Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 999 (2003) 145–153
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Hollow-fibre liquid-phase microextraction of phthalate esters from water

Elefteria Psillakis*, Nicolas Kalogerakis

Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis, GR-73100 Chania, Crete, Greece

Abstract

A simple and efficient liquid-phase microextraction (LPME) technique using a hollow-fibre membrane, in conjunction with gas chromatography–mass spectrometry has been developed for the extraction and analysis of six phthalate esters in water samples. Parameters such as extraction solvent, agitation of the sample, salt addition and extraction time were controlled and optimised. The developed protocol was found to yield a linear calibration curve in the concentration range from 0.02 to 10 μg l^{-1} for most target analytes and the limits of detection were in the low μg l^{-1} level, ranging between 0.005 and 0.1 μg l^{-1}. The repeatability of the method varied between 4% and 11%. Under the present experimental conditions, the performance of the method was found comparable to that of solid-phase microextraction (SPME). The advantage of the proposed method over SPME was that it eliminated carry-over of analytes between runs. The applicability of the developed hollow-fibre LPME method and SPME was demonstrated for real water samples. The ability of both microextraction methods to concentrate many organic analytes was demonstrated as both methods allowed the confirmation of the presence of an extra contaminant (ethyl *p*-ethoxybenzoate) in bottled mineral water samples.

Keywords: Hollow-fibre membranes; Liquid-phase microextraction; Extraction methods; Water analysis; Phthalates; Ethyl ethoxybenzoate

1. Introduction

The mechanical properties of rigid poly(vinyl chloride) (PVC) can be modified through the addition of low molecular mass compounds that mix with the polymer matrix. Addition of these so-called plasticisers (mainly phthalates and adipates) in various amounts generates materials with versatile properties that have led to the use of PVC in a vast range of applications [1].

Today, all the phthalates used as plasticisers in diverse applications are ubiquitous in the environment. Since they are not chemically but only physically bound to the polymer chains, they may be leached into food and beverages from the packaging material [2]. Likewise, penetration of phthalates from waste plastics into the ecosystem surrounding the waste disposal sites may occur. Certain phthalates, as well as their metabolites and degradation products, can cause adverse effects on human health (in particular on liver, kidney and testicles) [3]. Potential endocrine disrupting properties were also reported [4]. The most commonly used phthalates include bis-2-ethylhexyl phthalate (DEHP), di-*n*-butyl phthalate (DBP) and butylbenzyl phthalate (BBP). Due to their potential risks to human health and the environment [5], these phthalates are on the first three priority lists for risk assessment in accordance with

*Corresponding author. Tel.: +30-82-103-7435; fax: +30-82-103-7483.
E-mail address: epsilaki@mred.tuc.gr (E. Psillakis).

0021-9673/03/$ – see front matter
doi:10.1016/S0021-9673(03)00390-X

the European Union's Regulation 793/93 on existing substances [6]. The US Environmental Protection Agency (EPA) has set the maximum contamination level (MCL) for DEHP in water systems at 6 μg l^{-1} and recommended that concentrations above 0.6 μg l^{-1} be closely monitored [7].

Determination of phthalates in aqueous samples commonly requires the use of different preconcentration techniques such as liquid–liquid extraction (LLE) or solid-phase extraction (SPE), followed by gas chromatography (GC) or high-performance liquid chromatography (HPLC) [8,9]. These sample pretreatment methods are considered expensive, time-consuming, and labour-intensive methods, which often result in high blank values. This is due to phthalates present in many laboratory products including glassware, chemicals and plastic accessories, which can easily migrate into the water samples destined for analysis [8,10].

Solid-phase microextraction (SPME) is an innovative sample preconcentration technique that has been used for a wide variety of organic contaminants in environmental samples [11,12]. Recently, several published reports dealt with the development and validation of SPME methods in phthalate analysis [9,10,13–15]. In these studies, several commercially available SPME fibres were compared and the influence of temperature, salt addition and sample agitation were examined. The results confirmed that SPME is a fast, simple, solventless and efficient preconcentration technique that enables determination of phthalates at low μg l^{-1} contamination levels in water samples. More importantly though, they concluded that the use of SPME reduced the risk of secondary contamination during sample handling, a major concern in phthalate analysis.

