



# Surface Area and Pore Size Distribution via Gas Sorption Analysis

**A material's surface morphology plays a vital role in its interactions with the surrounding environment. Surface area and pore structure are important considerations in many fields, impacting diverse industry concerns.**

The measurement of a material's surface morphology is commonly performed using nitrogen sorption analysis, where nitrogen molecules adsorbed on or desorbed from the sample surface, analyzed using the appropriate model, provide values for these parameters.

Gas sorption analysis takes advantage of the attraction between an open surface and any gas molecules it encounters. Interactions between the surface molecules of the sample (the adsorbent) and a gas molecule (adsorbate) lead to the gas molecules becoming weakly attached to the surface as liquids. A surface free of interactions (as one is under vacuum) is in an unfavorable state, so when gas molecules are introduced to the adsorbent at low pressures, the molecules interact with the surface to form a film, as this is a more favorable state. Upon adsorption to the surface, these molecules are known as the adsorptive. This technique was originally developed to analyze mesoporous (pore diameter 2-50 nm) materials, though it can also be extended to microporous (< 2 nm diameter) and small macroporous (> 50 nm diameter) materials with the appropriate selection of analysis parameters.

Adsorption and desorption data collected by this instrument at a constant temperature is known as an isotherm. The volume of gas adsorbed is plotted against the relative or partial pressure introduced to the sample during the analysis. Figure 1 illustrates the progression of analysis:

A) In preparation, any species currently adsorbed must be removed from the sample surface. This is accomplished by placing the sample either under vacuum or a stream of inert gas to drive adsorbed

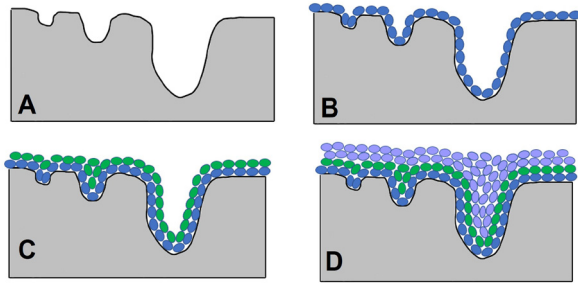
molecules from the surface. Elevated temperatures are frequently applied to speed the process, though care must be taken to avoid any changes to the sample's morphology due to heating.

B) Analysis begins with the sample under vacuum, where the sample's surface is free of adsorbed species. Carefully controlled doses of adsorbate (typically N<sub>2</sub>) are added to the sample to reach a partial pressure (P/P<sub>0</sub>) chosen by the operator. As gas is added to the system, molecules are adsorbed on the surface of the sample. The volume of gas required to increase the pressure to the requested value is plotted as a point on the isotherm. This process is repeated at a sequence of increasing partial pressures. As the pressure and adsorbed volume increase, samples are covered by an adsorbed nitrogen film the equivalent of a 1 molecule thick layer, known as a monolayer. This monolayer coverage can be used to calculate a sample's surface area using the Brunauer-Emmett-Teller (BET) method.

C) Incremental increase to chosen pressure setpoints leads to increased adsorption on the sample surface. As adsorption progresses, mesopores fill with adsorptive, starting from the smallest diameter and progressing to larger pore sizes as the pressure is incrementally increased.

D) As pressure approaches atmospheric pressure (P/P<sub>0</sub> = 1), the surface is fully covered by multiple layers of adsorptive. This marks the completion of the adsorption isotherm. To construct the desorption isotherm, the process is reversed, with P/P<sub>0</sub> incrementally decreased. During this process, the adsorptive is slowly removed from the surface, with largest pores being emptied first, and

decreasing pore sizes being emptied as  $P/P_0$  is decreased. This desorption data is commonly used to analyze the pore volume and size distribution using the Barrett-Joyner-Halenda (BJH) method. In select well-studied materials, density functional theory (DFT) based models can also be used to describe the pore size distribution and pore volume.



