Talanta 76 (2008) 718–723

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Screening method for phthalate esters in water using liquid-phase microextraction based on the solidification of a floating organic microdrop combined with gas chromatography–mass spectrometry

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ARTICLE INFO

Article history:
Received 8 December 2007
Received in revised form 2 March 2008
Accepted 4 March 2008
Available online 13 March 2008

Keywords:
Liquid-phase microextraction (LPME)
Phthalate esters
Gas chromatography–mass spectrometry (GC–MS)
Water samples

ABSTRACT

A simple and efficient liquid-phase microextraction (LPME) technique was developed using directly suspended organic microdrop coupled with gas chromatography–mass spectrometry (GC–MS), for the extraction and the determination of phthalate esters (dimethyl phthalate, diethyl phthalate, diallyl phthalate, di-*n*-butyl phthalate (DnBP), benzyl butyl phthalate (BBP), dicyclohexyl phthalate and di-2-ethylhexyl phthalate (DEHP)) in water samples. Microextraction efficiency factors, such as nature and volume of the organic solvent, temperature, salt effect, stirring rate and the extraction time were investigated and optimized. Under the optimized extraction conditions (extraction solvent: 1-dodecanol; extraction temperature: 60 °C; microdrop volume: 7 μL; stirring rate: 750 rpm, without salt addition and extraction time: 25 min), figures of merit of the proposed method were evaluated. The values of the detection limit were in the range of 0.02–0.05 $\mu g\,L^{-1}$, while the R.S.D.% value for the analysis of 5.0 $\mu g\,L^{-1}$ of the analytes was below 7.7% ($n = 4$). A good linearity ($r^2 \geq 0.9940$) and a broad linear range (0.05–100 $\mu g\,L^{-1}$) were obtained. The method exhibited enrichment factor values ranging from 307 to 412. Finally, the designed method was successfully applied for the preconcentration and determination of the studied phthalate esters in different real water samples and satisfactory results were attained.

1. Introduction

Phthalate esters (PEs) are well-known polymer additives that are used in formulations of pesticides, paints, poly (vinyl chloride) plastics, and etc. However, their most important use by far is as plasticizers, improving the flexibility and workability of polymeric materials. Having the mentioned properties, the phthalate esters production and their use have increased significantly in the recent years. The main drawback of PEs is that they can migrate from the material to the environment and, consequently, pollute water, soil, air, food products [1–5]. Furthermore, certain phthalate esters and/or their metabolites are suspected to be human cancer-causing agents and endocrine disruptors [6,7] which makes their trace determination of special importance.

The most commonly used phthalates include bis-2-ethylhexyl phthalate (DEHP), di-*n*-butyl phthalate (DnBP) and butyl benzyl phthalate (BBP). DEHP is the most widely used PE in the world and it represents a quarter of the total plasticizers production [8]. These phthalates are on the first three priority lists for the risk assessment, in accordance with the European Union's Regulation 793/93 on the existing substances [9,10]. The US Environmental Protection Agency (EPA) has set the maximum contamination level (MCL) for DEHP in water systems at 6 $\mu g\,L^{-1}$ and recommended that concentrations above 0.6 $\mu g\,L^{-1}$ should be closely monitored [11].

Gas chromatography (GC) [12–15] and high performance liquid chromatography (HPLC) [16–18] have been used commonly for the detection of these compounds in water samples. Nevertheless, when the concentration levels are low, a previous enrichment step is usually needed. The preconcentration techniques, which are commonly applied to monitor phthalates in water, are liquid–liquid extraction (LLE) with dichloromethane or hexane [2,15] and solid-phase extraction (SPE) [2,16,18]. However, these sample pretreatment methods are considered expensive, time-consuming and labor-intensive methods, which often result in high blank values [19].

Solid-phase microextraction (SPME), now a commercial product, was developed by Pawliszyn's group [20]. It is an innovative solvent-free procedure that has gained tremendous popularity. It

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0039-9140/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.talanta.2008.03.002

satisfies most of the desired characteristics of a sample preparation technique mentioned above, having been used for numerous applications particularly in environmental, biological and pharmaceutical analyses [21–27], including some PEs [4,5,17,27]. In addition, it is portable, relatively fast and it can be automated and coupled online with analytical instrumentation. Nevertheless, the coated fibers may be considered to be expensive and, for some applications, they have limited lifetimes [28,29].

