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CHARACTERIZATION OF CARBON SORBENTS FOR ENRICHMENT STEP IN ENVIRONMENTAL ANALYSIS

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The thorough study on physico-chemical properties of carbon sorbents belonging to different groups of sorbents—activated charcoal, molecular sieves—Carbosieve S-III, Carboxen 1000; porous carbons—Carb I, Carb II; graphitized carbon blacks—Carbopack B, Carbotrap, Carbotrap C is presented in this paper. Measurements of the surface area, pore size and volume on the base of adsorption isotherms and pore distribution measurements, measurement of particle size and evaluation of particle shape by microscopy, searching the sorbent morphology by scanning electron microscopy, evaluation of the quality of surface by ¹H MAS- and ¹³C MAS solid-state NMR spectroscopy and elemental analysis were employed as means for the sorbent materials characterisation.

Gas-solid chromatography (GSC) has been utilised to determine the specific retention volumes at 20°C, V_g(20°C), and isosteric heat of adsorption, qst, for organic compounds belonging to various groups—n-alkanes, aromatics, halocarbons, oxygenated compounds. On the base of V_g(20°C) and qst the advantages and drawbacks of porous carbon sorbents in contrary to commercial kinds of sorbents for preconcentration purposes of volatile organic compounds in environmental analysis are discussed.

Keywords: Carbon sorbents; physical characterization; solid-state NMR spectroscopy; scanning electron microscopy; specific retention volume; gas-solid chromatography

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INTRODUCTION

The use of adsorbent tubes for sampling and preconcentration of organic contaminants in various environmental matrices (particularly air, water) has become increasingly popular as the consequence of the development of improved adsorbents, which allows for better adsorption and desorption of the contaminants. There are available various kinds of carbonaceous sorbents, which may be utilised for enrichment of analytes in environmental samples: activated carbon, molecular sieves, graphitized carbon black, porous carbon. The review on carbon sorbents and their utilisation to trace analysis of organic pollutants in environmental samples was published recently.^[1] Sorbents differ in physico-chemical characteristics, as pore size and shape; surface area; size, volume of pores; functionality of surface; chemical inertness. Kinetic and thermodynamic properties of carbon sorbents (breakthrough volumes; adsorption isotherms; equation of state; intermolecular interaction mechanisms occurring at the adsorbate/carbon sorbent interface) strongly influence the preconcentration and/or preseparation step. The extent to which these often conflicting characteristics can be achieved will be dependent upon:

- the type of starting material
- the procedure chosen for preparation of the product
- the conditions under which it is used.

Interest in preparation of the novel carbonaceous adsorbents has recently increased because of theoretically non-polar character of these materials, mechanical and thermal stability the possibility of using them over a wide pH range and better defined surface properties in comparison to *e.g.* activated carbon and organic polymers.^[2-4] This is connected also with the development of porous carbonaceous packings with the defined pores size. Generally, porous carbon sorbents are prepared by controlled pyrolysis of appropriate carbon precursors either soaked within the pores of silica gel or in the presence of suitable porogens. Silica gel and/or porogens which, in fact, form porous structure of carbon are leached out after pyrolysis.^[5-7]

Identification and characterisation of the physical properties of adsorbents are important in understanding their performance characteristics. There is not yet a powerful method available that gives an exact and detailed picture of the chemical species formed on the surface. Therefore, for study of a solid material it is advisable to employ more methods.

The use of gas-solid chromatographic techniques for the characterisation of adsorbents provides insight into the adsorbent characteristics.^[8] Using a small gas chromatographic column to evaluate interactions adsorbent/adsorbate allows

for quick and effective extraction data that can be applied to the reconstruction of a sampling tube with known sampling parameters. These interactions in the low coverage region provide information such as adsorbent surface homogeneity, adsorbate specific retention volume (or breakthrough volume), and adsorbent capacity for the chosen adsorbate.

Specific retention volumes which relate to the adsorbent capacity have been studied by several authors^[9-12] for a number of carbon sorbents. This specific retention volume value can be used in constructing an adsorbent tube that possesses known breakthrough characteristics for known adsorbent bed weights. However, to make intercomparison of sorbents on the base of the V_g value is complicated, as authors choose variety of adsorbates and in addition, some results of specific retention volumes are published at different temperatures.

Valuable information about the structural details of the surface of materials can be obtained with the help of solid-state NMR spectroscopy.^[13-15] NMR spectra of solid material measured with the routine equipment would only result in line width increase owing to dipole-dipole interactions and the anisotropy of the chemical shift tensor. Dipolar decoupling^[16] in combination with magic angle spinning (MAS),^[17] however, results in spectra that show resolutions comparable to those of high resolution spectra.^[18-20]

Evaluations of physico-chemical properties of sorbents and their suitability to trap organic compounds were in this contribution focused on calculation of specific retention volumes of selected compounds belonging to different groups of adsorbates, measurements of the surface area, particle size and shape of particles, pore size and volume, the searching of the sorbent morphology by scanning electron microscopy, evaluation of the quality of surface on the base of elemental analysis results and ^1H MAS- and ^{13}C MAS solid-state NMR spectroscopy.

Physico-chemical properties of a novel porous carbon sorbent were compared with commercial types of carbon sorbents—activated charcoal, carbon molecular sieves, graphitized carbon blacks (GCB). The advantages and drawbacks of porous carbon sorbents for preconcentration purposes in environmental analysis are discussed.

EXPERIMENTAL PART

Materials

The following sorbents were used during this study:

molecular sieves — Carbosieve S-III, Carboxen 1000 (Supelco, Bellefonte, PA, USA),

porous carbons — Carb I (Anapron, Bratislava, SK), prepared by controlled pyrolysis of saccharose in the matrix of silica gel^[21] performed at 600°C in an inert atmosphere. In the next stage silica gel was leached out by NaOH.

