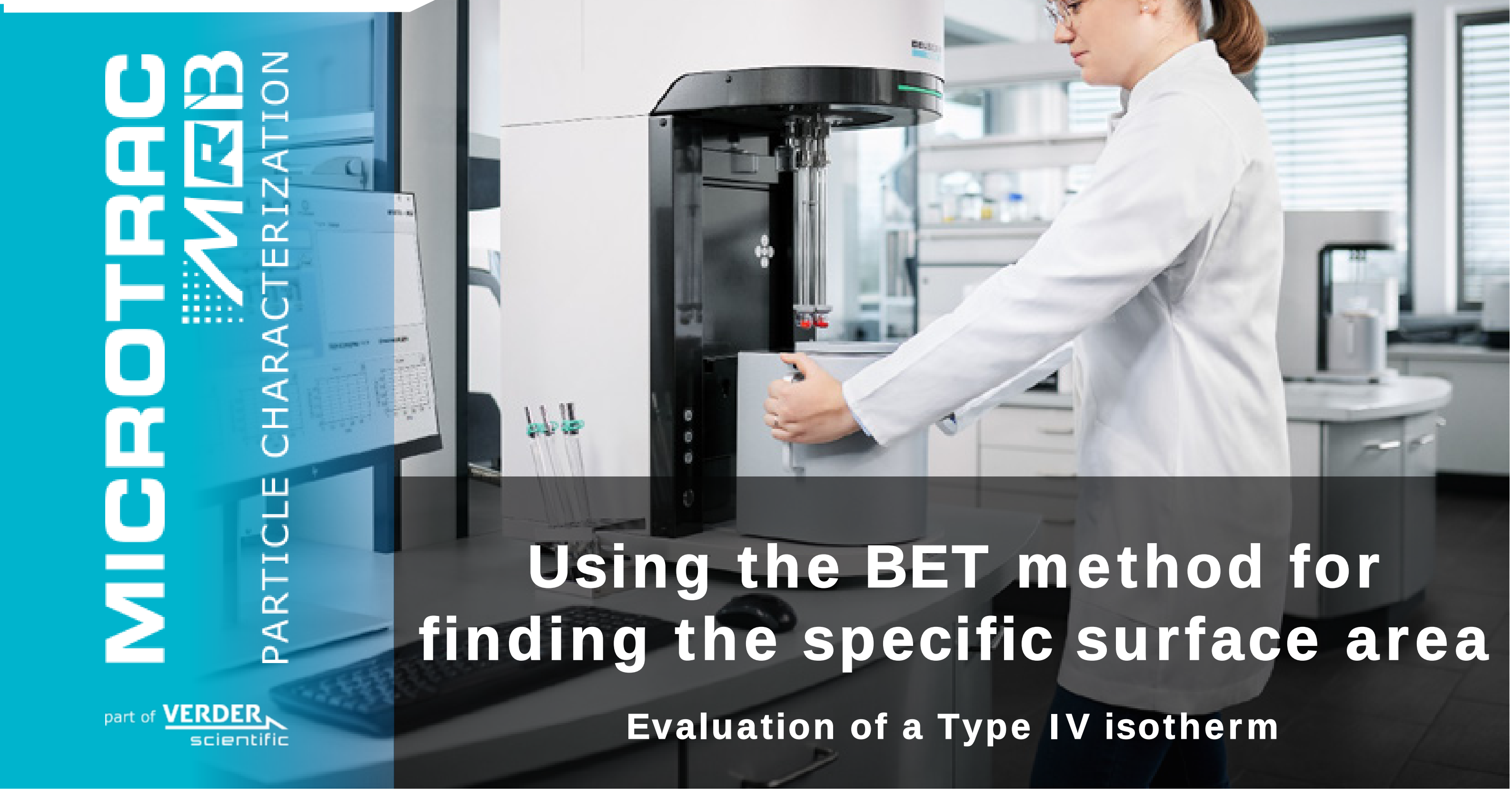

Using the BET method for finding the specific surface area

Evaluation of a Type IV isotherm

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Introduction

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.

Fig. 1 – Examples of the numerous applications for determining BET surface areas.

General information

The Brunauer-Emmett-Teller method (BET method, ISO 9277) is the most common method for the evaluation of specific surface areas. 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 possible to also 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.

