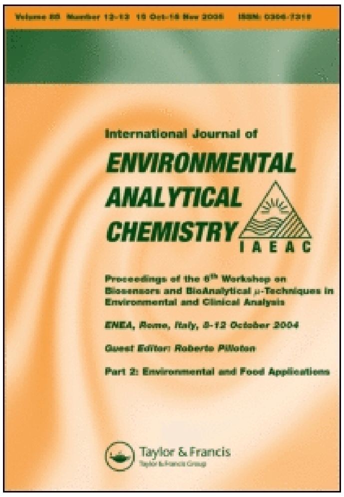

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Carbon Sorbents as a Mean for Enrichment of Atmospheric Oxygenated VOCs with Subsequent HRGC Determination

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CARBON SORBENTS AS A MEAN FOR ENRICHMENT OF ATMOSPHERIC OXYGENATED VOCs WITH SUBSEQUENT HRGC DETERMINATION

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The paper concerns the evaluation of sample preconcentration on the novel mesoporous carbons and the analytical determination of oxygenated VOCs (alcohols, aldehydes, ketones, acetates) from the gas phase. The trapped analytes were desorbed off-line by liquids and on-line by thermodesorption in combination with HRCGC, using a capillary column with a chemically bonded stationary phase under temperature programmed conditions, on-column injection and FID. Adsorption-desorption properties of the sorbents with simulated samples were evaluated by the recovery data at various concentration levels. Comparison with graphitized carbon sorbents and/or carbon molecular sieves in single bed or multibed arrangement is shown. The linearity range and limits of determination are given. An example of real sample analysis is reported (emissions measurements).

Keywords: Oxygenated VOCs; carbon sorbents; liquid desorption; thermodesorption; HRGC

INTRODUCTION

The demand for accurate, reliable and sensitive techniques for the determination of organic trace constituents in the atmosphere has increased tremendously in the recent past. The reasons include a growing concern for the quality of the environment and also the realisation that atmospheric pollution is not only a local problem. The number of different organic compounds which are emitted into the atmosphere has been risen steadily. Further, it has been recognised that several substances which had been considered harmless can pose serious hazards to the environment[1].

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There is a broad range of techniques for the determination of organic compounds at trace levels which are sufficiently sensitive and selective. Chromatography is the most widely used in connection with appropriate preconcentration and isolation techniques. The use of adsorbent tubes for sampling and preconcentration of organic contaminants in various environmental matrices has become increasingly popular as the consequence of the development of improved adsorbents, which allows the better adsorption and desorption of contaminants. There are various kinds of carbonaceous sorbents available, which may be utilised for enrichment of analytes in environmental samples: activated carbon, molecular sieves, graphitized carbon black, mesoporous carbons prepared by pyrolysis. The review on carbon sorbents and their utilisation for trace analysis of organic pollutants in environmental samples was published recently[2].

The stress in this paper is given to the analytical determination of oxygenated volatile organic compounds in air samples. Hydrocarbons, that can be emitted to the atmosphere (*e.g*. petrochemical industry, petrol stations, cars...) are involved in photochemical reactions resulting in the oxidants formation, that can contribute to the formation of regional and global tropospheric ozone. Oxygenated volatile compounds (in particular aldehydes and ketones) are often the by-products of these reactions. Acetates are frequently used in organic technologies (mainly the production and treatment of dyestuffs), pharmaceutical technologies and as solvents in electrotechnics and engineering. The mentioned groups of compounds are also emitted by vegetation. Biogenic volatile organic compounds (BOVOCs) were recently reported to be emitted from a large number of agricultural and natural plant species [3–5].

A novel mesoporous carbon sorbents had been characterised[6] and successfully applied for trapping non-polar compounds[7–9].

For oxygenated organic compounds only few data exist concerning analytical recovery on solid sorbents. The aim of this paper is to compare recoveries of a series of alcohols, ketones, aldehydes and esters for simulated sampling on two new and three commercial carbon sorbents for sampling from the gas phase. It should be stressed, however, that the study of the sorption-desorption process under simulated conditions is not the same as real conditions where co-adsorption can drastically reduce the breakthrough volumes.

EXPERIMENTAL

Sorbents

- Carb I (Anapron, Bratislava, SK), prepared by controlled pyrolysis of saccharose in the matrix of silica gel[10] 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[11], performed at 600°C in an inert atmosphere. In the next step the porogen was washed out.
- *Carbotrap 100* – Carbotrap B (Supelco, Bellefonte, PA, USA).
- *Carbotrap 300* – Carbotrap C/ Carbotrap B/ Carbosieve S-III (Supelco. PA, USA).
- *Carbotrap 301* – Carbopack C/ Carbopack B/ Carboxen 1000 (Supelco, PA, USA).