Carb II (Anapron, Bratislava, SK), prepared by controlled pyrolysis of cellulose beads in the presence of porogens,^[22] performed at 600°C in an inert atmosphere. In the next step the porogen was washed out.

graphitized carbon blacks—Carbopack B, Carbotrap, Carbotrap C (Supelco, Bellefonte, PA, USA).

Physical Characterisation

For electron microscopy experiments, the sample of sorbent was covered by a layer of Au and Pt in the Balzers/SCD 050 apparatus under vacuum conditions. The Tesla BS 300 scanning electron microscope was employed for observing the texture of sorbents at accelerating voltage of 15 kV and with the use of magnification in the range of 75-3000.

Adsorption isotherms were measured on volumetric apparatus according to Gregg and Sing^[23] using Ar as a sorbate at the temperature of 77.3 K. Surface area was calculated from adsorption data according to B.E.T. method.^[24] Pore volume was determined from adsorption at $p/p_s = 1$ (p —actual pressure of Ar, p_s —saturated vapour pressure of Ar). Pore size was calculated according to the modelless method of Brunauer-Mikhail-Bodor.^[25]

Elemental Analysis

Elemental analysis were done with a model 1104 CHN analyzer (Carlo Erba, Milan, Italy).

NMR Spectroscopy

All samples were measured by solid-state ¹H MAS- and ¹³C MAS NMR spectroscopy on a Bruker ASX 300 NMR spectrometer at 7.05 T equipped with a double bearing probe for rotors with 4 mm outer diameter. Quantities of 100 mg of each solid sample were packed into rotors of ZrO₂ which were spun at 10 kHz (for ¹³C NMR) and 14 kHz (for ¹H NMR), respectively, by dry air gas drive.

¹H MAS NMR experiments were performed using a single pulse excitation technique in combination with magic angle spinning (MAS) to reduce the homonuclear dipolare interactions. The 90° pulse length was 7 μs and the relaxation delay between two scans was 2s. 16 scans were accumulated to achieve an appropriate signal to noise ratio.

^{13}C MAS NMR experiments were carried out under MAS conditions using a single pulse excitation technique with high power proton decoupling during acquisition. Usually 4 K up to 20 K FIDs were accumulated with 90° pulse lengths of $7\ \mu\text{s}$ and the relaxation delay of 1s.

All chemical shifts were referenced to external liquid tetramethylsilane.

Gas-Solid Chromatography

Gas chromatographic measurements were performed on a HP-5890 Series II (Hewlett Packard, Avondale, PA, USA), equipped with an on-column injector, electronic pressure control and a flame ionisation detector. The carrier gas was hydrogen at a flow rate according to optimum of H_u curve (H —height equivalent of theoretical plate, u —linear velocity of carrier gas). The inlet pressure was 183 kPa, the column outlet pressure was measured to be atmospheric. Retention measurements were realised over the temperature range 150–420°C. The vapours of adsorbates were injected into the carrier gas stream by means of a $10\ \mu\text{L}$ Hamilton syringe in ng concentration level.

RESULTS AND DISCUSSION

Physical Characterization

The sorbents investigated are listed in Table I with detail description of electron microscopy observations and for having a possibility to view selected photographs some figure are presented. Chosen carbon molecular sieves are generally rigid spherical particles with homogeneous channel texture. The detail of the sorbent surface of Carbosieve S-III single particle is given in Figure 1a.

Scanning electron microscopy of porous carbons show that the particles have a sponge-like porous texture, the example of the view into a single particle of Carb I after its cracking is in Figure 1b. The shape of particles strongly depends both on a template and precursor used for preparation of sorbent. The example of the shape of Carb II is given in Figure 1c. The spherical form indicates that spherical cellulose was used as the precursor for pyrolysis in preparation procedure.

Graphitized carbon blacks are sorbents generally considered with insignificant porosity, math, irregular rounded particles. Similar picture of the surface of a single particle and the view into the particle after cracking indicates the homogeneous structure. In Figure 1d the picture of graining surface shows, that a single particle of the GCBs is composed of small particles arranged into aggregates.

TABLE I Summary of electron microscopy observations

Molecular sieves <i>Carbosieve S-III</i>	-microporous carbon with rigid, glistening perfect spherical particles -surface of a single particle with small inequalities uniformly laid out round the whole surface
<i>Carboxen 1000</i>	-particle after cracking, small flakes can be observed -ultramicroporous carbon, glistening, rigid, perfectly spherical particles -the surface of the particle is smooth, the structure is homogeneous, after cracking the same form of fragment surface at the same magnification was observed
Porous Carbons <i>Carb I</i>	-highly porous carbon, glistening, sharp-ended, hard but relatively brittle particles -particles with sponge-like porous texture similar to parent silica gel
<i>Carb II</i>	-after the cracking sharp-ended breaks can be seen -low porosity carbon, spherical particles with layer-arranged structure; the structure depends on the porogene used for sorbent preparation -cracks on the surface are formed during preparation (see in Figure 3) -inside—crater-like structure; with a reprint of crystals of not-dissolved porogenes
Graphitized Carbon Blacks <i>Carbopack B</i>	-almost non-porous carbon, insignificant porosity appeared above 40 Å (cylindrical pores assumed) -math, irregular, rounded particles, the surface of the particle is smooth -the view inside the particle after the cracking; small particles are arranged in aggregates
<i>Carbotrap</i>	-almost non-porous carbon, soft, matted irregular nearly spheroidal particles, -graining surface of a single particle, -some cracks between clusters of particles can be observed
<i>Carbotrap C</i>	-completely non-porous carbon, doesn't exhibit any adsorption-desorption hysteresis of non-polar gases, -rounded particles with graining surface of a single particle -after cracking the particle it can be seen, that the particles are homogeneous

The porosity of a variety of carbonaceous material forms ranges from highly porous active carbons to virtually non-porous GCB. Sorbents having a higher surface area per mass unit have a higher number of active accumulation media.^[1] The surface area can be increased by a porous structure of the sorbent. The factor of pore size is inversely proportional to the surface area. The pores should be as

