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The preparation, properties and application of carbon fibers for SPME

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Abstract

The conditions of preparation of new types of carbon fibers for solid phase micro extraction (SPME) prepared by methylene chloride pyrolysis (at 600 °C) on the quartz fiber (100 μm) as well as by supporting synthetic active carbon (prepared especially for this purposes) supported in a special epoxide-acrylic polymer is described. The properties of such carbon fibers for SPME were defined by determination of the partition coefficient of the tested substances (i.e., benzene, toluene, xylenes, trichloromethane and tetrachloromethane) and by the microscopic investigations with the application of the optical and scanning electron microscope.

The obtained carbon SPME fibers were applied to the analysis of some volatile organic compounds from its aqueous matrix. During chromatographic GC test, at the investigated SPME carbon fibers, we obtained different but mostly high partition coefficients for the determined compounds (Kfs from 120 for trichloromethane up to 11,500 for tetrachloromethane).

Owing to the high partition coefficients of the studied substances obtained on carbon fibers, it was possible to do the analysis of organic substances occurring in trace amounts in different matrices. In this paper, we present the analysis of BTX contents in the petrol analyzed with the application carbonized with CH_2Cl_2 SPME fiber (C1NM) and a headspace over the petrol sample (concentration of each BTX ~g/dm^3).

Keywords: SPME; Carbon adsorbents; GC; Carbon fiber

1. Introduction

Many environment samples as well as food and industrial products are complex from the analytical point of view as direct analysis by any instrumental method is difficult because only some substances in the studied matrix are the object of our interest. Therefore, technology of sample preparation for analysis is one of the most important analytical problems. The solid phase micro extraction method (SPME) is one of the sample preparation techniques.

SPME has been used for analysis relatively recently. It was elaborated and popularized by Pawliszyn [1–3]. This method is used for preliminary separation and enrichment of analytes based on sorption of the analytes present in the studied matrix or in the above surface gaseous phase on the microfibre covered with a sorption layer placed in a special micro syringe. The analytes sorbed on the stationary phase is removed to a gas chromatograph (GC) injector where it is subjected to thermal desorption. This technique not requiring dissolution has many advantages like, e.g., simplicity, not using a liquid extraction phase, low costs and compatibility with on-line analytical procedures.

Therefore, lately there have been carried out studies on preparation of new kinds of fiber coating for SPME as well as on their analytical application for removal and enrichment of micro-contamination from water samples and air. The stationary phases coating the extraction fiber in SPME can be of various types. At present over 30 types of fibers are commercially available. The most frequently used are: polydimethylsiloxane (PDMS), polyacrylic (PA) as well as those containing two or three components, e.g., polydimethylsiloxane-divinylbenzene (PDMS-DVB), carboxen-polydimethylsiloxane (CAR-PDMS), carbowax-divinylbenzene (CW-DVB).

Besides commercially available fibers, produced by SUPELCO, there are those produced on a laboratory scale. They include the coatings formed due to modification of the

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quartz capillary surface with the aliphatic phenyl groups of C_8, C_{18} types [4], graphitized carbon of low temperature glassy carbon type (LTGC) [5,6], layer of the carbon sorbent Carbopack™ [3], covered with gold or lead [7,8], coated with polyurethane–acrylate mixture [9,10], polydimethyl-ethoxy-siloxane stationary phase (PDES), ion-exchange coatings [11,12], liquid-crystalline phases for extraction of flat-structure molecules [1], metal fiber, which can be covered with an electrolytic coating [13,14], polymer of Nafion™ type [15], polypyrrole and *N*-phenylpyrrole [16–18].

The stationary phase can be also supported inside the steel needle of syringe to take up the analyte samples. The other way of supporting the sorbent bed inside the needle is called INCAT (Inside Needle Capillary Adsorption Trap) [19,20].

Carbon adsorbents are characterized by nonpolar properties and nonspecific interaction with the adsorbed substances, which could be useful in the SPME technique. The adsorption capacities of active carbons are the function of microporous structure and various functional groups which are present on their surface. Common active carbons used for organic substance traces enrichment have the specific surface area of the range 200–1200 m^2/g, whereby micropores constitute about 70% surface. Active carbons adsorb hydrocarbons, particularly aromatic ones and halogen derivative compounds strongly.

There are carbon sorbents of very large specific surface areas (e.g., over 2000 m^2/g) and very well developed microporous structure as well as nonporous carbon sorbents, i.e., graphitized carbon black Carbopack F of the surface smaller than several m^2/g. This gives possibilities for preparation of SPME fibers coated with carbon adsorbents which theoretically could be used for analysis of, e.g., very volatile, poorly sorbed substances (stable gases, freons) and on the other hand of strongly polar substances (e.g., aldehydes, ketones, carboxylic acids).

The paper describes the conditions of preparation of new types of carbon fibers for SPME prepared by methylene chloride pyrolysis on the quartz fiber (100 μm) as well as by supporting synthetic active carbon mixtures in a special epoxide-acrylic (EA) polymer. Structural and analytical properties of such fibers were defined by determination of the partition coefficient of the tested substances and possibilities of their application in the analysis of some volatile organic compounds from the air and aqueous matrix were discussed.

2. Experimental

2.1. Preparation of carbon fibers for SPME by methylene chloride pyrolysis

Carbon fibers of this type were prepared by pyrolysis of methylene chloride (CH_2Cl_2) on the quartz fiber (100 μm diameter) at 600 °C for 1 h (C1NM fiber) and at 700 °C (C2NM fiber) under dynamic conditions in the fluidal reactor designed and built by the authors of paper [21]. Methylene chloride was added to the reactor with the rate 0.6 cm^3/min through the vapor saturator (100 °C) using the peristaltic pomp of Master flex type (Cole Parmer Instrument Company, USA). Carrier gas (deoxidized N_2) of the flow rate 180 cm^3/min was passed through the system during sample heating and other stages of preparation. The amount of pyrocarbon deposited on the surface of the quartz fiber depended on reaction time and temperature. When methylene chloride pyrolysis was over, the samples were conditioned in nitrogen stream at 600 °C for 60 min to remove HCl and other volatile products.

