

2. Chambers, J., Cleveland, W., Kleiner, W., and Tukey, P., *Graphical Methods for Data Analysis*. Duxbury Press, Boston, 1983.
3. Hoaglin, D. C., Mosteler, F., and Tukey, J. W., *Exploring Data Tables, Trends and Shapes*. Wiley, New York, 1985.
4. Scott, D. W. and Sheater, S. J., *Commun. Statist.* **14**, 1353 (1985).
5. Lejenne, M., Dodge, Y., and Koelin, E., *Proceedings of the Conference COMSTAT'82 Toulouse*. P. 173 (Vol. III).
6. Hoaglin, D. C., Mosteler, F., and Tukey, J. W. (Editors), *Understanding Robust and Exploratory Data Analysis*. Wiley, New York, 1983.
7. Kafander, K. and Spiegelman, C. H., *Comput. Stat. Data Anal.* **4**, 167 (1986).
8. Hines, W. G. S. and Hines, R. J. H., *Am. Statist.* **41**, 21 (1987).
9. Hoaglin, D. C., *J. Am. Statist. Assoc.* **81**, 991 (1986).
10. Stoodley, K., *Applied and Computational Statistics*. Ellis Horwood, Chichester, 1984.
11. *Statistical package ADSTAT 2.0*. TriloByte, Pardubice, 1992.

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## The Testing of Carbon Sorbent for Preconcentration of Volatile Organic Trace Compounds

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Carbon sorbent Carb I (prepared by controlled pyrolysis of saccharose) was tested for preconcentration of volatile organic compounds from the gas phase. The model mixture of hydrocarbons (n-alkanes and aromatics) and mixture of aromatics with low-boiling polar solvents was used. For desorption of compounds several solvents were utilized, carbon disulfide was found to be the best. Adsorption—desorption process was studied in the concentration range of components in nitrogen 0.03—15  $\mu\text{g dm}^{-3}$ . Chromatographic measurements were performed on gas chromatograph with on-column and splitless injection, fused silica capillary columns with chemically bonded stationary phases under temperature programmed conditions and flame ionization detector. The recovery of n-alkanes and aromatics was found to be around 90 %, the recovery of low-boiling solvents, particularly of polar character was low.

The main part of toxicological analyses and analyses that have been required with regard to the control of the environment is concentrating upon compounds with very low concentration. In many cases the concentrations of contaminating components are so low, e.g. in air, that the common detectors used, e.g. in gas chromatography, do not detect them. Organic contaminating components in environmental samples generally occur in  $\text{ng kg}^{-1}$  to  $\mu\text{g kg}^{-1}$  as a part of a complex matrix [1]. Besides that, samples are usually not compatible with chromatographic system, therefore analysis with direct sample injection is not possible.

It is therefore necessary to perform sample pretreatment before an analysis. It is mainly preconcentra-

tion of components of interest, isolation of determined analytes from the matrix and removal of potential interferences. For this reason there have been utilized each time more special qualities of sorbent materials [2—4].

In the selection of a proper sorbent it is necessary to take into consideration general characteristics as functional groups at the surface, chemical and thermal stability, as well as inertness and catalytic properties, mechanical resistance, pores diameter and volume, specific surface area, size and shape of particles.

Affinity of sorbents towards various organic compounds depends on the type of functional groups bound on the surface of a sorbent and on their orientation on the surface.

Homogeneous sorbent surface influences the reproducibility of the sorption process. Catalytic properties of active sites may initiate changes in original analytes, which may lead to incorrect identification.

Pores diameter is indirectly proportional to the surface area size and from that it follows that for the effective compounds accumulation the pores size should be small. Sorbents with a large specific surface area have higher number of active sites and are, therefore, more effective accumulation media. The surface area may be increased by decreasing pores diameter. However, when the pores sizes start to be comparable with molecules diameter, the penetration of molecules into pores is slowed down. If large molecules block pores, they are not permeable for small molecules.

