

Novel Porous Carbons and their Utilization in Trace Analysis

^aE. MATISOVÁ*, ^aS. HROUZKOVÁ, ^bI. NOVÁK, ^bD. BEREK, and ^cJ. KOZÁNKOVÁ

^a*Department of Analytical Chemistry, Faculty of Chemical Technology,
Slovak University of Technology, SK-812 37 Bratislava*

^b*Polymer Institute, Slovak Academy of Sciences, SK-842 36 Bratislava*

^c*Department of Ceramics, Glass, and Cement, Faculty of Chemical Technology,
Slovak University of Technology, SK-812 37 Bratislava*

Received 9 February 1998

The physicochemical properties of novel mesoporous carbon sorbents and their application for the preconcentration of trace analytes in combination with HRGC are presented. For sorbent evaluation, scanning electron microscopy, elemental analysis, ¹H MAS and ¹³C MAS solid-state NMR spectroscopy were applied together with measurements of the surface area, particle size and shape, pore size and volume, as well as with determination of specific retention volumes of selected compounds belonging to different groups of adsorbates. The tested sorbents showed high sampling capacities and were successfully applied to the preconcentration and/or isolation of great variety of volatile compounds and semivolatile compounds from simulated samples and various environmental matrices.

For the solution of analytical problems in the field of trace analysis, particularly in the analysis of multicomponent mixtures, various preconcentration and/or preseparation steps have been utilized according to sample matrix [1–14]. In environmental samples the target of qualitative and quantitative analysis may be either the whole trace multicomponent mixture in various matrices, or only individual trace component(s). In this regard the whole preconcentration/preseparation strategy differs substantially. Nowadays also materials with selective sorption properties are being utilized to a large extent for these purposes. Besides a broad spectrum of “universal” sorbents much attention is given to tailored sorbents which allow the optimum solution of a particular separation problem. Carbonaceous materials belong to potential sorbents for preconcentration/preseparation purposes [10, 11].

There are available various kinds of sorbents the matrices of which are prevalingly built of carbon:

- Microporous carbon – activated carbon
 - molecular sieves
- Mesoporous carbon – pyrolytic carbon
 - some forms of graphitized carbon black (*e.g.* Carbotrap B)
- Nonporous carbon – some forms of graphitized carbon black (*e.g.* Carbotrap C)

They differ in physicochemical characteristics, such as pore size and shape; pore volume, surface area; particle size and bulk density; functionality of surface; chemical inertness. The other characteristics of carbon sorbents, as breakthrough volumes, shape of adsorption isotherms strongly influence the preconcentration and/or preseparation step. These often conflicting characteristics are dependent upon: the type of starting material, the procedure chosen for preparation of the product, and the application conditions.

The development of carbon sorbents for enrichment of analytes has been connected with the development of chromatographic sorbents generally. Interest in preparation of the novel carbonaceous adsorbents has recently increased because of the theoretical nonpolar character of these materials, the applicability over a wide pH range, and better defined surface properties in comparison to sorbents commonly used in the past [15–17]. In our review article on carbon sorbents and their utilization to trace analysis we have shown the advantages of some kinds of carbon sorbents compared to conventional sorbents (organic polymers, bare and bonded silica gels, activated carbon) [11].

The use of different carbons (in a single bed arrangement) depends strongly on the applications but also on the techniques used. Depending on volatile, semivolatile or nonvolatile compounds, both the sor-

*The author to whom the correspondence should be addressed.

bents and the techniques are not the same. Different techniques do not require the same characteristics of the carbons. We have evaluated and classified the utilization of carbon sorbents and preconcentration techniques according to the phase state of an analyte during sorption and desorption processes [11].

Generally, porous carbon sorbents are prepared by controlled pyrolysis of appropriate carbon precursors either soaked within the pores of silica gel [18–21] or in the presence of suitable porogens [22]. Silica gel and/or porogens which, in fact, form porous structure of carbon are leached out after pyrolysis. The surface chemistry is determined by the final heat treatment and any subsequent chemical treatment.

In the following sections we present an overview on novel porous carbon sorbents developed in the Polymer Institute of the Slovak Academy of Sciences (already commercially available), on their physicochemical characterization and application to the preconcentration of volatile and semivolatile organic compounds from environmental matrices and their subsequent analysis.

EXPERIMENTAL

Porous Carbon Sorbents

Carb I was prepared by pyrolysis of saccharose in the matrix of silica gel [20] at 600°C in an inert atmosphere. In the next stage silica gel was leached out by NaOH.

Carb II was prepared by pyrolysis of cellulose beads in the presence of porogen [22] at 600°C in an inert atmosphere. In the next step the porogen was washed out by water.

Physicochemical Characterization of Carbon Sorbents

For the physicochemical characterization of carbon sorbents in the most cases commercial instrumentation was utilized [23]. Elemental analysis (model 1104 CHN analyzer, Erba) was used for the determination of carbon, hydrogen, and nitrogen in sorbents samples. Scanning electron microscopy of samples covered by a layer of Au and Pt (Tesla BS 300) and solid-state ^1H MAS and ^{13}C MAS NMR spectroscopy (Bruker ASX 300 NMR at 7.05 T) were applied to characterize sorbents surfaces. Gas-solid chromatography on a HP-5890 Series II (Hewlett—Packard) equipped with an on-column injector, electronic pressure control, a flame ionization detector and connected to a stainless steel column packed with the tested sorbents was used for measuring breakthrough characteristics of selected analytes. Sorbents surface area, pore volume [24], and pore size distribution [25] were calculated from Argon adsorption data measured on apparatus constructed according to literature [26].

