

# Determination of carbon porosity from low-temperature nitrogen adsorption data. A comparison of the most frequently used methods

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## Abstract

This paper compares the most frequently used procedures for carbon porosity determination, i.e. the Dubinin–Radushkevich, Dubinin–Izotova,  $t$  and  $\alpha_s$  plot, Horvath–Kawazoe (HK) and micropore analysis methods. The correlations between the obtained results are presented, and the importance of the choice of reference material for  $t$  and/or  $\alpha_s$  plot construction is displayed. It is concluded that only the HK method predicts smaller pore sizes. Our results show also that nitric acid oxidation of carbon and desorption in a flow of He in the temperature range 493–573 K leads to considerable changes in its porosity. However, for carbon previously oxidized and desorbed at 573 K, a pore-blocking effect occurs which probably results from the production of anhydrides in the carbon micropores.

**Keywords:** Activated carbon; Adsorption; Pore size distribution

## 1. Introduction

There are two main factors determining the adsorption properties of a microporous solid: its porous structure and the chemical composition of its surface. The aim of this paper is to compare the most popular and widely used methods of porosity determination based on low-temperature (77.5 K) nitrogen adsorption data,  $t$  and  $\alpha_s$  plots [1,2] and micropore analysis (MP) [3], and the Dubinin–Radushkevich (DR) [4], Dubinin–Izotova (DI) [5] and Horvath–Kawazoe (HK) [6] methods. Despite their wide use in the determination of the porosity of different adsorbents, there is a lack of papers comparing the different methods for the same carbon.

## 2. Experimental

Microporous activated carbons obtained from polyfurfuryl alcohol were investigated. The initial carbon (carbon A) was obtained by carbonization of polyfurfuryl alcohol and activation with carbon dioxide [7] ( $T=1123$  K, burn-off 29.7%), followed by annealing in a flow of hydrogen ( $1 \times 10^{-3}$  m<sup>3</sup> h<sup>-1</sup>) at the same temperature for one hour. The carbon was oxidized with nitric acid at 353 K for two hours (carbon B), and desorbed at 493 K under vacuum (carbon B 493). Table 1 shows the characteristics of carbons A and B 493 which were determined previously [8].

The surface concentration of the oxygen functionalities was determined by the Boehm method [9]. Pore volumes and surfaces were established by the procedure given recently by Dubinin [10].

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Table 1  
Carbon A and B 493 characteristics

	Carbon A <sup>a</sup>	Carbon B <sup>b</sup> 493
Surface acidity (mol NaOH kg <sup>-1</sup> )	0.098	1.577
Surface basicity (mol HCl kg <sup>-1</sup> )	0.462	0.166
Surface concentration (mol kg <sup>-1</sup> ) of:		
carboxyls	—	0.569
phenols	—	0.247
lactones	—	0.765
carbonyls	—	1.250
Total volume of micro and mesopores (cm <sup>3</sup> g <sup>-1</sup> )	0.440	0.373
Volume of mesopores (cm <sup>3</sup> g <sup>-1</sup> )	0.057	0.029
Volume of micropores (cm <sup>3</sup> g <sup>-1</sup> )	0.383	0.344
Total surface of mesopores (m <sup>2</sup> g <sup>-1</sup> )	32.60	32.10

<sup>a</sup> Activated carbon annealed in hydrogen at 1123 K.

<sup>b</sup> Carbon A oxidized using nitric acid and desorbed under vacuum at 493 K.

which uses Ar adsorption–desorption isotherm data measured at 77.5 K in a semi-automatic adsorption manostat.

Nitrogen adsorption isotherms at 77.5 K, presented in this paper, were determined using a Gemini 2360 (Micromeritics, Atlanta, GA, USA), an automatic volumetric adsorption apparatus. Both carbons A and B were desorbed for three hours in a flow of He, carbon A at 573 K, and carbon B at 493 (B 493), 523 (B 523) and 573 (B 573) K. The resulting adsorption isotherms are given in Fig. 1.