Liquid-phase microextraction (LPME) is a fairly new method of sample preparation [30]. It is a miniaturized implementation of the conventional LLE, where only microliters of the solvents are used. LPME has been used to preconcentrate compounds from aqueous samples [31–38]. In 2003, Psillakis and Kalogerakis developed the hollow-fiber LPME (HFLPME), combined with GC for the PEs determination in water samples [39]. This technique is simple, inexpensive and providing minimal exposure to toxic organic solvents.

Recently, Yamini and co-workers have reported a simple and efficient preconcentration and microextraction method, based on LPME, which was initially applied for the determination of polycyclic aromatic hydrocarbons (PAHs) in water samples [40]. In this technique, a free microdrop of the organic solvent is delivered to the surface of an aqueous sample, while being agitated by a stirring bar in the bulk of the solution. Under the proper stirring conditions, the suspended microdrop can remain in the top-center position of the aqueous sample. After the completion of the extraction, the sample vial is cooled by placing it into an ice bath for 4 min. The solidified microdrop is then transferred into a conical vial, where it melts immediately. Finally, the analytes determination in the extractant can be performed by GC. This quantitative LPME method is a green and satisfactory analytical procedure, for which excellent accuracy and precision are demonstrated, being simpler and more convenient, compared with the conventional sample preparation methods.

The goal of this study was to assess the technique suitability for the detection of a group of the PEs compounds in water samples. The analytes were monitored by gas chromatography combined with mass spectrometry (GC–MS). The influence of different experimental parameters on the yield of the sample preparation step is described and discussed. In the end, this recommended method was employed to investigate the levels of the target species in several water samples.

2. Experimental

2.1. Reagents

The studied compounds were dimethyl- (DMP), diethyl- (DEP), diallyl- (DAP), di-*n*-butyl- (DnBP), benzyl butyl- (BBP), dicyclohexyl- (DCHP) and di-2-ethylhexyl- (DEHP) phthalate esters. All PEs were purchased from Merck (Darmstadt, Germany). The stock standard solutions of 2000.0 mg L^{-1} of each compound were prepared in methanol. The working standard solution of 100 mg L^{-1} was prepared weekly in methanol. The stock and working standard solutions were stored at 4 °C at the refrigerator. The aqueous solutions were prepared daily by diluting the working solution with water. The used reagent water was purified with a Milli-Q water purification system (Millipore, Bedford, MA, USA). 1-Undecanol, 1-dodecanol, 2-dodecanol and *n*-hexadecane as the extraction solvents, benzyl benzoate as the internal standard as well as sodium chloride were purchased from Merck (Darmstadt, Germany). A solution of the internal standard with the concentration of 2.0 mg L^{-1} in 1-dodecanol was used as the extracting solvent.

2.2. Instrumentation

The analysis was performed on a Hewlett-Packard (Agilent Technologies, Palo Alto, CA, USA) HP 6890 series GC, equipped with a split/splitless injector and a HP 5973 mass selective detector system. The MS was operated at the electron impact (EI) mode (70 eV). The chromatographic data were recorded using a HP Chemstation, which was controlled by Windows NT (Microsoft). Helium (99.999%) was employed as carrier gas at the flow rate of 0.8 mL min^{-1}. The analytes were separated on a 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5MS gas chromatographic column (J&W Scientific, Folsom, CA, USA) with the following oven temperature program: initial 60 °C, from 60 °C (held 3 min) to 180 °C at 20 °C min^{-1}, increased at 10 °C min^{-1} to 285 °C and held for 5 min. The injection port was operated at 350 °C and was used at the split mode with a split ratio of 1:10. The EI ion source, quadrupole mass analyzer and the interface temperature were maintained at 230, 150 and 280 °C, respectively. The MS was tuned to *m*/*z* 69, 219 and 502 for the EI corresponding to perfluorotetrabutylamine (PFTBA). It was equipped with the mass spectral library Wiley 275, which was used to compare the obtained experimental spectra. The MS was operated on the total ion current (TIC) mode, scanning from *m*/*z* 50 to 550 for identification purposes. To gain the highest possible sensitivity, the acquisition was performed at the selected ion monitoring (SIM) mode, based on the selection of some mass peaks of the highest intensity for each compound. Table 1 lists the retention times, selected masses and the start scan times for each compound studied by GC–MS.

