

Determination of the Specific Surface of Powdered Carbon by Small-Angle Scattering of X-Rays and Sorption Methods

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The specific surface of two activated charcoal samples was determined by the method of small-angle scattering of X-rays and the results were compared with the values of specific surface obtained by sorption methods. It was found that notwithstanding the great specific surfaces in systems with distinctly difform structures the results of both methods were in quite a good agreement.

The method of specific surface determination by small-angle scattering is based on the *Porod* theory of small-angle scattering of X-rays in closely-packed systems [1, 2]. According to *Porod*, the scattered intensity from such systems in a region of relatively higher angles („outer part“ of scattering curve) is inversely proportional to the third power of diffraction angle ϑ or distance of the measured point in scattering region from the centre of the primary beam m ($\tilde{I} = \tilde{k}/m^3$). By means of the constant \tilde{k} the inner specific surface of disperse phase in a binary system (in our case dispersion medium and disperse phase are air or carbon, respectively) may be calculated by using the expression

$$O_s = k \frac{w_2 \tilde{k}}{a \tilde{Q}}, \quad (1)$$

where a is the distance between the sample and registration plane; $k = 8\pi/\lambda = 16.32 \text{ \AA}^{-1}$ is a constant; w_2 is the volume fraction of dispersion medium; λ is the wavelength of the radiation used (for $\text{CuK}\alpha = 1.542 \text{ \AA}$); \tilde{Q} is the invariant of scattering curve. Moreover, it holds $O_s = O/V w_1$, where O/V and w_1 being the specific surface related to the volume of system and volume fraction of disperse phase, respectively. The quantity \tilde{Q} is defined by the integral

$$\tilde{Q} = \int_0^\infty \tilde{I} m \, dm. \quad (2)$$

It can be solved either by graphical integration (on assumption that the necessary experimental data are available) or by computation on the basis of relationship

$$\tilde{Q} = k P_s d a \Delta \sigma_{\text{el}}^2 w_1 w_2, \quad (3)$$

where P_s is the intensity of primary beam; d the thickness of sample; $\Delta\rho_{e1}$ is the difference between the electron densities of dispersion medium and disperse phase. The constant k is defined by the relation $k = (i_e/2\pi) \lambda^3 N_A^2 = 1.67 \times 10^{-2} \text{ mole}^{-2} \text{ cm}^6$, the symbols i_e and N_A denoting the Thomson factor and Avogadro constant, respectively.

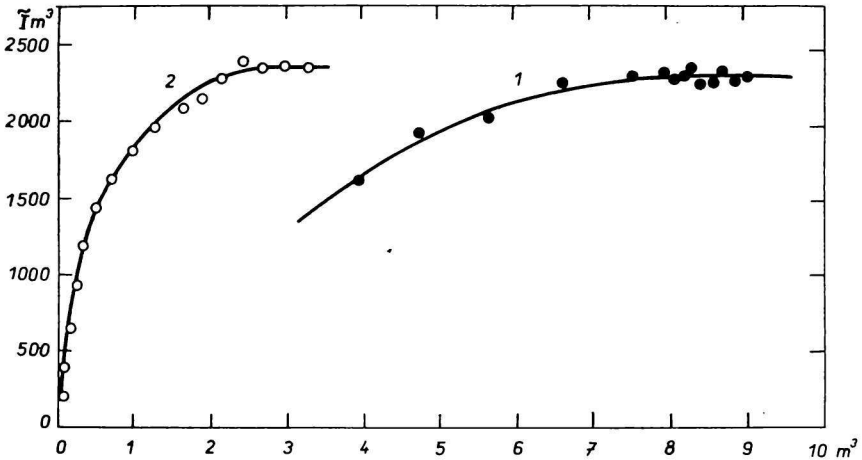


Fig. 1. Plot of the function $\tilde{I} m^3 = f(m^3)$; $[\tilde{I} m^3] = \text{imp min}^{-1} \text{ cm}^3$; $[m] = \text{mm}$.
1. 33; 2. G 1000.

The constant $\tilde{k} = \lim_{m \rightarrow \infty} (\tilde{I} m^3)$ in the expression (1) is to be found preferably from the plot $\tilde{I} m^3 = f(m^3)$ (Fig. 1). To determine the value of invariant by graphical integration, the graph of the function $\tilde{I} m = f(m)$ should be plotted.