The number of new types of sorbents used as stationary phases in HPLC and SPE (solid-phase extraction) has been increasing [5, 6]. Besides sorbents with a broad utilization the increased attention is paid to tailored sorbents, which allow optimal solution of a given separation problem. Among potential sorbents belong materials with matrix built prevalently of carbon. They are simply called carbon sorbents. Their preference is predominantly in the high chemical and thermal stability. In contradistinction to sorbents with SiO<sub>2</sub> matrix (silica gel, porous glass) it is possible to use them without any pH limitation and in comparison with sorbents based on organic polymers they resist to much higher temperatures. Sorbents with carbon matrix may serve as carriers of various active groups.

Adsorption properties of carbon sorbents depend besides mentioned parameters also on geometry arrangement of carbon atoms — amorphous (glassy carbon) and crystallinity (graphite), eventually on the presence of residues of precursors structures (in technology of sorbents by pyrolysis). On the surface of carbon sorbent various functional groups may be found. There may be compounds of carbon with other elements, particularly with oxygen and hydrogen, eventually with nitrogen, or there may be found also "xenobiotic" molecules, which contaminate the surface, e.g. molecules of metals [7].

In a review paper [6] suitability of 26 porous materials for the preconcentration of trace organic compounds in air was evaluated. One group of the tested sorbents formed graphitized and activated commercial carbon sorbents (Carbosieve S II, CPP-9, CF-17). They present good or very good retention properties with all tested organic compounds. The other groups of sorbents showed good retention properties only towards a certain group of organic compounds.

The aim of our paper was to test the possibility of application of carbon sorbent, prepared by controlled pyrolysis of saccharose [8, 9], for the

preconcentration of organic compounds from gas phase before the consequent determination by capillary gas chromatography (GC).

## EXPERIMENTAL

The used solvents are: carbon disulfide, puriss (Avondale Laboratories, UK), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>; n-hexane and dimethylformamide, pure (Soyuzkhimeksport, Russia), n-hexane was cleaned by washing with H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub>, and water. After drying it was rectified [10], dimethylformamide was cleaned by distillation with benzene and water [10]; dichloromethane, anal. grade (Lachema, Czech Republic).

Standard solutions of model mixtures of organic compounds (the composition is given in Tables 1 and 2) were prepared in hexane (weighing 30 mm<sup>3</sup> of individual standards/10 cm<sup>3</sup> of solvent). The solutions with lower concentration were prepared by dilution. The used standards were of minimal purity 98 %. The purity of individual standards was checked by capillary GC.

The tested carbon sorbent Carb I was prepared by controlled pyrolysis of saccharose in the matrix of silica gel. In the next stage silica gel was removed by dissolving in NaOH.

Physical and chemical characterization of carbon sorbent covered the measurement of particles size and shape using microscopy, the determination of surface size by B. E. T. technique, thermogravimetry, and IR spectroscopy. Diffuse reflectance FTIR was utilized for monitoring of the presence of chemical groups in material after pyrolysis. It was shown that carbon sorbents prepared from various precursors have different chemical composition of the surface and some chemical properties of the starting precursors pass into carbon structure. There were found particularly residual hydroxyl groups and newly formed C=O groups [5].

The basic physical properties of the tested sorbent are the following:

- particles size 125—60 μm,
- specific surface area 1200 m<sup>2</sup> g<sup>-1</sup>,
- irregular particles shape.

Chromatographic measurements were performed on gas chromatograph HP-5890 Series II (Hewlett—Packard, Avondale, PA, USA) equipped with a flame ionization detector (FID), split/splitless injector in on-line combination with computer Vectra ES/12 and on gas chromatograph C. Erba Model 4180 (Milan, Italy) equipped with FID and cold on-column injector and integrator HP 3396A.

Measurements were performed on the following capillary columns with chemically bonded stationary phases under temperature programmed conditions:

1. HP-1 (25 m × 0.2 mm × 0.33 μm) with dimethylsiloxane phase (Hewlett—Packard) connected *via* press-fit connector with 1.4 m retention gap (i.d. = 0.53 mm); C. Erba instrument with on-column injector, initial temperature 35 °C (1 min), temperature gradient 8 °C min<sup>-1</sup>, final temperature 180 °C (5 min); detector temperature 300 °C; carrier gas: hydrogen with linear velocity 50 cm s<sup>-1</sup> determined under isothermal conditions (70 °C); gases for detector: hydrogen (50 kPa), air (100 kPa).

