

# Micropore Size Analysis of Porous Carbons Using CO<sub>2</sub> Adsorption at 273 K

Relevant for: activated carbon, micropores, carbon dioxide

Activated carbons fibers, pellets, granules, or powders are used in air filters, in water purification systems, for removing organic impurities from various solutions, and in a variety of medical, environmental, and agricultural applications. These microporous, high surface area materials are often characterized by their apparent BET area and their pore size distribution (PSD). Filling the micropores and subsequently calculating the micropore size distribution using nitrogen or argon is a slow process, requiring high-resolution pressure transducers and a turbomolecular pump for achieving very low vacuum levels. Alternatively, the PSD can be determined faster using carbon dioxide as adsorbate at 273 K, at higher pressures than nitrogen or argon, thus increasing throughput and reducing equipment cost.



## 1 Introduction

The pore size distribution (PSD) is a key factor in characterizing porous materials. The PSD analysis can be useful in developing new porous materials for specific applications as well as for testing existing products. Traditionally, the PSD of a porous solid is evaluated from the analysis of nitrogen or argon adsorption isotherms measured at 77 K or 87 K, respectively. However, it is well-known that at such cryogenic temperatures, diffusion of adsorptive molecules into carbon micropores is very slow. Moreover, it has been proven that diffusional limitations at these temperatures might influence adsorption in ultra-micropores (pores smaller than 0.7 nm) [1].

For porous carbons, usually containing a wide distribution of pore sizes including ultra-micropores, these diffusional limitations lead to time-consuming measurements and under-equilibration of measured adsorption isotherms, giving erroneous results for

subsequent PSD calculations. It has long been recognized [2-4] that problems of this type can be eliminated by using CO<sub>2</sub> adsorption at 273 K (0 °C).

Although it is possible to perform CO<sub>2</sub> measurements on the Autosorb and Quadrasorb series instruments, the lower cost and ease of use of the Anton Paar Nova 600 and 800 instruments make them an excellent choice for this technique. The 273 K temperature can be maintained using the Dewar filled with an ice and water mixture. However, it is HIGHLY recommended that for stable temperature control and the most accurate measurement, a circulating chiller and jacketed Dewar (recirculating Dewar) filled with a suitable coolant (usually an antifreeze and water mixture) should be used.

## 2 Details of Experimental Setup

**Hardware:** Measuring CO<sub>2</sub> isotherms on a Nova 600 or 800 is similar to measuring N<sub>2</sub> isotherms. The main difference between N<sub>2</sub> and CO<sub>2</sub> is the temperature of the analysis and how it is controlled. For N<sub>2</sub>, the sample is immersed in a liquid nitrogen bath to maintain the constant 77 K temperature for the analysis. For CO<sub>2</sub>, the sample is immersed in a bath of either an ice/water mixture or a thermostatically controlled circulating bath held at 273 K (recommended). A picture of the recirculating bath and Dewar setup is shown in Figure 1. Please note that the CO<sub>2</sub> Dewar and connecting parts are not supplied with the instrument but are accessories that can be added if CO<sub>2</sub> experiments are of interest. The coolant level sensor (CLS) must be attached to the instrument for the software to start the measurement, but for a CO<sub>2</sub> analysis the Dewar will travel all the way to the top of the upper limit switch and remain there

for the entirety of the analysis. A research grade (99.999% purity) CO<sub>2</sub> compressed gas tank is required.

**Sample Preparation:** To minimize the void volume, the smallest sample cell stem down which the sample will fit is recommended for the analysis (i.e., for powder 6 mm stem, etc.) along with the smallest bulb that allows for an appropriate amount of sample. There are no straightforward guidelines about sample amount for CO<sub>2</sub> analyses as this is highly dependent on the sample characteristics and adsorbed amount. However, it is recommended that no less than 0.2 g of sample be used for the measurement for the best data quality. Also note that if it is intended for this experiment to be complementary to the measurement of the sample with N<sub>2</sub>, in order to merge the PSDs, the same aliquot of sample should be used for both measurements [5]. The sample must first be degassed at elevated temperature to remove any pre-adsorbed moisture or contaminants. Vacuum degassing is recommended for microporous materials, using N<sub>2</sub> gas to backfill the sample cell after the degassing. No filler rod should be used for the degassing in order to minimize elutriation, but should be added to the sample cell prior to the analysis.

**Software:** The Kaomi for Nova software contains a preset analysis profile for CO<sub>2</sub> analysis: *CO2 isotherm*. This profile contains the analysis parameters that have been found to be appropriate for a wide variety of microporous carbons. The profile can be modified as necessary for the carbon being analyzed by simply cloning it and changing the relevant parameters. The parameters in this profile are also given in Table 1. If the analysis will be run in *Nova mode*, *Nova He Mode* must be chosen for the *Void Volume Mode* to avoid introducing CO<sub>2</sub>, which adsorbs at room temperature, into the sample cell prior to the analysis.

### 3 Analysis of Results

Activated carbons F400, ACF-15, and BAM P109 were chosen as representative carbons for CO<sub>2</sub> (273 K) micropore analysis. The isotherms were measured using the setup and parameters given below and the resulting isotherms are shown in Figure 2. Prior to applying any data reduction to the measured isotherms, it is important to correct the p<sub>0</sub> value from the experimental value to the actual p<sub>0</sub> value of CO<sub>2</sub> at 273 K: 26141 Torr. This can be done from the Data Reduction Parameters (see Figure 3). This will re-scale the pressure axis of the isotherm to the correct p/p<sub>0</sub> values, with the highest p/p<sub>0</sub> ~ 0.03.

