

MICROPORE SIZE ANALYSIS OF POROUS CARBONS USING CO₂ ADSORPTION AT 273 K (0°C)

The pore size distribution (PSD) is a key factor characterizing porous materials. The PSD analysis can be useful in developing new porous materials for specific applications as well as for testing of the existing products. Traditionally, the PSD of a porous solid is evaluated from the analysis of nitrogen adsorption isotherms measured at 77 K. It is well known, however, that at such cryogenic temperature diffusion of nitrogen molecules into carbon micropores is very slow. Moreover, it was pointed out that diffusional limitations at this temperature might influence adsorption in ultramicropores (pores smaller than 7 Å) [1]. For porous carbons, usually containing a wide range of pore sizes including ultramicropores, this leads to time-consuming measurements and may cause under-equilibration of measured adsorption isotherms, which will give erroneous results of the analysis. It has been long time recognized [2-4] that problems of this type can be eliminated by using CO₂ adsorption analysis at 0°C. The saturation pressure of CO₂ at 0°C is very high (26200 torr), therefore low relative pressure measurements necessary for the micropore analysis are achieved in the range of moderate absolute pressures (1 – 760 torr). At elevated temperatures and under higher absolute pressures CO₂ molecules can more easily access ultramicropores than N₂ at 77 K in spite of the fact that molecular critical dimensions of both gases are similar. This kind of measurements can therefore be carried out without high vacuum equipment and without low-pressure transducers (e. g.; 1 torr or 10 torr transducers). The CO₂ adsorption isotherms measured under such conditions can be analyzed using modern molecular models such as Density Functional Theory (DFT) or Monte Carlo Simulations to provide detailed

information about carbon micropore structure.

Main advantages of CO₂ micropore analysis at 0°C versus nitrogen analysis at 77 K:

- Faster analysis. Due to higher diffusion rate equilibrium is achieved faster, which allows completing the isotherm measurement in a significantly shorter time: about 3 hours for CO₂ versus more than 30 hours for N₂.
- Faster diffusion to micropores ensures greater confidence that measured adsorption points are equilibrated.
- Range of analysis is extended to pores of smaller sizes that are accessible to CO₂ molecules but not to N₂.
- Technical simplification of instrumentation:
 - No need for high vacuum systems with turbomolecular pump; 10⁻³ torr vacuum is sufficient.
 - No need for a low-pressure transducer; 1000 torr transducer is sufficient.

Both the NOVA and Autosorb series instruments can perform the analysis. Data reduction is supported by Quantachrome software, which includes a comprehensive library of classical and modern methods for the calculation of PSD. In contrast to the classical macroscopic thermodynamic methods, modern approaches allow to describe the configuration of the pore fluid on the molecular level. Such microscopic methods for PSD analysis are available and listed in Table 1. More detailed description of these methods was given elsewhere [5-9]. Briefly, modern approach to the evaluation of PSD is based on the statistical mechanical

model calculations. The most important part of this approach is development of theoretical isotherms calculated for individual pores of a given adsorbate-adsorbent system, such as Carbon-CO₂. These isotherms, which constitute the so-called kernel, are generated using Grand Canonical Monte Carlo (GCMC) simulations or the Non-Local Density Functional Theory (NLDFT). Both of these statistical mechanical methods utilize fundamental molecular parameters characterizing the gas-gas and gas-solid interactions of the adsorption system. In the case of porous carbons the model of slit pores with graphite-like parallel walls is utilized. Mathematical procedure used to calculate PSD can be described as fitting a combination of the theoretical isotherms to the experimental data. The obtained PSD represents volumetric contributions of pores with different sizes whose theoretical isotherms best fit the experimental data.

Recognizing advantages of the CO₂ analysis Quantachrome Instruments introduced NLDFT / GCMC kernels for the PSD calculation from CO₂ isotherms. For illustration of the method, the CO₂ analysis results are compared with the results of well-established nitrogen DFT analysis for the two representative carbon samples. The PSDs are presented as histograms in Figure 1 for the activated carbon fiber ACF-10 (Nippon Kynol, Japan) and in Figure 2 for the coal based activated carbon F400 (Calgon Carbon). ACF-10 is a typical microporous carbon fiber with almost no mesopores while F400 has both micro and mesopores. Agreement between the results of the two methods is very good for both samples especially in the range of small micropores. The CO₂ isotherms measured at 0°C below 760 torr yield pore size distribution in the range up to about 15 Å.