To improve the properties of obtained fibers and modification of porous structure of the carbon deposits on the fiber surface, they were modified in various ways. C1NM fibers were impregnated with 30% styrene solution in toluene for 24 h. Then they were heated at 600 °C for 60 min (C1MS fiber).

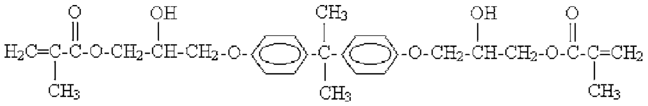
The third type of fibers was obtained after quartz core etching with 10% NaOH solution for 2 h. After careful washing of quartz fibers with distilled water, the fibers were carburized with methylene chloride at 600 °C for 1 h (C1MNa)

Another series of carbon fibers was obtained after spreading calcium acetate ($Ca(CH_3COO)_2$) on the fibers C2NM (carburized by carbonization of CH_2Cl_2 at 700 °C) and hydro thermally modified at 800 °C in water vapor for 1 h. After careful washing of calcium ions, the fiber designated C3NM was obtained.

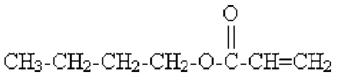
2.2. Preparation of SPME fibers by supporting carbon suspension in the polymer on the quartz core

The carbon fibers of this type were obtained by supporting the suspension of synthetic active carbons (M3P [22,23], PCV-1, PCV-3 [24] and A2PS [25] type) in epoxide resin with the active diluent (butyl acrylate) and photo-initiator agent on the quartz fiber. Then epoxide resin was hardened in UV light (254 nm).

In our investigations we used epoxide-acrylate (with bisphenol type A) with the active diluent (butyl acrylate) and the photo-initiator (2,2-dimethoxy-2-phenyl-acetophenone - Irgacure 651) mixed at the ratio 16:4:0.4. Epoxide resin (EA) obtained after hardening was thermo gravimetrically tested to determine its thermal resistance and emission of volatile contaminants during heating to higher temperatures.

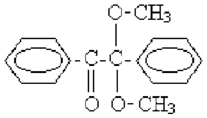


Structural formula of epoxide-acrylate monomer (with bisphenol type A)



$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH{=}CH_2$

Structural formula of butyl-acrylate (used as active diluent)



Structural formula of 2,2-dimethoxy-2-phenyl-acetophenone – Irgacure 651 (used as photo-initiator)

Structural properties of active carbons used for the preparation of carbon fibers (M3P, PCV-1, PCV-3 and A2PS) were determined from the adsorption–desorption isotherms at the temperature of liquid nitrogen [22–25].

The adsorbent M3P prepared in the process of controlled carbonization of polymer (4,4-diphenylsulfonodimethacrylate) had the specific surface area $S_{\mathrm{BET}} = 575\,\mathrm{m}^2/\mathrm{g}$, the micropore surface $S_{\mathrm{mi}} = 442\,\mathrm{m}^2/\mathrm{g}$ and pore volume $V_{\mathrm{p}} = 0.40\,\mathrm{cm}^3/\mathrm{g}$. The pore diameter of this carbon was 22 Å [22,23]. M3P carbon was used to prepare SPME fibers of C1M3P and C2M3P types.

Another types of carbon used for preparation of the SPME fibers was obtained in the process of carbonization of polyvinyl chloride at 600 °C, in the nitrogen stream (Ads. PCV-1). Before carbonization to PCV there was added the mixture of catalysts: NH_4Cl, $FeCl_3$, $ZnCl_2$ [24] (Ads. PCV-3). The specific surface area of the carbon PCV-1 was $S_{\mathrm{BET}} = 6.2\,\mathrm{m}^2/\mathrm{g}$, the pore volume $V_{\mathrm{p}} = 0.007\,\mathrm{cm}^3/\mathrm{g}$, average pore size $R = 46$ Å. The adsorbent (PCV-1) did not contain micropores [24]. The carbon PCV-1 was used for the preparation of the fiber type C1PP.

The specific surface area of the carbon PCV-3 was $S_{\mathrm{BET}} = 368\,\mathrm{m}^2/\mathrm{g}$, the micropore surface $S_{\mathrm{mi}} = 269\,\mathrm{m}^2/\mathrm{g}$, the pore volume $V_{\mathrm{p}} = 0.26\,\mathrm{cm}^3/\mathrm{g}$, the average pore size $R = 22$ Å [24]. This carbon was used for preparation of the fiber of C2PP type.

To obtain the fiber of CA2PS type there was used the adsorbent A2PS prepared by plum stone carbonization. Its specific surface area was $S_{\mathrm{BET}} = 1200\,\mathrm{m}^2/\mathrm{g}$, the micropore surface $S_{\mathrm{mi}} = 957\,\mathrm{m}^2/\mathrm{g}$, the pore volume $V_{\mathrm{p}} = 0.71\,\mathrm{cm}^3/\mathrm{g}$, the pore diameter $R = 22$ Å [25]. The conditions and physicochemical properties of the obtained active carbons are described in the papers [22–25].

Carbon fibers were also prepared using another technique: a thin layer of epoxide-acrylate polymer was supported on the quartz fiber surface (diameter 100 μm), and then M3P carbon grains were glutted on it (C2M3P fiber). The average carbon grain size was about 20 μm. Then the polymer was cured by means of UV light = 254 nm for 1 h. The fiber was fixed in the syringe SPME (SUPELCO) using epoxide polymer.

The extraction fiber was conditioned by placing the needle SPME in the gas chromatograph injector at 220 °C (30 min). Then volatile analytes from the studied matrices were adsorbed on the fiber adjusting the exposition time (from 5 to 50 min) at 18–20 °C. After sorption the needle was placed in sample injector and the thermo-desorption process was carried out (for 5 min). The analysis was conducted on the gas chromatograph GC 6000 Vega (Carlo Erba Instruments) with the flame-ionization detector and electron capture detector equipped with the capillary column of DB–5 type (30 m × 0.32 mm) produced by Altech. The injector temperature was 220 °C and the detector temperature was 250 °C. The oven temperature program: initial temperature 40 °C maintained for 10 min, next heating with the rate 10 °C/min up to 200 °C and maintained for 10 min.

