurs, and a small increase can be seen concurrent with the increasing pressure. Any sharp increases in the quantity adsorbed in the relative pressure of around 0.2 to 0.95 are due to the filling of any **mesopores** present in the material (pores of 2 to 50 nm in width). From 0.95 to 1, the filling of **macropores** (pores greater than 50 nm in width) can be seen; this region can also be difficult to collect due to the proximity to saturation pressure ($P/P_0 = 1$).

There are some patterns that have been recognized in the N_2 isotherm at 77 K. The International Union of Pure and Applied Chemistry (IUPAC) has recognized several of these isotherm 'shapes', though they have continued to be under discussion and revision since their initial inclusion. **Fig 3**. The most commonly produced isotherms are I, II, and IV, which are the shapes associated with microporous, non-porous, and mesoporous materials, respectively. Furthermore, just as materials can contain both **mesopores** and **micropores**, some combinations of these classes are possible, such as a type I + IV.

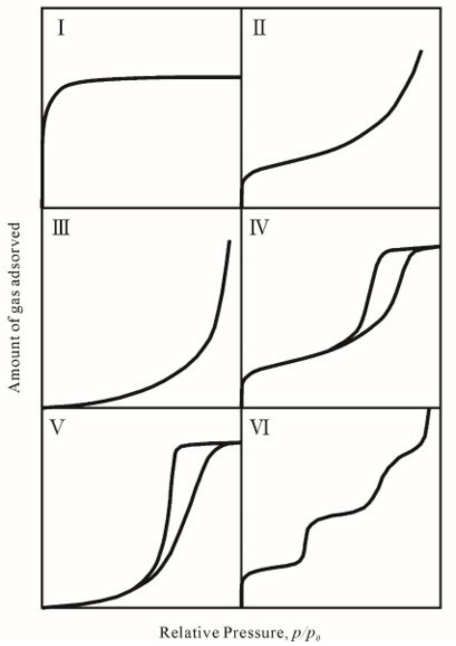


Figure 3 : IUPAC specified categories for the various shapes of **adsorption** isotherms.

1b) Data obtained from adsorption isotherms

Adsorption isotherms provide information about the **adsorbate**-adsorbent relationship, and can also provide specific surface area, pore size distribution, and pore volume, depending on analysis conditions. It is also possible to be able to gain some insight into whether an **adsorption** process is physisorption (no covalent bonding, reversible) or chemisorption (bonding occurs, irreversible) based. The specific surface area is commonly determined by the BET method (named after Brunauer-Emmett-Teller) for physisorption, while the Langmuir surface area is preferred for chemisorption processes (e. g., catalysis) where it can provide an 'active surface area'. According to IUPAC recommendations, the BET specific surface area can be calculated from $P/P_0 = 0.05$ to 0.30.[1] However, microporous materials can impact this range, and lower relative pressures may be used with proper care, utilizing the so-called Rouquerol criteria.[2] These topics are important enough that they are discussed in their own application notes on our website.

Pore size distributions (PSD) are another critical component of material analysis. Since **micropores** and **mesopores** behave differently, they are almost always considered separately and treated with different methods and models. Traditionally, mostly empirical and theoretical methods have been used for obtaining PSDs. If mesoporous materials are expected, BJH, DH, CI, and INNES plots can be used. For microporous materials, t-plots, α-s plots, HK, SF, CY, and MP plots are more appropriate. Again, these topics are important enough to the typical **adsorption** user that they will receive their own application notes.

In recent years, computational methods have become more and more prevalent for determining a material's PSD. These generally utilize **NLDFT** (Non-Localized Density Functional Theory) or **GCMC** (Grand Canonical Monte Carlo). **NLDFT** / **GCMC**- method can analyze from **micropores** to **mesopores** as a unified theory, which is an advantage compared to other pore size analysis theories. However, these models are heavily constrained by the computational 'kernel' that was used. In order to be confident in your fitting, the kernel must very closely represent the surface of the material. As such, it's still very common to see non-computational methods be used alone or in conjunction with these more modern methods.

Finally, the pore volume can be analyzed. Often, pore size distribution methods can be utilized to provide information on the associated pore volumes. Still, the simplest way to get the total porosity of a material from a nitrogen isotherm is by using the Gurvich rule (eq. 1).[4,5] It is assumed that the horizontal plateau of an isotherm represents the region where pore filling is complete.

$$V_{total} = \frac{V_{STP}\ M\,p}{\rho\,\mathrm{R}\,\mathrm{T}} = V_{STP} \times 1.547 \times 10^{-3} \quad \text{Equation 1}$$

V_{total} = total pore volume
V_a = adsorbed volume of nitrogen
M = molar mass of nitrogen molecule
p = pressure at STP
r = density of liquid nitrogen
R = gas constant
T = temperature at STP

Using the SBA-15 material shown in **Figure 2**, the total pore volume determined at $P/P_0 = 0.95$ (Va = 650 cm^3 g^{-1}) is approximately 1 $cm^3\,g^{-1}$.

1c) Summary

Understanding the basics of **adsorption** is the first step in fully utilizing **adsorption** for your research or work. Here at MICROTRAC, we specialize in **adsorption** and the instrumentation that enables high-quality measurements. If you're unsure of the application or how this technology could help your research or industrial needs, please contact us.

1d) References

1. Hommes, K. Kaneko, A. V. Neimark, J. P. Oliver, F. Rodriguez-Reinoso, J. Rouquerol, and K. S. W. Sing, Pure Appl. Chem. 2015, 87, 1051–1069

2. J. Rouquerol, P. Llewellyn, F. Rouquerol, Stud. Surf. Sci. Catal. 2007, 160, 49–56

3. L. Gurvich, J. Phys. Chem. Soc. Russ. 1915, 47, 805

4. J. Rouquerol, F. Rouquerol, K. Sing, Adsorption by Powders and Porous Solids, Academic Press, London, 1999.

5. C. Lippens, B. G. Linsen and J. H. de Boer, J. Catal., 1964, 3, 32–37 and J. H. de Boer, B. C. Lippens, B. G. Linsen, J. C. P. Broekhoff, A. van den Heuvel and T. J. Osinga, J. Colloid Interface Sci., 1966, 21, 405–414

2. SPECIFIC SURFACE AREA DETERMINATION OF A TYPE IV ISOTHERM USING THE BET METHOD

The evaluation of surface area is an important method in the toolkit of many research and industrial sectors relating to batteries, carbons, catalysts, medicines and cosmetics, adsorbents and separations, ceramics, semiconductors, and more. **(Fig 1)**. As discussed in greater detail in the application note on surface area, these measurements are based upon the phenomenon of **adsorption**. This application note focuses on one method of using **adsorption** data to determine specific surface areas, namely the **BET-method**.

Figure 1 : Examples of the numerous applications for determining BET surface area.

2a) General Information

The Brunauer-Emmett-Teller method (BET method, ISO 9277) is the most common method for the evaluation of specific surface areas. The BET method can determine the specific surface area of macroporous, mesoporous, and non-porous solids (i.e., type II and type IV isotherms) by measuring the amount of adsorbed gas. This is typically done with N_2 at its boiling point (77 K), using the relative pressure range of $P/P_0 = 0.05 – 0.30$, based on the IUPAC recommendation. It is also possible to evaluate type I isotherms using the BET method; however, since **micropores** can interfere with the validity of this method, the so-called Rouquerol criteria should be considered. For more information on evaluating type I isotherms using the Rouquerol criteria, see our application note on that topic, where it is discussed in further detail.

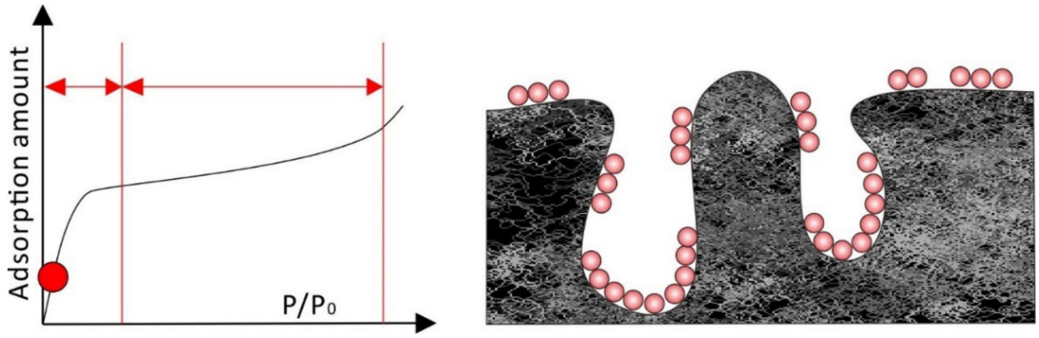
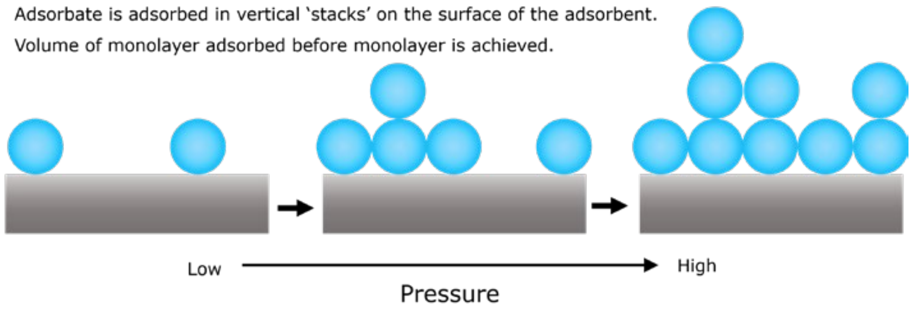


Figure 2 : Isotherms and graphical representations depicting **adsorption** before (a) and the completion of the first monolayer (b). Note that the second and third layers are produced in some regions before the completion of the first monolayer.

Relative pressures in the range of $P/P_0 = 0.05 – 0.30$ are used under these conditions for determining BET surface areas because this is the region in which a monolayer of gas is formed on the surface. **Figure 2**. It is important to note that a true monolayer is never achieved; there will always be some multilayer formation before monolayer completion in any physisorption process. The assumption of a perfect monolayer was the foundation for the BET equation's predecessor, the Langmuir equation. This distinction is what led Brunauer, Emmett, and Teller to produce a different model that better describes the process of **adsorption** during the region surrounding the completion of the first monolayer. This is the key consideration that led to BET's success when compared to the Langmuir model.

The BET theory is based on three assumptions;

1. Surface energy is uniform
2. There is no interaction between adsorbed molecules
3. Adsorption energy above the second layer is equal to the condensation energy



When selecting the appropriate region of the N_2 isotherm, it is conventional to use the **relative pressure** range of **P/P_0** = 0.05 – 0.3. This is selected because this region tends to reflect the point at which nitrogen will complete the initial monolayer. Using regions after **P/P_0** = 0.3 is typically invalid, as you are no longer adsorbing onto the surface, but rather onto already adsorbed layers of **adsorbate**. Before you reach **P/P_0** = 0.05, you are typically not close enough to achieving your monolayer for the BET model to be applied. Furthermore, in the case of **microporous** materials, there will likely be some pore filling occurring in this region.

