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Determination of phthalic acid esters in water samples by hollow fiber liquid-phase microextraction prior to gas chromatography tandem mass spectrometry

Javier González-Sálamo [a], Miguel Ángel González-Curbelo [b], Bárbara Socas-Rodríguez [a], Javier Hernández-Borges [a, *], Miguel Ángel Rodríguez-Delgado [a]

[a] Departamento de Química, Unidad Departamental de Química Analítica, Facultad de Ciencias, Universidad de La Laguna (ULL), Avda. Astrofísico Fco. Sánchez, s/nº, 38206, San Cristóbal de La Laguna, España
[b] Departamento de Ciencias Básicas, Facultad de Ingeniería, Universidad EAN. Calle 79 nº 11-45, Bogotá D.C., Colombia

HIGHLIGHTS

- A new HF-LPME-GC-MS/MS method was developed for the analysis of PAEs.
- Mineral, tap, pond and waste water samples were analyzed.
- Main parameters affecting the extraction efficiency were optimized.
- Recoveries ranged between 74 and 120% with RSD values below 20%.
- The developed method is simple, cheap and reliable.

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ABSTRACT

A new hollow fiber liquid-phase microextraction (HF-LPME) method has been developed for the extraction of a group of phthalic acid esters (PAEs) of interest from different water samples prior to gas chromatography tandem mass spectrometry analysis. HF-LPME was carried out using 1-octanol as extraction solvent followed by a back extraction step with cyclohexane. The different parameters that affect HF-LPME such as sample pH, ionic strength, extraction time, stirring rate, extraction temperature and back extraction conditions were investigated. The optimized conditions involved the extraction of 10 mL of sample without pH adjustment or addition of salt during 75 min under a stirring of 850 rpm at 60 °C and subsequent desorption with 200 μL of cyclohexane for 10 min in an ultrasonic bath. The method was validated in terms of calibration and recovery studies using dibutyl phthalate-d_4 as internal standard. The developed procedure gave satisfactory recovery (74–120%) and relative standard deviation values (<20%) for the studied PAEs in mineral, tap, pond and waste water samples.

1. Introduction

Phthalic acid esters (PAEs), generally known as phthalates, have been widely and increasingly used since 1920s in plastic manufacturing as polymer additives to improve the properties of plastic products such as flexibility, elasticity and durability (Abdel daiem et al., 2012), though they also have other different applications (Cao, 2016; Gao and Weng, 2016). These compounds are not covalently bound to the polymeric chains and may leak into the environment, constituting an important source of contamination that has to be continuously studied (Abdel daiem et al., 2012). In fact, several studies have demonstrated the occurrence of PAEs in the environment (Dargnat et al., 2009; Ko et al., 2008; Zeng et al., 2008). Moreover, since the molecular structure of PAEs is similar to that of certain hormones, it has been proved that a continuous exposure to PAEs, their metabolites and degradation products through drinking water and the food chain can lead to health problems for humans, including endocrine disrupting effects as well as increasing the risk of cardiovascular diseases and even cancer

* Corresponding author.
E-mail address: jhborges@ull.edu.es (J. Hernández-Borges).

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(Kay et al., 2014; Posnack, 2014; Trasande et al., 2013; Weuve et al., 2010). Because of these environmental and health risks, the US Environmental Protection Agency (EPA) classified certain PAEs as priority pollutants (i.e. dibutyl phthalate (DBP), di-isobutyl phthalate (DIBP), butyl benzyl phthalate (BBP) and bis-*n*-pentyl ester (DNPP), among others) (U.S. Environmental Protection Agency, EPA. Phthalates action plan. 2012). Therefore, the development of accurate and sensitive analytical methods for the determination of PAEs is an important issue for evaluating water quality and food safety as well as possible risks to human health.

The migration of PAEs to the environment is generally very slow, and their concentrations in the environment are frequently at the low μg/L or μg/kg levels (Abdel daiem et al., 2012; Gao and Wen, 2016). Hence, sample preparation and pre-concentration of the analytes from these matrices are needed before chromatographic analysis. In this sense, different approaches such as liquid-liquid extraction (LLE) (Farajzadeh et al., 2013), ultrasound assisted extraction (Ma et al., 2003) or solid-phase extraction (SPE) (Özer et al., 2017) have been traditionally and widely used to extract PAEs from aqueous samples, but most of them need large volumes of hazardous organic solvents. Moreover, given the high sensitivity of modern instruments, in many cases, and depending on the type of sample, it is desirable to use a sample preparation method which, in addition to enriching the target analytes, should also perform a simultaneous clean-up step. All of the above should be accompanied by a low consumption of solvents and materials as well as an easy implementation.

Compared with traditional sample preparation methods, liquid-phase microextraction (LPME) is a relatively recent and promising set of simplified and miniaturized techniques that require only several microliters of extraction solvents (Asensio-Ramos et al., 2011). Among the different LPME modes, hollow fiber (HF)-LPME enables to carry out extraction and clean-up in a single step with high selectivity, high enrichment factors, low cost, simplicity of operation and minimal waste (González-Curbelo et al., 2013; Pedersen-Bjergaard and Rasmussen, 1999). In earlier studies, some PAEs have been successfully extracted by HF-LPME but only in five occasions (Chao et al., 2013a, 2013b; Jiang et al., 2016; Mtibe et al., 2012; Psillakis and Kalogerakis, 2003). All these works were focused on a relatively low number of PAEs (no more than 3 or 6) and were applied to a single type of water sample. As a result, and despite its advantages, the application of the technique has not been fully explored.

