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Short communication

Comparison of different fibers for the solid-phase microextraction of phthalate esters from water

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Abstract

Solid-phase microextraction (SPME) coupled to gas chromatography–mass spectrometry (GC–MS) has been applied to determine six phthalate esters and one adipate ester in water. The SPME parameters were optimized for several commercially available fibers. A 65-μm polydimethylsiloxane-divinylbenzene (PDMS-DVB) was the fiber selected and was applied to analysis of water from the Ebro river and the industrial port of Tarragona. The studied compounds were found at concentrations ranging from 0.4 μg l^{-1} for di-*n*-butyl phthalate ester (DnBP) to 3.2 μg l^{-1} for bis(2-ethylhexyl) phthalate ester (DEHP). The linear range for real samples was from 0.1 to 10 μg l^{-1} for most phthalates, and the limits of detection of the method were between 3 and 30 ng l^{-1}. Repeatability and reproducibility between days ($n=5$) for 1 μg l^{-1} samples were below 13 and 18%, respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Solid-phase microextraction; Phthalate esters

1. Introduction

Phthalate esters and bis(2-ethylhexyl) adipate ester (DEHA) are well-known polymer additives and are also used in formulations of pesticides, paints, cosmetics, etc. Phthalate esters can migrate from the plastic material to the environment [1], and consequently, they are often found in water, soil, air, food products, and the human body [2–4]. Some of these compounds have toxic effects in algaes and some micro-organisms living in marine water samples [5]; they are also thought to be carcinogenic and endocrine disrupting [6,7]. Some phthalate and adipate esters are included in the priority lists of pollutants in several countries [8,9]. For instance, the Environmental Protection Agency (EPA) has set the maximum admissible concentration (MAC) for bis(2-ethylhexyl) phthalate ester (DEHP) and DEHA at 6 μg l^{-1} and 0.4 mg l^{-1}, respectively [10].

Gas chromatography (GC) [3,8,11,12] and high-performance liquid chromatography (HPLC) [2–4,13,14], preceded by different preconcentration techniques such as solid-phase (SPE) [2,7,14] or liquid–liquid (LLE) extraction [8], are the usual techniques for determining these compounds in environmental samples. Solid-phase microextraction (SPME) has been used to determine a wide variety of organic compounds from environmental samples [15–20], including some phthalate esters [4,12,13]. The first commercially available SPME fibers were

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coated with polydimethylsyloxane (PDMS) of different thicknesses (7, 30 and 100 μm) for relatively apolar compounds [16,18,19], and 85-μm polyacrylate (PA) for more polar compounds [12,15–17,20]. At present, more specific coatings that contain polymers such as carbowax (CWX), divinylbenzene (DVB) and carboxen (CAR) have been developed. The main aim of the present study is to compare different fibers in order to develop an optimized SPME method for the six commonly used phthalate esters and bis(2-ethylhexyl) adipate ester, in water.

2. Experimental

2.1. Reagents and standards

The compounds studied were dimethyl- (DMP), diethyl- (DEP), di-*n*-butyl- (DnBP), butylbenzyl (BBP), bis(2-ethylhexyl)- (DEHP), and di-*n*-octyl (BnOP) phthalate esters, and bis(2-ethylhexyl) adipate ester (DEHA). All the phthalate esters were purchased from Riedel-de Häen (Seelze-Hannover, Germany) and the adipate from Dr Ehrenstorfer (Augsburg, Germany). All compounds were more than 98% pure.

A stock standard solution of 2000 mg l^{-1} of each compound was prepared in ethyl acetate. Working standard solutions of 100 mg l^{-1} were prepared weekly in ethyl acetate. Stock and working standards were stored at 4°C in the refrigerator. The aqueous solutions were prepared daily by diluting the working solution with water (Milli-Q, sea and river water).

Ethyl acetate was of Suprasolv quality (for organic trace analysis) and was supplied by Merck (Darmstadt, Germany). Sodium chloride, more than 99.5% pure, was obtained from Prolabo (Fontenay S. Bois, France). Water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Helium carrier gas (99.995% quality) was supplied by Carburos Metálicos (Tarragona, Spain).