Analytes Preconcentration and GC Analysis

Solid phase extraction (SPE) was applied for preconcentration and isolation of trace volatile and semivolatile organic compounds from various matrices (gas and liquid) [27–33]. For the simulation of gas samples and the study of adsorption-desorption processes of volatile compounds (hydrocarbons [27, 30], halocarbons [29–31], oxygenated compounds [30]) with the utilization of carbon sorbents a home-made apparatus was used. Desorption of analytes was performed with a liquid with subsequent injection of the extract into a gas chromatograph [27–31]. Alternatively the desorption was accomplished with a carrier gas at elevated temperature, followed by on-line introduction of the desorbed analytes into the gas chromatographic column [30, 31]. Thermodesorption unit (Dynatherm Thermal Tube Desorber, Model 890/891, Supelco) with ballistic heating of the trap was utilized without cryo-cooling of the volatile analytes on the top of capillary GC column. The refocusing of the desorbed analytes was performed with the thick film of stationary phase (1.5 μm of polydimethylsiloxane) [30, 31]. For the emission measurements of real samples a custom-made sampling apparatus was used. Sampling was done by means of cartridges packed with adsorbent studied and followed by a liquid and/or thermodesorption and GC analysis [29–31]. To determine the volatile organic compounds in water samples by purge and trap method a home-made purge vessel was used with subsequent liquid desorption and off-line GC analysis [28]. Analysis of semivolatile compounds (selected pesticides) and their isolation from various matrices was realized with SPE in combination with capillary GC and/or GC-MS [32–36].

Capillary GC was performed in a gas chromatograph HP-5890 Series II in on-line combination with a Vectra ES/12 computer and/or HP 3396 integrator, with injection systems devoted to trace analysis (splitless and on-column) [27–36]. For detection and quantitation of individual analytes a universal flame ionization detector (FID) was used [27–33]. For halocarbons [29] and selected pesticides [32, 33] also an electron capture detector (ECD) was applied. In GC-MS combination a low resolution mass spectrometer with electron impact ionization was utilized with a full scan and multiple ion monitoring mode (Varian 3400 gas chromatograph equipped with a splitless injection system in direct connection with a mass spectrometer ITD 800, Finnigan) [32–36]. In all measurements commercial capillary columns with chemically bonded stationary phases were employed [27–36].

RESULTS AND DISCUSSION

Physicochemical Characterization of Sorbents

Identification and characterization of the physico-

Table 1. Summary of Electron Microscopy Observations of Porous Carbons

Carb I	highly porous carbon, glistening, sharp-ended, hard but relatively brittle particles – particles with sponge-like porous texture similar to parent silica gel – sharp-ended breaks can be seen after cracking
Carb II	– 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 Fig. 1e) inside – crater-like structure; with a replica of crystals of nondissolved porogenes

