Comparison of Adsorbents Containing Carbon Nanotubes for Express Pre-Concentration of Volatile Organic Compounds from the Air Flow

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Abstract: New composite adsorbents including silica supports (silica, aerosilogel, and diatomite) and carbon materials (multiwall carbon nanotubes and pyrolytic carbon) have been prepared and characterized. The analytical capabilities of the produced sorbents have been evaluated by their efficiency in the express pre-concentration of volatile organic compounds (butanol and phenols) from the air stream. The prepared surface-layered adsorbents containing multiwall carbon nanotubes placed onto the surface of aerosilogel by use of the carbon vapor deposition method with preloading cobalt nanostructures as a catalyst were found significantly more efficient than traditionally used graphitic carbon-based adsorbents Carbopacks B, C, and X. Additionally, a new adsorbent composed of diatomite Porochrome-3 support coated with a pyrocarbon layer was prepared. This low surface area composited adsorbent allowed both quantitative pre-concentration of phenol and isomeric cresols from the air and their thermal desorption. The developed adsorbents provided fast pre-concentration of selected phenols with a concentration factor of 2×10^3 in 5 min and were used for gas chromatographic determination of analytes in the air at low concentration levels starting from several $\mu g/m^3$ with a flame ionization detector.

Keywords: sorbents; surface-layered adsorbents; multiwall carbon nanotubes; pyrocarbon; aerosilogel; adsorption; air; analysis; phenols; alcohols

1. Introduction

Presently determination of most pollutants in the atmospheric air and the air of living accommodations necessitates pre-concentration of analytes [1]. Even in the case of employing the most sensitive detectors in gas chromatography (GC) or high-performance liquid chromatography (HPLC) for determining ecotoxicants, e.g., phenols, on the threshold limit value (TLV), the coefficient of pre-concentration should span (10^3–10^4) [2]. The sorption often referred to as the solid-phase extraction (SPE), falls into a predicament of the most efficient methodologies of volatile phenols pre-concentration [3,4]. Functionalities of SPE in its most widespread in the GC variant of the solid-phase microextraction (SPME) are restricted with a relatively small mass of the active absorbing phase (0.2–2.0 mg), and, consequently, relatively small adsorptive capacity of concentrators regarding concentrated analytes, the situation being insufficient for attaining low detection limits [5,6].

On this account it is preferable to resort to a dynamic SPE based on passing analyzed gas through a tube filled with a sorbent, a routine being followed by thermo-desorption or desorption by an organic solvent with consequent determination by GC or HPLC [2,3,7]. By now, various polymer and carbon-containing sorbents [8–11], i.a. highly selective

carbon [12] and nanocarbon components with different specific areas and hydrophobicity [13,14], have been proposed for usage in dynamic SPE. Polymer sorbents are remarkably inferior against carbon ones with regard to the absorption capacity [11], whilst carbon materials (carbon-black soot), and, specifically, nanocarbon ones (nanographene, carbon nanotubes, nanodiamonds, etc.), exhibit a substantial setback, linked with sizes of particles. Excessively small-size particles of the said materials prevent their direct usage in pre-concentration of micro-admixtures in the air analysis because of the low permeability of the tube sorption layer.

The problem of the low permeability of pre-concentration tubes was figured out by the use of composite surface-layered sorbents (SLS), in which microparticles of sorption-active materials resided in near-surface pores of relatively coarse-dispersed support [15]. In particular, the usage of carbon@Teflon agglomerated sorbents let the admissive rate of the analyzed air flow through sorption tubes increase several times with no lesion in the efficiency of the extraction of analytes. Thereby, the duration of the sorption pre-concentration of volatile organic substances has been tangibly shortened [16–18]. Additionally, yet, relatively big particulates of carbon materials in these sorbents, e.g., particles of activated carbon with sizes less than 40 μm, weakly hold on the surface of the polytetrafluroethylene support because of relatively weak physical adhesion. Stemming from this, small particulates drop off at a shake-up or at pouring a sorbent into a new container. Apart from that, in such a case the structure and size distribution of Teflon pores do not in full scale correspond to the shape and sizes of the carbon particles in use [18].

Thence, employing surface-layered composite sorbents containing sorption-active nanocarbon materials for pre-concentration of volatile compounds from the gaseous phase makes an appearance as a perspective scenario. Carbon nanotubes (CNTs) are among the most available and widespread nanocarbon materials germane to processing composite sorbents [19,20].