2.2. GC–MS

GC was performed on a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA, USA) equipped with a split-splitless injector and a HP 5972 mass spectrometer. A Merlin microseal high pressure septum and an insert liner of 0.75-mm I.D., both from Hewlett-Packard, were used. A Hewlett-Packard HP-5MS fused-silica capillary column (cross-linked 5% methyl silicone of 30 m×0.25-mm I.D. and phase thickness of 0.25 μm) was used. The GC temperature program was as follows [13]: initial temperature, 60°C; increased to 280°C at 20°C min^{-1}; hold for 5 min. The total run time was 16 min. The injector and detector temperatures were 250 and 280°C, respectively. The helium flow-rate was maintained at 1.2 ml min^{-1}. The samples were injected in the splitless mode and the splitter was opened after 4.5 min (delay time). The sample volume in the direct injection mode was 1 μl.

Electron ionization (EI) was used at 70 eV, the mass range scanned was 50–465 m/z and the base peak of each compound (149 for all phthalate esters except for DMP (163) and DEHA (129)) was selected for quantifying under full scan acquisition mode. The MS was tuned to m/z 69, 219 and 502 for EI corresponding to perfluorotributylamine (PFTBA). The data were acquired with the HP Chemstation equipped with the mass spectral library Wiley 198.

The response by direct injection of 1 μl of standard solutions under full scan acquisition mode was studied in the range between 0.05 and 25 mg l^{-1} and good linearity was obtained for most compounds with determination coefficients (R^2) above 0.995.

2.3. SPME

The SPME device, the 65-μm polydimethylsyloxane-divinylbenzene fibers and the other fibers tested (65-μm carbowax-divinylbenzene, 85-μm polyacrylate, 75-μm carboxen-divinylbenzene and 30-μm polydimethylsiloxane) were obtained from Supelco (Bellefonte, PA, USA). Before the initial application, fibers were conditioned in the hot port of the gas chromatograph at 260°C, according to the supplier's instructions.

For SPME, water samples (3.5 ml) spiked with an appropriate amount of each pesticide were introduced in 4-ml vials. The concentration of NaCl in the samples was 360 g l^{-1} and the pH was not adjusted (pH ≅ 6). In the extraction process, the 65-

μm PDMS-DVB fiber was directly immersed into the sample solution for 30 min at 80°C. The samples were heated and continuously stirred at a constant speed of 1400 rpm with a magnetic stirrer and heater unit from Selecta (Abrera, Spain). Finally, the compounds were thermally desorbed from the fiber into the GC injector, which was maintained at a temperature of 250°C. The fiber remained in the injector for 3 min. Desorption time was increased to 5 min when real water samples were analyzed in order to avoid carry-over effects.

Sea and river water samples were filtered through a 0.45-μm nylon membrane filter (Whatman, Maidstone, UK) before analysis. Moreover, all the glass material used (vials, volumetric material, etc.) to achieve the extractions was carefully cleaned to avoid contamination problems, as was observed in previous papers [3,8,21].

3. Results and discussion

3.1. Comparison of fibers and optimization of SPME conditions

The five commercially available fibers (Section 2.3) were tested to extract the phthalate and the adipate esters. First experiments with 75-μm carboxen-PDMS showed that it was not suitable for extracting phthalate and adipate esters. This fiber is recommended for extracting gases and low molecular mass compounds (<5 carbon atoms), and phthalate esters have higher molecular masses, so it was not considered for further studies [22].

The main parameters that affect the absorption and desorption processes in SPME were optimized for each fiber. Milli-Q water spiked with 2 μg l^{-1} of each compound was used.

Desorption time and temperature were the first parameters to be studied. The desorption temperature was set at 250°C because this temperature had been used for phthalate esters in a previous study [12]; additional experiments showed that it provided good results for all fibers. Fibers remained in the injector for different times at 250°C, from 2 to 16 min (total run time), and some blanks were run to confirm the absence of carryover. For example, polyacrylate fiber was kept in the injector throughout the run time (16 min), but the splitter was opened at 4.5 min, so only the analytes desorbed at this time were introduced into the analytical column. All the fibers were kept in the auxiliary injector of the gas chromatograph between desorption and the following extraction to prevent contamination by room atmosphere.