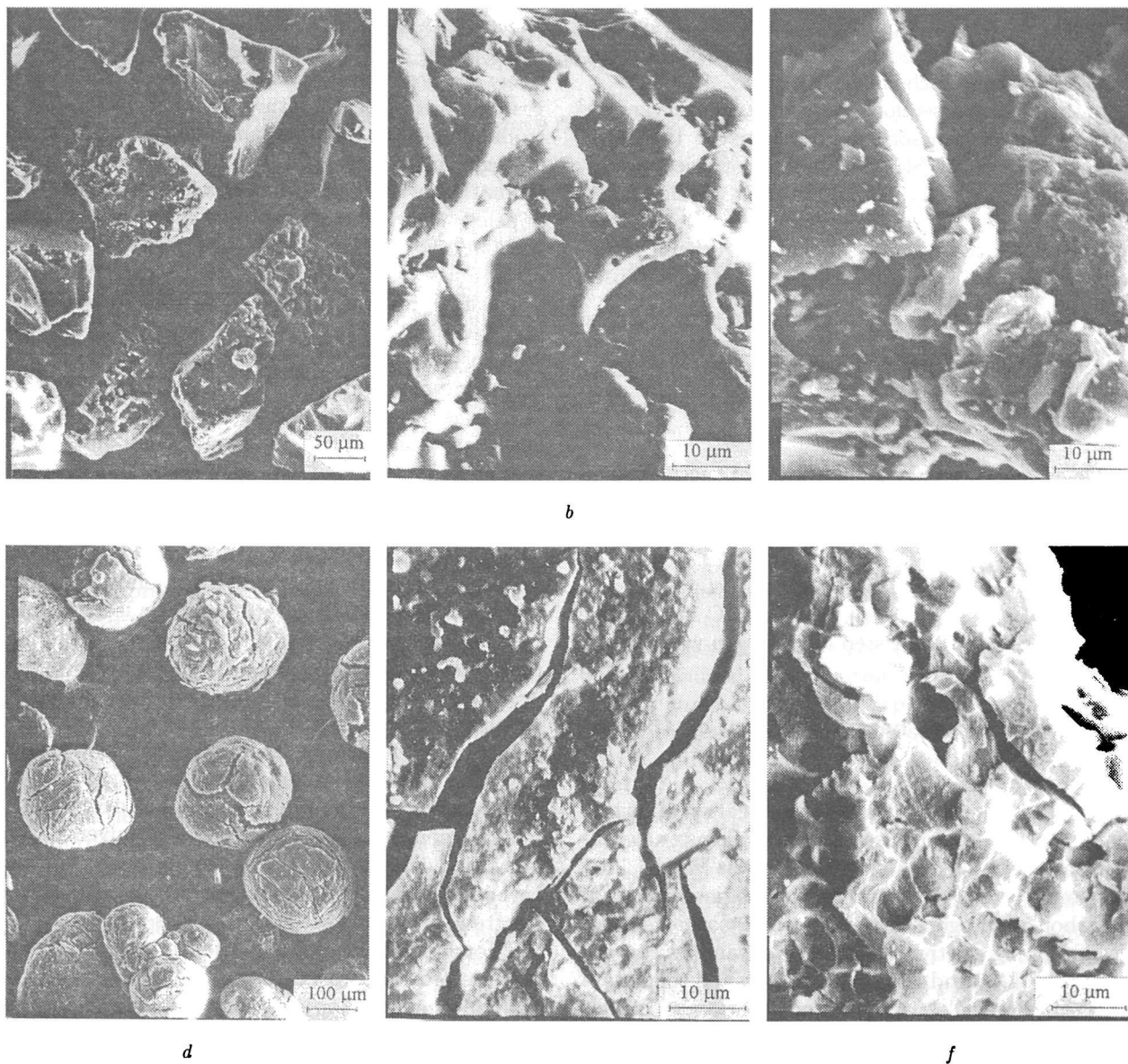


Fig. 1. Scanning electron microscopy photographs of porous carbon sorbents: *a*) Single particles of Carb I; *b*) the surface of a single particle of Carb I; *c*) the view into a single particle of Carb I after cracking; *d*) single particles of Carb II; *e*) the surface of a single particle of Carb II; *f*) the view into a single particle of Carb II after cracking.

chemical properties of adsorbents are important in understanding their performance characteristics. So far no powerful method is available that gives an exact

and detailed picture of the chemical species formed on the surface. Therefore, it is advisable to employ more methods for the study of solid materials.

Table 2. Physical Characteristics of Porous Carbons

Sorbent	Specific surface area	Specific pore volume	Bulk density	Particle size	Pore size
	m ² g ⁻¹	cm ³ g ⁻¹	g cm ⁻³	mm	nm
Carb I	1020	0.560	0.24	0.05—0.16	1.8—9.0
Carb II	632	0.475	0.35	0.12—0.30	4.0—25.0

Evaluations of physicochemical properties of sorbents and their suitability to trap organic compounds were in this contribution focused on the searching of the sorbent morphology by scanning electron microscopy, characterization of the sorbent surface based on results of elemental analysis and ¹H MAS and ¹³C MAS solid-state NMR spectroscopy, as well as on measurements of the surface area, particle size and shape of particles, pore size and volume, calculation of specific retention volumes of selected compounds belonging to different groups of adsorbates [23].

Electron Microscopy

The detailed description of electron microscopy observations of the investigated sorbents is listed in Table 1. Selected photographs are presented in Fig. 1. Scanning electron microscopy of porous carbons shows the shape and structure of particles, which strongly depend both on the template and the precursor used for the preparation of a sorbent. The example of the shape of Carb I and Carb II is given in Figs. 1a and d. The Carb I sharp-ended particles come from silica gel template (Fig. 1a). The spherical form of Carb II indicates that spherical cellulose was used as the precursor for pyrolysis in the preparation procedure (Fig. 1d). The high magnification enables a detailed view of surfaces texture (Figs. 1b and e) and a view into a single particle after cracking (Figs. 1c and f).

Characteristics from Adsorption Data Measurements

The porosity of carbonaceous materials ranges from highly porous active carbons to virtually non-porous graphitized carbon blacks (GCB). Sorbents having a higher surface area per mass unit have a higher number of active accumulation media [11]. The surface area can be increased by a porous structure of the sorbent. Besides mean pore size, also pore size distribution is a very important parameter for sampling and preconcentration of analytes. The pore size distribution of the studied sorbents was determined from adsorption measurements by the classical B.E.T. method with argon as a sorbate (77.3 K), which lead to adsorption isotherms [23]. Surface areas and physical characteristics calculated from adsorption isotherms and pore distribution curves [23] are summarized in Table 2. Particle size and shape influence the hydro-

Table 3. Elemental Analysis Results

Sorbent	w(N)	w(C)	w(H)
	%	%	%
Carb I	—	89.3	2.2
Carb II	0	94.1	1.8

dynamic conditions in the sorbent bed. The pore size of Carb I, Carb II is in the region termed “mesopores” The broader pore size distribution for Carb II reflects the preparation procedure, especially the nature of inorganic salts used as porogens. In few cases the porogen could not be well dissolved and created larger pores.

