

## Application of ordered micro-mesoporous carbon materials activated by steam and CO<sub>2</sub> or KOH in solid-phase extraction of selected phthalates from aqueous samples

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### ABSTRACT

Adsorption of six phthalate acid esters (PAEs) from aqueous samples by the solid-phase extraction (SPE) method was studied. As sorbents in the SPE method, two ordered micro-mesoporous carbon materials were used, obtained by the soft-templating method (STA) and activated by steam and carbon dioxide (STA-CO<sub>2</sub>) or potassium hydroxide (STA-KOH). The surface properties of investigated carbon materials were characterized by nitrogen adsorption isotherms and the scanning electron microscopy. Studied adsorbents have specific surface areas of 1,008 and 1,009 m<sup>2</sup> g<sup>-1</sup> for STA-CO<sub>2</sub> and STA-KOH, respectively. The recoveries obtained for six PAEs (DMP, DEP, DBP, BBP, DEHP, and DOP) in the SPE procedure with application of studied carbon materials as sorbents were in the range of 92%–99% for STA-CO<sub>2</sub> and 89%–98% for STA-KOH. The multiple SPE procedure without exchanging the carbon sorbents in SPE cartridge were also studied, obtaining recoveries for determined PAEs up to 90%. The determination of PAEs in extracts was performed by the gas chromatography-mass spectrometry (GC-MS) method. Applied to SPE method carbon materials were also compared to commercially available sorbents as C-18 and Florisil.

**Keywords:** Phthalate acid esters; Solid-phase extraction; Ordered micro-mesoporous carbon materials; KOH activation; CO<sub>2</sub> and steam activation; Gas chromatography-mass spectrometry

### 1. Introduction

One of the most important tasks of the modern analytical chemistry is the analysis of environmental pollutions and contaminants in foods and beverages. The analysis of these pollutions is usually related to the necessity of the sample preparation for the chromatographic analysis. The stage of collecting and preparing the sample is a very important step in every chemical analysis [1]. Phthalate esters (PAEs) are widely used as polymer additives in the production of plastics to improve their flexibility and

durability [2,3]. Phthalates have been commonly used in the manufacturing of water bottles, food package, cosmetics, medical equipment, pharmacy, textile, etc. [4,5]. PAEs can easily migrate from plastic to other matrices, because they are not chemically but only physically bound to the frame of the polymer forming plastics [6]. Because of the phthalates lipophilicity, the migration of these compounds is also possible from foils and packings to food and various elements of the natural environment [7]. Several PAEs are suspected to be human cancer-causing agents and endocrine disruptors. PAEs can also cause teratogenic

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effects and fetal damage [8–10]. Some of the PAEs are listed in several countries as the priority contaminants [11]. It is very important to develop a simple sample preparing method that can provide a high concentration of the analytes, interferences removal, and matrix change.

The concentration of PAEs in complex environmental samples can be very low, so sample pretreatment, especially before chromatographic analysis, is needed. Sometimes the concentration is below the detection limit of the analytical instrument and extraction techniques must be used to concentrate the analytes in the sample. There are several methods of PAEs extraction from aqueous matrixes such as liquid–liquid extraction (LLE) [12–20], solid-phase extraction (SPE) [21–29], solid-phase microextraction (SPME) [30–34], microextraction by packed sorbent (MEPS) [35], magnetic solid-phase extraction (MSPE) [36–39], microwave-assisted extraction (MAE) [40], and many other techniques. The most popular technique is SPE for environmental samples. The most important step in the SPE technique is the choice of the sorbent. There are many sorbents used in SPE of PAEs like most often used  $C_{18}$  [22–29], selected polymers [41,42], Florisil [43], multi-walled carbon nanotubes [44,45], and nowadays graphene [11,46–48]. There are also micro- and mesoporous carbon materials used as sorbents in the SPE technique. They have very good adsorption properties, large surface area, homogenous micro- and mesopores [49–51]. As the final method of PAEs identification gas chromatography (GC) [19,52–55], high performance liquid chromatography (HPLC) [56,57], and capillary electrophoresis (CE) [58,59] can be used.

Mesoporous carbons with pores dimensions from 2 to 50 nm are very interesting materials, especially useful for the adsorption of many organic compounds. To expand their range of application, it is necessary to develop microporosity in these carbon materials, which lead to enlarge their surface area and micropores volume (pores with dimension lower than 2 nm).

There are two main methods of synthesis of ordered mesoporous carbons. The first one is the hard-templating method with the application of mesoporous silica, silica colloids, or silica colloids crystals [60–65]. The second is the soft-templating method [66–71] in which surfactants or block copolymers are used (e.g. Pluronic F127) as soft matrices. In the soft-templating method, in contrast to the hard-templating method, the application of solid silica matrices was eliminated, which reduced the number of synthesis stages and made the process cheaper and easier from an industrial point of view. Nanoporous materials, containing large, homogenous mesopores and micropores, are needed in many applications. This structure provides a high adsorption capacity. Fast adsorbate transport inside nanopores is assured due to the well-developed mesoporous structure. Considering the nature of the soft and hard templating method, mostly carbons with well-developed mesoporosity are obtained, but low microporosity. To enlarge the range of application of mesoporous carbons, their surface area and pore volume must be increased. One of the methods to increase microporosity is physical or chemical activation. It can be achieved by KOH [69–74] or NaOH [75] chemical activation. Another way is

physical activation using steam and carbon dioxide in the temperature range from 800°C to 1,100°C [76–79].

The aim of this work was to verify the abilities of two carbon material sorbents obtained by the soft templating method in acidic environment (STA) and activated by steam and carbon dioxide or potassium hydroxide to work as sorbents in the SPE technique. Six phthalates were investigated in this work: dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP), and di-n-octyl phthalate (DOP).

## 2. Experimental

### 2.1. Reagents, materials, and instruments

The standard solution of six PAEs (DMP, DEP, DBP, BBP, DEHP, and DOP), in methanol, the concentration of each phthalate = 2,000  $\mu\text{g}/\text{cm}^3$  was purchased from Supelco (USA). Methanol, acetone, n-hexane, ethyl acetate, and acetonitrile all GC capillary grade (min 99%) were purchased from Pestinorm VWR (USA). Ethanol (98%), formaldehyde (36%–38%), hydrochloric acid (37%), and potassium hydroxide were purchased from Avantor (Poland). For the synthesis of carbon material, Pluronic F127 and resorcinol, were from Sigma-Aldrich (USA). The SPE C-18, Florisil (3  $\text{cm}^3/500$  mg) and empty glass cartridges (3  $\text{cm}^3$ ) were from Chromabond, Macherey-Nagel (Germany). SPE procedure was carried out using SPE vacuum manifold from J.T. Baker (USA). For final determination of PAEs gas chromatography coupled with mass spectrometry system was used, model Clarus 600/600T from Perkin Elmer (USA). Phthalates were separated on the Elite-5MS (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ) capillary column. Images of investigated carbon materials were obtained by SEM Zeiss model Ultra Plus, EDS Bruker Quantax 400 (USA). The porous structure of applied adsorbents was designated based on low-temperature nitrogen adsorption isotherms at 77 K (Structural Research Laboratory of Jan Kochanowski University in Kielce), using volumetric adsorption analyzer ASAP 2020 by Micromeritics (Norcross, GA, USA). Infrared spectra were determined by the Perkin-Elmer Spectrum 400 FT-IR/FT-NIR spectrometer with a smart endurance single bounce diamond, attenuated total reflection (ATR) cell. Spectra in the 4000–650  $\text{cm}^{-1}$  range were obtained by the co-addition of 40 scans with a resolution of 4  $\text{cm}^{-1}$ . Before the measurements, all samples were dried and powdered in an agate mortar.

