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Determination of phthalate esters in water samples by solid-phase microextraction and gas chromatography with mass spectrometric detection

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Abstract

Solid-phase microextraction (SPME) with an 85 μm polyacrylate fiber, coupled to gas chromatography–mass spectrometry was used to determine six phthalate esters and bis(2-ethylhexyl) adipate in water samples. The variables affecting the SPME absorption process were optimized and the method developed was applied to analyze both tap and commercial mineral water samples as well as water from the Ebro river and fishing and industrial ports. For real samples, the linear range in full scan acquisition mode was between 0.02 and 10 μg l^{-1} for most compounds, and the limits of detection of the method were between 0.006 and 0.17 μg l^{-1}. Commercial water samples contained in recipients which were made from different materials were analyzed, and the influence of the material of the recipients on the concentration of phthalates was evaluated.

Keywords: Water analysis; Environmental analysis; Food analysis; Phthalates

1. Introduction

Phthalate esters are widely used as additives in the manufacture of plastics to make them flexible. Because of their properties as plasticizers, in recent years phthalates production and use has increased significantly and, as a result, they are often found in environmental matrices such as waters and soils [1–3]. Little is known about the possible effects of these substances on the environment and human health [5] but some recent studies have shown that they may cause hormone disrupting activity [3,4].

The most commonly used phthalates (dimethyl-, diethyl-, di-*n*-butyl-, butylbenzyl-, bis(2-ethylhexyl)- and di-*n*-octyl phthalate esters) and another plasticizer, the bis(2-ethylhexyl) adipate, have been included on the list of priority pollutants in several countries. For example, the US Environmental Protection Agency (EPA) has established a maximum admissible concentration (MAC) in water of 6 μg l^{-1} for the bis(2-ethylhexyl) phthalate (DEPH) and 0.4 mg l^{-1} for the bis(2-ethylhexyl) adipate [6]. The bis(2-ethylhexyl) phthalate is the most used and it represents a quarter of the total production of plastizicers [7]. The European Union (EU) has not set any regulations on the maximum concentration

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allowed for phthalates or for bis(2-ethylhexyl) adipate in water, but they will probably be established in the near future.

Gas chromatography (GC) [1,2,8,9] and high-performance liquid chromatography (HPLC) [4,10] have been used for determining these compounds in water samples but when the levels of concentration are low, a previous enrichment step is usually needed. The preconcentration techniques which are commonly applied to determine phthalates in water are liquid–liquid extraction (LLE) [2,9] with dichloromethane or hexane, and solid-phase extraction (SPE) [2,4,10]. Solid-phase microextraction (SPME) is a preconcentration technique which has recently been introduced for the extraction of organic compounds [11–17]. To our knowledge, there are only a few papers in which the suitability of SPME has been tested for the extraction of phthalate esters [12,14,15]. Möder et al. [12] extracted some phthalate esters in a study on the characterization of water-soluble compounds of slurries by a SPME–HPLC–MS method, and Kelly and Larroque [14] used SPME–HPLC–UV to determine diethylphthalate ester in water samples. These studies have used polydimethylsiloxane–divinylbenzene (PDMS–DVB) [14] and Carbowax-coated [12] fibers.

The main aim of this study was to develop a method for determining the six phthalates mentioned above and the bis(2-ethylhexyl) adipate in water samples using SPME as the preconcentration technique and gas chromatography with mass spectrometric detection (GC–MS). The experimental conditions for SPME were optimized and the method was validated under the best conditions with real water samples.

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 (DnOP) phthalate esters, and the bis(2-ethylhexyl) adipate ester. The phthalate esters were purchased from Riedel-de Häen (Seelze–Hannover, Germany) and the adipate from Dr. Ehrenstorfer (Augsburg, Germany). All the 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, tap, sea, river and drinking water). Phthalate and adipate esters were completely solved in the water solutions because their solubilities were higher than the concentrations of the solutions prepared [5].

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. Instrumentation

Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA, USA) equipped with a split–splitless injector and an 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% methylsilicone) of 30 m×0.25 mm and with a phase thickness of 0.25 μm was selected to separate the analytes.

The temperature program used for the analyses was as follows: the initial temperature was 60°C which was then increased to 280°C at 20°C min^{-1}. This temperature was held for 5 min. The total run time was 16 min. The injector and detector temperatures were 250°C 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 2 μl.