Usage of siliciferous supports (e.g., silica gel, aerosilogel, or diatomites) as the matrix looks pertinent to the case. The choice of these supports shows up as an expedient one owing to their high thermal stability, a broad assortment of silica possessing strictly definite pore structure, and possibilities of varying their properties by chemical modification of silica surface for augmented adsorptive coating by layers of pyrocarbon and CNT [21,22]. Employing composites on the platform of silica and CNT as sorbents in the needle SPME pre-concentrators has already been reported [23,24], their shortcoming being low adsorptive capacity.

The present communication addresses functionalities of composite sorbents containing CB soot, pyrocarbon, or multiwall carbon nanotubes (MWCNTs), coating silica sorbents-supports. These sorbents have been tested regarding express pre-concentration of toxic volatile polar organic substances from the air flow, viz., medium alcohols, and phenols, whose determining demands high efficiency in pre-concentration [2,25].

2. Materials and Methods

2.1. Preparation of Adsorbents

Macroporous aerosilogels (ASGs) employed in the present work are synthetic silica with rigid porous structure and approximately homogeneous pores for their sizes [22]. A sorbent ASG-800 was gotten in accord with a standard methodology [22] by processing a gel aerosil with consequent hydrothermal treatment at 800 °C for 6 h. A sorbent ASG-900 was developed by a similar methodology, set aside the temperature of hydrothermal treatment, viz., 900 °C. In both cases a feed aerosol was the one of a brand A-200 (Evonik, formerly Degussa, Germany), with average particle sizes being 12 nm and a specific surface area −200 m^2/g. More tough conditions of hydrothermal processing, as is seen in Table 1, entailed a reduced specific area (S_{sp}) and increased pore sizes (D_{pore}) in the case of sorbent ASG-900. Silica gel KSK-2 ("Soyuzhimprom", Russia) was used as purchased.

Table 1. Characteristics of silica supports used for the growth of MWCNT (particle size *d* was in the range of 0.18–0.25 mm).

Silica Support	S_{sp}, $m^2\,g^{-1}$	D_{pore}, nm	V_{pore}, $cm^3\,g^{-1}$
Aerosilogel ASG-800	130	25	1.40
Aerosilogel ASG-900	70	80	0.70
Silica gel KSK-2	360	12	1.25

Surface-layered compositional sorbents (MWCNT@ASG) were gotten through MWCNT growth by chemical deposition from the gaseous phase or carbon vapor deposition onto the ASG surface in a hydrogen medium following a regime of a boiling layer following published methodology [26]. The temperature equaled 600 °C in the case of ASG-900 and KSK-2, whilst for ASG-800 it was 800 °C. Cobalt (II), which featured as a catalyst for carbon nanotubes growth, was spread in the form of ammonium complex along the surface of preliminary hydroxylated silica from 0.2 M solutions at pH = 8.1 [26].

Another type of composite sorbents, containing weight-equal amounts of silica and MWCNT, was processed by a sol–gel method making use of a gel aerosol A-380 (S_{sp} = 380 m^2/g, *d* = 7 nm), which was mixed with weighed samples of various industrially produced MWCNT: Taunid-MD (plc NanoTechCenter, Russia), Dealtom (SIV Center for nanotechnologies, Russia) and BayTUBES C-150P (Bayer, Germany), and an aerosilogel branded A-380.

Characteristics of industrially manufactured MWCNT, used in this study, are presented in Table 2.

Table 2. Characteristics of MWCNT used in this work.

MWCNT	S_{sp}, $m^2\,g^{-1}$	Outer Diameter, nm	Inner Diameter, nm	*L*, μm
Taunid-MD	270	8–30	5–15	≥ 20
Dealtom	97.6	49.3–72.0	13.3	~ 5
BayTubes C-150P	210	13–16	4	1–10

Processing of MWCNT@aerosil comprises several stages. At the first one, equally weight samples of MWCNT and A-380 were vigorously stirred in a mortar until getting a homogeneous matter. Next, a blend underwent pounding in a steel vessel by use of a planetary ball mill, then, grinding being initially (30 min duration) dry and eventually the one with the addition of 20% of water (duration 1 h). The gotten blend was exposed in a bake-oven for 1 h at 200 °C. The material obtained was sift-fractionated. Eventually, granules were annealed in nitrogen flow for 1 h at 800 °C.

Surface-layered sorbents with a layer of pyrocarbon on a macroporous diatomite support Porochrom-3, often employed in gas-adsorption chromatography, were processed in accord with the methodology of Ref. [27]. Silica content in the said support is 96–98%. For getting a pyrocarbon coating, vapors of propargyl alcohol were let pass through a layer of porochrome-3 in a regime of a boiling layer at 800 °C for 2 h using nitrogen as a carrier gas.

