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Development of a solid-phase microextraction method for the determination of phthalic acid esters in water

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Abstract

Solid-phase microextraction method (SPME) coupled to GC/ECD has been developed and validated for the determination of phthalic acid esters (dimethyl-, diethyl-, di-*n*-butyl-, butylbenzyl-, di-2-ethylhexyl- and di-*n*-octyl phthalate) in water samples. Two types of coatings (PDMS, PA), altogether four different kinds of fibers have been investigated. Both parameters affecting the partition of analytes between a fiber coating and aqueous phase (i.e. extraction time, extraction temperature, agitation) and conditions of the thermal desorption in a GC injector were optimized. The final SPME method employing the polyacrylate fiber, extraction time 20 min, heating and stirring of the sample enabled the determination of all six phthalates in water samples. The method showed linear response over four orders of magnitude and the limits of quantification of the method ranged between 0.001 and 0.050 $\mu g\,l^{-1}$. The repeatability expressed as R.S.D. was in the range 4–10% for the spiking level 7 $\mu g\,l^{-1}$ of each analyte. The applicability of the developed SPME method was demonstrated for real water samples.
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Keywords: Solid-phase microextraction; Phthalates; Water analysis; Gas chromatography

1. Introduction

Phthalic acid esters (phthalates, PAEs) are key additives in many plastics, mainly in polyvinylchloride (PVC) products. Due to their widespread use, relatively large amounts of these compounds are released into the environment. In the recent years, considerable attention has been paid to the human exposure to phthalates because of the suspicion of their carcinogenic and estrogenic properties. As phthalates are not chemically but only physically bound to the plastic structure, they may be leached into foods and beverages from the packaging material, likewise penetration of PAEs from waste plastics into ecosystem surrounding dumping sites may occur.

Analysis of phthalate esters in food and environmental samples may pose a serious problem because high blanks are often encountered. This is due to PAEs presence in many laboratory products, including chemicals and glassware.

Various liquid–liquid extraction (LLE) techniques employing organic solvents such as dichloromethane, hexane or petroleum ether have been widely used for isolation of PAEs from aqueous samples [1–4]. These procedures are typically time-consuming, tedious, and often require pre-concentration or other pre-treatment of the sample prior to analysis. As a modification of classic liquid extraction, miniaturized version (microextraction, ME) might be used. In this case analytes are extracted from a relatively large sample

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Table 1
Analytes characteristics: basic physico-chemical properties [15]

Analyte	Abbreviation	Molecular weight	H_2O solubility ($mg\,l^{-1}$)	$\log K_{ow}$
Dimethyl phthalate	DMP	194.19	4200	1.61
Diethyl phthalate	DEP	222.24	1100	2.38
Di-*n*-butyl phthalate	DnBP	278.35	11.2	4.45
Butylbenzyl phthalate	BBP	312.39	2.7	4.59
Di-2-ethylhexyl phthalate	DEHP	390.56	0.003	7.50
Di-*n*-octyl phthalate	DnOP	390.56	0.0005	8.06

volume (up to 1 l) by a very small amount of solvent (typically few hundreds of microliters) [5]. Unfortunately, microextraction configured in this manner, is suited mainly for non-polar analytes possessing strong affinity to solvent used. Accordingly, poor recoveries are obtained for the most polar phthalates such as DMP and DEP [2]. Alternative isolation technique conceivable for analysis of phthalates in aqueous samples is represented by solid-phase extraction (SPE). The use of solvents and consequently, secondary contamination are reduced significantly. In addition, automated sample handling can be realized in case of large series of samples.

Solid-phase microextraction method (SPME) is a solvent-free isolation technique that is distinctly faster and more simple to perform compared to conventional methods mentioned above. This method usually employs a polymeric stationary phase coated onto a fused-silica fiber to extract compounds from any type of sample (or adjacent vapor phase) placed in sealed vials. Extraction of analytes from aqueous samples can be performed either by direct immersion of the fiber into the liquid phase or by headspace sampling. Adsorbed analytes are then thermally desorbed in the injection port of a gas chromatograph and quantified using an appropriate column and detector. The SPME method coupled to gas chromatography (GC) has been also successfully employed for the determination of a wide variety of organic water pollutants such as volatile organic compounds [6], nitrobenzene and dinitrotoluenes [7], organochlorine pesticides [8] or polyaromatic hydrocarbons and polychlorinated biphenyls [9].

Nowadays, new interfaces have been also developed to couple the solid-phase microextraction to high-performance liquid chromatography (HPLC). Analytes are eluted from the fiber by a mobile phase and transferred directly onto the analytical column for separation. SPME/HPLC procedures of this kind have been successfully applied for the analysis of both non-volatile and semi-volatile substances [10–13].

Recently, studies employing SPME in phthalate analysis have been published [13,14]. It clearly seems to be an "ideal" technique, namely for the determination of these analytes in aqueous samples, because a risk of secondary contamination often occurring during sample handling (which is the major problem in phthalate analysis) is significantly reduced.

The purpose of our study was to develop a multi-residual SPME method encompassing six most common phthalates, which possess a wide range of physico-chemical properties (see Table 1). Applicability of this method for analysis of target analytes in real water samples was demonstrated.

2. Experimental

2.1. Chemicals and materials

Dimethyl phthalate (98.8%), diethyl phthalate (99.9%), di-*n*-butyl phthalate (99.4%), butylbenzyl phthalate (97%), di-2-ethylhexyl phthalate (99%) and di-*n*-octyl phthalate (94%) were obtained as neat compounds from Dr. Ehrenstorfer (Germany). The individual stock solutions of $1\,g\,l^{-1}$ were prepared in methanol and stored at 4 °C. Standards mixture was prepared in the final concentration about $50\,mg\,l^{-1}$ of each analyte in methanol (standard working solution). Solvents used (methanol and isooctane) were analytical grade (Merck, Germany) and were rectified to remove phthalates residues. The distilled water was prepared in all glass apparatus and stored in a glass bottle.