Chemicals

The following solvents were used: carbon disulphide, puriss (Avondale Labs.), methanol, pestiscan (LAB-SCAN, Analytical Sciences). The used standards (Aldrich. Milwaukee. WI) were of minimal purity 98 %.

Sampling

The preconcentration of oxygenated VOCs was evaluated in an experimental arrangement published elsewhere[7]. Standards were injected into the vaporiser and 10 dm^3 of purified nitrogen (at the flow rate of 25–100 $cm^3.min^{-1}$) was passed through the apparatus. After flushing the sorbent with nitrogen, sorbent from the sorption and the control part of the tube were separately transferred into the glass vials. Sorbates were desorbed by 1 mL of solvent for 15 min in ultrasonic bath. After sedimentation of sorbent the supernatant was analysed.

In the case of thermodesorption, the simulated sorption was performed in Dynatherm, Thermal Tube Desorber, Model 890/891 (Supelco, Bellefonte, PA, USA). Glass sampling tubes with 4 and 2 mm I.D. were filled by sorbents Carb I and Carb II. The removal of possible impurities was performed by activation at 380 °C for 40 min. During the sampling simulation 1 µL of standard solution was slowly injected into the empty glass tube placed in the desorption chamber with the temperature held at 350 °C for 10 min. Volatile compounds were transferred by the stream of an inert gas at the flow rate of 33 $cm^3.min^{-1}$ into the secondary chamber and trapped into the adsorption tube. The total volume of helium was 1 dm^3. Then the adsorption tube was replaced in the desorption chamber and the analytes were directly injected into chromatographic column or were first refocused on the tube with smaller internal diameter. During the refocusation of the trapped components from the 4 mm tube to the 2 mm tube the temperature of the desorption chamber was held at 350 °C for 5 min. From the refocusation tube the analytes were desorbed at 350 °C and carried directly to the chromatographic column. Direct injection of a liquid into the chromatographic column was performed via the injection port of desorption chamber (held at 330 °C for 5 min) by a syringe. The temperature of transfer line and valve compartment was 220°C.

Gas chromatography

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 following capillary columns and conditions were used:

- SPB-1 (60 m × 0.32 mm I.D. × 1 μm film thickness) connected with 1 m retention gap (0.53 mm I.D.), the carrier gas was hydrogen with a linear velocity of 40 cm.s^{-1}, on-column or splitless injection 1 μL, temperature programme: 35°C, gradient 1.5°C.min^{-1} to 50°C, then gradient 10°C.min^{-1} to 180°C,
- CP Sil-8 CB (50 m × 0.32 mm I.D. × 5 μm film thickness) connected with 1 m retention gap (0.53 mm I.D.), the carrier gas was hydrogen with a linear velocity of 40 cm.s^{-1}, on-column injection 1 μL, pressure program 20 kPa - 0.1 min, gradient 680 kPa.min^{-1}, final pressure 70 kPa, FID,

  * TPG1 conditions: 35°C, gradient 4°C.min^{-1} to 180°C,
  * TPG2 conditions: 35 °C – 1 min, gradient 8 °C.min^{-1}, final temp. 220 °C – 10 min.,
- in the case of thermodesorption: SPB-1 (60 m × 0.53 mm I.D. × 1.50 μm film thickness) under TPG conditions: 27°C – 3 min, gradient 1.6°C.min^{-1} to 40°C, then 10°C.min^{-1} to 180°C, the carrier gas was helium with the flow rate of 5 cm^3.min^{-1}, 0.5 μL of the sample was injected via the injection port. The temperature of the desorption chamber was 350°C.

RESULTS AND DISCUSSION

Alcohols, aldehydes and ketones

Chromatographic measurements were carried out on the non-polar chemically bonded dimethylsiloxane stationary phase and on the methylphenylsiloxane phase with the thick film of stationary phase. The column with dimethylphenylsiloxane stationary phase exhibits good properties for the separation of mentioned polar components, all separated compounds had good shape of chromatographic peaks. Sufficient resolution and peak form was obtained with the use of dimethylsiloxane phase as well. The linearity range was checked in the range of 1.8 to 120 ng per injection and was proved to be linear (correlation coefficient >0.999).

Recoveries of the adsorption-desorption process were calculated from chromatographic peaks areas using n-nonane and toluene as internal standards. Recovery values of liquid desorption are shown in Table I, where also the limits of determination are summarised. Limits of determination were calculated as 10 times the noise signal level. Practically, for all studied compounds the recoveries with the use of liquid desorption were above 60 % on the concentration range of 3 – 15 μg.dm^{-3}. The smallest values were obtained for alcohols with the greatest polarity. This observation and measured recovery data of vinylacetate (see next section) suggests that strong sorbent – solute interactions were taking place during the adsorption. We suppose, there are the specific interactions of polar compounds with the residual active functional groups of polar character on the sorbent surface. Such residual polar groups were proved by FTIR spectroscopy on sorbents prepared from saccharose[12] and by solid-state NMR spectroscopy[6].