A magnetic heater-stirrer (IKA-Werke, Staufen, Germany) and an 8 mm × 1.5 mm PTFE coated stirring bar were used to stir the solutions. A simple water bath placed on the heater-stirrer was used for control the temperature of the sample solutions. All injections were carried out using a 1.00 μL microsyringe (zero dead volume, cone tip needle, SGE, Australia).

Table 1
Retention times, selected ions, scan start time and some quantitative data of the PEs studied by the LPME–GC–MS

Compound	Retention time (min)	Selected ions (*m*/*z*)	Scan start time (min)	LOD[a,b] (μg L^{-1})	r^2	LR[b,c] (μg L^{-1})	EF[d]	R.S.D.%[e] (*n* = 4)
DMP	10.5	163, 194	10.0[f]	0.03	0.9947	0.05–100	391	5.8
DEP	11.4	149, 177	11.0	0.02	0.9959	0.05–100	358	6.4
DAP	13.8	149, 189	13.3	0.02	0.9953	0.05–50	412	7.7
DnBP	15.5	149, 223	15.0	0.03	0.9960	0.05–50	376	5.5
BBP	18.8	149, 206	18.3	0.03	0.9940	0.05–100	389	7.3
DCHP	20.2	149, 167	19.8	0.05	0.9971	0.1–50	307	6.9
DEHP	20.4	149, 279	20.3	0.02	0.9955	0.05–100	409	6.1

[a] Limit of detection for S/N = 3.
[b] Concentration unit is μg L^{-1}.
[c] Linear range.
[d] Enrichment factor.
[e] Relative standard deviation at the concentration of 5.0 μg L^{-1} of each PE.
[f] The MS detector was OFF before the time point of 10.0 min.

2.3. Analytical procedure

A total of 10.0 mL of the aqueous PEs solution (containing 5.0 μg L^{-1} of each PE) was transferred into an 11.0 mL vial. 10.0 μL of 1-dodecanol were delivered to the solution surface using a 10.0 μL model 701 N microsyringe (Reno, NV, USA). The vial was sealed and then the magnetic stirrer was turned on. Under the proper stirring conditions, the suspended microdrop could remain in the top-center position of the aqueous sample. In an immiscible liquid–liquid system with the proper interface tension, the microdrop would not break up even in the absence of any support from the microsyringe needle, polymer rod or other supporting material like hallow fibers. On the other hand, the microdrop movement was affected by the flow field, which favored the promotion of the mass transfer inside the microdrop [40]. After the desired extraction time, the sample vial was transferred into an ice beaker and the organic solvent was solidified after 4 min. Then, the solidified solvent was transferred into a conical vial and it melted immediately. Finally, 1.00 μL of the extractant was injected into the gas chromatograph.

A univariate approach was employed to optimize the influential factors in this method. All quantifications, made in this study, were based on the relative peak area of the analyte to the internal standard (benzyl benzoate) from the average of three replicate measurements.

3. Results and discussion

3.1. Selection of the extracting solvent

The selection of an appropriate extraction solvent is of great importance for the optimization of the LPME process. To choose a suitable organic solvent, the following points should be considered. Firstly, the chosen solvent should illustrate a high boiling point and a low vapor pressure in order to reduce the risk of evaporation [41]. Secondly, it should exhibit a good chromatographic behavior [42] and, thirdly, the partitioning coefficient of the analyte should be high. Furthermore, the solvent must have a good affinity for the target compounds [43] and, finally, it should demonstrate a melting point near the room temperature (in the range of 10–30 °C) [40]. According to these considerations, several extracting solvents, including 1-undecanol, 1-dodecanol, 2-dodecanol and *n*-hexadecane were considered. Among the tested extracting solvents, 1-dodecanol presented the best extraction efficiency (Fig. 1). Thus, 1-dodecanol was chosen as the extracting solvent in this investigation. In order to improve the precision and accuracy of the method, benzyl benzoate was used as the internal standard and was added into the extracting solvent.