2.2. Real water samples

Potable tap water from the Prague water-supply network and deionized water from purification system (Milli-Q RG, Millipore, USA) were examined. Samples of bottled potable water were obtained at a retail market: (i) mineral water "Mattoni" (Mattoni, CZ) distributed in glass bottles with metal caps sealed with PVC inserts plasticised by DEHP; (ii) spring water "good water" (HBSW, CZ) distributed in polyethylene terephthalate (PET) bottles.

2.3. Instrumentation

Gas chromatographic analyses were carried out using a HP 5890 series II gas chromatograph equipped with electronic pressure control (EPC), an electron capture detector (^{63}Ni ECD) and an autosampler HP 7673 (Hewlett-Packard, USA). A capillary column DB-35 (35% phenyl, 65% polymethylsiloxane) of 30 m length × 0.25 mm i.d. coated with 0.15 μm film (J&W Scientific, USA) was employed for separation of analytes. All GC data were stored and reprocessed using HP Vectra 386s/20 and software ChemStation HP 3365 (Hewlett-Packard).

The oven temperature was programmed from 45 °C (held 5 min = splitless period), then increased to 130 °C at 20 °C min^{-1}, then increased to 240 °C at 3 °C min^{-1}, then increased to 270 °C at 20 °C min^{-1} (held 2.5 min, total GC run time = 50 min). Nitrogen was used both as carrier and make-up gas at flow rates 1 ml min^{-1} and 30 μl min^{-1}, respectively. The injector and detector temperatures were 250 and 300 °C, respectively. The volume of injected liquid samples was 1 μl.

2.4. SPME procedure

The SPME fibers used in this study were purchased from Supelco (USA). Silica fibers coated with polydimethylsiloxane film—thickness 100, 30 and 7 μm (PDMS 100, PDMS 30, PDMS 7) and polyacrylate film—thickness 85 μm (PA 85) were used. Before the first usage, the fibers were conditioned according to the recommendations of the producer. Each day, before analysis, the fibers were conditioned for 30 min in the GC injector held at 250 °C and then, prior to starting set of experiments, a blank analysis was performed to verify that no extraneous compounds were desorbed from the fiber.

In preliminary trials in which PDMS 100 fiber was used, 3 ml of distilled water spiked with 2 μl of methanolic standard working solution (spiking level 30 μg l^{-1} of each analyte) were placed into 4 ml screw cap vials with Teflon lined septa. Extraction time profiles were measured under various extraction conditions (heating and stirring of the sample) while the desorption conditions were fixed (desorption period 5 min, position 3 on the manual holder, the fiber was left in the GC injector till the end of analysis). The precision of the method expressed as R.S.D. was determined from a set of five replicates.

In consequent method development, based on the PDMS 30, PDMS 7 and PA fibers, 3 ml of distilled water spiked with 2 μl of methanolic standard working solution (spiking level 3.5 or 7.0 μg l^{-1} of each analyte) were placed into 4 ml screw cap vials with Teflon lined septa. Parameters affecting both SPME procedure and chromatographic process were optimized: (i) desorption conditions (position of the fiber in GC injector, carry-over effect); and (ii) extraction conditions (time, heating and stirring of the sample). The precision of the method expressed as R.S.D. was determined from a set of five replicates. The linearity was investigated over the range 0.001–10 μg l^{-1} with PA 85 fiber. The concentration of phthalates in real water samples was calculated using the calibration curves obtained for distilled water (spiking level 0.001–10 μg l^{-1}) after subtraction of blank analysis.

2.5. Liquid–liquid microextraction

The method developed by Holadová and Hajšlová [2] was used for isolation of phthalates. The samples of bottled potable water were left prior to extraction in a sonication bath for 10 min to remove carbon dioxide. A 300 ml sample together with 1 ml of isooctane was agitated for 2 h in 0.5 l glass flask. Then, 1 μl of isooctane layer was directly injected into the gas chromatograph. The recovery of this method was tested using spiked distilled water (spiking level of PAEs 1 μg l^{-1} each).

3. Results and discussion

Although many kinds of SPME fibers are nowadays available at the market, those extracting analytes mainly by absorption were chosen for our experiments. PDMS coating effective for non-polar compounds and PA coating with high affinity for aromatic analytes were examined in our study.