The parameters affecting the absorption process were optimized for each fiber in the following order (the ranges tested are in parentheses): absorption time (5–90 min), absorption temperature (25–80°C), and addition of salt to the sample (0–360 g l^{-1}). The initial conditions selected for the optimization were an absorption temperature of 45°C and no salt addition. The pH of the sample was not adjusted since it did not appear to affect the amount of analyte extracted. Table 1 shows the optimum conditions for each fiber. The results show that absorption times were lower with polydimethylsiloxane-containing fibers and that adding NaCl increased the amount of analyte extracted, mainly for the 65-μm PDMS-DVB fiber.

Fig. 1 shows the mean peak area of the phthalate and adipate esters for each fiber at the optimum conditions from a 2 μg l^{-1} standard solution. Obviously, responses of all compounds studied but

Table 1
SPME optimum conditions for each fiber studied

Fiber	Absorption process			Desorption process	
	Time (min)	Temperature (°C)	NaCl (g l^{-1})	Time (min)	Temperature (°C)
30-μm PDMS	30	60	25	10	250
65-μm PDMS-DVB	30	80	360	3	250
85-μm PA	90	45	180	16[a]	250
65-μm CWX-DVB	60	45	100	3	250

[a] Total run time.

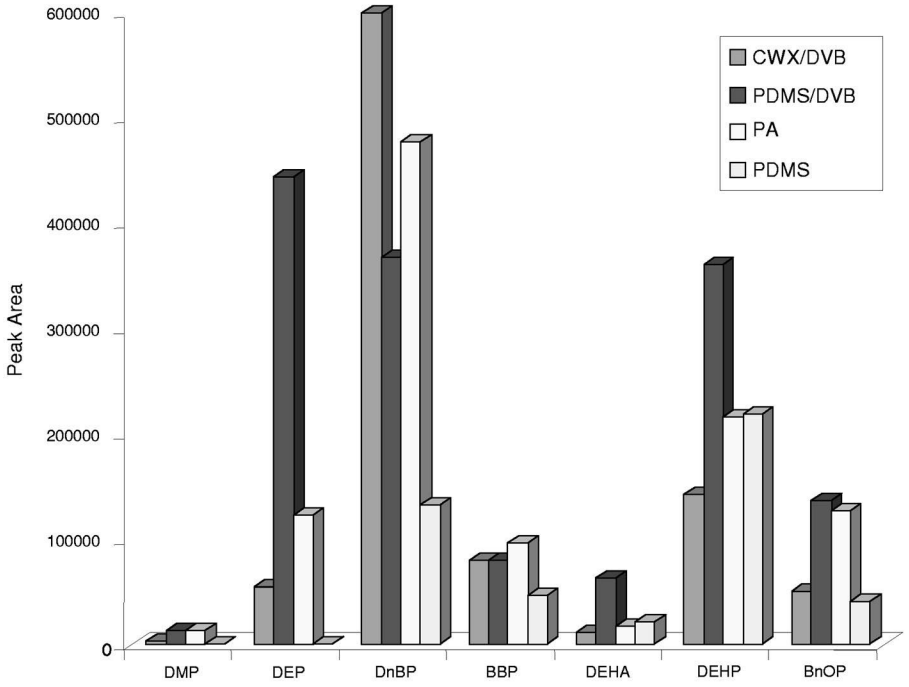

Fig. 1. Peak area obtained for each fiber at optimum conditions in Milli-Q water samples spiked with 2 μg l^{-1} of phthalate and adipate esters.

for DnBP and BBP were higher with the PDMS-DVB fiber. It was also observed that the PA fiber, except for DEHA and DEHP, provided better responses than the apolar PDMS fiber. The more polar (DMP and DEP) compounds were not extracted by the PDMS fiber. PA fibers, in general, have a great affinity for aromatic compounds, such as the phthalate esters, probably due to π–π interactions [22]. These results agree with a previous study by Kelly et al. [13], who determined diethylphthalate (DEP) in water by SPME coupled to HPLC. They tested different fibers and reported that 65-μm PDMS-DVB was the best for extracting this phthalate.