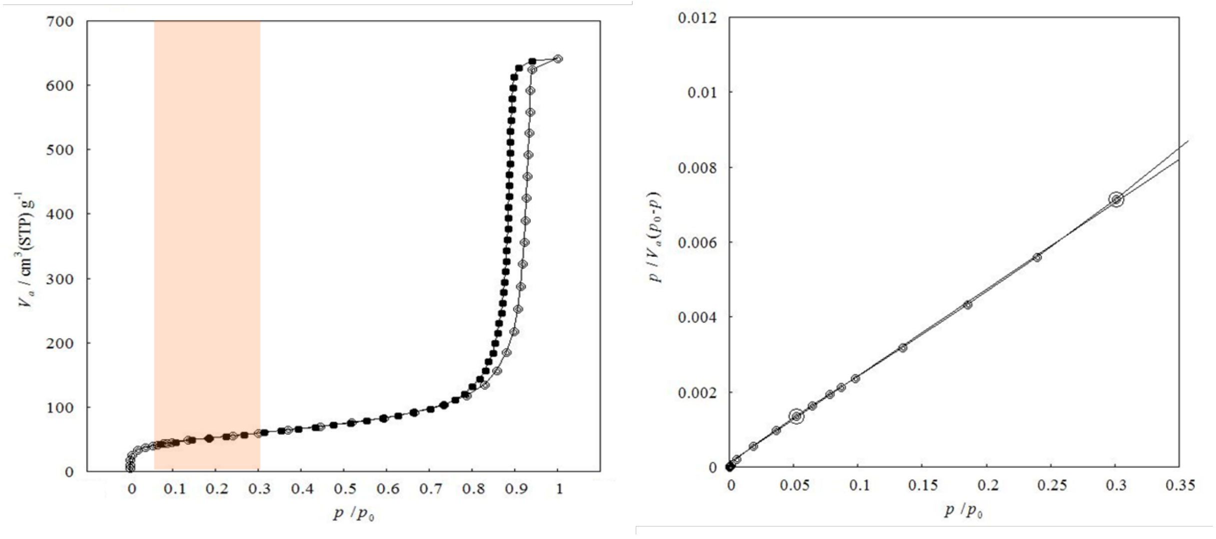


Figure 3 : An example isotherm (a) and the respective BET plot (b) for a **mesoporous** material with a BET **specific surface area** of ~ 187 m^2 g^{-1}

It should be noted that the BET theory has noteworthy flaws. The most important flaws are that **micropores** are ignored, **adsorbent** surfaces are considered energetically homogenous, and that lateral (**adsorbate-adsorbate**) interactions are not considered. In particular, **micropores** are considered to be highly problematic when seeking accurate surface areas. As such, when reporting the surface areas of **microporous** materials, one should reflect this and report these surface areas as “BET characteristic surface areas”. Recently, much work has been put into methods of properly selecting the **relative pressures** used and validating these reported surface areas, e.g., the so-called **Rouquerol criteria**.

2b) BET Surface Area Calculation

The **BET equation** (eq. 1) is used to convert the isotherm plot to a ‘BET plot’ (**Figure 4**). The appropriate region of this plot is then used to determine the BET intercept and slope (eq. 2 and 3). These are, in turn, used to determine the **monolayer volume** (eq. 4). Finally, the properties of your **adsorbate** can be used in conjunction with the **monolayer volume** to determine the BET surface area and BET **specific surface area** (eq. 5 and 6).

$$\frac{1}{W_{ads}[(P_0/P)-1]} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right)$$

Equation 1 – BET equation

$$i = \frac{1}{W_{mono} C}$$

Equation 2 – BET plot intercept

$$s = \frac{C-1}{W_{mono} C}$$

Equation 3 – BET plot slope

$$W_m = \frac{1}{s+i}$$

Equation 4 – Monolayer volume

$$S_t = \frac{W_m \times N_A \times A_{cs}}{M}$$

Equation 5 – BET surface area

$$S = \frac{S_t}{w}$$

Equation 6 – BET specific surface area

***Where C is the **BET constant**, N_A is Avogadro's constant, W_m is the weight of the monolayer, M is the molecular weight of the **adsorbate**, A_{cs} is the cross-sectional area of the **adsorbate**, and w is the weight of the sample.

An example of this can be seen in the calculation of the surface area of Develosil 100, a **mesoporous** material with a type IV isotherm. **Figure 4a** (left). First, the data is replotted using the **BET equation**. (**Figure 4b** (right)). Next, the **relative pressure** range is selected, trying to achieve a correlation coefficient of R ≥ 0.99. In this case, the entire **relative pressure** range of **P/P_0** = 0.05 – 0.30 was used, and a correlation coefficient of 0.998 was achieved. It was also checked that the 'C' value was positive, a requirement for valid BET surface areas. Since everything looks good, the BET **specific surface area** of 296 m^2 g^{-1} is accepted.

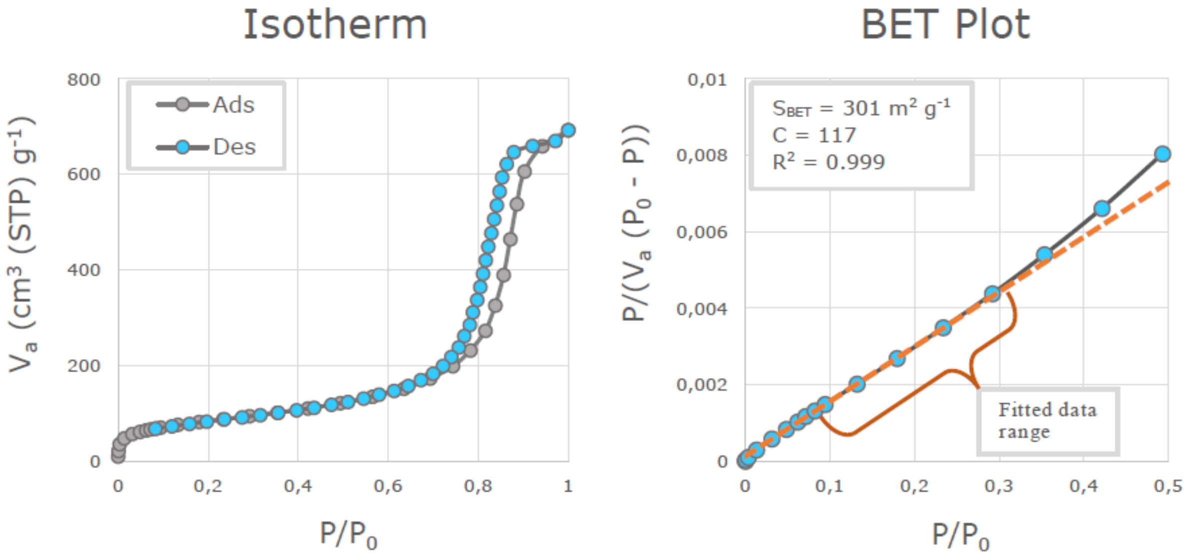


Figure 4 : Nitrogen sorption isotherm of Develosil 100 at 77 K activated under vacuum at room temperature for 15 h (left) and BET plot of Develosil 100 (right).

2c) Gas Adsorption Analyzers

Modern instrumentation makes these measurements quite feasible for all varieties of research and industrial needs. MICROTRAC BEL product line constitutes a series of manometric/volumetric and dynamic flow measurements. These systems are capable of collecting data automatically and efficiently.

Figure 5 : A selection of gas adsorption analyzers from MICROTRAC, capable of collecting high-quality measurements (from left to right: **BELSORP MAX G, BELSORP MAX X, BELSORP MINI X, BELSORP MR1**).

All information about our instruments is available on www.microtrac.com

Manometric (sometimes referred to as volumetric) systems are the type of system that is typically used to collect isotherms for the determination of a BET surface area. Manometric systems initially reduce pressure, followed by slowly re-pressurizing the system at pressures set by the user. Dynamic flow systems can be used to collect single-point BET surface areas, a quality control method that is discussed in its own application note found on www.microtrac.com.

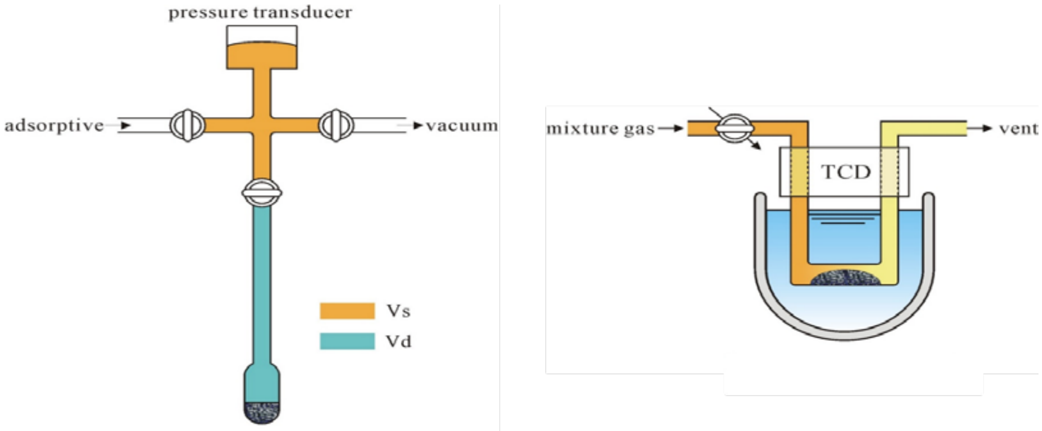


Figure 6 : Two types of systems capable of collecting **adsorption** data, including manometric/volumetric (a) and dynamic flow (b) methods.

Manometric systems also have considerable variations. Generally, BET surface areas only require achieving **P/P_0** = 10^{-2}. Most instruments, such as the **BELSORP MINI X**, can achieve **P/P_0** = 10^{-4} and are therefore perfectly suited to determining isotherm type and finding the BET **specific surface area** of a material. For a more thorough understanding of the **micropore** structure, some instruments, such as the **BELSORP MAX G** and **BELSORP MAX X**, can collect isotherms down to **P/P_0** $< 10^{-8}$.

2d) Summary

The collection of BET surface areas is an industrially and academically important tool. While the BET model has flaws, its usefulness and broad applicability have contributed to it being ubiquitous in material analysis.

If you're unsure of the application or how this technology could help your research or industrial needs, please contact us.

3. THE BET METHOD FOR MICROPOROUS MATERIALS

3a) Applying the Rouquerol Criteria to Validate the BET Surface Area of a Type I Isotherm

The Brunauer-Emmett-Teller (BET) method is the most common method for the evaluation of **specific surface area**s. It applies to sorption isotherms Type II and Type IV, and the evaluation is carried out in the **relative pressure** range **P/P_0** from 0.05 to 0.30 as recommended by IUPAC.[1] This range is used because, to oversimplify, it is around these pressures that the completion of the monolayer occurs. However, the presence of **micropores** can interfere with the isotherm in the same region, and cause reported values to not represent the true surface area of a material.

Therefore, Rouquerol *et al.* expanded the **BET method** for **Type I isotherm**s by developing the so-called **Rouquerol criteria**. In-part, these criteria state that the **BET constant** 'C' must be positive, that the selected **P/P_0** range must be limited to where the term $n(1 - P/P_0)$ continually increases with **P/P_0**, and the **P/P_0** value corresponding to the monolayer capacity should fall within the selected range.

Applying the Rouquerol Criteria

In order to apply these criteria with ease, the 'Rouquerol-Plot' is utilized. The maximum of this plot (blue-marked measurement point) provides a very easy-to-recognize upper limit for the acceptable **P/P_0** range for use in determining BET surface area. Relative pressures past this point should not be used. Usually, activated carbon and zeolite with **micropores** deliver Type I **adsorption** isotherms. In the following **Figure 1**, the nitrogen sorption measurement (top left) of activated carbon is shown. The data is then used to produce a Rouquerol Plot, where an upper limit can be easily identified (right). Finally, the corresponding BET plot is presented and shows the upper limit for the respective material (bottom left).