3.1. Preliminary trials using PDMS 100 fiber

The fiber coated with polydimethylsiloxane (thickness 100 μm) was used within preliminary studies aimed at recognition of a behavior of the whole group of selected phthalates in SPME system. In this study, the influence of heating and stirring of the sample on amount of extracted analyte was investigated. Extractions were performed at 5, 10, 20, 40 and 60 min (120 and 150 min) and either at laboratory (22 °C) or at elevated (66 °C) temperature. Extraction time profiles for individual analytes under various extraction conditions are shown in Fig. 1. Comparable extraction time profiles for a pairs of phthalates with similar K_{ow} values and other physico-chemical properties (DMP–DEP, DnBP–BBP, DEHP–DnOP, see Table 1) were obtained. For the most polar phthalates, such as DMP and DEP the equilibrium was reached quickly because of their low affinity to fiber used. Heating and stirring of the sample did not accelerate an equilibration of DMP and DEP in the system, the amounts extracted at higher temperature were lower than in the case of extraction at laboratory temperature. For medium/non-polar analytes represented by DnBP, BBP, DEHP and DnOP, the equilibrium in the system was obtained very slowly, the amounts of extracted analytes were higher when either heating or stirring of the sample were used. The repeatability of the method using PDMS 100 fiber was determined by performing the 40-min extraction of five spiked water samples (30 μg l^{-1}). The values of R.S.D. obtained both for stirred samples at laboratory temperature and for unstirred heated samples are summarized in Table 2. Generally, either method in this configuration is suitable for the determination of high/medium polar phthalates, such as DMP, DEP, DnBP and BBP: the R.S.D. values ranged from 1 to 6%. On the other hand, the 40-min extraction is not sufficient for DEHP and DnOP, the equilibrium in the system is not attained and the repeatability of method is poor (R.S.D. values ranged from 29 to 37%). One of the conceivable solution providing faster equilibration and, consequently, improved R.S.D. values for non polar analytes was the use of a fiber with a thinner polydimethylsiloxane film. Alternatively the use of a fiber coated with a more polar phase can be used. Accelerated equilibration in the system for non-polar analytes resulting in improved LODs and simultaneous increased extraction efficiency for polar phthalates were the main benefits that were anticipated.

Table 2
Repeatability of SPME method using PDMS 100 fiber for 40-min extraction under various extraction conditions (spiking level 30 μg l^{-1})

Analyte	Repeatability as R.S.D. (%), $n = 5$	
	66 °C without stirring	22 °C with stirring
DMP	6	6
DEP	1	5
DnBP	4	5
BBP	5	4
DEHP	36	29
DnOP	37	36

3.2. Optimization of the SPME method using PDMS 30 fiber

3.2.1. Position of the fiber in the GC injector

The location of the fiber in the GC injector was the first parameter to be optimized. Considering the results obtained for all the target analytes, the position marked on the manual holder as "3" was obviously the optimal one, the highest detector responses were obtained. Fig. 2 well illustrates the consequence of temperature gradient existing across the injection port. Compared to central part, which is reached with fiber located in position 3, the bottom (fiber in position 3.5) and namely the upper (fiber in position 2.5) are cooler what results in decreased desorption of phthalates—proportionally to their increasing molecular weight. It should be noted that the optimal position of fiber in GC injector may vary among different GC instruments and it has to be always experimentally determined.

3.2.2. Carry-over effect

To avoid carry-over effects that may occur among subsequent SPME analyses, the time needed for complete desorption of analytes from a fiber has to

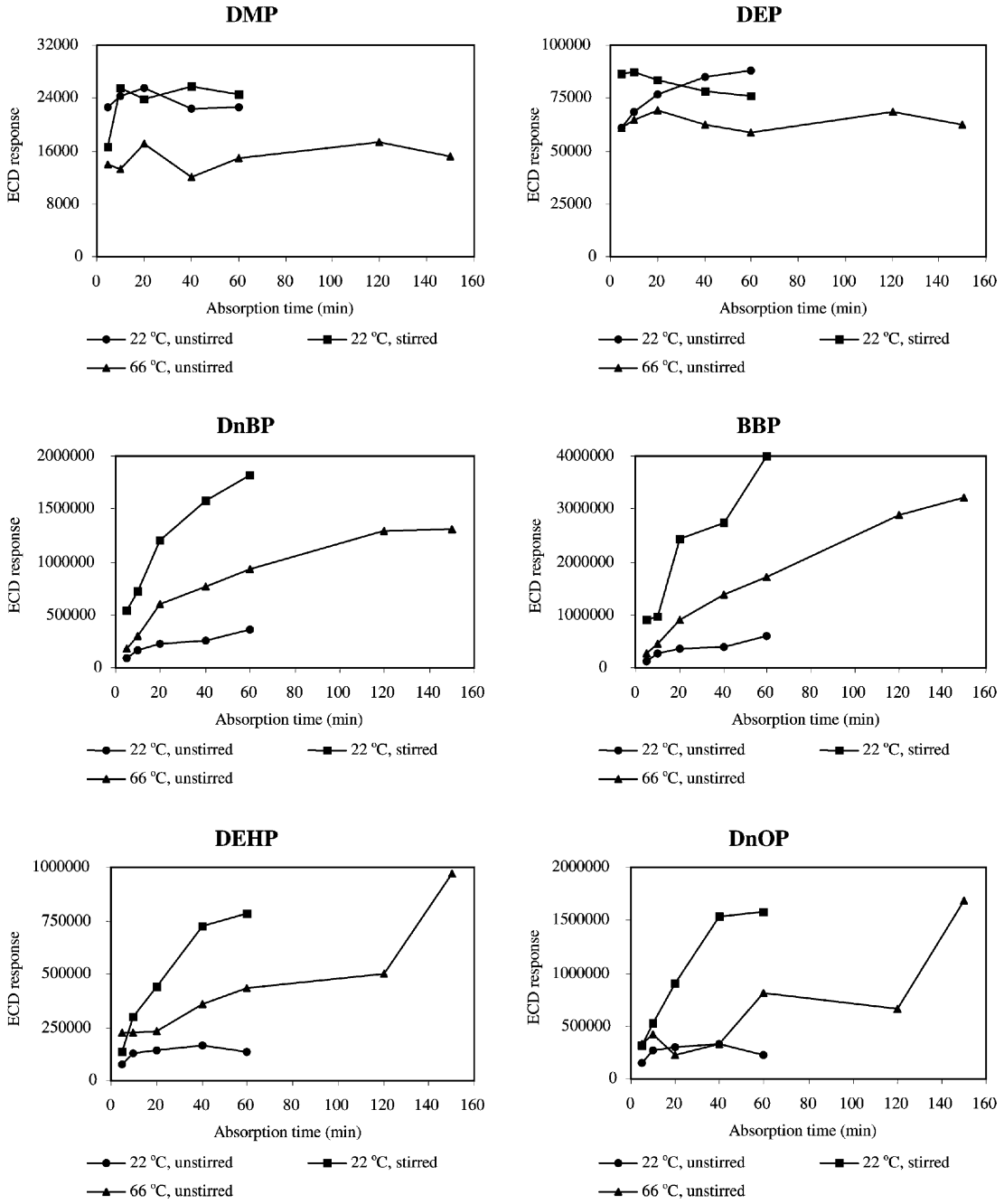

Fig. 1. The influence of heating and stirring of the sample on the extraction time profiles of PAEs, PDMS 100 fiber.

