APPNOTE 2-01

How exact can we determine the specific surface area of porous materials?

Characterization of
particles · powders · pores

Introduction

The specific surface area of powders and porous solids is usually described with the BET theory, however especially in the micropore range we should cast a critical spotlight on the term "surface area" on an atomic scale. On one hand, this will be in reference to the "real surface", which incorporates irregularities and impurities of any given porous material. On the other hand it is also in relation to other representations of a surface area determined by a variety of analytical instruments employing the method of physisorption such as the 3P meso 400 (Fig. 1). This will be especially important during the determination of micropores. Furthermore the apparent contradiction, that surface area analysis in microporous materials is theoretically questionable but a sample characterization based on it is very useful from a practical point of view, needs to be considered.

Figure 1 *3P meso 400 as an example for an analytical instrument for surface area analysis equipped with four fully independent analysis stations for high throughput*

The unified standard BET model of analysis

The specific surface area of a substance can be determined by a variety of methods and usually certain analytical models are attributed towards a specific type of analysis. When solely focusing on gas adsorption as an analytical method, this still leaves the question open which analytical model should be used for calculations? Only when using the method of Brunauer, Emmett and Teller (BET) one can speak of the BET-surface area, and to be fully correct, this requires the standard BET equation

$$V_a = V_m \frac{Cp/p_0}{(1-p/p_0)(1-p/p_0+Cp/p_0)} \tag{1}$$

as there are other models to be used.

Being able to compare results of the same methods and models has gained increasing value in industrial practices, when it comes to handling materials in quality and delivery control as well as research and development, thus requiring simple parameters to be compared. This also applies to the determination of specific surface area, meaning in order to obtain comparable results, these results must be obtained from or with

- the same method (gas adsorption)
- the same analysis gas (traditional standard for BET is nitrogen, but argon becomes more popular because of physical reasons)
- the same analysis temperature (77 K for N_2, but 87 K for Ar)
- the same range of relative pressures (standard-BET-analysis is carried out at p/p_0=0.05 to 0.3, but special procedure for microporous materials)
- the same equation (Standard-BET-equation)

Changing any parameter can lead to different results and would not be comparable with decades of results and database entries. The answer to the question “should I change my analytical method” would undoubtedly be different, if newer and more modern models would yield the „true surface area“. But is there any hope for an universal method for surface area determination at the current state of science and technology?

Why we are still waiting for a universal method…

The BET-equation is usually applied in its linear form and the monolayer capacity V_m is calculated from the slope and the intercept of the linear regression curve. The monolayer capacity combined with the Avogadro constant results in the number of molecules required to fill the monolayer and multiplying with the area required by one adsorbate molecule results in the specific surface area O_{sp}

$$O_{sp} = V_m \cdot N_A \cdot a_m \tag{2}$$

According to various recommendations, the area required for one molecule of N_2 is 0.162 nm². This value is derived from the adsorbates liquid density, independent from the type of surface and without considering the elliptical shape of the N_2 molecule and thereby ignoring that the molecule can take different conformations when interacting with the surface of the adsorbent. The interatomic distance between the two nitrogen atoms (specifically the range of the repulsive force of the Lennard-Jones potential) in an N_2 molecule is considered to be rigid at an atomic diameter of 0.1659 nm. This results in a minimum molecular width of 0.33 nm and a maximum molecular expansion of 0.44 nm. This is further illustrated in fig. 2, where the total area of the enveloping rectangle of 0.33 nm x 0.44 nm = 0.1452 nm² deviates from the IUPAC standard of 0.162 nm² by roughly 10 %.