**Figure 1:**

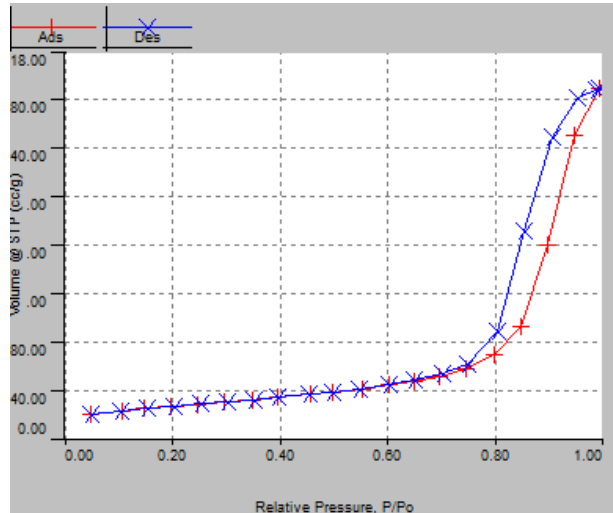
A) Prior to analysis, the surface is outgassed to remove adsorbed species. Analysis begins on an open surface under vacuum.

B) As pressure is increased in the cell, a coating approximately 1 molecule thick is formed on the surface, known as the monolayer. For mesoporous materials, this usually occurs at  $P/P_0 \sim 0.3$ .

C) With increasing pressure, multiple layers of gas molecules are adsorbed. Pores begin to fill, with the smallest pores filling first, and increasingly larger pores filling at incrementally higher pressures.

D) As the pressure approaches  $P/P_0 \sim 1$ , the surface is fully covered. This point marks the completion of the adsorption isotherm. From here, the process can be reversed to form the desorption isotherm: pressure is incrementally decreased, and adsorbed molecules are removed from the surface, starting from the largest pores and the outermost adsorbed layer.

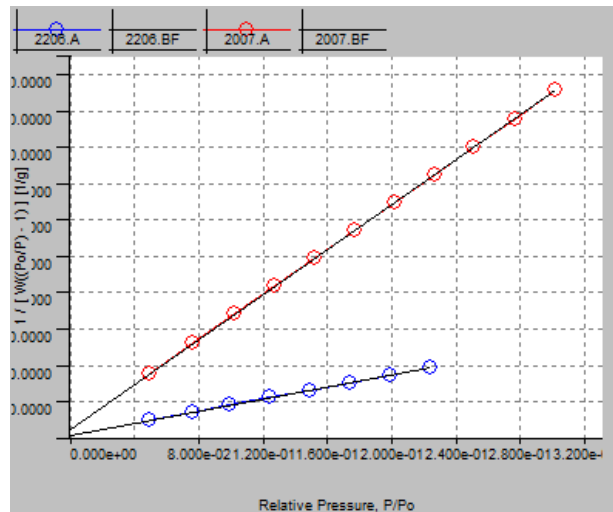
Once the isotherm is obtained (Figure 2), various models are used to calculate different values related to pore structure; a few examples are listed below. In a sense, it may be helpful to think of the isotherm as the raw data obtained by the instrument, and applications listed below as the analyzed data, since all calculated values are derived from the isotherm. Some common applications include surface area by BET, pore volume and distribution by BJH or DFT, and separation of the micro- versus meso-pore volume using the statistical thickness method to construct a t-plot. ASTM methods exist for these analyses for some materials; methods and the material they apply to are listed in the application section below. Materials without specific ASTM methods can also be tested using this technique.