TABLE I Characteristics and results of recoveries for selected oxygenated compounds on sorbent Carb I with liquid desorption (CS_2)

Compound	*boiling point [°C]*	*limit of determination [ng]*	**limit of determination [μg.m^{-3}]*	*R_{LD} [%]*	*RSD_{LD} [%]*
2-butanol	99-100	0.49	25	78	1.9
3-methyl-3-buten-1-ol	130-132	0.54	27	70	0.3
2-methyl-1-butanol	130	0.84	42	82	0.8
4-penten-1-ol	134-137	0.94	47	64	1.1
1-pentanol	136-138	1.83	92	76	0.6
cis-3-hexene-1-ol	156-157	1.53	77	68	0.9
2-hexanol	136	1.52	76	85	0.4
1-heptanol	176	2.23	112	80	1.6
1-octanol	196	1.43	72	78	4.3
hexanal	131	0.40	20	98	0.8
heptanal	153	0.52	26	94	4.7
2-heptanone	149-150	0.45	23	60	0.3

R_{LD} - recovery of liquid desorption (CS_2), concentration 3 μg.dm^{-3}.
RSD_{LD}- relative standard deviation of recovery determination by liquid desorption, number of measurements n=3.
* sample volume 20 dm^3, liquid desorption, 1 cm^3 of desorption agent.

When analysing oxygenated compounds with lower concentration some of them remained strongly bonded and the repeatability of the chromatographic area became unacceptable. The extract had to be immediately analysed as the decomposition of some compounds after standing in solvent and the formation of new components, *e.g.* acetales was observed after few days.

For the analysis of real samples it was necessary to calibrate the preconcentration method, because it was found that the recovery of polar compounds is concentration dependent. This observation is a limitation in comparison to aromatics and alkanes, which provide the recovery close to 100 % up to the lowest studied concentration level (1.5 ng. dm^{-3})[9].

For the study of thermodesorption, recoveries in the sorption-desorption process were determined with the use of n-heptane as internal standard for various concentration levels. The obtained results of recoveries at 150 ng. dm^{-3} are summarised in Table II. 3-Methyl-2-butene-1-ol was not evaluated as it co-elutes with a solvent impurity (Figure 1). Recovery values were in the interval 60 – 100 % for Carb I, for Carb II 89–106 % and the RSD_{TD} value was ≤ 8.8 % for the majority of components. On the other hand, in most measurements on Carb I and Carb II the recovery for 1-heptanol was unsatisfactory ($R_{TD} \gg 100$ %); unsatisfactory results on Carb I were also observed for 2-hexanol, and on Carb II for 1-octanol. Values in Table II are marked by *. In the case of the latter compounds decomposition takes place (low recoveries) and the reaction products could coelute with another compounds leading to $R_{TD} \gg 100$ %. On graphitized commercial sorbent Carbotrap 100, which is a more pure form of carbon, the results are in the range of 90 – 102 % with $RSD_{TD} \leq 5.4$ %. From the results it follows that the recoveries with the use of Carb II are comparable to the values with the use of Carbotrap 100 (with the exception of the three mentioned compounds), Carb I exhibits stronger interactions with the investigated compounds and the recoveries are lower than on both, Carb II and Carbotrap 100.

An example of the GC separation of studied oxygenated compounds after thermodesorption from Carb I with concentration of 150 ng. dm^{-3} is shown in Figure 1.

In all series of measurements the repeatability of the chromatographic area by direct injection of liquid standards and after desorption was calculated. The results obtained on the concentration level 150 ng. dm^{-3} are summarised in Table III. The RSD values were calculated for the ratios between the chromatographic areas of the studied compounds and the internal standard. From the Table III it follows that the specified standard deviation is comparable for both, direct injection and injection with the use of sorbent preconcentration. The repeatability of the relative areas exhibited in both cases for all studied components a RSD ≤ 11.1%.

TABLE II Results of preconcentration recovery determinations for oxygenated compounds with the use of carbon sorbents, concentration level 150 ng. dm^{-3}

Sorbent	*Carb I*		*Carb II*		*Carbotrap 100*	
Compound	R_{TD}	RSD_{TD}	R_{TD}	RSD_{TD}	R_{TD}	RSD_{TD}
2-butanol	79	5.1	91	1.6	98	4.7
2-methyl-1-butanol	83	5.8	95	3.0	97	0.1
1-pentanol	62	8.8	94	2.5	102	2.4
2-hexanol	49*	18.1	100	4.3	97	2.7
1-heptanol	124*	20.6	115*	3.2	94	1.0
1-octanol	82	7.4	131*	3.5	90	4.0
3-methyl-3-butene-1-ol	92	4.1	90	3.5	98	5.4
4-pentene-1-ol	85	3.4	95	2.3	98	3.2
hexanal	72	4.1	92	1.9	97	5.2
cis-3-hexene-1-ol	85	5.5	100	1.9	98	2.5
2-heptanone	104	4.9	106	4.5	96	4.1
heptanal	80	0.4	94	3.4	98	5.0

R_{TD}- preconcentration recovery calculated from relative ratios of chromatographic areas, expressed in %, number of measurements n = 3–4.