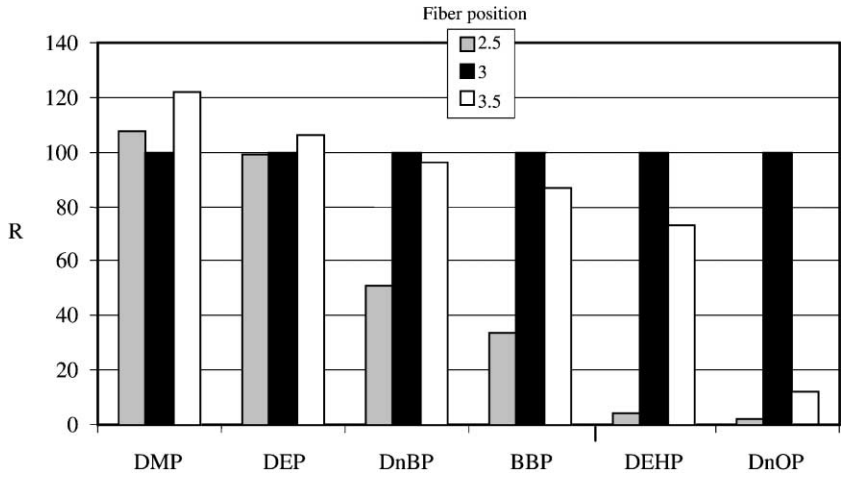

Fig. 2. The relationship between the position of the fiber (PDMS 30) in the injection port and the detector responses (R) of analytes (area of peak obtained for the positions 3 = 100%).

be carefully determined. Three analyses differing in residence times of a fiber in the injection port (5, 30 and 50 min at 250 °C) were carried out prior to the following "blank analysis". As shown in Fig. 3, total desorption of DMP and DEP was obtained even at the shortest time setting (i.e. 5 min, which correspond to the duration of splitless period). Similarly, BBP was weekly retained by this fiber and only negligible carry-over effects were observed. Contrary to these results, considerable carry-over effects were encountered for DnBP, DEHP and DnOP. To complete desorption of these analytes and to minimize carry-over effect, it was necessary to leave PDMS 30 fiber in the GC injector till the end of GC run (50 min). It should be noticed that the extent of carry-over effects is reduced with decreasing thickness of stationary phase film and is dropping with lowering affinity of analytes to the stationary phase.

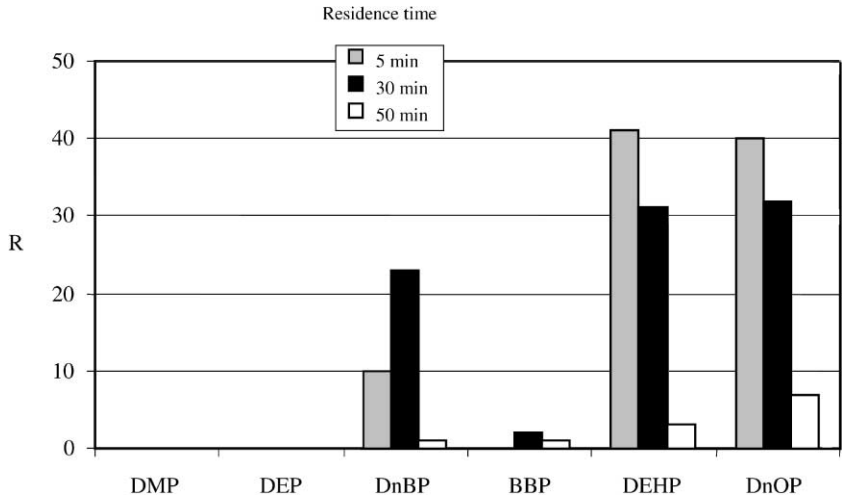

Fig. 3. Carry-over effects recorded in SPME analysis of phthalates expressed as detector responses (R) of analyte left on PDMS 30 fiber after different fiber residence time in GC injector (100% = amount desorbed during analysis after exposition to the spiked sample).

3.2.3. Extraction conditions

Extractions were performed at 2, 5, 10, 15, 20, 30, 40 and 60 min and either at laboratory (22 °C) or at elevated (66 °C) temperature. Extraction time profiles of analytes under various extraction conditions are shown in Fig. 4. Heating and stirring had a distinct effect on the extraction profiles. As expected, for medium/non-polar analytes represented by DnBP, BBP, DEHP and DnOP, the equilibrium in the heated and stirred system was obtained more quickly in about 20 min. The amounts of extracted analytes were higher when simultaneous heating and stirring of the sample were applied. On the other hand, for relatively polar analytes, such as DMP and DEP, higher temperature setting resulted in reduced yields of analytes, nevertheless, the time necessary to reach the equilibrium was not affected—the plateau for DMP and DEP was achieved very rapidly, within 5 min. The highest responses for these relatively polar phthalates were obtained when sample was left at laboratory temperature with stirring. The reason is probably lower value of distribution constant in heated system while in the case of other esters positive effect of faster diffusion is more pronounced. Considering the whole set of generated data, heating and stirring of the sample was necessary to reach the equilibrium for the most of analytes.