2.3. Thermogravimetric studies

The fibers with carbon deposits and the polymer (epoxide-acrylate with bisphenol of type A) mixed with the active diluent (butyl acrylate) and the initiator (2,2-dimethoxy-2-phenyl-acetophenone (Irgacure 651)) at the ratio 16:4:0.4 and cured with UV radiation – 254 nm were subjected to the thermogravimetric analysis in the temperature range 20–1000 °C in air using the Derivatograph PC (Paulik, Paulik, Erdey, Budapest, Hungary). The measurements were made using the linear temperature increase with the rate 10 °C/min. The sample mass was 30–100 mg. The TG, DTG and DTA curves were registered. The values of mass loss from the TG curve in the temperature range 400–600 °C were used, among others, for determination of carbon adsorbent mass and hence the average content and thickness of carbon deposit layer on the SPME fiber.

2.4. Microscopic studies (SEM and projective microscopy)

Studies of carbon fiber structure were made by means of scanning electron microscopy Tesla BS 300 and projective microscope Nikkton. The magnification 500 to 4000x (for SEM microscopy) and from 100 to 400x was obtained using the projective microscope.

3. Results and discussion

3.1. Properties of fibers carburized with CH_2Cl_2

Basic properties and conditions of carbon fibers preparation are presented in Table 1. Fig. 1 shows the microscopic photograph of the quartz fiber (100 μm) covered with carbon deposit (obtained by the carbonization of methylene chloride at 600 °C). To determine the carbon deposit layer thickness, part of deposit was mechanically removed from the fiber. The carbon deposit layer thickness was determined to be 8.15 μm.

Carbon deposits formed on the quartz fiber due to methylene chloride pyrolysis have a shape of spherical globules (from 20 to 250 nm diameter) [21]. The reaction used in carbon fiber preparation:

$$CH_2Cl_2 \rightarrow C + 2HCl \qquad (1)$$

allows to obtain any amount of carbon deposit on the surface of neutral support, e.g., quartz fiber. Though reaction (1) seems to be very simple, the process of quartz fiber surface carburization is complex and depends on such factors as: temperature, pyrolizate concentration and rate of removal of forming hydrogen chloride from the reaction area. The reaction yield increases rapidly with increasing temperature. Fibers with several to scores percent of carbon deposit on the surface can be obtained owing to the large yield of reaction (1). With the sufficiently large amount of carbon (already from about 1%), the quartz fiber surface can be completely covered with carbon deposit (Fig. 1). In such case properties of quartz fibers covered with carbon deposit should be like those for typical carbon adsorbents.

For carbon fibers prepared by pyrolysis of CH_2Cl_2 there was observed high efficiency of sorption and desorption (measured from the chromatographic band broadening after thermodesorption in the injector of GC) which can be explained by lack of specific interaction of the studied adsorbates with the carbon surface and relatively low specific surface area and small volume of micropores obtained in carbonization reaction (1) [21].

Table 1
The types of fiber used in this study

Fiber	Type of SPME phases	Thickness of SPME phases (μm)
C1NM	Fiber obtained by methylene chloride pyrolysis at 600 °C	∼8
C1MS	Fiber obtained by methylene chloride pyrolysis at 600 °C, and next modified with styrene and heated at 600 °C	∼8
C1MZ	Fiber obtained by etching with 10% NaOH solution and next carbonized with methylene chloride at 600 °C	∼8
C2NM	Fiber obtained by methylene chloride pyrolysis at 700 °C	∼10
C3NM	Fiber obtained by methylene chloride pyrolysis at 700 °C, and next hydrothermally modified at 800 °C	∼8
C1M3P	Fiber obtained by supporting the suspension of synthetic active carbons (M3P) and epoxide-acrylate polymer (EA)	70–80
C2M3P	Fiber obtained by supporting a thin layer of epoxide-acrylate polymer (EA) on the quartz capillary and then glutted on M3P carbon grains	∼40
C1PP	Fiber obtained by supporting the suspension of synthetic active carbons (PCV-1) and epoxide polymer (EA)	∼80
C2PP	Fiber obtained by supporting a thin layer of epoxide-acrylate polymer (EA) on the quartz capillary and then glutted on PCV-3 carbon grains	∼40
CA2PS	Fiber obtained by supporting a thin layer of epoxide-acrylate polymer (EA) on the quartz capillary and then glutted on A2PS carbon grains	∼70–90
EA	Fiber obtained by supporting a thin layer of epoxide-acrylate polymer (EA) on the quartz capillary	20
PDMS/DVB	Standard fiber manufactured by SUPELCO	65
Car/PDMS	Standard fiber manufactured by SUPELCO	85

3.2. *Properties of epoxide-acrylate resin*

To study the possibility of epoxide-acrylate resin application as the material joining carbon adsorbents with the quartz fiber surface, it was studied gravimetrically (100 mg sample containing epoxide-acrylate polymer + active diluent (butyl acrylate) + photo-initiator (2,2-dimethoxy-2-phenyl-acetophenone (Irgacure 651)) mixed at the ratio 16:4:0.4 and then hardened with UV radiation −254 nm for 1 h.

The DTA curve (Fig. 2) shows a distinct maximum (exothermic transformation) in the temperature range ∼100–300 °C not resulting in mass change of the studied polymer (DTG curve). In this temperature range polymerization of part of polymer uncured with UV radiation −254 nm can be completed. In the temperature range ∼300–600 °C on the DTA curve a distinct minimum for endothermic transformation, connected with significant mass loss (about 80% of the polymer initial mass), occurs. During heating in this temperature range (over 300 °C), thermal depolymerization of epoxide-acrylate resin can take place. Hence, the endothermic effect and significant mass loss are observed. During further heating of EA polymer (at over 600 °C), most probably polymer carbonization to the carbon matter and then its combustion in air took place. In this temperature range (600–900 °C) two exothermic effects connected with mass loss are observed. Complete polymer combustion is observed here.