### 3. Results

#### 3.1. DR and DI analysis

According to the theory of the volume filling of micropores, an amount ( $W$ ) adsorbed at the relative pressure  $p/p_0$  (where  $p_0$  stands for the saturation vapour pressure of an adsorbate), is given by

the relation [4]

$$W = W_{0\text{ DR}}[\exp(-A/\beta E_0)^2] \quad (1)$$

where  $W_{0\text{ DR}}$  is the total micropore volume,  $A$  is the differential free energy of adsorption, and  $\beta$  and  $E_0$  are, respectively, the affinity coefficient and standard free energy of adsorption. According to Eq. (1) the plot of an adsorption isotherm in the coordinates  $W$  vs.  $\ln^2(p/p_0)$  (a so-called DR plot) should be a straight line. However, Fig. 2 shows that, for the investigated carbons, the DR plots demonstrate slight C-type deviation, according to Marsh and Randt [11]. It was established [12] that this type of deviation can be taken as the consequence of multilayer adsorption and capillary condensation in mesopores. Izotova and Dubinin [5] proposed the following equation for such DR plots (called here the DI equation):

$$W = W_{0\text{ DI}}[\exp(-A/\beta E_0)^2] + W_{1\text{ DI}}[\exp(-A/\beta E_1)^2] \quad (2)$$

in which  $W_{0\text{ DI}}$ ,  $W_{1\text{ DI}}$  and  $E_0$ ,  $E_1$  characterize the adsorption in the primary and secondary porous space. It was shown [13] that the second term of the DI equation is usually negligibly small compared with the first term.

On the basis of the theory of the volume filling of micropores, pore surfaces ( $S_{\text{DR}}$ ,  $S_{W_{0\text{ DI}}}$ ,  $S_{W_{1\text{ DI}}}$ ) and average pore diameters ( $L_{\text{DR}}$ ,  $L_{0\text{ DI}}$ ,  $L_{1\text{ DI}}$ ) were calculated according to semi-empirical relations recently proposed by Stoeckli [14]:

$$S_{\text{DR}} = W_0 N A_m \rho / M \quad (3)$$

$$L_{\text{DR}} = K / E_0 \quad (4)$$

where  $N$  is Avogadro's constant,  $A_m$  and  $\rho$  are the molecular area and the density of an adsorbate in the liquid state respectively (1.62 nm<sup>2</sup> [15] and 0.808 cm<sup>3</sup> g<sup>-1</sup> are usually used for nitrogen at 77.5 K), and  $M$  is the molecular weight of an adsorbate.  $K$  is a constant usually taken to be equal to 16.5 kJ nm mol<sup>-1</sup> [14], when  $L$  is in nm.

#### 3.2. $\alpha_s$ and $t$ plots

Fig. 3 shows  $\alpha_s$  plots for nitrogen adsorption on investigated carbons. They were constructed using carbon provided by Rodriguez-Reinoso et al. [16]