A recent trend in sample pretreatment techniques involves the miniaturisation of the LLE extraction procedure by greatly reducing the solvent to aqueous phase ratio, leading to solvent microextraction methodologies [16]. A technique that evolved from this approach is single-drop microextraction, where the extractant phase is a microdrop of a water-immiscible solvent suspended on the tip of a conventional microsyringe, immersed in a contaminated water sample [17]. Although single-drop microextraction proved to be a simple, inexpensive, fast, and virtually solvent-free sample pretreatment technique, problems of drop stability and low sensitivity were often encountered [16,18].

The quest for novel micro-LLE methods has never ceased and a new microextraction method, termed liquid-phase microextraction (LPME), using porous polypropylene hollow-fibres was recently introduced [19]. In one of the possible configurations, the fibre is connected at one of its ends to the needle tip of a microsyringe while the other end is left suspended in the sample solution [20]. This fibre configuration is considered an evolution of single-drop microextraction, because the organic microdrop is protected by the hollow-fibre.

The aim of the present study was to investigate the applicability of hollow-fibre LPME method for the determination of phthalates in water samples. Parameters such as extraction solvent, agitation speed, ionic strength of the aqueous sample and sampling time were controlled and optimised. The resulting method was validated and compared to SPME for the extraction of phthalates from real water samples. Overall, both techniques allowed the low μg l^{-1} level analysis of phthalates in aqueous samples and reduced the risk of secondary contamination. The advantages of hollow-fibre LPME over SPME included a low analysis cost per sample and elimination of sample carry-over between analyses due to the disposability of the polypropylene fibre.

2. Experimental

2.1. Chemicals and sample preparation

The Accurel Q 3/2 polypropylene hollow fibre membrane used here was obtained from Membrana (Wuppertal, Germany). The wall thickness of the fibre was 200 μm, the inner diameter was 600 μm, and the pore size was 0.2 μm.

Methanol, hexane and acetonitrile were Suprasolv quality (for organic trace analysis) and were obtained from Merck (Darmstadt, Germany). Deionized water used for sample preparation was prepared on a water purification system (EASYpure RF) supplied by Barnstead/Thermolyne (Dubuque, IA, USA). Ethyl 4-ethoxybenzoate (>99%) was purchased from Eurolabs (Poynton, UK). Sodium chloride more than

99.5% pure was obtained from Merck. The six phthalates selected for investigation were purchased from Supelco (Bellefonte, PA, USA) in the form of a standard methanolic stock solution containing 2000 mg l^{-1} of dimethyl phthalate (DMP), diethyl phthalate (DEP), DBP, BBP, DEHP and di-*n*-octyl phthalate (DOP). From this solution, working mixtures in methanol (100 mg l^{-1}) were prepared weekly. Standard solutions in hexane were also prepared for direct injection calibration containing all phthalates in the range 0.1–50 mg l^{-1}. All solutions were stored in the dark at 4 °C.

The spiked aqueous solutions were prepared daily at the concentration levels of interest. For extraction, a 5-ml spiked aqueous sample was placed each time in a 7-ml clear glass vial (Supelco). For the SPME experiments, the vials were fitted with aluminium foil and screw caps with a hole (Supelco). Unless otherwise stated, magnetic stirring at 1000 rev./min was applied at all times using a glass-coated flea micro spinbar (8 mm×3 mm).

2.2. Hollow-fibre liquid-phase microextraction

Before use, the hollow fibre membrane was sonicated in acetone for several minutes to remove any contaminants. The fibre was then removed from the solvent solution and allowed to dry completely. It was then cut, manually and carefully, into 1.3-cm pieces.

A 10-μl Hamilton gas-tight syringe (Hamilton, Bonaduz, Switzerland), Model 1701RNR, with a blunt needle tip (length, 5.1 cm; O.D., 0.071 cm; I.D., 0.015 cm), was used to introduce the acceptor phase, support the hollow fibre and act as the injection syringe. A 3-μl portion of a water immiscible organic solvent was withdrawn into the syringe followed by 3.4 μl of water. The tip of the microsyringe's needle was then inserted into the hollow fibre, which was then immersed into the organic solvent for 10 min, to ensure that the pores were filled with the extraction solvent. After solvent impregnation, water in the microsyringe was injected carefully into the hollow fibre, removing thus any excess of organic solvent from the inside. The fibre was then removed from the organic solvent and immediately immersed into the stirred water sample destined for analysis. The plunger was depressed and the 3-μl portion of the organic phase was injected into the hollow fibre. The use of stands and clamps ensured reproducible and stable positioning of the hollow fibre. After extracting for a prescribed period of time (typically 20 min) at room temperature, the organic solvent was withdrawn into the microsyringe and then injected into the GC–MS for analysis. Due to the low cost, a new fibre was used for each extraction.