Elemental Analysis

The results of CHN elemental analysis of samples are summarized in Table 3. The content of carbon is significantly lower than 100 %. The technology of sorbent preparation evidently led to formation of oxygen-containing groups in the matrix. The carbonization of precursor was not complete and also some hydrogen-containing groups could be detected. The content of nitrogen was expected to be 0 %, which was proved with the sorbent Carb II, for Carb I it was therefore not determined.

Solid-State NMR Spectroscopy

Valuable information about the structural details of the surface of materials can be obtained with the help of solid-state NMR spectroscopy [37—39]. Porous carbon samples were investigated by ¹H MAS and ¹³C MAS solid-state NMR spectroscopy [23]. Samples of Carb I and Carb II show similar ¹H and ¹³C NMR spectra with similar chemical shifts, line widths, and signal intensities. The maxima of the ¹³C resonances appear in both spectra at δ = 125 to 130, the signal intensities are relatively high in comparison to the other carbon sorbents studied (molecular sieves and graphitized carbon blacks) [23]. The region of these maxima is due to the resonance of olefinic and/or aromatic carbon atoms. Single resonance cannot be resolved in any spectrum. The ¹H NMR spectra show a broad resonance at δ = 7 due to the presence of aromatic

Table 4. Specific Retention Volumes V_g and Isothermic Heats of Adsorption q^{st} for Selected Organic Adsorbates on Carb I and Carb II Adsorbents

Adsorbate	M_r	B.p.	V_g	V_g	q^{st}	q^{st}
		°C	cm ³ g ⁻¹ (Carb I)	cm ³ g ⁻¹ (Carb II)	kJ mol ⁻¹ (Carb I)	kJ mol ⁻¹ (Carb II)
Dichloromethane	84.93	39.8—40	1.5×10^5	5.9×10^5	42.7	43.2
Hexanal	100.16	131	4.5×10^6	1.7×10^7	53.9	56.8
Tetrachloroethylene	165.83	121	5.7×10^7	1.9×10^7	58.7	53.1
Hexane	86.18	69	6.4×10^7	1.4×10^8	62.4	62.0
Octan-1-ol	130.23	196	1.1×10^8	5.3×10^8	61.1	64.1
Ethylbenzene	106.17	134.6	1.7×10^9	4.2×10^9	70.1	70.0
Octane	114.23	125—127	4.0×10^9	2.2×10^{10}	74.2	77.1
Decane	142.29	174	6.8×10^{11}		90.7	
Dodecane	170.34	216.2	5.4×10^{14}		114.2	

hydrogens. A shoulder at $\delta = 2.5$ is also visible due to the remaining aliphatic rests.

To check the potential changes of sorbents in atmosphere (particularly the presence of the moisture) NMR spectra of Carb I, Carb II were measured after one-week exposure to air. The spectra did not show any changes [23].

Gas-Solid Chromatography

The use of gas-solid chromatographic techniques for the characterization of adsorbents provides valuable insight into the adsorbent characteristics [40—44]. Using a small gas chromatographic column to evaluate interactions between adsorbent and 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 on the adsorbent surface homogeneity, adsorbate specific retention volume (or breakthrough volume), and on the adsorbent capacity for the chosen adsorbate.

The specific retention volume is the calculated volume of carrier gas, per mass unit 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 [40—44]. The determined values of the specific retention volumes V_g at 20°C for selected organic adsorbates [23] are summarized in Table 4. The isothermic heats of adsorption at zero uptake [45] were determined from the variation of $\ln\{V_g\}$ on $1/T$. The derived values of q^{st} for Carb I and Carb II are listed in Table 4.

It can be seen from the results in Table 4 that the specific retention volumes at 20°C measured on sorbents Carb I and Carb II generally increase with the increasing of molecular mass in groups of adsorbates with similar chemical properties. Representative plots of the dependence of $\ln\{V_g\}$ vs. $1/T$ for selected unbranched alkanes and halocarbons showed that the higher the molecular mass of adsorbates belonging to

specific group, the higher is the slope of the linear dependence [23].

The increase in differences of the q^{st} values on Carb I with the increase of the carbon atoms number of alkanes indicates the enhancement in the adsorbent-adsorbate interaction energy [23]. As the sorbent material is porous with pores up to tens of nm, the release of larger molecules becomes more difficult. Consequently higher isothermic heats are observed. The length of dodecane 1.65 nm reaches the border of Carb I pore range (1.8 nm). The values of q^{st} for alkanes measured on mesoporous sorbents are considerably higher than the corresponding values measured on GCB [46] and lower than values given by microporous samples of carbon sorbents, e.g. the difference of isothermic heats measured on sorbent Carb I and on microporous carbon sorbent CC1 [47] for hexane is about 20 kJ mol⁻¹.

The differences between q^{st} values for Carb I and Carb II are very small (max. $q^{st} = 5.6$ kJ mol⁻¹, see Table 4). This is not surprising because as it can be seen in pore distribution curves [23] the range of pore sizes of both sorbents is overlapped in the broad range of 4—9 nm (Table 2). Moreover, one can expect similar surface properties of adsorbents prepared by pyrolysis of mono- and polysaccharides. Thus, very similar adsorption-desorption behaviour is expected.