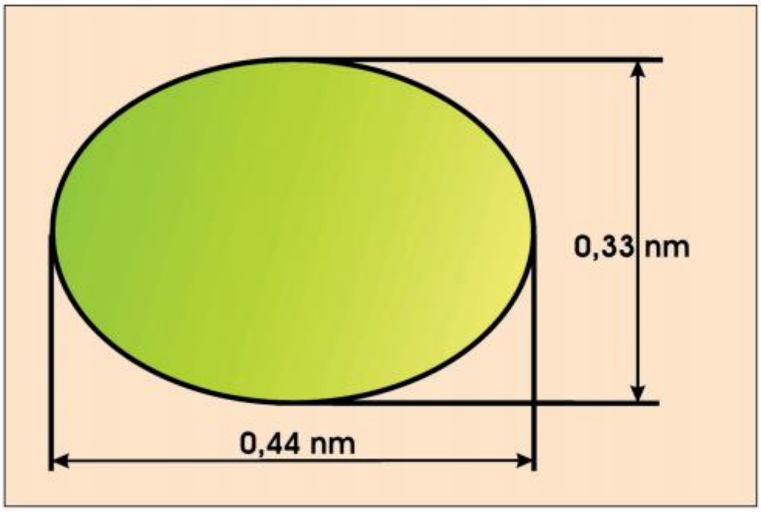

Figure 2 *Schematic representation of a N_2 molecule according to the dimensions*

The actual area occupied by one molecule of adsorbate on a surface is further dependent on other parameters, such as polarity of the sample, and may vary. While for N_2 a standard value of 0.162 m² is assumed, literature values for calcined silica-based materials, such as mesoporous M41-S-materials of 0.134 nm² can be found. This is mainly due to the stronger interaction of hydroxyl-groups on the surface with the high quadrupole moment (non-spherical symmetry of charge distribution in the electron density) of the N_2 molecule. Assuming the noble gas argon as a mono-atomic gas instead of the molecular N_2, it is to be expected, that due to the spherical symmetry of the argon atom no quadrupole moment is present. It stands to note, that while working with a mean value for the adsorbates area of occupation, we will never determine the “true” surface area of all materials. This problem becomes even more pronounced under the influence of micropores.

The special problem with microporous surface areas

If the BET model is applied on microporous materials to determine surface areas, the linear section of the isotherm is supposed to be used as described in the appendix of ISO 9277. This linear section is usually shifted towards lower pressures when measuring microporous materials and is usually found within a relative pressure range from 0.001 to 0.1. The analytical software normally includes tools in order to properly identify and analyze this linear section. However, even though the analysis of the linear BET section can be carried out, the assumptions of the BET model are no longer valid for adsorption processes in the smallest micropores. This is one of the reasons, why more or less severe differences can be observed when analyzing specific surface areas of microporous materials with BET or NLDFT methods. The main reasons are based in the founding theories of the analytical model. The standard BET method is assuming that adsorption takes place on a level surface with indefinite space for multi-layer adsorption. These properties are not given in microporous materials, since the curvature of cylinder pores becomes more distinct with smaller pore diameters. Independent of these and other shortcomings of the BET model for micropores, the BET analysis does not require a pore model and requires only a small number of measurement points, which are significant practical advantages making the method viable.

The strengths of the non-local density functional theory (NLDFT) lie in the calculation of pore size distributions and a unified analysis of micro- and mesopores. The NLDFT method takes the behavior of pore fluids at the analysis temperature in pores of variable diameters and thereby the thermodynamic properties of the adsorbate on a microscopic scale into consideration while also accounting for interaction between adsorbate and adsorbate as well as adsorbate and adsorbent. Furthermore, geometry and chemical composition of the adsorbent is also taken into account, thus considering its properties in the respective analysis kernels. On the other hand, the disadvantages of the DFT method are obvious if there is not a suitable evaluation kernel for the special materials available. It is very likely, that the DFT analysis when applied with a non-optimal kernel (for example assuming a certain pore geometry even though the pore geometry is uncertain or not well defined) will result in faulty results when calculating a specific surface area.

In practice this number of assumptions such as space requirements, chemical composition, pore geometry and others can lead to deviations between a surface area calculated by BET and NLDFT model. This leads to different applications of both models:
- BET surface area can be obtained by a minimum of effort and with small data sets. If data sheets are available, BET surface areas should be compared only to other BET surface areas and according to the criteria stated earlier in this text
- NLDFT analysis is an outstanding method for special reference materials. Calculated surface areas and their comparison with calculated BET surface area can yield additional information and give a better feeling about possible differences between the results of special reference materials.