2.3. Solid-phase microextraction

SPME was performed using a manual 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB) SPME fibre and an SPME fibre holder assembly, all purchased from Supelco. The fibre was initially conditioned according to the recommendations of the producer. Each day and prior to extracting any samples, the fibre was immersed for a few minutes in a stirred acetonitrile solution, and a blank analysis was then run to ensure that the fibre was free of contaminants. For extraction, the SPME fibre holder assembly was clamped at a fixed location above the 7-ml glass vial containing 5 ml of the spiked sample solution, stirred at 1000 rev./min. The SPME fibre was exposed to the aqueous phase and after sampling for 20 min at room temperature, the fibre was retracted and transferred to the heated injection port (260 °C) of the GC–MS where it remained for 5 min.

2.4. GC–MS analysis

All analyses were carried out on a Shimadzu GC-17A (Version 3) QP-5050A GC–MS system. The instrument was equipped with a 30 m×0.25 mm, 0.25 μm HP-5MS capillary column (Agilent Technologies). All analyses were performed in the splitless mode with the split closed for 5 min. An 8-min solvent delay time was used. The injector's temperature was 260 °C. Helium (>99.999% pure) was used as a carrier gas at a flow-rate of 1.2 ml min^{-1}. The column oven was initially set at 60 °C for 1 min and then programmed to 300 °C at a rate of 10 °C min^{-1}, where it was held for 5 min. The

interface temperature was set at 310 °C and the detector voltage at 1.40 kV. The ionization mode was electron impact (70 eV). Based on the literature, the selected ion monitoring (SIM) mode was used as a sensitive tool for quantitative measurements [15]. The esters were monitored according to the following target ions m/z DMP: 163, 194, DEP: 149, 177, DBP: 149, 223, BBP: 149, 206, 91, DEHP: 167, 149, 279, DOP: 149, 279. Prior to quantification in the SIM mode, the full scan mode (m/z 50–465) was used for identification of all target compounds based on their mass spectra and GC retention times. The limits of detection (LODs) were calculated from the calibration curves that defined linearity and the value of the Winefordner and Long criterion [23]. The value of the slope of the calibration curves (b) and the standard error of the independent term of the regression (S_b) were substituted for each target analyte in:

$$\mathrm{LOD} = \frac{3S_b}{b}. \quad (1)$$

The response of the mass detector in the SIM mode by direct injection of 1 μl of the different standard solutions was investigated and was found to be linear within the range of 0.1–50 μg ml^{-1}. The correlation coefficients were above 0.99 and were comparable with previously reported values [15].

The linearity of each microextraction method was checked within the range of 0.2–10 μg l^{-1} for most target analytes by using spiked deionised water. The concentration of phthalates in real water samples was calculated by using the calibration curves obtained for each microextraction method after subtraction of the blank analysis (deionised water) values.

Shimadzu GC instruments require a thick septum. Although thermo-resistant Thermogreen LB-2 septa (Supelco) were used here, the thick needle-protector of the SPME fibre as well as the thick needle of the 10-μl Hamilton microsyringe (Model 1701RNR) were damaging it irreversibly. This resulted in phthalate contamination due to the small polymer pieces introduced into the inlet liner of the GC injector and even carrier gas leaks and extraneous peaks. This problem could be overcome simply by drilling the septum prior to its use.