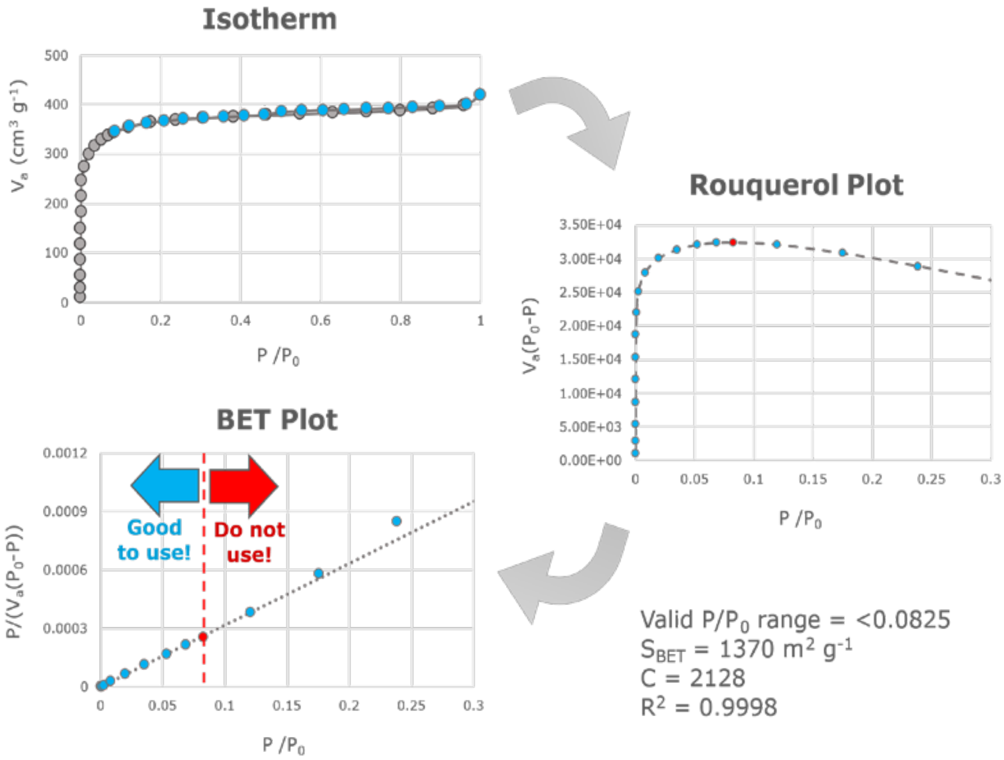


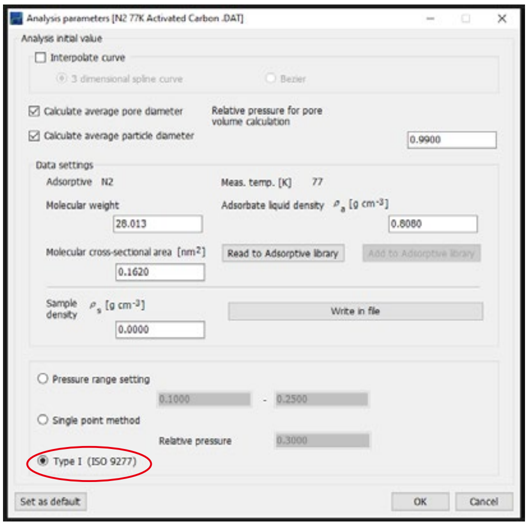
Figure 1 : Rouquerol-plot (left) and BET-plot of activated carbon in relative pressure range according to Rouquerol et al. (right).

3b) Software Analysis

Our analysis software, BELMaster, can automatically determine the upper limit per the **Rouquerol plot**, so anyone can easily determine the proper BET range in type I materials.

To use this function, follow these steps:

1. Select the isotherm to be analyzed
2. Click on 'Analysis' → 'BET plot.'
3. Select the generated BET plot
4. Click on 'Settings' → 'Analysis parameters settings.'
5. Select Type I (ISO 9277), then 'OK.'



Analysis parameters [N2 77K Activated Carbon .DAT]

Analysis initial value

☐ Interpolate curve

● 3 dimensional spline curve ○ Bezier

☑ Calculate average pore diameter

☑ Calculate average particle diameter

Relative pressure for pore volume calculation: 0.9900

Data settings

Adsorptive N2

Meas. temp. [K] 77

Molecular weight: 28.013

Adsorbate liquid density ρ_a [g cm^{-3}]: 0.8080

Molecular cross-sectional area [nm^2]: 0.1620

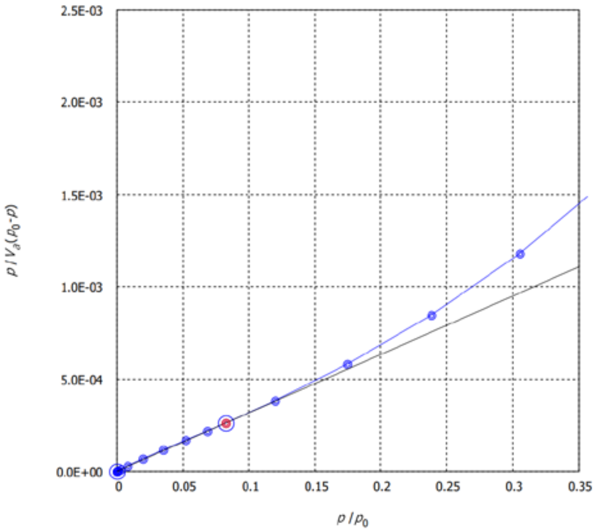
Sample density ρ_s [g cm^{-3}]: 0.0000

○ Pressure range setting: 0.1000 - 0.2500

○ Single point method: Relative pressure 0.3000

● Type I (ISO 9277)

The BET range limit will be marked in a color that stands out, regardless of the selected data color.



3c) Summary

When it comes to analyzing **micropores**, great care must be taken. Fortunately, methods such as the **Rouquerol criteria** exist to help validate data. The **BET method** is very widely used, and unfortunately, the **Rouquerol plot** is not as widely considered. Hopefully, this document has provided you with an entry point into the utility of this method.

If you're unsure of the application or how this technology could help your research or industrial needs, please contact us.

4. IMPROVED REPRODUCIBILITY OF BET SPECIFIC SURFACE AREA BY AFSM™ (ADVANCED FREE SPACE MEASUREMENT)

The gas sorption isotherm (ísos “equal” and thérmē “heat”) is measured at a specific temperature. Commonly, liquid refrigerants (e. g., liquid nitrogen, short LN_2) are used to keep the temperature constant, 77 K in case of nitrogen (boiling point). The liquid nitrogen in the Dewar vessel vaporizes during the **adsorption** measurement, and the level of the liquid decreases gradually.

In the volumetric system, the adsorbed amount is calculated from the pressure change before and after **adsorption** based on the ideal gas equation. A certain amount of gas with pressure pi is filled into a manifold with known volume Vs. The valve to the sample port is opened, and the pressure after reaching equilibrium pe is measured.

$$N = n_1 - n_2 = [(p_i - p_e)\, V_s - p_e V_d]/RT$$

N = **adsorbed amount of substance**
n_1 = amount of gas at pressure Pi
n_2 = amount of gas at pressure Pe
p_i = initial pressure (before **adsorption**)
P_e = equilibrium pressure (after **adsorption**)
V_s = geometric volume of manifold
V_d = dead volume
R = universal gas constant 8,314 J/mol K
T = temperature

From the pressure difference pi and pe and the **dead volume** Vd, the adsorbed amount can be calculated. The **dead volume** in the sample cell changes gradually along with this level of refrigerant. However, there are two options to consider the **dead volume** during measurement. The **dead volume** is determined at the beginning or at the end of the measurement and is tried to keep constant during the whole measurement.

Our patented **AFSM™** (**Advanced Free Space Measurement**) determines an initial **dead volume** of the sample cell and an initial **dead volume** of a reference cell at the same time.[1]

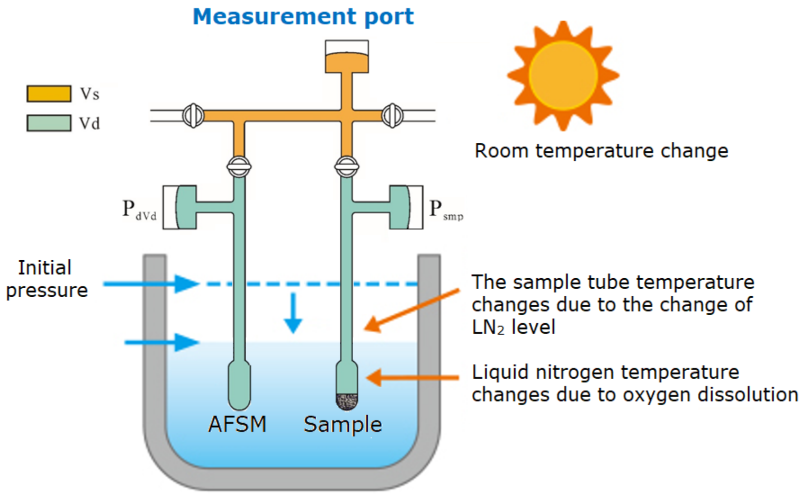


Figure 1 : Adsorption isotherm measurement using LN_2 and LAr by **AFSM™**

Since the change of the **dead volume** in the sample and reference cell is equal, the **dead volume** change is continuously followed via the reference cell. Therefore, **AFSM™** enables the calculation of the adsorbed quantity based on the measured **dead volume** at any time during measurement without keeping the liquid level of the refrigerant constant during the whole measurement (see **Figure 1**). Changes in room temperature during measurement and changes in liquid nitrogen temperature due to oxygen dissolution can be considered, enabling accurate and highly reproducible **adsorption** quantity evaluation. The change of **dead volume** in the sample cell is expressed by the following equation:

$$dVd = [1-(p_i/p_e)] * V_{d,ref}$$

$$V_{d,sample} = V_{d,ini} - dVd$$

DVD = Free space change
$V_{d,ref}$ = dead volume of reference cell
$V_{d,\text{ échantillon}}$ = dead volume of sample cell
$V_{d,\text{ ini}}$ = initial dead volume of sample cell

Figure 2 shows a graph with the total surface area on the horizontal axis and reproducibility on the vertical axis for three exemplary materials with different surface areas.

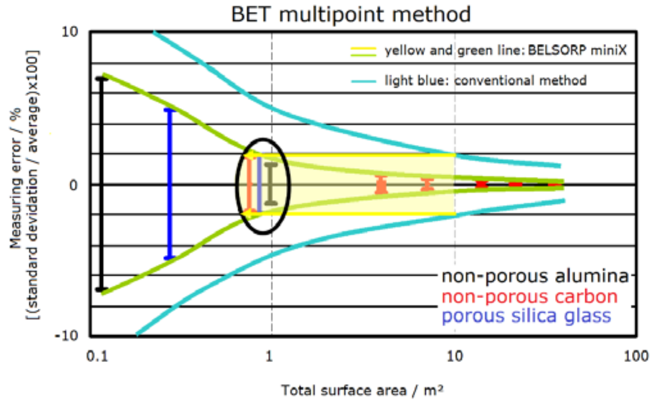


Figure 2 : Reproducibility of the BET surface area of non-porous alumina, non-porous carbon, and porous silica.

The comparison between the conventional method (keeping VD constant; light blue) and **AFSM™** (continuously measuring VD; green) shows that **AFSM™** is more reproducible in the whole surface area range, especially for smaller BET surface areas. With **AFSM™**, it is possible to measure low total surfaces down to 1 m2 with a reproducibility of ±2%, while conventional methods are limited to 10 m² with similar reproducibility. Summarized, the sensitivity is improved by 10 times by **AFSM™**.

5. REPRODUCIBILITY OF PORE SIZE DISTRIBUTION MEASUREMENT BY AFSM™

The patented **Advanced Free Space Measurement** (**AFSM™**; US Patent:6.595.036) is a highly accurate method for the determination of **dead volume**, which does not require keeping the level of liquid refrigerant constant. With **AFSM™**, it is possible to measure the free-space change continuously, considering the change of liquid refrigerant level, the room temperature change during sorption measurement, and the temperature change of the refrigerant due to oxygen dissolution. Therefore, the **pore size distribution** as well as the **specific surface area** can be evaluated with the highest accuracy (see Application Note No. 4 **AFSM™**: Improved reproducibility of the BET **specific surface area** by **AFSM™**).

Figure 1 shows up to five nitrogen sorption isotherms of **mesoporous** alumina (BAM-PM-104), carbon black (LGC2102), and porous glass (BAM-PM-122) at 77 K (left), including an enlarged section of the relevant **relative pressure** range (right).