For unbiased estimates of sorbents synthesized in the work, they were juxtaposed with carbon sorbents Carbopack C, Carbopack B, Carbopack X, and Carbograph X (Sigma-Aldrich, USA), which are ubiquitous in pre-concentration of volatile substances from the gaseous phase with subsequent thermodesorption and GC determination [28]. We also verified the adsorption activity of a sorbent exemplified by unmodified porochrom-3, used as a matrix for processing surface-layered sorbents with pyrocarbon.

Assessment of Pore-Metric Parameters of the Sorbents

Determining specific area and size distribution of pores was performed in accord with Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) algorithms from the data on low-temperature nitrogen adsorption [29]. Before measurements, samples of sorbents underwent vacuum degassing at 300 °C for 10 h for removing absorbed gases and water.

2.2. Assessment of Pore-Metric Parameters of the Sorbents

Model gaseous mixtures with a constant concentration of analytes (50 mg/m^3) were used for estimation of the studied sorbents' efficacy. These mixtures were prepared by flowing air through aqueous solutions with a preset concentration of analytes, the purity being never less than the analytical reagent grade in accord with the known methodology [30]. It was determined that the equilibrium distribution of test samples between aqueous and gaseous phases and the constancy of their concentrations in the saturated gaseous phase was attainable. One can infer these conditions from the constancy of the analyte's concentration in the flow of the model gaseous mixtures, formed at various air flow rates. Values of the analyte's distribution coefficients between aqueous and gaseous phases were determined following a common routine [31].

2.3. Processing Model Gaseous Mixtures

The model gaseous mixtures of analytes with a given volume gas flow rate (W_G) were let pass through tubes filled with weighted samples of the sorbents for estimation of their efficacy. The sorption completeness control was carried out by sampling a portion of a gaseous phase at the tube outlet with subsequent determination of analytes by a gas chromatograph. Next, retention curves for the test substances were plotted as dependences C/C_0 vs. V, where C and C_0 are concentrations of the test substance in the gas phase by the column outlet and inlet correspondingly; and V (L)—a volume of the model gas phase passed through the column. Suchlike dependences were giving the retention volume, the latter being assumed equal to such volume of the gas phase passed through the column, which conforms to a constraint $C/C_0 = 0.5$. The number of theoretical plates, N, was also determined from the dependences to characterize efficacy of the sorption column according to the formula, suggested for the frontal variant of chromatography [32]:

$$N = \frac{V_R^2}{(V_R - V_{0.16})^2} \tag{1}$$

where V_R—retention volume and $V_{0.16}$—such volume of the gas phase passed through the column, which holds a constraint $C/C_0 = 0.16$. A height equal to an equivalent theoretical plate (HETP) was calculated from the relationship: $H = l/N$, where l is the length of the chromatographic tube.

The estimation of sorbents hydrophilicity, known for exerting a detrimental effect on the analysis of humid gaseous media, was carried out by mass determination of the absorbed air vapor during the passing of the air with the relative humidity of 99% through the tube with a studied sorbent at the temperature 22 ± 1 °C. The determined mass was reduced by the sorbent mass in the tube. The sorbent underwent degassing at the temperature of 190 °C for 4–5 h until attaining the constant mass. To ensure the air flow with the said humidity this flow was passed through the 1% aqueous solution of NaCl.

2.4. Instrumentation

Pore-metering studies of the sorbents were performed employing a setup ASAP 2020 MP (Micromeritics, USA). The investigation of the surface morphology was performed by scanning electron microscopy, viz., Zeiss Supra 40 VP setup with 10 kV voltage. Carbon content in the synthesized compositional sorbents was determined with differential-thermogravimetric analysis using a setup SETSYS Evolution 16 (Setaram, France) by heating the sorbent samples

in the air at 900 °C. Determination of the test substances was implemented on a gas chromatograph Crystal-5000.2 (Chromateck, Russia) equipped with a flame ionization detector (FID) and a quartz capillary column (10 m × 0.53 mm × 2.65 μm) with 100% dimethylpolysiloxane coating. Regulation of the air flow during the preparation of the model gaseous mixtures was performed with a regulator of gaseous flows Chromatec-Crystal FPG. Gas sampling was carried out with an automatic heated six-port sample valve. One-step thermo-desorber NDS-1 (Chromatec, Russia) was used for thermodesorption, the device rendering thermo-desorption viable in the interval 150–400 °C with the step of 50 °C. HPLC determination of phenol compounds was performed by using liquid chromatograph LC-20 Prominence (Shimadzu, Japan) with a spectroscopic detector (λ = 269 nm) and a chromatographic column 250 mm × 4.6 mm ID packed with 5 μm sorbent Supelco Discovery C_{18}. The column temperature was 30 °C.