3. Results and discussion

3.1. Optimisation of the hollow-fibre LPME method

3.1.1. Extraction solvent

A crucial step in hollow-fibre LPME is choosing the most suitable extraction solvent [20]. As in LLE the principle ''like dissolves like'' is applied. The water immiscible solvent used should fulfil several requirements [19,20]. Firstly, it should be able to provide high solubility for the target analytes, and be compatible with direct injection into the capillary GC column. In addition, it should have a low solubility in water to prevent solvent dissolution during extraction, especially when faster stirring rates and extended extraction times are applied. Finally, it should have a polarity matching that of the polypropylene hollow-fibre, namely, the solvent must be able to impregnate and become immobilised within the pores of the hollow-fibre, in order to enhance transfer of analytes into the organic phase, as extraction occurs onto the surface of the immobilised organic solvent. For the purpose of the present experiments, three solvents were investigated: toluene, hexane and cyclohexane. Solvent selectivity was evaluated for 20-min extractions of 5-ml water samples spiked at 10 μg l^{-1} of each target analyte and stirred at 1000 rev./min. The results showed that toluene was the most suitable extraction solvent as it resulted in an increased response of the analytical instrument. In addition, toluene combined low solvent loss during extraction and, compared to the other organic solvents tested, had the ability to be easily immobilised in the pores of the hollow-fibre within seconds [20].

3.1.2. Agitation of the sample

Magnetic stirring enhances extraction and reduces the time required to reach thermodynamic equilibrium. Since the solvent here is protected by the hollow-fibre, faster stirring rates may be applied. This was not the case for single-drop microextraction where the solvent-drop was directly exposed to the aqueous phase and higher stirring rates usually resulted in drop displacement and/or drop dissolution [21]. The instrument's response was examined

for several stirring rates ranging from 0 to 1250 rev./min for a 20-min extraction of 5-ml aqueous samples spiked at 10 μg l^{-1} of each target analyte. As shown in Fig. 1, the results confirmed that agitation of the sample greatly enhances extraction. Although the instrument's response was at maximum at the highest agitation speed attainable by the magnetic stirrer (1250 rev./min), the results were difficult to reproduce due to solvent dissolution. Thus, the 1000-rev./min stirring rate was used for all subsequent experiments.

3.1.3. Salt addition

Increasing the ionic strength of the aqueous solution may have several effects upon extraction [12]. Usually, depending on the solubility of the target analytes, adding salt to the sample enhances extraction of the more polar analytes. In the case of single-drop microextraction, salt addition was generally found to limit or not to affect extraction of analytes. It was assumed, that apart from the salting-out effect, the presence of salt was causing a second effect, adverse for the extraction, whereby the physical properties of the extraction film were changed, reducing thus the diffusion rates of the analytes into the drop [16]. For the purpose of the present experiments, the effect of NaCl concentration (ranging from 0 to 30%) was investigated and the extraction efficiency was monitored. The results revealed that in hollow-fibre LPME, addition of salt restricted extraction of target analytes except in the case of the more polar DMP.

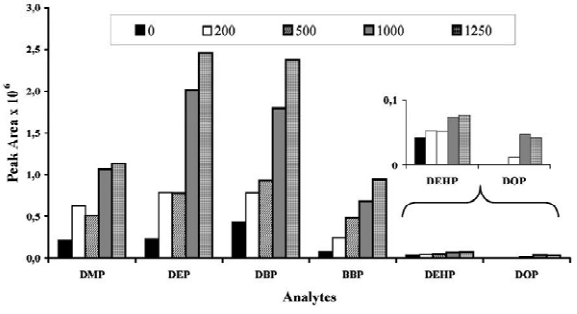

Fig. 1. Effect of sample agitation (rev./min) on hollow-fibre LPME extraction of phthalates from water samples: concentration 10 μg l^{-1}; 20 min extraction time.

During the SPME extraction of DEP from water samples, blank aqueous solutions of NaCl were found to contain DEP, possibly originating from the plastic containers in which the salt was stored, and it was found necessary to extract the salt twice with acetonitrile to remove any traces of DEP [13]. Taking into account all the above considerations and in accordance with Luks-Betlej et al. [15] who made similar observations concerning the effect of salt on the SPME analysis of phthalates, we decided not to alter the salt content of the sample solutions in the subsequent extractions as the sensitivity of the procedure was not poor.

3.1.4. Extraction time

The extraction time profile was then investigated. Standard aqueous solutions (10 μg l^{-1}) were prepared and extracted by varying the exposure of the extraction solvent to the sample from 5 to 30 min. Extraction times longer than 30 min could not be investigated as they typically resulted in significant solvent dissolution. As shown in Fig. 2, extraction increased with increasing exposure times and it seems that only DEHP and DOP reached equilibrium after 20 min of extraction. For routine analysis however, it is not necessary to attain equilibrium if constant extracting conditions are maintained [13,15,16,20–22]. Therefore, a 20-min extraction was used for all subsequent experiments as it matched the chromatography run time and maximised sample throughput.