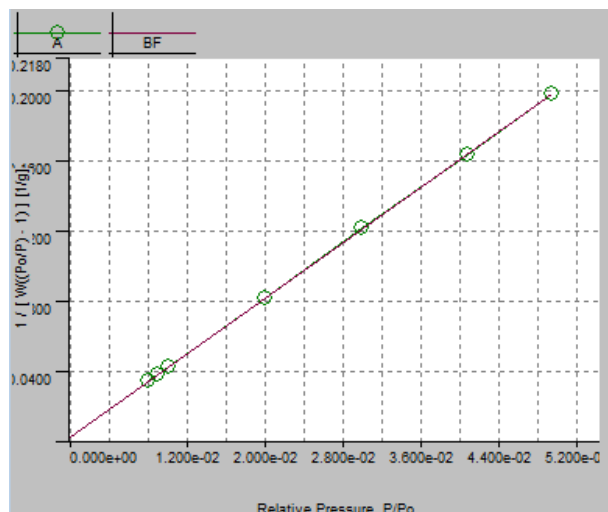
**Figure 2:** Sample isotherm obtained from nitrogen sorption analysis. As partial pressure increases, the amount of nitrogen adsorbed increases; plotting the adsorbed volume vs the partial pressure produces the adsorption branch of the isotherm (red). Reversal of this process, with removal of nitrogen at incrementally lower partial pressures, produces the desorption branch (blue).

## Applications

One of the most common applications of this analysis is the measurement of surface area. Surface area is calculated by the BET method in the pressure range where a monolayer is formed (see Figure 3.)



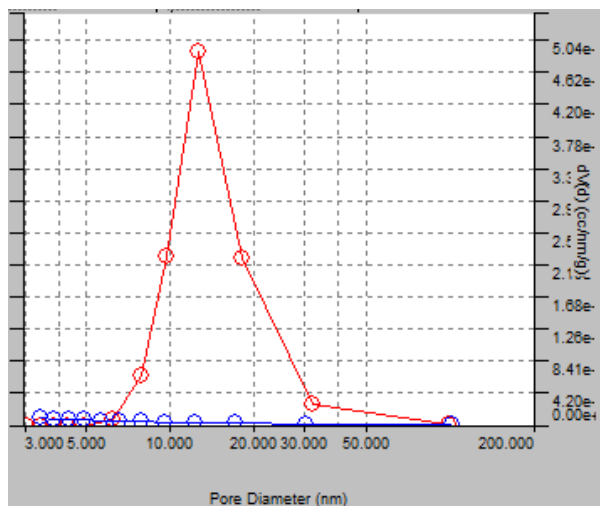
**Figure 3A:** BET plots for two alumina and one activated carbon material. Relative pressure ranges used to construct the plots vary due to presence of micropore structure. A) alumina samples show a larger portion of mesoporous structure, so relative pressures of 0.05 to 0.25 and 0.3 are used for plot construction.



**Figure 3B:** BET plots for two alumina and one activated carbon material. Relative pressure ranges used to construct the plots vary due to presence of micropore structure. B) graphite sample, with its much larger micropore structure, where pressure range 0.008-0.05 is used for calculation of the BET surface area.

Classical BET analysis uses the relative pressure range from 0.05-0.3, where monolayer formation of mesoporous materials occurs. In materials with a wider variety of pore sizes, BET analysis can still yield useful information in the form of an apparent surface area to compare materials. For materials with a wider variety of pore sizes, the recommended partial pressure range for this analysis can shift. In the figure below, BET surface area for one of the alumina samples (red), because it exhibits mesoporous structure, is calculated using the 0.05-0.3 relative pressure range. BET surface area for the second alumina sample (blue), which contains a mix of meso- and micro pores, is calculated using a narrower pore size range. For a material with primarily microporous structure (green), relative pressures below the classical range are used ( $> 0.05$ ) to obtain the apparent surface area. The pressure range used to calculate the BET area is calculated by the analysis software to yield the best results.

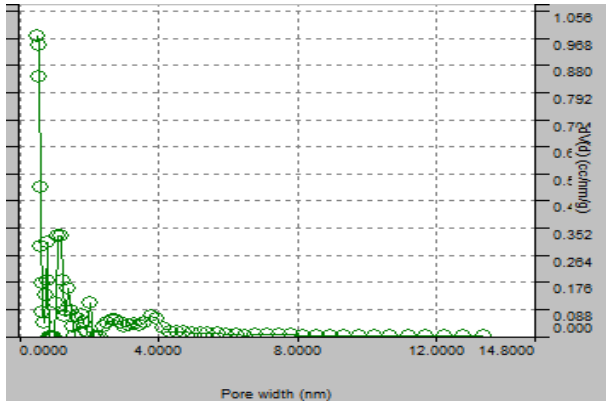
Another common application is the measurement of pore size distributions by various methods. One frequently used method for investigating the pore size distribution and pore volume of a material, the Barrett-Joyner-Halenda (BJH) method, is illustrated for two alumina samples in Figure 4a.