The conditions for electron impact ionization (EI) were an ion energy of 70 eV and the mass range scanned was 50–465 m/z. The MS was tuned to m/z

69, 219 and 502 for EI corresponding to perfluorobutylamine (PFBA). The data were acquired with the HP Chemstation. It was equipped with the mass spectral library Wiley 198 which was used to compare the experimental spectra obtained.

2.3. SPME procedure

The SPME device and the 85 μm polyacrylate fibers were obtained from Supelco (Bellefonte, PA, USA). Before the initial application, the fiber was conditioned in the hot port of the gas chromatograph at 300°C for 3 h, according to the supplier's instructions. After the conditioning process, a fiber blank was run to confirm that there were no extraneous peaks which could be assigned to compounds introduced during the manufacture of the fiber.

For the SPME process, water samples (3.5 ml) spiked with an appropriate amount of each pesticide were put in 4-ml vials. The concentration of NaCl in the samples was 180 g l^{-1}, which is half the saturated concentration of NaCl in water, and the pH was not adjusted. In the extraction process, the fiber was directly introduced into the sample solution for 90 min at 45°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 in the gas chromatograph injector at 250°C. The fiber remained in the injector throughout the run time.

Real samples (tap, drinking, Ebro river and sea water) were filtered through a 0.45-μm nylon membrane filter (Whatman, Maidstone, UK) before analysis.

3. Results and discussion

3.1. Chromatographic separation

First, the separation of the six phthalates and the adipate was optimized and the optimal conditions are described in the Experimental section.

To determine the linearity of the response, 2 μl of standard solutions in ethyl acetate was injected under full scan acquisition mode. Linearity was good in the range from 0.05 to 25 mg l^{-1} for most of the analytes with determination coefficients higher than 0.9949 in full scan acquisition mode. The limits of detection (LODs), the repeatability and the reproducibility of the method were also studied. The LODs were calculated by Winefordner and Long's criterion with the K value equal to 6 [18]. They were between 0.015 and 0.05 mg l^{-1}. Repeatability, expressed as a percentage of relative standard deviation, RSD ($n=5$), was lower than 6.2% and reproducibility, RSD ($n=5$), between-days was lower than 8.4%.

3.2. Optimization of SPME

The fiber selected was 85 μm polyacrylate since this kind of fiber coating gave good results in previous works [13,15,16] and, to our knowledge, this fiber has not been previously used to extract phthalate esters. The main parameters that can affect the SPME process were optimized under full scan acquisition mode: the time and the temperature of the absorption process, and the addition of NaCl to the sample. Standard solutions containing 2 μg l^{-1} of each phthalate and adipate in Milli-Q water were used to evaluate the effect of these parameters. Desorption parameters were the same as in previous papers [13,16], since good results were obtained with additional experiments with phthalate esters. In the desorption step, the fiber remained in the injector of the gas chromatograph at 250°C for the total run time. The splitter was opened at 4.5 min, so only the analytes desorbed at this time were transferred to the analytical column, but the fiber was maintained in the injector throughout the run to avoid carryover effects in subsequent analyses. If the fiber was kept in the injection port for shorter times, some peaks appeared at the same retention times as the phthalates indicating that they had not been completely removed from the fiber. This was also observed by other authors [15]. The same fiber was used to analyze about 20 real samples. The fact that the lifetime of the 85 μm polyacrylate was shorter than in other studies [13,16,17,19] is due to the long exposure time of the fiber in the injector port. Likewise, to prevent the fiber from being contaminated by the room atmosphere it was kept in the auxiliary injector of the gas chromatograph between analyses. All the material used (e.g., glassware and

stirring bars) had to be also carefully cleaned and three blanks were run to verify the absence of phthalate peaks.

3.2.1. Absorption time

The absorption time profile was studied by monitoring the area counts as a function of the absorption time. The standard solution was exposed for times which ranged from 5 to 120 min. The temperature of absorption was set at 45°C throughout the extraction process and NaCl was not added to the sample. The sample was continuously stirred to decrease the time required for the analytes to reach the equilibrium.

After the absorption time, the phthalates and the adipate were desorbed from the fiber which had been kept throughout the run at 250°C in the injector of the gas chromatograph. The equilibrium was reached for most of compounds at 120 min. However, an absorption time of 90 min was selected for subsequent analysis so the analysis time was shortened and the response was acceptable. At absorption times lower than the equilibrium time and if the stirring rate, the absorption time and the temperature are held constant, quantification is possible [20].