RSD_{TD}- relative standard deviation of recovery determination in %.

* – explanation in text.

TABLE III Repeatability of chromatographic area determinations (expressed by relative standard deviation in %) in direct injection and after thermodesorption (sorbents Carb I, Carb II, Carbotrap 100) on concentration level 150 ng. dm^{-3}

Compound	*Direct injection*	*Carb I*	*Carb II*	*Carbotrap 100*
	RSD [%]			
2-butanol	1.5	6.7	3.3	7.0
2-methyl-1-butanol	1.1	6.8	1.6	3.0
1-pentanol	1.9	7.8	1.1	3.7
2-hexanol	2.7	1.9	1.4	2.0
1-heptanol	2.7	3.3	2.5	2.0
1-octanol	6.4	8.2	4.0	5.3
3-mehtyl-3-butene-1-ol	1.7	7.5	6.4	1.9
4-pentene-1-ol	1.4	6.0	2.4	3.0
hexanal	2.3	4.1	3.5	0.5
cis-3-hexene-1-ol	0.8	9.3	3.1	1.4
2-heptanone	1.3	8.7	1.9	1.4
heptanal	7.2	9.6	3.8	1.7

number of repeated measurements n = 4.

At the concentration of 15 ng. dm^{-3} the RSD_{TD} values for relative areas of oxygenated compounds were ≤ 25 %. After thermodesorption from Carbotrap 100 a RSD ≤ 12 % was found for the majority of components. Recoveries on Carb I and Carb II were in the range between 50 – 106 %, $RSD_{TD} \leq 20$ % for the majority of components. On Carbotrap 100 higher recoveries at this concentration level were obtained ($R_{TD} \geq 92$ %, $RSD_{TD} \leq 10.4$).

According to our knowledge the following sorbent combinations Carbotrap C/ Carbotrap and Carbotrap C/ Carbotrap/ Carbosieve S-III were used for the sampling of oxygenated compound, but the preconcentration recoveries were not reported [13,14].

Acetates

The linearity range of the GC detector response of individual components was tested in the mass range 2 ng to 3 μg per injection. These are amounts expected to be injected after their trapping and desorption from adsorbent tubes. It was found, that the correlation coefficient in all cases was better than 0.999. For all studied components the RSD of the chromatographic area determination by FID was ≤ 3% (n=4).

The limits of determination are expressed in absolute amounts and in concentrations of acetates per m^3 of air sample, if 20 dm^3 of the air sample are passed through the sorption tube and liquid desorption is performed (1 cm^3 of solvent). The results are summarised in Table IV. The volume of 20 dm^3 was chosen as the highest usable under the given experimental conditions, because it equals to safety sampling volume (SSV) of methylacetate[9]. SSV for other studied acetates are higher and the possibility of breakthrough is eliminated. When 1 dm^3 of gas sample passes through the sorbent bed and 1 – 3 cm^3 of solvent are used for extraction, the mentioned method allows the determination of acetates in air samples at concentrations higher than 200 μg.m^{-3}.

With the use of thermodesorption the limits of determination for the studied acetates per 1 dm^3 of air sample are similar to those shown in Table IV. With 20 dm^3 of sample the limits of determination are 20 times lower, so they are in the region of some hundrets of ng.m^{-3}.

For the adsorption-desorption recovery determination the calibration with liquid solutions of acetates was performed. The recovery was calculated from the ratio of the absolute chromatographic peak areas of the standard solution and the peak areas obtained with the application of the preconcentration step with the sorbent or the method of internal standards. In the case of liquid desorption the recovery of methylacetate and vinylacetate with Carb I and a sampling flow rate of 200 cm^3.min^{-1} was low (30 %; 50 %), but the recovery of ethyl- and butylac-