2. SP-Nucol (25 m × 0.25 mm × 0.25 μm) (Supelco, Bellefonte, PA, USA) with modified polyethylene glycol phase connected with 2 m retention gap (i.d. = 0.53 mm); Hewlett—Packard instrument with splitless injector, initial temperature 35 °C (5 min), temperature gradient 8 °C min<sup>-1</sup>, final temperature 180 °C (10 min); injector temperature 220 °C, detector temperature 280 °C; carrier gas hydrogen with linear velocity 40 cm s<sup>-1</sup> determined under isothermal temperature (70 °C); gases for detector: nitrogen (260 kPa), hydrogen (110 kPa), air (250 kPa).

On-column injection: 1 mm<sup>3</sup> of sample was injected with 5 mm<sup>3</sup> Hamilton syringe by fast injection.

Splitless injection: 1 mm<sup>3</sup> of sample with 0.8 mm<sup>3</sup> solvent plug was injected by "hot needle injection" technique with 10 mm<sup>3</sup> Hamilton syringe.

The preconcentration of organic compounds from gas samples was evaluated in an experimental arrangement shown in Fig. 1.

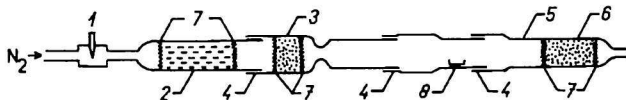


Fig. 1. An apparatus for preconcentration: 1. needle valve, 2. molecular sieve 5 Å, 3. sorbent Carb I, 4. gas tight connections, 5. sorption tube, 6. sorbent, 7. silanized wool, 8. glass vessel for sample.

A controlled volume of nitrogen (10 dm<sup>3</sup> with a flow 200 cm<sup>3</sup> min<sup>-1</sup>) was dried by molecular sieve "5 Å" and purified by sorbent Carb I. Adsorption cartridges were prepared by packing glass tubes with 150 mg of activated carbon sorbent, whereby sorbent was placed between two layers of silanized glass wool. The standards were injected into glass vessel or directly into sorbent by 10 mm<sup>3</sup> or 50 mm<sup>3</sup> syringe. 10 dm<sup>3</sup> of nitrogen was transferred through apparatus. The parts of apparatus (2) and (3) in Fig. 1 may be used only in the case of simulated analysis to prevent potential contamination of tested sorbent by impurities from gas.

In trace analysis it is very important to use all parts made of glass to prevent adsorption and/or to minimize potentiality of contamination.

As desorption reagent the following solvents were used: hexane, dichloromethane, dimethylformamide, and carbon disulfide. After flashing the sorbent with nitrogen sorbent was transferred into glass vial and the trapped components were desorbed by 1 cm<sup>3</sup> of solvent for 20 min in ultrasonic bath. After sedimentation of sorbent the supernatant was analyzed.

## RESULTS AND DISCUSSION

In the first stage of work the model mixture consists of hydrocarbons — n-alkanes and aromatics, later the other model mixture was used containing besides aromatics also some low-boiling organic solvents of polar character.

In the study of recovery of adsorption—desorption process standards were injected with syringe directly into sorbent (to avoid eventual losses by incomplete evaporation from glass vessel).

The selection of solvent for desorption was evaluated according to the following criteria: efficiency of desorption, suitability from the chromatographic point of view, purity for trace analysis.

The following solvents were tested with on-column and splitless injection and capillary column with chemically bonded dimethylsiloxane phase (HP-1) under the optimal temperature programmed condition was used.

Hexane was a suitable solvent from the point of view of chromatography (solvent effect) and purity; however, as desorption reagent for the whole studied mixture it was not suitable. As n-hexane is a nonpolar compound, recovery of n-alkanes was good (90—100 %). Recovery of aromatics was, however, maximum 30 %.

The mixture hexane—dichloromethane ( $\varphi_r = 1 : 1$ ) was used in an effort to desorb both polar and nonpolar compounds. Sedimentation of suspension of sorbent and solvent was very slow and was sped up by centrifugation. Recovery of some aromatics was 70 %, that of naphthalenes up to 20 %.

Acetone — there was a problem with peaks splitting and peaks broadening.

Dimethylformamide is a solvent with high boiling point, it elutes after the studied standard mixture and causes peaks broadening and deformation.