3. Results and Discussion

Currently, there are three principal options of processing sorbents on the platform of silica with immobilized CNT. The first one includes covalent affixing of CNT via the reaction with aminopropyl groups on the silica surface modified with 3-aminopropyltrialcoxysilanes [19,32–34]. The shortcoming of the method consists in a multistage synthesis, low content of CNT in the sorbents [19], and the presence of residual reactive aminopropyl- and silanol groups, deteriorating the specificity of sorption. The other option is a sol–gel method of producing silica sorbents with the addition of CNT [35]. However, there is a high probability of hydrophobic CNT aggregation in this method, which issues serious concerns regarding the homogeneity of the CNT distribution and their accessibility for the adsorption interaction with sorbates. The authors of the present work stepped forward with the introduction of a novel technique for the preparation of CNT-containing sorbents [26]. In this method, MWCNTs are synthesized by a routine of chemical deposition or growth from the gaseous phase onto the surface of the silica matrix activated by cobalt nanoparticles.

Composite silica-based sorbents with MWCNT are more promising against analogs with single-wall CNT, insofar as they procure more strong interactions with sorbates. It is also commonly admitted that long MWCNTs (5–15 μm) exhibit higher adsorption ability as compared to short ones (1–2 μm) [13].

A pivotal assignment of the present work addressed the development of new sorbents for the pre-concentration of polar compounds from the gaseous phase. To this end, alongside porometric investigation of sorbents, determination of the adsorptive capacity of the composites regarding butanol-1 and phenol has been implemented. The experimental data obtained are summed up in Table 3.

Table 3. Characteristics and sorption properties of the sorbents studied. Measurements of values shown as $X \pm S_X$ (X is the purpose value, S_X-standard deviation, confidence probability = 0.95) have been performed in 3 experiments.

Sorbent	d, m	D_{pore}, nm	V_{pore}, cm³/g	S_{sp}, m²/g	Carbon Content, %	Hydro-Phylicity, %	Specific Retention Volume, dm³/g	
							Butanol-1	Phenol
1 Carbopack C	180–250	n/a	n/a	12 ± 1	>98	0.3 ± 0.03	-	29 ± 2
2 Carbopack B	180–250	n/a	n/a	110 ± 8	>98	1.3 ± 0.2	29 ± 3	340 ± 20
3 Carbopack X	180–250	6–80	0.62	240 ± 20	>98	1.5 ± 0.2	69 ± 7	730 ± 50
4 Carbograph-1	180–250	20–80	0.65	100 ± 10	>98	0.9 ± 0.08	23 ± 2	580 ± 30
5 MWCNT@ASG-800	180–500	-	1.25	250 ± 20	3.4 ± 0.3	5.9 ± 0.6	95 ± 6	690 ± 40
6 MWCNT@ASG-900	180–250	-	0.65	330 ± 30	17 ± 1	5.4 ± 0.5	115 ± 8	1340 ± 60
7 MWCNT @KSK-2	180–250	-	0.95	290 ± 30	16 ± 1	13 ± 1	105 ± 7	650 ± 40
8 Bayer C150P/A-380	200–500	24	1.09	200 ± 20	49 ± 3	15 ± 2	32 ± 3	680 ± 50
9 Dealton/A-380	200–500	25	0.77	140 ± 15	48 ± 4	13 ± 1	60 ± 5	740 ± 60
10 Taunid-MD/A-380	200–500	25	1.07	230 ± 20	50 ± 4	18 ± 1	93 ± 7	1220 ± 50
11 Porochrom-3	350–500	-	1.5–1.8	2.6 ± 0.2	<0.1	0.8 ± 0.07	-	5.9 ± 0.4
12 Porochrom-3-PC [a]	350–500	-	-	2.8 ± 0.2	1.2 ± 0.1	0.26 ± 0.02	-	10.0 ± 0.9

[a] PC—pyrocarbon.