### 2.2. STA materials synthesis and activation

The synthesis of mesoporous carbon materials was based on the work of Wang [80] modified according to work of Choma [81]. First, 7.5 g of Pluronic F127 and 7.5 g of resorcinol were dissolved in 35.7  $\text{cm}^3$  and 19.8  $\text{cm}^3$  of distilled water, respectively. Then both solutions were mixed. Next 2.2  $\text{cm}^3$  of hydrochloric acid (37%) was added. The mixture was mixed on a magnetic stirrer for 30 min. Then 7.5  $\text{cm}^3$  of formaldehyde was added to the solution and mixed until it became cloudy. After mixing, the solution was left until two layers were separated. The bottom

layer, polymer-rich, was transferred into quartz boat and heated in the furnace at 100°C for 24 h. The last step of synthesis was carbonization in a tube furnace under nitrogen flow of 20 dm<sup>3</sup> h<sup>-1</sup>. The temperature program of the furnace was from room temperature up to 400°C (1°C min<sup>-1</sup>), then up to 850°C (5°C min<sup>-1</sup>) and hold for 2 h.

Obtained STA material was activated in two ways. First was the activation with CO<sub>2</sub> and steam in 850°C in gas mixture: steam – CO<sub>2</sub> – nitrogen (2:3:5) under flow of 20 dm<sup>3</sup> h<sup>-1</sup> for 4 h, then in mixture of CO<sub>2</sub> – nitrogen (1:1) under flow of 10 dm<sup>3</sup> h<sup>-1</sup> for 4h and pure nitrogen under flow of 15 dm<sup>3</sup> h<sup>-1</sup> for 4 h. This material was named STA-CO<sub>2</sub>.

Another activation was performed with KOH. The mixture of STA and KOH (3:9 mass ratio) was heated in the atmosphere of nitrogen under flow of 20 dm<sup>3</sup> h<sup>-1</sup> per 2 h in 700°C. Next, the material was washed with 0.1 M hydrochloric acid to obtain neutral pH, then washed with distilled water and dried to a constant mass. This material was named STA-KOH.

Both materials STA-CO<sub>2</sub> and STA-KOH were grinded and sieved to separate fractions of 0.4–0.8 mm grain size.

### 2.3. STA-CO<sub>2</sub> and STA-KOH structural properties

Before adsorptive measurements, both studied carbon materials were degassed in temp. 200°C for 2 h. Experimental nitrogen adsorption isotherms were used to determine the standard parameters of the porous structure such as specific surface area, pore volume, and pore size distribution. The specific surface area ( $S_{\text{BET}}$ ) was determined in the relative pressure range from 0.05 to 0.20 considering the surface (0.162 nm<sup>2</sup>) occupied by a single nitrogen molecule in a monolayer [82]. The total pore volume ( $V_t$ ) was determined from one point of the adsorption isotherm corresponding to the relative pressure  $p/p_0 = 0.99$  [83]. The pore size distribution (PSD) functions were calculated by the non-local density functional theory method (NLDFT) for carbon slit-shaped pores with surface energetical heterogeneity and geometrical corrugation [84,85]. The calculations were performed using the numerical program SAIEUS (Micromeritics).

### 2.4. Elaborated procedure of solid-phase extraction

100 mg of STA-CO<sub>2</sub> or STA-KOH were packed in 3 cm<sup>3</sup> glass cartridges, between two polytetrafluoroethylene frits. The prepared cartridges were placed in an SPE vacuum manifold. The SPE procedures in case of both carbon materials were the same. The first step was conditioning with 3 cm<sup>3</sup> of methanol and 3 cm<sup>3</sup> of distilled water prior to each SPE extraction. 50 cm<sup>3</sup> of distilled water spiked with six PAEs (final concentration in water 300 ng cm<sup>-3</sup>) was passed through prepared STA-CO<sub>2</sub> and STA-KOH sorbents in cartridges at the flow rate of 5 cm<sup>3</sup> min<sup>-1</sup>. After this step, the sorbent was rinsed with 3 cm<sup>3</sup> of distilled water and dried for 10 min in the nitrogen flow. The next step was elution with 3 cm<sup>3</sup> ethyl acetate – n-hexane (50:50 v/v). The final step was to evaporate the excess of the effluent with nitrogen flow to obtain 1 cm<sup>3</sup> of the extract. Finally, the extracts were analyzed by GC-MS.

### 2.5. GC-MS analysis conditions

The flow of helium carrier gas (99.9999% purity) was maintained constant at a rate of 2 cm<sup>3</sup>/min. The injection port temperature was 250°C in the split (1:10) mode. The sample volume injected was 5 µl. The ion source and transfer line temperature were set as 250°C. The electron ionization was 70 eV. The compounds were separated using the following temperature program: 100°C maintained for 1 min, then increased at a rate of 10°C/min up to 310°C and hold for 9 min. The total analysis time was 31 min.

## 3. Results and discussion

### 3.1. STA-CO<sub>2</sub> and STA-KOH properties

Experimental nitrogen adsorption isotherms for studied adsorbents are shown in Fig. 1. The course of isotherms for investigating carbon materials suggests IV type isotherms (which are characteristic for mesoporous solids) with well-developed hysteresis loops H1 type (the presence of accessible mesopores is confirmed), according to IUPAC classification [86]. The parameters of the porous structure determined from nitrogen adsorption isotherms are presented in Table 1.

The pore volume distribution functions are shown in Fig. 2. Each of the presented plots of examined carbon materials contains two maximums. One maximum corresponds to micropores and the other to mesopores. However, the height and the dispersion of the selected peak is different for both carbon materials and they point to the participation of selected pores in the total porosity. Carbon materials STA-CO<sub>2</sub> and STA-KOH are characterized by a relative high peak in the microporosity section, while low in the mesoporosity section. The detailed data concerning the dimension of micropores  $w_{\text{mi}}$  and mesopore  $w_{\text{me}}$  are presented in Table 1.