When Milli-Q water samples were analyzed, chromatograms were cleaner with PA and PDMS fibers than with CWX-DVB, PDMS-DVB and carboxen-DVB fibers. It has recently been reported that the SPME extraction process with fibers containing carbowax and divinylbenzene polymers is achieved via adsorption, whereas with PDMS and PA fibers the analytes are extracted via absorption [23]. Some studies [24,25] show the increase of adsorption contribution in the extraction step when the molecular mass of analytes increases. Adsorption is less selective than absorption, so the amount of analyte extracted by DVB and carbowax fibers may be more affected by matrix composition, especially when real water samples are analyzed. Therefore, all fibers were evaluated in the extraction of Ebro river water spiked with 2 μg l^{-1} of the analytes at optimum conditions. The responses thus obtained were similar to those obtained with Milli-Q water. Since 65-μm PDMS-DVB fiber provided the best results for the compounds in both Milli-Q and Ebro river water, it was selected for the subsequent studies.

3.2. Validation of the SPME–GC–MS method

The SPME–GC–MS optimized conditions for 65-μm PDMS-DVB fiber were used to validate the method in Milli-Q water samples. Results are shown in Table 2. Some small peaks appeared at the same retention time as DEP, DnBP and DEHP in the Milli-Q water blank chromatograms so their limits of detection were estimated by using the calibration curves and the Winedfordner and Long criterion

Table 2
Linear range, determination coefficients and limits of detection (LOD) of phthalates in Milli-Q water by SPME–GC–MS (65-μm PDMS-DVB)

Compound	Linear range (μg l^{-1})	R^2	LOD (ng l^{-1})[a]
DMP	0.1–10	0.997	26
DEP	0.05–10	0.994	20[b]
DnBP	0.05–10	1.000	15[b]
BBP	0.01–10	0.999	2
DEHA	0.05–10	0.999	6
DEHP	0.05–10	0.993	15[b]
BnOP	0.1–10	0.994	27

Reproducibility, RSD (%) (spiking level ($n=5$): 1 μg l^{-1}): 7–15%; repeatability, RSD (%) (spiking level ($n=5$): 1 μg l^{-1}): 4–11%.

[a] Calculated using Winefordner and Long criterion [26].

[b] Estimated value (see text).

Table 3
Concentration (μg l^{-1}) of phthalate and adipate esters found in Ebro river and water from Tarragona industrial and fishing ports

Compound	Ebro river	Tarragona fishing port	Tarragona industrial port
DMP	–	1.6	2.1
DEP	0.6	1.4	1.8
DnBP	0.4	1.3	1.9
BBP	–	0.5	1.1
DEHA	–	0.7	1.6
DEHP	1.1	2.1	3.2
BnOP	–	0.8	1.5