3.3. Comparison of PDMS and PA fibers

Three different fiber types were evaluated for the analysis: PDMS 30, PDMS 7 and PA 85. Since the extraction efficiency of the respective compound strongly depends on its affinity to the particular fiber coating, the use of the polar PA 85 fiber provided excellent extraction efficiency of the most polar analytes, DMP and DEP, as well as of moderately polar DnBP and BBP (see Figs. 5 and 6). However, for DnBP and BBP, the equilibrium in this system could not be reached even after 60 min. For phthalates with a long alkyl chain, such as DEHP and DnOP, the highest responses were obtained using fiber PDMS 30; in this case the equilibrium was reached after 20 min.

3.4. Validation of SPME method

Based on the results described above, the experimental set-up employing simultaneous heating and stirring of the sample was used. To compromise between laboratory sample throughput and limits of quantification (LOQs) method, extraction time was set only to 20 min, although the equilibrium can not be achieved for all tested phthalates within this period. In spite of this fact, the amounts of extracted analytes are, thanks to high sensitivity provided by ECD, still sufficient for most of applications. The repeatability of the SPME method was determined by performing the extraction of five equally spiked water samples (7 $\mu g\,l^{-1}$). The values of R.S.D. obtained for all types of fibers are summarized in Table 3. Considering obtained results, the use of polyacrylate fiber is preferred whenever all of six phthalates are to be determined in single analysis. The linearity of the method was checked in the range 0.001–10 $\mu g\,l^{-1}$ using PA 85 fiber. The method showed good values of correlation coefficients (r^2), LOQs ranged between 0.001 and 0.050 $\mu g\,l^{-1}$ (see Table 3).

3.5. Liquid–liquid microextraction

As mentioned in Section 1, microextraction is a very simple and non-laborious method widely used for

Table 3
Performance characteristics of SPME method

Analyte	Repeatability as R.S.D. (%) for particular fiber			Linearity using PA 85	
	PDMS 30	PDMS 7	PA 85	r^2	LOQ ($\mu g\,l^{-1}$)
DMP	5	16	4	0.990	0.050
DEP	12	19	4	0.985	0.020
DnBP	12	3	4	0.989	0.001
BBP	3	2	7	0.999	0.010
DEHP	19	14	8	0.992	0.003
DnOP	12	11	10	0.987	0.050