From the thermal analysis curve course, it can be stated that EA resin under investigation is characterized by thermal stability up to about 300 °C. No emission of any volatile products from polymer (lack of mass loss on the TG and DTG curves) and no polymer decomposition (depolymerization, carbonization) are observed. Therefore, this EA polymer was chosen for further studies of carbon fiber preparation for SPME.

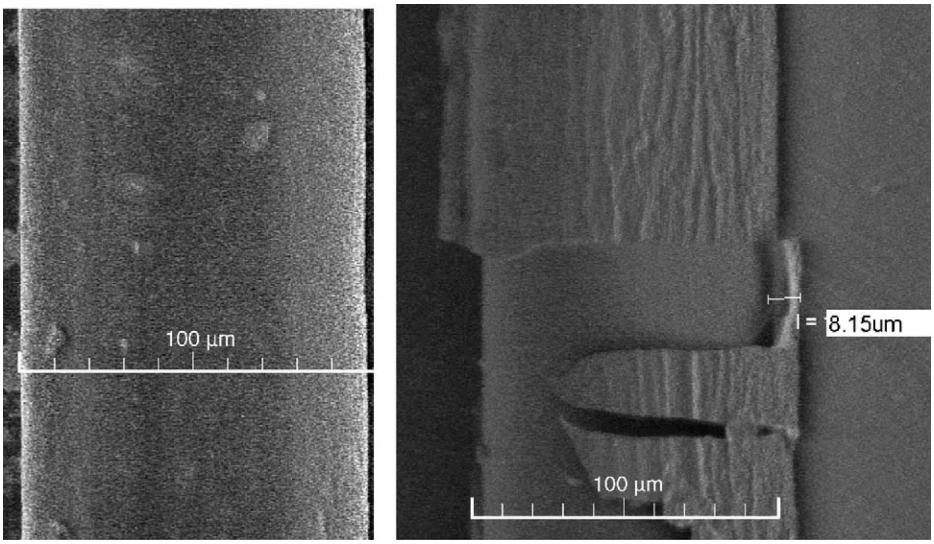


Fig. 1. The SEM of the SPME fiber obtained after dichloromethane pyrolysis on the quartz fiber (C1NM) (magnitude 1000x). (a) Initial fiber. (b) Fiber after partial removing of the carbon deposit.

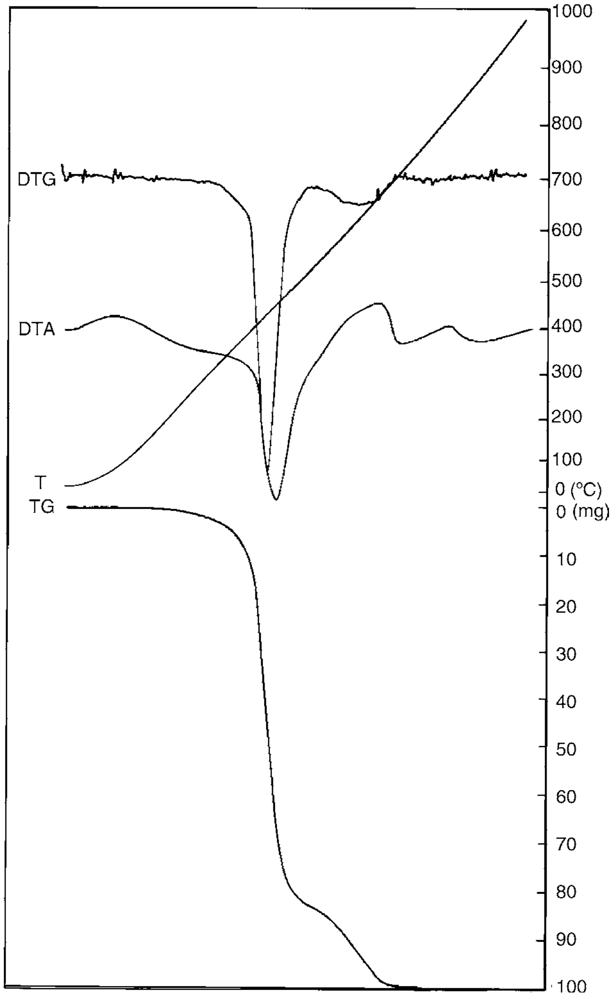


Fig. 2. Thermo gravimetric analysis of polymer EA.

The fibers with carbon deposit prepared by carbonization of methylene chloride (C1NM, C1MS, C1MNa, C2NM and C3NM) were subjected to thermal analysis. As follows from the thermogravimetric analysis made in air atmosphere, the largest changes of sample mass are observed in the temperature range 400–600 °C. The TG curve course indicates that complete mass loss (practically 100% registered mass changes) took place in this temperature range. This is probably due to combustion of carbon deposit formed on the quartz fiber accompanied by exothermic effects registered on the DTA curves. The results of derivatographic analysis of fibers in the form of mass loss (mg/sample) were used for the determination of the carbon percentage content and from it carbon deposit volume on the quartz fiber surface. Assuming that carbon deposit covers the quartz fiber homogeneously, the approximate thickness of carbon deposit layer was determined from these data (Table 1) in the range 8–10 μm. These data are in agreement with those obtained by scanning electron microscopy (Fig. 1).

3.3. Properties of fibers with synthetic carbons and EA polymer

There were made microscopic photographs (projective microscope Nikkton) of the fibers of C1M3P type obtained by supporting the mixture of synthetic active carbon (M3P) and epoxide polymer on quartz core to determine the thickness of stationary phase (Fig. 3a). The thickness of polymer layer mixed with carbon adsorbent was from 72 to 80 μm. Fig. 3b presents the general picture of SPME fiber. Fig. 4 shows the photograph of M3P adsorbent grains built of spherical globules used for preparation of fibers of C1M3P and C2M3P types.