Carbon disulfide — its application is problematic, as it has to be preserved under water and before using it has to be dried with anhydrous nitrogen sulfate. It fulfils all criteria. In all next experiments carbon disulfide was used for liquid desorption. Chromatogram of analysis of blank experiment of the whole adsorption—desorption procedure without injection of standards is given in Fig. 2. From the figure it is seen that there are not interferences in blank with analyzed compounds (for comparison see Fig. 3).

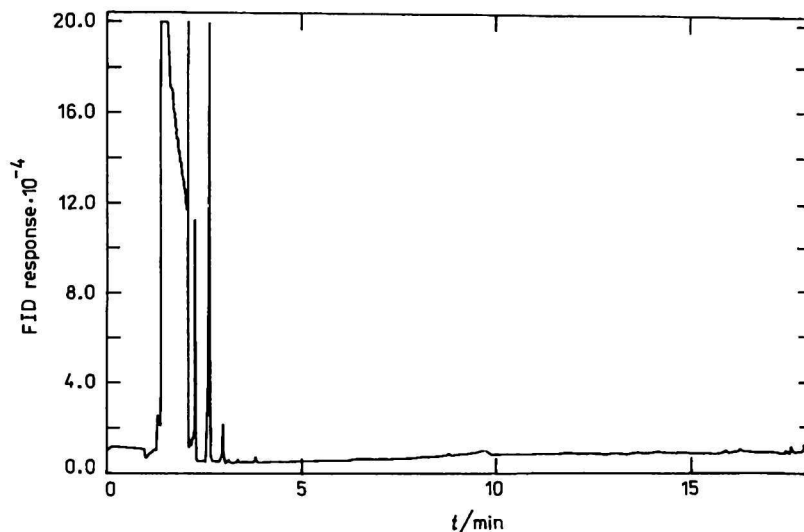


Fig. 2. Chromatogram of analysis of blank experiment of the adsorption—desorption procedure on fused silica capillary column HP-1 under temperature programmed conditions: initial temperature 35 °C (1 min), temperature gradient 8 °C min<sup>-1</sup>, final temperature 180 °C (5 min), carrier gas hydrogen, on-column injection, temperature of FID 280 °C.

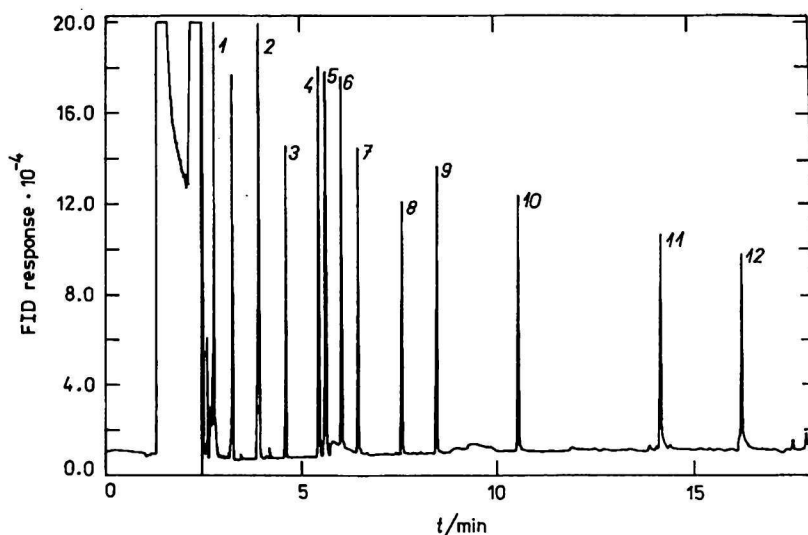


Fig. 3. Chromatogram of separation of the standard model mixture (n-alkanes and aromatics), experimental conditions as in Fig. 2. 1. n-heptane, 2. toluene, 3. n-octane, 4. ethylbenzene, 5. *m*-xylene, *p*-xylene, 6. *o*-xylene, 7. n-nonane, 8. 1,3,5-trimethylbenzene, 9. n-decane, 10. n-undecane, 11. 2-methylnaphthalene, 12. 1,6-dimethylnaphthalene.