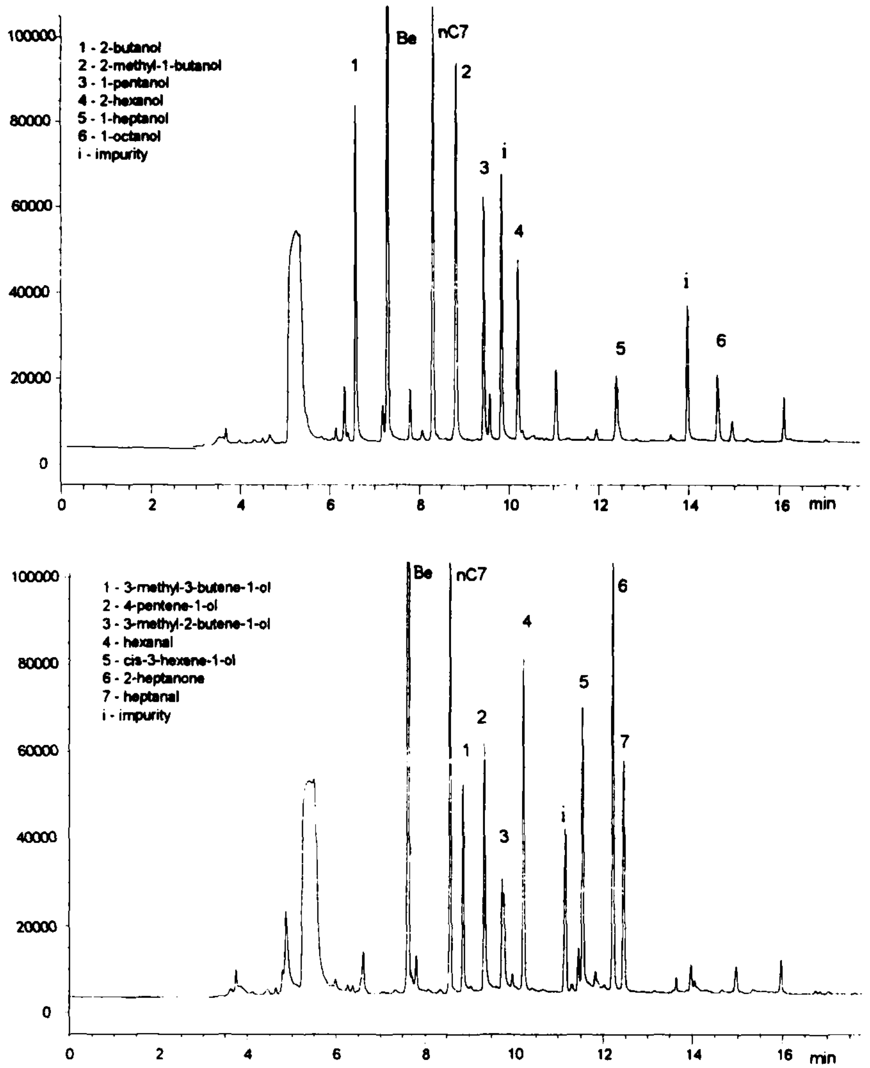

FIGURE 1 *a*, *b* Chromatographic separation of oxygenated volatile compounds (two simulated mixtures *1a*, *1b*) on capillary column SPB – 1 with polydimethylsiloxane phase (60 m × 0.53 mm I. D. × 1.5 µm film thickness) under TPG conditions (35 °C – 3 min. gradient 8 °C.min^{-1}, 200 °C – 5 min). carrier gas He (at the flow rate of 13.5 cm^3.min^{-1}), FID, concentration level 150 ng. dm^{-3}, after desorption (temperature of desorption 350 °C) from Carb I (from 4 mm I.D. tube and refocused on a tube with 2 mm I.D.). *Assignment:* Be – benzene, nC_7 – n-heptane

etates was acceptable (around 90 %). Under the same experimental conditions with Carbosieve S-III the recoveries were the following: methyl- 69 %, vinyl- 88 %, ethyl- 94 % and butylacetate 100 %. It was found, that the recovery for the most volatile compounds was flow-dependent. The optimal flow rate for the sampling of acetates was found to be 25 $cm^3.min^{-1}$. The recovery values of the sorption-desorption process under the optimal sampling flow rate with Carbosieve S-III were close to 100 %, the values for Carb I are summarised in Table IV.

TABLE IV Characteristics of acetates (boiling point, limit of determination measured with the use of FID and on-column injection system) and results of recovery determinations of acetates on sorbent Carb I with the use of liquid desorption

Analyte	*boiling point [°C]*	*limit of determination [ng]*	**limit of determination [$\mu g.m^{-3}$]*	R_{LD} %	RSD_{LD} %
Methylacetate	57.5	0.28	14	96	2.6
Vinylacetate	72–73	0.31	15	85	1.9
Ethylacetate	76.5–77.5	0.20	10	85	3.2
Butylacetate	124–126	0.18	9	105	1.8

* sample volume 20 dm^3, liquid desorption, 1 cm^3 of desorption agent;
R_{LD} – recovery of liquid desorption (desorption agent CS_2 with 1% of methanol), conc. 1–3 $\mu g.dm^{-3}$; number of repeated analyses n=3, RSD_{LD} – relative standard deviation in %.