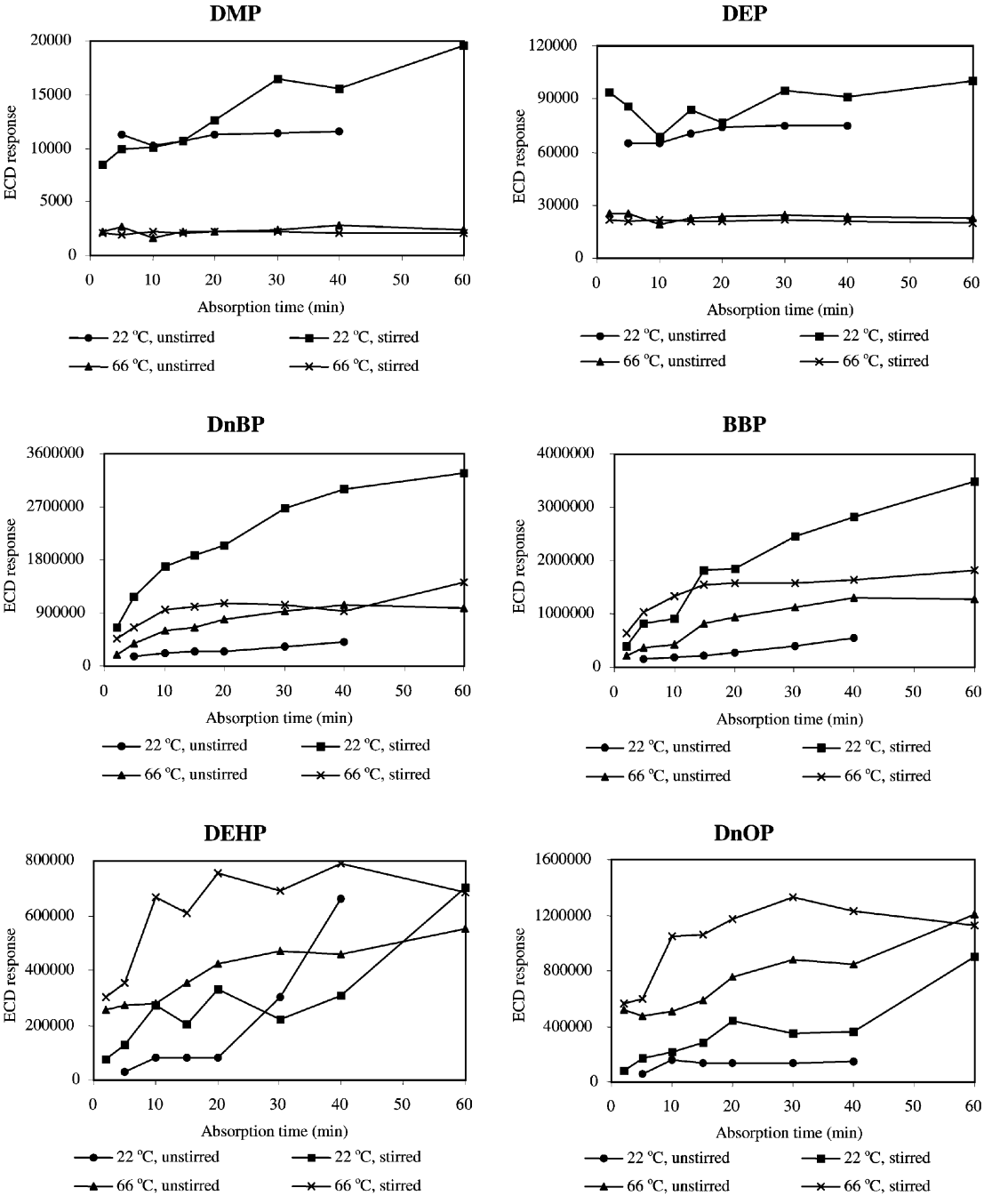

Fig. 4. The influence of heating and stirring of the sample on the extraction time profiles of PAEs, PDMS 30 fiber.

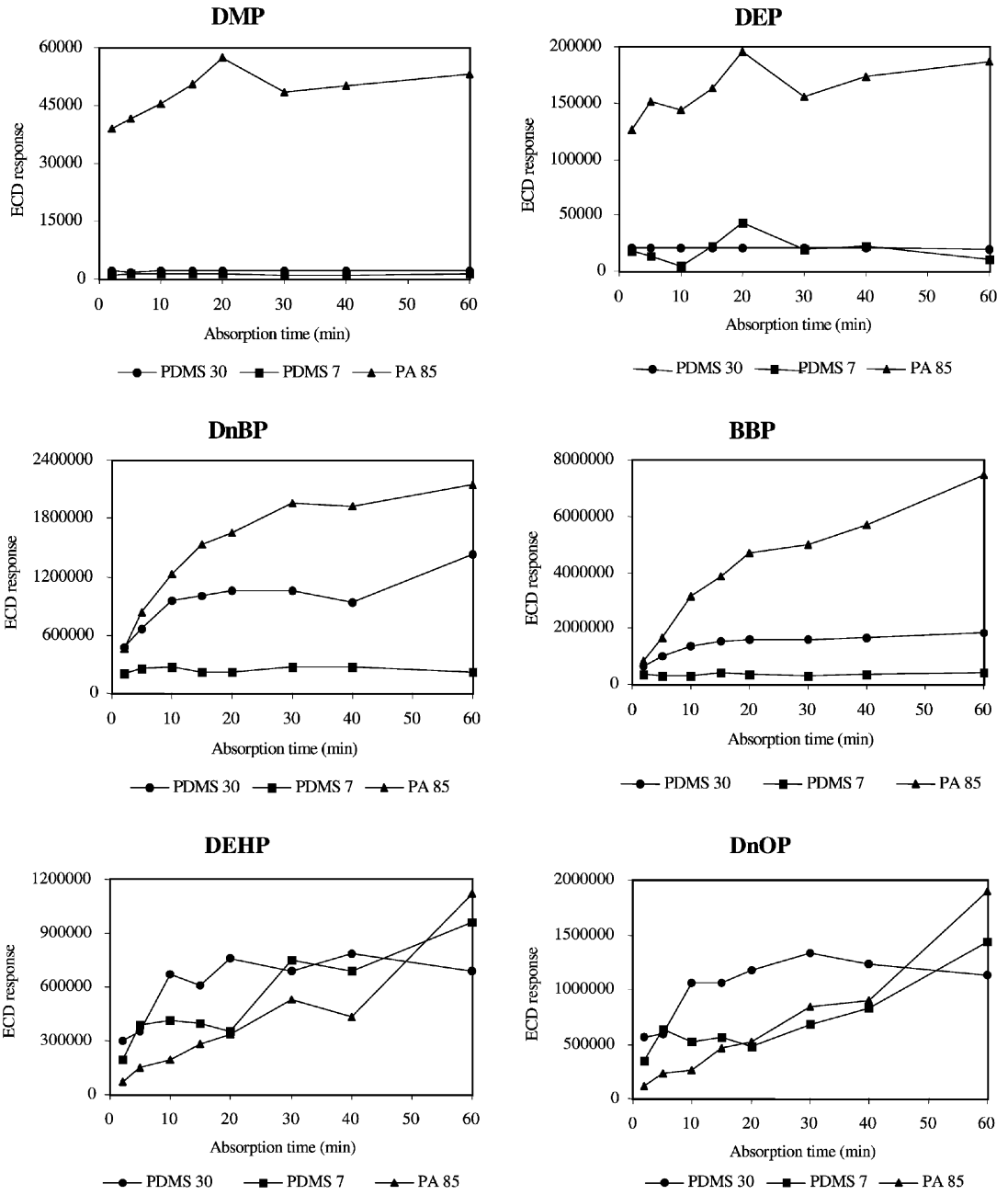

Fig. 5. Effect of fiber type on PAEs peak area and extraction time profile (simultaneous heating and stirring of the sample).