As follows from Table 3, a change in the temperature of MWCNT deposition onto silica supports (sorbents 5–7) gives way to varying the carbon content (the amount of carbon nanotubes) in the resulting surface-layered carbon-silica absorbents, which is reflected in their sorption properties. In the sorbents MWCNT@ASG-900 and MWCNT@KSK-2, processed at 600 °C, the carbon content was almost 3 times higher as compared to MWCNT@ASG-800, synthesized at 800 °C. Noteworthy is that in the sorbents MWCNT@ASG-800 and MWCNT@ASG-900 an increase in specific surface area was from 130 to 250 and from 70 to 330 m^2/g was accordingly observed as compared with the pristine non-modified macro-porous aerosil gels. At the same time, the decrease in specific surface area from 360 to 290 m^2/g was noted for the bare mesoporous silica gel and MWCNT@KSK-2 sorbent on its basis, which is caused by blocking the bulk of mesopores with carbon nanotubes.

The sorption capacity of the compositional sorbents with MWCNT processed in this work is not inferior to the capacity of absorbents based on graphitized thermal carbon black sorbents of Carbopack and Carbograph types. Particularly attractive is the surface-layered absorbent MWCNT@ASG-900, which not only has a maximum sorption capacity of 115 and 1340 dm^3/g to butanol-1 and phenol, respectively, but is also the most hydrophobic in comparison with its analogue based on silica gel, MWCNT@KSK-2, and composites 8–10 obtained by the sol–gel technology. The latter ones, despite a significantly higher content of CNT (50%) in their formulation, are inferior to MWCNT@ASG-900 in terms of sorption capacity and hydrophobicity.

High hydrophilicity of composites 8–10 impedes the usage of these adsorbents for sorption pre-concentration in the analysis of humid atmospheric or exhaled air with an orientation towards subsequent thermal desorption of analytes. Nonetheless, the possibility of desorbing the tested compounds using suitable organic solvents, followed by HPLC-determination of analytes [36], remains. Figure 1 shows an electron microphotograph of the Bayer C150P@A-380 composite: obviously, carbon nanotubes do not form dense agglomerates and retain their individuality. This ensures the accessibility of their surface for adsorbates. According to the data of the differential thermogravimetric analysis, a noticeable decrease in the mass of nanotubes caused by oxidation with atmospheric oxygen occurs at temperatures above 400 °C. This information is essential when planning conditions of thermal desorption of adsorbed analytes.
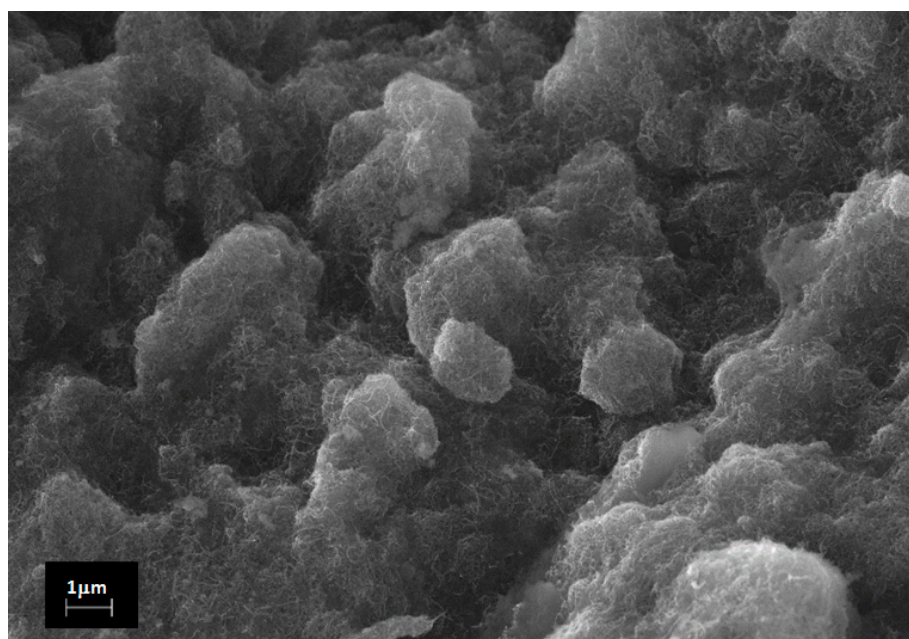

Figure 1. SEM image of Bayer C150P@A-380.