A qualitative indicator of the particle irregularity of disperse phase is the factor f defined by the expression

$$f = \tilde{k} \tilde{E} \tilde{Q}^{-1}. \quad (4)$$

The quantity \tilde{E} given by the integral

$$\tilde{E} = \int_0^{\infty} \tilde{I} dm, \quad (5)$$

is to be estimated by graphical integration of the scattering curve. If the value of f equals approximately 0.5, it does indicate a regular, almost spherical form of scattering objects. For granular structure the value of f is equal to one or a little more. A rather higher value of the factor f indicates a fibrous or sheet structure [3].

Experimental

A Kratky-camera [4–7] and $\text{CuK}\alpha$ radiation filtered through Ross difference filters [8] were used for fixing the scattering curve. A powdered specimen was placed in a capillary with the inside diameter of about 1 mm the volume of which was determined by

means of mercury. The intensity of scattered radiation was measured by means of a Geiger—Müller-counter recording the number of impulses per minute. The intensity „impaired“ by the effect of collimation \tilde{I} [9] was employed for calculations. The value of absolute intensity was obtained by use of a calibrated polyethylene plate Lupolen in accordance with the method of Pílz and Kratky [10, 11]. The plate was calibrated by means of a rotator [12]. Graphical integration was performed by use of a planimeter.

Parameters used

Specimen 33 — Voltage in X-ray tube 30 kV, intensity 20 mA, point focus, primary beam „infinitely“ screened, entrance slit 100 μm , counter slit 50 μm , the distance between specimen and registering plane $a = 185$ mm, the measurement of a single point (Ni and Co filter) for 10 minutes. Since only a region of relatively high angles was involved, it was not necessary to eliminate the scattering in the empty capillary which was constant in this region.

Specimen G 1000 — The parameters used were the same as with the specimen 33; entrance slit 150 μm , counter slit 75 μm . The scattering curves of both specimens are presented in Fig. 2.

To corroborate the values of specific surfaces obtained from small-angle scattering, the same values were measured by an independent sorption method. These measurements were carried out in three ways by using:

1. The relative dynamical method of thermal nitrogen desorption (MTD method) at the boiling temperature of liquid nitrogen, employing F-charcoal with $O_s = 581.0$ $\text{m}^2 \text{g}^{-1}$ as a standard [13].

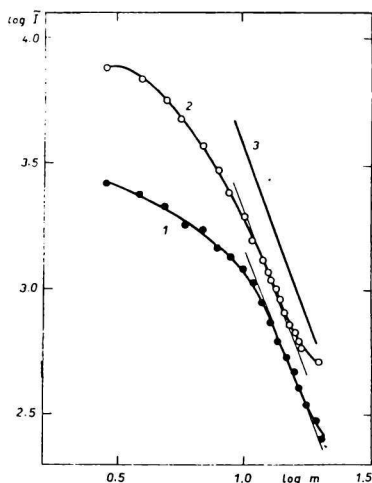


Fig. 2. Scattering curve $\log \tilde{I} = f(\log m)$.
1. 33; 2. G 1000; 3. $\text{tg } \alpha = -3$.

2. The instrument „Sorptomatic“ of C. Erba Inc. with nitrogen also at its boiling point [14]. The corresponding measurements were carried out in the Certified Checking and Testing Institute in Pardubice-Rybitví.

3. The static method employing a spiral sorption balance and benzene at 20°C ($\omega = 41$ Å) according to BET [15].

Results and Discussion

A survey of values of the quantities necessary for the evaluation of specific surface by the method of small-angle scattering is given in Table 1. The results of specific surface determinations by both small-angle scattering and sorption methods are summarized in Table 2.

Table 1

Quantities necessary for the calculation of specific surface by small-angle scattering method

Specimen	G 1000	33
d	0.105 cm	0.100 cm
w_1	0.1817	0.0972
w_2	0.8183	0.9028
ρ	1.904 g cm ⁻³	2.283 g cm ⁻³
ρ_{el}	0.952 mole cm ⁻³	1.141 mole cm ⁻³
\tilde{P}_a	1.904×10^6 imp min ⁻¹ cm	1.901 imp min ⁻¹ cm
\tilde{k}	2350 imp min ⁻¹ cm ³	2300 imp min ⁻¹ cm ³
\tilde{Q}_{theor}	8315 imp cm ² min ⁻¹	6714 imp cm ² min ⁻¹
\tilde{Q}_{exp}	7800 imp cm ² min ⁻¹	4800 imp cm ² min ⁻¹

Table 2

Comparison of the results of specific surface determination from small-angle scattering with the results of adsorption methods

Specimen	Adsorption methods [m ² g ⁻¹]			Small-angle scattering method [m ² g ⁻¹]	
	MTD	Sorptomatic	Sorption balance	\tilde{Q}_{theor}	\tilde{Q}_{exp}
33	1605	1424	1392	1195	1617
G 1000	1277	1152	1300	1071	1142