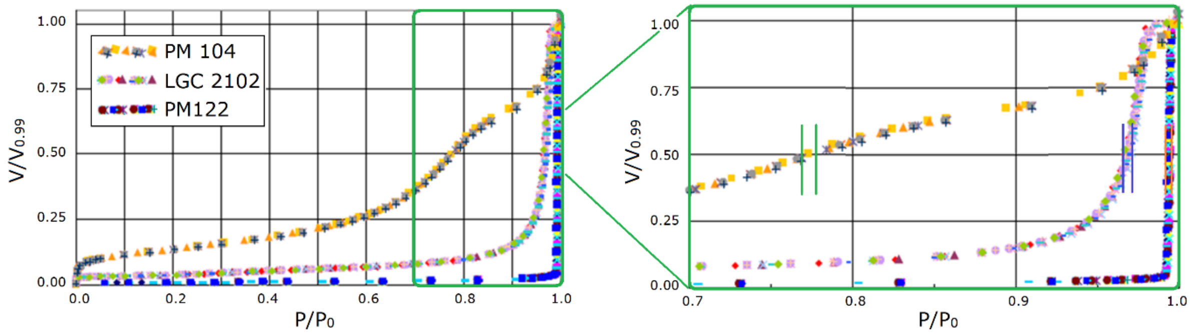


Figure 1 : Nitrogen sorption isotherms at 77 K and reproducibility of PM104, LGC2102, and PM122 (left) and enlarged section of relevant **relative pressure** range (right).

It is shown that the nitrogen sorption isotherms are highly reproducible with small deviations by using the **AFSM™** technique. As shown in **Figure 1**, the gas uptake of each material occurs at different **relative pressures**, while the strongest increase of gas uptake is marked (marking in **Figure 1**, right). Consequently, all three materials have different **pore size distribution**, respectively mean pore radius.

Figure 2 shows the reproducibility of **pore size distribution** calculation of the aforementioned materials with different mean pore radius. The calculation of **pore size distribution** is based on the compensation of the meniscus radius rc and the thickness t using the Kelvin equation at 77 K (see Equations 1 and 2).

Kelvin equation at 77 K :

$$r_c = \frac{-0.416}{\log(p/p_0)} \qquad (1)$$

$$\rightarrow \quad r_p = r_c + t \qquad (2)$$

Figure 2 points out that the calculation of **pore size distribution** is highly reproducible. The highest increase of uptake of PM 122 is at a **relative pressure** of ~0.995, which corresponds to a pore radius of ~195 nm (diameter: 390 nm; cf. **Figure 2**, orange). Although this pore diameter is near the maximum of resolution (pore diameter of 500 nm), the measurement error is about 6%.

In the case of PM 104, the smallest pores of our examples, the highest increase of nitrogen uptake is about a **relative pressure** of 0.76, which corresponds to a pore radius of ~4 nm. A measuring error of about 1% (see green marking, **Figure 2**) is obtained. Consequently, the smaller the pores are, the smaller the deviation/ measurement error.

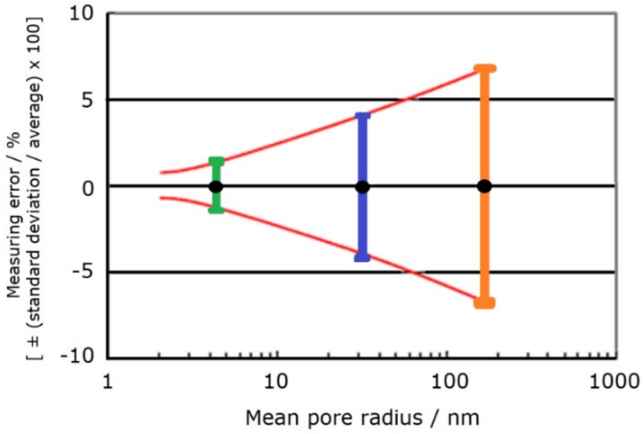


Figure 2 : Reproducibility of pore size distribution of PM 104 (green), LGC 2102 (blue), and BAM PM 122 (orange) – corresponding to **Figure 1**, right.

Summarized, the **AFSM™** technique of the **BELSORP series** delivers isotherms with high accuracy. As a result, the calculation of pore size distribution has lower measuring errors compared to other common techniques.

6. EVALUATION OF LOW SPECIFIC SURFACE AREA BY KRYPTON SORPTION MEASUREMENT

The characterization of low **specific surface area** materials, such as non-porous metallic materials, glass substrates, and films, with traditional gases like nitrogen (77 K) and argon (77 K or 87 K) is insufficient due to detection limits. Alternatively, krypton gas **adsorption** can be used at liquid nitrogen temperature to determine the BET-**specific surface area**.

Normally, the adsorbed quantity at a certain **relative pressure** (equilibrium pressure p/ saturation vapor pressure p0) is calculated using the following simplified equation:

(Adsorption amount) = (Amount of **adsorbate** introduced) - (Amount of **adsorbate** remaining without **adsorption**)

In case of low **specific surface area**s, the number of non-adsorbed nitrogen molecules in the void volume of the cell can be large compared to the number of molecules adsorbed on the surface. The end point of **relative pressure** commonly used for BET **specific surface area** evaluation for N_2 and Kr at 77 K is 0.3 (N_2: ~30400 Pa /101325 Pa and Kr: ~100 Pa /331 Pa; cf. Table 1). If there is a material that adsorbs 50 Pa at a **relative pressure** of 0.3, the absolute pressure of N_2 slightly changes from 30450 Pa to an equilibrium pressure of 30400 Pa. The change rate is bellow of 0.2%. In contrast, a pressure change from 150 Pa to 100 Pa results in a change rate of 33.3%. In low **specific surface area** materials, the change rate of pressure is crucial. Consequently, the use of Kr gas with low saturation vapor pressure is increasing the accuracy of measurement significantly. However, to measure low **specific surface area** using Kr gas, equipment with low leakage and outgassing, 1 torr pressure transducers, and high vacuum pumps must be used (optional in **BELSORP MAX, MAX X et MAX G**).

Gas	Adsorption Temperature / K	Saturation Vapor Pressure / Pa	Cross-sectional Area / nm²	Scope / m²
N_2	77	101325	0.162	1 or more
Ar	77	26664	0.166	0,1~10
Kr*	77	331	0.202	0,01~1
Xe	77	0.23	0.232	Around 1 cm²
CO_2	298	6,45x106	0.216	Coal and activated carbon

**Kr is a solid at 77 K. The saturated vapor pressure is calculated from the Clausius-Clapeyron equation for a supercooled fluid.*

Table 1 : Adsorption temperature, saturation vapor pressure, **adsorption** cross-sectional area, and application area of different gases.

Figure 1 hows the total surface area of a blank sample tube, α-alumina BAM-PM101, α-alumina BCR169, and carbon black (#3845; CB) on the horizontal axis and reproducibility on the vertical axis. The measurements are performed on **BELSORP MAX X** using a high-precision sample tube.

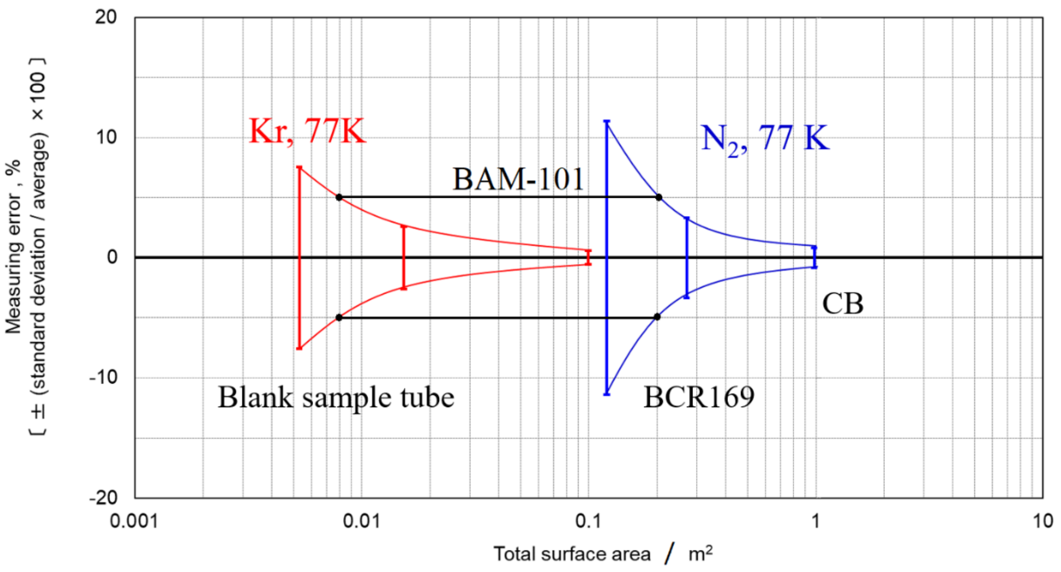


Figure 1: Reproducibility of Kr sorption of 77 K **BELSORP MAX X**

If sorption measurements with a measuring error of less than 5% is desired, N_2 **adsorption** measurements can be performed starting with total surface areas of 0.2 m² or more. However, Krypton sorption measurements with max. A measuring error of 5 % can be obtained in the total surface area range starting from 0.008 m². The results are consistent with Table 1.

7. CASE STUDIES IN POROUS MATERIALS CHARACTERIZATION

7a) Adsorption Behavior of N_2 and Ar Molecules in Type Y Zeolite with Different Surface Properties (SiO_2/Al_2O_3)

The surface areas and pore-size distributions of porous and non-porous solids are frequently inferred from nitrogen **adsorption** measurements. Nitrogen **adsorption** is the method of choice because of its sensitivity, precision, and low cost. However, in some cases, nitrogen **adsorption** isotherms can provide misleading estimates of pore-size distributions. In such cases, inert gases such as argon are typically used instead. In this application note, we examine the differences between the **adsorption** isotherms of N_2 at 77.4 K and Ar at 87.4 K in Y-type zeolites.

Molecular nitrogen, N_2, which has a quadrupole moment, is strongly adsorbed on Al cation sites in zeolites, while non-polar argon does not interact as strongly with these **adsorption** sites. The isotherms plotted in **Figure 1** (middle and right) below are shown in terms of adsorbed amount (given in units of gas volume at STP) against **relative pressure**. The **relative pressure** is the ratio of the actual measurement pressure (*p*) to the saturation vapor pressure (*p0*) of the gas phase at the measurement temperature. As synthesized, Y-type (FAU) zeolites have high aluminum contents and low hydrothermal stability. Before these materials can be used as industrial catalysts, they are usually converted to ultra-stable Y (USY) zeolites with low aluminum contents by steaming at high temperature. The de-alumination process preserves the zeolites' **micropore** structures while increasing their Si/Al ratios and creating meso- and **macropores**. The FE-SEM surface images in **Figure 1** (left (1)) and the cross-sectional images after BIB (broad ion beam) treatment in **Figure 1** (left (2)) show this for samples of Y-type zeolite 320HOA (SiO_2/Al_2O_3=5.5), and its ultra-stable, de-aluminated analog 390HUA (SiO_2/Al_2O_3=400) provided by Tosoh Corp. **Figure 1** (middle and right) shows the **adsorption** isotherms of N_2 and Ar at 77.4 K and 87.3 K, respectively, on both zeolites. These isotherms were measured using the **BELSORP MAX** after pretreatment at 300 °C for 8 hours *in vacuo*.