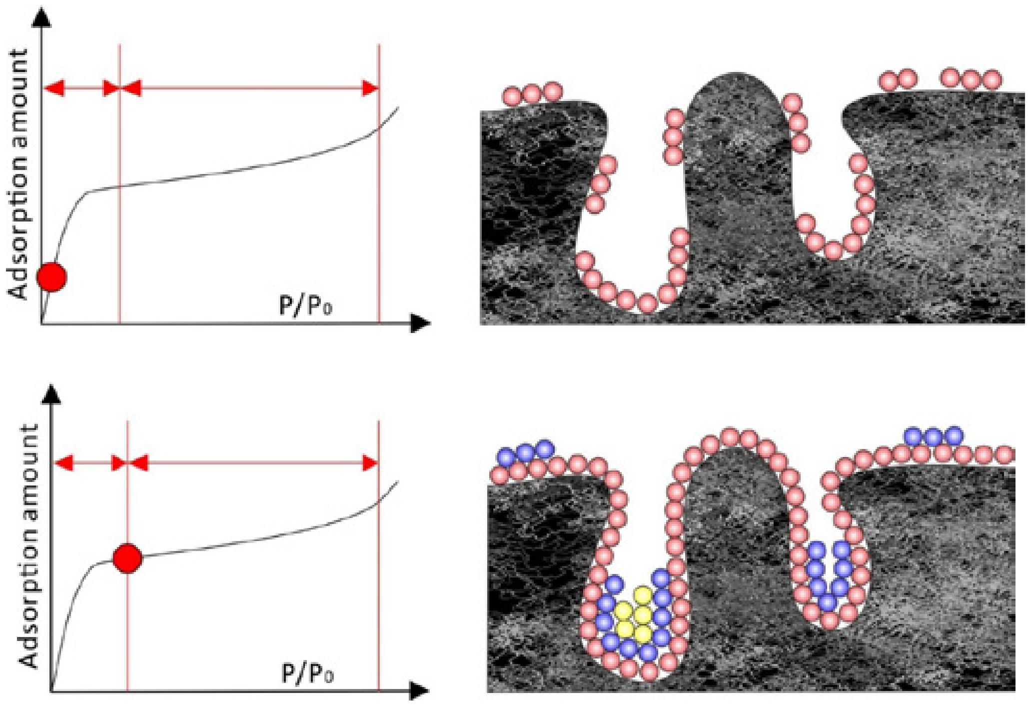
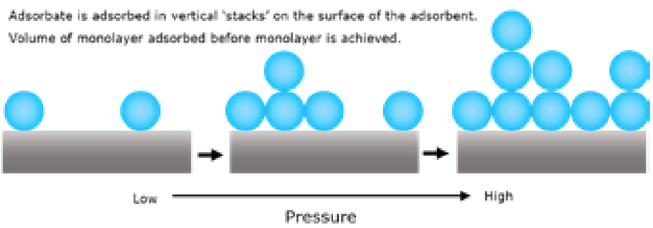


Fig. 2 – Isotherms and graphical representations depicting adsorption before (a) and at (b) the completion of the first monolayer. Note that second and third layers are produced in some regions before the completion of the monolayer.

Relative pressures in the range of P/P_0 = 0.05 – 0.30 is 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 prior to 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:



Assumptions of BET Theory:

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 are 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.