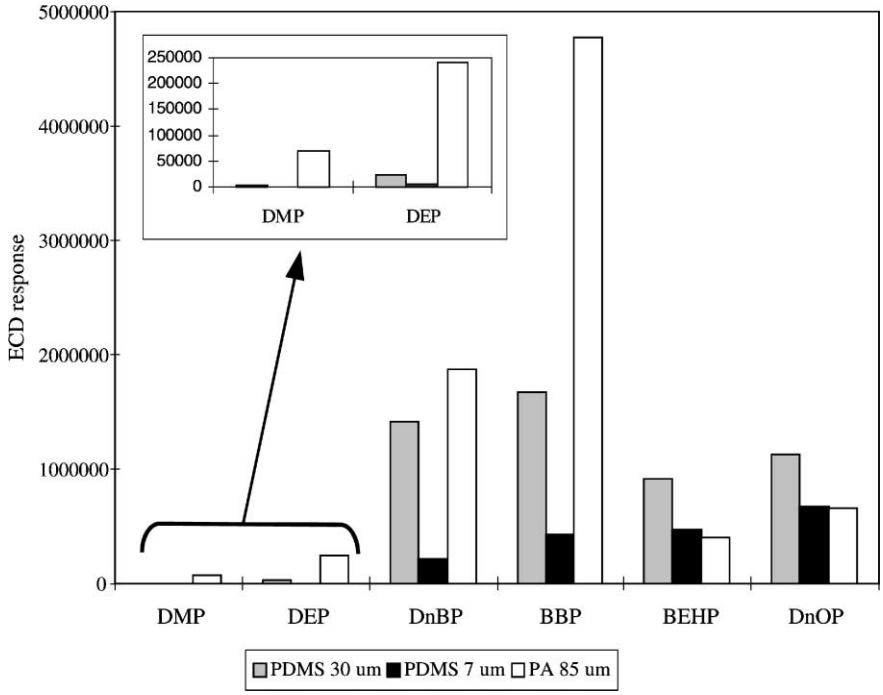

Fig. 6. Effect of fiber type on PAEs peak area (20 min sorption, stirring, extraction temperature 66 °C).

the isolation of non-polar organic compounds. In our experiments this procedure was employed for determination of selected phthalates in aqueous samples to compare results obtained by recently introduced SPME method. In accordance with our assumptions, the recoveries of more polar phthalates (DMP and DEP, see Table 4) were very low. On the other hand, practically complete extraction with good repeatability was obtained for other phthalates (moderately polar DnBP and BBP and non-polar DEHP and DnOP) even at low spiking level ($1\,\mu g\,l^{-1}$). Evidently, as long as a great attention is paid to a careful elimination of potential contamination, liquid–liquid microextraction is a method of choice for determination of low levels (ppb–ppt) of most of common phthalates.

Table 4
Performance characteristics of microextraction (concentration of phthalates $1\,\mu g\,l^{-1}$ each)

	Analyte					
	DMP	DEP	DnBP	BBP	DEHP	DnOP
Recovery (%)	0	32	115	116	111	109
R.S.D. (%)	–	6	10	2	5	4
LOQ ($\mu g\,l^{-1}$)	n.d.[a]	0.2	0.1	0.05	0.1	0.1

[a] Not determined.

3.6. Real samples

To demonstrate performance of the optimized SPME method, potable water from Prague water-supply network and deionized water from purification system Milli-Q RG were analyzed for the phthalate presence. Commercial products represented by mineral water Mattoni distributed in glass bottles with metal caps sealed with PVC inserts plasticised by DEHP and spring water “good water” distributed in bottles from PET were analyzed, too. Simultaneously ME was used for analysis of the above real samples (see Table 5). As demonstrated earlier, the optimized SPME method enabled determination of all tested analytes including DMP and DEP, which could not be isolated by microextraction because of low affin-

Table 5
Phthalates determined in real water samples ($\mu g\,l^{-1}$) using SPME and ME

	Potable tap water		Deionized water		Mineral water (Mattoni)		Spring water (good water)	
	SPME	ME	SPME	ME	SPME	ME	SPME	ME
DMP	0.08	[a]	n.d.[b]	[a]	n.d.	[a]	0.10	[a]
DEP	0.07	0.02[a]	0.04	[a]	n.d.	[a]	0.04	[a]
DnBP	0.05	0.05	0.15	0.08	0.18	0.37	0.20	n.d.
BBP	0.002	n.d.	0.005	n.d.	n.d.	n.d.	0.002	n.d.
DEHP	0.66	0.24	0.49	0.14	9.78	9.93	2.88	0.14
DnOP	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[a] Low recovery (DMP 0%, DEP 32%).
[b] Not detected.