In case of both specimens large specific surfaces are involved. The small-angle scattering the intensity of which is inversely proportional to the third power of diffraction angle thus occurs in the region of relatively high angles what is advantageous in view of graphical solution of the integral (2). The scattering curve could be measured in a relatively broad interval involving the region of smaller angles what enabled us to get the points of invariant plot before its maximum and to extrapolate it without difficulties to zero (Fig. 3). On the other hand, the extrapolation to infinity was more difficult since the last available experimental data were relatively high and their extrapolation was not unambiguous. For this reason, the scattering curve $\tilde{I} = f(m)$ the course of which was unambiguous in this region was extrapolated to higher angles. The intensities thus obtained were used for the calculation of invariant points presented in Fig. 3 and marked with small triangles. This procedure enabled us to find out the character of the curve course what resulted in an essentially better

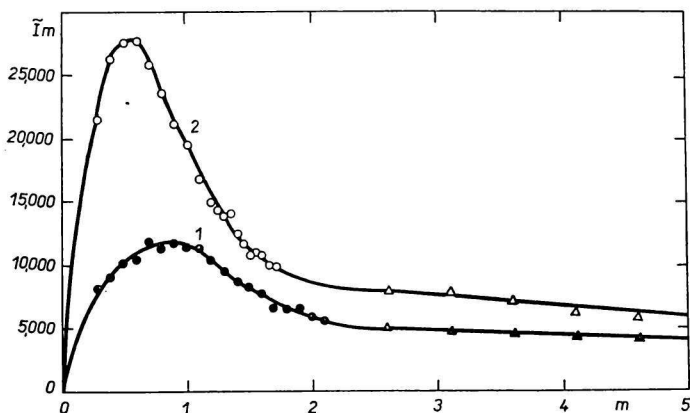


Fig. 3. Plots of the invariant integral $[\tilde{I} m] = \text{imp min}^{-1} \text{ cm}$; $[m] = \text{mm}$.
1. 33; 2. G 1000.

extrapolation. The difference between the invariant values which were calculated and found by graphical integration was due to the fact that only a part of disperse phase effected scattering in an experimentally observable region, whereas the other part (too large and too small particles) caused scattering in extreme regions. In our case about 71% of the specimen 33 and about 94% of the specimen G 1000 scattered in an experimentally observable region. This portion is defined by the ratio $\tilde{Q}_{\text{exp}}/\tilde{Q}_{\text{theor}}$. It is evident that the specific surfaces calculated by means of \tilde{Q}_{exp} are more likely to be true.

It may be assumed for both specimens that the value of the function (5) is equal. It is justified by the nearly identical intensity value for zero diffraction angle (values P_s) and for the graphical integration of practically negligible region given by the experimental curve in the range of higher angles. The obtained value of the integral (5) $\tilde{E} = 3 \times 10^4 \text{ imp min}^{-1}$ has enabled us to calculate the value of shape factor according to (4). It holds $f \doteq 3$ for the specimen 33 and $f \doteq 1$ for G 1000. The value $f_{\text{G 1000}}$ indicates a corpuscular (granular) structure while the value f_{33} indicates a lamellar structure of scattering objects what is in agreement with a greater value of the specific surface of this specimen.

In case of adsorption method the three measuring methods have given absolute differences of 181, 213 and $32 \text{ m}^2 \text{ g}^{-1}$ for the specimen 33 and 125, 23 and $148 \text{ m}^2 \text{ g}^{-1}$ for the specimen G 1000. The mutual agreement of these results is relatively good.

Since the MTD method is a relative one and the results may be impaired by the error of the specific surface of standard and the method involving benzene adsorption has a smaller importance and more limited validity for an accurate determination of specific surfaces, the values obtained with the instrument „Sorptomatic“ on the basis of nitrogen adsorption are most likely to be true. The specific surfaces calculated on the basis of small-angle scattering by means of \tilde{Q}_{exp} differ from those results by $247 \text{ m}^2 \text{ g}^{-1}$ in case of the specimen 33 and by $10 \text{ m}^2 \text{ g}^{-1}$ in case of the specimen G 1000. Considering the fact that these results have been obtained by two quite independent methods, the agreement is rather good.

The results achieved confirm the rightness and correctness of specific surface measurements by the small-angle scattering method.

Some authors [3] assume that the small-angle scattering method does not afford any sufficiently accurate values of specific surface for a rather lamellar or fibrous structure of disperse phase (in case of distinctly difform systems). Nevertheless, it has been found that even in such systems it is possible to obtain the specific surface values which are in a good agreement with the results of „classical“ sorption methods.

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