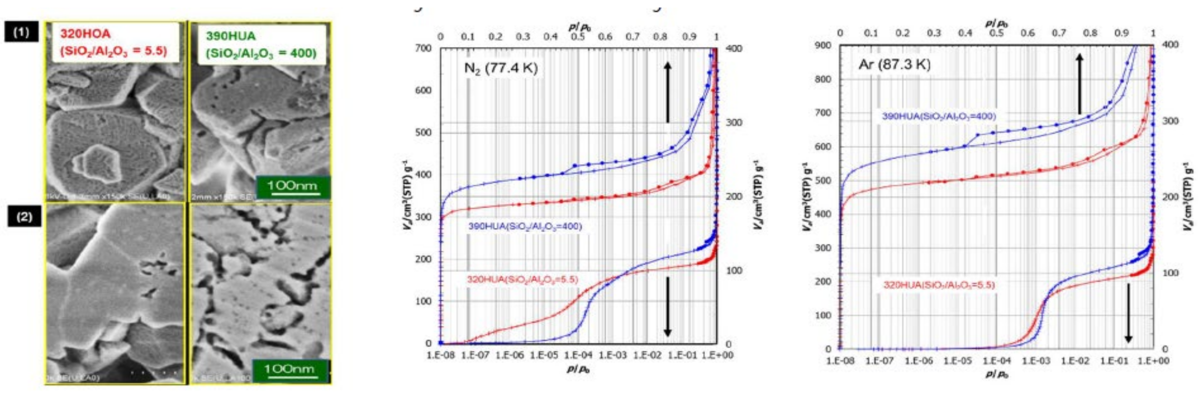


Figure 1: Left: FAU zeolite SEM image of different SiO_2/Al_2O_3 = 5.5 and 400 – (1) Surface image of HSZ particles / (2) Cross-sectional image – Middle and right: Adsorption isotherms of Y-type zeolite (N_2@77.4K, Ar@87.4K).

The isotherms were measured from extremely low **relative pressure**s (10-8) to near saturation (ambient) pressure. In the IUPAC isotherm classification scheme, both sets of **adsorption** isotherms are classified as Type I+IV. **Type I isotherm**s are characteristic of purely **microporous** solids. In **micropores** (pore diameter < 2 nm), adsorbed molecules interact strongly with the atoms of the pore walls because of their close physical proximity (up to approximately two or three times the molecular diameter), resulting in the classical Langmuir **isotherm shape**. The low- pressure portions of the isotherms in **Figure 1** (middle and right) show this type of behavior. At higher pressures, the **micropores** are almost filled, and **adsorbate** molecules begin coating the surfaces of **mesopores** (2 nm < pore diameter < 50 nm) and **macropores** (diameter $\geq$ 50 nm). Further increases in pressure result in **multilayer adsorption** or condensation within the **mesopores** and **macropores**. Condensation/multilayer formation cannot occur within **micropores** because of spatial constraints. The isotherms in **Figure 1** show both the **adsorption** (increasing pressure) and desorption (decreasing pressure) branches; when the **adsorption** and desorption branches of an isotherm do not coincide, i.e., when there is *hysteresis* in the isotherm, this indicates condensation within meso- and **macropores**. Attractive forces between sorbate molecules and pore walls favor the condensed phase over the gas phase. As a result, the desorption branches of the hysteresis loops in **Figure 1** are above the **adsorption** branches.

The lower (logarithmic scale) N_2 isotherm plots in **Figure 1** (middle and right) show significant differences in the N_2 loadings of the two zeolites at low **relative pressure**s. The loading of N_2 in the smallest **micropores** (corresponding to the lowest pressures) of 320HUA is enhanced relative to the N_2 loading in its de-aluminated analog 390HUA because of attractive interactions between the N_2 quadrupoles and the Al^+ cation centers in 320HUA. This effect is not observed for non- polar Ar. **Figure 2** (left) shows that N_2 is strongly adsorbed within the **micropores** of 320HOA (SiO_2/Al_2O_3 = 5.5) even at very low pressures (on the order of 10^{-8}). Nitrogen **adsorption** in the **micropores** of de-aluminated 390HUA (SiO_2/Al_2O_3 = 400) begins at much higher **relative pressure**s because the number of cation sites that can interact with N_2 quadrupoles is much lower than in 320HOA. The enhancement in 320HOA N_2 loading due to quadrupole-cation interactions persists throughout the **micropore**-filling pressure range, until the isotherms coincide at a value as close to 1.

Figure 2 (right) shows that for Ar **adsorption** at 87.4 K, by contrast, little difference is found between 320HOA and 390HUA. Micropore filling begins at approximately $p/p0=10^{-3}$ in both zeolites, and the Ar loadings are similar throughout the **micropore**-filling pressure range.

Argon **adsorption** can therefore be used to characterize **micropore** structure regardless of whether cationic **adsorption** sites are present. If cation sites are present, they interact strongly with the quadrupoles in molecular nitrogen and enhance nitrogen loading in the **micropore**-filling pressure range.

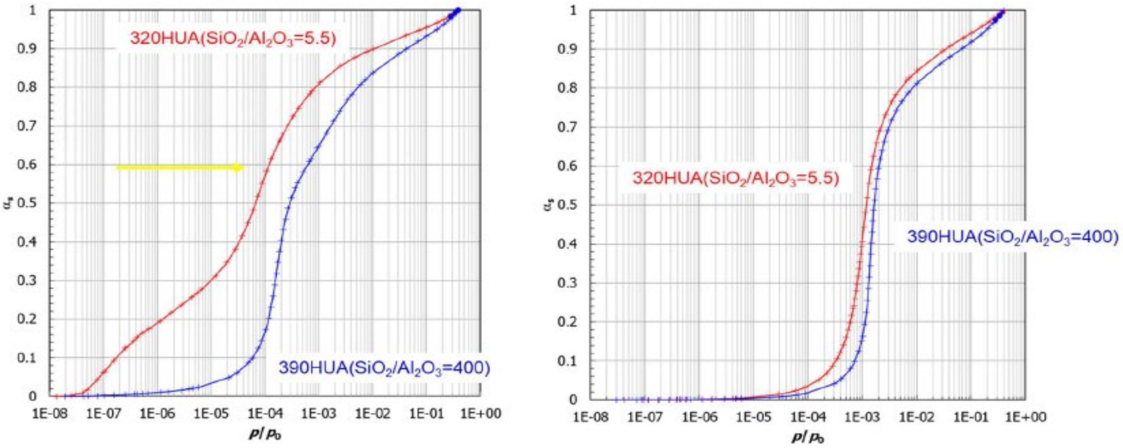


Figure 2 : Strong **adsorption** of N2 on Al cation

7b) Investigation of Micropore Structures of Mesoporous MFI Zeolite by the SF Method

The **Saito-Foley** (SF) method assumes **a cylinder-shaped micropore,** and Eq.1 relates pore size and **relative pressure** that can be applied to MFI zeolite by extending the HK method.

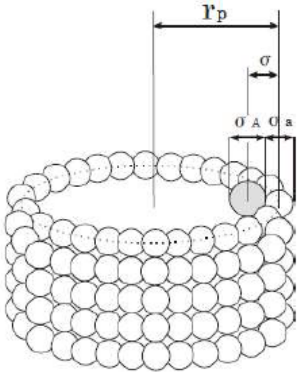


Image for cylinder type pore model

$$\boxed{\ln(p/p_0) = \frac{3}{4}\frac{\pi L}{RT}\frac{N_s A_s + N_a A_a}{\sigma^4}\sum_{k=0}^{\infty}\left[\frac{1}{k+1}\left(1-\frac{\sigma}{r_p}\right)^{2k}\left\{\frac{21}{32}\alpha_k\left(\frac{\sigma}{r_p}\right)^{10} - \beta_k\left(\frac{\sigma}{r_p}\right)^{4}\right\}\right]} \quad \text{(Eq. 1)}$$

$$A_s = \frac{6\,m\,c^2\,\alpha_s\,\alpha_a}{\frac{\alpha_s}{\chi_s}+\frac{\alpha_a}{\chi_a}}$$

$$A_a = \frac{3}{2}\,m\,c^2\,\alpha_s\,\alpha_a$$

$$\alpha_k^{0.5} = \frac{\Gamma(-4.5)}{\Gamma(-4.5-k)\,\Gamma(k+1)}$$

$$\beta_k^{0.5} = \frac{\Gamma(-1.5)}{\Gamma(-1.5-k)\,\Gamma(k+1)}$$

L: Avogadro number
N_s ,N_a: Number of atoms per unit area of adsorbent
s:adsorbent a:adsorbate in adsorption state
m: mass of electron, c: speed of light
α_s ,α_a: Polarization ratio of adsorbent atoms and adsorbent molecules
χ_s ,χ_a: Magnetization ratio of adsorbent atoms and adsorbent molecules

Figure 1 shows the SEM image of H^+-type ZSM-5 prepared by heat treatment of NH_4-type ZSM-5 (MFI-type zeolite) at 535 °C for 3 h under atmospheric pressure. The image shows an agglomerate of polyhedral layered particles of around 200 nm, and the interparticle space consisted of slit-type pores. The N_2@77.4 K **adsorption**/desorption isotherms of H^+-type ZSM- 5 (**Figure 1**) were classified as Type I+IV, with the interparticle pores and the hysteresis that is closed at p/p_0=0.42 confirmed that they included **mesopores** and **micropores** within the particles.

The SF-plot from N_2@77.4 K **adsorption** isotherm is shown in **Figure 1** (right). It can be confirmed that the pore diameter and **pore volume** of the **micropores** existing in the ZSM-5 sample were 0.41 nm and 0.13 cm^3 g^{-1}, respectively.

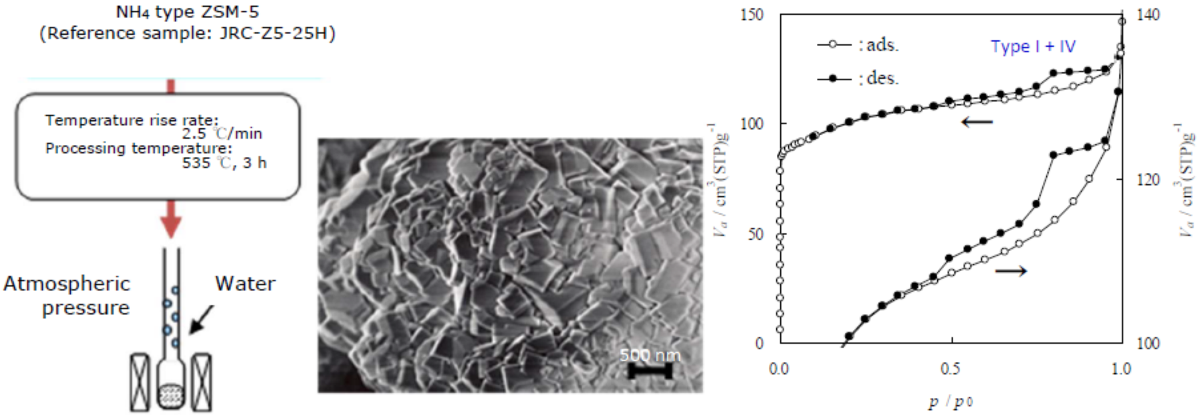


Figure 1 : N_2@77,4 K adsorption isotherm for H+ type MFI zeolite

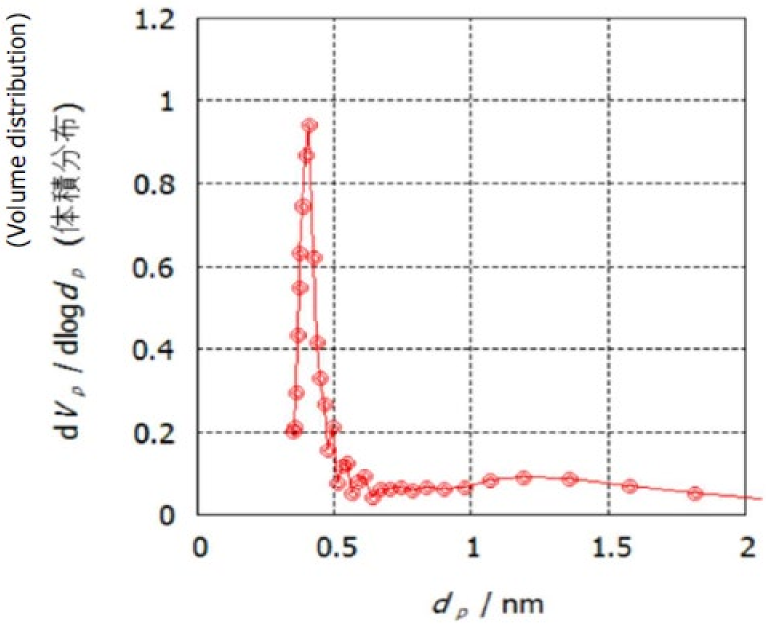


Figure 2 : Micropore size distribution for H+ MRI zeolite by the SF method

In addition, the **SF method** result can be referred to application note B-AD-013 (t-plot) and B-AD-008 (graphique INNES) regarding the structural evaluation of the same mesoporous zeolite sample.