3.2.2. Absorption temperature

The absorption temperature was the next parameter to be optimized. The effect on the amount of analyte absorbed was studied by exposing the fiber to the sample for 90 min at temperatures ranging from 25°C (room temperature) to 65°C. The other experimentation parameters were the same as for the optimization of the absorption time. The results obtained show an increase in the peak area of the phthalates and adipate when temperature increases. Increasing the absorption temperature enhances the diffusion of the analytes from the solution to the fiber. However, at temperatures over 45°C, there is a decrease in the amount of DEHP, BnOP and BBP extracted. This is because the absorption of the analytes by the fiber is an exothermic process and high temperatures can decrease the amount extracted [7]. For this reason, the plot of the area peak versus the absorption temperature usually shows a maximum for some analytes. An absorption temperature of 45°C was selected since at this temperature the peak area for most compounds was maximum.

3.2.3. NaCl addition

NaCl is often added to the sample in order to increase the ionic strength and enhance the amount of analyte extracted by the fiber [16,17,21,22]. The optimum concentration of NaCl was determined by analyzing a set of samples which contained amounts of NaCl which ranged from 0 to 360 g l^{-1} (the NaCl saturation concentration). The absorption time and temperature were set at 90 min and 45°C, respectively, and the desorption conditions were the same as those for the optimization of the absorption time. The results obtained show that the peak areas were highest at 180 g l^{-1} NaCl for most of the analytes studied except for DEP and DEHP. The maximum peak area of these two compounds was at 360 g l^{-1}. Results were best, for most compounds, at a NaCl concentration of 180 g l^{-1}, so this was the concentration selected to the next experiments.

3.3. SPME–GC–MS

Once the SPME parameters were optimized, the method was checked by analyzing 3.5 ml Milli-Q water samples spiked with the compounds studied. Full scan was the acquisition mode used since low levels of concentration were achieved and the presence of the phthalates could be confirmed with the mass spectra.

The linearity of the response in Milli-Q water was checked in the range 0.02 to 10 μg l^{-1} using full scan acquisition mode. The LODs were calculated using Winefordner and Long's criterion and they were between 0.006 μg l^{-1} and 0.1 μg l^{-1}. The repeatability and the reproducibility of the method, expressed as a percentage of RSD and calculated at a spiking level of 1 μg l^{-1} ($n=4$) were between 4.2% and 14.2% for repeatability and between 7.8% and 17.4% for reproducibility. Reproducibility was calculated with the results obtained by analyzing a sample in consecutive days. These results are typical for SPME. The addition of an internal standard to decrease the RSD was not considered since a previous work [19] showed that it did not improve significantly the repeatability and the reproducibility of the SPME–GC–MS method.

3.4. Real samples

The performance of the method was tested with

water from Tarragona's fishing and industrial ports, the Ebro river and also commercial water samples. The quantity of NaCl added to sea water samples depended on the initial concentration in these samples.

The linearity of the method was checked in tap water samples. The results were similar to those for Milli-Q water and they are given in Table 1. Analytical data were calculated in the same way as for Milli-Q water. Fig. 1 shows the chromatograms obtained when both unspiked tap and Milli-Q water and tap water spiked with 1 μg l^{-1} of each compound were analyzed. No phthalate or adipate ester peaks were observed in Milli-Q and tap water blank chromatograms and the peaks that appeared could not be identified by the mass spectral databases.

Samples from the Tarragona fishing port and the Ebro river were analyzed in order to verify the presence of different peaks at the same retention time as the compounds studied. Some peaks appeared at the retention times corresponding to DEP, DnBP and DEHP. The spectra of these peaks confirmed that they correspond to these three phthalates. Then, we determined whether the calibration curves obtained for tap water were valid for these samples. Therefore, the samples were spiked at two different levels of concentration (0.5 μg l^{-1} and 2 μg l^{-1}) and the values of the areas of DEP, DnBP and DEHP were subtracted from the mean of the areas obtained in the blank chromatograms ($n=5$). The concentration of the phthalate and adipate esters in these samples, calculated by means of the calibration curves for tap water, agreed with the spiked concentration. The concentration of these compounds in the blanks was calculated with the calibration curves obtained for tap water. DEHP was found in a concentration of 0.6 μg l^{-1} and 0.7 μg l^{-1} in fishing port and Ebro river water, respectively. However, DEP and DnBP could not be quantified because their concentrations were between the detection limit and the quantification limit of the method.

