

Accounts of Materials & Surface Research

Characterization of Micro/Mesoporous Materials by Physisorption: Concepts and Case Studies

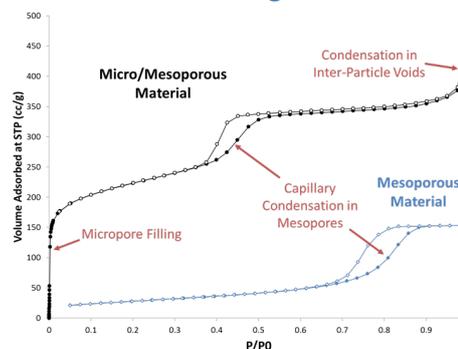
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Utilizing case studies of selected materials, including hierarchical zeolites, controlled pore glasses, and mesoporous carbons, we demonstrate that physisorption analysis is a valuable tool in the structural characterization of a broad range of nanoporous materials. In conjunction with the selected case studies, we illustrate how application of advanced methodologies allows for the determination of surface areas, pore volumes, and pore size distributions over the complete range of micro-, meso-, and even narrow macropores. We discuss important aspects of state-of-the-art gas adsorption methodologies, in line with recent recommendations by the IUPAC. Rather than serving as a broad review of gas adsorption literature, this paper highlights basic concepts and resources for understanding gas adsorption characterization in a modern context and offers practical guidance for users of gas adsorption instruments, especially those in industrial settings.



Keyword: Physisorption Isotherms, Nanoporous Adsorbents, Surface Area and Pore Size Characterization

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1. Introduction

Measurement of gas adsorption isotherms is a well-established technique in the characterization of porous materials with over a century of dedicated research and development. Gas adsorption isotherms were already being measured in analysis of adsorbents and catalysts at the end of the 19th century and pioneering experimental and theoretical work in the early 20th century laid the ground work for our understanding of gas adsorption phenomenon and its employment for the characterization of porous materials.¹ However, it is only within the last 30 years that advances in material synthesis have enabled the development of nanoporous materials with uniform, tailor made pore structures (e.g., mesoporous molecular sieves, carbon nanotubes and nanohorns,, and tailored hierarchical materials).^{2,3} These novel materials have both furthered understanding of characterization techniques by serving as model materials and necessitating the development of advanced experimental protocols for analysis and characterization. High resolution experimental protocols now exist for measuring the adsorption of various subcritical fluids, organic vapors and supercritical gases. These high resolution isotherms can be combined with advanced characterization theories and procedures like density functional theory and molecular simulation to obtain accurate and comprehensive analyses of surface area and pore structure.⁴⁻⁷

The purpose of this short paper is not to provide a comprehensive review of adsorption literature, but rather to highlight some basic concepts and resources for understanding gas adsorption characterization in a modern context and offer practical guidance for the analysis of meso- and microporous materials using methodology which is consistent with the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) and international standards organizations. For this purpose, a broad range of selected materials are used as case studies to showcase how state-of-the-art gas adsorption methodologies can be reliably implemented for advanced characterization of material structure.

2. Gas Adsorption Phenomena and Physisorption Isotherms

Before discussing various procedures that are currently recommended for the determination of pore size and surface area, it is necessary to describe in broad strokes gas adsorption phenomena and how these phenomena are used in the characterization of materials. For a complete guide to recommended terminology and symbols, the reader is encouraged to review the 2015 IUPAC technical report on physisorption of gases.⁴ *Physisorption* refers to the general phenomenon which occurs whenever an adsorbable gas (*adsorptive*) is brought into contact with the surface of a solid (the *adsorbent*). Due to van der

Waals forces, the density of gas molecules increases in the vicinity of the solid surface. This region of increased gas density is referred to as the *adsorption space* and the adsorbed gas molecules within this space, previously the adsorptive, are now referred to as the *adsorbate*.⁴ *Chemisorption*, which is a separately classified phenomenon and not covered here, deals with the formation of chemical bonds between the adsorptive and the adsorbent.

To assess the adsorption of gas on an adsorbent of interest, it is generally expedient to perform an experiment at constant temperature where the adsorbed amount is recorded as a function of the pressure or concentration of the adsorptive. This relation, at constant temperature, between the adsorbed amount and the equilibrium pressure of the gas is known as the *adsorption isotherm*. The adsorption isotherm is a function of the general and specific interactions between the adsorptive and the adsorbent as modulated by the adsorbent's surface structure and pore geometry. From the isotherm itself it is possible to broadly classify the adsorbent's pore characteristics and the strength of adsorbent/adsorbate interactions. It is recommended that the isotherm be so characterized prior to the application of any data reduction techniques. A classification of physisorption isotherms (Figure 1) which are broadly useful in the characterization of subcritical isotherms on rigid adsorbents has been published by the IUPAC.⁴ Gas adsorption is readily used in the characterization of *nanoporous* (pores < 100 nm) materials. In this work, focus will be placed on Type I and Type IV isotherms which are associated with adsorption in *microporous* (containing pores < 2 nm in width)

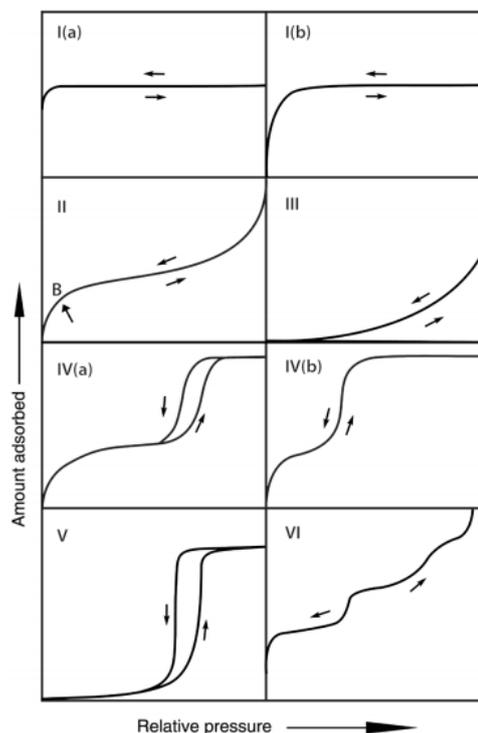


Figure 1. IUPAC Classification of Isotherms⁴

and *mesoporous* (containing pores 2-50 nm in width) materials respectively. Furthermore, we will focus on argon at 87K and nitrogen at 77K isotherms, which are widely used in industrial and research settings for surface area and pore size characterization. For structural characterization of primarily macroporous materials (containing pores > 50 nm in width), alternative techniques, such as mercury porosimetry, should be considered.⁸