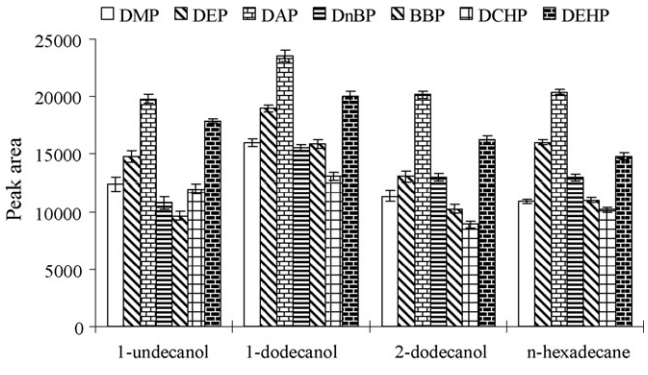

Fig. 1. The effect of the organic solvent type on the extraction efficiency. Conditions: sample volume, 10.0 mL; extraction temperature, 60°C; extraction solvent volume, 10.0 μL; stirring rate, 600 rpm; extraction time, 30 min, and without salt addition.

3.2. Sample solution temperature

Solution temperature affects extraction kinetics. At higher temperatures, diffusion coefficients of analytes increase, therefore, this process facilitated the mass transfer of the analyte from the sample to the organic solvent and the time required to reach equilibrium decrease [44]. The effect of the sample solution temperature on the extraction efficiency was studied in the temperature range of 30–70 °C by floating a 1-dodecanol microdrop for 30 min on the surface of the water samples. The experimental results clearly exhibited that by increasing the temperature, the extraction efficiency increased for all the analytes. However, high temperatures (>60 °C) can alter the microdrop size dramatically and cause over-pressurization in the sample vial, making the extraction system unstable. For this reason, the solution temperature was held at 60 °C for the subsequent experiments.

3.3. Effect of the ionic strength

The effect of salt concentration on the extraction efficiency was studied with different NaCl concentrations in the range of 0–4 mol L^{-1} (Fig. 2). The results revealed that in this method the salt addition restricted the extraction of the target analytes, except for that of DMP. A possible explanation for this observation may be that apart from the salting-out effect, NaCl dissolved in the aqueous solution may have changed the physical properties of the Nernst diffusion film and reduced the rate of diffusion of the target analytes into the drop [44]. This means that by increasing salt concentration, the diffusion of analytes towards the organic drop becomes more and more difficult and thus limits extraction [34,45]. Hence, we decided not to alter the salt content of the sample solutions in the following extractions as the sensitivity of the procedure was not poor.

3.4. Organic solvent volume

Based on LLE equations, the rate of the analytes transport into the microdrop is directly related to the interfacial area between the two liquid phases and inversely related to the organic-phase volume [46–48]. Therefore, by increasing the drop volume, the effect of the interfacial area predominates and the analytical signals increase. By further increasing of the microdrop volume, the effect of the solvent volume is predominated and the analytical signals are decreased [49,50]. The influence of the organic solvent volume on the analytical signal was studied in the range of 6.0–12.0 μL. Fig. 3 depicts that the PEs analytical signals increase by increasing

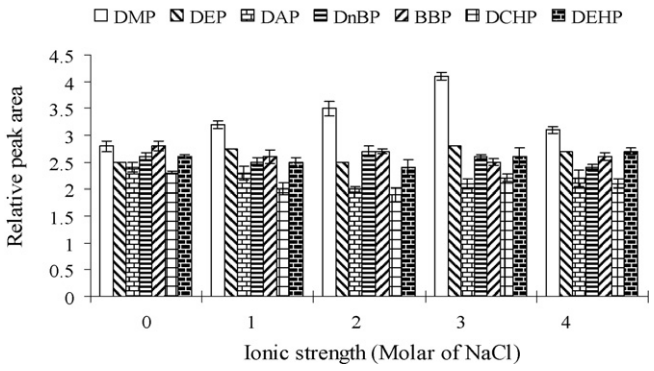

Fig. 2. The effect of the salt addition on the relative peak area. Extraction conditions as with Fig. 1, extraction solvent: 1-dodecanol.