Various samples from the Tarragona industrial port and another from the Ebro river were analyzed by SPME–GC–MS, and the same three phthalates, which appeared in the water samples from Tarragona fishing port and Ebro river, were found. The concentrations and RSD obtained by SPME–GC–MS for these water samples are shown in Table 2. Fig. 2 shows the total ion chromatogram for one of the samples from the Tarragona industrial port and the insert corresponding to the spectrum of the DEHP. The other peaks that appear in the chromatograms could not be identified.

Various commercial mineral waters were also analyzed since it is described in literature that the additives of poly(vinyl chloride) (PVC) packaging materials, especially adipate and phthalate esters, can migrate from the container to the water [23]. In this study, DEPH and DnOP were the principal compounds identified.

The original recipients containing the water samples analyzed were made from materials such as polyethylene terephthalate (PET), PVC, glass and tetra-brick. The phthalate esters are used in the manufacture of some of these recipients, so the influence of the material on the concentration of the phthalates has also been evaluated. Fig. 3a shows the results obtained for mineral water samples from the same brand but with different recipient material (PVC, PET and glass). Different concentrations of

Table 1
Linear range, determination coefficients, limits of detection and repeatability and reproducibility for tap water by SPME–GC–MS

Compound	Linear range (μg l^{-1})	r^2	LOD (μg l^{-1})	RSD (%) ($n=4$)[a,c]	RSD (%) ($n=4$)[b,c]
DMP	0.5–10	0.9948	0.17	10	13
DEP	0.05–10	0.9961	0.02	10	16
DnBP	0.02–10	0.9986	0.007	17	18
BBP	0.05–10	0.9965	0.02	19	21
Bis(2-ethylhexyl) adipate	0.1–10	0.9936	0.03	15	18
DEHP	0.02–10	0.9990	0.006	7	10
BnOP	0.1–10	0.9991	0.03	10	14

[a] Under repeatability conditions.
[b] Under reproducibility between-days conditions.
[c] Spiking level: 1 μg l^{-1}.