(Référence) K. Nakai, M. Hakuman, H. Naono, Zeolite,**23** 2(2006) (in Japanese).

7c) Investigation of the Hydrophilicity of Carbon Nanotubes (CNT) by Water Vapor and Nitrogen Adsorption

While N_2 molecules can cover the surface of a material uniformly, H_2O molecules preferentially adsorb on the hydrophilic sites, making it possible to evaluate the hydrophilicity of the material using both **adsorbates.**

The N_2@77.4K **adsorption** isotherms of carbon nanotubes CNT-A and B, shown in **Figure 1** (left), indicate that they are Type VI and Type II, respectively. The results indicate that CNT-A presents a more homogeneous and, therefore, more stable surface than that of CNT-B when exposed to similar conditions. The BET-plot yields the BET(N_2) **specific surface area** of 10.4 m^2 g^{-1} for CNT-A and 44.6 m^2 g^{-1} for CNT-B. Additionally, the results of the H_2O@298.15 K **adsorption** isotherm are shown in **Figure 1** (right), where the y-axis is the number of H_2O molecules per BET(N_2) **specific surface area** (ɼ = v/ 22414 × 6.022 × 1023 /as × 10^{-18} (as is the N_2 surface area / m^2 g^{-1})). It can be confirmed from the isotherm that CNT-B has a larger number of hydrophilic sites than CNT-A, indicating that there are about 10 times more water molecules at a **relative pressure** of 0.2. From these results, it could be concluded that the surface of CNT-A is homogeneous, CNT-B is heterogeneous, and CNT-B has about 10 times more hydrophilic sites than CNT-A. (Table 1)

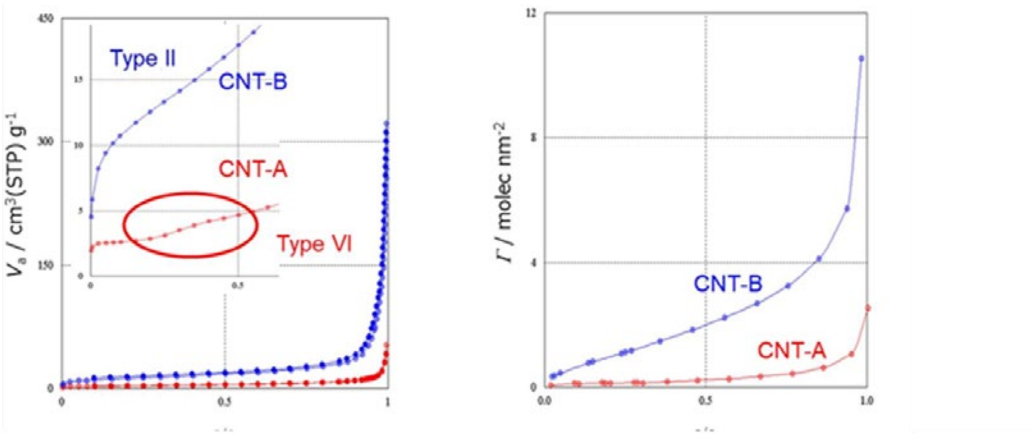
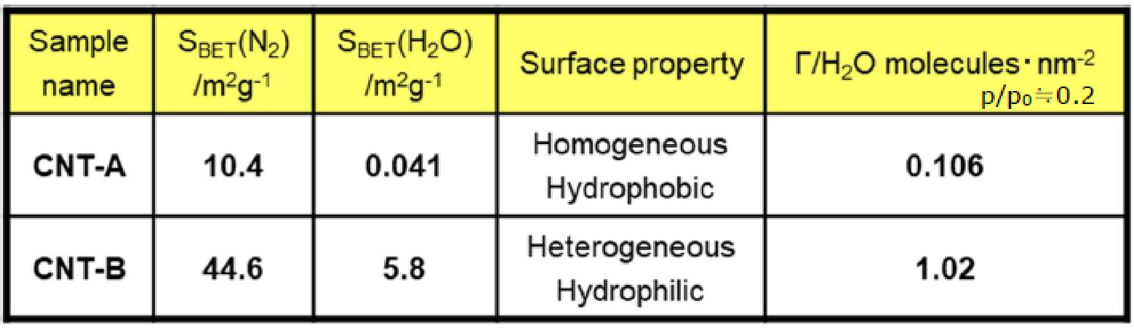


Figure 1 : Adsorption/desorption isotherms of CNT-A and -B (N_2@77.4K) (left) and Adsorption/desorption isotherms (H_2O molecules per BET (N_2)) of CNT-A and -B (H_2O@298.15K) (right)



Sample name	$S_{BET}(N_2)$ /m^{2}g^{-1}	$S_{BET}(H_2O)$ /m^{2}g^{-1}	Surface property	Γ/H_2O molecules · nm^{-2} p/p₀≒0.2
CNT-A	**10.4**	**0.041**	Homogeneous Hydrophobic	**0.106**
CNT-B	**44.6**	**5.8**	Heterogeneous Hydrophilic	**1.02**

Table 1 : Surface structure evaluation of CNT-A and -B

7d) Investigation of Materials with Cylindrical Pore Structures (Zeolite and Mesoporous Silica) by NLDFT and GCMC

In the past, the HK (slit), SF (cylinder), and CY (cage) methods based on the **adsorption** potential theory were used to evaluate the pore structure of various porous materials in the **micropore** region due to the difference in pore structure, while the INNES (slit) and BJH (cylinder) methods based on the **capillary condensation** theory were used in the meso- and **macropore** region.

On the other hand, in recent years, computer simulation methods such as **NLDFT** (Non- localized density functional theory) and **GCMC** (grand canonical Monte Carlo) methods have been attracting attention for their ability to analyze pore structures from **micropores** to meso- and **macropores** using a unified theory. It is known that the pore size peaks and **pore size distribution**s (PSD) obtained from the same **adsorption** isotherm are different between classical and novel analysis, and even between novel theories, because the filling pressure obtained from each theory is different.

In the **NLDFT** method, the pore shape is assumed. Moreover, at any given **adsorption** temperature and pressure, parameters such as the interaction between adsorbed molecules, the interaction between atoms constituting the **adsorbent**, and the interaction between adsorbed molecules and atoms constituting the **adsorbent** are determined. From this, the **adsorption** density in the pore is calculated using an approximate equation based on the density functional theory. The **GCMC** method calculates the **adsorption** density using a computer simulation that simulates the **adsorption** phenomenon by setting the same parameters as above, placing the adsorbed molecules in the virtual pore space, repeating the movement, generation, and disappearance of the adsorbed molecules, and accepting the molecules if the ground potential becomes negative (stable), and restoring the molecules if the ground potential is the opposite.

Figure 1 depicts a relationship between **adsorption** densities and **relative pressure** for the local isotherm of 4nm (left) and 10nm (right) by **NLDFT** and **GCMC** calculations. From these results, it can be seen that the **NLDFT** method underestimates the adsorbed phase density and overestimates the filling pressure compared to the **GCMC** method.

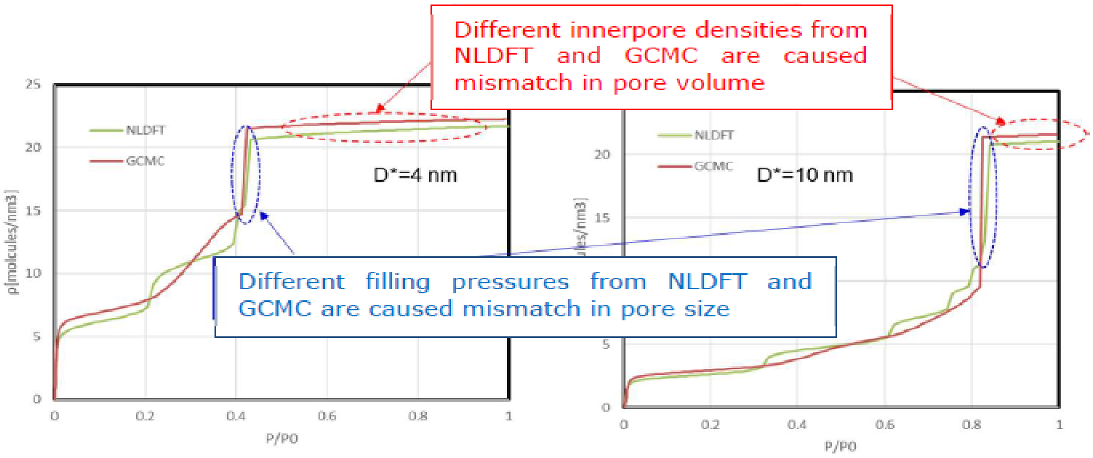


Figure 1 : Local isotherms of 4 nm and 10 nm by **NLDFT** and **GCMC** (adsorbed branch Ar@87.3 K)

In other words, the **NLDFT** method can be considered to be overestimating the **pore volume** and underestimating the pore size.

This paper discusses the viability and applicability of both **NLDFT** and the **GCMC** method for determining PSD. Furthermore, the continued use of N_2 vs Ar as an **adsorbent**, which was recommended by IUPAC in 2015, comes into question. Adsorption measurements were performed for N_2 (77.4K) and Ar (87.3 K) on **mesoporous** silica MCM41, MFI (10-membered ring), and MTW (12-membered ring) zeolites with cylinder pores.

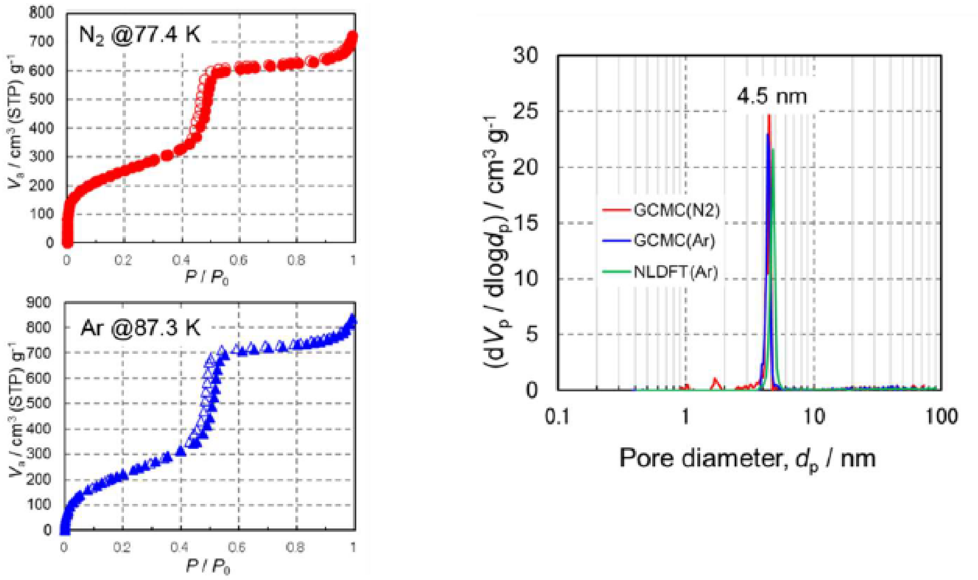


Figure 2 : Adsorption isotherms of MCM41 (N_2@77. 4 K, Ar@87.3 K) (left) and PSD of MCM41 (N_2@77. 4 K, Ar@87.3 K) (right)

The **mesoporous** silica MCM41 N_2@77. 4 K and Ar@87.3 K **adsorption**/desorption isotherms (**Figure 2**) are classified as Type IVb, indicating the presence of **mesopores**. **Figure 2** (right) shows the PSD of MCM 41 calculated by **GCMC** and **NLDFT** method from Ar@87.3 K isotherm, as well as PSD by **GCMC** from N_2@77.4K isotherm. This confirms that all results of the analysis of PSD by the **GCMC** and **NLDFT** methods using N_2@77.4K and Ar@87.4 K **adsorption** isotherms for **mesoporous** MCM41 are in good agreement.