**Figure 4a:** Pore sizes for two alumina samples are described in the 2-200 nm range using a BJH desorption plot. One material (red) shows a nominal pore size ~12 nm, while the other (blue) contains pores spread over a wide range of diameters.

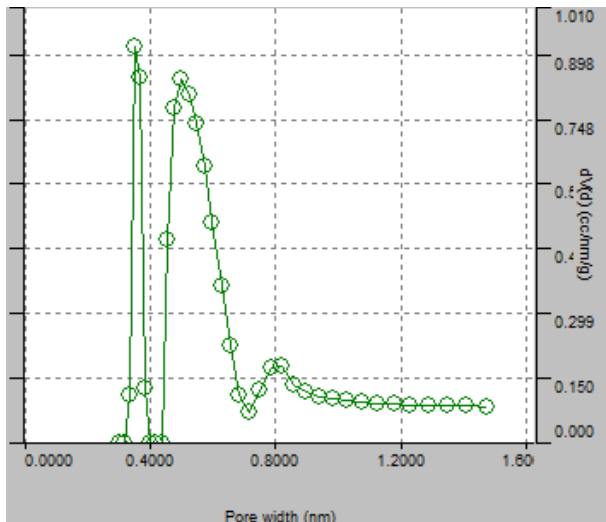
This approach, based on the ability of different pore sizes to fill with adsorptive at different pressures, is widely applicable to a variety of materials, and pore sizes of varying materials can be compared in a relatively straightforward manner. However, caution must be exercised when applying this model to the smaller mesopore range, as for pore sizes  $< 10$  nm diameter, it has been shown to underestimate the pore size by up to 30% (<sup>1</sup>IUPAC 17).

A more recent approach for understanding a material's pore structure makes use of density functional theory (DFT), a model which takes interactions between surface and adsorbate in the micropore size region into account more effectively than BJH. The DFT method allows description of the pore structure down to 0.35 nm for select materials, while the BJH method is limited to the mesopore/small macropore size range. Because this method is based on modelling work done for specific materials, only some materials have a well-defined model which can be used for this analysis. Figure 4b shows the pore size distribution for an activated carbon calculated using the DFT method.



**Figure 4b:** Pore sizes calculated using nitrogen sorption for one activated carbon material. Using this technique, pore sizes can be modelled down to 0.35 nm for select materials, though micropore analysis can be time-consuming.

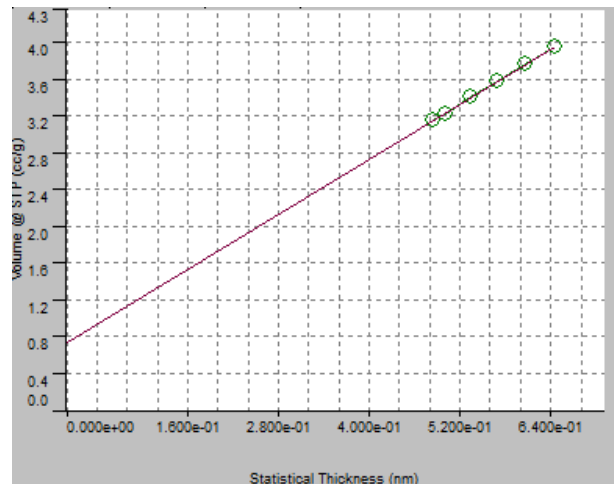
For this material, a single analysis using N<sub>2</sub> as adsorbent can provide the BET surface area and the pore size distribution covering both the meso- and micropore region; however, this entire analysis can be very time-consuming. To increase the efficiency of the measurement in the micropore region, analysis can be performed using CO<sub>2</sub> at higher temperatures and relative pressures to allow faster diffusion of gas molecules into the micropores. Figure 4c shows an example of the micropore size distribution calculated for the same activated carbon material.