In general, pore filling occurs on a continuum, with smaller pores filling at lower relative pressures (p/p^0 , where p^0 is the saturation pressure of the adsorptive) and larger pores filling at higher relative pressures. This relation between pore filling pressures and pore size is clear in the progression in isotherm shape from Type I(a) \rightarrow Type I(b) \rightarrow Type IV(b) \rightarrow Type IV(a) isotherms. For nitrogen at 77K and argon at 87K isotherms, Type I(a)

isotherms are given by microporous materials having mainly narrow micropores, such as ultramicropores (< 0.7 nm); while Type I(b) isotherms are found in materials having wider micropores, such as supermicropores (0.7 – 2 nm). The steep uptakes at very low p/p^0 in Type I isotherms are associated with enhanced adsorbent-adsorptive interactions in very narrow pores (approaching molecular dimensions), which results in pore filling at very low p/p^0 . For example, in many microporous zeolites and metal-organic frameworks (MOFs) the initial stage of physisorption for nitrogen at 77 K can begin at $p/p^0 = \sim 10^{-7}$.^{4,9} The limiting uptake is governed by the accessible micropore volume. For materials with pores in the mesopore range (2-50 nm), the isotherm transitions to the patterns of Type IV(b) and IV(a). The adsorption behavior in mesopores consists of multilayer adsorption followed by pore condensation, which represents a shifted vapor-liquid phase transition, determined by the adsorbent-adsorptive interactions and also by the interactions between the adsorbate molecules in the condensed state. For narrow mesopores (cylindrical pores less than ~ 4 nm for argon at 87K and nitrogen at 77K isotherms) the isotherm is completely reversible (i.e., Type IV(b)). When the pore width exceeds a certain critical width, dependent on adsorption system and temperature (greater than ~ 4 nm for argon at 87k and nitrogen at 77K isotherms) pore condensation is accompanied by hysteresis (i.e., Type IV(a)). The appearance of hysteresis and the shape of the hysteresis loop is associated with adsorption metastability (delayed condensation due to the metastability of the adsorbed multilayer) and, in some cases,

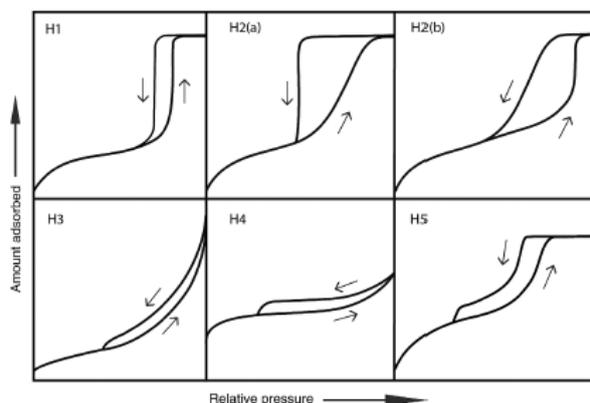


Figure 2. IUPAC Classification of Hysteresis Loops⁴

pore network effects affecting the desorption branch. Type V isotherms are a special case of adsorption in micro- and/or mesopores where the interactions between the adsorbent and the adsorptive are relatively weak. Isotherms of Types II, III, and VI are associated with non-porous or macroporous materials and are of limited interest with regard to pore size analysis (although surface area analysis can be readily performed using isotherms of Type II and Type VI).

For a complete physisorption analysis, it is required that the adsorption isotherm be collected under both ascending pressure (*adsorption*) and descending pressure (*desorption*) conditions. The presence or absence of *hysteresis* (where adsorption and desorption curves do not overlay) will give additional information about the overall quality of the isotherm and the material's pore structure. For nitrogen at 77K and argon at 87K isotherms on rigid adsorbents, hysteresis between the adsorption and desorption branches should close by $p/p^0 = \sim 0.38$. Mesoporous isotherms showing hysteresis can be further classified by the type of hysteresis. The IUPAC classifications of hysteresis loops are shown in

Figure 2. Each of these six characteristic types is closely related to particular features of the pore structure and underlying adsorption mechanism. For the purposes of an initial material characterization prior to application of data reduction methods, it should be identified whether the hysteresis is Type H1 (narrow range of uniform mesopores where networking effects are minimal) or not Type H1 (i.e., Type H2-H5, where complex pore structures exist and networking effects are important). As discussed in various reviews¹⁰⁻¹³, for materials with Type H1 hysteresis, the pore size distribution can be reliably obtained from either the adsorption or desorption branches using appropriate methods. For materials with Type H2-H5 hysteresis, in addition to adsorption metastability, the desorption branch is delayed due to various phenomena (e.g., pore blocking, cavitation) associated with pore evaporation in networked structures (e.g., ink-bottle pores). A complete pore size distribution for such materials can only be obtained using a statistical mechanics based approach which correctly accounts for delayed (spinodal) condensation on the adsorption branch (e.g., an adsorption branch DFT method). Collection of the desorption branch is still useful in characterizing the observed pore evaporation phenomena and, in certain cases, can be used to determine the distribution of neck sizes in the material's pore network.

It should be emphasized that more complex materials may exhibit features from multiple isotherm types depending on the adsorbent's pore characteristics. Furthermore, the IUPAC classifications are specific to rigid adsorbents. Adsorption in non-rigid materials has historically difficult to interpret¹ and may show low

pressure hysteresis or apparent isotherm transitions associated with contraction or expansion of the adsorbent structure. Characterization of non-rigid materials requires specialized methods which account for the flexible nature of the adsorbent structure¹⁴ (see also available case studies of flexible MOF materials⁶).