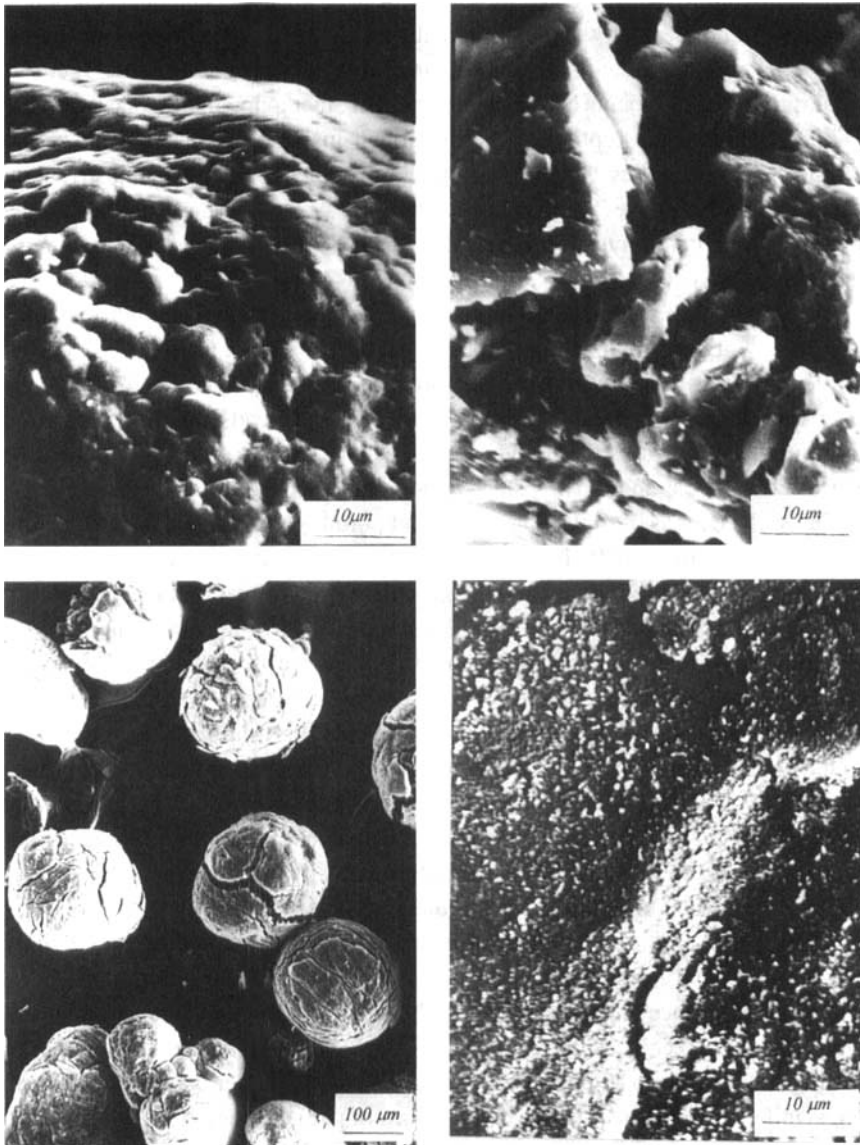


FIGURE 1 SEM of carbon sorbents a./ a single particle of Carbosieve S-III; magn. 1500 b./ a single particle of Carb I after cracking; magn. 1500 c./ Carb II; magn. 100 d./ a single particle of Carbopack B after cracking; magn. 1500

small as possible for effective accumulations, but the size of molecules should be taken into consideration not to hinder the molecules penetration within the pores. Therefore, beside pore size, the characteristic normally specified by the producer, also pores distribution is very important phenomenon for sampling and analytes preconcentration. In further step the choice of the sorbent depend on a compound volatility and molecular weight/size and the technique used for the preconcentration. The pore distribution of the studied sorbents can be seen in Figure 2. Adsorption measurements by the classical B.E.T. method with argon as a sorbate (77.3 K) leads to adsorption isotherms drawn in Figure 3. Surface areas and physical characteristics calculated from adsorption isotherms and distribution curves are summarised in Table II. Particle size and shape influence the hydrodynamic conditions in the bed of a sorbent and are related to the value of the surface area.

Molecular sieves according to their characteristics have a highly porous structure with almost uniform micropores. The pore size of Carb I, Carb II is in the region termed "mesoporous". The broader pore size range for Carb II—the distribution curve in Figure 2 is a broad peak—depends on the preparation procedure. In few cases the porogene used as a template to form pores could be not well dissolved and thus clusters of porogene can create larger pores.

The surface areas of molecular sieves and porous carbons are generally in 1 to 2 orders higher than GCB. This is connected with graphitization of materials that causes the material reordering and the growth of graphite crystallites, particles in which are arranged in the form of polyhedrons.^[26-28] GCB are almost non-porous material, however, a number of them in dependence to preparation treatment present some porosity, but the degree of porosity in comparison to other studied sorbents as we can see in the third column of Table II is minimally 4-times lower. In the case of Carbotrap high pore size values (80-300 Å) were measured, but the number of pores is small, what follows from pore volume (0.17 mL/g). The highest bulk density of Carbotrap C is in an agreement with non-porous character of sorbents and on the contrary the ultramicroporosity is the reason in the case of Carbosieve S-III. The value of pore volume was calculated from the point $p/p_s \approx 1$ of the adsorption curve, when all pores are filled by liquid Ar by capillary condensation and recalculated according to equation of state into mL/g.

Values of surface area determined in this study are more or less in agreement with Supelco specified values (see in Table II). Smaller surface area of Carbopack B in comparison to Carbotrap agrees with smaller pore volume. There are significant differences between the values of particles measured and specified by Supelco for graphitized carbon blacks—Carbopack B and Carbotrap (after recalculation 60/80 mesh into size of sieve opening is in mm equals to 0.250-0.177 mm; and 20/40 mesh is 0.841-0.420 mm).