It is commonly accepted that the model substances used in this work (butanol-1 and phenol) can be adsorbed both on the surface of polar silica absorbents and on the surface of hydrophobic carbon ones. However, the adsorption mechanisms of these substances differ significantly. Adsorption on bare silica adsorbents occurs due to the interactions between the hydroxyl and phenyl groups of the sorbates and silanol groups of the sorbent in the form of hydrogen bonding. In the case of carbon adsorbents, the main contribution to retention is due to the hydrophobic interactions between alkyl radical from 1-butanol molecule and the aromatic ring of phenol molecule with a neutral hydrophobic surface. For composite sorbents, containing both CNT and silica, a mixed mechanism of adsorption of alcohols and phenols can be anticipated. In this case, π–π interactions of the aromatic ring of phenols with the condensed aromatic structure of CNT are added to the hydrophobic interactions and formation of hydrogen bonds.

The dependences of the adsorption capacity of the studied sorbents (specific retention volumes) vs. specific surface area are shown in Figure 2.
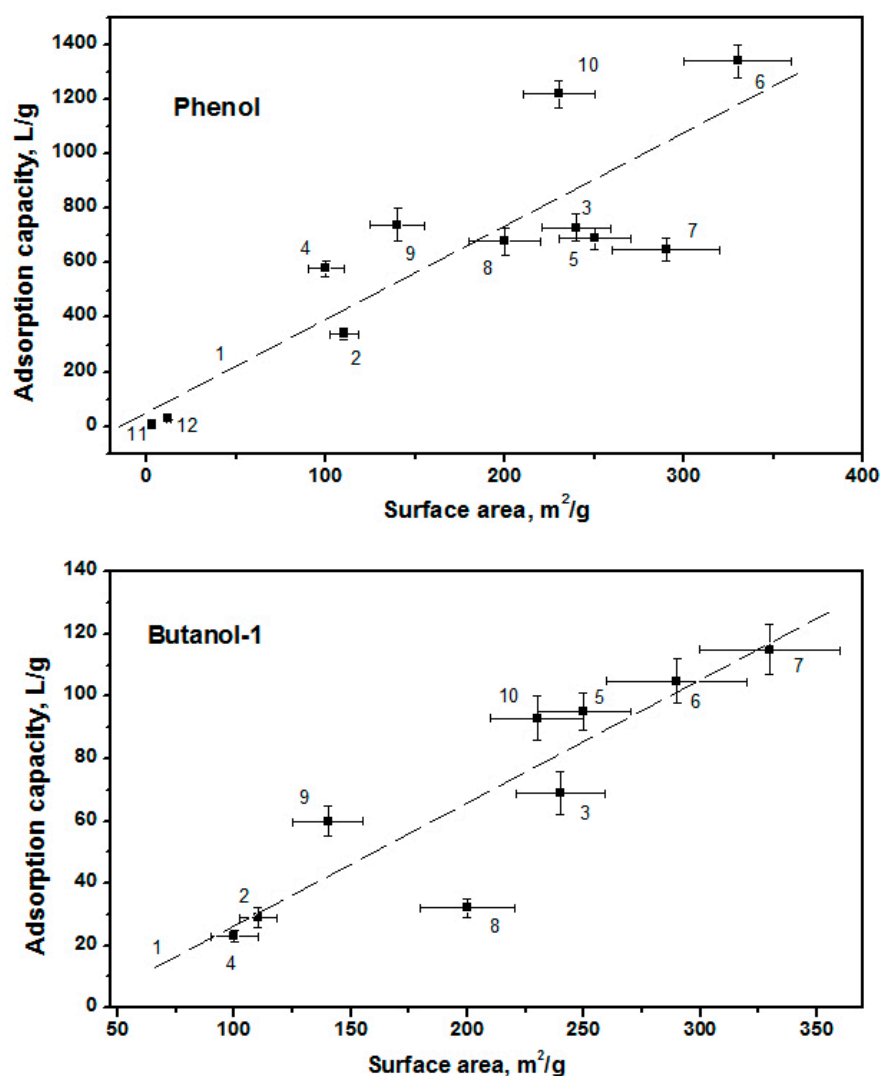

Figure 2. Dependences of the adsorption capacity of the sorbents (retention volumes) towards phenol and butanol-1 vs. specific area. 1—least squares regression for these correlations, notations 2–12 correspond to the sorbents from the Table 3.

The presented dependences show that the adsorption capacity of the studied sorbents was proportional to their specific surface area. For fully carbon sorbents of the Carbopack series (sorbents 1–3), this dependence was strictly linear in the cases of, both, phenol and

butanol-1. As it comes to the composite sorbents, the dependence was less pronounced, which is due to the differences in the adsorption capacity of the silica matrix and MWCNTs, and to differences in the specific surface area of different types of MWCNTs used for the synthesis of sorbents (Table 2). In this case, for sorbents having MWCNT deposited from the gas phase, the surface of carbon nanotubes should be fully accessible for low-molecular-weight sorbates, so, an additional correlation was observed based on the calculations considering the surface of only the carbon phase S_C (m^2 g^{-1}).