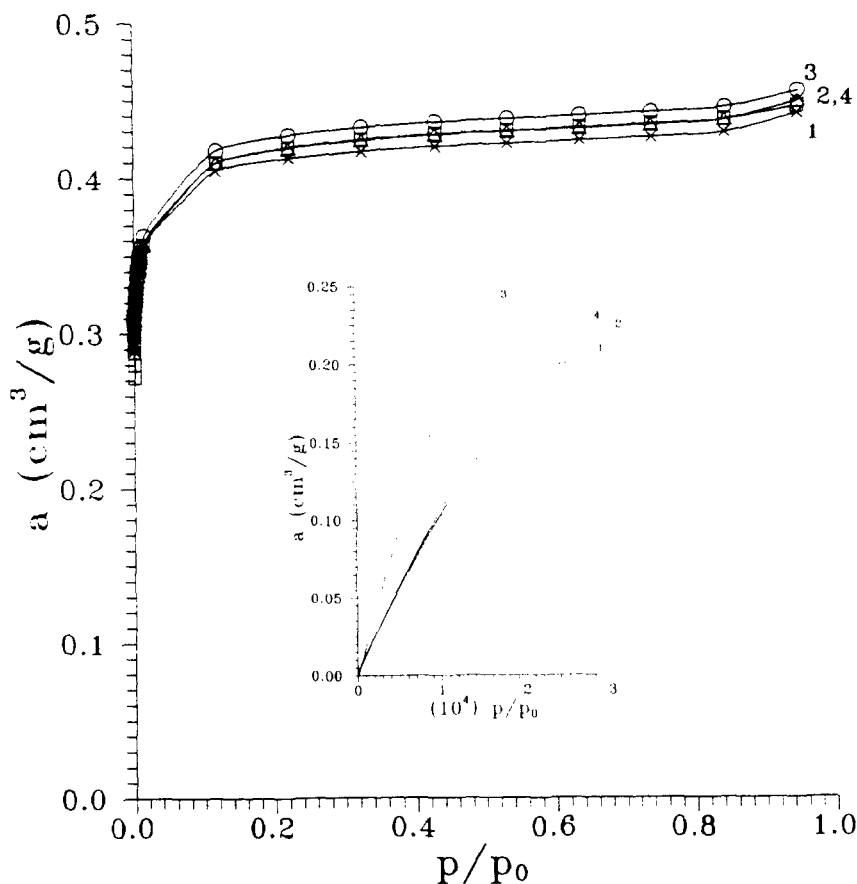


Fig. 1. Nitrogen adsorption isotherms at 77.5 K on A (1), B 493 (2), B 523 (3) and B 573 (4) carbons (low-pressure isotherms below  $5 \times 10^{-4} p/p_0$  were extrapolated).

as the reference material. The  $\alpha_s$  plots obtained can be classified as plots belonging to group (1a) following the classification of Selles-Perez and Martin-Martinez [17]. Such a type of  $\alpha_s$  plot was established for carbons with relative homogeneity and narrow porosity.

The external surface areas of carbons ( $S_{EX \alpha_s}$ ) were obtained from the  $\alpha_s$  plots by the relation [18]

$$S_{EX \alpha_s} = 60.76 dn_x / d\alpha_s \quad (4)$$

where the factor 60.76 was obtained by calibration against the BET surface area of the reference carbon [18], and  $n_x$  is the adsorbed amount in  $\text{mmol g}^{-1}$ . Pore volumes were evaluated by extrapolation of horizontal parts of the plots from Fig. 3 to  $\alpha_s = 0$ .

Taking the same carbon as the reference material,  $t$  plots were constructed following the relation [19]

$$t = 0.354 \alpha_s \quad (5)$$

where 0.354 is assumed to be the thickness ( $\text{\AA}$ ) of the unimolecular nitrogen layer in the micropores [1]. From the slope of the obtained  $t$  plots, the pore surface areas were calculated ( $S_{MP}$ ) according to the procedure of Mikhail et al. [3].

### 3.3. Pore size distributions

The MP and HK methods were applied to determine the pore size distributions. The resulting data are given in Figs. 4 and 5.

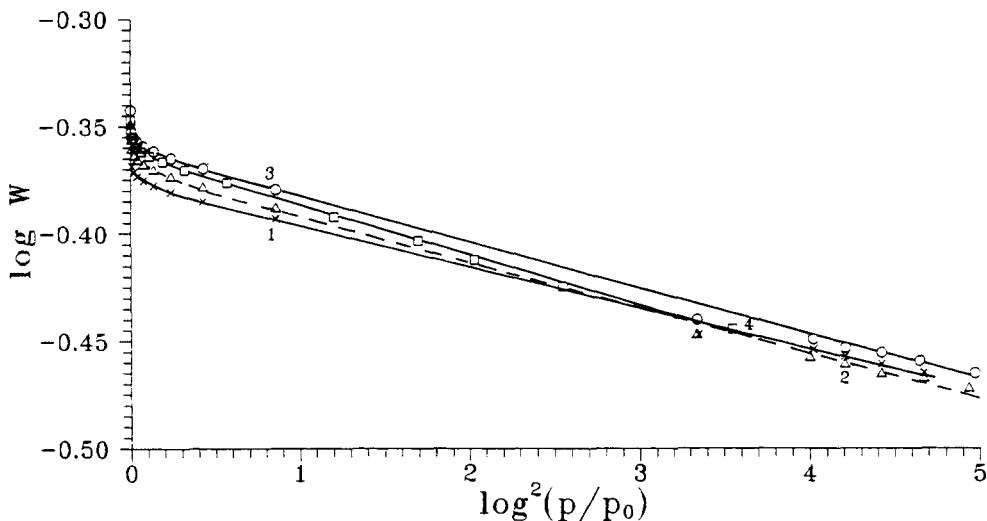


Fig. 2. Dubinin–Radushkevich plots for nitrogen adsorption at 77.5 K onto A (1), B 493 (2), B 523 (3) and B 573 (4) carbons.