As it follows from NMR results [23], 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 [19] also confirmed the mixed character of polar and nonpolar groups and some of the chemical features of the starting materials are still present in the charred structures.

According to classification scheme by Kiselev [48], porous carbons can belong between the first and particularly the third class of adsorbents. The Carb I and Carb II retention characteristics show that the upper end of the functional range (the range of molecular sizes that can be trapped efficiently, and then desorbed at medium temperatures) in comparison to

Carbotrap [49] is similar. For Carbotrap and Carb I, Carb II sorbents, extremely large sample volumes may be treated with adsorbates larger than decane [23], which follows from Table 4. On the other hand, the increase in molecular lengths results in an increase in the surface-to-surface interactions. Consequently it is necessary to utilize very high temperature for quantitative analyte desorption. The lower end of the functional range is broader than the one of Carbotrap. Due to the large surface area Carb I covers also a part of molecular sieves range. Dichloromethane can serve as an example. The solvent is a typical adsorbate for studies on carbon molecular sieves and it was successfully trapped by porous carbon [30]. The V_g (20°C) on Carbosieve S-III is $2.56 \times 10^5 \text{ cm}^3 \text{ g}^{-1}$ [40]. The V_g values of dichloromethane on Carb I and Carb II (Table 4) are of the same order. In few applications Carb I or Carb II could replace the multibed sorbent tubes, particularly composed of Carbotrap/Carbosieve S-III [30].

Testing and Application of Porous Carbon Sorbents for the Preconcentration of Analytes in Combination with HRGC

Volatile Organic Compounds

Mesoporous carbon sorbents have shown a high adsorption capacity for the broad range of volatile organic compounds [23]. They were tested for their potential utilization on preconcentration purposes of trace analytes from environmental matrices, air [27, 29–31] and water [28]. Adsorption-desorption properties of sorbents were evaluated according to the determined recovery values, whereby physicochemical interactions of both sorbent and solute were taken into consideration. It was shown that some chemical properties of the starting precursors are transferred into the carbon structure. In particular, residual hydroxyl groups and newly formed C=O groups were found by diffuse reflectance FTIR spectroscopy [19]. From the interpretation of ^1H MAS and ^{13}C MAS solid-state NMR [23] the presence of aromatic, olefinic, and aliphatic moieties was confirmed. So besides nonspecific interactions also specific interaction between polar residual groups on the sorbents surface and analytes of polar character could be anticipated.

Preconcentration of Organic Compounds from Air

In our recent work we have studied possibilities of application of mesoporous carbons for preconcentration of compounds, which can be expected in anthropogenic and natural emissions at various levels of concentration [27, 29–31]. Individual searched compounds differed in polarity and volatility. They belonged to various chemical groups, as alkanes and aro-

matic hydrocarbons with carbon atoms number C_7 – C_{12} , halocarbons (derivatives of methane, ethane, ethylene), and oxygenated compounds (alcohols, aldehydes, ketones, acetates).

After sorption of analytes from simulated samples (in adsorption cartridges prepared by packing the glass tubes with sorbents) under controlled conditions the off-line liquid desorption and GC analysis was performed. The selection of a solvent for the desorption was evaluated according to the following criteria: efficiency of desorption, chromatographic properties, and the presence of potential interferences [27, 29, 30]. Conditions of desorption were optimized (volume of displacing solvent, the utilization of co-displacer, time of desorption, application of ultrasound). From the series of nonpolar and polar displacers carbon disulfide showed superior properties when applying splitless and on-column injection system. For ECD detection of chlorinated compounds it was necessary to apply a displacer which does not disturb the determination, *e.g.* pentane [29]. From the study of adsorption-desorption process of hydrocarbons in the concentration range of the sample components in nitrogen (0.03–15 $\mu\text{g dm}^{-3}$) it was shown that the recovery data were above 90 % [27, 30]. No statistical differences were found in the recovery data when in the loading procedure sample was injected into the vaporizer and directly into the sorbent. Recovery data of 60–100 % were found for the oxygenated compounds, whereas the result was dependent on the compound polarity. The lowest recoveries were found for alcohols, particularly those, which were the most polar (alcohols with the shortest branched chain and/or the double bond). These observations indicate the presence of active sites (residual polar groups) on the surface of the sorbent. This agrees with the FTIR [19] and NMR spectroscopy [23] characteristics for these sorbents.

Carbon sorbents were tested also for the preconcentration of real samples, acetates [30], halocarbons [29], and epichlorohydrin [30, 31]. With emission measurements, where fairly high concentration could be expected ($(\mu\text{g}–\text{mg}) \text{ m}^{-3}$) with liquid desorption low limits of determination were reached (in the order of $\mu\text{g m}^{-3}$ with FID and with ECD up to ng m^{-3}).