Synthetic carbon adsorbents used for preparation of SPME fibers were chosen due to their specific structural and surface properties. The carbon M3P possesses heterogeneous surface and micro porous structure as well as slit – like pore shape [26]. Moreover, it is characterized by high thermal and mechanical resistance. However, the carbon PCV-3 contains homogeneous micro porous structure with the pores of 0.2–1.3 nm.

Fig. 5 shows the appearance of the fiber C2PP obtained by supporting a thin EA resin layer on which the PCV-3 carbon (of spherical grains) was glutted. Fig. 5b shows carbon globules distinctly projecting from the polymer layer. The advantage of fibers of this type is that the studied adsorbates have complete access to the carbon adsorbent surface owing to the fact that carbon grain is only partially fused into polymer. This results in higher sorption and quicker desorption of analytes on such phases compared to those obtained by supporting the mixture of carbon adsorbent grains with polymer on the SPME fiber. In the fibers containing the polymer and carbon adsorbent mixture on the quartz capillary surface, diffusion to and from polymer is a slower process than that directly on the carbon adsorbent surface (e.g., on the fibers of C1M3P type). These fibers are

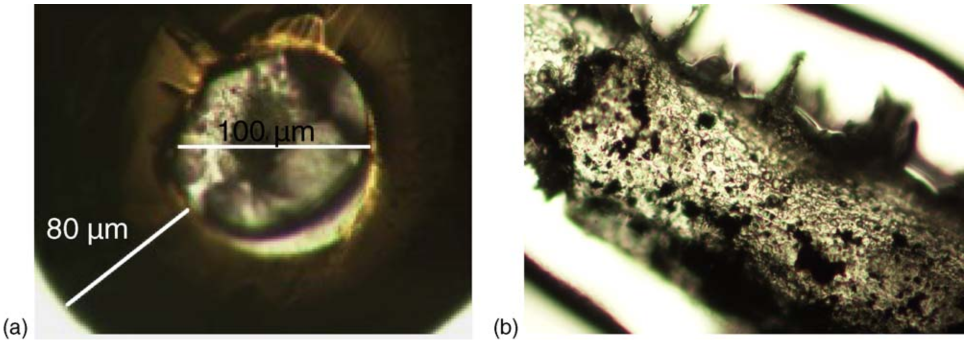


Fig. 3. The SEM micrographs of the mixture EA polymer and carbon adsorbent (M3P), supported on quartz fiber (100 μm) (fiber C1M3P). (a) Cross-section of C1M3P fiber. (b) View showing the quartz fiber on which the attached carbon of spherical structure is to be visible. Magnitude: (a) x200; (b) x100.

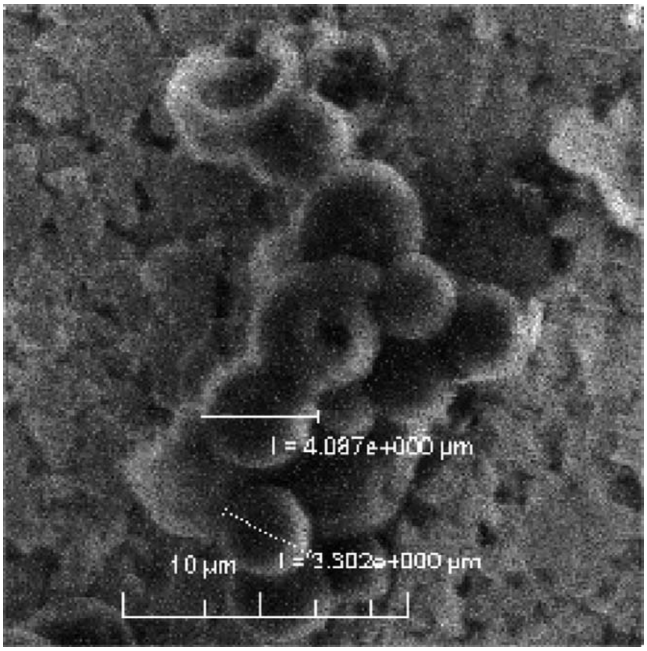


Fig. 4. The SEM of synthetic carbon adsorbent M3P (magnitude x2000).

mechanically stronger and more durable than those obtained by CH_2Cl_2 carbonization on quartz fiber.

The drawback of the fibers prepared by sticking carbon adsorbents to the quartz capillary by means of epoxide-acrylate polymer is possibility of penetration of volatile fragments evolving from resin during thermo-desorption at the temperatures over 300 °C. This may cause "ghost" peak formation on the chromatograms.

High physical homogeneity of active carbon surface obtained by polyvinyl chloride carbonization and nonspecific character of adsorption of studied analytes allow obtaining symmetric peaks after the SPME process for the compounds of the halogen derivatives group, e.g., trichloromethane and tetrachloromethane. Lack of developed interior porosity of synthetic adsorbents of PCV type provides quite good conditions for quick exchange of mass and ensures high efficiency of carbon fiber prepared by supporting carbon of this type on the quartz fiber.

High broadening of chromatographic bands observed while using the fiber covered with active carbon A2PS results from the slow exchange of mass with carbon of large porosity and large specific surface area ($S_{\mathrm{BET}} = 1200\,\mathrm{m}^2/\mathrm{g}$). Large porosity of the carbon A2PS can also cause slower thermo-desorption. High adsorption capacity of such carbon leads to longer time of the analyte–fiber surface equilibrium establishment in adsorption