Elemental Analysis

Results of CHN elemental analysis of samples are summarised in Table III. They were rather unusual, with the high deviation of analyses of the same sample. In the case of presence of metals in the samples the results of elemental analyses can

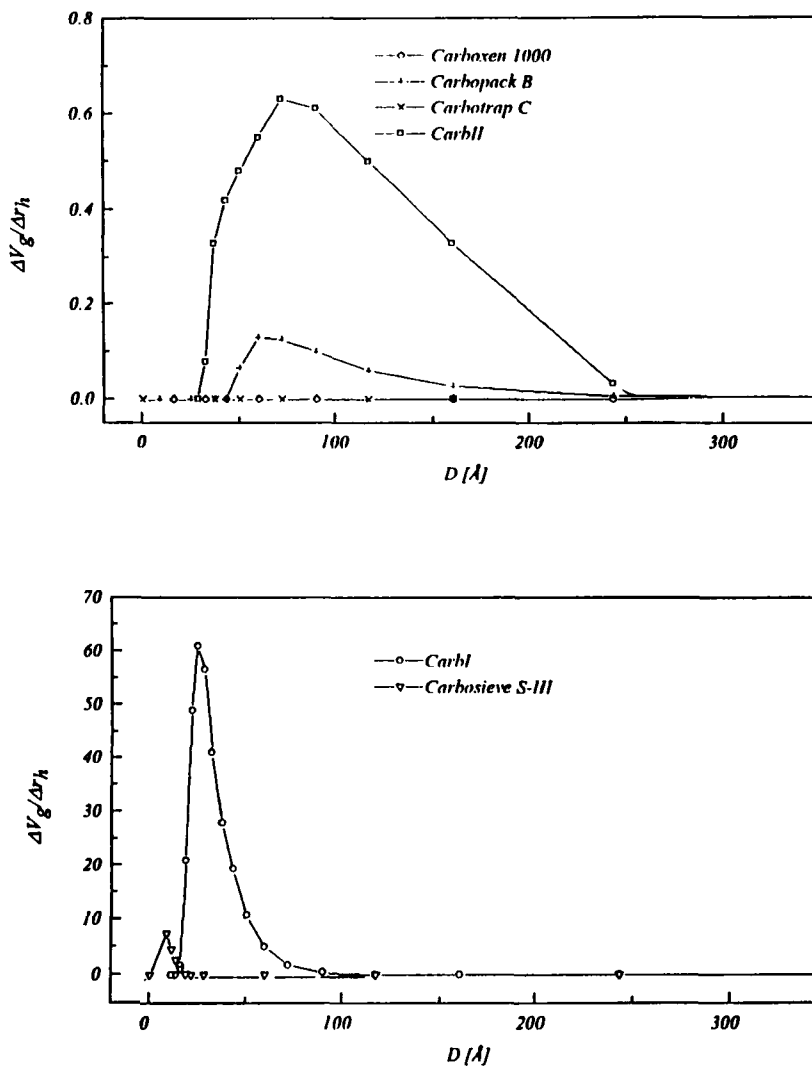


FIGURE 2 Distribution curves of pore size of sorbents. (D —pore diameter, V_g —volume of Ar, r_h —hydraulic modul)

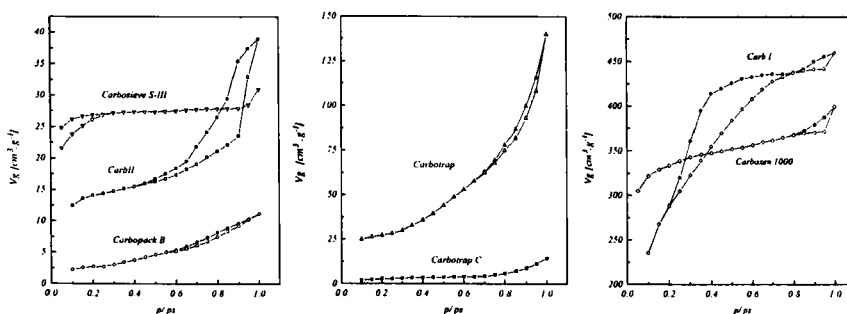


FIGURE 3 Adsorption isotherms of Ar on studied carbons (opened symbols = adsorption, full symbols = desorption). (V_g —volume of Ar, p —actual pressure of Ar, p_s —saturated vapour pressure of Ar)

get uncertain. This fact could explain the samples with a measured carbon content higher than 100%. In the case of these samples, particularly all studied graphitized carbon blacks, the presence of metals was observed by solid state MAS NMR, where the highfield-shifted signals in the ^1H MAS solid-state NMR spectra in the region between -2 up to -26 ppm were detected. These chemical shifts unusual for ^1H NMR signals are due to organometallic compounds and hydridometal complexes.

NMR Spectroscopy

All samples were investigated by ^1H MAS- and ^{13}C MAS solid-state NMR spectroscopy. The usually applied cross-polarisation experiment for the ^{13}C NMR measurements wasn't efficient in the case of these samples but as the relaxation time of the ^{13}C atoms was short enough we could use the direct excitation technique for the measurements.

All samples gave ^{13}C -NMR spectra with one very broad peak with maxim in the region between 110 and 135 ppm dependent on the sample. The region of these maxima is due to the resonance of olefinic or aromatic carbon atoms. Single resonance cannot be resolved in any spectrum. Differences could be seen in the signal to noise ratio, in the chemical shift of the maximum and in the line width of the peak.

