APPLICATION NOTE

MICROTRAC MRB

PARTICLE CHARACTERIZATION

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Evaluation of low specific surface area by krypton sorption measurements at 77 K

BELSORP instruments

The characterization of low specific surface area materials, such as non-porous metallic materials, glass substrates and films, with traditional gases like nitrogen (77 K) and argon (77 K or 87 K) is insufficient due to detection limits. Alternatively, krypton gas adsorption can be used at liquid nitrogen temperature to determine the BET-specific surface area.

Normally, the adsorbed quantity at a certain relative pressure (equilibrium pressure p/ saturation vapor pressure p0) is calculated using the following simplified equation:

(Adsorption amount) = (Amount of adsorbate introduced) - (Amount of adsorbate remaining without adsorption)

In case of low specific surface areas, the number of non-adsorbed nitrogen molecules in the void volume of the cell can be large compared to the number of molecules adsorbed on the surface. The end point of relative pressure commonly used for BET specific surface area evaluation for N2 and Kr at 77 K is 0.3 (N_2: ~30400 Pa /101325 Pa and Kr: ~100 Pa /331 Pa; cf. Table 1). If there is a material that adsorbs 50 Pa at a relative pressure of 0.3, the absolute pressure of N2 slightly changes from 30450 Pa to an equilibrium pressure of 30400 Pa. The change rate is bellow of 0.2%. In contrast, a pressure change from 150 Pa to 100 Pa results in a change rate of 33.3%. In low specific surface area materials, the change rate of pressure is crucial. Consequently, the use of Kr gas with low saturation vapor pressure is increasing the accuracy of measurement significantly. However, to measure low specific surface area using Kr gas, equipment with low leakage and outgassing, 1 torr pressure transducers and high vacuum pumps must be used (optional in BELSORP max, maxII and max G).

Table 1 Adsorption temperature, saturation vapor pressure, adsorption cross-sectional area and application area of different gases [1,2]

Gas	Adsorption temp. /K	Saturation vapor pressure /Pa	Cross-sectional area /nm²	Scope /m²
N_2	77	101325	0.162	1 or more
Ar	77	26664	0.166	0.1~10
Kr*	77	331	0.202	0.01～1
Xe	77	0.23	0.232	approx. 1 cm²
CO_2	298	$6.45x10^6$	0.216	Coal and activated carbon

*Kr is solid state at 77 K. The saturated vapor pressure is calculated from Clausius-Clapeyron equation as a supercooled fluid.

Fig. 1 shows the total surface area of a blank sample tube, α-alumina BAM-PM101, α-alumina BCR169 and carbon black (#3845; CB) on the horizontal axis and reproducibility on the vertical axis. The measurements are absolved on BELSORP max using a high-precision sample tube.

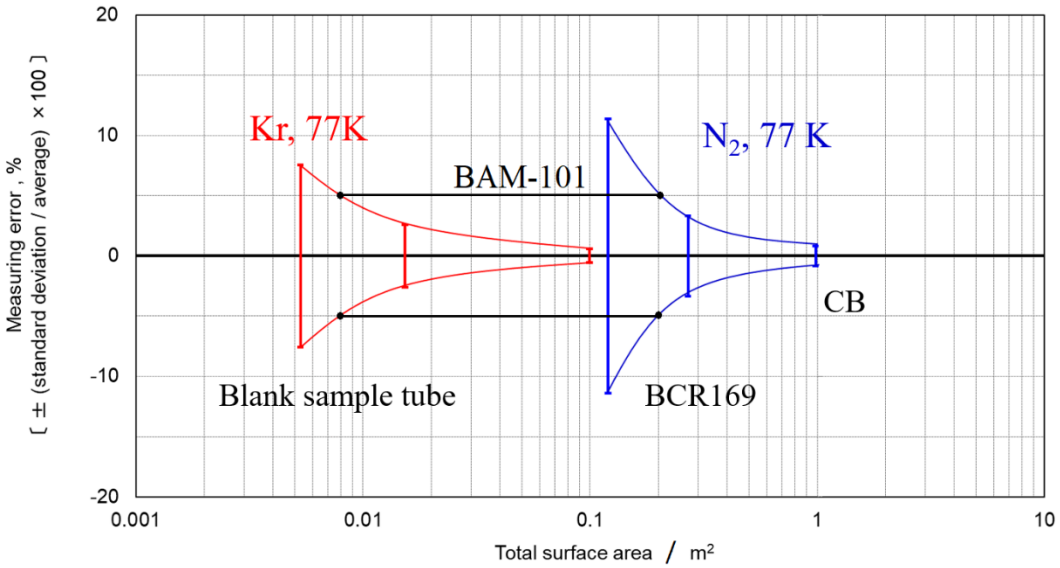

Fig. 1 Reproducibility of Kr sorption of 77 K BELSORP max

If sorption measurements with measuring error of less than 5% is desired, N2 adsorption measurements can be performed starting with total surface areas from 0.2 m² or more. However, Krypton sorption measurements with max. measuring error of 5 % can be obtained in total surface area range starting from 0.008 m². The results are consistent with Table 1.

[1] A. L. McClellan and H. F. Harnsberger. J. Colloid and Interface Sci. 1967, 23, 577
[2] ASTM D 4780-95