The data in Table 1 show that STA-CO<sub>2</sub> carbon material has the specific surface area of 1,008 m<sup>2</sup> g<sup>-1</sup> and the total

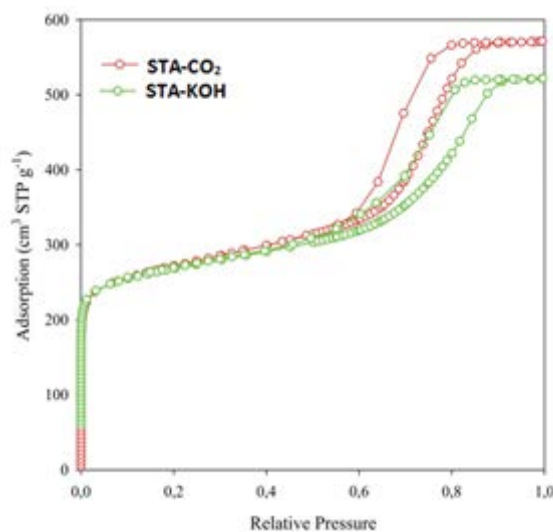


Fig. 1. Experimental nitrogen adsorption isotherms for studied micro-mesoporous carbon materials.

Table 1  
Porous structure parameters obtained for STA-CO<sub>2</sub> and STA-KOH materials

Carbon material	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_t$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{\text{ultra}}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{\text{micro}}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{\text{meso}}$ (cm <sup>3</sup> g <sup>-1</sup> )	$w_{\text{mi}}$ (nm)	$w_{\text{me}}$ (nm)	Mesoporosity (%)
STA-CO <sub>2</sub>	1,008	0.88	0.24	0.33	0.55	0.56	6.10	63
STA-KOH	1,009	0.81	0.25	0.35	0.46	0.50	7.28	57

$S_{\text{BET}}$  – specific surface area BET,  $V_t$  – total pore volume calculated from single-point on nitrogen adsorption isotherm at  $p/p_0 \approx 0.99$ ,  $V_{\text{ultra}}$  – ultramicropore volume (pores < 0.7 nm) obtained from DFT (density functional theory) method and PSD (pore size distribution),  $V_{\text{micro}}$  – micropores volume (pores < 2 nm) obtained from DFT PSD,  $V_{\text{meso}}$  – mesopores volume (pores 2–50 nm) obtained DFT PSD,  $w_{\text{mi}}$  or  $w_{\text{me}}$  – dimension of micro- or mesopores obtained from maximum of PSD by DFT method

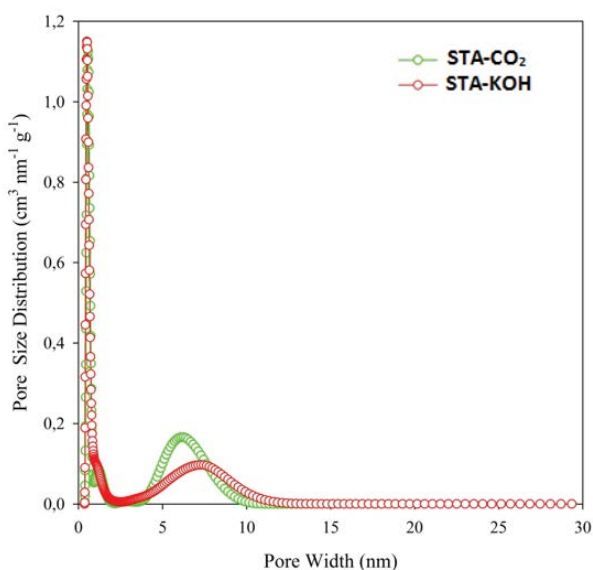


Fig. 2. The pore volume distribution functions for studied micro-mesoporous carbon materials.

pore volume of 0.88 cm<sup>3</sup> g<sup>-1</sup>. STA-KOH carbon material has a specific surface area of 1,009 m<sup>2</sup> g<sup>-1</sup> and a total pore volume of 0.81 cm<sup>3</sup> g<sup>-1</sup>. The comparison of these values indicates that activation by carbon dioxide and steam allows to obtain micro-mesoporous carbon with slightly better-developed porosity ( $V_t$ ) than activation by KOH.

In Fig. 3, SEM images of studied micro-mesoporous carbons are shown. During the measurements, a voltage of 2 kV was applied. These images confirm the ordered, layered structure. It can be observed in the images that STA-CO<sub>2</sub> material is slightly better ordered.

In order to confirm what kind of functional groups are present on the surface of both studied materials, FTIR analysis were performed. The obtained spectra for studied sorbents are presented in Fig. 4.

The ATR-FTIR spectra confirmed the presence of oxygen functional groups on the surface of both activated carbon materials studied in this work. The bands in 3,800–3,300 cm<sup>-1</sup> range of low intensity correspond to stretching vibrations of –OH groups [87,88]. The presence of the bands in 3,000–2,800 cm<sup>-1</sup> range (2,987, 2,843 cm<sup>-1</sup> for STA-CO<sub>2</sub> and 2,906, 2,850 cm<sup>-1</sup> for STA-KOH) can be related to asymmetric group stretching of –CH<sub>3</sub>, –CH<sub>2</sub> from Pluronic F127 matrix [89]. Bands 2,551 cm<sup>-1</sup> for STA-CO<sub>2</sub>

and 2,585 cm<sup>-1</sup> for STA-KOH can be related to vibrations in O–H group [90]. Bands 2,174 and 2,102 cm<sup>-1</sup> prove the CO presence in studied sorbents [91]. For band 1,740 cm<sup>-1</sup>, present in spectra of both sorbents, are responsible vibrations related to double bonds between carbon atoms or between carbon and oxygen atoms [92,93]. The band at 1,570 cm<sup>-1</sup> for both studied sorbents is characteristic for C=C bond [94]. The bands in 1,500–1,100 cm<sup>-1</sup> range (1,214, 1,110, 1,007 for STA-CO<sub>2</sub>; 1,208, 1,139, 1,007 cm<sup>-1</sup> for STA-KOH) are related to carbonyl groups C=O [90]. The range between 900 and 750 cm<sup>-1</sup> represents bending vibration C–H [95]. Summarizing, FTIR spectra of both sorbents are very similar, no matter which method of activation was applied. These results confirmed that both sorbents have the same functional groups on their surface.

### 3.2. Effect of eluent

Three solvents: methanol, acetone, acetonitrile, and one mixture: ethyl acetate – n-hexane (50:50, v/v) were investigated as eluents in SPE of six PAEs. The eluent should be chosen to eluate all six PAEs from the STA-CO<sub>2</sub> and STA-KOH sorbents. The polarity of the eluent should be also similar to the polarity of the analytes. The influence of the solvents on recovery of the PAEs are shown in Fig. 5 for STA-CO<sub>2</sub> sorbent and in Fig. 6. For STA-KOH sorbent.