Therefore, the main objective of this study was to develop a sensitive, simple and cheap method based on HF-LPME prior to gas chromatography-tandem mass spectrometry (GC-MS/MS) for the analysis of a group of PAEs widely used in the plastic industry (i.e. dipropyl phthalate (DPP), DIBP, DBP, bis-isopentyl phthalate (DIPP), bis-2-ethoxyethyl ester (DEEP), DNPP, BBP, bis-2-*n*-butoxyethyl ester (DBEP) and dicyclohexyl phthalate (DCHP)), including three priority pollutants indicated by the US EPA (DBP, DIBP, BBP and DNPP), in four real water samples (mineral, tap, pond and waste water). To the best of our knowledge, this is the first time that some of these analytes have been extracted by HF-LPME from water samples. It is also the first application of HF-LPME to phthalates in which the highest number of water samples of different type has been analyzed and also the application in which the highest number of phthalates has been extracted by HF-LPME.

2. Materials and methods

2.1. Chemicals

Phthalates analytical standards of DPP, DIBP, deuterated DBP (DBP-d_4) as internal standard (IS), DBP, DIPP, DEEP, DNPP, BBP, DBEP and DCHP were obtained from Sigma-Aldrich (Madrid, Spain) and Dr. Ehrenstorfer (Augsburg, Germany). Purity of the phthalates standards was higher than 98.4%. Individual stock solutions of each analyte were prepared in cyclohexane (concentrations in the range 400–1050 mg/L) and stored in the darkness at −18 °C. Mix standard solutions of all phthalates were prepared at different concentrations by combination and dilution with an appropriate volume of cyclohexane. Spiking was carried out using different volumes of these solutions.

All chemicals were of analytical reagent grade and were used as received. Distilled water was deionized (conductivity of 18.5 μS/cm at 25 °C) by using a Milli-Q A10 system from Millipore (Bedford, MA, USA). Acetonitrile (ACN) and methanol (MeOH), both liquid chromatography-mass spectrometry (LC-MS) grade, and cyclohexane, GC-MS grade and acetone were from Merck (Darmstadt, Germany). Sodium hydroxide was from Scharlau Chemie S.A. (Barcelona, Spain) and hydrochloric acid from Panreac (Barcelona, Spain). Sodium chloride and 1-octanol were from Sigma-Aldrich Chemie (Madrid, Spain).

Accurel Q3/2 polypropylene HF membranes (600 μm id, 200 μm wall thickness and 0.2 μm pore size) were acquired from Membrana GmbH (Obernburg, Germany) and used as received after a previous washing with cyclohexane with ultrasounds assistance.

2.2. Apparatus and software

Analysis were performed with two different apparatus: (A) The optimization of the HF-LPME method was developed on a Varian 3800 GC-flame ionization detector (FID) system (Walnut Creek, CA, USA), equipped with a Varian Combipal Autosampler. For instrument control, the Varian Star Chromatography Workstation v.6.41 Software was used. Separation was carried out in a SPB-5 fused silica capillary column (30 m × 0.25 mm, 0.25 μm film, poly (5% diphenyl/95% dimethylsiloxane)) from Supelco (Bellefonte, PA, USA). The column temperature was increased from 70 °C to 160 °C at a rate of 30 °C/min, then increased to 260 °C at a rate of 3 °C/min and finally increased to 300 °C at a rate of 30 °C/min and held for 10 min. Total run time was 35.66 min. Nitrogen was employed as the carrier gas (1.2 mL/min) and also as make-up (30 mL/min). Hydrogen and air flows were kept at 30 and 300 mL/min, respectively. Two microliters of a standard or sample solution were injected in the split/splitless mode (ratio of 1:50) at 280 °C and the FID was maintained at 300 °C. (B) The validation of the method was developed on a Bruker Scion 436GC triple quadrupole equipped with an 8400 Autosampler (Bruker Daltonik GmbH, Bremen, Germany). For instrument control, Bruker MSWS 8 Software was used. Separation was carried out in a BR-5ms fused silica capillary column (30 m × 0.25 mm, 0.25 μm film, poly (5% diphenyl/95% dimethyl arylene siloxane)) from Bruker Daltonik GmbH (Bremen, Germany). The column was initially maintained at 70 °C for 2 min, and then the temperature was increased to 200 °C at a rate of 25 °C/min, then increased to 260 °C at a rate of 3 °C/min and finally increased to 300 °C at a rate of 30 °C/min and held for 4 min at that temperature. Total run time was 32.53 min. Helium was employed as the carrier gas (1.5 mL/min). The injection volume was 2 μL in the splitless mode at 280 °C. The MS transfer line and ion source were set at 280 °C with electron ionization energy of −70 eV. Argon was used as collision gas at 1.5 mL/min. A list of the studied phthalates including their retention times (t_R) and MS/MS transitions is provided in Table 1.

2.3. HF-LPME procedure

A 2-cm hollow fiber was used for each extraction previously cleaned with 2 mL of cyclohexane for 5 min in an ultrasonic bath

Table 1
Retention times, quantifier and qualifier transitions in GC-MS/MS analyses of the selected PAEs.