3. Measurement Techniques

The most frequently used methods for physisorption analysis are the volumetric (manometric) and gravimetric methods. Static or dynamic techniques may be used in either case. State-of-the-art static volumetric systems are based on calibrated volumes, pressure measurements, and gas equations of state. The adsorbed amount is determined from the difference between the total amount of adsorptive admitted to the sample cell with the adsorbent and the amount of gas remaining in the void space of the cell after equilibration. The gravimetric method is based on a sensitive microbalance and determines the adsorbed amount based on the weight change of the adsorbent after exposure to the adsorptive. The gravimetric technique has deficiencies for adsorption measurements at cryogenic temperatures, such as the boiling temperatures of nitrogen (77K) and argon (87K), which are primarily used for surface area and pore size characterization. Hence, the volumetric technique is recommended for physisorption characterization (see also 2015 IUPAC recommendations⁴). For more detailed descriptions of measurement methods we refer to various textbooks and reviews.^{1,4-6,12,15,16}

Volumetric instruments can be further distinguished based on their available p/p^0

measurement range for argon at 87K and nitrogen at 77K isotherms. Instruments which measure adsorbed amount in a narrow range of $p/p^0 = 0.05$ to 0.3 provide useful assessments of surface area. Further determination of total pore volumes and mesopore size distributions require instruments capable of measuring isotherms over a broader range of moderate relative pressures ($p/p^0 = 0.05$ to 0.99). For accurate measurement of large mesopores which fill near saturation (i.e., near $p/p^0 = 1$), the saturation pressure should be recorded for every point by means of a dedicated saturation pressure transducer.⁴ In contrast, full characterization of microporous materials requires the collection of isotherms to very low relative pressures (to as low as $p/p^0 = 10^{-7}$, as mentioned previously). For accurate measurement of the low pressure isotherm, it is necessary to use special equipment in the form of highly efficient turbomolecular vacuum pumping systems and low-pressure transducers.^{4,5,9}

4. Sample Preparation

Prior to a physisorption experiment, it is required to remove all physically adsorbed material from the adsorbent surface while avoiding irreversible changes to the surface (see IUPAC⁴ and also ISO 9277¹⁶). The adsorbed amount should be obtained in reference to the outgassed sample. This can be accomplished by vacuum pumping or purging with an inert gas (e.g., Helium) at elevated temperatures.⁴⁻⁶ Vacuum outgassing to a residual pressure <1 Pa is generally preferred, especially for microporous materials.⁴ For known materials, well defined outgassing protocols are often available from the material provider or described in standard analysis

methodology from the applicable standards organizations.

For unknown samples, the maximum temperature at which the sample can be outgassed should be determined by thermogravimetric analysis, by spectroscopic methods, or by trial experiments using different degassing conditions of time and temperature.^{4,16} In vacuum systems, it is recommended that the current readiness of the sample be evaluated by isolating the sample from vacuum and monitoring the cell for pressure change associated with a vapor pressure from the sample. If the pressure is nearly constant over a prolonged period (15-30 minutes), degassing is complete. This method also confirms the absence of leaks.

A pressure-controlled heating regime is recommended for sensitive samples which are susceptible to elutriation (e.g., fine powders) or steaming induced structure changes (e.g., hydrophilic microporous zeolites).¹⁶ Under this procedure a fixed pressure limit (typically 7-10 Pa) is set to control the heating rate in relation to the gas pressure emanating from the sample. When the pressure limit is exceeded due to desorbing gas from the adsorbent surface, the temperature ramp is paused and the temperature is held constant until the pressure falls below the set pressure limit. When the pressure returns below the pressure limit, the system can continue the temperature ramp. In this way, vigorous vapor release associated with aggressive heating regimes, which can damage fragile micropore structures or cause elutriation of fine powders, is avoided. To ensure valid and repeatable measurements, the conditions chosen for pretreatment of the adsorbent (e.g., outgassing time, temperature, and residual

pressure) should be carefully controlled and recorded.

5. Choice of Adsorptive for Structural Analysis

Prior to performing a physisorption analysis the experimental goals should be identified and an appropriate adsorptive selected. Proper choice of adsorptive is crucial for reliable and meaningful results. The suitability of various adsorptives is covered in great detail in a number of books and reviews.^{4-6,9,10,17,18}

For pore size and surface area determination, argon at liquid argon temperature (87K) is the adsorptive recommended by IUPAC.⁴ Argon does not exhibit specific interactions with surface functional groups and therefore can be reliably employed in the determination of surface areas and pore size for both microporous and mesoporous materials down to ~0.45 nm with minimal concern for the influence of surface chemistry.

Nitrogen at liquid nitrogen temperature (77K) is another potential adsorptive for pore size and surface area analysis. In spite of nitrogen's numerous deficiencies as compared with argon at 87K, due to the nitrogen molecule's potential for specific interactions with the adsorbent surface, nitrogen at 77K can readily be used in analysis of mesopores.^{4-6,9,10,17} However, it is not possible to obtain reliable micropore size information using nitrogen in materials with functionalized, polar, or oxidic surfaces (e.g., zeolites, MOFs, oxides).^{5,6,9,18} The specific interactions of nitrogen with adsorbent surfaces not only affects the orientation of the adsorbed nitrogen molecule on the adsorbent surface, but also strongly affects the micropore filling pressure, shifting it to extremely low pressures.^{4,9} As

mentioned previously, this can be as low as ~ 10^{-7} for many microporous zeolites and MOFs. At pressures below 10^{-5} , the adsorptive is in a regime of Knudsen diffusion where the rate of diffusion is extremely slow, making it difficult to measure equilibrated adsorption isotherms. These problems are avoided through the use of argon at 87K. The micropore filling pressures of argon at 87 K are often shifted 1–1.5 decades higher in relative pressure as compared to nitrogen at 77K.^{9,10}

Surface area analysis by nitrogen or argon measurement can routinely measure surface areas as low as 0.5 m². To analyze lower surface areas (down to <0.05 m²), krypton at 77K is routinely employed. For various reasons krypton at 77K is more or less exclusively used for surface area assessment.^{4,5} For pore size analysis of low volume samples, methods based on krypton adsorption at 87K are available, although they are limited to analysis of pores < 10 nm.^{19,20}