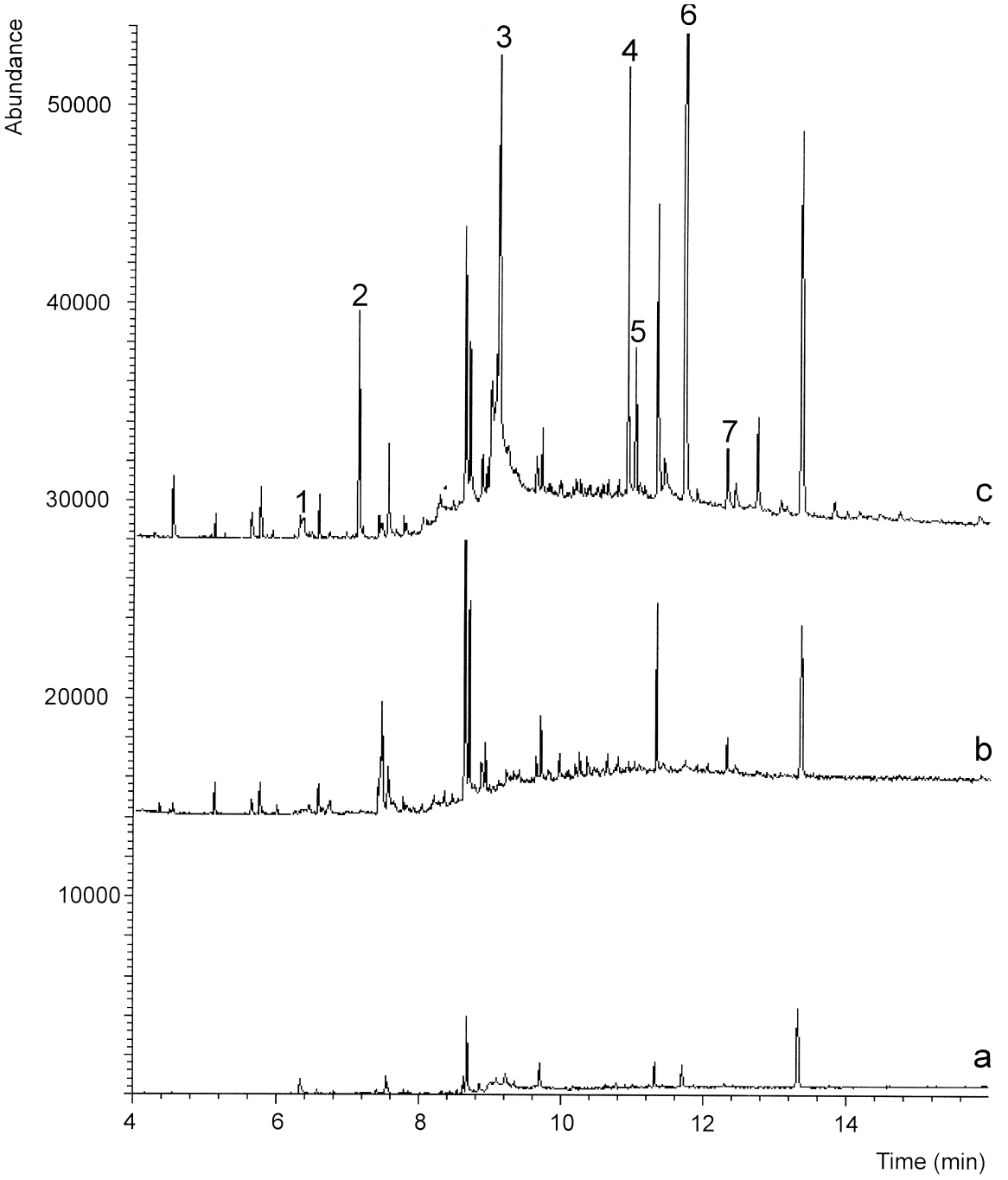

Fig. 1. Chromatograms obtained by SPME–GC–MS under full scan acquisition mode of (a) Milli-Q water (b) tap water and (c) tap water spiked with 1 μg l^{-1} of the compounds studied. Peak assignation: (1) DMP, (2) DEP, (3) DnBP, (4) BBP, (5) bis(2-ethylhexyl) adipate ester, (6) DEHP, (7) BnOP.

Table 2
Concentration ($\mu g\ l^{-1}$) and RSD ($n=3$) of phthalates found in water samples from the Tarragona industrial port and the Ebro river by SPME–GC–MS

Compound	Industrial port I		Industrial port II		Ebro river	
	Concentration ($\mu g\ l^{-1}$)	RSD (%)[a]	Concentration ($\mu g\ l^{-1}$)	RSD (%)[a]	Concentration ($\mu g\ l^{-1}$)	RSD (%)[a]
DMP	n.d.	–	n.d.	–	n.d.	–
DEP	0.62	8	0.39	9	0.26	11
DnBP	0.16	13	0.12	13	n.q.	–
BBP	n.d.	–	n.d.	–	n.d.	–
Bis(2-ethylhexyl) adipate	n.d.	–	n.d.	–	n.d.	–
DEHP	1.62	12	2.12	11	0.70	16
BnOP	n.d.	–	n.d.	–	n.d.	–

[a] $n=3$.
n.d.=Not detected.
n.q.=Not quantified.

DEP, DnBP and DEHP were found in all samples. Each sample was analyzed three times and Fig. 3a shows the mean values. Nevertheless, no peaks corresponding to the other phthalate and adipate esters appeared in the chromatograms. As can be observed in Fig. 3a, the concentration of DEHP and DEP was similar in all the samples, and DEHP was the phthalate ester with the highest concentrations, about 1.0 $\mu g\ l^{-1}$. This has been also observed by other authors [23]. This phthalate ester is the most widely used and EPA has established that its MAC in drinking water is 6 $\mu g\ l^{-1}$ [6]. It can be also observed that the concentration of DnBP in the water samples from PVC bottles was higher than the samples from the other materials.

On the other hand, Fig. 3b shows the results obtained for mineral water samples which are from different brands (see numbers 1 to 3 in the categories axis) and two materials (PVC and PET). The same three phthalates (DEP, DnBP and DEHP) were found and the concentration of two of the phthalates, DEP and DEHP, in brand 3 was higher than in the other two brands. Moreover, a similar distribution in the concentrations of the three phthalates can be observed between PET and PVC containers. Fig. 4 shows the total ion chromatogram for brand 1 in PVC bottles, and the insert corresponding to the spectrum of the DEHP.