Analyte	Retention time (min)	Quantifier transition (*m*/*z*)	Collision energy (V)	Qualifier transition (*m*/*z*)	Collision energy (V)
DPP	9.02	144 → 121	10.0	191 → 149	15.0
DIBP	9.84	149 → 93	12.5	149 → 121	17.5
DBP-d_4 (IS)	10.84	153 → 125	12.5	153 → 97	17.5
DBP	10.86	149 → 121	12.5	149 → 93	15.0
DIPP	12.33	149 → 121	15.0	149 → 93	17.5
DEEP	12.84	149 → 121	10.0	149 → 93	15.0
DNPP	13.49	149 → 121	15.0	149 → 93	17.5
BBP	16.98	149 → 121	10.0	149 → 93	15.0
DBEP	19.40	149 → 121	10.0	149 → 93	10.0
DCHP	20.27	149 → 121	10.0	167 → 149	15.0

and air dried. Subsequently, it was inserted into the needle tip of a 25 μL microsyringe and its pores and lumen were filled with 20 μL of 1-octanol in duplicate. The fiber was submerged in 10 mL of mineral, tap, pond or waste water and the extraction was performed for 75 min under stirring of 850 rpm at 60 °C. After extraction, the fiber was taken out of the vial and introduced into a 300 μL GC micro-vial containing 200 μL of cyclohexane for 10 min in an ultrasonic bath to back extract the analytes. Then, the solvent was evaporated under a gentle steam of nitrogen, reconstituted in 200 μL of cyclohexane and injected in the GC-MS/MS system.

3. Results and discussion

PAEs have enough volatility and thermostability to be analyzed by GC without derivatization using apolar columns (Fan et al., 2017; Qureshi et al., 2016). In this work, a total of 9 targeted PAEs were totally separated by GC-FID, for optimization purposes, and by GC-MS/MS, for validation purposes (the separation conditions as well as the temperature gradients are indicated in Section 2.2). In this last case, in which DBP-d_4 was used as IS, the MS system was operated in the multiple reaction monitoring (MRM) mode using 1 or 2 precursors, 2 product ions and relative ion intensities with a ±20% maximum permitted tolerance as well as the retention time as identification points (European Commission Decision, 2002/657/EC). Those peaks which did not meet these requirements were not considered as the target analyte. MRM transitions as well as the collision energy values are shown in Table 1, in which it can clearly be seen that most PAEs have common characteristic transitions (149 → 121 and 149 → 93) as already indicated in the literature (Barp et al., 2015; Liao et al., 2010).

The selection of the target PAEs was carried out taking into account their classification as priority pollutants as well as their applicability in products intended to be in contact with water and food, and therefore, be susceptible to being ingested by humans. As examples, among the PAEs commonly used in the industry DIBP, DBP and BBP stand out since they have been detected in leachate samples at average concentrations of 26.27, 14.20 and 5.52 μg/L, respectively (Zhang and Wang, 2009). Concentrations of these PAEs have also been routinely reported in water and sediment (Zeng et al., 2008; Gao and Wen, 2016). For example, DBP has been quantified in the ranges 1.69–11.8 μg/L (Gao et al., 2014), 2.8–122 μg/L (Fatoki and Noma, 2002) and 1.00–13.5 μg/L (Yuan et al., 2002) in river water samples. Regarding sediments, DIBP was found in the range 77.7–147.2 μg/kg and DEEP and DBEP at average concentrations of 8.3 and 75.1 μg/kg, respectively, in lake water samples (Zheng et al., 2014).

3.1. HF-LPME optimization

In order to obtain the best conditions for the analysis of the studied analytes, the parameters influencing the extraction (type of extraction solvent, pH, ionic strength, extraction time, agitation, back extraction time and temperature) were studied using 10 mL of spiked Milli-Q water with the selected PAEs at a concentration of 1.5 mg/L. In this sense, two-phase HF-LPME using 1-octanol as the acceptor phase was applied since it has been the most widely used approach to extract different groups of analytes obtaining satisfactory results due to its low volatility and immiscibility in aqueous solution as well as its high extraction capacity (Asensio-Ramos et al., 2011; González-Curbelo et al., 2013). Therefore, a polypropylene HF of 2.0 cm long was employed for all experiments. For this purpose, the HF was previously washed with 2 mL of cyclohexane in an ultrasonic bath to remove any impurity and even PAEs residues and air dried. Afterwards, it was inserted into the needle tip of a 25 μL Hamilton microsyringe pre-filled with 1-octanol. Then, 20 μL of extraction solvent was slowly introduced into the fiber, allowing its correct distribution through the pores and lumen. Subsequently, the syringe was filled again with 20 μL of 1-octanol and the procedure was repeated to ensure correct impregnation without bubbles formation and thus to avoid irreproducibility problems during extraction. Moreover, after extraction, a back extraction procedure based on the use of 200 μL of different solvents (sufficient to completely immerse the fiber in a micro-vial of 300 μL) for 8 min in an ultrasonic bath and subsequent evaporation under a gentle steam of nitrogen was employed. Finally, the analytes were reconstituted in 200 μL of cyclohexane before injection.

3.1.1. Effect of the type of solvent used during the back extraction procedure

After the extraction process, the development of a back extraction has shown to provide better results than the conventional retraction of the acceptor phase (González-Curbelo et al., 2013; Wang et al., 2011; Zorita et al., 2007). That is why the analytes were back extracted from the fiber by immersing it in a micro-vial containing 200 μL of solvent in all cases. In this sense, four organic solvents of different polarity were initially tested including ACN, acetone, MeOH and cyclohexane maintaining the rest of the parameters as follows: a 2-cm HF impregnated with 1-octanol, 10 mL of Milli-Q water without pH adjustment, extraction time of 25 min at ambient temperature, a stirring speed of 1000 rpm and a back extraction with 200 μL of solvent for 8 min under ultrasounds. As can be seen in Fig. 1, the results obtained showed that the best extraction efficiencies were obtained with acetone and cyclohexane for all analytes. However, due to the high volatility of acetone, which could lead to repeatability problems, and the fact that cyclohexane provided slightly higher results for 5 of the 9 studied compounds, this was selected. In the case of DEEP, it could not be initially detected, probably due to the initial conditions selected that did not favor the extraction of this analyte.