The composition of the desorption agent was optimised. The addition of 1–3 % of methanol to carbon disulphide and the chromatographic resolution of methylacetate from the solvent components was studied. The addition of 1 % of methanol leads to the enhancement of recovery values by approximately 10 % at the studied concentration level 180 $ng.\mu L^{-1}$ (in solvent after desorption). The recovery results are given in Table IV, with $RSD_{LD} \leq 3.9$ % for n = 3. The further increase of the methanol content (2 %) did not increase the recovery, but the addition leads to an improvement in the shape of the chromatographic peak of vinylacetate. For comparison, the values published in the literature[15] for activated carbon and CS_2 desorption are the following: methylacetate 88 %, ethylacetate 89 % and butylacetate 95 %.

In the case of thermodesorption the standards were injected into the empty tube of the desorption chamber (350 °C), the volatile components were carried by the stream of helium and trapped on the adsorption tube with Carb I, Carb II or on a multibed tube Carbotrap 300 with 4 mm I.D. in the secondary trapping chamber. After flushing of 1 dm^3 of inert gas the adsorption tube was transferred into the desorption chamber. The compounds if necessary can be refocused on the tube with the lower internal diameter (*e.g.* 1 mm I.D.). From the focusation tube the compounds were desorbed at 350 °C via a heated transfer line into the chromatographic column.

The values of the recoveries with the use of Carb I, Carb II and Carbotrap 300/ Carbotrap 301 on three studied concentration levels are listed in Table V. An example of chromatographic separation of acetates desorbed from Carb II is shown in Figure 2.

TABLE V Results of recovery determinations of acetates with the use of thermodesorption on Carb I, Carb II and Carbotrap 300 (refocused on Carbotrap 301)

			Carb I			
Concentration	*600 ng. dm^{-3}*		*50 ng. dm^{-3}*		*5 ng. dm^{-3}*	
↓analyte	*R_{TD} [%]*	*RSD_{TD}[%]*	*R_{TD} [%]*	*RSD_{TD}[%]*	*R_{TD} [%]*	*RSD_{TD} [%]*
Methylacetate	91	1.3	100	3.8	84	18.5
Vinylacetate	54	2.2	37	0.6	-	-
Ethylacetate	100	1.7	103	3.3	100	13.4
Butylacetate	99	1.1	103	1.8	126	1.6
			Carb II			
Concentration	*600 ng. dm^{-3}*		*50 ng. dm^{-3}*		*5 ng. dm^{-3}*	
↓analyte	*R_{TD} [%]*	*RSD_{TD} [%]*	*R_{TD} [%]*	*RSD_{TD} [%]*	*R_{TD} [%]*	*RSD_{TD} [%]*
Methylacetate	86	1.0	80	3.1	53	1.0
Vinylacetate	52	4.8	39	2.1	94	5.8
Ethylacetate	93	1.1	92	2.6	102	8.4
Butylacetate	95	0.5	90	1.9	89	2.2
			Carbotrap 300 (refocused on Carbotrap 301)			
Concentration	*600 ng. dm^{-3}*		*50 ng. dm^{-3}*		*5 ng. dm^{-3}*	
↓analyte	*R_{TD} [%]*	*RSD_{TD} [%]*	*R_{TD} [%]*	*RSD_{TD} [%]*	*R_{TD} [%]*	*RSD_{TD} [%]*
Methylacetate	97	1.4	91	3.7	108	2.6
Vinylacetate	86	4.9	80	1.8	78	6.0
Ethylacetate	99	1.8	101	0.9	129	3.3
Butylacetate	97	0.8	102	2.5	97	9.0

the number of measurements n = 3–4, R_{TD} – recovery in %, RSD_{TD} – relative standard deviation of the recovery determination in %.

The recoveries for methyl-, ethyl- and butylacetate on Carb I were close to 100 %, whereas on Carb II were slightly lower. At lower concentrations the relative standard deviation of the recoveries were higher for both sorbents. At the concentration level of 5 ng. dm^{-3}, the RSD_{TD} was ≤ 18.5 %. The interactions of vinylacetate with Carb sorbents are supposed to be very strong, so that a temperature of 350 °C gave around 50 % recovery (600 ng. dm^{-3}). Higher desorption temperatures can cause the thermal decomposition of the acetates. The recoveries at the concentration level of 5 ng. dm^{-3} are low, the background interference lead to a difficult chromatographic data evaluation. Recovery values obtained with the commercial multibed sorbent Carbotrap 300 are comparable with the data measured on Carb sorbents with the exception of vinylacetate. The recovery for vinylacetate on the multibed sorbent arrangement Carbotrap 300 is significantly higher. The recovery data values reported in the literature[16] for butylacetate are the following: 92.9 % for Tenax TA and 64 % for Carbotrap B. Hsu et al.[17] reported the utilisation of Carbopack B and Carbosieve S-III for sampling vinylacetate, but the recovery data are not given.