The obtained surface-layered nanocarbon-silica sorbents and, above all, MWCNT@ASG-900 open up a way to the express pre-concentration of alcohols and phenols from the humid air flow at high flow rates through a tube with a sorbent, providing a pre-concentration factor of 10^4 for analytes within 8–10 min. In Figure 3 there is a juxtaposition of the output retention curves of butanol-1 in sorption columns filled with equal weights (50 mg) of Carbopack X and MWCNT@ASG-900. Similar results were obtained for phenol.
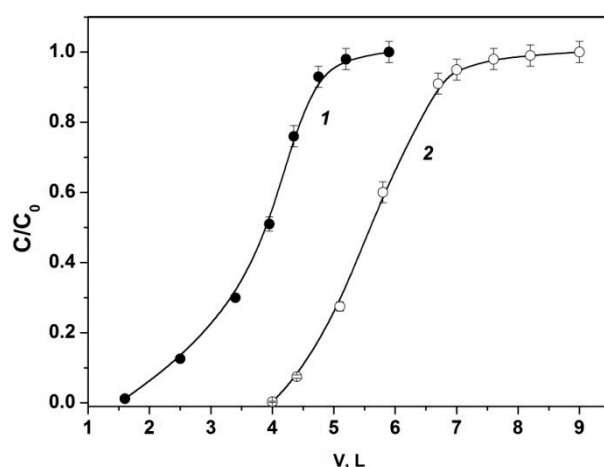

Figure 3. Output retention curves of butanol-1 from the air flow (200 mL/min) in 20 mm × 2.5 mm ID columns filled with Carbopack X (1) and MWCNT@ASG-900 (2) with particle sizes of 0.18–0.25 mm.

The advantages of the surface-layered sorbents are especially noticeable at high flow rates of the analyzed air. This is illustrated in Figure 4, which shows the dependence of HETP on the volumetric air flow rate through sorption columns of equal sizes.
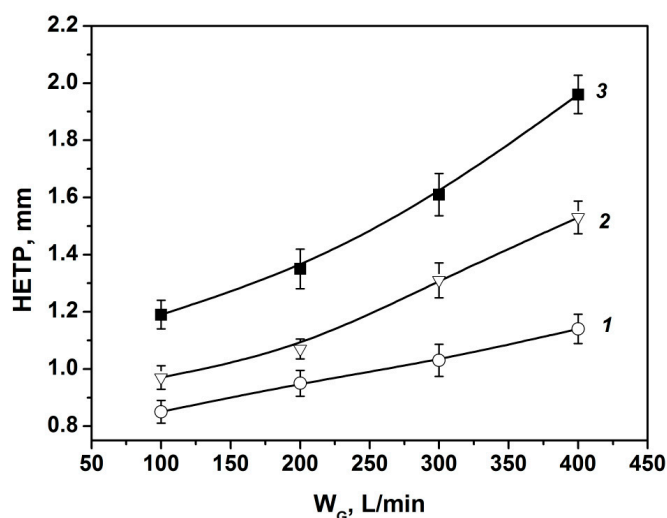

Figure 4. HETP values obtained for phenol vs. the volume rate of the gaseous phase flow through 20 mm × 2.5 mm ID columns, filled with MWCNT@ASG-900 (**1**), Carbopack X (**2**), and MWCNT@KSK-2 (**3**) with particle sizes of 0.18–0.25 mm.

Quantitative desorption of phenol compounds retained from the flow of the analyzed air through the short 20 mm × 2.5 mm ID column filled with the MWCNT@ASG-900 sorbent can be performed using 0.2 mL of acetonitrile, which was analyzed by using the reversed-phase HPLC with a spectrophotometric detector. Figure 5 shows a chromatogram obtained for a model gas mixture with a phenol concentration of 0.05 mg /m^3 after passing 2 L of this mixture through the sorption column during 10 min. It should be noted that the sensitivity of the detection of separated phenols can be increased more than 10 times by using an electrochemical detector instead of a spectrometric one.
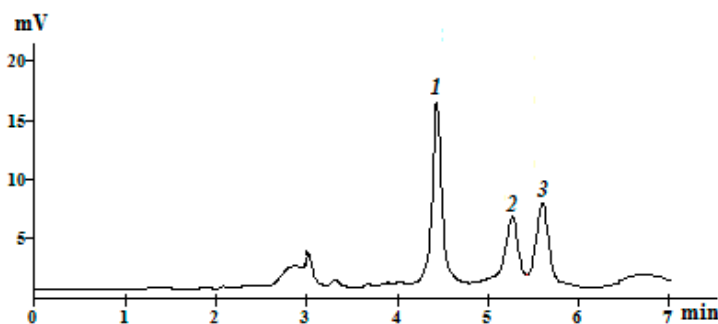
Figure 5. HPLC chromatogram of the concentrate obtained with the model gaseous mixture containing 0.05 mg m^{-3} each of phenols. The eluent is a mixture of acetonitrile–water (30:70 *v/v*), flow rate—1.0 mL/min. 1-phenol; 2-m-cresol; and 3-o-cresol.