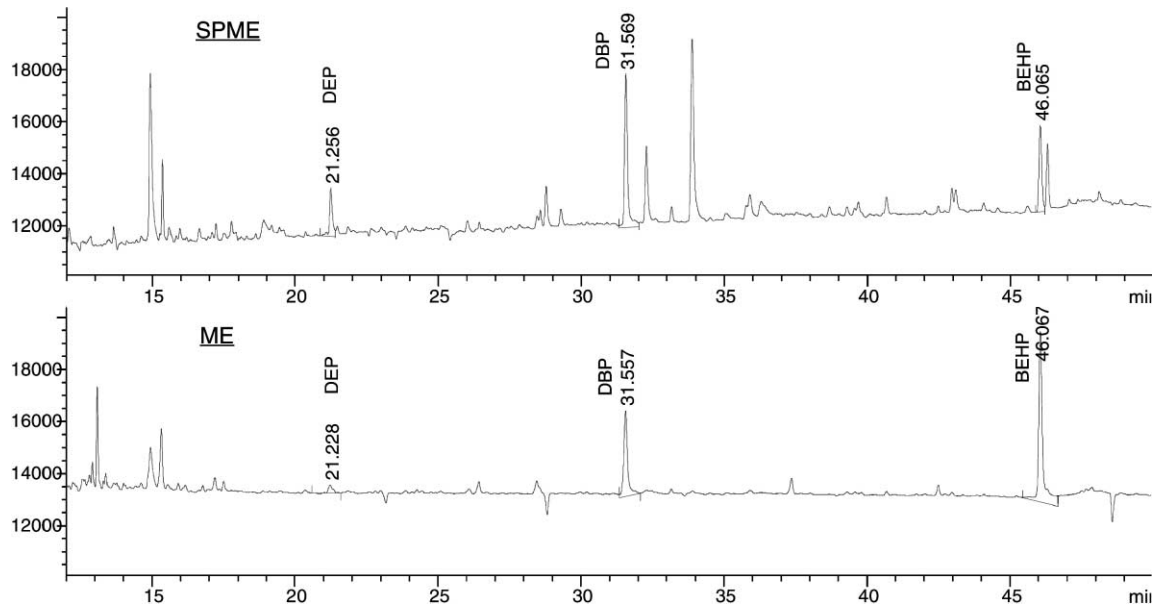

Fig. 7. Chromatograms of drinking (tap) water analyzed by SPME–GC/ECD and ME–GC/ECD.

ity to extraction solvent. DnBP and DEHP were the analytes found to occur at the highest concentrations in all examined samples. The concentration of DEHP in potable tap water and in deionized water was 0.66 and 0.49 $\mu g\,l^{-1}$, respectively. To our experience, these levels correspond to common background contamination. However, DEHP concentrations in bottled waters were significantly higher: 9.78 and 2.88 $\mu g\,l^{-1}$ in mineral water Mattoni and spring water "good water", respectively. These findings may indicate migration of DEHP from the caps into the content of bottle, namely in the former case.[1] The concentration of DnBP in the mineral water samples distributed in glass bottles with metal cap was higher than in the other water samples, on the other hand, DnOP was not found in any analyzed samples. The

[1] Based on these results, the analyses of large set ($n = 20$) of mineral waters distributed in glass bottles with PVC sealed metal caps were carried out using liquid–liquid microextraction. Elevated levels of DEHP in this type of samples were confirmed. The mean concentration of DEHP was 17 $\mu g\,l^{-1}$ (range 5–27 $\mu g\,l^{-1}$).

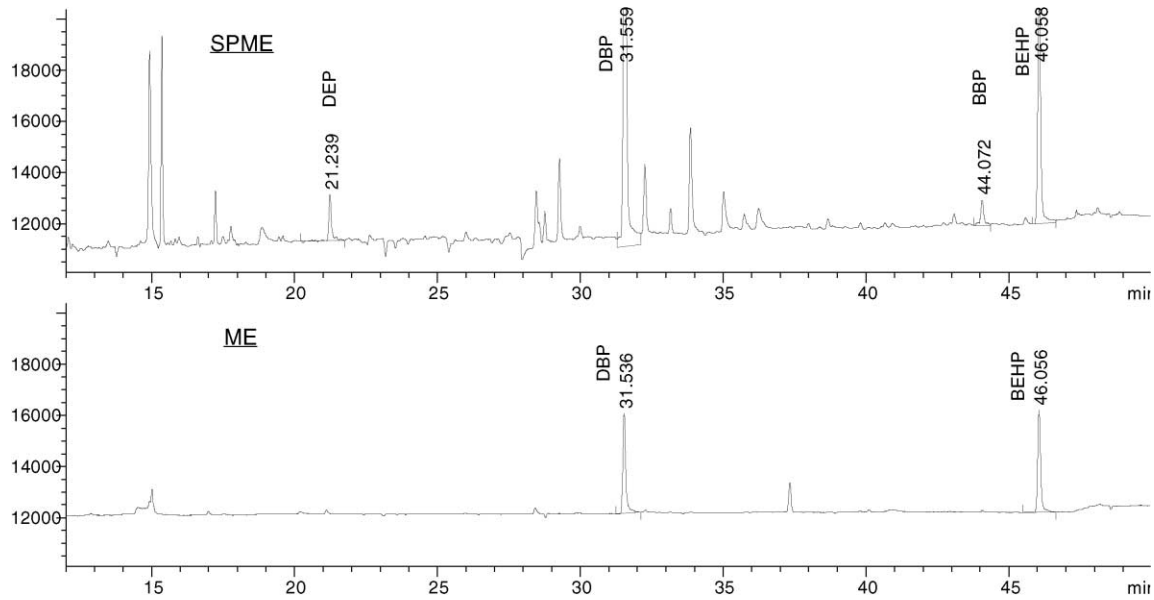

Fig. 8. Chromatograms of bottled spring water sample "good water" distributed in PET bottles analyzed by SPME–GC/ECD and ME–GC/ECD.

occurrence of other phthalates was less frequent: BBP was identified and quantified in three samples using SPME, while it was not detected using ME. Figs. 7 and 8 show the chromatograms of potable tap water and bottled spring water sample "good water" analyzed by SPME and ME. Although not identified in this study, the presence of many other compounds was demonstrated by SPME, what provides additional proof of capability of this technique to concentrate efficiently even ultra-trace levels of many organic substances contained in aqueous samples.

4. Conclusions

The SPME method for the determination of six PAEs in water samples has been developed and validated within this study. The influences of different desorption and extraction conditions as well as various types of fibers were investigated. Considering relatively high yields of polar phthalates, such as DMP and DEP, as well as good repeatability of measurements, fiber coated with polyacrylate was selected as the most suitable for the determination of the whole group of target analytes involving both polar and non-polar phthalates.

The accuracy of results obtained by optimized SPME for most common phthalates occurring in real water samples was good and comparable to that achievable by ME procedure. Analyses of bottled water indicate that the type of packaging material could affect the phthalates concentrations.

Besides of general advantages (reduced sample volume, omitting of organic solvents, low costs), the application of SPME in the phthalate analysis poses a great benefit thanks to decreased risk of secondary contamination during sample handling.

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