Combined use of carbon dioxide at 273K with argon at 87K or nitrogen at 77K is considered a standard methodology for pore size analysis of microporous carbons.^{5,6,9,17} Carbon dioxide at 273K can access smaller pores (down to ~0.35 nm) as compared with nitrogen or argon at their respective liquid temperatures. Due to specific interactions between carbon dioxide and adsorbent surfaces, this method cannot be recommended for the pore size characterization of microporous materials with polar/oxidic surfaces (e.g., zeolites and MOFs).⁴ However, carbon dioxide adsorption at 273 K may still be useful to assess solely the micropore volume of pores where the entrances are too small to allow argon or nitrogen to enter at cryogenic temperatures.²¹

6. Evaluation of Adsorption Data

Isotherm Quality. Once an adsorptive has been chosen and an experiment performed, the adsorption isotherm should be evaluated for quality. It is the intention of the authors to provide a detailed guide to evaluation of isotherm quality in a future publication. In general, for analyses with argon at 87K or nitrogen at 77K, the following isotherm features should be considered suspect as they are typically associated with an instrumentation issue (e.g., leaks or poor calibrations) or incorrect analysis parameters (e.g., insufficient sample mass or equilibration parameters): (i) crossing of the desorption branch below the adsorption branch, (ii) *non-monotonic* behavior (where the adsorbed amount does not continuously increase with increasing pressure or, conversely, decrease with decreasing pressure), (iii) hysteresis of the adsorption and desorption branches which extends below relative pressures of ca. 0.38. Below this relative pressure pore condensation is fully reversible in argon at 87K and nitrogen at 77K isotherms (i.e., Type IV(b) isotherms). Closure of low pressure hysteresis at relative pressures below 0.38 is often an indication of insufficient equilibration parameters, whereas prolonged low pressure hysteresis (i.e., no closure) is more typically associated with experimental artifacts and/or leaks. Notable exceptions (i.e., materials with real low pressure hysteresis) do exist. The low pressure hysteresis in these cases is often associated with flexibility of the adsorbent structure. Flexible adsorbents can display prolonged low pressure hysteresis (e.g., swelling in charcoals)¹ or low pressure hysteresis loops which are not associated with pore condensation in mesopores (e.g., gate opening or breathing transitions in flexible MOFs)^{6,7}. As discussed previously, the isotherms measured on such materials will not

fit into typical IUPAC isotherm classifications for rigid adsorbents.

For low pressure analyses used in the investigation of microporous materials, special attention should be paid to the low pressure data where micropore filling occurs. It is recommended that the isotherm be graphed on a log scale and any problematic regions identified, as any pore size analyses using these regions will be suspect. If an issue with the isotherm has been identified or is suspected, it is typical and recommended to run a reference material obtained either from the instrument manufacturer or from an international reference organization (e.g., BAM, NIST) to identify whether the issue is associated with instrument performance (i.e., instrument does not meet certification criteria) or, alternatively, is only associated with the analysis parameters or sample characteristics (i.e., instrument does meet certification criteria).

Surface Area. Evaluation of the isotherm typically begins with determination of the BET surface area. The Brunauer-Emmet-Teller (BET) method, despite weaknesses in its theoretical foundations, is still the state-of-the-art and most widely used procedure for evaluating the surface area of porous materials.⁴⁻⁶ Under carefully controlled conditions, the BET area of Type II or Type IV(a) isotherms can be regarded as the true probe accessible surface area.⁴ The classical range for application of the BET method in Type II or Type IV(a) isotherms is $p/p^0 = 0.05$ to 0.3 . The BET theory is not applicable to microporous materials; i.e., if the BET method is applied to Type I isotherms one can only determine an apparent or “fingerprint” area, which is characteristic for the material, provided an appropriate linear range for application of the BET method can be found. For reliable

determination of the linear BET range for Type I isotherms, the Rouquerol method is recommended.⁴ The BET method cannot be applied in a straightforward way in the case of Type IV(b) isotherms as the start of pore condensation may begin well within the classical BET range. A linear range for the application of the BET equation may not be found or, if found, may lead to significant overestimation of the monolayer capacity. The BET method is not applicable to either Type III or Type V isotherms. Reported values for BET areas should include the range of application of the BET equation, the adsorptive used, and the assumed cross-sectional area.

Comparison to Standard Isotherms. The empirical comparison of the measured isotherm to a reference isotherm, which represents adsorption on a non-porous material of similar chemical composition, is a useful technique in the determination of micropore volume and in the evaluation of “external” surface area. “External” in this case refers to the surface area of pores > 2 nm. Two such methods are the t-plot and a_s -plot methods (for detailed description we refer to various textbooks and reports^{1,4-6,22}). The a_s -plot method is generally considered more adaptable than the t-plot method as the a_s -plot method can be applied even when the BET method is not strictly applicable. A high resolution a_s -plot method is available, which allows one to obtain additional information concerning micro- and mesoporosity in the adsorbent.^{5,23} In comparison plot methods the measured adsorbed amount is plotted as a function of the expected adsorbed amount from a reference or standard isotherm. In the range of multilayer adsorption, assuming the reference isotherm correctly describes adsorption in the experimental

isotherm, the comparison plot will show a linear relationship between measured adsorbed amount and expected adsorbed amount or film thickness (typically in the range of $p/p^0 = 0.15$ to $0.4/0.5$). The slope and extrapolated y-intercept of the linear region of the comparison plot can be used to determine the “external” surface area and micropore volume respectively. The application of conventional comparison plot methods is not possible in a straightforward way in materials containing narrow mesopores (Type IV(b) and some Type IV(a) isotherms where hysteresis extends well below $0.5 p/p^0$) as the start of pore condensation may begin very near the start of multilayer adsorption. In such cases the linear range for the comparison plot may be extremely limited or not present.