It can be noticed that the mixture of ethyl acetate with n-hexane (50:50, v/v) is the most effective eluent in case of both investigated STA sorbents. Phthalates are semi-polar or non-polar compounds so nonpolar eluent is very effective. Moreover, the pH effect on the extraction was also studied and it was determined that the pH of sample in the range 5.0–8.0 had no influence on the recoveries.

### 3.3. Effect of the eluent volume

To be completely sure that all the analytes were eluted from the sorbent during the SPE procedure and no carry-overs occur it is needed to optimize the volume of ethyl acetate – n-hexane eluent. The volume of the eluent was tested in the range of 1–5 cm<sup>3</sup> with 50 cm<sup>3</sup> sample of distilled water spiked with PAE's standard at 300 ng cm<sup>3</sup>. The recovery values for all six phthalates increased with the increase of ethyl acetate – n-hexane volume in the range of 1–3 cm<sup>3</sup> and remained almost constant over 3 cm<sup>3</sup>. In all further experiments, 3 cm<sup>3</sup> of the eluent was used. Recovery values for STA-CO<sub>2</sub> and STA-KOH vs. eluent volume are shown in Figs. 7 and 8 respectively.

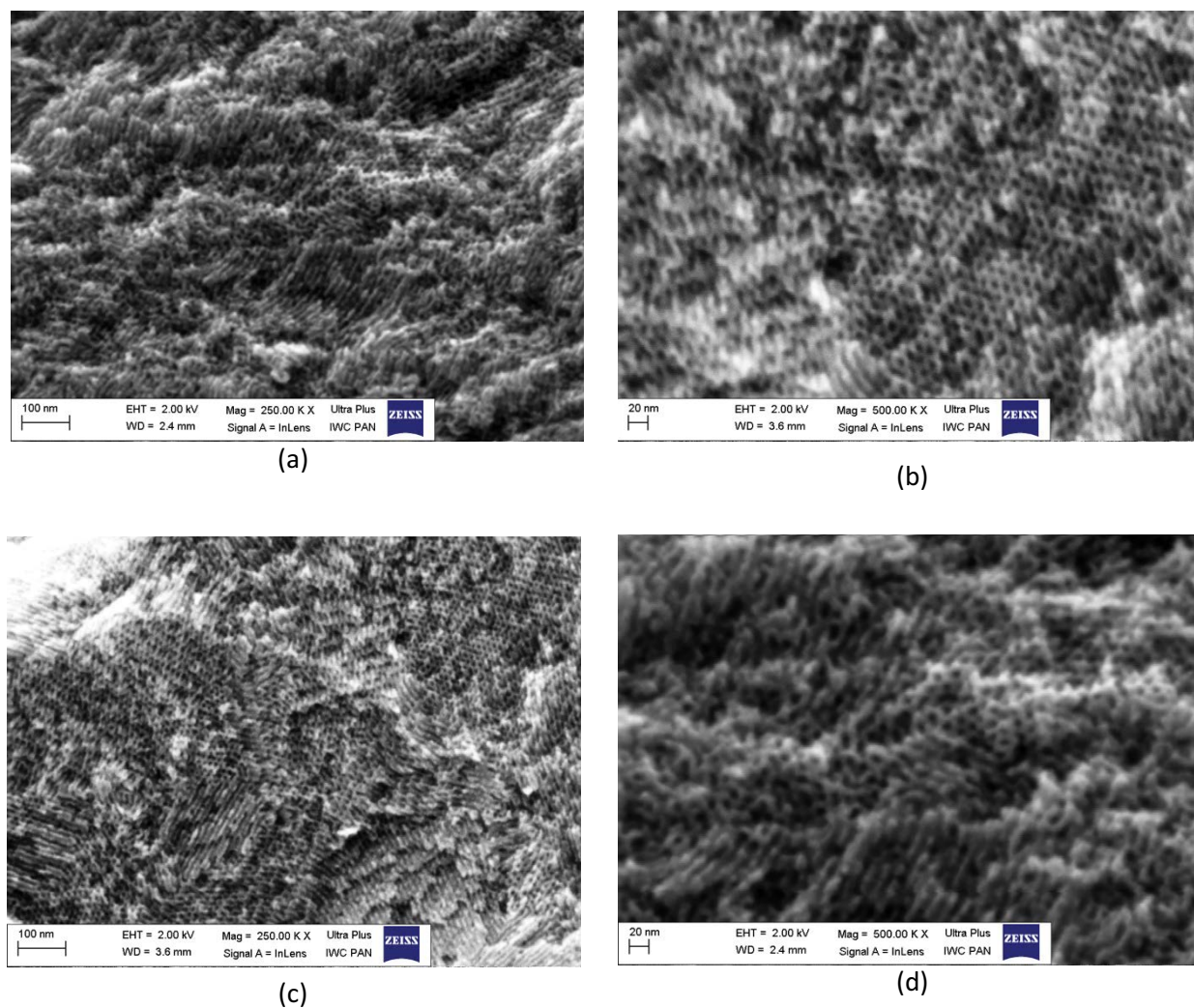


Fig. 3. The SEM images of studied micro-mesoporus carbon materials: STA-CO<sub>2</sub> (a, b) and STA-KOH (c, d).

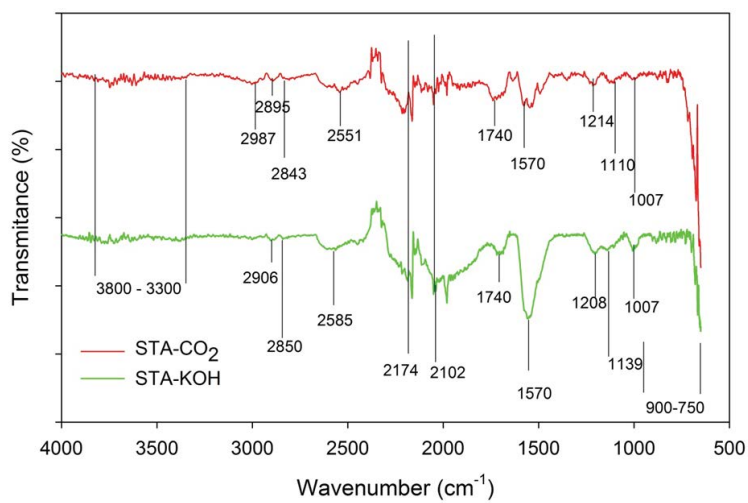


Fig. 4. The FTIR spectra of STA-CO<sub>2</sub> and STA-KOH sorbents.