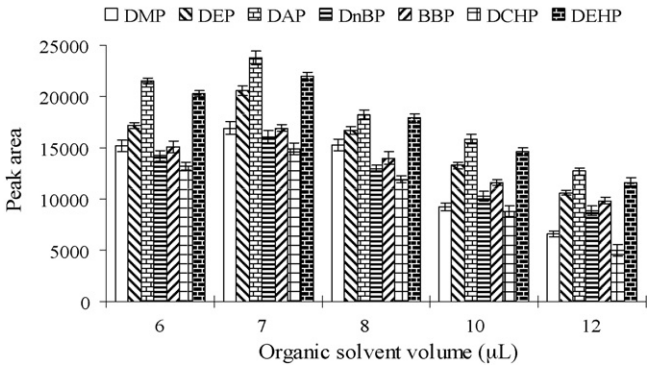

Fig. 3. The effect of the organic solvent volume on the extraction efficiency. Extraction conditions as with Fig. 2.

the solvent volume to 7 μL, but it diminished when the solvent volume was increased to 12.0 μL. So, volume of 7 μL was selected as the optimum.

3.5. Stirring rate

Magnetic stirring enhances extraction and reduces the time required to reach thermodynamic equilibrium, and facilitate the mass transfer process and thus improves the extraction efficiency [51,32,33]. In this work, samples with the volume of 10.0 mL were agitated at different stirring rates (0, 150, 300, 450, 600 and 750 rpm). According to obtained results, the relative peak area of all analytes increases with the stirring rate up to 750 rpm. Higher stirring rates (>750 rpm) were not used, because, in this case the microdrop was spattered and damaged. Hence, for the following studies, the stirring rate of 750 rpm was chosen.

3.6. Extraction time

Like SPME, LPME is not an exhaustive extraction method under real conditions [52–54]. To increase repeatability of the extraction, it is necessary to choose an extraction time during which the equilibrium between the aqueous and the organic phase is reached. The time for reaching equilibrium determines the maximum amount of analyte that can be extracted by the microdrop [31,55]. The extraction time was investigated in the range of 5–35 min at the optimized experimental conditions. The relative peak areas increased with the extraction time up to 25 min (Fig. 4). After 25 min, the extraction system basically reached a steady state and no dramatic increase in the relative peak areas was observed with an additional extraction time. Therefore, a 25 min extraction time was selected for subsequent experiments.

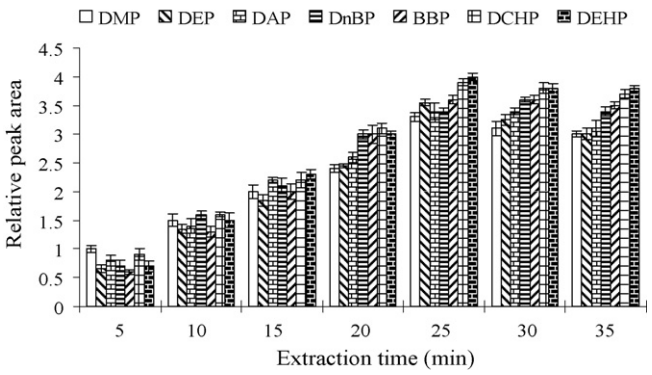

Fig. 4. The effect of the extraction time on the extraction efficiency. Extraction conditions as with Fig. 2, organic solvent volume: 7.0 μL and stirring rate: 750 rpm.

3.7. Evaluation of the method performance

Under the selected optimum experimental conditions, the suggested methodology was applied to a series of standard solutions containing various analytes concentrations, in order to develop the respective calibration curves. For each level, three replicate extractions were conducted. The limit of detections (LODs), based on the signal-to-noise ratio (S/N) of three, the correlation coefficients (r^2), the linear ranges (LRs), the relative standard deviations (R.S.D.s) and the enrichment factors (EFs) were calculated and summarized in Table 1.

For the EF calculation of each analyte, three replicate extractions were performed at the optimal conditions from the aqueous solution, containing 5.0 μg L^{-1} of the analytes. The EF was calculated as the ratio of the final analyte concentration in the microdrop and its concentration in the original solution. The PEs standard solutions were prepared in 1-dodecanol as solvent and the calibration curves were drawn in the concentration range of 0.25–2.5 mg L^{-1} with three replicate direct injections. The actual concentration of each extracted analyte in 1-dodecanol was calculated from the calibration curves and the EFs were determined.

As it is illustrated in Table 1, LODs for the tested PEs were found to be 0.02 up to 0.05 μg L^{-1}. The linearity values varied from 0.05 to 100 μg L^{-1} with a correlation coefficient of 0.9940–0.9971. The precision of the method was investigated with a 5.0 μg L^{-1} PEs mixed standard solution. Regarding the R.S.D.s for four replicates, they varied from 5.5 to 7.7%, while the EF values ranged from 307 to 412.