Thermodesorption allows for several advantages [11]. The main advantage is the possibility to analyze samples with low concentration of organic compounds. Therefore, we have systematically studied the repeatability and hysteresis of sorption-desorption processes. The obtained data allowed optimization of experimental conditions of thermodesorption in an on-line combination with HRGC [30, 31, 50, 51]. The recoveries of nonpolar compounds (hydrocarbons and most of halocarbons) were close to 100 % also at low concentration levels (1.5 ng dm^{-3}) with good reproducibility of analytic determination. The recoveries of oxygenated compounds determined by thermodesorption considerably increased (for most compounds ≥ 90 %)

compared to liquid desorption, however, the recoveries and reproducibility of measurements were dependent particularly on the investigated sample concentration level (15–600 ng dm⁻³). Better results were obtained with sorbent Carb II for the lower sorbed amounts (≤ 15 ng l dm⁻³, or higher) [50, 51].

Physicochemical properties of recently developed carbon sorbents show their superiority compared to traditional materials, such as porous polymers, for adsorbing different compounds encountered within the environment [11]. Sorption-desorption properties of the tested porous carbon were shown to be very good for nonpolar compounds [27, 29–31] and they are comparable to *e.g.* graphitized carbon blacks materials [11]. There is higher affinity of the tested sorbents to polar compounds [30, 50, 51]. For oxygenated compounds only few data exist concerning analytical recovery on solid sorbents. To our knowledge, there are only a few sorbents, graphitized carbon blacks (Carbotrap C/Carbotrap) and graphitized carbon blacks in combination with carbon molecular sieves (Carbotrap C/Carbotrap/Carbosieve S-III) described in literature for the enrichment of alcohols, aldehydes, ketones, however, without giving the recovery data [52, 53]. According to our results [51] for these compounds graphitized carbon black material Carbotrap 100 is excellent for sampling C₄–C₈ alcohols, aldehydes, and ketones. Recovery data values reported in literature for acetates sampling with carbon sorbents are limited, for butyl acetate 64 % for Carbotrap B [54]. The tested mesoporous carbon Carb I is excellent for sampling methyl, ethyl, and butyl acetates, sorbent Carb II is recommended, too [51]. For sampling acetates including vinyl acetate it is recommended to utilize the multibed arrangement Carbotrap 300 (Carbotrap C/Carbotrap B/Carbosieve S-III).

If we want to compare the tested porous carbon with other carbon materials for the application to real sample analysis, besides good sorption-desorption properties also some other parameters are important, such as breakthrough volumes (BTVs), which are related to specific retention volumes, and affinity to water.

BTVs of air needed to elute adsorbate were determined for various particular sorbents by several authors. As it was already discussed, the tested mesoporous carbon sorbents have shown the high sampling capacity for a great variety of compounds [23]. *Figge et al.* [41] performed a systematic study on the determination of BTVs for 26 adsorbents (including carbon sorbents) by the use of 29 test compounds differing in polarity and volatility. A presently tested porous carbon Carb I (the other batch denominated as CF-17) belonged to group of sorbents I, which consisted of the adsorbents CF-17 and Carbosieve S-II, which exhibit good or very good retention properties with all tested organic compounds. Graphitized carbon blacks (Carbopack B and Carbopack C) belonged to group II

with good retention properties for all nonpolar, high-boiling test compounds.

Moisture in air samples presents problems, particularly with canister sampling, as it can extinguish the FID hydrogen flame, plug column at sub-zero temperatures. Sampling with carbon sorbents, such as tubes with activated charcoal [5], multilayerbed tubes with graphitized carbons and carbon molecular sieves (Carbotrap C, Carbotrap, and Carbosieve S-III) [55] led to a reduced adsorptive capacity to some chemical, particularly low molecular mass compounds under high humidity conditions. With the tested porous carbons under humid conditions in the workplace the collection of water was not observed (no presence of condensed water droplets in the sample tube) and no problems occurred with GC analysis after liquid desorption. According to the results with thermodesorption some affinity to water was observed, but to prevent water from entering the GC column a refocusing tube (with narrower internal diameter than the sampling tube) was used which served at the same time as a prefocusing device instead of the cryogenic technique [56].

Preconcentration of Organic Compounds from Water

Porous carbon sorbent Carb II was tested for the preconcentration of volatile organic pollutants (particularly hydrocarbons in the gasoline range) from water matrices by the purge and trap method [28]. The trapped compounds were desorbed by carbon disulfide and analyzed by HRGC applying on-column injection. Due to the presence of multicomponent mixture much attention was devoted also to the optimization of the separation of hydrocarbons mixture under temperature-programmed conditions. The studied concentration range of individual hydrocarbons in water was 10 ppb–10 ppm. Recoveries of hydrocarbons with carbon atom number $C \leq 10$ were close to 100 %. Higher boiling compounds, particularly naphthalenes, showed significantly lower values of recoveries. Drinking water, spring water, and gasoline-contaminated water are given as examples of real sample analysis. In gasoline-contaminated water 163 compounds were identified, predominantly aromatics. Concentrations of individual components were found to be in the range 7 ppb–3.5 ppm.

Semivolatile Compounds

Graphitized carbon black cartridges have successfully been applied for SPE of various pollutants including pesticides [11]. Carbopack cartridges proved to be more efficient than C₁₈ silica [57, 58] with higher accuracy analyzing drinking water samples [59]. With respect to chemically bonded silica, an apparent weakness of graphitized carbon black is that its surface framework is contaminated by few oxygen complexes,

having a structure similar to benzpyrylium salts [57]. This apparent weakness is, in fact, an advantage in that acidic analytes can be completely isolated from base-neutral ones.