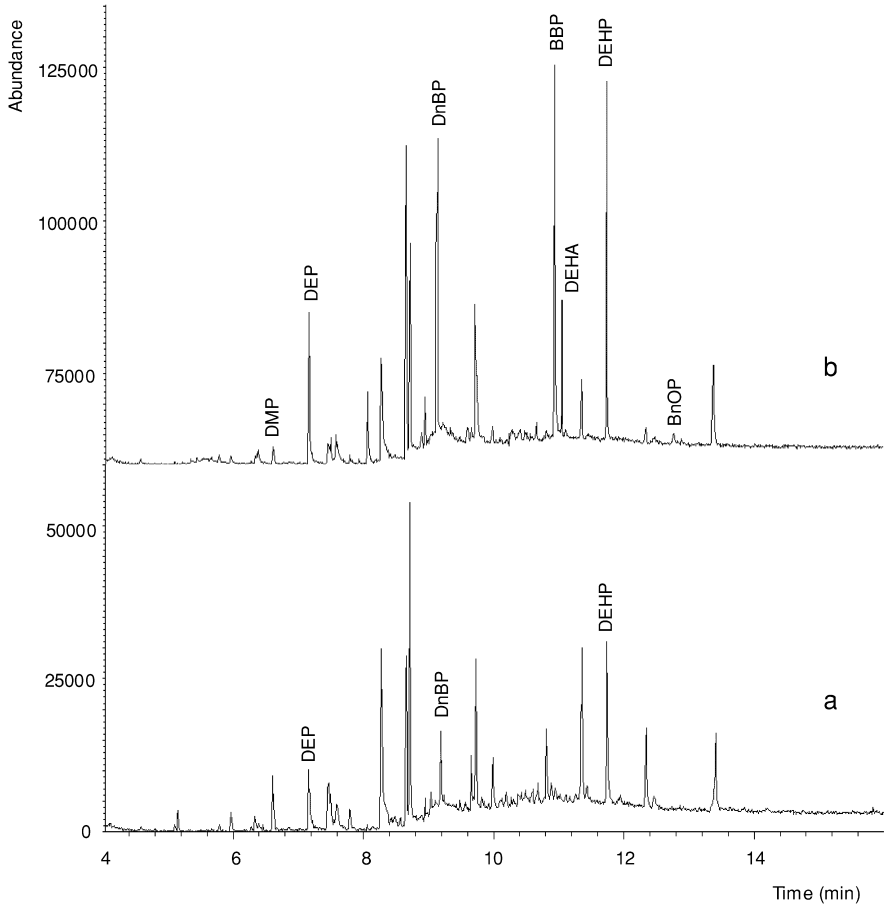

Fig. 2. Total ion chromatograms obtained by SPME–GC–MS of: (a) unspiked Ebro river water; and (b) Ebro river water spiked with 2 μg l^{-1} of each compound.