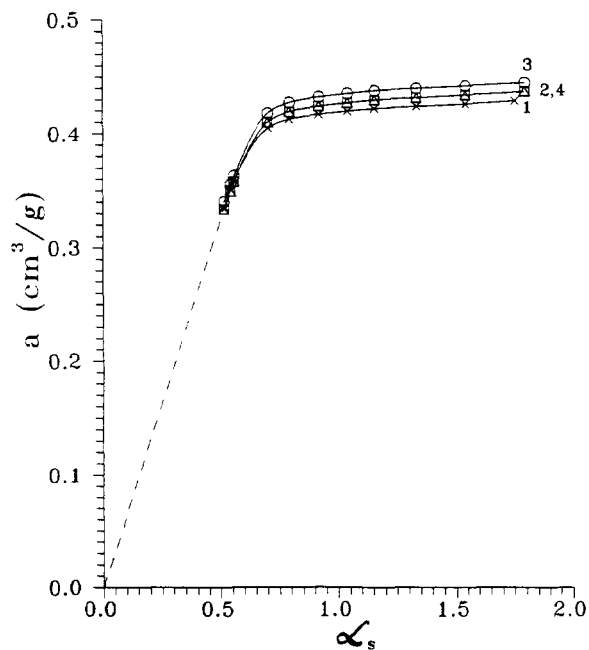


Fig. 3.  $\alpha_s$  plots of A (1), B 493 (2), B 523 (3) and B 573 (4) carbons.

#### 4. Discussion

Tables 2 and 3 summarize the results obtained using the methods described above and show the correlations existing between them.

The apparent surface areas given by the MP, DR, and DI methods are in good agreement, the best correlation existing between  $S_{MP}$  and  $S_{TOT DI}$  (Table 3). However, there are large differences between the apparent surface areas determined from the three methods and those calculated from the BET model. The lower apparent surface area given by the BET equation in comparison with the MP method is a consequence of the choice of the reference material for the construction of  $\alpha_s$  and  $t$  plots. It was suggested by Mikhail et al. [20] that for correct application of  $t$  plots, the reference material should have the same  $c$ -BET constant as the investigated material. However, IUPAC has recently recommended [21] that the standard isotherm should be obtained for the particular adsorption system and not by choosing a type II isotherm which happens to have the same  $c$ -BET value as the isotherm on a particular microporous solid. The  $c$ -BET values for the studied carbons (Table 2) are so large that it is practically impossible to find a reference material with the same surface chemical nature, and the same  $c$ -BET constant (for example, this constant for nitrogen adsorption on carbon blacks, which could be used as the reference material here, is in the range 100–285 [22]). Comparison of the external surface areas shows that there are differences (4–10  $m^2 g^{-1}$ ) between the areas calculated using the DI and  $\alpha_s$  methods,

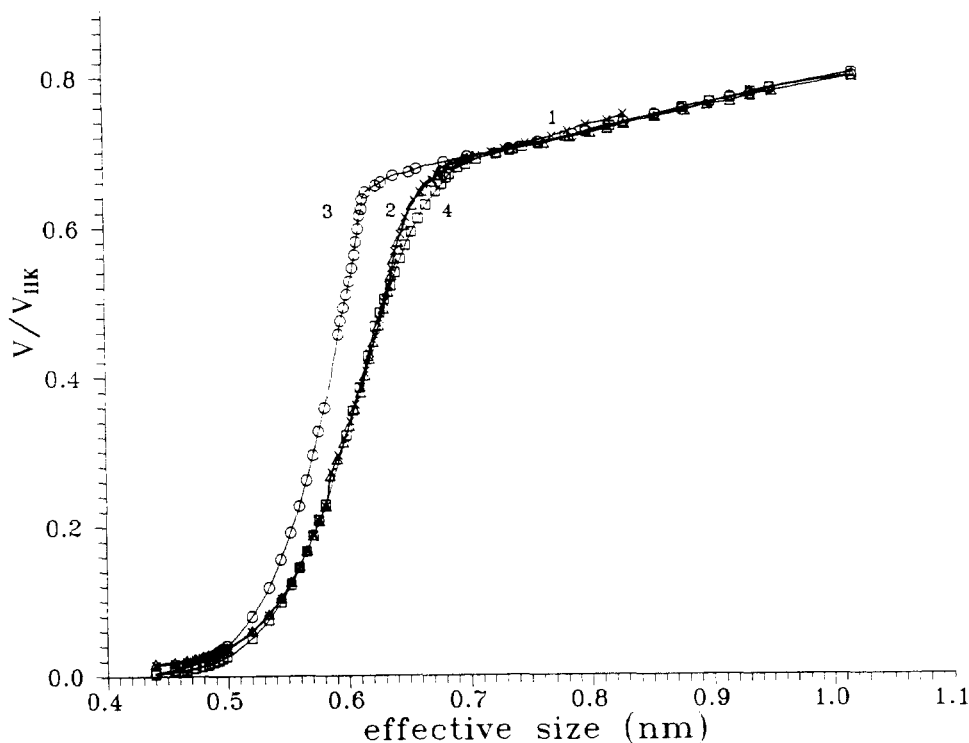


Fig. 4. Pore size distributions of A (1), B 493 (2), B 523 (3) and B 573 (4) carbons obtained using the Horvath-Kawazoe method.

and the method based on Ar adsorption-desorption data.