3.1.2. Effect of pH of the aqueous phase

The influence of the pH of the donor phase on extraction efficiency over the range of 2.0–9.0 (including Milli-Q water without pH adjustment) was studied using 10 mL of Milli-Q water under the conditions indicated previously, including a back extraction procedure with 200 μL of cyclohexane for 8 min. In general, and as expected, owing to the fact that analytes are non-ionizable in aqueous solution, pH did not significantly affect the extraction of PAEs (data not shown). Therefore, it was decided not to adjust it in future experiments as it has been suggested several times in the

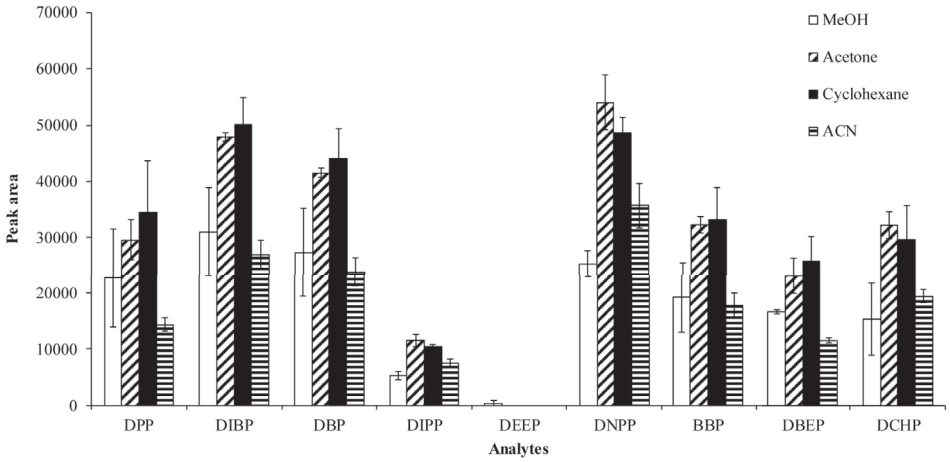

Fig. 1. Effect of type of solvent during the back extraction procedure on the peak areas of the selected PAEs after the HF-LPME procedure. Extraction conditions: a 2-cm HF impregnated with 1-octanol, 10 mL of spiked Milli-Q water at 1.5 mg/L without pH adjustment nor addition of salt, 25 min of extraction at 1000 rpm and ambient temperature and desorption with 200 μL of each solvent for 8 min assisted by ultrasounds.

literature (Chao et al., 2013a), unless a certain irreproducibility was observed in the final application of the procedure which, as can be seen in the following section, did not happen.

3.1.3. Effect of the ionic strength (NaCl addition) of the aqueous phase

Under the previously described conditions, the effect of the addition of NaCl at concentrations varying from 0 to 15% (w/v) was studied. As can be seen in Fig. 2, and especially for compounds such as DIBP, DIPP, DNPP, BBP, DBEP and DCHP, a clear decreasing trend of the peak areas was observed by increasing the percentage of NaCl added. This effect is quite significant for DBP for which extraction efficiency decreased drastically when NaCl is added. In the case of DEEP, the addition of NaCl slightly improved the extraction but not significantly. Therefore, it could be concluded that the addition of NaCl negatively affect the extraction of 8 of the 9 analytes studied, as some authors have previously suggested for a reduced number of PAEs (Chao et al., 2013a; Mtibe et al., 2012). This is because the addition of salts may exert a certain influence on the physicochemical conditions of the diffusion layer, to the point of hindering the transport of the analytes through it and towards the organic phase (Xiong and Hu, 2008; Palit et al., 2005).

3.1.4. Effect of the extraction time

Mass transfer is a process that depends on the extraction time, as long as there is no saturation of the analytes in the extraction solvent; in such case the equilibrium condition is reached. Taking into account that HF-LPME is a technique in which extraction is usually carried out under non-equilibrium conditions, the influence of extraction time up to 75 min was initially studied. In the obtained data shown in Fig. 1S of the Supplementary Material, it could be

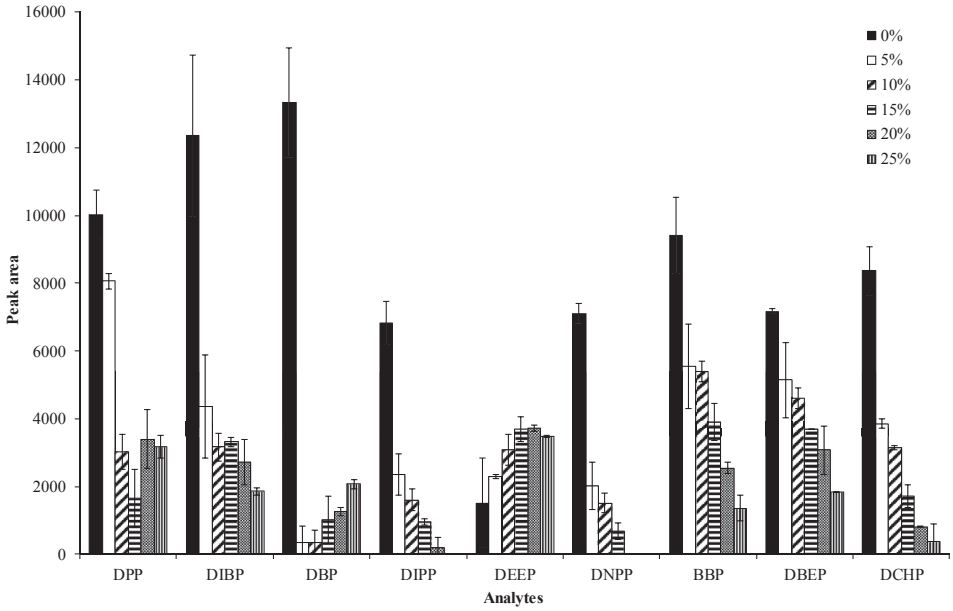

Fig. 2. Effect of the percentage (w/v) of NaCl on the peak areas of the selected PAEs after the HF-LPME procedure. Extraction conditions: a 2-cm HF impregnated with 1-octanol, 10 mL of spiked Milli-Q water at 1.5 mg/L without pH adjustment, 25 min of extraction at 1000 rpm at ambient temperature and desorption with 200 μL of cyclohexane for 8 min assisted by ultrasounds.