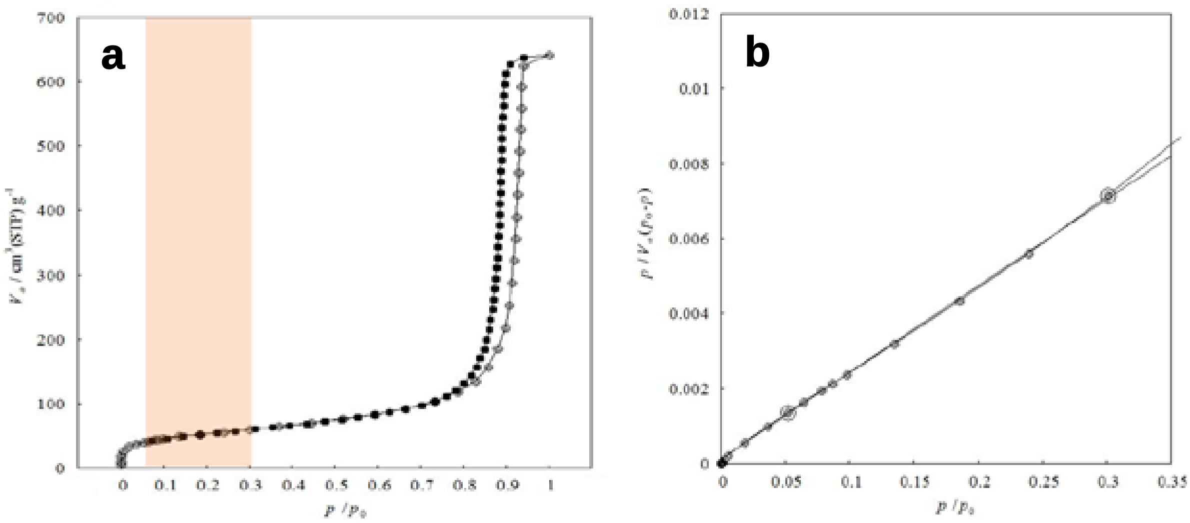


Fig. 3 – An example isotherm (a) and the respective BET plot (b) for a mesoporous material with a BET specific surface area of ~187 $m^2\ g^{-1}$.

It should be noted, that 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.

BET Surface Area Calculation

The BET equation (eq. 1) is used to convert the isotherm plot to a ‘BET plot’ (fig. 5). 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).

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

$$i = \frac{1}{W_{mono} C}$$ eq. 2 – BET plot intercept

$$s = \frac{C-1}{W_{mono} C}$$ eq. 3 – BET plot slope

$$W_m = \frac{1}{s+i}$$ eq. 4 – Monolayer volume

$$S_t = \frac{W_m \times N_A \times A_{cs}}{M}$$ eq. 5 – BET surface area

$$\mathrm{S} = \frac{S_t}{w}$$ eq. 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. First the data is replotted using the BET equation. Figure 4b. 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 is 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.

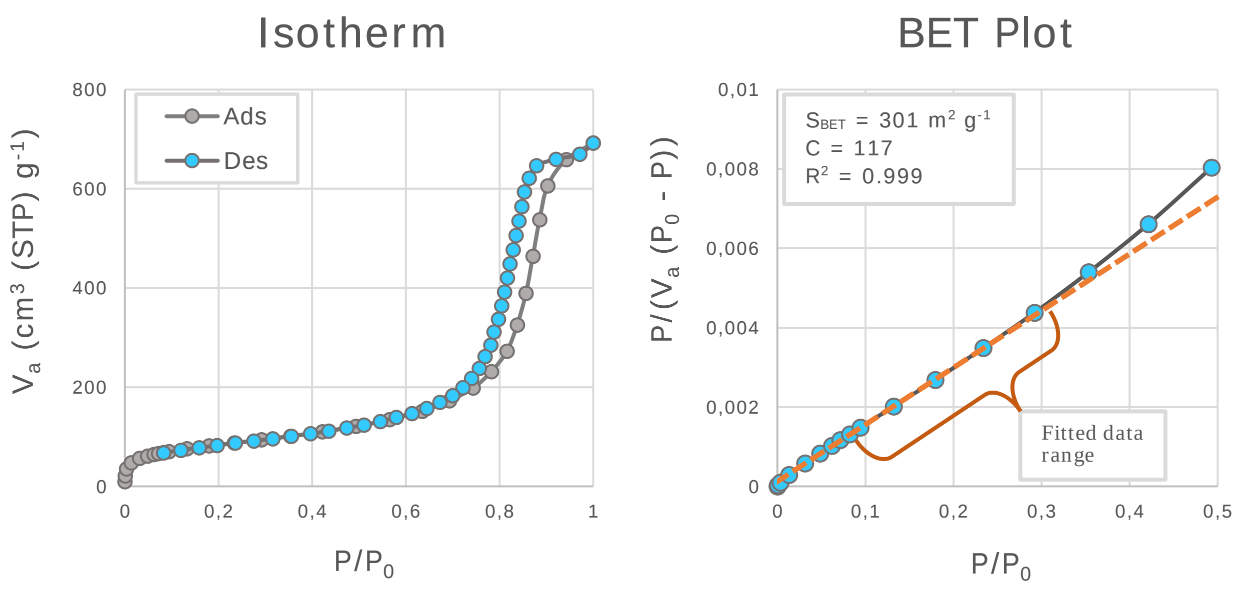


Fig. 4 – Nitrogen sorption isotherm of Develosil 100 at 77 K activated under vacuum at room temperature for 15 h (left) and BET plot of Develosil 100 (right).

Gas Adsorption Analyzers

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

Fig. 5 – A selection of gas adsorption analyzers from Microtrac capable of collecting high quality measurements.

Manometric (sometimes referred to as volumetric) 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 Microtrac.com.