Samples of Carb I and Carb II show similar ^1H - and ^{13}C -NMR spectra with similar chemical shifts, line widths and signal intensities. Typical results for ^{13}C NMR measurements are given in Figure 4. The maxima of the ^{13}C resonances appear in both spectra at 125 to 130 ppm, the signal intensities are relatively high

TABLE II Physical Characteristics of Adsorbents

Sorbent	Surface determined [$\text{m}^2 \cdot \text{g}^{-1}$]	area Supelco specif. [$\text{m}^2 \cdot \text{g}^{-1}$]	Pore volume [$\text{mL} \cdot \text{g}^{-1}$]	Bulk determined [$\text{g} \cdot \text{cm}^{-3}$]	density Supelco specif. [$\text{g} \cdot \text{cm}^{-3}$]	Particle determined [mm]	size Supelco specif. [mesh]	Pore size [Å]
Carbosieve S-III	940	820	0.377	0.71	0.61	0.2	60/80	8-16
Carboxen 1000	1340	1200	0.486	0.48	0.48	0.2	60/80	<15
Carb I	1020				0.560	0.24	0.05-0.16	18-90
Carb II	632				0.475	0.35	0.12-0.30	40-250
Carbopack B	86	100	0.136	0.41	0.38	0.6-1	60/80	>40
Carbotrapp	102	100	0.170	0.42		1-1.5	20/40	80-300
Carbotrapp C	9.6	12	-	0.83		0.5-1	20/40	-

TABLE III Elemental Analysis Results

Sorbent	% N	% C	% H
Carbosieve S-III	0	97.7	0.05
Carboxene 1000	0	94.7	0.14
Carb I	-	89.3	2.2
Carb II	0	94.1	1.8
Carbotrap	0	101.2	-
Carbopack B	0.03	100.7	-
Carbotrap C	-	101.6	-

in comparison to the other samples. In Figure 5 it can be seen, that the ^1H NMR spectra show a broad resonance at 7 ppm due to the presence of aromatic hydrogens. A shoulder at 2.5 ppm is also visible due to the remaining aliphatic rests.

The signal intensities of ^{13}C -NMR spectra of activated charcoal, Carbosieve S-III and Carboxene 1000 are similar and relatively small. All three samples show in the ^1H MAS NMR spectra resonance in the region between -2 and -6 ppm due to the presence of metalorganic compounds which can disturb the NMR signal intensity. Additionally, there are broad resonances in the region between 5 and 7 ppm which show the presence of olefinic and aromatic compounds.

The samples of Carbotrap and Carbotrap C gave only a very weak signal in the ^{13}C NMR spectrum. These samples contain no hydrogen, therefore this supports the idea that these samples consist mainly on graphite with a high amount of free electrons which destroy the NMR signal. A similar result was obtained in the case of Carbopack B. In this sample elemental analysis couldn't show any hydrogen too, but the ^1H -NMR spectrum shows a relative weak resonance. The interesting here is the chemical shift of this resonance: the peak appears in a region between -20 and -26 ppm. This extreme highfield shift can only be due to the resonance of metalhydrides (Figure 5c). This behaviour can also explain the result of elemental analyses (values over 100% of carbon) as the presence of metals with paramagnetic attributes. The presence of metal traces on GCB surface is a new finding which is contradictory to the general consideration on non-polar character of this sorbent.

To check the potential changes of sorbents in atmosphere (particularly the presence of the moisture) we made at least NMR spectra of Carb I, Carb II and of activated charcoal after 1 week exposure to air. The spectra did not show any changes or deviation. For illustration the repeated measurement of spectrum of Carb I after 1 week is given in Figure 4.

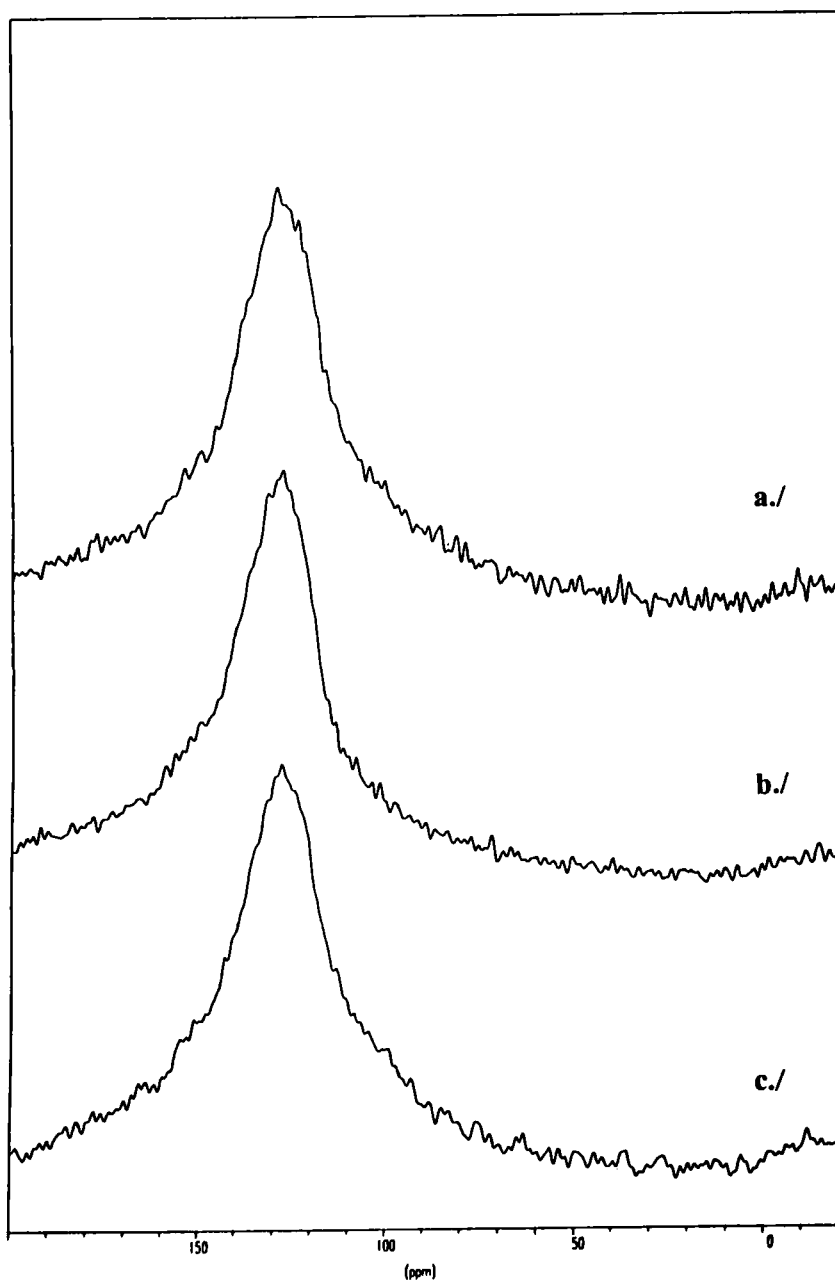


FIGURE 4 ^{13}C MAS NMR spectra of carbon sorbents a./ Carb I; b./ Carb II; c./ Carb I after 1 week exposition to air.