Table 2
Method calibration data of the selected PAEs in water samples after the HF-LPME-GC-MS/MS method.

Analyte	Sample	Studied linear range (μg/L)	Regression equation (n = 7)		$s_{y/x}$	R^2
			$b \pm s_b \cdot t_{(0,05;5)}$	$a \pm s_a \cdot t_{(0,05;5)}$		
DPP	Mineral water	1–100	$2.53 \cdot 10^{-2} \pm 9.22 \cdot 10^{-4}$	$-3.87 \cdot 10^{-2} \pm 4.06 \cdot 10^{-2}$	$3.10 \cdot 10^{-2}$	0.9990
	Tap water	1–100	$2.42 \cdot 10^{-2} \pm 2.78 \cdot 10^{-3}$	$-1.23 \cdot 10^{-1} \pm 1.22 \cdot 10^{-1}$	$9.32 \cdot 10^{-2}$	0.9901
	Pond water	1–100	$2.41 \cdot 10^{-2} \pm 1.32 \cdot 10^{-3}$	$-6.04 \cdot 10^{-2} \pm 5.64 \cdot 10^{-2}$	$4.27 \cdot 10^{-2}$	0.9982
	Waste water	1–100	$2.37 \cdot 10^{-2} \pm 1.54 \cdot 10^{-3}$	$-7.49 \cdot 10^{-2} \pm 6.79 \cdot 10^{-2}$	$5.18 \cdot 10^{-2}$	0.9968
DIBP	Mineral water	1–100	$3.74 \cdot 10^{-2} \pm 1.26 \cdot 10^{-3}$	$-6.09 \cdot 10^{-2} \pm 5.52 \cdot 10^{-2}$	$4.21 \cdot 10^{-2}$	0.9991
	Tap water	1–100	$3.46 \cdot 10^{-2} \pm 2.02 \cdot 10^{-3}$	$-6.59 \cdot 10^{-2} \pm 8.81 \cdot 10^{-2}$	$6.72 \cdot 10^{-2}$	0.9974
	Pond water	1–100	$3.68 \cdot 10^{-2} \pm 2.96 \cdot 10^{-3}$	$-1.07 \cdot 10^{-1} \pm 1.29 \cdot 10^{-1}$	$9.84 \cdot 10^{-2}$	0.9951
	Waste water	1–100	$3.38 \cdot 10^{-2} \pm 2.61 \cdot 10^{-3}$	$-8.59 \cdot 10^{-2} \pm 1.14 \cdot 10^{-1}$	$8.68 \cdot 10^{-2}$	0.9955
DBP	Mineral water	1–100	$5.27 \cdot 10^{-2} \pm 1.86 \cdot 10^{-3}$	$-3.92 \cdot 10^{-2} \pm 8.53 \cdot 10^{-2}$	$6.51 \cdot 10^{-2}$	0.9991
	Tap water	1–100	$5.02 \cdot 10^{-2} \pm 4.56 \cdot 10^{-3}$	$2.98 \cdot 10^{-2} \pm 2.09 \cdot 10^{-1}$	$1.59 \cdot 10^{-1}$	0.9938
	Pond water	1–100	$5.22 \cdot 10^{-2} \pm 1.09 \cdot 10^{-3}$	$-2.01 \cdot 10^{-2} \pm 4.98 \cdot 10^{-2}$	$3.80 \cdot 10^{-2}$	0.9997
	Waste water	1–100	$5.06 \cdot 10^{-2} \pm 9.55 \cdot 10^{-4}$	$-4.54 \cdot 10^{-2} \pm 4.37 \cdot 10^{-2}$	$3.34 \cdot 10^{-2}$	0.9997
DIPP	Mineral water	1–100	$2.45 \cdot 10^{-2} \pm 1.32 \cdot 10^{-3}$	$-5.90 \cdot 10^{-2} \pm 5.78 \cdot 10^{-2}$	$4.42 \cdot 10^{-2}$	0.9978
	Tap water	1–100	$2.14 \cdot 10^{-2} \pm 4.38 \cdot 10^{-4}$	$2.66 \cdot 10^{-3} \pm 1.91 \cdot 10^{-2}$	$1.46 \cdot 10^{-2}$	0.9997
	Pond water	1–100	$2.35 \cdot 10^{-2} \pm 7.98 \cdot 10^{-4}$	$-4.56 \cdot 10^{-2} \pm 3.49 \cdot 10^{-2}$	$2.66 \cdot 10^{-2}$	0.9991
	Waste water	1–100	$2.15 \cdot 10^{-2} \pm 1.97 \cdot 10^{-3}$	$-7.53 \cdot 10^{-2} \pm 8.62 \cdot 10^{-2}$	$6.58 \cdot 10^{-2}$	0.9937
DEEP	Mineral water	1–100	$8.91 \cdot 10^{-4} \pm 7.90 \cdot 10^{-5}$	$-2.53 \cdot 10^{-3} \pm 3.46 \cdot 10^{-3}$	$2.62 \cdot 10^{-3}$	0.9953
	Tap water	1–100	$1.05 \cdot 10^{-3} \pm 9.19 \cdot 10^{-5}$	$-3.47 \cdot 10^{-3} \pm 3.13 \cdot 10^{-3}$	$3.16 \cdot 10^{-3}$	0.9942
	Pond water	1–100	$8.55 \cdot 10^{-4} \pm 7.31 \cdot 10^{-5}$	$4.90 \cdot 10^{-4} \pm 2.29 \cdot 10^{-3}$	$2.51 \cdot 10^{-3}$	0.9945
	Waste water	1–100	$1.03 \cdot 10^{-3} \pm 1.04 \cdot 10^{-4}$	$-3.24 \cdot 10^{-3} \pm 4.68 \cdot 10^{-3}$	$3.57 \cdot 10^{-3}$	0.9924