Porous carbon Carb I was successfully applied for the isolation of fungicide residues, which have been utilized for the protection of vine [32, 33]. SPE with porous carbon was developed for the clean-up step of dicarboxyimide and *N*-acylalanine fungicides from the variety of Slovak grape wines with subsequent capillary gas chromatography – flame ionization detection, electron-capture detection, and mass-spectrometry-ion-trap detection (MS-ITD) analysis.

Capacity of SPE cartridges packed with porous carbon sorbent was found to be high. The Carb capacity was influenced besides properties of analytes (fungicides) also with the matrix complexity (sugars, esters, compounds of proteins nature, acids, colours). Recoveries were tested at various concentration levels in standard solutions. The value of recovery in spiked wines depends on the sample concentration level (studied in the range $5.9 \mu\text{g dm}^{-3}$ – 1.96 mg dm^{-3}) and the variety of wine ($R = 80$ – 99%) with excellent reproducibility. Low limits of determination were received for fairly small sample volume (25 cm^3 ; 50 cm^3).

To our knowledge, there is not published literature on the preconcentration and/or isolation of the studied groups of fungicides utilizing other types of carbon sorbents either from wine, or from other matrices for the comparison.

CONCLUSION

Novel mesoporous carbon sorbents were prepared with the technology which allows for tailor-made pore size and shape, so 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 these sorbents. Due to their defined physical characteristics carbon sorbents can be used for trapping organic pollutants from environmental samples for emission measurements. Subsequently analytes are subject to liquid or thermal desorption and HRGC separation and quantitation. An important advantage of tested sorbents is their high sampling capacity and successful applicability for thermodesorption of volatile adsorbates at temperatures where the catalytic transformations and chemical changes of adsorbates to different products were not observed. In certain applications Carb I and Carb II replace multibed sorbent tubes, particularly composed of graphitized carbon black and carbon molecular sieves. Porous carbons were also used in purge and trap method for analysis of volatile compounds in water samples. The developed SPE method with carbon sorbent for the isolation of fungicides from very

complex matrix (wines) showed important field of application also for semivolatile compounds.

The measured physicochemical characteristics of sorbents and their soption-desorption behaviour represent contribution to further sorbent technology and to trace analysis in the field of combination of preconcentration and/or isolation techniques with high-resolution separation technique.

Acknowledgements. This study was partially supported by EC project CIPA-CT 94-0180 and the Slovak Grant Agency.

REFERENCES

1. Onuska, F. I., *J. High Resolut. Chromatogr.* 12, 4 (1989).
2. Liška, I., Krupčík, J., and Leclercq, P. A., *J. High Resolut. Chromatogr.* 12, 577 (1989).
3. Poole, S. K., Dean, T. A., Oudsema, J. W., and Poole, C. F., *Anal. Chim. Acta* 236, 3 (1990).
4. Namiešnik, J., Górecki, T., and Biziuk, M., *Anal. Chim. Acta* 237, 1 (1990).
5. *Annual Book of ASTM Standards, 11.03 Atmospheric Analysis, Occupational Health and Safety*, D 3686-89, D 3687-89, Philadelphia, USA, 1991.
6. Berezkin, V. G. and Drugov, Y. S., *Gas Chromatography in Air Pollution Analysis (J. Chromatogr., Library Vol. 49)*. Elsevier, Amsterdam, 1991.
7. Lai, J. Y. K., Matisová, E., He, D., Singer, E., and Niki, H., *J. Chromatogr.* 643, 77 (1993).
8. Matisová, E. and Lehotay, J., *Vodní hospodářství a ochrana ovzduší* 44, 6 (1993).
9. Matisová, E. and Škrabáková, S., *Ropa Uhlie* 37, 88 (1995).
10. Škrabáková, S. and Matisová, E., *Chem. Listy* 89, 192 (1995).
11. Matisová, E. and Škrabáková, S., *J. Chromatogr. A* 707, 145 (1995).
12. Mol, H. G. J., Janssen, H. G. M., Cramers, C. A., Vreuls, J. J., and Brinkman, U. A. Th., *J. Chromatogr. A* 703, 277 (1995).
13. Poole, C. F., *LC-GC* 9, 274 (1996).
14. Straková, M. and Matisová, E., *Chem. Listy* 91, 330 (1997).
15. Knox, J. H., Unger, K. K., and Mueller, H., *J. Liq. Chromatogr.* 6, 1 (1983).
16. Knox, J. H., Kaur, B., and Millward, G. R., *J. Chromatogr.* 352, 3 (1986).
17. Unger, K. K., *Anal. Chem.* 55, 361A (1983).
18. Gilbert, M. T., Knox, J. H., and Kaur, B., *Chromatographia* 16, 138 (1982).
19. Chiantore, O., Novák, I., and Berek, D., *Anal. Chem.* 60, 638 (1988).
20. Novák, I., Berek, D., Štamberg, J., Peška, J., Philipp, B., Gensrich, H., Gröbe, V., and Bartsch, D., *Czech. J. Chem.* 230 297 (1984); *Ger. DD* 21 864 (1985).
21. Škuchtanová, E., Feltl, L., and Smolková-Keulemansová, E., *J. Chromatogr.* 292, 233 (1984).
22. Novák, I. and Berek, D., *Czech. J. Chem.* 221 197 (1982).
23. Hrouzková, S., Matisová, E., Novák, I., Slezáčková, M., Brindle, R., Albert, K., and Kozánková, J., *J. Environ. Anal. Chem.* 69, 31 (1998).