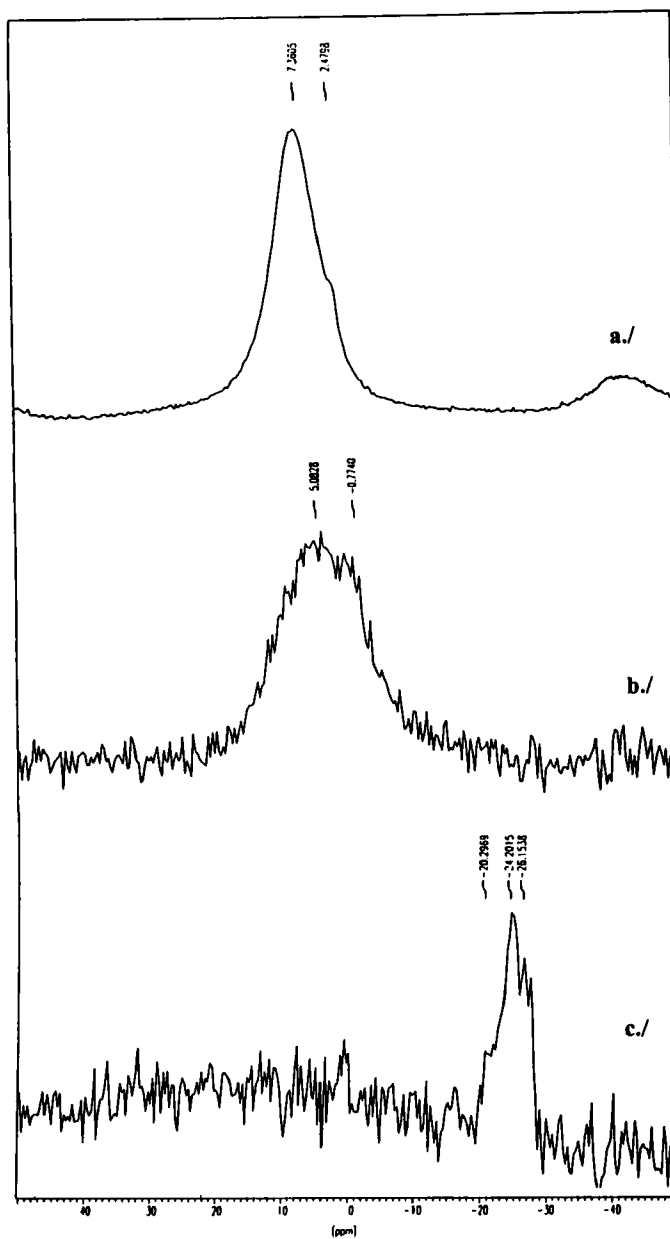


FIGURE 5 ^1H MAS NMR spectra of carbon sorbents a./ Carb I; b./ Carboxen 1000; c./ Carbopack B.

Gas-Solid Chromatography

The specific retention volume is the calculated volume of carrier gas, per unit mass of adsorbent, passing through an adsorbent bed that causes a "challenge slug" of adsorbate molecules to migrate from the front of the adsorbent bed to the back of the bed^[8]. The equation (1) for calculating V_g is as follows:^[29]

$$V_g = j \cdot F_a \cdot \left[\frac{T_c}{T_a} \right] \cdot \left[\frac{(t_r - t_a)}{W_a} \right], \text{ where } j = \frac{3}{2} \cdot \left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right]$$

V_g -specific retention volume,

j -pressure correction factor,

F_a -flow rate at ambient temperature,

T_c -column temperature,

T_a -ambient temperature,

t_r -peak maximum retention time,

t_a -dead volume retention time,

w_a -adsorbent weight,

p_i -inlet pressure,

p_o -outlet pressure.

After calculating retention volumes at least at 4 different temperatures usually higher than the trapping temperature, the specific retention volumes at 20°C were obtained by linear extrapolation of the graph $\ln V_g$ vs. $1/T$. The determined values of the specific retention volumes at 20°C for selected organic adsorbates are summarised in Table IV.

The agreement of measured and published values was checked on the example of chlorobenzene on Carbopack B (measured $1.89 \cdot 10^5$ vs. published $1.58 \cdot 10^6$ mL/g^[9] and $4.8 \cdot 10^5$ mL/g^[30]) and 1,2-dichloroethylene on Carbopack B (measured $2.7 \cdot 10^3$ mL/g vs. published $1.94 \cdot 10^3$ mL/g^[30]). When we take into account, that there are in all cases small differences in experimental conditions, there is an acceptable variance in results among different authors.

The isosteric heats of adsorption at zero uptake^[31] were determined from the variation of $\ln V_g$ on $1/T$ according to the equation (2):

$$q^{st} = R \cdot \frac{d(\ln V_g)}{d(1/T)}$$

q^{st} -isosteric heat of adsorption,

R -universal gas constant.

The derived values of q^{st} for Carb I and Carb II are listed in Table IV.