Based on the above data, the calibration curves and analyses of real samples were obtained under the following conditions: 3 μl toluene, 5 ml water samples, 1000 rev./min stirring rate and 20 min sampling time.

3.2. SPME method

Previous studies dealing with the optimisation of the SPME procedure for the analysis of phthalates in water samples revealed that the SPME fibres containing a DVB phase were more suitable, as they yielded high extraction efficiency [15] and were less affected by the composition of the matrix since extraction with this type of fibre occurs via absorption [9]. When using the PDMS–DVB fibre, sam-

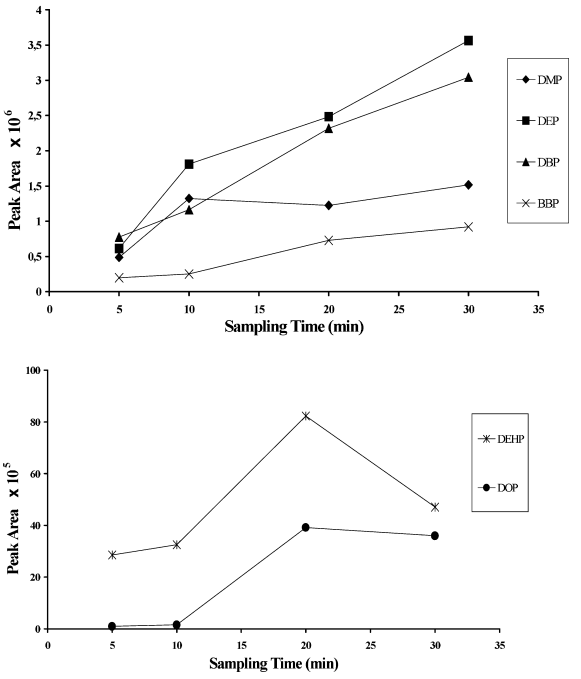

Fig. 2. Extraction time profiles for hollow-fibre LPME extraction of phthalates from water samples: concentration 10 μg l^{-1}; stirring rate 1000 rev./min.

pling time was reduced which maximised sample throughput [9,13]. The experimental conditions for the SPME procedure were comparable to the ones used for hollow-fibre LPME to allow direct comparison and were: PDMS–DVB fibre, 5 ml water samples, 1000 rev./min stirring rate and 20 min sampling time.

The main drawback of SPME when compared to hollow-fibre LPME is the possibility of analyte carry-over between runs during phthalate analysis [10]. In order to eliminate such a possibility in the present studies, after desorption, the SPME fibre was immersed in a stirred solvent solution for 5 min and was subsequently transferred to the heated injection port of another GC system until the next extraction to avoid contamination between runs. In hollow-fibre LPME, since the price of each extraction unit was low, each hollow-fibre was used only for a single extraction. The disposable nature of hollow-fibre LPME eliminated the possibility of analyte carry-over.

3.3. Method validation and comparison with the SPME method

Calibration curves for most analytes were calculated in the concentration range from 0.02 to 10 μg l^{-1}. As shown in Table 1, linearity for hollow-fibre LPME was very good with correlation coefficients r^2 being greater than 0.9984 ($n=5$) except in the case of DEHP and DOP where the r^2 values were 0.9888 and 0.9875, respectively. For SPME, the r^2 values were all greater than 0.9974 ($n=5$). The repeatability of the method, expressed as relative standard deviation (RSD), was evaluated by extracting five consecutive aqueous samples spiked at 1 μg l^{-1} with

Table 1
Main method parameters (linear range, correlation coefficients, limits of detection and repeatability) of phthalates in water when using hollow-fibre LPME and SPME