The isotherms that were used for the PSD calculations of ACF-10 are shown in Figure 3.

It is important to note that for nitrogen, adsorption in carbon micropores begins at relative pressures well below 10^{-6} p/p_0 (<0.001 torr). At 10^{-6} p/p_0 , the adsorbed amount is already about 20% of total adsorption of this sample, so in order to measure the initial part of the isotherm much lower pressure is necessary. On the other hand, CO₂ adsorption begins at about 10^{-4} which in terms of absolute pressure is significantly higher compared to the nitrogen experiment (~ 1 torr). It follows that the initial parts of adsorption isotherms are accessed more easily for CO₂ than for N₂. This comparison clearly demonstrates that in order to follow and analyze adsorption in micropores it is more convenient and beneficial to use CO₂ rather than N₂.

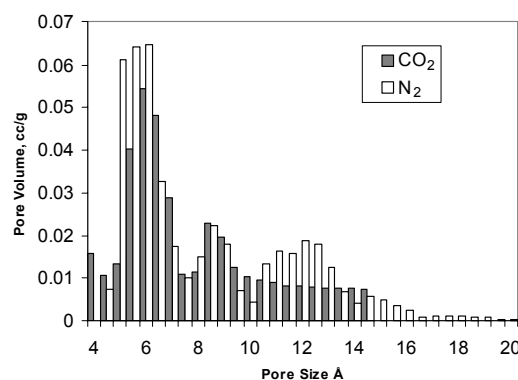


Figure 1. PSD histograms for ACF-10 activated carbon fiber. Analysis times: 3 hours for CO₂ and 40 hours for N₂.

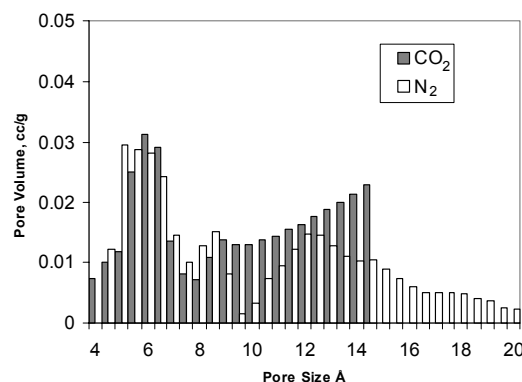


Figure 2. PSD histograms for F400 activated carbon. Analysis times: 3 hours for CO₂, and 35 hours for N₂.

Obviously, when the range of mesopores is of interest, the CO₂ analysis may be combined with the classical nitrogen mesopore analysis. Combination of the two methods allows for the micro and mesopore characterization of carbons avoiding time consuming and more costly low-pressure nitrogen measurements at 77 K.

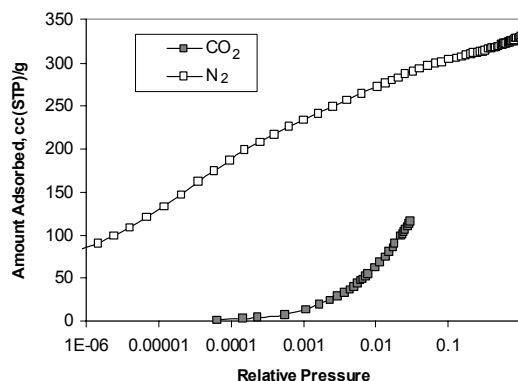


Figure 3. Adsorption isotherms of N₂ at 77 K and CO₂ at 273 K on activated carbon fiber ACF-10.

Table 1

NLDFT / GCMC Kernels available in Autosorb and NOVWin software

NLDFT / GCMC Kernel File	Applicable Pore Diameter Range
<i>NLDFT – N₂ - silica at 77 K</i> , based on a cylindrical pore model . In case of sorption hysteresis pore size analysis is possible from both adsorption and desorption branches of the hysteresis loop.	1.8 nm - 100 nm
<i>NLDFT – N₂ - carbon at 77 K</i> based on a slit-pore model	0.35 nm - 8 nm
<i>NLDFT - Ar-zeolite/silica at 87 K</i> , based on a cylindrical pore model . In case of sorption hysteresis pore size analysis is possible from both adsorption and desorption branches of the hysteresis loop.	0.35 nm - 100 nm
<i>NLDFT – Ar - carbon at 77 K</i> based on a slit-pore model	0.35 nm - 8 nm
<i>NLDFT – CO₂ - carbon at 273 K</i> based on a slit-pore model	0.35 nm - 1.5 nm
<i>GCMC – CO₂ - carbon at 273 K</i> based on a slit-pore model	0.35 nm - 1.5 nm