**Figure 4c:** Pore sizes calculated using CO<sub>2</sub> sorption for the activated carbon material. Use of CO<sub>2</sub> as adsorbate can increase the efficiency of micropore analysis in porous carbon materials, but the pore diameter range is limited.

It should be noted that currently, models using CO<sub>2</sub> as adsorbate are only available for porous carbon materials, so application of this analysis is limited.

If a full pore size distribution is not needed, information about a material's micropore structure can also be obtained by creating a t-plot. This method takes advantage of widely applicable equations to evaluate a sample's micropore volume and surface area (some methods refer to this value as STSA, or statistical thickness surface area.) Taken together with the surface area obtained by BET analysis, this analysis allows the user to determine the micropore contribution to the total surface area. Figure 5 shows a t-plot created for the same activated carbon material shown in Figure 3B.



**Figure 5:** t-plot created for the same activated carbon material shown in Figure 3c, used to calculate the micropore volume. In combination with the measured BET value, the relative contributions of micro- and mesopores can be obtained.

T-plot results indicate a micropore surface area of 220 m<sup>2</sup>/g; with a total BET surface area of 880 m<sup>2</sup>/g; the micropores account for one-quarter of the material's accessible surface area.

## Sample Requirements/Industries

- Because the sample must first be outgassed, information about the material's thermal stability is essential to the preparation procedure. A heating program must be found that effectively removes contaminants from the surface, while avoiding any morphological changes to the sample. For many thermally

stable materials (alumina, silica, silicon carbide, etc) recommendations based on historical data exist, but more novel materials might require investigation to avoid morphological changes during the outgassing process.

- Nitrogen is the most common adsorbate, as it generally provides the necessary information. However, for some samples, such as those with a very low surface area or micropores, use of either krypton or carbon dioxide may be necessary to obtain accurate values. Use of these gases requires additional experimental considerations, and therefore may require additional resources.
- For DFT-based pore size distribution analysis, it is essential that the correct model be chosen for the specific material. Types of material that have been studied using sorption analysis, including zeolites, activated carbon, and some porous glasses, have models available; however, this may not be the case for more novel materials.
- Nitrogen sorption analysis was primarily developed for analysis of mesoporous materials, then expanded to allow micropore analysis. While analysis of smaller macroporous materials (< 200 nm pore size) is possible, other methods must be used for analysis of larger macropores.

## Industries

- Additive manufacturing
- Automotive
- Battery and Energy storage
- Catalysts
- Ceramics
- Graphite Production
- Medical implants
- Pharmaceutical
- Size-exclusion Separation Materials

## Relevant ASTM Method

### Surface Area

<b>B922</b>	Standard Test Method for Metal Powder Specific Surface Area by Physical Adsorption
<b>C1069</b>	Standard Test Method for Specific Surface Area of Alumina or Quartz by Nitrogen Adsorption
<b>C1274</b>	Standard Test Method for Advanced Ceramic Specific Surface Area by Physical Adsorption
<b>D1993</b>	Standard Test Method for Precipitated Silica-Surface Area by Multipoint BET Nitrogen Adsorption
<b>D5604</b>	Standard Test Methods for Precipitated Silica—Surface Area by Single Point B.E.T. Nitrogen Adsorption

### Pore Size Distribution

<b>D4641</b>	Standard Practice for Calculation of Pore Size Distributions of Catalysts and Catalyst Carriers from Nitrogen Desorption Isotherms
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### T-plot ASTM Method

<b>D6556</b>	Standard Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption
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## Gas Analysis Services at Eurofins EAG

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### Sources:

<sup>1</sup>Matthias Thommes, K. K.-R. (2015). *Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution* (IUPAC Technical Report). IUPAC.