A commercial water sample in tetra-brick recipient was also analyzed. This recipient also contains a plastic film. The results were similar to the other commercial waters except for DEP, the concentration of which was slightly lower. On the basis of these results, the material of the recipient which contains the mineral water affect the concentrations of phthalates. Moreover, glass and tetra-brick showed lower concentrations of some of the phthalates.

4. Conclusions

In this study, SPME was used to determine a group of plasticizers in aqueous samples. Parameters that affect the SPME absorption process were optimized. Optimum conditions were 90 min at 45°C for the absorption process. Adding NaCl to the water samples increased the amount extracted of most phthalates. The combination of SPME with GC–MS in full scan acquisition mode enables these compounds to be determined at low $\mu g\ l^{-1}$ concentration levels in real water samples. A similar relation between the concentrations of the phthalate esters found in mineral water samples bottled with the same material (PVC, PET) was observed.

Real water samples from different sources were analyzed by the SPME–GC–MS method developed and phthalates were found in some of them. The material of the recipient which contains the water samples affect the concentration of phthalates found in the commercial mineral water studied.

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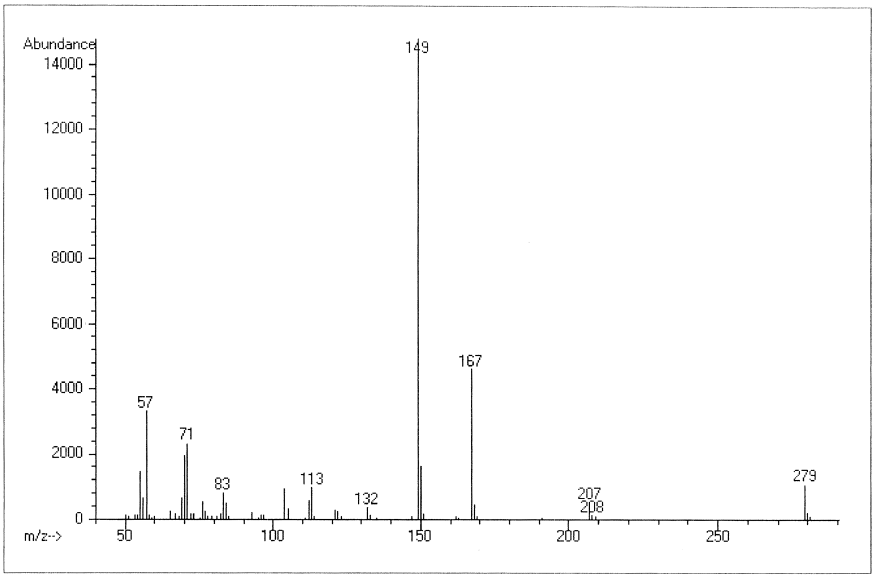