24. Brunauer, S., Emmett, P. H., and Teller, E., *J. Am. Chem. Soc.* **60**, 309 (1938).
25. Brunauer, S., Mikhail, R. Sh., and Bodor, E. E., *J. Colloid Interface Sci.* **24**, 451 (1967).
26. Gregg, S. J. and Sing, K. S. W., *Adsorption Surface Area and Porosity*. Academic Press, London, 1982.
27. Škrabáková, S., Matisová, E., Onderová, M., Novák, I., and Berek, D., *Chem. Papers* **48**, 169 (1994).
28. Škrabáková, S., Matisová, E., Benická, E., Novák, I., and Berek, D., *J. Chromatogr. A* **665**, 27 (1994).
29. Matisová, E. and Škrabáková, S., *Anal. Chim. Acta* **309**, 181 (1995).
30. Matisová, E., Straková, M., and Škrabáková, S., *Fresenius' J. Anal. Chem.* **352**, 660 (1995).
31. Škrabáková, S., Matisová, E., Straková, M., and Slezáčková, M., *Chem. Prům.* **71**, 21 (1996).
32. Kakalíková, L., Matisová, E., and Leško, J., *Int. J. Food Res. Technol.* **203**, 56 (1996).
33. Matisová, E., Kakalíková, L., Leško, J., and de Zeeuw, J., *J. Chromatogr. A* **754**, 445 (1996).
34. Leško, J., Jakubík, T., Matisová, E., and Kakalíková, L., *Vinohrad* **2**, 40 (1996).
35. Leško, J., Jakubík, T., Kakalíková, L., and Matisová, E., *Vinohrad* **4**, 83 (1996).
36. Leško, J., Jakubík, T., Kakalíková, L., and Matisová, E., *Vinohrad* **2**, 40 (1997).
37. Albert, K. and Bayer, E., *J. Chromatogr.* **544**, 345 (1991).
38. Sullivan, M. J. and Maciel, G. E., *Anal. Chem.* **54**, 1606 (1982).
39. Dec, S. F., Bronnimann, C. E., Wind, R. A., and Maciel, G. E., *J. Magn. Res.* **82**, 454 (1989).
40. Betz, W. R., Maroldo, S. G., Wachob, G. D., and Firth, M. C., *Am. Ind. Hyg. Assoc. J.* **50**, 181 (1989).
41. Figge, K., Rabel, W., and Wieck, A., *Fresenius Z. Anal. Chem.* **327**, 261 (1987).
42. Betz, W. R., Hazard, S. A., and Yearick, E. M., *International Labmate XV* (1) (1991).
43. Betz, W. R. and Lambiase, S. J., *J. Chromatogr.* **556**, 433 (1991).
44. Brunner, F., Crescentini, G., and Mangani, F., *Chromatographia* **30**, 565 (1990).
45. Kiselev, A. V., in *Advances in Chromatography*, Vol. 4, p. 113. Dekker, New York, 1967.
46. Avgul, N. N. and Kiselev, A. V., in *Chemistry and Physics of Carbon*. (Walker, P. L., Editor.) P. 1. Dekker, New York, 1965.
47. Cao, X. L., Colenutt, B. A., and Sing, K. S. W. *J. Chromatogr.* **555**, 183 (1995).
48. Kiselev, A. V. and Yashin, J. P., *Gas Adsorption Chromatography*. Plenum Press, New York, 1969.
49. *Supelco GC Bull.* **846 C** (1986).
50. Matisová, E., Straková, M., Škrabáková, S., Marcová, M., and Puxbaum, H., *26th International Symposium on Environmental Chemistry*. Vienna, Austria, Book of Abstracts, FR 44, 1996.
51. Hrouzková, S., Straková, M., Matisová, E., Marcová, M., and Puxbaum, H., *J. Environ. Anal. Chem.*, in press.
52. Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., and Liberti, A., *J. High Resolut. Chromatogr.* **15**, 75 (1992).
53. Kruschel, B. D., Bell, R. W., Chapman, R. E., Spencer, M. J., and Smith, K. V., *J. High Resolut. Chromatogr.* **17**, 187 (1994).
54. Hsu, J. P., Miller, G., and Moran, V., *J. Chromatogr. Sci.* **29**, 83 (1991).
55. Sharp, G. J., Yokouchi, Y., and Akimoto, H., *Environ. Sci. Technol.* **26**, 815 (1992).
56. *Supelco Sample Handling Bulletin* **850 A** (1991).
57. DiCorcia, A., Marchetti, M., and Samperi, R., *Anal. Chem.* **58**, 2048 (1986).
58. DiCorcia, A. and Samperi, R., *Anal. Chem.* **62**, 1490 (1990).
59. DiCorcia, A. and Marchetti, M., *Anal. Chem.* **63**, 580 (1991).