Figure 3 illustrates the deviation of surface areas as a result of different analytical models.

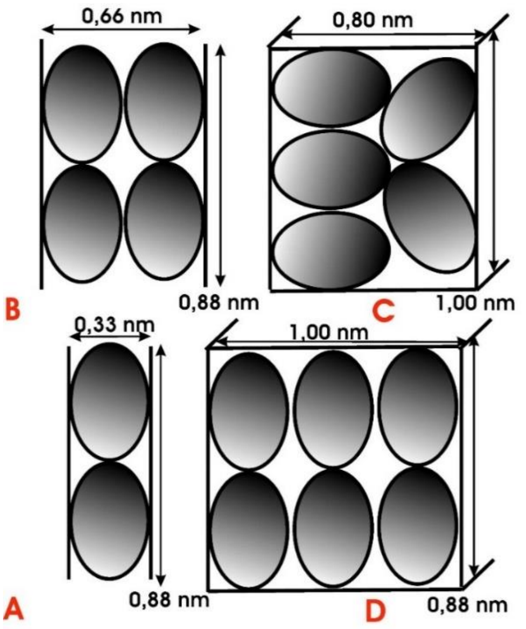

Figure 3 *Schematic representation of micropores with geometric arrangement of N_2 adsorbate molecules for estimating surface areas*

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Case A: It is assumed, that in a 0.33 nm cylinder pore two N_2-molecules on a length of 0.88 nm can fit. In this case, a simple surface area model is attributed to these two N_2-molecules with a surface area requirement of 0.162 nm^2 which results in a surface area of 2 x 0.162 = 0.324 nm^2. In case of an exact surface area determination from pore size data based on precise values of cylinder circumference x pore length = 3.14 x 0.33 nm x 0.88 nm = 0.912 nm^2, which is a value 2.8 times larger than the model suggests.

Case B: At a pore diameter of 0.66 nm and a pore length of 0.88 nm four N_2-molecules would fit. The calculation results in the same factor of 2.8, since both the number of molecules and the cylinders circumference have doubled: 4 x 0.162 nm^2 = 0.648 nm^2. With the BET model this results in a value of 3.14 x 0.66 nm x 0.88 nm = 1.824 nm^2.

Case C: In this case, a section from a cuboid is assumed – such as a slit pore in an activated carbon with the dimensions a = 1.00 nm, b = 0.80 nm and a depth of c = 0.33 nm. The pore is open on both ends, meaning the available surface area of the pore walls is 2 x 0.33 nm x 1.00 nm = 0.66 nm^2. The five N_2-molecules have a space requirement of 5 x 0.162 nm^2 = 0.810 nm^2, leading to a factor of only 0.81.

Case D: Similar to Case C a factor of 0.60 is obtained, even smaller than before and resulting from 2 x 0.33 nm x 0.88 nm = 0.581 nm^2 vs. 6 x 0.162 nm^2 = 0.972 nm^2.

Based on these factors the influence of the surface curvature and thus the pore width can be showcased and illustrates a special problem occurring in micropores, where the factor becomes larger with smaller pore sizes, when a portion of the pore cannot be filled with adsorbate due to the ratio of pore width and molecular diameter.

Conclusion

From a practical point of view, the different analytical methods for specific surface area determination can be employed individually or in parallel, as long as the calculated surface areas are not considered as absolute surface area values, but rather as a measure for surface area. A BET surface area is not an absolute true surface area in this sense, but rather a measure for the characterization of a specific surface area based on the BET equation for adsorption measurements. A NLDFT surface area is a value based on information from full isotherm data and thus a measure obtained from a specific analysis kernel under an assumed pore geometry. Sample comparisons should be relying on the same bases (e.g. analytical conditions such as adsorptive, temperature, pressure range) and the same model assumptions (such as space requirements of an adsorbate molecule and material characteristics). From a scientific point of view it is of course useful, to use analytical methods tailored towards a specific sample type in order to obtain results based on further developed models describing reality as best as possible. However, since there are no DFT evaluation kernels with comprehensible mathematical evaluations for many materials, the BET evaluation remains a useful method for sample comparison.

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