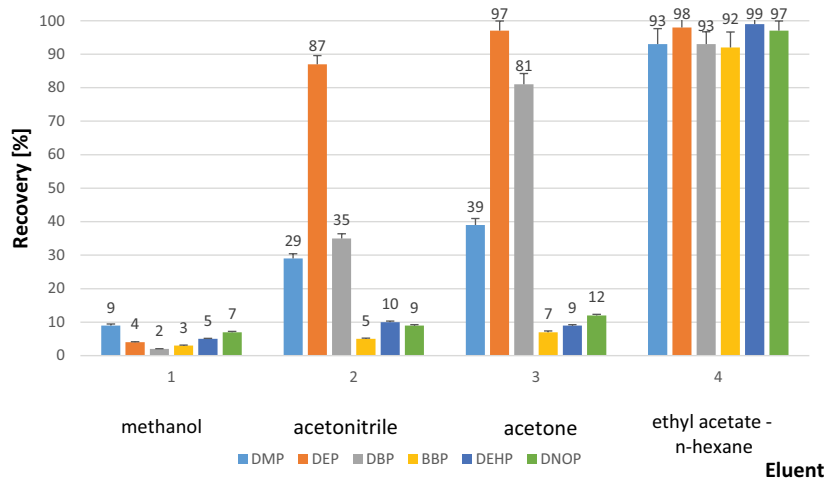


Fig. 5. Effect of the eluent on SPE efficiency for 100 mg of sorbent STA-CO<sub>2</sub>; 50 cm<sup>3</sup> of sample loading volume; concentration of six PAEs: 300 ng cm<sup>-3</sup>.

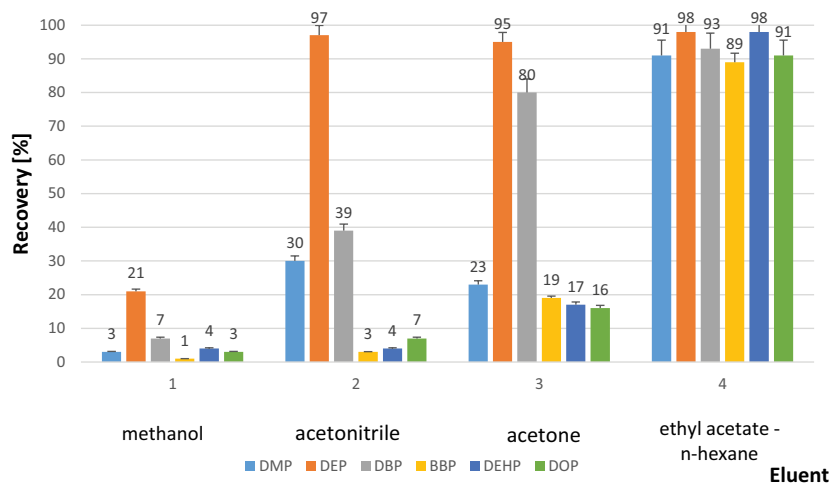


Fig. 6. Effect of the eluent on SPE efficiency for 100 mg of sorbent STA-KOH; 50 cm<sup>3</sup> of sample loading volume; concentration of six PAEs: 300 ng cm<sup>-3</sup>.

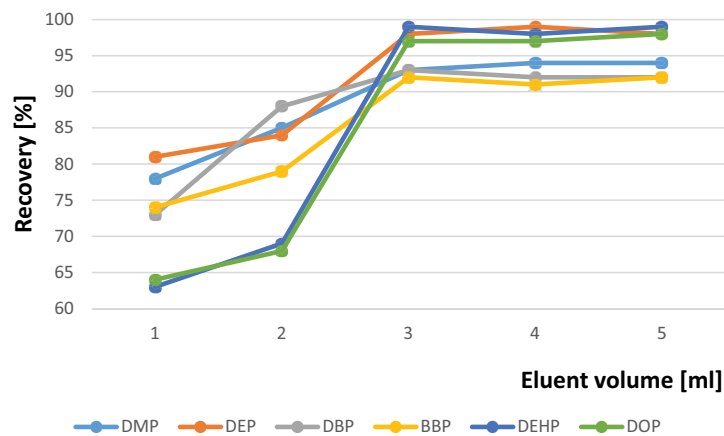


Fig. 7. Effect of the eluent volume on SPE efficiency for 100 mg of sorbent STA-CO<sub>2</sub>; 50 cm<sup>3</sup> of sample loading volume; concentration of six PAEs: 300 ng cm<sup>-3</sup>.

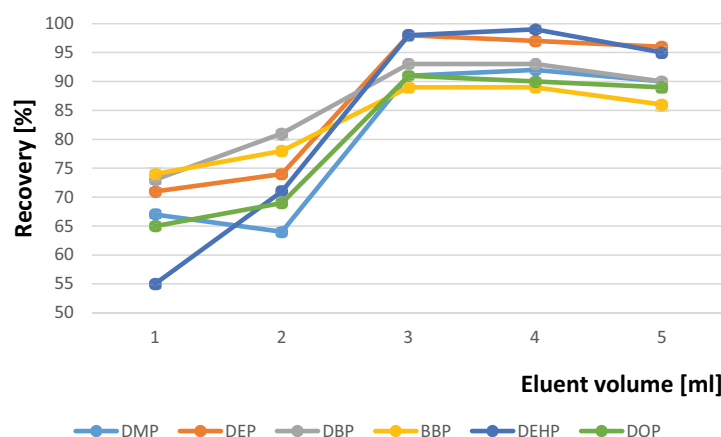


Fig. 8. Effect of the eluent volume on SPE efficiency for 100 mg of sorbent STA-KOH; 50 cm<sup>3</sup> of sample loading volume; concentration of six PAEs: 300 ng cm<sup>-3</sup>.

### 3.4. Effect of the sample volume

The effect of sample volume on recovery of extraction was also studied. Various volumes of aqueous solutions were tested, from 25 to 250 cm<sup>3</sup>. The effect of sample loading volume on the recovery is presented in Figs. 9 and 10 for STA-CO<sub>2</sub> and STA-KOH respectively.

From Fig. 9 can be seen that the highest recovery values were reached when 50 cm<sup>3</sup> of sample was loaded into the SPE cartridges. All recovery values in this case were higher than 90% and the best efficiency was obtained for DEHP, DOP, DEP which is 99%, 97%, and 97%, respectively. It is presented in Fig. 10 that the highest recoveries were obtained also for 50 cm<sup>3</sup>. All the recovery values were higher than 90%, except BBP (89%). The highest efficiency was reached for DEP and DEHP, both at 98%. In case of both studied adsorbents, the difference between recovery values for 50 and 100 cm<sup>3</sup> weren't large. Loading 250 cm<sup>3</sup> of the sample showed a decrease in recovery, which might be caused by the partial sample loss or the breakthrough of the sorbents.

### 3.5. Comparison of STA-CO<sub>2</sub> and STA-KOH with other sorbents

The STA-CO<sub>2</sub> and STA-KOH sorbents were compared to other commonly used sorbents like C-18 and Florisil, so the SPE procedure of PAEs were carry out whit the application of C-18 and Florisil sorbents. The studied carbon sorbents were also compared with literature data concerning sorbents as: graphene nanoplatelet (GN), active carbon, HLB (Hydrophilic-Lipophilic-Balanced) and multi-walled carbon nanotubes (MWCNTs). In order to different densities of studied sorbents, different amounts of them were packed in the SPE cartridges to receive the same level of packing. The results are presented in Table 2.