Total Pore Volume. If there is no significant macroporosity, the isotherm will remain nearly horizontal over the upper range of p/p^0 , indicating that the accessible pore volume has been completely filled with adsorbate and no significant further adsorption can occur prior to bulk condensation. Under these conditions the total pore volume can be assessed from a point on the plateau near unity (e.g., $p/p^0 = 0.95$ or 0.99) by assuming the fluid in the pores is at bulk liquid density (i.e., applying the Gurvich rule).⁴ If macropores are present (e.g., a composite Type I/II or Type IV/II isotherm), the isotherm will not be nearly horizontal near $p/p^0 = 1$ and the “total” pore volume cannot be evaluated.

Pore Size Distribution. The state-of-the-art for obtaining accurate and reliable pore size distributions over the complete nanopore range is application of methods based on statistical mechanics and molecular simulation (e.g., DFT methods).^{4,9,13} Methods for pore size analysis

based on DFT and molecular simulation are now widely used and are commercially available for many important adsorptive/adsorbent systems. DFT methods accurately describe adsorption and phase behavior of fluids confined in pores structures and it has been shown that the application of DFT methods allows one to obtain reliable pore size distributions over the complete range of micro- and mesopores.¹³ Classical methods for pore size analysis (e.g., BJH, HK, SF), in addition to not being applicable over the complete nanopore size range, do not realistically treat the behavior of the molecules adsorbed in pore structures and may underestimate the pore size significantly (i.e., by up to 20–30%, if not properly corrected for pores of width smaller than 10nm).^{4,10,11,17}

DFT methodology, as applied to pore size analysis of nanoporous materials, is highlighted as indicated in the recent IUPAC recommendations, but also in international standards such as ISO 15901-3²². Meanwhile comprehensive libraries of DFT and Monte-Carlo simulation based methods are commercially available for many adsorbent/adsorptive pairs. Detailed and concise introductions to DFT methodology can be found in various texts.^{5,12,17} It should be stressed that application of DFT methodology can only be expected to lead to a reasonably accurate evaluation of the pore size distribution if the nanoporous system is compatible with the DFT kernel selected for analysis. The DFT *kernel* is the collection of theoretical adsorption or desorption isotherms representing adsorption of a particular adsorptive on a model adsorbent with pores of differing widths of a given pore shape(s). The quality of the fit of the theoretical isotherm to the measured experimental isotherm, especially in regions of pore filling, is one necessary criterion in evaluating the

compatibility of a given DFT kernel with a particular material. Reported pore size distributions determined using a DFT methodology should include a description of the DFT kernel applied (e.g. adsorptive/adsorbent pair, assumed pore geometry, adsorption/desorption branch).

Many commercially available DFT kernels are based on Non-Local Density Functional Theory (NLDFT). A drawback of the NLDFT method is that the solid surface is treated as molecularly smooth, whereas it is known that surface roughness and defects can affect the shape of adsorption isotherms on real surfaces.^{10,17} This is especially problematic for carbon materials, where the assumption of a structure-less graphitic pore wall can lead to unrealistic layering transitions in the theoretical DFT isotherm (i.e., Type VI isotherms) not observed in experimental isotherms. A way to account quantitatively for the effects of surface heterogeneity is the application of commercially available quenched solid density functional theory (QSDFT) methods, where the solid is modeled using a more realistic distribution of solid atoms. Application of QSDFT methods substantially improves the pore size characterization of nanoporous carbons.^{13,17}

7. Case Studies

Comparison of BET surface areas by nitrogen at 77K and argon at 87K adsorption. Typical BET surface areas ($p/p^0 = 0.05$ to 0.3) determined by measurement with nitrogen at 77K, and corresponding surface areas measured by argon at 87K on the same aliquot of material, are shown for a variety of primarily mesoporous, macroporous, or non-porous materials in Table 1. As can be seen in the table, there can be significant discrepancy between the nitrogen at 77K and argon at 87K BET

surface areas, in some cases approaching or exceeding 20%. Because these measurements were performed on the same aliquot of material, discrepancies in measured surface area values between argon and nitrogen can primarily be attributed to uncertainty in the assumed molecular cross-sectional areas (σ_m). A cross-sectional area for nitrogen at 77K of 0.162 nm², based on the assumption of a close-packed monolayer, is typically used to calculate the BET surface area. However, as discussed previously, it has been recognized that nitrogen at 77K is sensitive to the adsorbent's surface chemistry and that the effective cross-sectional area can vary significantly from this typically assumed value.⁴ For fully hydroxylated surfaces a cross sectional area for nitrogen of 0.135 nm² has been derived, which was obtained by measuring the adsorption of nitrogen on silica spheres of known surface area.¹² If one uses the standard cross-sectional (0.162 nm²) the BET surface area can therefore be overestimated by ca. 20%.^{4,5} For argon at 87K a cross-sectional area of 0.142 nm² is usually assumed. Because of the absence of a quadrupole moment and the higher temperature, the adsorption of argon is less sensitive to differences in the nature of the adsorbent surface as compared with nitrogen at 77K.⁴ Previous work on mesoporous silica materials like such as MCM-41 (which consist of independent cylindrical-like pores), also strongly suggest that the argon at 87K BET surface areas are more consistent with the expected geometrical area.^{5,24}

Application of the alternative nitrogen cross-sectional area (0.135 nm²) to a similarly fully hydroxylated surface, the controlled pore glass in Table 1, reduces the apparent

discrepancy between nitrogen at 77K and argon at 87K BET surfaces areas from ca. 20% to <1%, essentially eliminating the observed difference. Similar benefits are observed for oxidic materials generally. With the alternative cross-sectional area of 0.135 nm² applied, the discrepancies in nitrogen

Table 1. Surface areas of selected materials determined by nitrogen at 77K and argon at 87K isotherms.