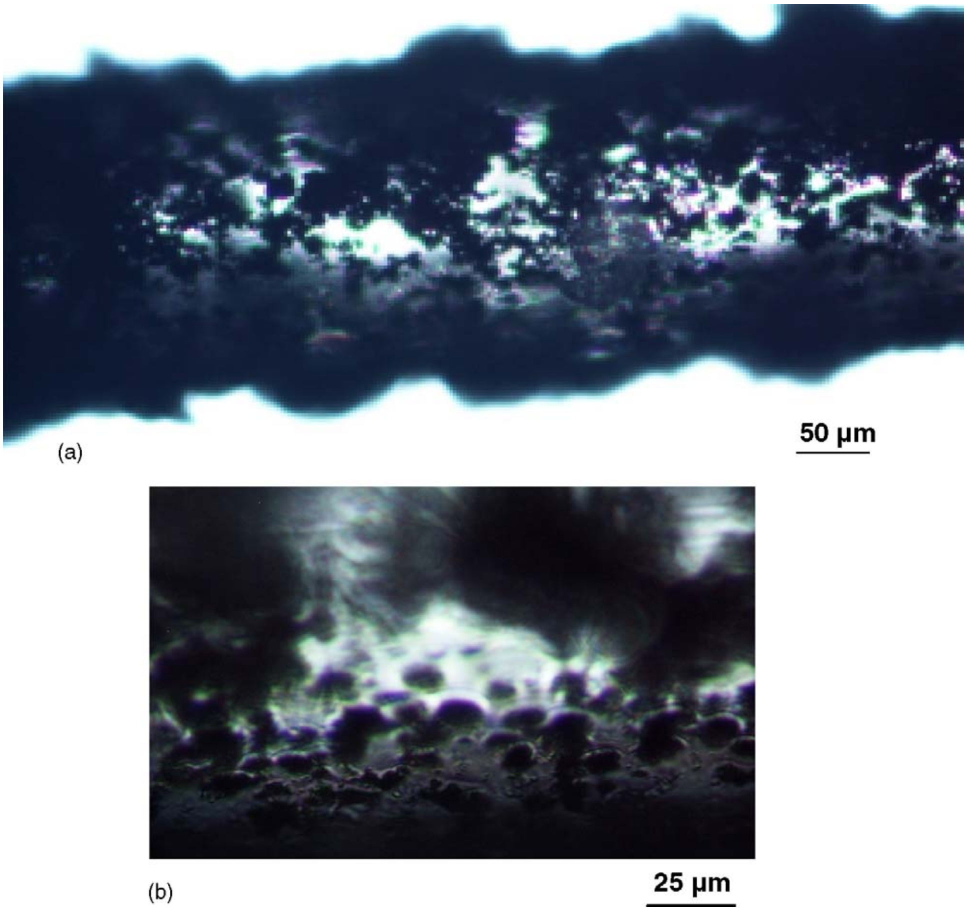


Fig. 5. The SEM micrographs of C1PP SPME fiber with carbon adsorbent (PCV-3) supported on EA polymer covering quartz fiber (100 μm) (a) magnitude x200; (b) magnitude x400.

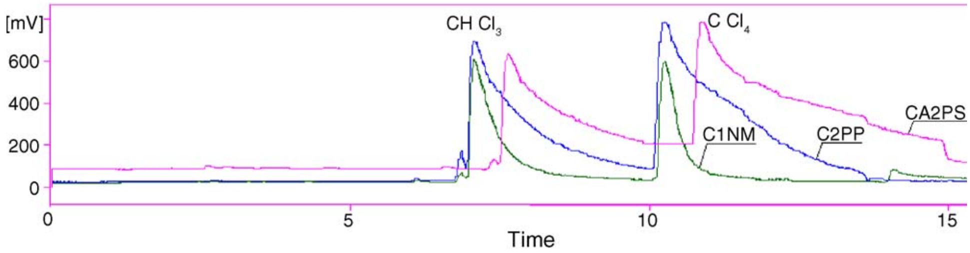


Fig. 6. Comparison of the chromatograms of the mixture of $CHCl_3$ and CCl_4 obtained after the adsorption–desorption process on SPME carbon fibers C1NM, C2PP and CA2PS and GC-ECD analysis (concentration analytes 10 μg/dm^3).

and slow desorption of studied substances to broadening of descending part of chromatographic band. As the processes of adsorption and desorption proceed differently, the broadening of the chromatographic band can be asymmetrical.

Fig. 6 presents three chromatograms obtained after sorption and desorption of trichloromethane and tetrachloromethane mixture on the three SPME fibers:

(1) C1NM – the fiber prepared by methylene chloride carbonization.
(2) C2PP – the fiber prepared by supporting the carbon obtained by polyvinyl chloride (PCV-3) carbonization.
(3) CA2PS – the fiber prepared by supporting the active carbon A2PS.

As follows from Fig. 6, the increase in specific surface area of the carbon adsorbent supported on the quartz fiber causes broadening of the chromatographic bands of the tested substances ($CHCl_3$ and CCl_4). It can be quantitatively expressed by giving e.g., chromatographic bandwidth at the half height ($w_{1/2}$) or the asymmetry coefficient (A_s). Slow carbon fiber thermodesorption affects also plate efficiency of the chromatographic capillary column (N_{ef}). Distinct shift of retentions time is also observed for the fiber CA2PS (Fig. 6).

Adsorption on carbon fibers proceeds in three stages: movement of analyte molecules towards the fiber surface, diffusion between grains (external diffusion), movement of molecules inside pores (internal diffusion in pores) and proper adsorption in the final stage. To decrease the effect of diffusion in the adsorbent pores on band broadening, the adsorbents of most homogeneous mesoporous structure should be used.

3.4. SPME tests

Rate of establishing adsorption equilibrium: adsorbate – SPME fiber surface for some organic compounds from the head space phase was studied measuring changes of peak surface areas obtained depending on extraction fiber exposition time in the standard gaseous mixture over their aqueous solution. Figs. 7 and 8 present the course of changes in the amount of the adsorbed analytes on the cover of the carbon SPME fiber depending on the exposition time. The obtained results indicate that after the first 30 min of the course, the changes of the surface area of the peaks versus the time of extraction of the BTX compounds proceed more slowly then previously (Fig. 7). In case of