The difficulties of thermal desorption of phenolic compounds from the surface of the carbon adsorbents are well known. To fix this problem, a sorbent with a layer of pyrocarbon on the surface of a macroporous porochrome-3 GC support with a small specific surface area was synthesized (see Table 3, sorbent 12). The resulting sorbent is ca. 40% more efficient regarding retention of phenol against Porochrom-3 (sorbent 11) and allows for the pre-concentration of phenol and isomeric cresols with a concentration factor of 2·10^3 from 2 dm^3 of the air in 5 min using sorption column 100 mm × 2.5 mm ID. The subsequent thermal desorption of analytes at 250 °C ensures their GC determination with an FID detector, starting from a few µg/m^3. Figure 6 shows a chromatogram of phenols pre-concentrated from 2 L of the model gas mixture with phenol concentrations of 0.05 mg m^{-3} and thermally desorbed.
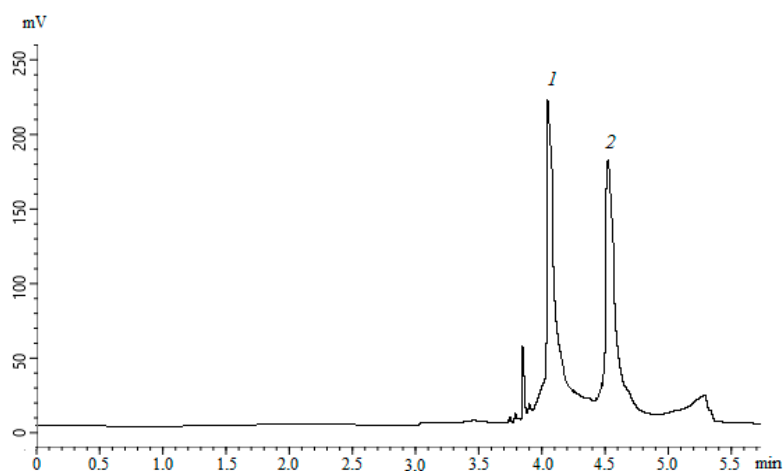

Figure 6. Gas chromatography (GC) chromatogram of phenols pre-concentrated from the model gaseous mixture analysis with concentration 0.05 mg/m^3 after thermodesorption at 250 °C from the column packed with the sorbent 12 (Table 3). 1-phenol, 2-m-cresol.

The optimization of HPLC and GC separation conditions for cresol isomers was not on a list of the issues set to be resolved in this article. Since the same TLV values have been established for cresol isomers, their separate determination and analysis at a microconcentration level in the atmospheric air are only of theoretical interest.

4. Conclusions

The possibilities of new carbonaceous sorbents (graphitized thermal soot, carbon nanotubes, and pyrocarbon) for the express pre-concentration of volatile organic compounds (medium alcohols and phenols) from the air stream were evaluated. The highest efficiency was found for surface-layered sorbents obtained by growing multilayer carbon nanotubes onto the aerosilogel surface using cobalt as a catalyst. The efficiency of these sorbents in terms of HETP was significantly higher than that of graphitized thermal soot-based sorbents (Carbopacks) having similar specific surface areas. Quantitative desorption of phenol compounds from these sorbents was carried out using acetonitrile followed by HPLC determination of analytes. Especially for the pre-concentration of phenols, sorbents based on diatomite supports (porochrome-3) modified with pyrocarbon are prepared to allow simplified thermal desorption of analytes. The proposed sorbents make it possible to pre-concentrate phenol and isomeric cresols in 5 min with a pre-concentration factor of $2 \cdot 10^3$, followed by GC-FID determination of analytes at the level of several $\mu g/m^3$.

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