Analyte	Hollow-fibre LPME				SPME[a]			
	Linear range (μg l^{-1})	Correlation coefficient (r^2)	LODs (μg l^{-1})[a]	RSD $n=5$[c] (%)	Linear range (μg l^{-1})	Correlation coefficient (r^2)	LODs (μg l^{-1})[a]	RSD $n=5$[c] (%)
DMP	10–0.02	0.9992	0.01	12	10–0.05	0.9985	0.01	7
DEP	10–0.02	0.9991	0.01[b]	19	10–0.02	0.9985	0.01[b]	4
DBP	10–0.02	0.9999	0.005[b]	4	10–0.02	0.9998	0.003[b]	7
BBP	10–0.02	0.9984	0.01	5	10–0.02	0.9993	0.008	7
DEHP	10–0.1	0.9888	0.02[b]	12	10–0.05	0.9974	0.01[b]	11
DOP	10–0.5	0.9875	0.1	18	10–0.1	0.9989	0.04	10

[a] Calculated using the Winefordner and Long criterion [23].
[b] Estimated values (see text).
[c] Spiking level 1 μg l^{-1}; mean values for five determinations.

each target analyte. The RSD of the hollow-fibre LPME ranged from 4% to 19% with a mean value of about 12%. For SPME, the RSD values varied between 4% and 11% (8% mean value). Regarding the r^2 and RSD values obtained here for the SPME method, similar values have been published elsewhere [9]. The LODs for DEP, DBP and DEHP under the MS-SIM conditions were calculated by using the calibration curves and the Winefordner and Long criterion [23]. Despite all precautions taken to avoid secondary contamination during extraction, the deionised water used for preparing the water solutions was found to contain trace amounts of the above-mentioned analytes. Similar observations have been previously reported [9,10]. The LODs when using hollow-fibre LPME and SPME techniques were found to be in the low $\mu g\ l^{-1}$ level and ranged between 0.005 to 0.1 $\mu g\ l^{-1}$ and 0.003 to 0.04 $\mu g\ l^{-1}$, respectively. Under the present experimental conditions, the two techniques seem to be comparable in terms of linearity and sensitivity. It should be noted however, that in the case of SPME better LODs are expected by prolonging the extraction time. Nevertheless, the wide linear range combined with the low detection limits obtained with the two extraction methods studied here, suggests a high potential for monitoring phthalates in water samples. The performance of hollow-fibre LPME reflects the fact that the extraction solvent is protected by the hollow-fibre, improving the stability and repeatability of extraction compared to that of the single-drop microextraction method.

3.4. Application to real samples

The performance of hollow-fibre LPME and SPME was also tested by analysing potable water from the Chania water-supply network. As shown in Table 2, DEP, DBP, and DEHP were the principal contaminants and found in low concentration levels. In the case of DEHP, the concentration was ca. 0.9 $\mu g\ l^{-1}$ when using both extraction methods. As stated earlier, the US EPA suggests that DEHP concentrations in potable water above 0.6 $\mu g\ l^{-1}$ be closely monitored [7].

In addition, two different brands of commercial bottled mineral water were analysed. They were both distributed in PET bottles having a push–pull closure, which enables consumers to drink straight from the bottle without removing the cap from the bottle. Analyses of the samples by using both microextraction techniques revealed that DEP, DBP and DEHP were also the principal contaminants (Table 2). Similar findings in PET bottles have been reported previously [10,14] and it was assumed that such levels of phthalate contamination corresponded to common background contamination during production.

The ability of these techniques to concentrate many organic analytes in aqueous samples was demonstrated in the case of brand B where an extra peak appeared at 13.04 min (Fig. 3). The mass spectrum of this peak (Fig. 3) in the full-scan mode corresponded to ethyl *p*-ethoxybenzoate (PEEB) with a 0.95 match factor. The identity of this compound was also confirmed in terms of retention time, by running a hexane solution of the commercially available analyte under the same chromatographic conditions. Detection of the above-mentioned analyte was also possible under the MS-SIM mode (194 ion in the ion set for the DMP). PEEB forms part of the fourth generation Ziegler–Natta catalyst in polypropylene production [24]. The European Union has recently set regulations for this compound and the maximum permitted concentration of this substance in materials intended to come into contact with foodstuffs is currently 3.6 mg kg^{-1} [25]. In the present studies, it was assumed that

Table 2
Concentration ($\mu g\ l^{-1}$) of phthalates found in tap water and in two brands (PET A and PET B) of bottled mineral water

Analyte	Hollow-fibre LPME			SPME		
	Tap water	PET A	PET B	Tap water	PET A	PET B
DEP	0.30	0.05	0.13	0.11	0.12	0.07
DBP	1.04	0.32	0.51	0.44	0.08	0.14
DEHP	0.93	0.65	0.57	0.87	0.36	0.46