From the group of sorbents studied in the experiment STA-CO<sub>2</sub> yielded the highest recoveries (92.5%–99.4%) of the PAEs extraction. For STA-KOH a little bit lower recovery values (89.4%–98.5%) were obtained than for STA-CO<sub>2</sub>, the lowest for BBP (89.4%). However, all recovery values obtained for studied STA-CO<sub>2</sub> and STA-KOH are higher than 90%, except for BBP on STA-KOH. In case of C-18 sorbent recoveries are from 68.7% to 95.5%. These

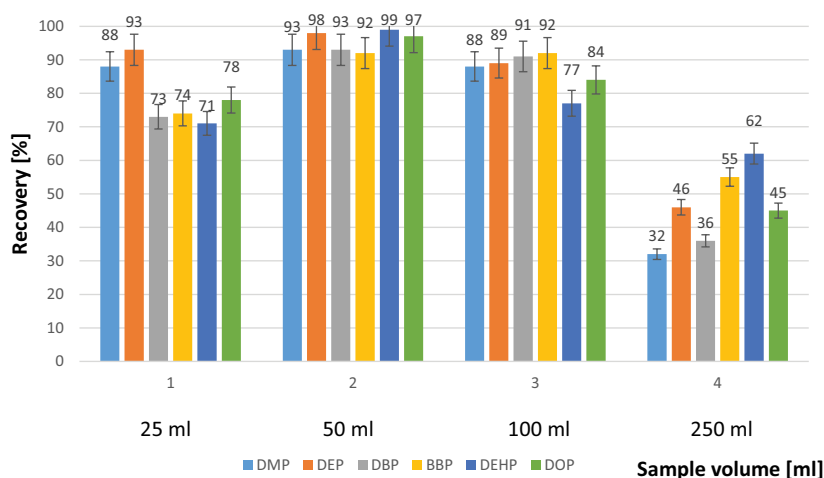


Fig. 9. Effect of the sample volume on SPE efficiency for 100 mg of sorbent STA-CO<sub>2</sub>; 3 cm<sup>3</sup> of eluent; concentration of six PAEs: 300 ng cm<sup>-3</sup>.

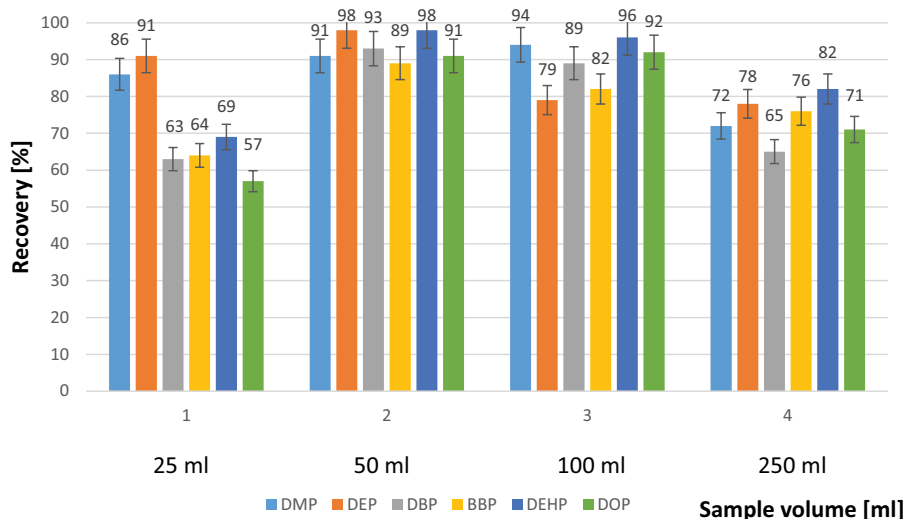


Fig. 10. Effect of the sample volume on SPE efficiency for 100 mg of sorbent STA-KOH; 3 cm<sup>3</sup> of eluent; concentration of six PAEs: 300 ng cm<sup>-3</sup>.

Table 2  
Comparison of sorbents for SPE of six PAEs

Sorbent <sup>a</sup> name	Sorbent mass (mg)	Recovery (%)						Reference
		DMP	DEP	DBP	BBP	DEHP	DOP	
STA-CO <sub>2</sub>	100	93.2 ± 0.6	98.2 ± 0.7	93.5 ± 0.3	92.5 ± 0.7	99.4 ± 0.5	96.9 ± 0.9	This work
STA-KOH	100	91.1 ± 0.4	98.5 ± 0.9	93.3 ± 0.4	89.4 ± 0.5	98.3 ± 0.4	91.4 ± 0.7	This work
C-18	500	79.4 ± 0.2	68.7 ± 0.5	82.1 ± 0.6	95.5 ± 0.4	85.4 ± 0.4	84.4 ± 0.7	This work
Florisil	500	57.8 ± 0.9	72.1 ± 1.1	48.3 ± 0.9	87.1 ± 1.3	81.5 ± 1.2	77.1 ± 1.5	This work
GN	30	86.2 ± 0.7	95.3 ± 0.5	89.4 ± 1.0	NA <sup>b</sup>	NA	NA	[11]
Active carbon	50	40.0 ± 0.8	65.2 ± 0.6	66.1 ± 1.0	NA	NA	NA	[11]
HLB	100	100.0 ± 1.7	90.1 ± 3.0	104.1 ± 0.7	NA	NA	NA	[11]
MWCNTs	50	68.9 ± 0.8	95.8 ± 3.4	93.7 ± 1.1	NA	NA	NA	[11]

<sup>a</sup>The eluent solvent for STA-CO<sub>2</sub>, STA-KOH, C-18 and Florisil was ethyl acetate with n-hexane (50:50, v/v); for GN and MWCNTs was acetonitrile; for HLB an active carbon was methanol;

<sup>b</sup>not available.

values are lower than for STA carbon materials, except BBP (95.5%) which is higher. The recoveries of six PAEs did not exceed 87% in case of Florisil application. The highest recovery on Florisil was for BBP. It should be noticed that the amount of STA-CO<sub>2</sub> and STA-KOH in SPE cartridge is five times smaller than in case of C-18 and Florisil, but the recoveries are higher. Recovery values of tested sorbents were also compared with literature data [11] concerning three PAEs: DMP, DEP, DBP. In case of HLB sorbent, the amount of sorbent is the same (100 mg) as in case of both STA materials and the recovery values are higher for DMP and DPB than for studied STA carbon materials, but lower for DEP. GN material showed good recovery values but a little bit lower than in case of STA carbon sorbents. For MWCNTs there is only 68.9% recovery for DMP, but 95.8% and 93.7% for DEP and DBP respectively. The recovery values obtained for active carbon were quite poor and didn't exceed 66% for three tested phthalates.