TABLE IV Specific retention volumes V_g and isosteric heats of adsorption q^s for selected organic adsorbates on Carb I and Carb II adsorbents

Adsorbate	M.W	V_g [mL/g] (CpockB)*	V_g [mL/g] (Carb I)	V_g [mL/g] (Carb II)	q^s [kJ/mol] (Carb I)	q^s [kJ/mol] (Carb II)
methanol	32.04		$5.6 \cdot 10^4$		38.8	
methylacetate	74.08		$1.3 \cdot 10^5$		39.2	
dichloromethane	84.93		$1.5 \cdot 10^5$		42.7	43.2
hexanal	100.16		$4.5 \cdot 10^6$		53.9	56.8
trichloroethylene	131.39	$1.27 \cdot 10^4$	$6.1 \cdot 10^6$		52.5	57.3
tetrachloroethylene	165.83		$5.7 \cdot 10^7$		58.7	53.1
hexane	86.18	$7.99 \cdot 10^4$	$6.4 \cdot 10^7$		62.4	62.0
1-octanol	130.23		$1.1 \cdot 10^8$		61.1	64.1
chlorobenzene	112.56	$1.58 \cdot 10^6$	$6.0 \cdot 10^8$		66.4	64.7
ethylbenzene	106.17	$2.03 \cdot 10^7$	$1.7 \cdot 10^9$		70.1	70.0
n-octane	114.23	$1.61 \cdot 10^7$	$4.0 \cdot 10^9$		74.2	77.1
n-decane	142.29	$4.79 \cdot 10^9$	$6.8 \cdot 10^{11}$		90.7	
n-dodecane	170.34	$1.63 \cdot 10^{14}$	$5.4 \cdot 10^{14}$		114.2	

*—values obtained from Supelco firm literature

It was found that under the employed experimental conditions, almost all studied compounds give symmetrical chromatographic peak, with specific retention volume independent on the amount of injected sample, with exception of few oxygenated compounds—*e.g.* 4-pentene-1-ol on both Carb sorbents. Therefore, values for 4-pentene-1-ol were not determined because of the irreproducible retention data.

It can be seen from the results in Table IV, that the specific retention volumes at 20°C on sorbents Carb I and Carb II generally increase with the increasing molecular weight in groups of adsorbates with similar chemical properties. Representative plots of the dependence $\ln V_g$ vs. $1/T$ for selected *n*-alkanes are given in Figure 6, for chlorinated compounds in Figure 7. It can be seen, that the higher is the molecular weight of *n*-alkanes, resp. halocarbons, the higher is the slope of the linear dependence.

The increase in differences of the q^{st} values on Carb I with the increase of the carbon atoms number of *n*-alkanes

$$nC_8 - nC_6 \quad 11.8 \text{ kJ.mol}^{-1}$$

$$nC_{10} - nC_8 \quad 16.5 \text{ kJ.mol}^{-1}$$

$$nC_{12} - nC_{10} \quad 23.5 \text{ kJ.mol}^{-1}$$

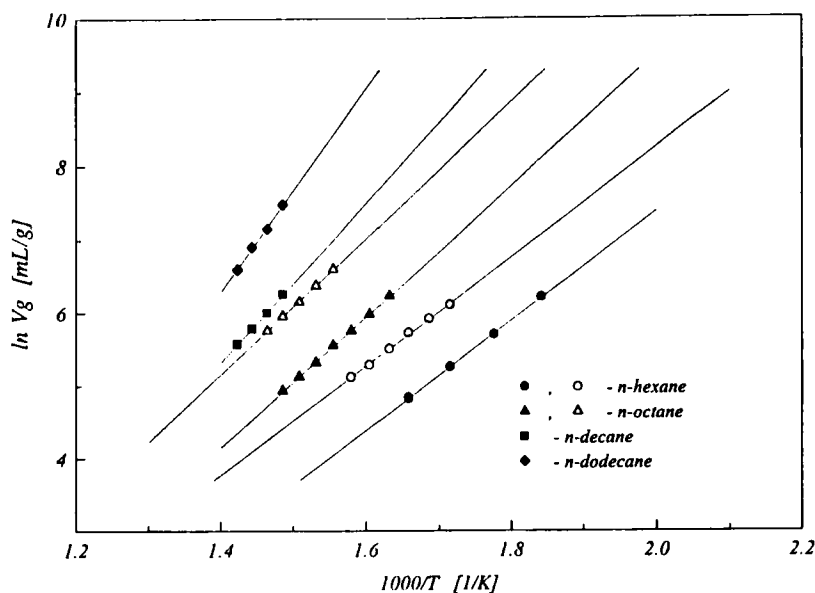


FIGURE 6 Dependence of $\ln V_g$ (V_g —specific retention volume) on $1/T$ (T —temperature) for *n*-alkanes on Carb I (full symbols) and Carb II (opened symbols).

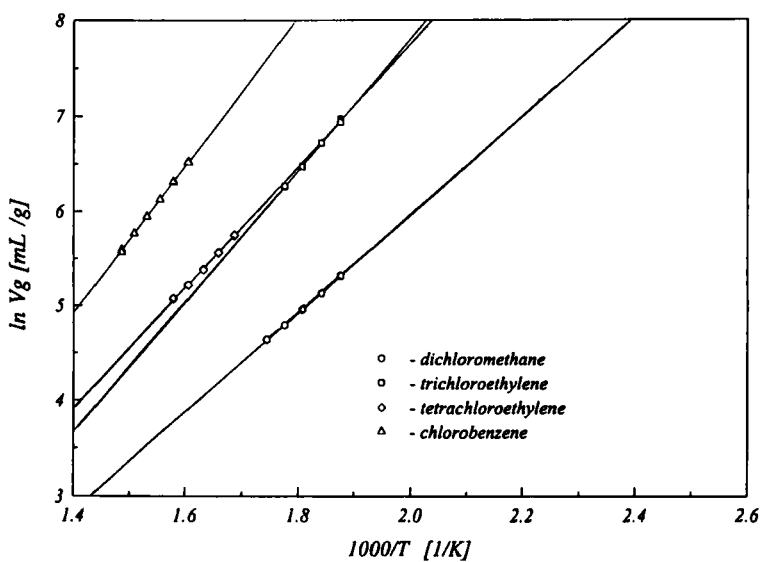
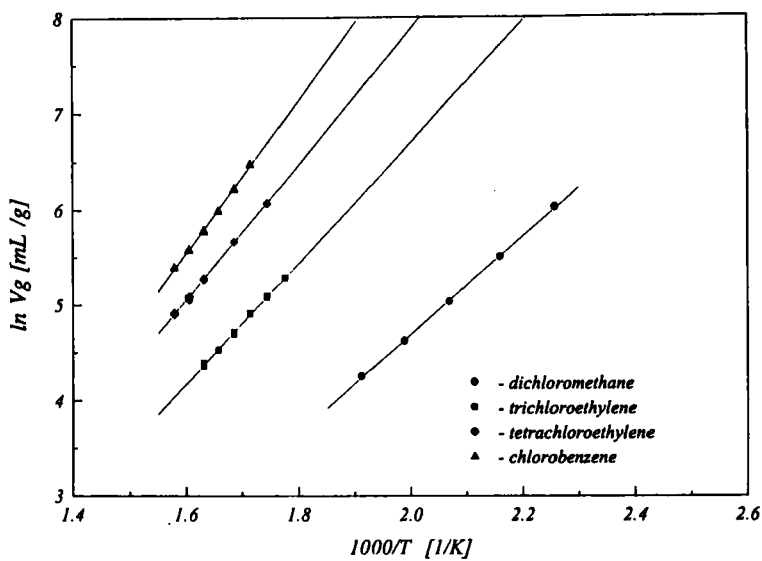