### Model Mixture (n-Alkanes and Aromatics)

A possibility of using carbon sorbent for preconcentration of trace organic compounds from the gas phase was tested by the simulation of preconcentration recovery determination. Standards were applied directly into sorbent by syringe (about 3 µg of individual standards), 10 dm<sup>3</sup> of inert gas flashed through the apparatus and 1 cm<sup>3</sup> of carbon disulfide was used for desorption. 1 mm<sup>3</sup> of solution over sorbent was analyzed by capillary GC with on-column injection. In the same way the standard solution (concentration 3 µg of individual standards in 1 cm<sup>3</sup>) was analyzed. Chromatogram of standard model mixture is given in Fig. 3. As the relative standard deviation of the peak area determination from

three analyses was in no case higher than 10 %, the recovery was determined from the ratio of peak areas of standards analyzed before and after preconcentration.

The recovery of preconcentration on this concentration level was searched without and with using ultrasonic bath. The solution with sorbent was mixed several times, GC analyses were performed after sorbent sedimentation. In the next experiment compounds were determined after 24 h. The highest recovery values were achieved after application of ultrasound. For the comparison in Table 1 there are given results of individual recoveries. The lower recovery of n-heptane (87.1 %) in comparison with n-octane (95.7 %) may be connected with higher losses of sorbate having higher volatility during flashing the



**Table 1.** Comparison of Recovery Results after Adsorption on Sorbent Carb I with and without Use of Ultrasound; Concentration Level  $0.3 \mu\text{g dm}^{-3}$ 

Compound	$R_a/\%$	$R_b/\%$	$R_{us}/\%$	$S_r/\%$
n-Heptane	70.6	86.7	87.1	3.2
Toluene	72.6	89.0	91.3	3.7
n-Octane	74.8	86.5	95.7	0.5
Ethylbenzene	71.8	85.4	95.4	2.5
<i>m</i> -, <i>p</i> -Xylene	71.9	85.0	97.3	6.7
<i>o</i> -Xylene	71.7	86.8	92.9	0.4
n-Nonane	75.3	89.1	96.9	0.5
Trimethylbenzene	72.7	90.5	94.9	1.1
n-Decane	71.8	93.6	95.3	1.2
n-Undecane	69.2	97.0	91.2	0.3
2-Methylnaphthalene	66.0	87.4	86.9	2.2
1,6-Dimethylnaphthalene	70.6	83.5	91.2	0.4

$R_a$  — recovery of desorption after mixing,  $R_b$  — recovery of desorption determined after 24 h,  $R_{us}$  — average value of two parallel recovery determinations after application of ultrasound (sonication 20 min),  $S_r$  — relative standard deviation of recovery determinations after application of ultrasound.

sorbent. The value of recovery of n-heptane is however satisfactory for its determination, e.g. in real samples.

The other attempts were realized with higher compound concentration to determine capacity of sorbent in the case of analysis of highly contaminated samples (e.g. measurements of emissions). The concentration  $15 \mu\text{g dm}^{-3}$  ( $50 \text{ mm}^3$  of standard solution with 20–30 mg of compounds in  $10 \text{ cm}^3$  of n-hexane) was applied on sorbent; compounds were desorbed in  $0.5 \text{ cm}^3$  of  $\text{CS}_2$ . Standard reference solution for recovery determination was prepared by spiking  $0.5 \text{ cm}^3$  of  $\text{CS}_2$  with  $50 \text{ mm}^3$  of stock standard solution. Recovery results showed that the capacity of sorbent is sufficient for the trapping of these higher concentrations. The results of recoveries were found in the range 88–99 %.

For the lower concentrations of compounds in gas ( $3 \text{ ng dm}^{-3}$ ) recoveries were around 90 %, however, the noise level at the higher sensitivity of GC measurement was high and there were interferences with some peaks of model mixture, which was possible to solve by subtracting the value of blank experiment. The analyses for the given concentration level could be improved by  $\text{CS}_2$  cleaning and/or placing cartridge for purifying carrier gas.

### Model Mixture (Hydrocarbons and Other Low-Boiling Organic Solvents)

With regard to the character of compounds in model mixture chromatographic measurements were performed on intermediate polarity column SP-Nucol with modified polyethylene glycol. The advantage of this column besides other things is, that in contrast to nonpolar dimethylsilicone phase, on this

column it is possible to analyze benzene, which is often monitored as cancerogene from the point of view of environment. On nonpolar column benzene coelutes with the used solvent.