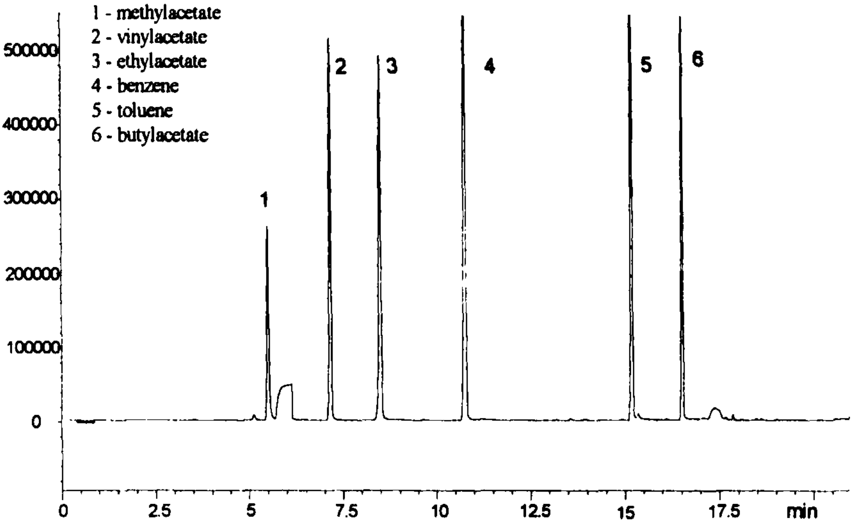

FIGURE 2 Chromatographic separation of acetates on capillary column SPB 1 (60 m × 0.53 mm I. D. × 1.5 μm film thickness) under the temperature programmed (TPG) conditions (init. temp. 27 °C - 3 min, grad. 1 : 1.6 °C.min^{-1} to 40 °C, grad. 2: 10 °C.min^{-1} to 180 °C) after thermodesorption from sorbent Carb II (temperature of desorption 350 °C), carrier gas He with the flow rate 13.5 cm^{3}.min^{-1}, concentration 600 ng. dm^{-3}, FID

Novel porous carbons were applied also for real sample measurements. The samples of emissions from a paint factory (colour mixing chamber) were trapped on the sorption tubes with Carb I and desorbed by CS_2 with 2 % of MeOH. In Figure 3 an example of the chromatographic separation of components trapped in the adsorption part of the tube is presented *(a)*, where methyl-, ethyl- and butylacetate were identified. In the control part of the tube *(b)* the components of interest were below the detection limit. Another example of a real measurement is the determination of emissions of butylacetates in a pharmaceutical plant. The sampling conditions and the results of quantitative analysis calculated with the method of calibration curve are summarised in Table VI. The calibration curve method is useful for routine measurements, as it includes the recovery data for the whole concentration range of interest. For both examples of real sampling the expected emission concentrations were high, the use of liquid desorption was advantageous over thermodesorption.

TABLE VI Sampling conditions and results of determination
a.l emissions from the paint factory

Sampling conditions		*Compound*	*Concentration [mg.m^{-3}]*	*RSD$_c$ [%]*
Sampling time	113 min	MeOAc	12.4	7.3
Sampling volume	8 dm^3	EtOAc	128.5	6.4
Atm. pressure	98.4 kPa	BuOAc	20.0	4.7
Temperature	15 °C			

Concentration is an average value from 3 parallel determinations.
RSD$_c$- relative standard deviation of concentration determination.
Relative standard deviation RSD of GC determinations (n=3) for 1 tube is ≤ 4.7 %.

b.l emissions of butylacetate from pharmaceutic plant

Sampling conditions		*Concentration [mg. m^{-3}]*	*RSD$_c$ [%]*
Sampling time	100 min		
Sampling volume	7.5 dm^3	3.11	5.52
Atm. pressure	98.6 kPa		
Temperature	16°C		

number of measurements n=3; RSD$_c$ – relative standard deviation of concentration determination, RSD – relative standard deviation RSD of GC determinations ≤ 2.2.