DNPP	Mineral water	1–100	$3.95 \cdot 10^{-2} \pm 2.04 \cdot 10^{-3}$	$-9.39 \cdot 10^{-2} \pm 8.76 \cdot 10^{-2}$	$6.69 \cdot 10^{-2}$	0.9980
	Tap water	1–100	$3.90 \cdot 10^{-2} \pm 2.32 \cdot 10^{-3}$	$-4.89 \cdot 10^{-2} \pm 1.00 \cdot 10^{-1}$	$7.63 \cdot 10^{-2}$	0.9973
	Pond water	1–100	$3.83 \cdot 10^{-2} \pm 1.56 \cdot 10^{-3}$	$-5.49 \cdot 10^{-2} \pm 6.72 \cdot 10^{-2}$	$5.13 \cdot 10^{-2}$	0.9987
	Waste water	1–100	$3.68 \cdot 10^{-2} \pm 3.02 \cdot 10^{-3}$	$-1.17 \cdot 10^{-1} \pm 1.30 \cdot 10^{-1}$	$9.92 \cdot 10^{-2}$	0.9949
BBP	Mineral water	1–100	$1.78 \cdot 10^{-2} \pm 1.53 \cdot 10^{-3}$	$-5.65 \cdot 10^{-2} \pm 6.65 \cdot 10^{-2}$	$5.08 \cdot 10^{-2}$	0.9945
	Tap water	1–100	$2.30 \cdot 10^{-2} \pm 1.98 \cdot 10^{-3}$	$-1.46 \cdot 10^{-1} \pm 1.92 \cdot 10^{-1}$	$1.71 \cdot 10^{-1}$	0.9933
	Pond water	1–100	$2.38 \cdot 10^{-2} \pm 2.04 \cdot 10^{-3}$	$-1.46 \cdot 10^{-1} \pm 1.98 \cdot 10^{-1}$	$1.76 \cdot 10^{-1}$	0.9934
	Waste water	1–100	$2.42 \cdot 10^{-2} \pm 1.80 \cdot 10^{-3}$	$-1.58 \cdot 10^{-1} \pm 1.74 \cdot 10^{-1}$	$1.56 \cdot 10^{-1}$	0.9950
DBEP	Mineral water	1–100	$5.08 \cdot 10^{-3} \pm 4.28 \cdot 10^{-4}$	$-1.51 \cdot 10^{-2} \pm 1.91 \cdot 10^{-2}$	$1.45 \cdot 10^{-2}$	0.9947
	Tap water	1–100	$5.16 \cdot 10^{-3} \pm 4.60 \cdot 10^{-4}$	$-6.96 \cdot 10^{-3} \pm 2.05 \cdot 10^{-2}$	$1.56 \cdot 10^{-2}$	0.9940
	Pond water	1–100	$5.51 \cdot 10^{-3} \pm 2.95 \cdot 10^{-4}$	$-1.01 \cdot 10^{-2} \pm 1.31 \cdot 10^{-2}$	$1.00 \cdot 10^{-2}$	0.9978
	Waste water	1–100	$6.29 \cdot 10^{-3} \pm 7.11 \cdot 10^{-4}$	$-3.06 \cdot 10^{-2} \pm 3.17 \cdot 10^{-2}$	$2.42 \cdot 10^{-2}$	0.9904
DCHP	Mineral water	1–100	$3.17 \cdot 10^{-2} \pm 2.05 \cdot 10^{-3}$	$-7.84 \cdot 10^{-2} \pm 9.05 \cdot 10^{-2}$	$6.91 \cdot 10^{-2}$	0.9969
	Tap water	1–100	$3.43 \cdot 10^{-2} \pm 9.59 \cdot 10^{-4}$	$-3.34 \cdot 10^{-2} \pm 4.13 \cdot 10^{-2}$	$3.12 \cdot 10^{-2}$	0.9995
	Pond water	1–100	$3.26 \cdot 10^{-2} \pm 1.50 \cdot 10^{-3}$	$-3.77 \cdot 10^{-2} \pm 6.61 \cdot 10^{-2}$	$5.05 \cdot 10^{-2}$	0.9984
	Waste water	1–100	$3.40 \cdot 10^{-2} \pm 2.66 \cdot 10^{-3}$	$-9.33 \cdot 10^{-2} \pm 1.17 \cdot 10^{-1}$	$8.96 \cdot 10^{-2}$	0.9954

b: slope; S_b: standard deviation of the slope; a: intercept; S_a: standard deviation of the intercept; R^2: determination coefficient; $S_{y/x}$: standard deviation of the estimate.

observed an increasing trend of the extraction over time for the majority of the analytes. In the case of DPP, DBP and DEEP, this increase was not significant. However, and because of the improvement of the extraction efficiency for most of the studied PAEs at high extraction times, it was decided to carry out the extraction for 75 min. It is possible that the longer the extraction time, the better results are obtained for some of the analytes, however, it was decided not to increase the time since it is not functional to employ long extraction if good performance is obtained at shorter times.