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Additional Technical Information for CO₂ Adsorption Measurements

The following technical changes should be done to switch from the standard N₂ (77 K) setup to CO₂ measurement at 273 K or other near ambient temperature.

1. The liquid nitrogen bath has to be replaced by a water bath with controlled temperature. The technical options and accessories for such a bath include:
 - a. For a 0°C measurement one can use a dewar filled with crushed ice/water mixture. The drawback of this method is that in the absence of stirring, as ice melts, some temperature gradient may develop around the sample cell and thus maintaining a constant temperature during the measurement is not fully ensured.
 - b. To maintain constant temperature (0°C or other near ambient temperature) it is recommended to use a recirculating dewar which is built as a double walled stainless steel vessel where the inside is filled with water or a suitable antifreeze mixture, and the cooling/heating liquid is circulated through the outer "jacket" by means of a thermostatic system. The available recirculating dewar is p/n 74097 with hose barbs on opposite sides facing opposite directions and its modified version, p/n 01541-6428, where hoses are attached facing the same direction (liquid flow still enters and leaves on opposite sides). Using dewars with hoses one should pay attention to avoid that the hoses may pull the dewar over.
2. Specific recommendations for CO₂ adsorption on the Autosorb-1/3/6:
 - a. For maintaining the level of bath liquid, the water level float switch (p/n 0080-H₂O) should be used with any kind of dewar. This sensor simply plugs into the same coaxial connector as the LN₂ cryogen level sensor (thermistor). Setup example of thermostatic system with Autosorb 1 is shown in Figure 4.
 - b. When ice/water mixture is used a dewar with wide mouth is recommended (e.g., p/n 74070 as used on Nova 1000 through 3000 series or p/n 04000-7224 as used on NOVAe series). The standard dewar as supplied for use with liquid nitrogen is too narrow at the neck for the float switch.
 - c. The P₀ measurement cell should be removed.
 - d. A foam block (p/n 04000-7188) is recommended to assist in fixing position of either recommended version of dewar within the elevator pan.
3. Specific recommendations for CO₂ adsorption on the Nova Series:
 - a. If the sample outgassing is performed in the Nova outgasing station and CO₂ is connected as the adsorption gas then the Isolation Valve Assembly p/n 01369-5305 (Figure 5) should be used. After the sample is outgassed, the valve should be closed before sample cell removal to avoid back fill with CO₂ which is an adsorbing gas at ambient temperature.
4. Analysis and data reduction parameters:
 - a. For both Autosorb and Nova series in the analysis parameter sections the User Entered P₀ should be selected and P₀=760 torr should be entered. This tells the instrument to measure in the range of absolute pressure up to 760 torr.
 - b. After the analysis, and before, the data reduction process, this value should be changed in the Analysis Information panel to a correct value (P₀=26,140 torr for CO₂ at 273 K).
 - c. In the Autosorb and Novawin software, the PSD analysis based on NLDFT and GCMC models is available for carbonaceous materials. The CO₂ isotherms should be measured at 273 K for this type of analysis.