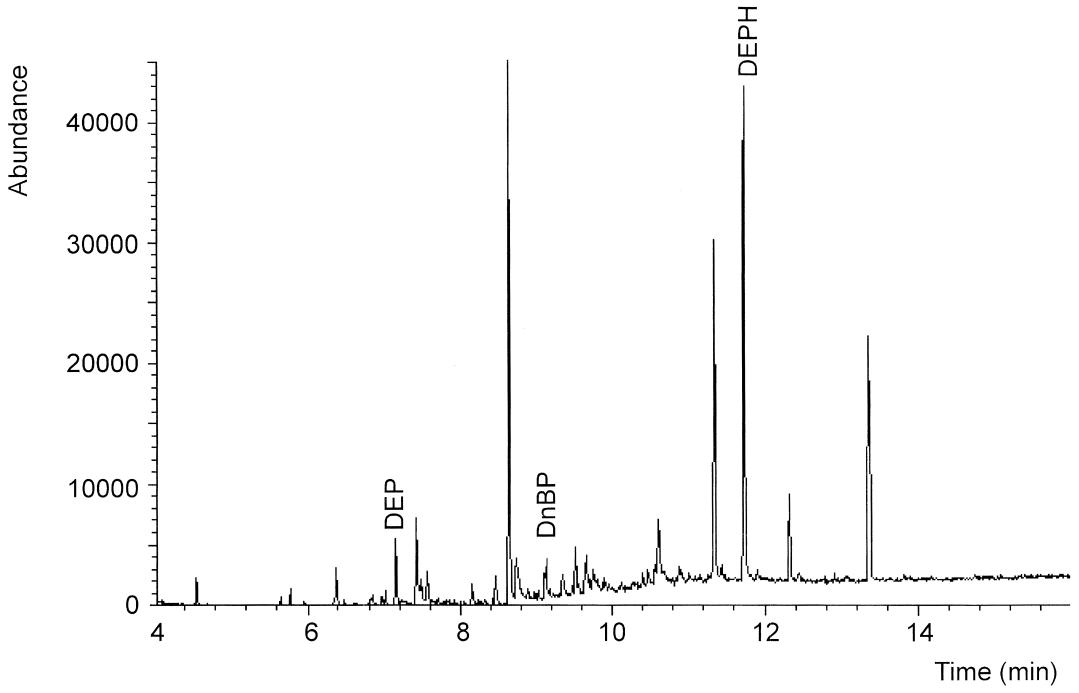


Fig. 2. Total ion chromatogram of marine water sample 1 analyzed by SPME–GC–MS. The insert corresponding to the spectrum of the DEHP.

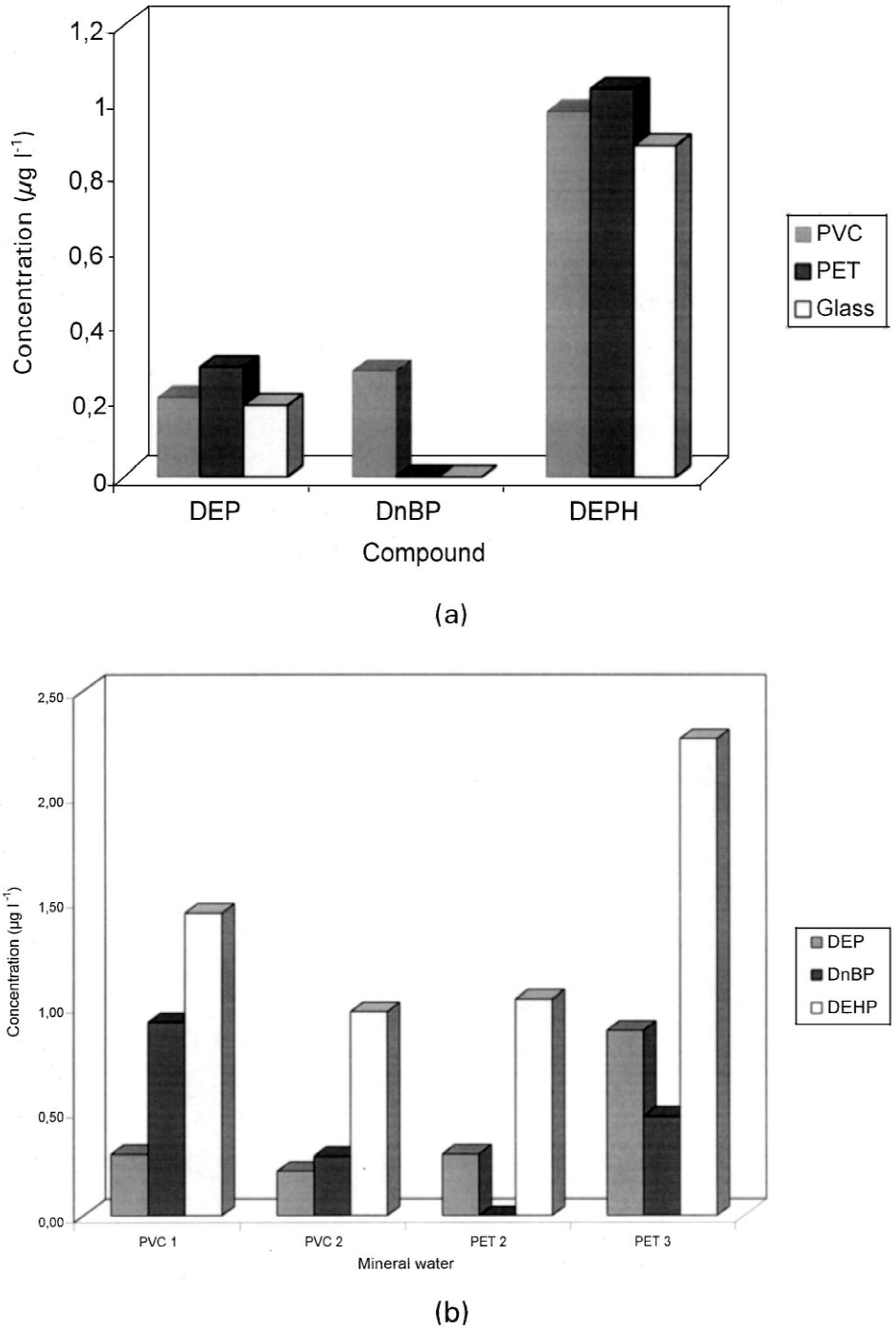
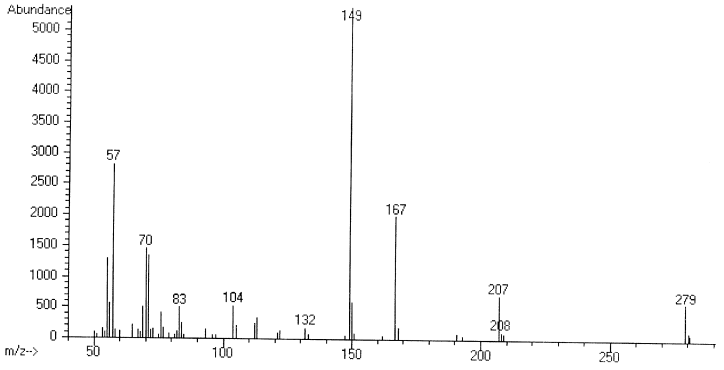