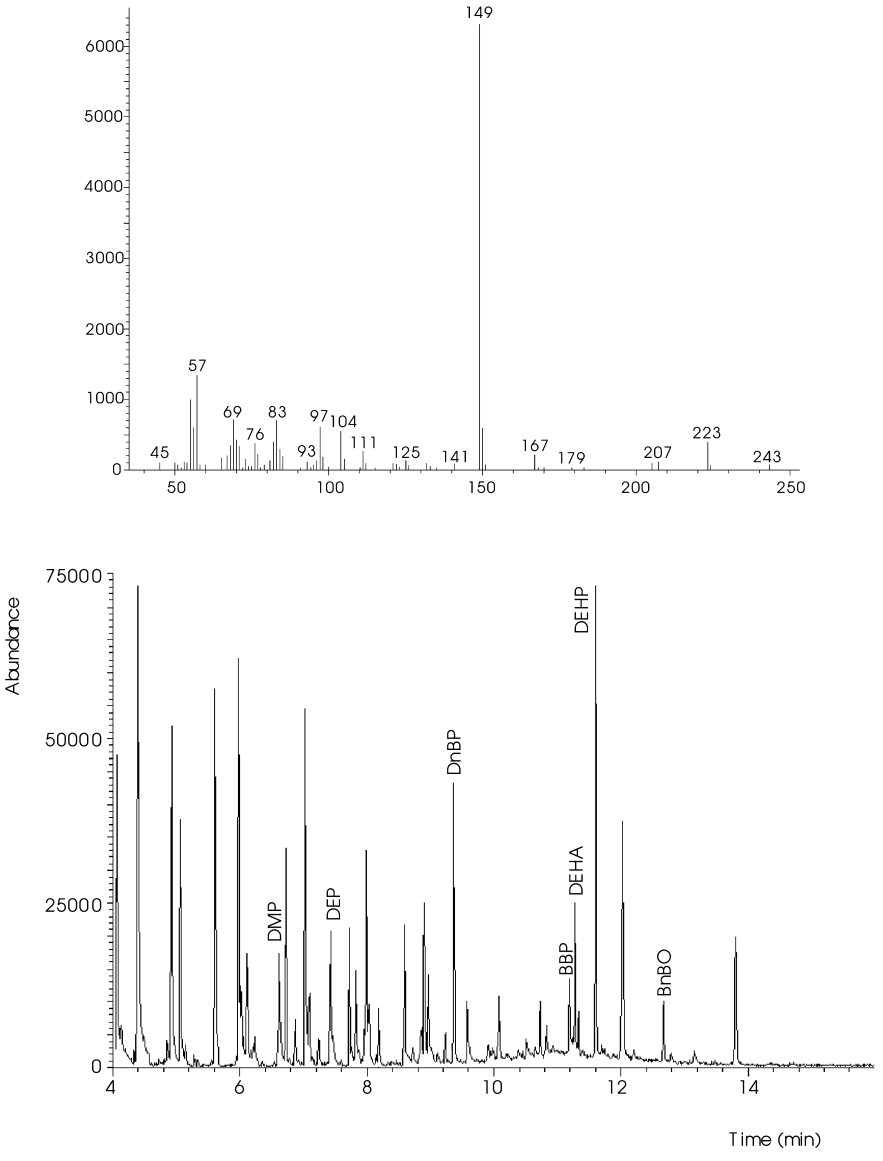

Fig. 3. Total ion chromatogram, obtained by SPME–GC–MS, of a water sample from Tarragona industrial port. The insert shows the mass spectrum of BBP.

[26]. The mass spectra of these peaks corresponded to the three phthalate esters.

3.3. Application to real samples

The performance of the method was tested with Ebro river water. Analysis of Ebro river water showed the presence of different peaks at the same retention time as the compounds studied. Some peaks were observed at the retention time of DEP, DnBP and DEHP and the spectra of these peaks corresponded to those of the three phthalates. For this reason, the linearity of the method was calculated by the standard addition method, in which Ebro

river water spiked with 0.01–10 μg l^{-1} of the phthalate and the adipate esters was analyzed. Linearity was good for most compounds in the range between 0.1 and 10 μg l^{-1} with determination coefficients above 0.984. Limits of detection were not calculated for DEP, DnBP or DEHP because of their presence in the sample. For the other compounds, they ranged between 3 and 30 ng l^{-1}. Repeatability and reproducibility between days, expressed as relative standard deviation, RSD (%) ($n=5$), were calculated for the sample spiked with 1 μg l^{-1}. The results were also similar to those for Milli-Q water and they were below 13 and 18% for repeatability and reproducibility, respectively. To determine whether the calibration curves for Milli-Q water can be used to analyze Ebro river water, the calibration curves for the phthalate and adipate esters in Ebro river water were statistically compared to those for Milli-Q water samples. There were no significant differences between them at a confidence level (α) of 0.05. The concentrations of DEP, DnBP and DEHP in Ebro river water were therefore calculated by the calibration curves for Milli-Q water and are shown in Table 3. DEHP, the most often used phthalate ester, had the highest concentration, 1.1 μg l^{-1}. Fig. 2 shows chromatograms obtained for unspiked Ebro river water and river water spiked with 2 μg l^{-1} of each compound.

Table 3 includes data of water from Tarragona industrial and fishing ports. It was confirmed that calibration curves for Milli-Q water could be used. DEHP was also the phthalate ester with the highest concentration (2.1 and 3.2 μg l^{-1}). A similar concentration has already been found in a previous study [12], in which a 85-μm PA fiber was used. Fig. 3 shows a typical full scan GC–MS chromatogram and the mass spectra recorded for BBP.

4. Conclusions

Important differences were observed in the amount of phthalate esters extracted by different SPME fibers. The 65-μm PDMS-DVB provided the best results. An absorption time of 30 min was sufficient to extract the analytes from the samples. The absorption temperature was 80°C and the samples were NaCl-saturated to increase the efficiency of the extraction process. Desorption was performed at 250°C for 3 min. SPME combined with GC–MS enables the compounds to be determined at low μg l^{-1} levels in surface water.

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