### 3.6. Multiple SPE extraction

Three repetitions of SPE extractions of six PAEs from aqueous samples were performed without exchanging the STA-CO<sub>2</sub> or KOH sorbent in the SPE cartridge. After first extraction the sorbent was rinsed with 2 cm<sup>3</sup> with a mixture of ethyl acetate – n-hexane (50:50, v/v) and heated in the laboratory dryer at 120°C for 12 h. Then the SPE cartridges were applied for the extraction for the second time. Next, rinsing and heating were repeated and SPE cartridges were applied for the extraction for the third time. Every time after the rinsing step, ethyl acetate - n-hexane eluate was checked by the GC-MS method to be sure that there aren't any PAEs washed out from the sorbent (there aren't any PAEs still adsorbed). The results of the experiment are shown in Fig. 11.

It can be seen from Fig. 11 that the recovery values decreased after multiple extractions in case of both investigated carbon sorbents for six studied PAEs. For DMP and



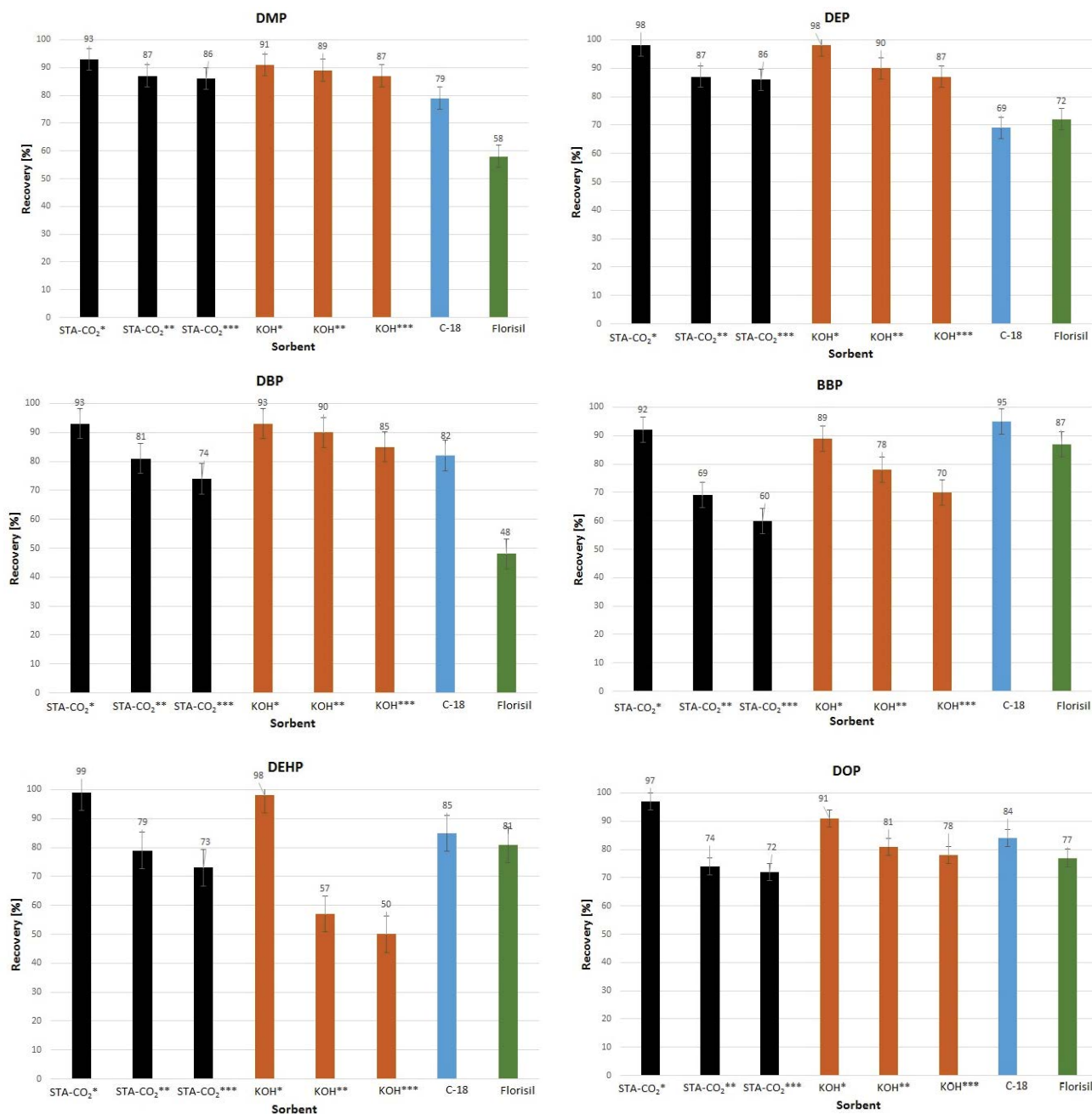


Fig. 11. Effect of the multiple SPE on recovery using 100 mg of STA-CO<sub>2</sub> or KOH; 3 cm<sup>3</sup> of eluent; concentration of six PAEs: 300 ng cm<sup>-3</sup>; mass of C-18 and Florisil = 500 mg. Symbol: \*means one repetition of SPE, \*\*means two repetitions of SPE and \*\*\*means three repetitions of SPE. Florisil and C-18 were used only once in SPE procedure.

DEP recovery values are in range from 86% to 90% in case of both carbon materials after second and third extraction. For STA-CO<sub>2</sub> the recovery values for DBP, BBP, DEHP, and DOP are between 60% and 81%. In case of STA-KOH sorbent the recovery values for DBP are quite high, 90% and 85% after second and third extraction respectively. For BBP and DOP recoveries for STA KOH are between 70% to 81%. The lowest recoveries were obtained for STA-KOH sorbent in case of DEHP, 57% and 50% after second and third extraction respectively. Florisil and C-18 were also

rinsed and heated, but it was very hard to use them for the second time, because it was almost impossible to pass any liquid through the sorbent. In the experiment with Florisil and C-18 multiple extractions were abandoned.