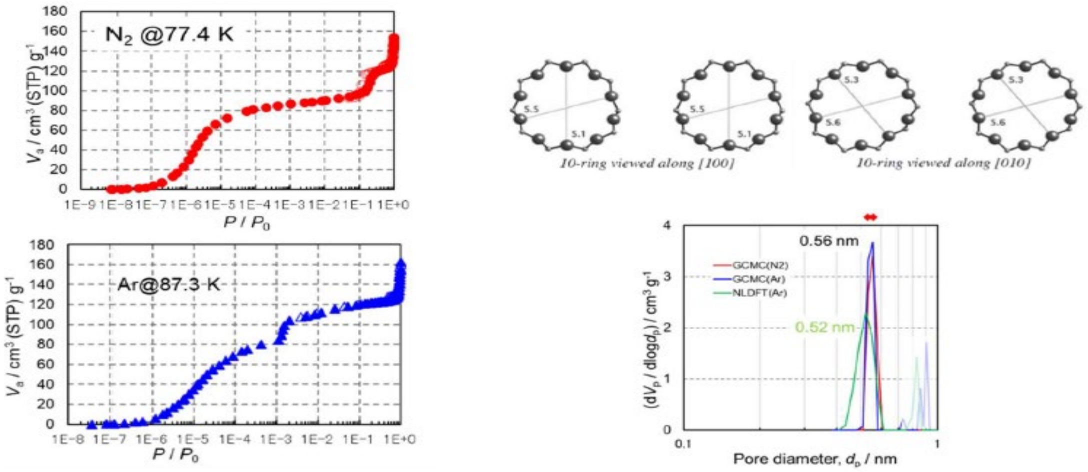


Figure 3 : Adsorption isotherms for MFI 1000H (N_2@77. 4 K, Ar@87.3 K) (left) and MFI pore structures provided by IZA and **pore size distribution** from **GCMC** and **NLDFT** of MFI 1000H (N_2@77. 4 K, Ar@87.3 K).

The **microporous** MFI (10-membered ring) zeolite 1000H (Si/Al=500) with N_2 @ 77.4K, Ar@87.3 K **adsorption**/**desorption** isotherms (**Figure 3**) are classified as Type I, indicating the presence of **micropores**. **Figure 4** shows the PSD for each **adsorbate** N_2@77.4K and Ar@87.3 K, calculated by the **GCMC** method and the **NLDFT** method. The **pore size distribution** analysis by the **GCMC** method is in good agreement with the pore size obtained from the XRD provided by IZA (International Zeolite Association), shown in Fig 5. On the other hand, the **pore size distribution** from the **NLDFT** method is broad due to its kernel problem, showing a **pore size distribution** of 0.4-0.5 nm, which does not exist in reality.

In **Figure 4**, **N_2@77.4** K and **Ar@87.3K adsorption**/desorption isotherms for MFI (25H) of Si/Al=12.5 were compared with those for MFI (1000H) of Si/Al=500. The isotherms for 25H show a gradual increase in **adsorption** branch from low **relative pressure** and **micropore** filling due to the involvement of the N_2 quadrupole and strong **adsorption** on the zeolite pore surface, whereas for 1000H, the **adsorption** increases rapidly at around p/p_0=1E-6, and **micropore** filling can be identified. For the **Ar@87.4** K isotherm, since Ar is non-polar, the behavior of the amount of **adsorbate** increases around p/p_0=1E-6 for both 25H and 1000H, regardless of the surface condition. 25H **N_2@77.4** K by the **GCMC** method (**Figure 5**), N_2 molecules are strongly adsorbed on Al^+ sites due to their quadrupole moment, resulting in a small pseudo- pore distribution around 0.4 nm. The **pore size distribution** of 25H from the **NLDFT** method by Ar molecule is broad, 0.4-0.5 nm, and the same can be observed for 1000H.

From the above, it can be concluded that for MFI zeolites with 10-membered rings, the **GCMC** method using N_2 **adsorption** gas can be used to obtain the appropriate pore distribution (>0.5 nm) except for the Al^+ site, while the **GCMC** method using Ar **adsorption** gas can analyze the appropriate pore distribution and **pore volume**.

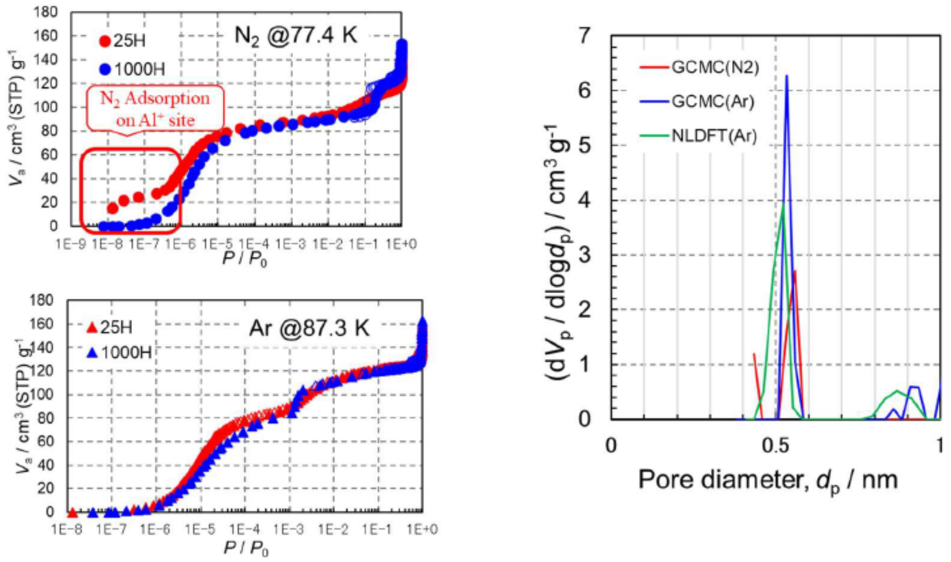


Figure 4 : Adsorption isotherms of MFI 25H and 1000H (N_2@77.4K, Ar@87.3 K) (left) and Pore distribution (pore volume) of MFI25H (N_2@77.4K, Ar@87.3K).

From the **GCMC** and **NLDFT** pore distribution analysis of MTW (ZSM-12, 12-membered ring) Ar@87.3K (**Figure 5**), the **GCMC pore size distribution** agrees well with the pore structure shown by IZA, while the **NLDFT pore size distribution** is underestimated due to its kernel problem (**Figure 1**). The **pore volume** of the **NLDFT** method was overestimated to 0.17 cm³ when compared to an ideal **pore volume** of 0.14 cm³ of the 0.58 nm cylinder shape, assuming a molecular diameter of 0.34 nm that is called the Ar molecule. The **pore volume** calculated from **GCMC** is in agreement with the ideal volume.

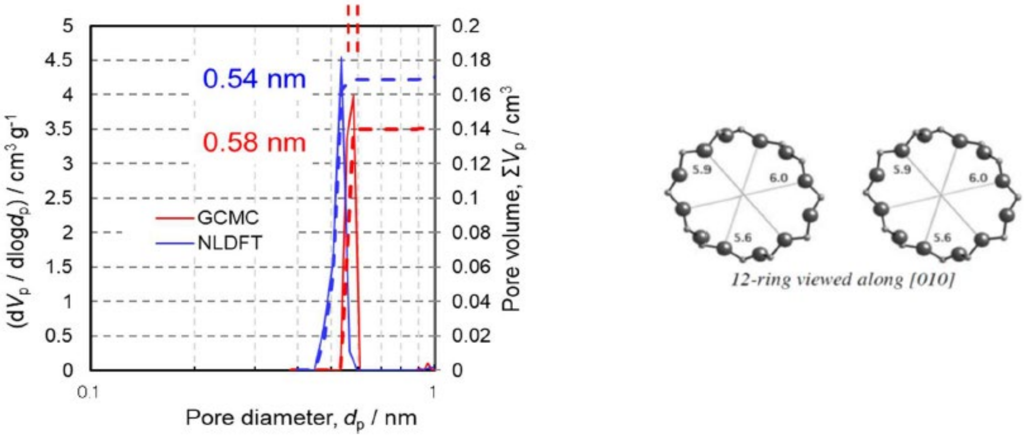


Figure 5 : Pore distribution and cumulative **pore volume** distribution of MTW 12-membered rings by **GCMC** and **NLDFT** methods [∑Vp] (Ar@87.3K).

In summary (Table 1), the **NLDFT** and **GCMC** methods can be used to evaluate the **pore size distribution** of materials with cylinder-shaped **mesopores**, regardless of whether the **adsorbate** is N_2 or Ar. For zeolites with micro-pores of the same shape, the Ar **adsorption GCMC** method is the best method to analyze the pore distribution when the pore size is larger than 0.4 nm (confirmed separately by an 8-membered ring zeolite; not shown in this report), and the N_2 **adsorption GCMC** method can also be employed to analyze the **pore size distribution** (>0.5 nm) except for zeolite with the Al cation site-rich surface. In addition, the **NLDFT** method underestimates the pore distribution and overestimates the **pore volume**, regardless of the **adsorbent**, when evaluating the pore structure of **microporous** zeolites, so the **GCMC** method is recommended.

	NLDFT Method		GCMC method	
	N_2	Ar	N_2	Ar
Poresize > 2 nm (**mesopore**)	○	○	○	○
Pore size > 0,5 nm (10-membered ring **micropore**)	△	△	○	○
Pore volume	×	×	○	○
Al $^+$ site-rich surfacee	△	△	△	○

Table 1 : Evaluation of pore structure by **NLDFT/GCMC** method and N_2 and Ar for porous materials with cylinder shape.

○ **(circle) → Recommended / reliable** (The method performs well for this case and gives accurate results)

△ **(triangle) → Moderate / acceptable but limited** (The method can be used, but with restrictions, lower accuracy, or only in specific conditions)

× **(cross) → Not recommended** (The method gives poor or unreliable results and should not be used)

7e) Characterization of Pore Structures for Slit Microporous Carbon Fiber by GCMC

We demonstrated earlier that the **GCMC** method can be used to evaluate pore size and **pore volume** more accurately than by **NLDFT**. This was the case for cylinder-type pores in materials like zeolites and **mesoporous** silicas. For the following study, the pore structure of activated carbon fiber (ACF) with slit-type shape pores was evaluated using the **GCMC** method, and the pore shape structure was examined based on these results.

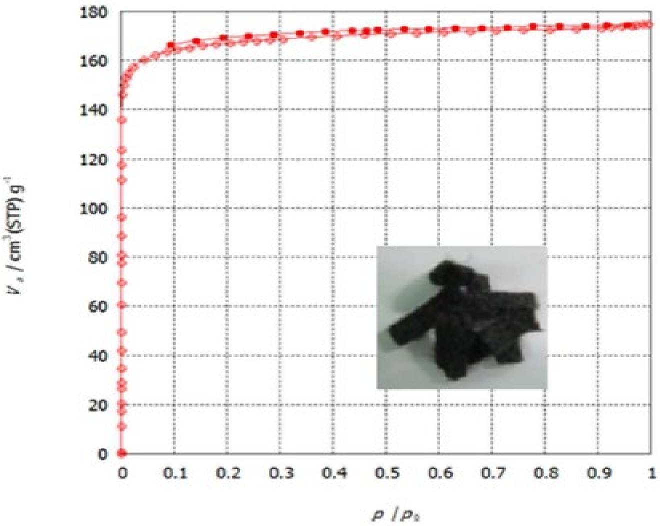


Figure 1 : Adsorption isotherm of activated carbon fiber (ACF) (N_2@77.4K) – Pretreatment: 573K, 12h, vac).

