Evaluation of the specific surface area of activated carbon (Type I isotherm) by the BET method

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The Brunauer-Emmett-Teller method (shortly BET) is the most common method for the evaluation of specific surface areas. It is applicable to sorption isotherms Type II and Type IV and the evaluation is carried out in the relative pressure range p/p_0 from 0.05 to 0.30 as recommended by IUPAC.[1] Although this method is primarily not applicable to Type I isotherms, it is often used especially since Langmuir equation is not simply usable. The Langmuir equation is established for the specific case of chemisorption in a single layer in free contact with the gas phase. Further, it does not apply to composite isotherms such as Type I and II (microporous and external surface area) or Type I and IV (micro- and mesoporous surface area).

When evaluating the BET specific surface area in the standard pressure range recommended by IUPAC, the specific surface area is underestimated. Therefore, Rouquerol *et al.* expand the BET method to Type I isotherms developing a such called Rouquerol-plot. The maximum of this plot (blue-marked measurement point) shows the upper limit for BET surface area. All measurement values upon this limit should not be used for calculation of the surface area. Usually activated carbon and zeolite with micropores deliver Type I adsorption isotherms. In the following Fig. 1 the nitrogen sorption measurement (left) of activated carbon is shown. Also, the corresponding BET plot in the pressure range from 0.05 to 0.30 is presented (right).
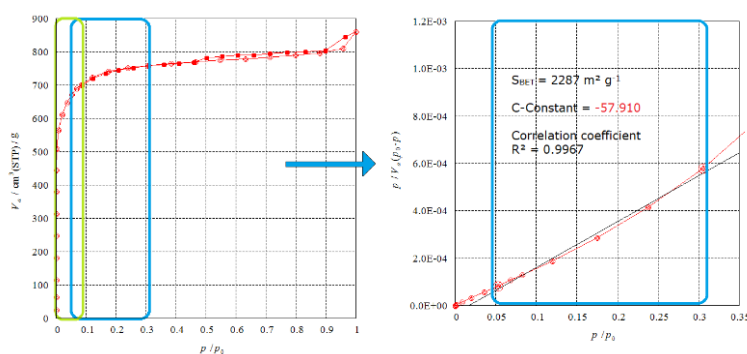
Fig. 1 Nitrogen sorption isotherm of activated carbon at 77 K pretreated at 573 K in vac. for 2 h (left) and corresponding BET-plot in standard relative pressure range

[1] 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
[2] J. Rouquerol, P. Llewellyn, F. Rouquerol, Stud. Surf. Sci. Catal. 2007, 160, 49–56.

In this case, the plot proposed by Rouquerol *et al.* for determining the relative pressure range can be applied to fulfill the criteria of the BET equation. This graph shows the relation between $V_a(p_0-p)$ to the relative pressure as shown in Fig. 2. The maximum value on the y-axis marks the end of BET range that can form a multilayer in the micropores. The BET-specific surface area is determined by taking the relative pressure determined by this method as the end point of BET plot. The lower point is selected as low as possible and with good linearity giving a positive C-constant. Herein, the BET surface area is calculated to be 2791 m²/g (C-constant: 3565.8; R²: 0.9998) and is much higher than the value determined in "wrong" pressure range (2287 m²/g; cf. Fig. 1).
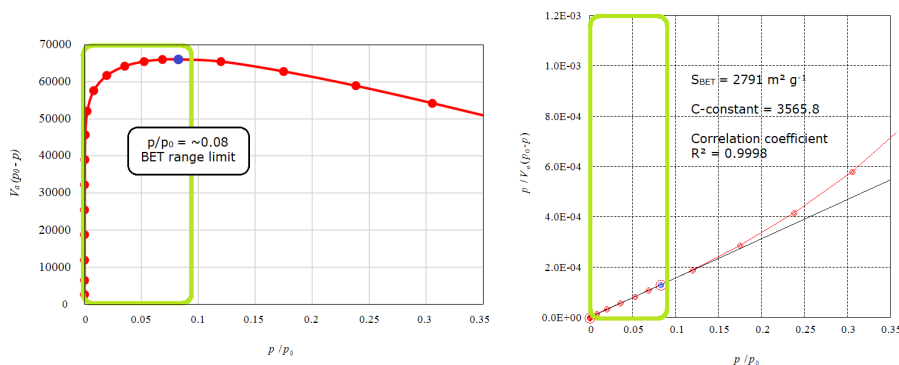

Fig. 2 Rouquerol-plot (left) and BET-plot of activated carbon in relative pressure range according to Rouquerol *et al.* (right)

This method is also described in Annex of ISO9277. Our analysis software BELMaster7 has a function that anyone can easily determine the BET range limit.

To activate the function, please run the following steps:

1.   Select isotherm

2.   Click on Analysis → BET plot

3.   Open BET plot → Settings → Analysis parameters settings

4.   Select Type I (ISO 9277)
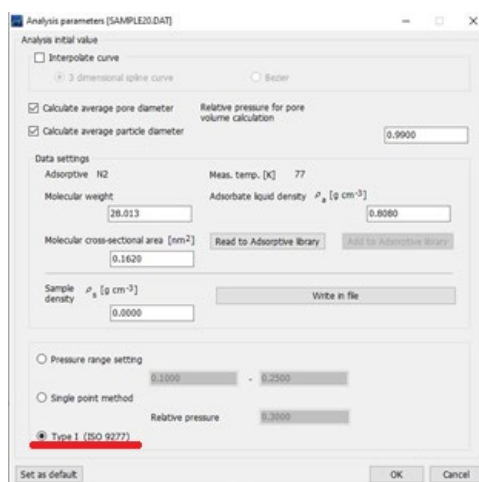
The BET range limit will be marked in blue as shown in Fig. 2 (right).