

# MICROTRAC

# MRB

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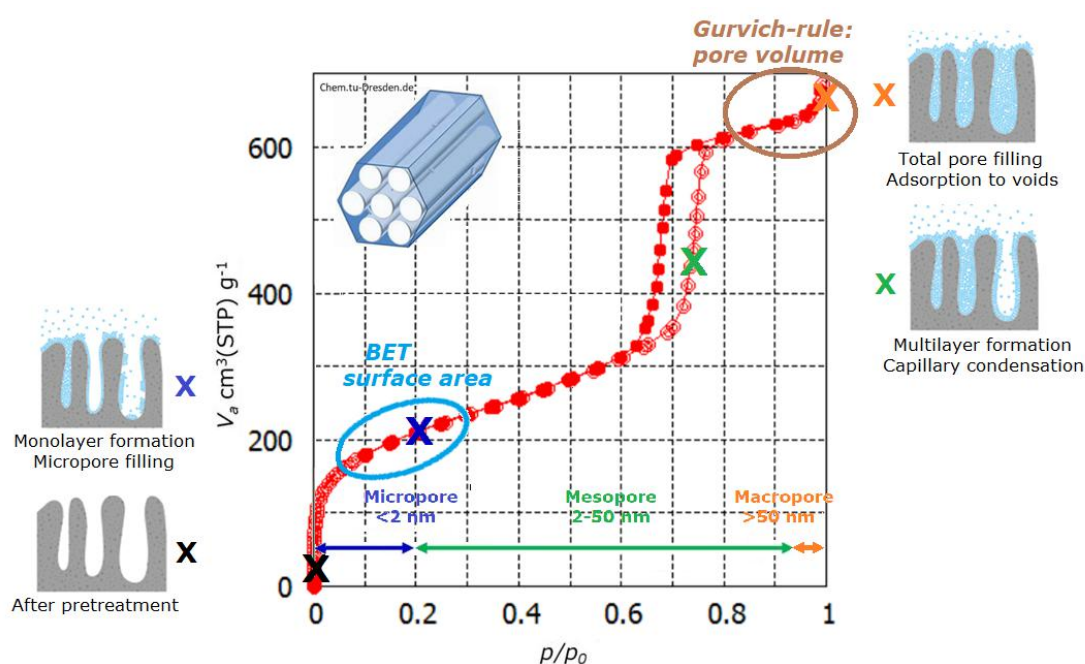
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Which information do we obtain from the adsorption isotherm?

## BELSORP instruments

The adsorption isotherm is known as the relation between the adsorbed amount onto an adsorbent and the equilibrium pressure of the adsorptive gas/vapor at constant temperature. The adsorbed quantity is shown on the vertical axis (STP: standard temperature 273.15 K, and pressure 101.325 kPa) and is commonly related to the dry mass of the adsorbent. The horizontal pressure axis is presented as absolute pressure above the critical temperature of the adsorptive or as relative pressure ( $p/p_0$ ;  $p$  = equilibrium pressure and  $p_0$  = saturation vapor pressure) below the critical temperature of the adsorptive.



**Fig. 1** Nitrogen sorption isotherm of mesoporous silica SBA-15 at 77 K

When analyzing sorption isotherms, the pressure is often given as relative pressure ranging from 0 to 1. Starting at a relative pressure close to 0 adsorption occurs onto the adsorbent. Formation of adsorbed multilayers can be accompanied by stepwise filling of micropores. At higher relative pressures capillary condensation occurs in the mesopores. At relative pressure of 1 the pores are filled completely with molecules and the saturated state is reached. Fig. 1 shows an exemplary nitrogen sorption isotherm of a mesoporous SBA-15.

In general, the sorption isotherm delivers information about the specific surface area, pore size distribution and pore volume. The specific surface area is commonly determined by the BET method (named after Brunauer-Emmett-Teller) for physisorbed gases, while the Langmuir surface area is preferred for chemisorption processes (e. g. catalysis). According to IUPAC recommendations the BET specific surface area can be calculated in  $p/p_0$  from 0.05 to 0.30.<sup>1,2</sup> Lower relative pressures can be used for microporous materials applying the Rouquerol-plot (see Application Note 3).<sup>3</sup>

Traditionally, the pore size distribution is evaluated depending on micro- or mesoporosity of the material. If mesoporous materials are expected BJH, DH, CI, INNES plots can be used, while HK, SF, CY, MP plots are used for microporous materials. As shown in Fig. 1, the low relative pressure range starting from  $1 \times 10^{-8}$  to  $\sim 0.2$  gives information about the micropores from 0.35 nm up to 2 nm. Further,  $p/p_0$  from  $\sim 0.20$  to  $\sim 0.96$  deliver information about the mesopores (2-50 nm) by the capillary condensation theory. Herein, a high increase in adsorption amount is observed at a relative pressure range from  $10^{-6}$  to 0.1 and around 0.75, confirming the presence of micro- and mesopores. The macropores can be analyzed in the relative pressure range starting from  $\sim 0.96$ , respectively pores from 50 up to 500 nm can be determined.

In recent years, NLDFT (Non-Localized Density Functional Theory) and GCMC (Grand Canonical Monte Carlo)- method from the computer simulation have been developed as the evaluation method of pore size distribution of porous materials. NLDFT / GCMC- method can analyze from micropores to mesopores as a unified theory, which is an advantage compared to other pore size analysis theories. Also, the accuracy of micropore size analysis is improved by these theories.

Finally, the pore volume can be analyzed. The simplest way to get porosity information from nitrogen sorption isotherms is using Gurvich-rule.<sup>4,5</sup> It is assumed that the adsorbed amount at the limiting horizontal plateau of an isotherm is like the total adsorption capacity.

$$V_{total} = \frac{V_{STP} \cdot M \cdot p}{\rho \cdot R \cdot T} = V_{STP} * 1.547 * 10^{-3}$$

$V_{total}$	= total pore volume
$V_a$	= adsorbed volume of nitrogen
$M$	= molar mass of nitrogen molecule
$p$	= pressure at STP
$\rho$	= density of liquid nitrogen
$R$	= gas constant
$T$	= temperature at STP

This means, the total pore volume at relative pressure of 0.95 ( $V_a = 650 \text{ cm}^3/\text{g}$ ) is about  $1 \text{ cm}^3/\text{g}$  for the shown SBA-15 in Fig. 1. Further, the pore volume can be differed in micro-, meso- and macropores by the t-plot.<sup>6</sup> The upon mentioned analysis methods will be discussed in the following Application Notes in detail.

<sup>1</sup> M. Thommes, K. Keneko, A. V. Neimark, J. P. Oliver, F. Rodriguez-Reinoso, J. Rouquerol and K. S. W. Sing, Pure Appl. Chem. 2015, 87, 1051-1069

<sup>2</sup> Calculation of BET surface area is explained in AppNote 2

<sup>3</sup> J. Rouquerol, P. Llewellyn, F. Rouquerol, Stud. Surf. Sci. Catal. 2007, 160, 49-56

<sup>4</sup> L. Gurvich, J. Phys. Chem. Soc. Russ. 1915, 47, 805

<sup>5</sup> J. Rouquerol, F. Rouquerol, K. Sing, Adsorption by powders and porous solids, Academic Press, London 1999.

<sup>6</sup> C. Lippens, B. G. Linsen and J. H. de Boer, J. Catal., 1964, 3, 32-37 and J. H. de Boer, B. C. Lippens, B. G. Linsen, J. C. P. Broekhoff, A. van den Heuvel and T. J. Osinga, J. Colloid Interface Sci., 1966, 21, 405-414.