The **adsorption** isotherms of ACF (KURACTIVE FT-07) at very low **relative pressures** (p/p_0=1E- 8) **N_2@77.4** K (pretreatment: 300 °C, 12h) were measured with the **BELSORP MAX**, and the results are shown in **Figure 1** (linear plot) and **Figure 2** (semi- log plot). From **Figure 1**, the **adsorption** isotherm is classified as Type Ia with well-developed **micropores**, and since there is no increase in **adsorption** after medium **relative pressure**, it can be said that the activated carbon fiber has no **mesopores**.

The measured **adsorption** isotherm and the ideal **adsorption** isotherm (simulation result) calculated from the carbon **N_2@77.4K GCMC** slit kernel are shown in **Figure 2** (left), respectively. The **pore size distribution** and the integrated **pore volume** are shown in **Figure 3**. The **pore size distribution** in **Figure 2** (right) is highly reliable because both the measurement of the **adsorption** isotherm and the simulated **adsorption** isotherm of activated carbon in **Figure 2** are in good agreement. From these results, it can be concluded that this activated carbon has ultra-**micropores** with 0.4- 0.7 nm that can contain about 1-2 molecules of N_2 molecules, and super**micropores** with 0.7- 2 nm that can contain about 2-5 molecules, respectively. Pore capacities are 0.23cm^3/g (86%) and 0.04 cm^3/g (14%), respectively (Table 1), and it can be inferred that the ACF has a pore structure as shown in **Figure 3**. As described above, the **GCMC** method can be used to predict the pore structure of porous carbon more accurately.

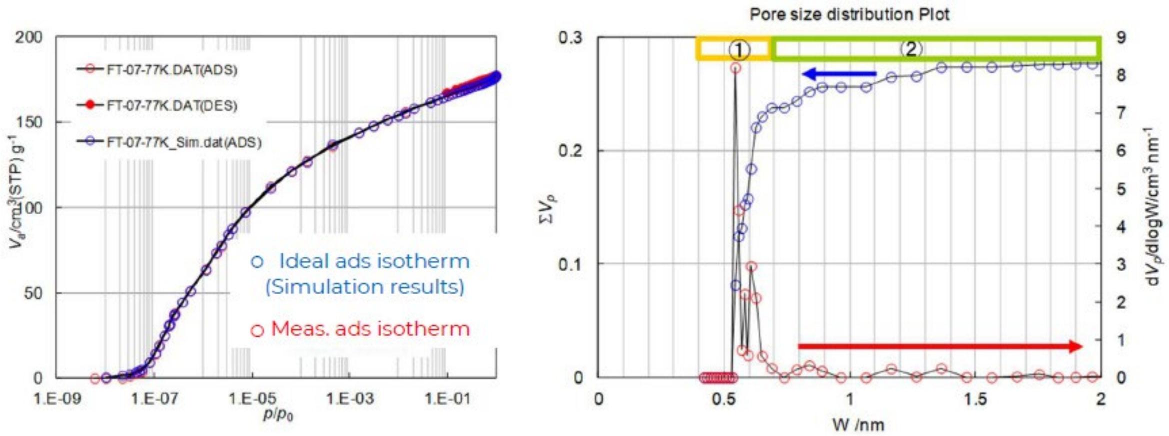


Figure 2 : Measurement result of **adsorption** isotherms of ACF (N_2@77.4K) and ideal **adsorption** isotherms calculated from **GCMC** method (left) – Pore size distribution (pore volume) and cumulative pore volume distribution (∑Vp) for ACF (FT-07) by **GCMC** (right).

	Pore volume / cm³ (liq.) g⁻¹	(dw) Pore width / nm	Pore volume ratio / %
Ultra-micropores 1 (1-2 N2 molecules)	0.23	0.4-0.7	86
Super micropores ② (2-5 N2 molecules)	0.04	0.7-2.0	14
Total pore volume (-2 nm)	0.27	-	-

Table 1 : Comparison of Ultra and Super Micropore Capacity of ACF by **GCMC** method

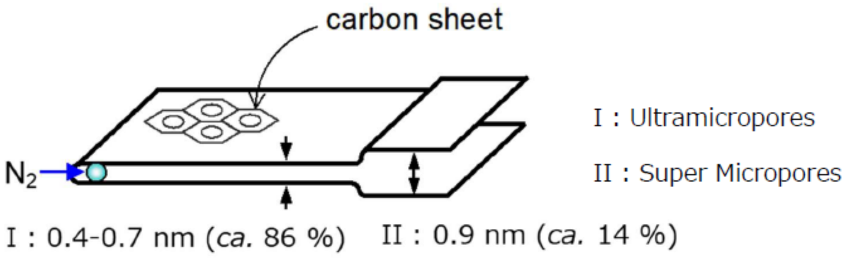


Figure 3 : Predicted slit pore structure of ACF (FT-07) calculated from **GCMC**.

7f) Characterization of Pore Size Distribution of Type A Zeolite by Molecular Probe Method

One method to evaluate the **pore size distribution** of **micropores** in zeolites is the molecular probe method. This technique uses the molecular sieving effect of probe molecules and thus can directly evaluate the pore distribution in zeolites. In this document, the pore distribution of three 3 different A-type zeolites (3A, 4A, and 5A) was evaluated using 5 different probe molecules (H_2O: 0.28 nm (dc), CO_2: 0.31 nm (dm), C_4H_{10}: 0.40 nm (dm), 4n-C_4H_{10}: 0.45 nm (dm), iso-C_4H_{10}: 0.58 nm (dm), molecular size of d_c and d_m is defined in **Figure 1**). The materials were characterized by volumetric sorption under the following conditions: @298.15 K are shown. H_2O, CO_2, and C_2H_6 were utilized as probe molecules for zeolite 3A, and CO_2, C_2H_6, n-C_4H_{10}, and iso-C_4H_{10} were utilized as probe molecules for zeolites 4A and 5A (see **Figure 2**).

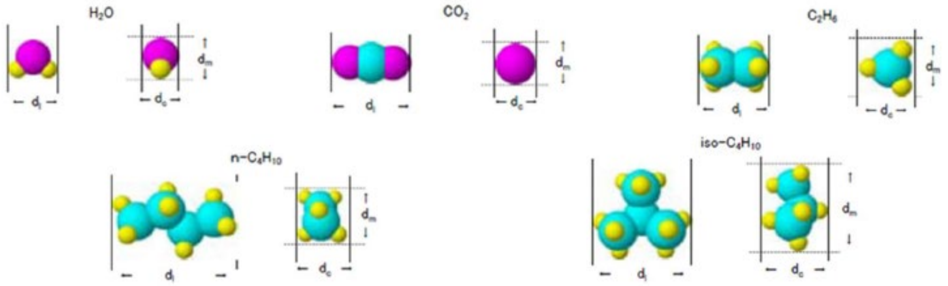


Figure 1 : *Probe molecule size* H_2O, CO_2, C_2H_6, n-C_4H_{10} and iso-C_4H_{10}.

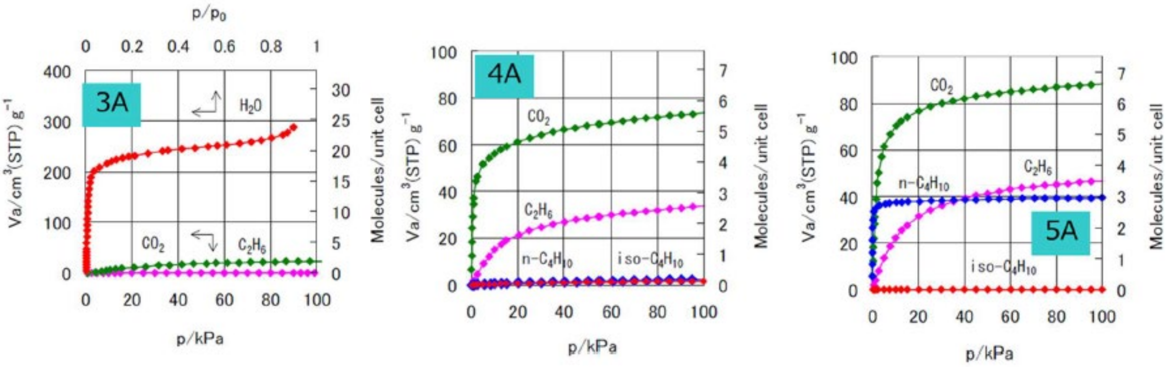


Figure 2 : Adsorption/desorption isotherm of type A zeolite (@298.15K) pretreatment: 400 °C, 4h.

The **pore volume** and **pore size distribution** of each zeolite were determined from these **adsorption** isotherms using the Dubinin-Astakov (DA) method, as shown in **Figure 3**. A value of 0.31 nm was obtained as the peak pore distribution for 3A, 0.42 nm as the peak pore distribution for 4A, and 0.50 nm as the peak pore distribution for 5A. It can be concluded that the molecular probe method is a viable method to evaluate the pore distributions of zeolites 3A, 4A, and 5A, as it allows the calculations to be obtained directly from the **adsorption** isotherms of each probe molecule.

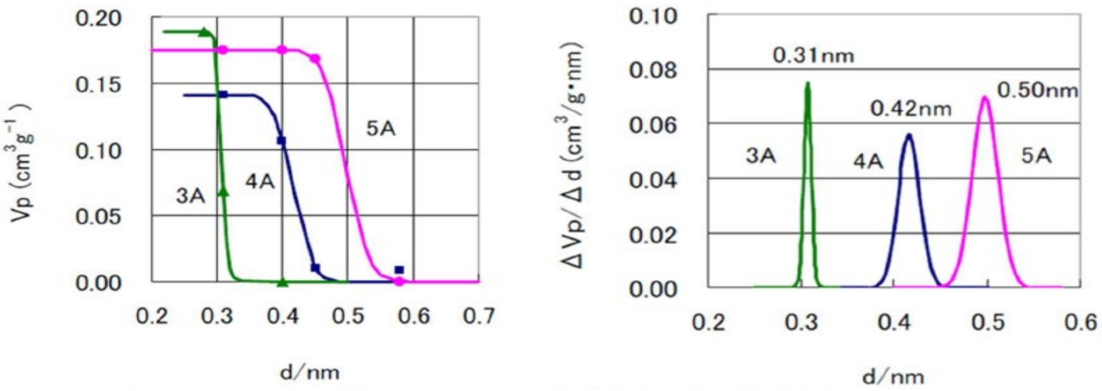


Figure 3 : Cumulative pore volume distribution and pore size distribution of 3A, 4A, and 5A zeolites.

8. CONCLUSION

The comprehensive evaluation of porous materials using advanced **adsorption** techniques demonstrates the critical role of measurement methodology, **adsorbate** selection, and computational analysis in obtaining accurate and reproducible pore structure data. The **AFSM™** technique provides high-precision nitrogen sorption isotherms, enabling highly reproducible calculations of **specific surface area** and **pore size distribution**, with smaller pores exhibiting lower measurement errors. For materials with very low surface areas, krypton **adsorption** at 77 K significantly improves measurement accuracy compared to nitrogen or argon, highlighting the importance of choosing the appropriate **adsorbate** for the material's characteristics.

Case studies on carbon nanotubes, zeolites, **mesoporous** silica, and activated carbon fibers confirm that the hydrophilicity, surface homogeneity, and **micropore**-to-**mesopore** distribution can be effectively characterized by combining traditional **adsorption** measurements with modern computational methods. The **NLDFT** method, while useful for **mesopores**, tends to underestimate **micropore** filling and overestimate **pore volume** due to kernel limitations. In contrast, **GCMC** simulations provide highly reliable **pore size distribution**s and **pore volume**s for both cylindrical and slit-shaped pores, closely matching experimental data and known structural parameters. Molecular probe methods further complement these approaches, offering direct evaluation of **micropore** sizes in zeolites with high accuracy.

Overall, the combination of precise experimental techniques, proper **adsorbate** selection, and advanced computational modeling allows for a detailed, reproducible, and reliable characterization of porous materials. These methods together provide insights into the interplay between pore geometry, surface chemistry, and **adsorption** behavior, enabling a better understanding and utilization of porous materials in applications ranging from catalysis and gas storage to separation and sensor technologies.

8a) Industry Standards

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