3.1.5. Effect of the stirring speed

The stirring rate is another parameter of great importance in a technique such as HF-LPME since it will inevitably affect the movement of the analytes in the sample and, consequently, the mass transfer. That is why the stirring speed was varied between 500 and 1000 rpm maintaining the rest of the conditions constant: a 2-cm HF impregnated with 1-octanol, 10 mL of Milli-Q water, without pH adjustment, without addition of salt, extraction time of 75 min at ambient temperature and 200 μL of cyclohexane for 8 min under ultrasounds. The results obtained are shown in Fig. 2S of the Supplementary Material. As can be seen, further agitation leads to better extraction of the analytes. In the case of DPP and DBP the effect is not sufficiently clear, as a result of the low extraction of these analytes. However, although the increment is progressive, it was possible to verify experimentally that at maximum speed, the magnetic bar could not provide a homogenous agitation thus reducing the efficiency of the extraction at 1000 rpm. It is important to take into account that excessive agitation may negatively influence the extraction, since in these cases the movement prevents the analytes from remaining long enough on the fiber surface to be able to penetrate through diffusion. Based on these results, it was decided to select a stirring speed of 850 rpm.

3.1.6. Effect of the back extraction time

As already indicated, the back extraction procedure consists on putting in contact the fiber (after extraction) with a solvent, in this case cyclohexane, under ultrasounds. The back extraction time is also a variable to be optimized and it was carried out by modifying the time between 5 and 20 min (see Fig. 3S of the Supplementary Material). The results showed that the extraction was higher at 10 min, except for DPP and DEEP for which there were hardly any variations. Hence, 10 min was selected for future experiments. At higher times the efficiency decreased, suggesting that the analytes return to the fiber. It is important to emphasize that it was not decided to carry out experiments between 8 and 10 min or between 10 and 15 min, given the few differences between the areas obtained in both cases (at 8 and 15 min).

3.1.7. Effect of the extraction temperature

Temperature may also influence the efficiency of the extraction through two opposed contributions. On the one hand, and as it is known, an increase in temperature favors the mass transfer and,

therefore, the displacement of the analytes towards the acceptor phase. But on the other hand, an increase causes a decrease in the K_{ow} of the analytes (Xiong and Hu, 2008) which decreases the affinity for that phase. In this case, the effect of the temperature was studied by developing extractions at 30, 40, 60, 70 °C and at room temperature, under the previous conditions: a 2-cm HF impregnated with 1-octanol, 10 mL of Milli-Q water, without pH adjustment, without addition of salt, extraction time of 75 min, stirring speed of 850 rpm and 200 μL of cyclohexane for 10 min under ultrasounds. In all cases, the vial containing the aqueous sample was immersed in a glycerin bath on a heated stirring plate and a temperature probe was submerged therein. The results obtained are shown in Fig. 4S of the Supplementary Material. As can be seen, an increase in temperature produces an enhancement of the extraction efficiency for most of the selected analytes up to a maximum of 60 °C, which has already been described in the literature for some of these analytes (Psillakis and Kalogerakis, 2003), and falling drastically at temperatures above 60 °C. Based on the results obtained, it was decided to select 60 °C as the appropriate extraction temperature.

3.2. Validation of the HF-LPME-GC-MS/MS method in water samples

To validate the optimized HF-LPME-GC-MS/MS method, calibration and recovery studies were carried out after a blank sample analysis. It is necessary to take into account the possible existence of contamination by PAEs from the impurities in the reagents, the laboratory material and also the particles suspended in the air. Therefore, in order to assure the quality of the experiments performed in terms of trueness, a laboratory blank sample was carried out by the direct back extraction of the HF impregnated with 1-octanol without performing the previous extraction step. The results showed the absence of the PAEs studied at least at concentrations equal to and higher than the lowest calibration level (LCL) set at 1 μg/L.

Calibration was evaluated by spiking mineral, tap, pond and waste water at seven concentration levels (n = 7) before extraction and injecting each level in triplicate using DBP-d_4 as IS in all cases at a concentration of 35 μg/L in the sample. As can be seen in Table 2, calibration curves were linear in the range studied (1.0–100.0 μg/L) with R^2 higher than 0.9901 in all cases.

Recovery of the overall method was studied spiking mineral, tap, pond and waste water before the extraction procedure at three concentration levels (IS was added at 35 μg/L in the sample), performing five consecutive replicates (n = 5) at each level (see Table 3). It can be observed that a good level of agreement was obtained between the concentration calculated at the end of the extraction process and the spiked one. In particular, recovery percentages ranged between 74 and 120% with RSD values lower than 20%. This analytical performance shows the feasibility of the procedure for the analysis of this group of PAEs from mineral, tap, pond and waste water with suitable sensitivity.

Finally, the method was applied to the analysis of the studied real samples, by carrying out a duplicate analysis in each case. Results are shown in Table 4 in which it can be seen that only DIBP and DBP were determined above the LCL of the method in mineral and waste water, respectively, though other compounds could also be detected depending on the sample. Both, DIBP and DBP have been previously found in similar samples (Wu et al., 2017; Keresztes et al., 2013). Fig. 5S of the Supplementary Material shows a GC-MS/MS chromatogram of DIBP in mineral water sample and of DBP in waste water sample.

Concerning previous applications of HF-LPME for the extraction of the selected analytes in water samples, among the PAEs

Table 3
Results of the recovery study (n = 5) of the HF-LPME-GC-MS/MS method for the selected PAEs in the different water samples at three levels of concentration.