| Material | Nitrogen BET Area [m ² /g] $\sigma_m = 0.162 \text{ nm}^2$ | Argon BET Area [m ² /g] $\sigma_m = 0.142 \text{ nm}^2$ |
|--|--|---|
| Graphitized Carbon Black (ASTM SRB8-G) | 8.98 | 8.1 |
| Graphitized Carbon Black (ASTM SRB8-D) | 21.2 | 19.1 |
| Graphitized Carbon Black (ASTM SRB8-F) | 36.4 | 32.9 |
| 3D Ordered Mesoporous Carbon ²⁵ | 1160 | 1050 |
| Non-porous Alumina | 2.76 | 2.22 |
| Controlled Pore Glass | 8.7 | 7.3 |
| Mesoporous Alumina | 96.7 | 80.1 |
| Mesoporous Titania (BAM P106) | 97.5 | 80.8 |
| Mesoporous Silica Gel | 282 | 229 |
| Mesoporous Silica (MCM-48E) ²⁴ | 1092 | 945 |

and argon BET surface areas for the oxide materials in Table 1 are reduced from ca. 20% to <4% in all cases. Although there are differences between the nitrogen and argon BET surface areas for the carbonaceous materials shown in Table 1, likely due to residual elemental impurities and the existence of polar surface functionality, the differences are much smaller than is apparent for oxidic materials (ca. 10 % and smaller for the examples given in Table 1). The examples given in Table 1 confirm that BET surface area analyses with argon at 87K adsorption are generally much more reliable as compared with analyses by nitrogen at 77K.

Case Study of BAM-P106. BAM-P106 is a mesoporous titanium dioxide (TiO₂, also called titania) powder with spherical particles and 100% crystalline structure.²⁶ As a primarily mesopor

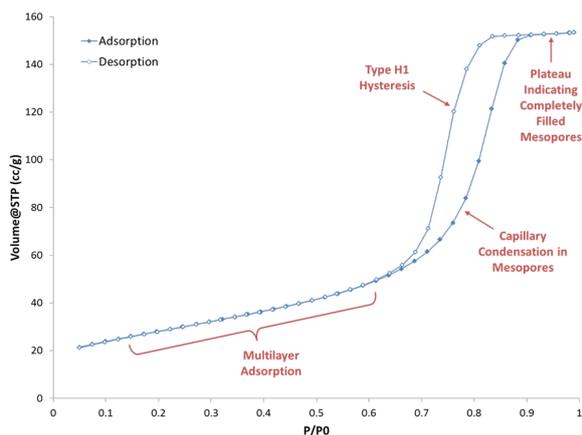


Figure 3. BAM-P106 Nitrogen at 77K Isotherm.

ous material, BAM-P106 can be structurally characterized with the collection of an isotherm in the relative pressure range of 0.05 to 0.99 p/p^0 , using either nitrogen at 77K or argon at 87K. The nitrogen at 77K isotherm of BAM-P106, shown in Figure 3, includes a number of classical features associated with primarily

mesoporous materials. The adsorption branch contains a low slope region associated with multilayer adsorption on pore walls, followed by pore condensation in mesopores, ending with a plateau region indicating completely filled mesopores and limited or non-existent macroporosity. The desorption branch proceeds into a narrow hysteresis loop, with the desorption branch parallel to the adsorption branch, indicative of a narrow distribution of uniform mesopores and limited networking effects. Based on these features, the isotherm is Type IV(a) with Type H1 hysteresis.

As BAM-P106 does not have any significant microporosity, application of the BET method in the classical range results in a linear plot (see Figure 4(a)). The resulting nitrogen BET surface area, assuming $\sigma_m(N_2) = 0.135 \text{ nm}^2$ (0.162 nm^2), is $83.6 \text{ m}^2/\text{g}$ ($100 \text{ m}^2/\text{g}$). Here, the t-plot method

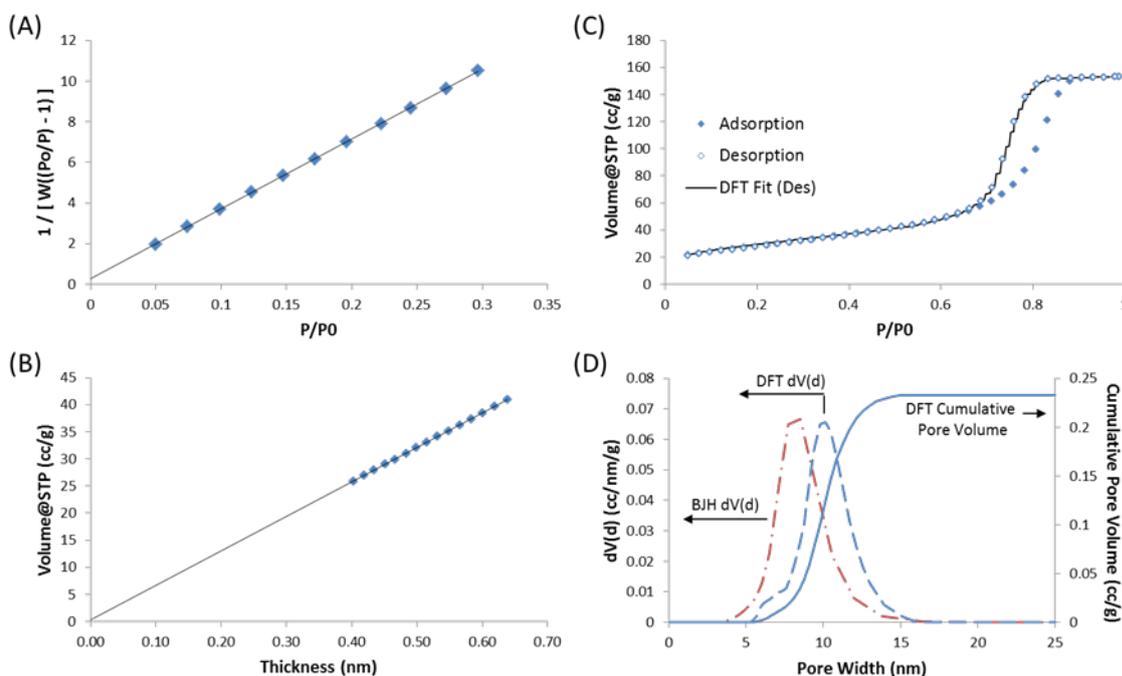


Figure 4. Adsorption methodologies applied to BAM-P106. (A) Bet plot in the classical range. (B) t-plot method applied in the typical range ($p/p^0 = 0.15$ to 0.5). (C) Comparison of DFT theoretical desorption branch isotherm with experimental nitrogen at 77K adsorption isotherm. (D) Comparison of BJH and DFT derived pore size distributions as well as the cumulative pore volume obtained from the DFT method.

can be applied in the typical range of $p/p^0 = 0.15$ to 0.5 associated with the broad region of multi-layer adsorption. Evaluation of the slope and intercept of the t-plot based on the thickness equation of de Boer⁵ (representing nitrogen adsorption on oxidic surfaces) confirms a negligible micropore volume (see Figure 4(b)), obviating the need for further micropore characterization by time-consuming low pressure adsorption measurements.