Chromatographic measurements were realized on a chromatograph with splitless injection. In this type of injector high reproducibility of injected volumes is required and in quantitative analysis it is recommended to use the standard addition or internal standard method. In our case it was convenient to use the internal standard method.

The recovery of preconcentration of model mixture was determined in the following way: on the sorbent in tube  $10 \text{ mm}^3$  of stock standard solution was applied, the system was flashed with  $10 \text{ dm}^3$  of nitrogen and the sorbent was transferred into  $1 \text{ cm}^3$  of  $\text{CS}_2$ . After ultrasound acting, internal standard n-C<sub>13</sub> (ca.  $30 \mu\text{g}$ ) was added and the supernatant was analyzed by capillary GC. From the ratio of peak area of compounds ( $A_i$ ) and peak area of internal standard ( $A_{st}$ ) the values of variables  $A_i/A_{st}$  were calculated. For the comparison the model mixture containing the same amounts of individual compounds, which was applied on sorbent, was analyzed with standard addition of n-alkane C<sub>13</sub>. From the peak areas ratio the values  $A_i/A'_{st}$  were calculated. The recovery was calculated according to the equation

$$R = \frac{A_i/A_{st}}{A_i/A'_{st}}$$

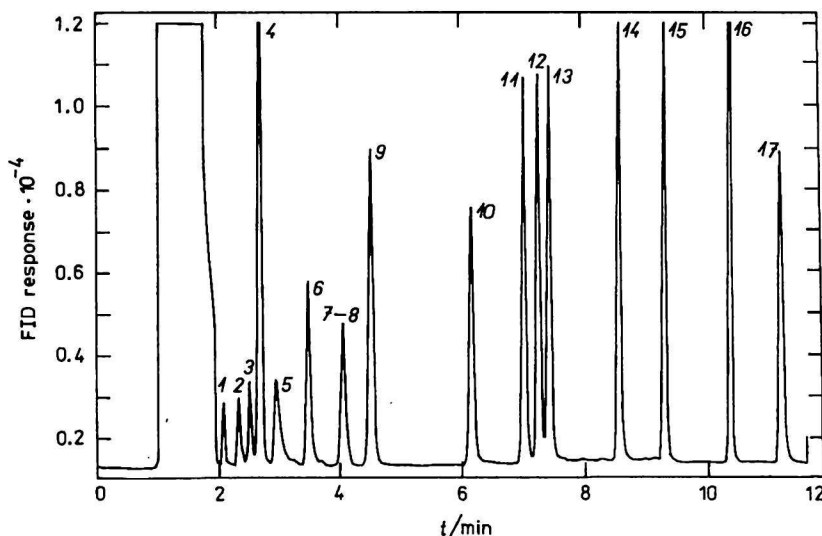
The values of ratios  $A_i/A_{st}$  and recoveries for individual standards are given in Table 2.

In the evaluation of results interfering peaks in blank were subtracted as the average value of blank experiments. Chromatogram of the model mixture of

**Table 2.** Results of Preconcentration Recovery Determination of Model Mixture Compounds on Sorbent Carb I

Compound	$A_i/A'_{st}$	$A_i/A_{st}$	$R/\%$
Tetrachloromethane	0.1611	0.1364	84.7
Methanol	0.2259	—	—
Dichloromethane	0.2553	0.1321	51.8
Benzene	1.6883	1.3306	78.8
Ethanol	0.2953	0.0684	23.2
Acrylonitrile	0.7826	0.4005	51.2
Trichloromethane + tetrachloroethylene	0.6192	0.4418	71.4
Toluene	1.3531	1.3389	98.9
n-Undecane	1.0232	0.9324	91.1
Ethylbenzene	1.3103	1.2200	93.1
<i>p</i> -Xylene	1.2918	1.2129	93.9
<i>m</i> -Xylene	1.3471	1.2490	92.7
<i>o</i> -Xylene	1.3607	1.2551	92.2
Chlorobenzene	1.1845	1.0854	91.6
Styrene	1.3686	0.9805	71.6

The ratio  $A_i/A'_{st}$  is an average value of four GC determinations, the ratio  $A_i/A_{st}$  is an average value of two parallel recovery determinations.