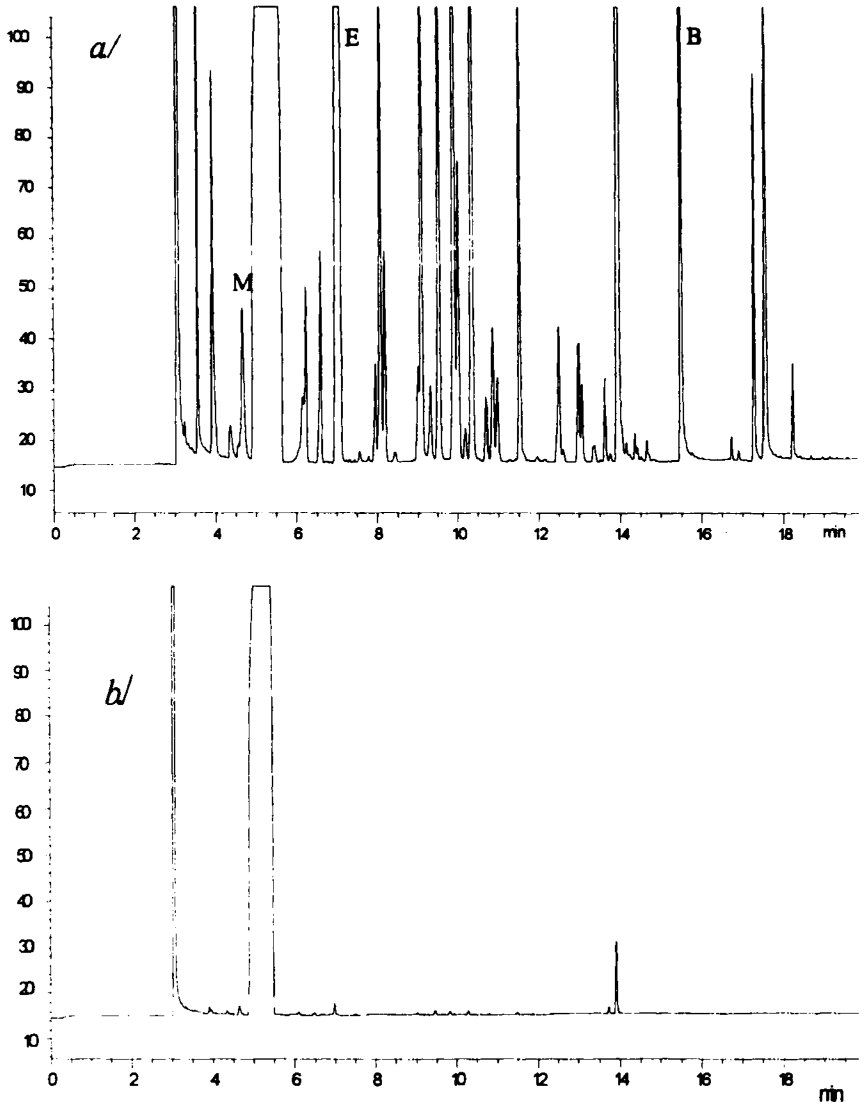

FIGURE 3 *a*, *b* Chromatographic separation of emissions from the paint factory on capillary column SPB-1 (60 m × 0.32 mm I. D. × 1 μm film thickness) under TPG conditions (init. temp. 35 °C, grad. 1: 1.5 °C.min^{-1} to 50 °C, grad. 2: 10°C.min^{-1} to 180 °C), on-column injection, FID, *a*/ adsorption part of the sampling tube, desorption agent – CS_2 with 2 % MeOH, *b*/ control part of the tube. Assignment: M – methylacetate, E – ethylacetate, B – butylacetate

CONCLUSION

Two novel mesoporous carbon sorbents were applied for preconcentration of oxygenated compounds (acetates, alcohols, aldehydes and ketones) in simulated conditions. The recovery was determined by GC measurements of series of compounds at various concentration levels with FID, the linearity range of the detector was checked and limits of determination were measured. A systematic study of sorption-desorption process of oxygenated compounds (going down to the lowest concentration according to an acceptable recovery data and reproducibility of preconcentration step) was performed for the comparison with commercial carbon sorbents. The example of practical utilisation for emission measurement is given.

Carb I is recommended for sampling all studied compounds with the subsequent liquid desorption. It was found to be excellent for sampling acetates and C_6, C_7 aldehydes (recoveries > 85 %) and it provides satisfactory recovery data for C_7 ketones and $C_4 - C_8$ alcohols (> 60%) with very good reproducibility of determination.

For thermodesorption we found the following results which could serve in the selection of an appropriate sorbent for isolation and preconcentration of oxygenated compounds from air matrices:

- Carbotrap 100 is excellent for sampling $C_4 - C_8$ alcohols (recoveries > 90%);
- Carb II can replace Carbotrap 100 for trapping the majority of $C_4 - C_8$ alcohols (recoveries > 91 %);
- for trapping C_7 ketones and C_6, C_7 aldehydes Carb II and Carbotrap 100 are fully recommended (recoveries > 92 % with good reproducibility). Carb I is applicable also, but with lower recoveries and thus with higher limits of detection;
- Carb I is excellent for sampling methyl-, ethyl- and butylacetates. Carb II is recommended too. For sampling acetates including vinylacetate it is recommended to utilise the multibed arrangement Carbotrap 300.

The results of the systematic study represent also a contribution to improve the technology process for the preparation of porous carbons without residual functional groups. The research in the area of porous carbons is a promising way to prepare a tailor made sorbent and also from the economical point of view. However, it should be emphasised, that recovery data should be obtained under real conditions. The carbons proposed need to be further tested for their ability to prevent artefacts formation in the presence of e.g. ozone, NO_2, SO_2 and water.

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