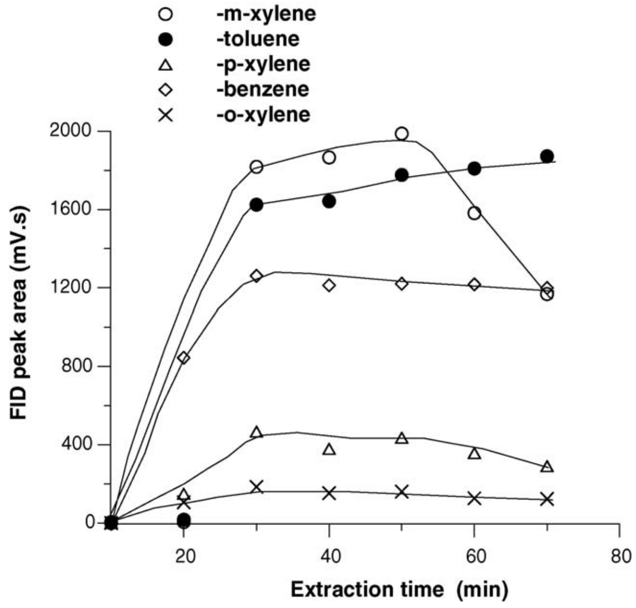


Fig. 7. Adsorption time profiles for BTX after adsorption–desorption on SPME fiber C1NM from its gaseous mixture (concentration analytes 2 μg/dm^3).

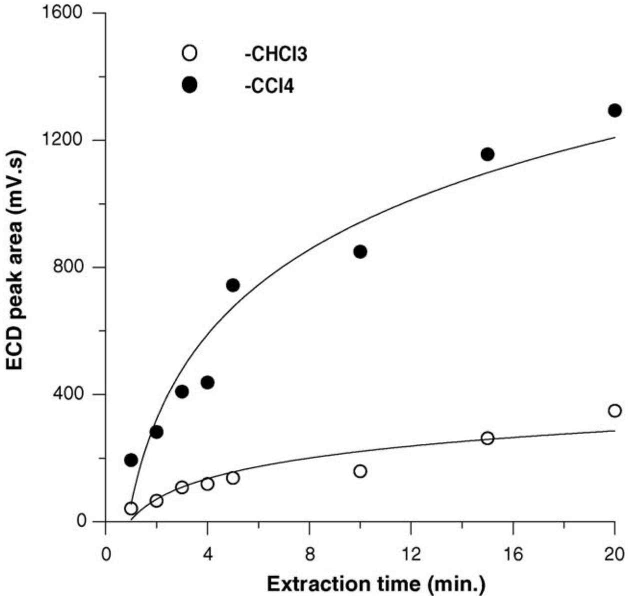


Fig. 8. Adsorption time profiles for trichloromethane and tetrachloromethane obtained from its gaseous mixture after adsorption and desorption on SPME fiber C1NM (concentration analytes 2 μg/dm^3).

Table 2
The partition coefficients for trichloromethane and tetrachloromethane determined on carbon phases of SPME fiber

The partition coefficients SPME phases – head space		
Type of SPME fiber	Analytes	
	Trichloromethane	Tetrachloromethane
C1NM	240	263
CNMS	125	450
CNMNa	385	357
C2NM	1191	6284
C3NM	596	1732
C1PP	365	336
C1M3P	453	1369
C2M3P	547	216
CA2PS	8032	11521
EA	23	34
PDMS/DVB	693	946

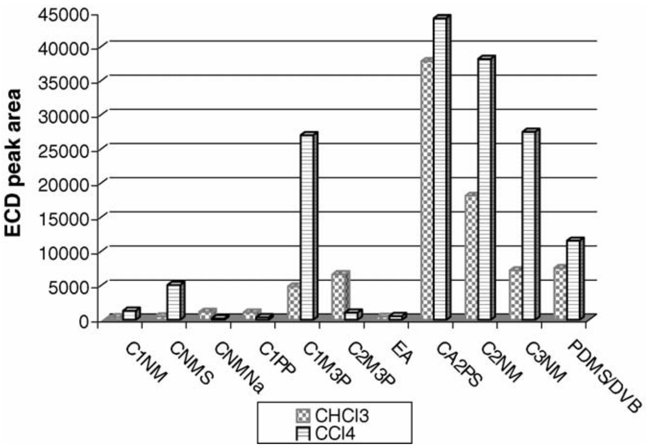


Fig. 9. Comparison of peak area for trichloromethane and tetrachloromethane after adsorption and desorption on different SPME fibers: extraction time of 15 min at 22 °C, desorption time of 5 min at 220 °C (concentration analytes 2 μg/dm^3).

trichloromethane and tetrachloromethane the same phenomena can be observed after 10 min (Fig. 8).

Fig. 7 shows evident decrease in adsorption depending on the time of fiber exposition for *m*-xylene and a slight decrease in adsorption for benzene and *p*-xylene. This can suggest competitive adsorption and mutual displacement of substances from the carbon surface on the extraction fiber. Competition of substances on the adsorbent surface becomes distinct in the case of concentrations close to saturation of SPME phase surface. Large sorption capacities are observed for carbon fibers, which are connected with large specific surface areas of carbon. Then competitive adsorption in analytes occupying the fiber surface is less probable.

The partition coefficients (K_{fs}) [27] were determined from surface area of peaks on the chromatogram for studied analytes obtained after their extraction from matrices in the SPME process and the analysis with the application of gas chromatograph. They are the ratio of studied substances concentration on the fiber of the device for SPME and their concentration in the studied matrix. For comparison similar determination was made on the standard fibers of: PDMS-DVB (65 μm), Carboxen-PDMS (85 μm) types produced by SUPELCO (Tables 2 and 3).

The analysis of the chromatographic data indicates that for the carbon fibers prepared by us different but very large values of the partition coefficients even over 8000 for trichloromethane and 11,000 for tetrachloromethane were obtained. The values of these coefficients indicate how many times the studied substances were enriched on the cover of the fiber during the adsorption–desorption process.