**Fig. 4.** Chromatogram of separation of the standard model mixture (hydrocarbons and low-boiling organic solvents) on fused silica capillary column SP-Nucol under temperature programmed conditions: initial temperature 35 °C (5 min), temperature gradient 8 °C min<sup>-1</sup>, final temperature 180 °C (10 min), carrier gas hydrogen, splitless injection system, temperature of injector 220 °C, temperature of FID 280 °C. 1. Tetrachloromethane, 2. methanol, 3. dichloromethane, 4. benzene, 5. ethanol, 6. acrylonitrile, 7. trichloromethane, 8. tetrachloroethylene, 9. toluene, 10. n-undecane, 11. ethylbenzene, 12. *p*-xylene, 13. *m*-xylene, 14. *o*-xylene, 15. chlorobenzene, 16. styrene, 17. n-tridecane as internal standard.

n-alkanes and low-boiling solvents is given in Fig. 4. The potentiality of adsorption of internal standard on carbon sorbent, after adding to solvent and action of ultrasound, was not controlled. It was supposed that sorption of internal standard was not significant after its adding to the mixture of sorbent, sorbate, and CS<sub>2</sub>. This may be concluded from the results of recoveries of some hydrocarbons, which were obtained from the first (Table 1) and the second model mixture, as *o*-xylene, ethylbenzene, n-undecane, where recoveries do not differ considerably. Toluene is an exception, the relative high value of recovery of which may be explained by higher inaccuracy of measurements (relative standard deviation higher than 10 %) in the used splitless injection.

The results of recoveries showed that the low-boiling solvents (methanol, dichloromethane, ethanol, tetrachloromethane, chloroform, tetrachloroethylene) give much lower recoveries in comparison to hydrocarbons and the method is not suitable for the analysis of compounds of polar character.

In the first part of work nonpolar capillary column was used, which is suitable for the separation of nonpolar compounds and there was not obtained the resolution of low-boiling solvents. Therefore, for the analysis of the second model mixture medium polar column was used, which is suitable for the analysis of both mixtures.

Unconventional sorbents were successfully applied also for the analysis of volatile hydrocarbons in water using "purge and trap" technique [11], and are the subject of the further paper [12].

The scientific work was devoted to testing unconventional carbon sorbent (prepared by controlled

pyrolysis of saccharose) for the preconcentration of trace organic volatiles from the gas phase. Recoveries of adsorption—desorption process of model analytes (n-alkanes, aromatics, volatile organic compounds) were studied. In sorption of sorbates from the gas phase and the liquid desorption (CS<sub>2</sub>) with the subsequent capillary GC good recoveries of n-alkanes and aromatic compounds at various studied concentration levels were obtained.

## REFERENCES

1. Onuška, F. I., *J. High Resolut. Chromatogr.* 12, 4 (1989).
2. Namiešnik, J., Górecki, T., and Bizziuk, M., *Anal. Chim. Acta* 237, 1 (1990).
3. Liška, I., Krupčík, J., and Leclercq, P. A., *J. High Resolut. Chromatogr.* 12, 577 (1989).
4. Rudolph, J., Muller, K. P., and Koppmann, R., *Anal. Chim. Acta* 236, 197 (1990).
5. Chiantore, O., Novák, I., and Berek, D., *Anal. Chem.* 60, 638 (1988).
6. Figge, K., Rabel, W., and Wieck, A., *Fresenius Z. Anal. Chem.* 237, 261 (1987).
7. Smišek, M. and Černý, S., *Aktivné uhlie (Active Carbon)*. Nakladatelství technické literatury (Publishers of Technical Literature), Prague, 1964.
8. Novák, I. and Berek, D., *Czech.* 221 197 (1982).
9. Novák, I., Berek, D., Štamberg, J., Peška, J., Philipp, B., Gensrich, H., Gröbe, V., and Bartsch, D., *Czech.* 230 297 (1984).
10. Černý, J., Černý, M., Paleček, M., and Procházka, M., *Organická syntéza (Organic Synthesis)*. Academia, Prague, 1971.
11. Škrabáková, S., *Thesis*. Slovak Technical University, Bratislava, 1992.
12. Škrabáková, S., Matisová, E., Novák, I., and Berek, D., *J. Chromatogr.* 665, 27 (1994).

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