The total pore volume calculation from the DI equation revealed that the second pore volume is very small ( $0.01 \text{ cm}^3 \text{ g}^{-1}$ ) as suggested previously by Dubinin [13]. This effect provides good correlation between  $W_{0 \text{ DR}}$  and  $W_{\text{TOT DI}}$ , and causes the ratio  $W_{0 \text{ DR}}/V_{zs}$  to be nearly equal unity, as was expected from the shapes of  $\alpha_s$  plots [17]. Taking the second pore volume into account hardly changes this proportion (and results in nearly the same ratio  $W_{\text{TOT DI}}/V_{zs}$ ). The good correlation between  $V_{\text{MP}}$ ,  $W_{\text{TOT DI}}$ , and  $V_{\text{HK}}$  leads to the suggestion that the HK method assumes too high a micropore volume (it assumes that an adsorbent comprises only micropores). Taking this into account leads to the conclusion that the total pore volume should be diminished by the volume of mesopores as far as the accurate application of this method is concerned. Average pore diameter comparison reveals that only the HK method gives smaller effective pore sizes. This is hard to explain,

especially since this method only works in the range of pore diameters up to 1.4 nm [6]. It is clear that the HK method is the most sophisticated method because it is based on the statistical mechanics of gases adsorbed in slit-like micropores. However, it uses the Kirkwood-Muller formula which yields overly large dispersion energies [23] and, as was shown by de Boer, may give false results [24].

Besides the quantitative differences given by all the methods, qualitative results show that nitric acid oxidation of the carbon surface and gradual desorption in a flow of He lead to considerable changes in carbon porosity. Desorption in the range 493–523 K causes development of primary and secondary porosity. Table 2 shows that  $V_{\text{HK}}$  increases in this temperature range. However, it is noticed from Fig. 3 that pore size distributions of carbons A and B 493 are nearly the same. Because the results of the HK method are plotted as  $V/V_{\text{HK}}$  (where  $V$  denotes the pore volume filled with adsorbed nitrogen) vs. pore diameter, there must

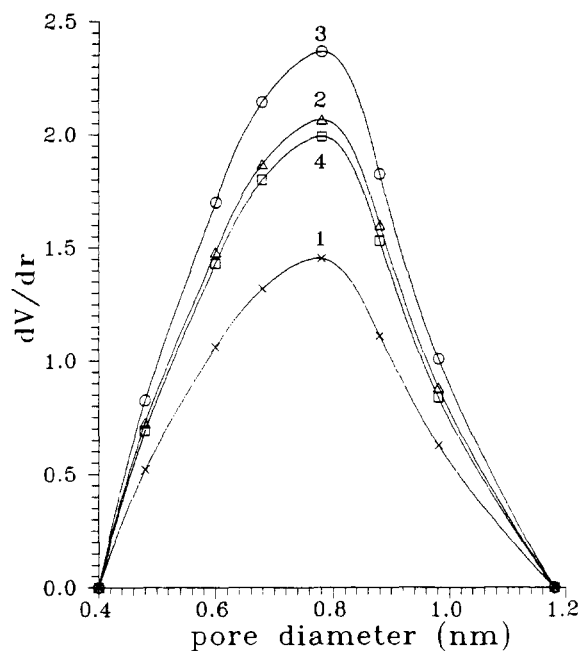


Fig. 5. Pore size distributions of A (1), B 493 (2), B 523 (3) and B 573 (4) carbons obtained on the basis of the MP method.

be an increase in carbon B 493 porosity. The same effect is shown by the DI and MP methods. Both of them reveal an increase in total pore volume, only including those pores with the same average diameter. For carbon B 523 the HK method exhibits the opening of very narrow pores, which does not confirm the theory of volume filling of micropores. All the methods used indicate that oxidized carbon desorption at 573 K causes the blocking of some pore entrances. This confirms the IR spectroscopy results [25,26], which suggest the possibility of cyclic acid anhydride structure formation in carbon micropores near this temperature.