For pore size characterization, two NLDFT kernels based on adsorption of nitrogen at 77K in cylindrical siliceous pores were applied to the adsorption branch (i.e. application of the so-called metastable adsorption branch kernel) and desorption branch (equilibrium NLDFT kernel) of the isotherm. The adsorption branch and desorption branch DFT kernels are in excellent agreement, indicating the absence of pore network effects (such as pore blocking) on the desorption branch of the hysteresis loop.

The total pore volume is 0.233 cc/g which is in good agreement with the total pore volume as calculated by the Gurvich rule (0.237 cc/g) applied at a relative pressure of $p/p^0 = 0.99$, which is in the plateau-region of the isotherm. The mode pore size for both DFT kernels is 10.1 nm. Figure 4(c) compares the fitted theoretical

NLDFT desorption isotherm with the measured isotherm. The resulting cumulative pore volume and pore size distribution curves for the desorption branch kernel are shown in Figure 4(d). Also shown in figure 4(d) is the pore size distribution obtained by application of the classical BJH method to the desorption branch of the isotherm. The pore size by BJH method, which does not take into account the true microscopic density profile of the adsorbed fluid in narrow mesopores, is shifted to smaller pore size significantly underestimating, as discussed previously, the pore size (here by ca. ~16%) as compared with the NLDFT methods. For BAM-P106 the surface area calculated from the DFT method applied to the desorption branch (93.5 m²/g) is quite comparable to the BET method, likely due to the material's well defined mesopore structure with non-existent microporosity and solid pore walls.

Case Study of C16 Meso-Y. C16 Meso-Y is a micro/mesoporous zeolite prepared from a commercially available zeolite (Zeolyst CBV720).²⁷ C16 Meso-Y has a hierarchical structure with cylindrical mesopores which cut through a faujasite type zeolite structure with spherical micropore cavities. Due to their

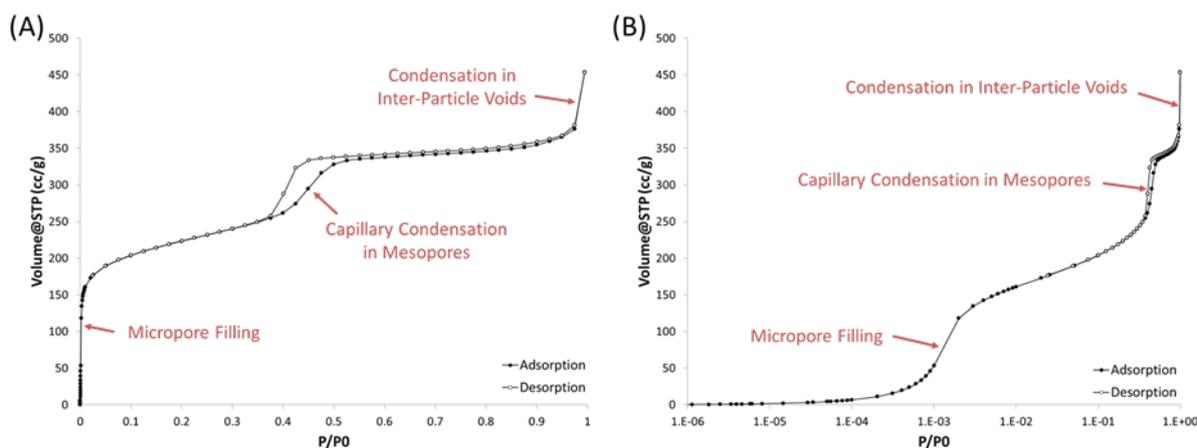


Figure 5. C16 Meso-Y Argon at 87K Isotherm. (A) Linear plot. (B) Semi-logarithmic plot.

surface chemistry, comprehensive structural characterization of microporous zeolites requires collection of a low pressure isotherm using argon at 87K. An argon isotherm of C16 Meso-Y is shown in figure 5(a) and 5(b). Due to the complex hierarchical structure, C16 Meso-Y has a composite Type I/IV(a) Isotherm and includes a number of features typically associated with micro-/mesoporous materials. At low pressures the adsorption isotherm exhibits a steep rise at low pressures associated with micropore filling. The adsorption isotherm in the higher pressure range exhibits multilayer adsorption, followed by pore condensation which is accompanied by an apparent type H1 hysteresis. C16 Meso-Y also shows a sharp rise in adsorbed amount near saturation associated with condensation in inter-particle voids.

Inspection of the isotherm on the log scale (Figure 5(b)) shows that the pore filling pressure of the micropores in C16 Meso-Y is on the order of 10^{-3} p/p⁰.