To calculate the micropore size distribution, a density functional theory (DFT) method was used. This method is programmed in the Kaomi for Nova

software and can be manually selected or pre-selected using the *defaultCO2* data reduction parameter set that is included in the software. The resulting DFT pore size distributions are shown in Figure 4. With measurement up to atmospheric pressure, CO<sub>2</sub> fills pores from ~0.35-1.5 nm. When the range of larger micro- and mesopores is also of interest, the CO<sub>2</sub> analysis can be combined with other adsorptives (e.g., nitrogen or argon analysis). Complementary combination of multiple adsorptive measurements allows one to obtain the complete micro- and mesopore size characterization of carbons while avoiding the time-consuming and costlier low-pressure measurements at cryogenic temperatures.



Figure 1. Recirculating Dewar and bath setup

Parameter	Value
p <sub>0</sub> mode	Material Specific: 800 Torr
Void Volume Mode	Helium Measure
Backfill Mode	Helium
Bath Thermal Delay	600 sec
Eq. Band %	Variable from 0.5 to 0.01
Eq. Interval	10 sec below p/p <sub>0</sub> = 0.2; 5 sec above p/p <sub>0</sub> = 0.2
Eq. Min.Time	--
Re-dose Tol.	25 %
Re-dose Max	3 Torr

Table 1: Parameters for CO<sub>2</sub> (273 K) analysis

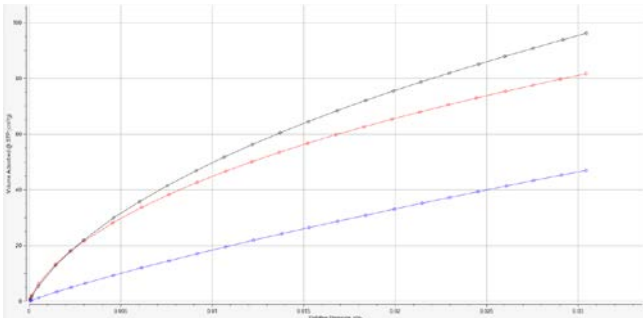


Figure 2: CO<sub>2</sub> (273 K) isotherms of F400 (red), ACF-15 (blue), and BAM P109 (black)

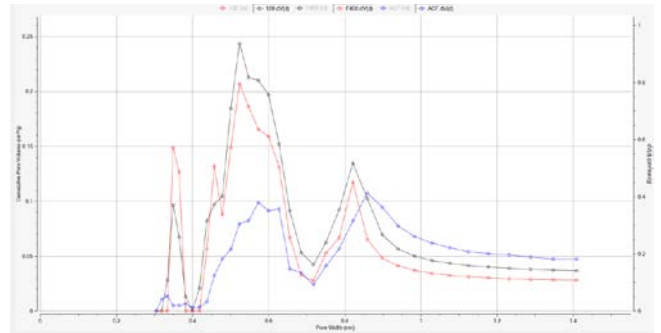


Figure 4: CO<sub>2</sub> (273 K) NLDFT pore size distributions of F400 (red), ACF-15 (blue), and BAM P109 (black)

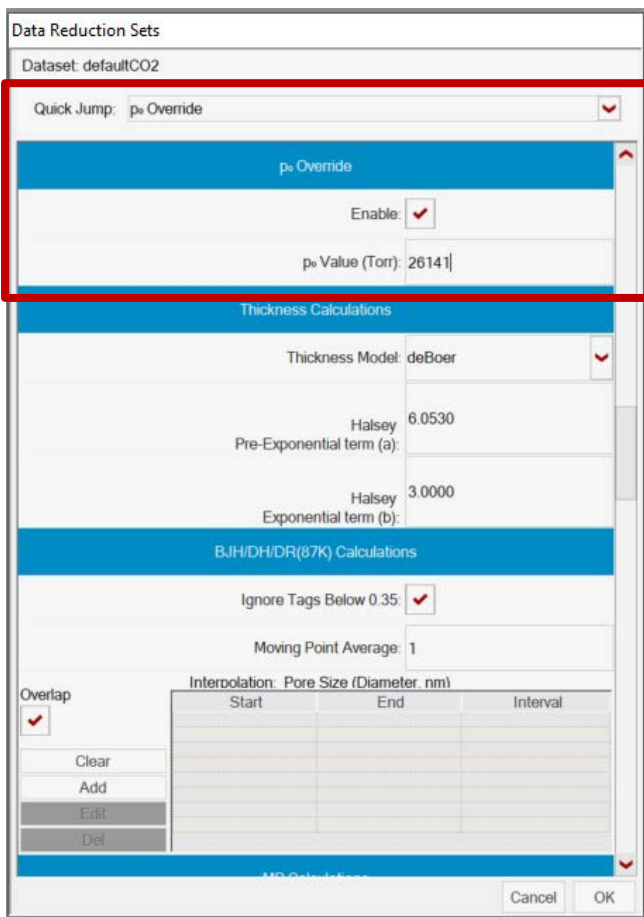


Figure 3: p<sub>0</sub> override in the Data Reduction Parameters

#### 4 Conclusions

The Anton Paar Nova 600 and 800 instruments are widely used in quality assurance and research labs to measure BET surface area and mesopore size distributions, but are generally not known as micropore analyzers. However, as can be seen here, these Nova models can be useful tools in determining the micropore size distribution of carbon samples using CO<sub>2</sub> adsorption. This method duplicates the results of more expensive instruments, and does it in significantly less time. In addition, the new “pore size distribution merge” feature is an incredibly useful tool in the Kaomi for Nova software - now data from two different experiments can be merged to obtain one continuous and complete pore size distribution, where previously they could only be overlaid.

#### 5 References

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- [Merging Pore Size Distributions from CO<sub>2</sub> and N<sub>2</sub> Adsorption Measurements](#)