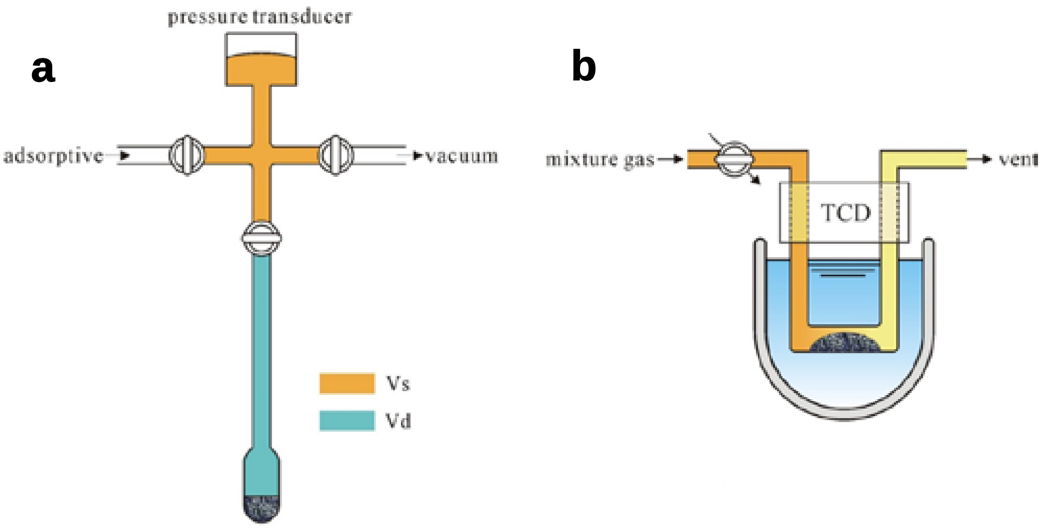


Fig. 7 – Two types of systems capable of collecting adsorption data including manometric/volumetric (a) and dynamic flow (b) methods.

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 are capable of achieving $P/P_0 = 10^{-4}$ 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 $P/P_0 < 10^{-8}$.

Industrial Standard Methods

Standard methods are important for validating industrial processes. What follows are a list of some important industrial standards relating to the collection of BET specific surface areas. All the listed methods are capable of being collected using instrumentation here at Microtrac MRB. As there are a vast number of accepted standard methods, as well as new ones being accepted continuously, there will certainly be soe missing from this list. If you don't see exactly what you're looking for, or the standard method of your choice isn't on the list but you're unsure if it would still apply, please reach out to us as info@microtrac.com and we'll be happy to work with you to find out if adsorption is right for you.

ASTM B922
Standard Test Method for Metal Powder Specific Surface Area by Physical Adsorption

ASTM C1069
Standard Test Method for Specific Surface Area of Alumina or Quartz by Nitrogen Adsorption

ASTM C1240
Standard Specification for Silica Fume Used in Cementitious Mixtures

ASTM C1274
Standard Test Method for Advanced Ceramic Specific Surface Area by Physical Adsorption

ASTM D1993
Standard Test Method for Precipitated Silica-Surface Area by Multipoint BET Nitrogen Adsorption

ASTM D3663
Standard Test Method for Surface Area of Catalysts and Catalyst Carriers

ASTM D4780
Standard Test Method for Determination of Low Surface Area of Catalysts and Catalyst Carriers by Multipoint Krypton Adsorption

ASTM D5604-96
Standard Test Methods for Precipitated Silica -- Surface Area by Single Point B.E.T. Nitrogen Adsorption

ASTM D6556
Standard Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption

ASTM D8325
Standard Guide for Evaluation of Nuclear Graphite Surface Area and Porosity by Gas Adsorption Measurements

ASTM E2864
Standard Test Method for Measurement of Airborne Metal Oxide Nanoparticle Surface Area Concentration in Inhalation Exposure Chambers using Krypton Gas Adsorption

ISO 8008

Aluminium oxide primarily used for the production of aluminium — Determination of specific surface area by nitrogen adsorption

ISO 9277
Determination of the specific surface area of solids by gas adsorption — BET method

ISO 12800
Nuclear fuel technology — Guidelines on the measurement of the specific surface area of uranium oxide powders by the BET method

ISO 18757
Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of specific surface area of ceramic powders by gas adsorption using the BET method

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 has 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 info@microtrac.com.

Produced by:

Nathan R. Bays, Ph.D.

Serkan Gökpinar, Ph.D.