### 3.7. GC-MS analysis

In Fig. 12, the standard chromatogram of six PAEs determined by GC-MS method is shown. The proposed STA-CO<sub>2</sub> and STA-KOH-based method were first evaluated

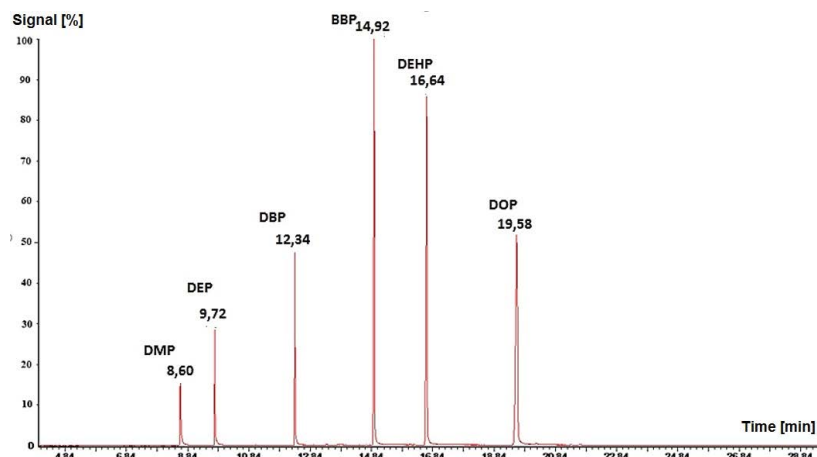


Fig. 12. Chromatogram of six phthalates in aqueous solution ( $300 \text{ ng cm}^{-3}$ ) after SPE procedure on STA- $\text{CO}_2$  with ethyl acetate – n-hexane elution, determined by GC-MS method.

using calibration solutions of investigated phthalates, prepared by spiking the distilled water with methanol PAEs standard solution. Calibration curves were determined for six phthalates, in the range of  $50\text{--}500 \text{ ng cm}^{-3}$ . The results obtained are shown in Table 3. The limits of detection (LODs), based on signal to noise ratio (S/N) of 3 were in range of  $0.11\text{--}0.83 \text{ ng cm}^{-3}$  for both studied carbon materials. The obtained results for STA- $\text{CO}_2$  were comparable with those of SPE method for MWCNTs ( $0.18\text{--}0.86 \text{ ng cm}^{-3}$ ) [44].

The described SPE-GC-MS method was applied for the analysis of commercial bottled water and water boiled in a plastic kettle. Three samples were prepared: spring water in a PET bottle hidden from sunlight influence; the same spring water but left for sunlight influence for ten weeks (left on the windowsill) and distilled water boiled in a plastic kettle. All three samples were investigated according to STA- $\text{CO}_2$  and STA-KOH based SPE-GC-MS method in order to PAEs determination. The results are shown in Table 4.

In bottled water no. 1 of six examined PAEs was detected which is a very good information. In bottled water no. 2 three PAEs were determined (DBP, BBP, DEHP) in case of both STA sorbents used in the SPE method. In Poland for example, the maximum allowed concentration of DBP and BBP in drinking water is  $20 \text{ ng cm}^{-3}$  and  $100 \text{ ng cm}^{-3}$ ,

respectively and is determined by the Regulation of the Minister of Health [96]. The concentrations of DBP determined in real water samples are higher than the acceptable standard and for BBP are acceptable. No regulations concerning DEHP level in drinking water in Poland were found. It was confirmed that storage of water in plastic bottles in sunny places can lead to phthalate esters migration from the bottle into the water and then into the human organism. In case of distilled water boiled in a plastic kettle two PAEs were determined (DBP, DEHP) which means that phthalates can migrate also under influence of high temperature. The DEHP concentration determined in water from the kettle is very high.

#### 4. Conclusion

In this work, two ordered carbon micro-mesoporous materials activated by  $\text{CO}_2$  and steam (STA- $\text{CO}_2$ ) or KOH (STA-KOH) were applied as sorbents in the SPE method for extraction of six phthalate esters from aqueous solutions. For the final determination of PAEs in obtained extracts, the GC-MS method was applied. Both carbon materials are characterised by a large surface area over  $1,000 \text{ m}^2 \text{ g}^{-1}$  and well-developed porosity. FTIR analysis

Table 3

Linear ranges, correlation coefficients, detection and quantification limits of STA- $\text{CO}_2$  and STA-KOH based SPE method ( $n = 3$ )

Phthalate	Linearity ranges ( $\text{ng cm}^{-3}$ )		$R^2$		LOD ( $\text{ng cm}^{-3}$ ) <sup>a</sup>		LOQ ( $\text{ng cm}^{-3}$ ) <sup>a</sup>	
	STA- $\text{CO}_2$	STA-KOH	STA- $\text{CO}_2$	STA-KOH	STA- $\text{CO}_2$	STA-KOH	STA- $\text{CO}_2$	STA-KOH
DMP	50–500	50–500	0.997	0.996	0.41		1.24	
DEP	50–500	50–500	0.992	0.998	0.19		0.66	
DBP	50–500	50–500	0.997	0.998	0.11		0.28	
BBP	50–500	50–500	0.994	0.995	0.11		1.19	
DEHP	50–400	70–400	0.991	0.990	0.47		1.36	
DOP	50–400	70–400	0.995	0.991	0.83		1.36	

<sup>a</sup>Limit of detection (LOD) and limit of quantification (LOQ) calculated based on signal/noise = 3 and 9, respectively.

Table 4  
Determination of PAEs in real water samples

Sample	STA-CO <sub>2</sub>					
	Phthalate (ng cm <sup>-3</sup> )					
	DMP	DEP	DBP	BBP	DEHP	DOP
<sup>a</sup> bottled water no.1	ND <sup>d</sup>	ND	ND	ND	ND	ND
<sup>b</sup> bottled water no. 2	ND	ND	51.2 ± 0.9	63.7 ± 1.6	80.4 ± 2.6	ND
<sup>c</sup> water from kettle	ND	ND	62.5 ± 1.9	ND	279.1 ± 4.3	ND
Sample	STA-KOH					
	Phthalate (ng cm <sup>-3</sup> )					
	DMP	DEP	DBP	BBP	DEHP	DOP
<sup>a</sup> bottled water no.1	ND	ND	ND	ND	ND	ND
<sup>b</sup> bottled water no. 2	ND	ND	50.8 ± 1.1	66.1 ± 1.6	88.4 ± 2.3	ND
<sup>c</sup> water from kettle	ND	ND	64.2 ± 1.2	ND	289.3 ± 4.4	ND

<sup>a</sup>spring water in PET bottle hidden from sunlight influence; <sup>b</sup>spring water but left for sunlight influence for six weeks; <sup>c</sup>distilled water boiled in plastic kettle; <sup>d</sup>ND – not detected

showed that on the surface of both studied sorbents the same functional groups are present, after the activation process. In comparison with several common SPE sorbents, including C-18 and Florisil appeared to be more effective considering recovery values of PAEs extraction. The recovery for STA-CO<sub>2</sub> yielded the highest values (92%–99%) of the PAEs extraction. For STA-KOH a little bit lower recovery (89%–98%) were obtained than for STA-CO<sub>2</sub>, the lowest for BBP (89%). However, all recovery values obtained for studied STA-CO<sub>2</sub> and STA-KOH are higher than 90%, except for BBP on STA-KOH. It should be noticed that the amount of used carbon sorbents (100 mg) was five times smaller than in case of C-18 or Florisil (500 mg). The advantage of applied carbon sorbents is the possibility of multiple extractions of PAEs from an aqueous solution without exchanging the sorbent in the SPE cartridge. Even after the third repetition of the SPE procedure without exchanging the cartridge the recovery values are quite high, even up to 90%. Both STA sorbents can be applied with good results for PAEs extraction from real aqueous samples.

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