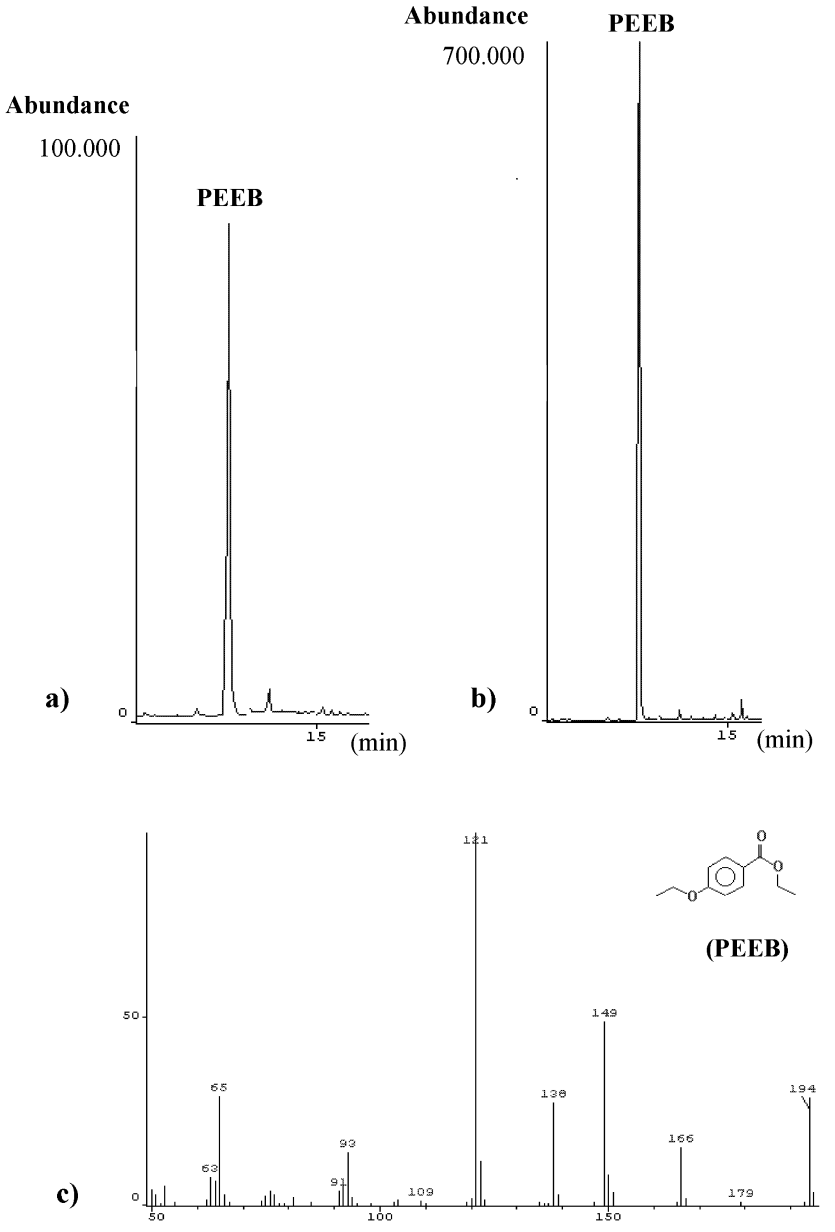

Fig. 3. Part of the SIM chromatogram of bottled mineral water (brand B) analysed by (a) hollow-fibre LPME and (b) SPME, revealing the presence of ethyl *p*-ethoxybenzoate (PEEB); (c) mass spectrum recorded at 13.04 min in the total ion chromatogram of mineral water brand B when using SPME–GC–MS, identified as PEEB.

PEEB originated from the push–pull closure of the particular brand. It should be mentioned here that caps are often responsible for phthalate contamination of bottled mineral water. For example, even commercially available mineral waters distributed in glass bottles are suspected of such a contamination,

as it has been reported that metal caps may be sealed with PVC inserts contributing to a high level of DEHP contamination [10].