## 5. Conclusions

The aim of this paper was to compare the most popular methods of carbon porosity determination from low-temperature nitrogen adsorption data. It is shown that the MP method — despite neglecting interactions between molecules adsorbed on opposing pore walls, and the increase in adsorption energy in the small micropores due to overlapping

Table 2

$c$ -BET values, surface areas ( $\text{m}^2 \text{g}^{-1}$ ), pore volumes ( $\text{cm}^3 \text{g}^{-1}$ ) and average pore diameters (nm) of investigated carbons obtained on the basis of methods described in the text

	Activated carbon			
	A	B 493	B 523	B 573
$c$ -BET	3455.90	3559.84	3539.60	3374.25
$S_{\text{BET}}$	1004.88	1001.63	1017.33	994.00
$S_{\text{MP}}$	1242.01	1285.10	1293.11	1269.02
$S_{\text{DR}}$	1193.16	1193.16	1210.74	1210.74
$S_{\text{W}_o \text{ DI}}$	1189.25	1198.14	1215.725	1206.83
$S_{\text{W}_i \text{ DI}}$	21.08	29.43	35.48	31.11
$S_{\text{TOT DI}}$	1210.34	1227.58	1251.29	1237.94
$S_{\text{EX } \alpha_s}$	123.16	24.21	23.67	23.73
$V_{\text{MP}}$	0.4131	0.4393	0.4488	0.4157
$W_{\text{O DR}}$	0.4242	0.4242	0.4304	0.4256
$W_{\text{O DI}}$	0.4228	0.4259	0.4322	0.4256
$W_{\text{I DI}}$	0.0075	0.0105	0.0126	0.0102
$W_{\text{TOT DI}}$	0.4303	0.4364	0.4448	0.4358
$V_{z_s}$	0.4080	0.4140	0.4244	0.4160
$V_{\text{HK}}$	0.4402	0.4481	0.4546	0.4447
$L_{\text{DR}}$	0.891	0.891	0.891	0.891
$L_{\text{O DI}}$	0.890	0.890	0.890	0.890
$L_{\text{I DI}}$	3.300	3.300	3.300	3.300
$L_{\text{MP}}$	0.780	0.780	0.780	0.780
$L_{\text{HK}}$	0.610	0.610	0.580	0.610

Table 3

Correlations existing between the porous structure parameters from Table 2

	Activated carbon			
	A	B 493	B 523	B 573
$S_{\text{MP}}/S_{\text{BET}}$	1.236	1.283	1.271	1.277
$S_{\text{MP}}/S_{\text{DR}}$	1.041	1.077	1.068	1.048
$S_{\text{MP}}/S_{\text{TOT DI}}$	1.026	1.047	1.033	1.025
$S_{\text{W}_i \text{ DI}}/S_{z_s}$	0.910	1.216	1.500	1.311
$V_{\text{MP}}/W_{\text{O DI}}$	0.960	1.007	1.009	0.954
$V_{\text{MP}}/V_{z_s}$	1.013	1.061	1.057	0.999
$V_{\text{MP}}/V_{\text{HK}}$	0.939	0.980	0.987	0.935
$W_{\text{O DR}}/V_{z_s}$	1.040	1.025	1.014	1.023
$W_{\text{TOT DI}}/V_{z_s}$	1.055	1.054	1.048	1.048
$W_{\text{O DR}}/V_{\text{HK}}$	0.964	0.947	0.947	0.957
$W_{\text{TOT DI}}/V_{\text{HK}}$	0.978	0.974	0.978	0.980
$L_{\text{DR}}/L_{\text{O DI}}$	1.001	1.001	1.001	1.001
$L_{\text{DR}}/L_{\text{MP}}$	1.142	1.142	1.142	1.142
$L_{\text{DR}}/L_{\text{HK}}$	1.461	1.461	1.536	1.461

wall potentials [27] -- gives results which are in good agreement with the Dubinin theory. However, the method is usable only when the reference material is chosen according to the IUPAC suggestion. Unfortunately, the application of this procedure gives differences between the BET and MP apparent surface areas. Despite the quantitative differences given by all the methods, qualitative results show that oxidation and gradual desorption lead to considerable changes in carbon porosity. The HK method predicts the smallest (by about 50%) pore diameters of all the methods.

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