FIGURE 7 Dependence of $\ln V_g$ (V_g —specific retention volume) on $1/T$ (T —temperature) for selected chlorinated hydrocarbons on Carb I (full symbols) and Carb II (opened symbols).

indicates the enhancement in the adsorbent-adsorbate interaction energy. As the sorbent material is porous with pores in tens of Å, the release of longer molecules becomes more difficult and thus higher heats are observed. The length of n-dodecane 16.5 Å reaches the border of Carb I pore range. The values of q^{st} for n-alkanes measured on mesoporous sorbents are considerably higher than the corresponding values measured on GCB^[32] and lower than values given by microporous samples, e.g. the difference of isosteric heats measured on sorbent Carb I and the one on microporous carbon sorbent CCI^[33] for n-hexane is about 20 kJ.mol⁻¹.

The differences between q^{st} values for Carb I and Carb II respectively, are very small (max. $q^{\text{st}} = 5.6$ kJ.mol⁻¹, see Table IV), what is not surprising, because as it can be seen in pore distribution curves (in Figure 2) the range of pore sizes of both sorbents is overlapped in a broad range of 40-90 Å and the preparation treatment is very close for both sorbents. Thus, very similar adsorption/desorption behaviour is expected.

As it follows from NMR results, some functional groups are observed on the surface of porous carbon sorbents, so specific interactions with adsorbates mainly of polar character can take place. The FTIR study on porous carbonaceous sorbents^[6] also confirmed the mixed character of polar and non-polar groups and some of the chemical features of the starting materials are still present in the charred structures.

Owing to the presence of remaining some functional groups on the sorbent surface higher differences in adsorption heats (Table IV) are observed with sorbates possessing double bonds or oxygenated functional groups. That means, not only non-specific dispersion forces in both cases play a role in adsorption. This supports also the study of sorption-desorption process of the same compound, where lower recoveries were observed mainly for sorbates of slightly polar character.^[34]

According to classification scheme by Kiselev^[27], porous carbons can belong between the first and particularly the third class of adsorbents.

Mesoporous carbon sorbents are more advantageous in enrichment of volatile organic compounds from environmental samples over activated charcoal, as there is the possibility of tailor made pore size, therefore the choice of sorbent can be regulated by the molecule size of expected sorbates. The large surface area, defined pore size, chemical, mechanical and thermal resistance are the perspective properties of this sorbent. Due to its defined physical characteristics it can be used in sorption of organic pollutants from environmental samples for emission measurements and their subsequent liquid desorption, mainly by CS₂,^[35-37] but it was also successfully used for thermodesorption of volatile adsorbates^[34] at temperatures much lower than are temperatures necessary with

the use of activated carbons and the catalytic transformations and chemical changes of adsorbates to different products were not observed. The Carb I, Carb II retention characteristics show that the upper end of the functional range (the range of molecular sizes that can be trapped successfully, and than desorbed not at extremely high temperatures) in comparison to Carbotrap^[30] is similar. For Carbotrap and Carb I, Carb II sorbents, extremely large sample volumes may be used with adsorbates larger than n-decane, what follows from Table IV. On the other hand, the increase in molecular lengths results in an increase in the surface-to-surface interactions and for quantitative compound desorption it is necessary to utilise very high temperature. The lower end of functional range is broader than the one of Carbotrap and due to the large surface area Carb I covers a part of molecular sieves range. As the example can serve dichloromethane, which is typical adsorbate for studies on carbon molecular sieves and it was successfully trapped by porous carbon.^[34] The Vg (20°C) on Carbosieve S-III is $2.56 \cdot 10^5$ mL/g.^[8] The value on Carb I and Carb II (see Table IV) is of the same order. In few applications Carb I, resp. Carb II could replace the multibed sorbent tubes, particularly composed of Carbotrap/Carbosieve S-III.^[34]

CONCLUSION

The techniques of scanning electron microscopy, techniques based on the adsorption of vapours, elemental analysis, MAS NMR, GSC have assisted in understanding the physico-chemical properties of variety of carbonaceous materials. Adsorption isotherms and pore distribution were measured and physical characteristics as specific surface area, pore volume, bulk density, particle size and pore size were calculated. The target in GSC measurements was given to porous sorbents Carb I and Carb II.

The research in the area of porous carbon sorbents is a promising way, by the choice of an appropriate precursor and the treatment procedure to look for the sorbent without residual functional groups on the surface with inert, high purity surface, and this way to regulate the adsorption exclusively by non-specific interactions, to regulate the sorption under defined conditions, reproducibly under the repetitive use and to decrease the adsorption energy for quick desorption of the enriched compounds without decomposition by heating.

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