Efficiency of analytes enrichment on the tested fibers was compared by graphical presentation of the dependences of surface area sizes of the analyzed substances (trichloromethane and tetrachloromethane) (Fig. 9) and BTX (Fig. 10) on individual SPME fibers with the same concentrations of analytes. As follows from Fig. 9 the largest surface areas of peaks in the studies of trichloromethane and tetrachloromethane sorption are observed for the fibers CA2PS (coated with carbon of the specific surface area 1200 m^2/g) and the fibers prepared by methylene chloride carbonization on the quartz core (C2NM). The fibers coated with pure epoxide-acrylate polymer (EA −20 μm) and PDMS-DVB are characterized by much smaller surface areas of peaks. In Fig. 10, the largest peak surface areas are observed in the case of BTX sorption on the fibers Carboxen-PDMS and C2PP. Slightly smaller surface areas of peaks are observed on the fibers formed by methylene chloride carbonization (though the thickness of carbon deposit layer was only about 8 μm).

Table 3
The partition coefficients for BTX (benzene, toluene, -*p*, -*m*, -*o*-xylene) determined on carbon phases of SPME fiber

The partition coefficients SPME phases – head space						
Analytes	Type of SPME fiber					
	C1NM	C2NM	EA	C2PP	PDMS/DVB	Car/PDMS
Benzene	381	273	116	450	354	845
Toluene	890	946	163	1243	876	1024
p-Xylene	1240	1280	251	1746	1608	2350
m-Xylene	1150	1096	235	1202	1342	2243
o-Xylene	1340	1256	263	1723	1854	2440

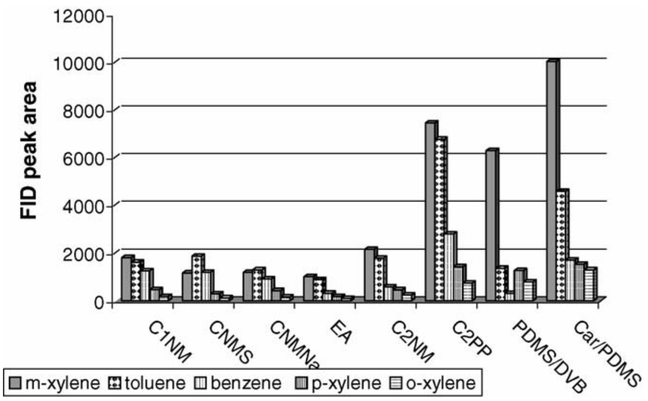


Fig. 10. Comparison of peak area for BTX (benzene, toluene, -*p*, -*m*, -*o*-xylene) after adsorption and desorption on different SPME fibers: extraction time of 30 min at 22 °C, desorption time of 10 min at 220 °C. (concentration analytes 2 μg/dm^3).

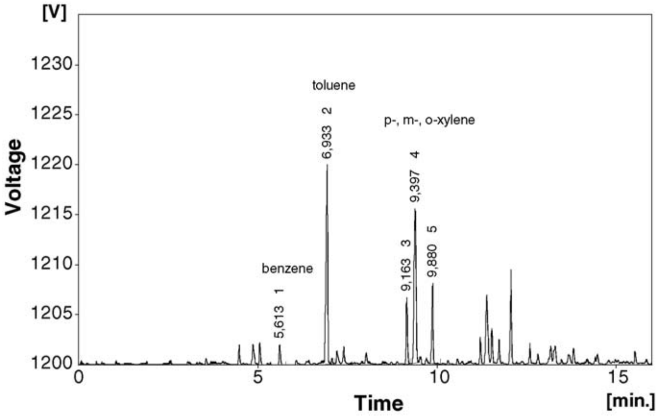


Fig. 11. An example chromatogram of the analysis of the of BTX contents in petrol, obtained after HAS-SPME concentration process proceeded on C1NM fiber and determination on GC-FID (concentration analytes several g/dm^3).

The analysis of Fig. 6 denotes that not only the partition coefficient analyte–fiber must be taken into account in choosing of the coating of fiber for SPME. Possibility of analytical fiber use is also affected by sorption rate (it determines the time of analyte–fiber equilibrium establishment) and thermal desorption rate. The latter process causes broadening of analytes chromatographic bands with the slow course, which diminishes efficiency of chromatographic separation and worsens resolution of the peaks of the substances under investigation.

Using SPME fibers coated with active carbon it was possible to make some analyses of the substances occurring in trace concentrations. Fig. 11 presents the chromatogram of *p*-, *m*-, and *o*-xylene (BTX) occurring in the petrol. The analysis was made after sorption and desorption of these substances by means of the HS-SPME technique on the fiber C1NM. The average concentration of BTX in petrol equals several g/dm^3.

4. Conclusions

Carbon fibers obtained by the direct pyrolysis of methylene chloride (C1NM) on the quartz core possessed the thickness of carbon deposit layer about 8–10 μm.

Another kind of carbon fibers can be prepared by supporting the mixture of synthetic carbon adsorbent and polymer with photo curing agent on the quartz fiber surface (e.g., C1M3P, C1PP, and CA2PS) or by sticking carbon grains on the thin layer of this polymer. In this process, the synthetic active carbons (M3P, PCV) prepared by carbonization of the different polymer can be applied. A thin layer of carbon stationary phase (40–90 μm thick) on the quartz fiber was obtained (C2M3P, C2PP fibers). Such kind of fibers exhibit similar surface properties to those of the typical carbon adsorbents. The chromatographic tests showed that the fibers coating only epoxide-acrylate polymer possess minimal adsorption properties.

The partition coefficients determined for the studied substances (benzene, toluene, *p*-, *m*-, *o*-xylene, trichloromethane and tetrachloromethane) were different but of very high values: from 381 for benzene to 1340 for *o*-xylene (on the carbon fiber C1NM) and 8032 for trichloromethane and 11521 for tetrachloromethane (on fiber CA2PS).

Owing to the high partition coefficients of the substances obtained on carbon fibers, the fibers can be used for the analysis of organic substances occurring in trace amounts, e.g., in the air or in liquid matrices. The paper presents the application of the fiber coated with carbon deposit (prepared by carbonization of methylene chloride at 600 °C) to the analysis of BTX contents in petrol (with the application of SPME–HSA over of petrol sample) The concentration of analytes equals several g/dm^3.

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