Fig. 3. Concentrations of DEP, DnBP and DEHP obtained (a) in three recipient materials for the same brand, and (b) in different mineral waters (numbers 1 to 4) and recipient materials determined by SPME–GC–MS. The legend shows the type of material of the recipient in which the water was contained.



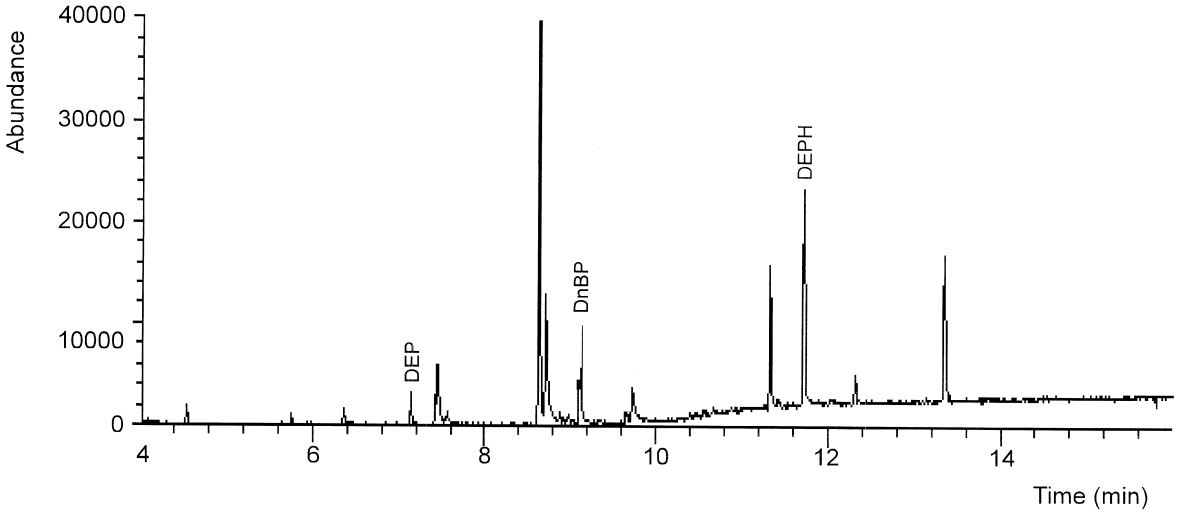


Fig. 4. Total ion chromatogram of mineral water number 1 in PVC bottle analyzed by SPME–GC–MS. The insert corresponding to the spectrum of the DEHP.

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