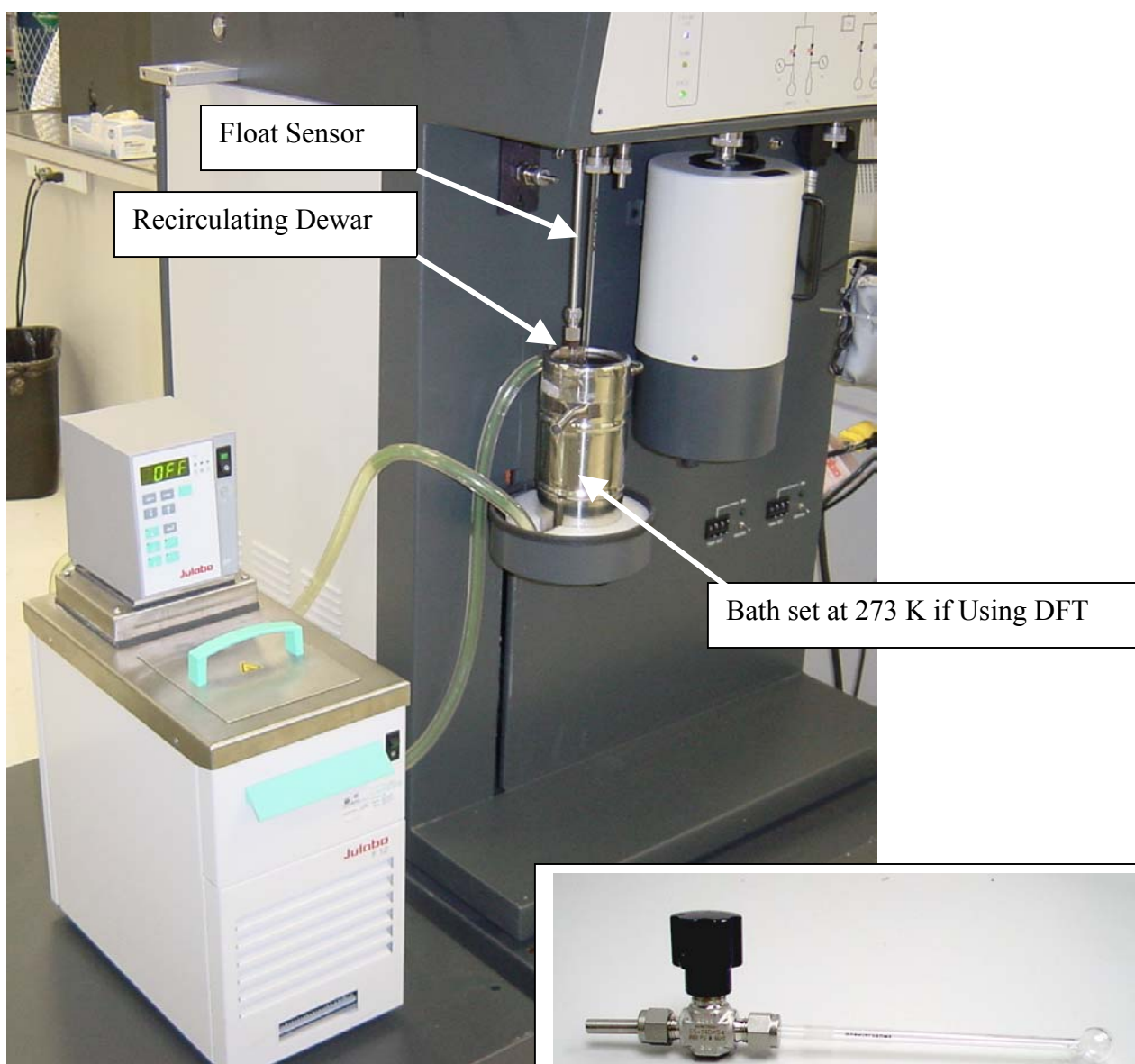


Figure 4. Setup of thermostatic system with Autosorb 1 for CO₂ adsorption measurements.

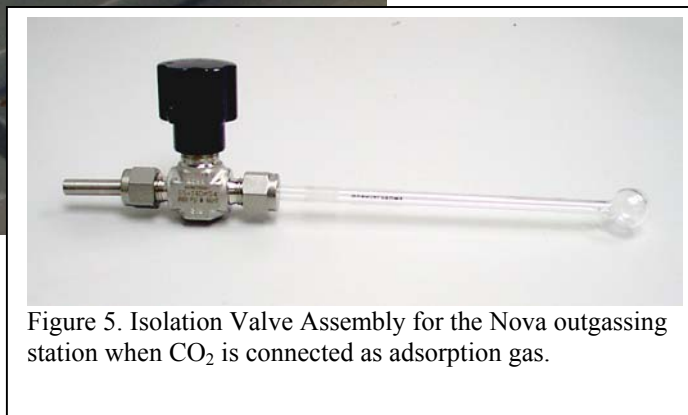


Figure 5. Isolation Valve Assembly for the Nova outgassing station when CO₂ is connected as adsorption gas.