4. Conclusions

Hollow-fibre LPME coupled to GC–MS was successfully applied for the analysis of trace levels of phthalates in water samples. The developed protocol proved to be a simple, rapid, inexpensive, precise and sensitive analytical procedure. The advantages of this extraction method over other microextraction methods follow from the presence of the hollow fibre, which protected the extraction solvent and allowed the use of high stirring rates without drop displacement and drop dissolution as in single-drop microextraction. The disposable nature of the hollow-fibre eliminated the possibility of carry-over effects seen in SPME. Hollow-fibre LPME and SPME minimise the risk of secondary contamination during analysis, a major problem in phthalate analysis. In addition, the performance of hollow-fibre LPME was comparable to that of SPME and, overall, both extraction methods can be recommended for trace analysis of phthalates in water samples.

Application to potable water samples suggested continuous monitoring of the water, as the DEHP concentration exceeded the 0.6 $\mu g\ l^{-1}$ limit set by the EPA. Analyses of bottled mineral waters indicated phthalate contamination possibly originating from production. However, in one brand both methods revealed the presence of an extra contaminant, demonstrating their ability to concentrate many organic analytes in aqueous samples.

References

[1] J.M. Cano, M.L. Marín, A. Sánchez, V. Hernandis, J. Chromatogr. A 963 (2002) 401.
[2] D. Balafas, K.J. Shaw, F.B. Whitfield, Food Chem. 65 (1999) 279.
[3] F.A. Arcadi, C. Costa, C. Imperatore, A. Marchese, A. Rapisarda, M. Salemi, G.R. Trimarchi, G. Costa, Food Chem. Toxicol. 36 (1998) 693.
[4] M. Petrović, E. Eljarrat, M.J. López de Alda, D. Barceló, Trends Anal. Chem. 20 (2001) 637.
[5] Council Directive 88/378/EEC of 3 May 1988 on the Approximation of the Laws of the Member States Concerning the Safety of Toys, European Union, Brussels, 1988.
[6] Council Regulation (EEC) No. 793/93 of 23 March 1993 on the Evaluation and Control of the Risks of Existing Substances (OJ L 84, 5 April 1993), European Union, Brussels, 1993.
[7] National Primary Drinking Water Regulations, Federal Register; Part 12, 40 CFR Part 141, US Environmental Protection Agency, Washington, DC, 1991, p. 395, 1 July.
[8] SW-846, Method 8061A, Phthalate Esters by Gas Chromatography with Electron Capture Detection (GC/ECD), US Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, 1996.
[9] A. Peñalver, E. Pocurrull, F. Borrull, R.M. Marcé, J. Chromatogr. A 922 (2001) 377.
[10] G. Prokůpková, K. Holadová, J. Poustka, J. Hajšlova, Anal. Chim. Acta 457 (2002) 211.
[11] R.E. Clement, P.W. Yang, C.J. Koester, Anal. Chem. 73 (2001) 2761.
[12] R. Eisert, J. Pawliszyn, Crit. Rev. Anal. Chem. 27 (1997) 103.
[13] M.T. Kelly, M. Laroque, J. Chromatogr. A 841 (1999) 177.
[14] A. Peñalver, E. Pocurrull, F. Borrull, R.M. Marcé, J. Chromatogr. A 872 (2000) 191.
[15] K. Luks-Betlej, P. Popp, B. Janoszka, H. Paschke, J. Chromatogr. A 938 (2001) 93.
[16] E. Psillakis, N. Kalogerakis, Trends Anal. Chem. 21 (2002) 53.
[17] M.A. Jeannot, F.F. Cantwell, Anal. Chem. 69 (1997) 235.
[18] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 938 (2001) 113.
[19] S. Pedersen-Bjergaard, K.E. Rasmussen, Anal. Chem. 71 (1999) 2650.
[20] G. Shen, H.K. Lee, Anal. Chem. 74 (2002) 648.
[21] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 907 (2001) 211.
[22] F. Hernandez, J. Beltran, F.J. Lopez, J.V. Gaspar, Anal. Chem. 72 (2000) 2313.
[23] G.L. Long, J.D. Winefordner, Anal. Chem. 55 (1983) 713A.
[24] A.G. Mattos Netto, J.C. Pinto, Chem. Eng. Sci. 56 (2001) 4043.
[25] Commission Directive 2001/62/EC of 9 August 2001 amending Directive 90/128/EEC relating to Plastic Materials and Articles Intended to Come into Contact with Foodstuffs, European Union, Brussels, 2001.