Analyte	Sample	Level 1[a,d] (n = 5)	Level 2[b,d] (n = 5)	Level 3[c,d] (n = 5)
		Recovery % (RSD %)	Recovery % (RSD %)	Recovery % (RSD %)
DPP	Mineral water	94 (9)	91 (10)	78 (9)
	Tap water	110 (2)	95 (15)	80 (3)
	Pond water	92 (8)	93 (6)	89 (10)
	Waste water	95 (6)	88 (12)	80 (8)
DIBP	Mineral water	95 (7)	102 (8)	87 (6)
	Tap water	105 (5)	99 (10)	87 (1)
	Pond water	120 (12)	95 (6)	90 (5)
	Waste water	90 (7)	92 (7)	88 (6)
DBP	Mineral water	108 (5)	103 (5)	87 (4)
	Tap water	106 (4)	108 (4)	90 (2)
	Pond water	104 (3)	102 (3)	96 (2)
	Waste water	99 (6)	103 (2)	91 (3)
DIPP	Mineral water	104 (5)	95 (13)	84 (4)
	Tap water	100 (11)	104 (5)	98 (6)
	Pond water	99 (5)	96 (3)	95 (7)
	Waste water	94 (6)	94 (7)	96 (8)
DEEP	Mineral water	109 (12)	84 (11)	74 (18)
	Tap water	116 (9)	85 (19)	79 (18)
	Pond water	95 (19)	95 (6)	104 (20)
	Waste water	83 (20)	93 (19)	88 (20)
DNPP	Mineral water	102 (4)	96 (11)	90 (7)
	Tap water	98 (8)	98 (3)	99 (5)
	Pond water	102 (4)	96 (4)	102 (5)
	Waste water	92 (4)	92 (4)	99 (6)
BBP	Mineral water	116 (5)	100 (6)	104 (12)
	Tap water	110 (7)	98 (5)	109 (7)
	Pond water	108 (7)	97 (5)	115 (5)
	Waste water	120 (2)	87 (9)	90 (5)
DBEP	Mineral water	109 (4)	99 (5)	106 (14)
	Tap water	109 (9)	96 (6)	120 (7)
	Pond water	119 (13)	100 (5)	120 (3)
	Waste water	100 (4)	92 (8)	102 (7)
DCHP	Mineral water	109 (5)	103 (6)	92 (15)
	Tap water	108 (10)	103 (9)	103 (2)
	Pond water	110 (7)	99 (7)	112 (7)
	Waste water	96 (4)	96 (10)	98 (4)

[a] Concentration of the analytes in the sample (level 1): 10 μg/L.
[b] Concentration of the analytes in the sample (level 2): 50 μg/L.
[c] Concentration of the analytes in the sample (level 3): 100 μg/L.
[d] Concentration of the IS in the sample: 35 μg/L.

Table 4
Concentration of the studied PAEs found in real water samples.

Analyte	Sample	Found concentration (μg/L)	Analyte	Sample	Found concentration (μg/L)
DPP	Mineral water	n.d.	DNPP	Mineral water	n.d.
	Tap water	n.d.		Tap water	< LCL
	Pond water	n.d.		Pond water	< LCL
	Waste water	< LCL		Waste water	< LCL
DIBP	Mineral water	2.56 ± 2.23	BBP	Mineral water	n.d.
	Tap water	< LCL		Tap water	n.d.
	Pond water	< LCL		Pond water	n.d.
	Waste water	< LCL		Waste water	< LCL
DBP	Mineral water	< LCL	DBEP	Mineral water	n.d.
	Tap water	< LCL		Tap water	n.d.
	Pond water	< LCL		Pond water	n.d.
	Waste water	2.46 ± 1.31		Waste water	< LCL
DIPP	Mineral water	n.d.	DCHP	Mineral water	n.d.
	Tap water	n.d.		Tap water	n.d.
	Pond water	< LCL		Pond water	n.d.
	Waste water	< LCL		Waste water	< LCL
DEEP	Mineral water	n.d.			
	Tap water	n.d.			
	Pond water	n.d.			
	Waste water	n.d.			

n.d.: not detected.

selected in this work, only BBP and DBP have been previously evaluated (Chao et al., 2013a, 2013b; Mtibe et al., 2012; Psillakis and Kalogerakis, 2003). In those publications, only three compounds were determined, except in one case in which six different analytes, including BBP and DBP were extracted from bottled mineral water (Psillakis and Kalogerakis, 2003). The LOQs obtained for both analytes in such works were slightly lower than the ones achieved in this case, although much more complex procedures were used in two of these applications in which push/pull flow approaches (Chao et al., 2013a,b) were necessary to assist the HF-LPME procedure. Concerning the work developed by Mtibe et al. (2012), no validation of the developed methodology was carried out, and, consequently, no comparison can be made since data regarding the quality parameters of the method were not provided.

In general, it should be highlighted that the procedure proposed in this work is very simple and constitutes the first application in which this group of PAEs has been simultaneously analyzed in such variety of water samples (i.e. mineral, waste, tap and pond water) and the first time in which the HF-LPME is applied for the evaluation of this kind of compounds in tap and pond water.

4. Conclusions

A new HF-LPME method was developed and validated for the extraction of 9 PAEs from mineral, tap, pond and waste water samples. The effects of sample pH, ionic strength, extraction time, stirring rate, extraction temperature and desorption procedure were studied. The analytical performance of the optimized method was evaluated and good linearity, recovery and reproducibility were demonstrated for all samples.

As inherent characteristics of this approach, the consumption of solvents was significantly low, high pre-concentration factors were achieved and, since the fibers are extremely cheap, they can be replaced in each extraction (reason why carry-over effects are discarded). In addition, the procedure is simple and several samples can be simultaneously extracted, so the potential of the method for routine analysis (also for more complex samples) is relatively high.

Conflict of interest

Authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.02.180.

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