As compared with BAM-P106, the application of classical characterization methods are of limited value in the study of C16 Meso-Y. The linear range of the BET method in C16 Meso-Y, due to significant microporosity, is no longer in the classical range of 0.05 to 0.3. A linear range for the BET plot can be found in the range of p/p⁰ = 0.009 to 0.1; however as discussed previously, the BET area calculated from this range (712 m²/g) cannot be considered the true probe accessible surface area, but rather a “fingerprint” area which is characteristic for C16 Meso-Y. Comparison plot methods, to determine external surface area and micropore volume, cannot

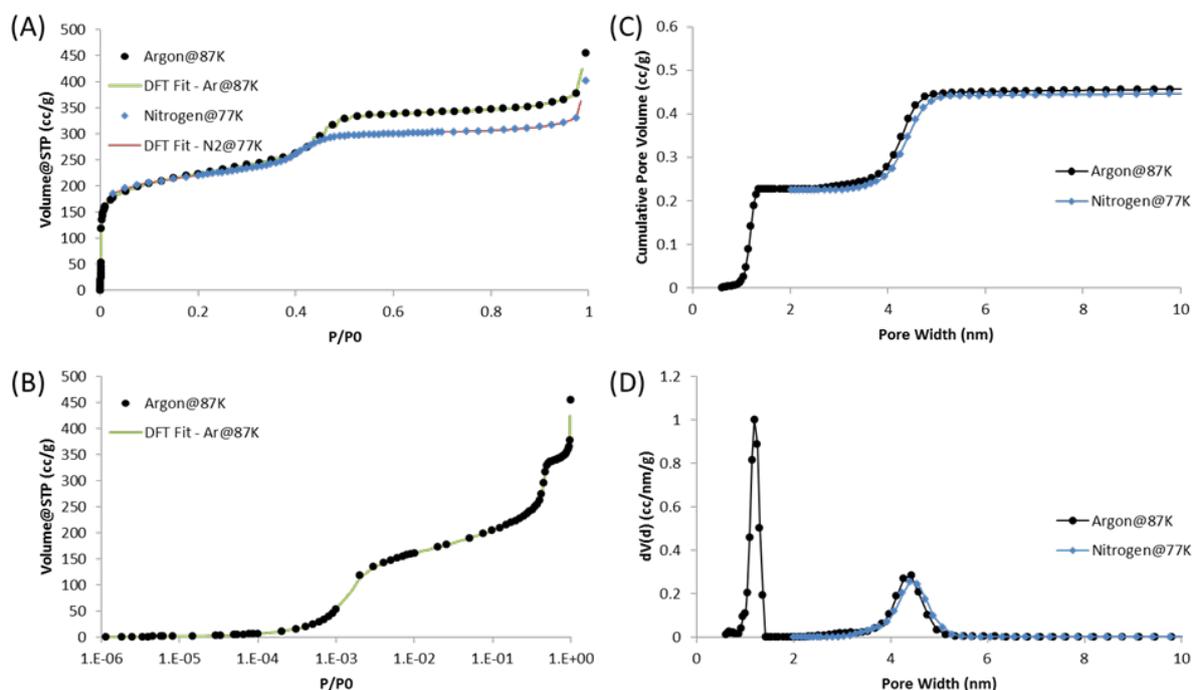


Figure 6. Application of DFT methodology to C16 Meso-Y. (A) Comparison of DFT theoretical adsorption branch isotherms with experimental argon at 87K and nitrogen at 77K adsorption isotherms (linear plot). (B) Comparison of DFT theoretical adsorption branch isotherm with experimental argon at 87K adsorption isotherm (semi-logarithmic plot). (C) Cumulative pore volumes derived from DFT methods applied to argon at 87K and nitrogen at 77K adsorption isotherms. (D) Pore size distributions derived from DFT methods applied to argon at 87K and nitrogen at 77K adsorption isotherms.

reliably be applied to C16 Meso-Y due to the presence of pore condensation and hysteresis well below $p/p^0 = 0.5$. The only way to obtain here a reliable and comprehensive pore size distribution over the complete range of micro- and mesopores is to apply a proper DFT based methodology.

An NLDFT kernel based on adsorption of argon at 87K in spherical zeolitic micropores (in line with the cage-like structure of the accessible pores in Y-zeolite) and cylindrical siliceous mesopores was applied to the adsorption branch of the of the argon isotherm. For comparison, a nitrogen at 77K isotherm is also shown and an NLDFT kernel based on adsorption of nitrogen at 77K in cylindrical siliceous pores was applied to the adsorption branches of the nitrogen isotherm. Figures 8(a) and 8(b) compare the fitted theoretical NLDFT adsorption isotherms with the measured nitrogen and argon isotherms. The resulting cumulative pore volume and pore size distribution for the adsorption branch kernels are shown in Figure 8(c) and 8(d) respectively. There is excellent agreement in the mesopore distribution centered on a diameter of 4.4 nm in both the nitrogen and argon derived pore size distributions, which confirms the suitability of nitrogen for the determination of mesopore size distributions even in materials with polar/oxidic surfaces. The determination of the micro, meso- and total pore volume follows directly from the from the cumulative pore volume plot. Excellent agreement is observed with regard to meso- and total pore volume obtained from argon and nitrogen isotherms. The NLDFT total pore volume is also comparable to the Gurvich pore volume, calculated from the plateau-like region of the argon adsorption isotherm at 0.8 p/p^0 (0.44 cc/g), i.e. prior to the region where interparticle condensation occurs as

indicated in the steep rise of the adsorption isotherms very close to the saturation pressure.

Despite the good agreement in mesopore size distribution and micropore volume between the nitrogen and argon isotherms, it should again be stressed that determination of micropore size distributions for materials with polar/oxidic surfaces, such as C16 Meso-Y, can only be reliably determined with argon at 87K. The micropore size distribution as determined by argon at 87K adsorption is centered on ~1.2 nm, consistent with the diameter of the inner cavity of a Y/faujasite type zeolite.

8. Conclusion

Practical guidance for users of gas sorption instruments has been provided, including brief discussion of gas sorption phenomena as well as sample preparation and measurement techniques. Advanced methodologies for the determination of surface area, pore volume, and pore size distributions over the complete nanopore range are discussed in the context of the recent IUPAC recommendations and other international standards.

The proper choice of adsorptive, critical for accurate material characterization has been presented and, through use of a comprehensive BET surface area case study, we confirm that nitrogen, due to its quadrupole moment and the associated uncertainty in the effective cross-sectional area, is less than optimal for a reliable surface area determination, especially for oxidic materials. In additional selected case studies of mesoporous and micro/mesoporous adsorbents, we illustrate the characterization of micro- and mesoporous materials using methodology which is consistent with the recommendations of the IUPAC and international standards organizations. The collected case studies

showcase how physisorption analysis can be reliably implemented for advanced characterization of material structure for research and quality control applications.

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