3.8. Comparison of this technique with other methods

Table 2 indicates the LOD, LR and R.S.D. values, the extraction time and the sample volumes of other methods together with LPME (present method) for the PEs extraction and determination from water samples. In comparison with other microextraction methods, LPME provided a comparable LOD value and a wider linear range. Moreover, the precision of the recommended method was better than those of SPME and HFLPME and also comparable with that of single drop microextraction (SDME). The required volume of the sample solution for this procedure was small, same as SPME and HFLPME. Also, the extraction time was relatively short and was comparable with the other methods. All these results revealed that this technique is sensitive, rapid and reproducible that can be used for the PEs preconcentration in water samples and be extended to other applications.

3.9. Real water analysis

The performance of this system was tested by analyzing the PEs in four different water samples – tap water from our chemical laboratory (University of Tehran), two drinking mineral water samples available at the supermarket packed in polymeric containers (Cheshmeh and Koohrang) and Jajrood river water (Tehran, Iran). The tap and river water samples were collected in glass bottles. The river water sample was filtered before the analysis using a 0.45 μm nylon membrane filter (Whatman, Maid-stone, UK) to eliminate the particles. All water samples were transported and stored at the refrigerator at 4 °C until their analysis time. The results showed that the analyzed samples had not been contaminated by PEs. All the real water samples were spiked with the PEs standard solutions at different concentration levels to assess the matrix effects. The relative recoveries of the analytes are given in Table 3. The obtained relative recoveries were between 84–115%, exhibiting that the real water matrices in our present context had little effect on LPME. After performing LPME, the chromatograms obtained by GC–MS of the mineral water (Koohrang) are displayed in Fig. 5, prior to (a)

Table 2
The results obtained from the analysis of the real water samples

Sample	DMP	DEP	DAP	DnBP	BBP	DCHP	DEHP
Tap water (0.20 μg L^{-1} added)							
Concentration (μg L^{-1})	ND[a]	ND	ND	ND	ND	ND	ND
Found (μg L^{-1})	0.181	0.188	0.214	0.219	0.192	0.167	0.228
Relative recovery (%)	91	94	107	110	96	84	114
R.S.D.% (n = 4)	7.1	7.9	8.1	6.5	6.8	8.4	8.8
Mineral water, Cheshmeh (0.80 μg L^{-1} added)							
Concentration (μg L^{-1})	ND	ND	ND	ND	ND	ND	ND
Found (μg L^{-1})	0.705	0.735	0.876	0.762	0.905	0.914	0.898
Relative recovery (%)	88	92	110	95	113	114	112
R.S.D.% (n = 4)	6.9	8.5	5.7	6.8	8.2	9.0	7.2
Mineral water, Koohrang (5.0 μg L^{-1} added)							
Concentration (μg L^{-1})	ND	ND	ND	ND	ND	ND	ND
Found (μg L^{-1})	4.59	5.35	5.29	5.68	5.77	4.81	4.44
Relative recovery (%)	92	107	106	114	115	97	89
R.S.D.% (n = 4)	7.5	7.4	6.1	8.2	5.9	9.40	7.8
Jajrood river water (20.0 μg L^{-1} added)							
Concentration (μg L^{-1})	ND	ND	ND	ND	ND	ND	ND
Found (μg L^{-1})	21.71	19.05	220.91	22.26	19.31	18.12	21.97
Relative recovery (%)	109	95	105	111	97	91	110
R.S.D.% (n = 4)	7.4	9.1	6.4	8.1	9.8	8.7	8.4

[a] Not detected.

Table 3
Comparison of the LPME with the other methods performing PEs determination

Method	LOD[a] (μg L^{-1})	LR[b] (μg L^{-1})	R.S.D.[c] (%)	Extraction time (min)	Sample volume (mL)	References
SDME–GC–FID	0.02–0.1	0.1–50	3.5–8	25	20	[55]
SPME–GC–MS	0.003–0.01	0.1–10	4–11	20	5	[39]
HFLPME–GC–MS	0.005–0.1	0.5–10	4–19	20	5	[39]
LPME–GC–MS	0.02–0.05	0.05–100	5.5–7.7	25	10	Present method

[a] Limit of detection.
[b] Linear range.
[c] Relative standard deviation.

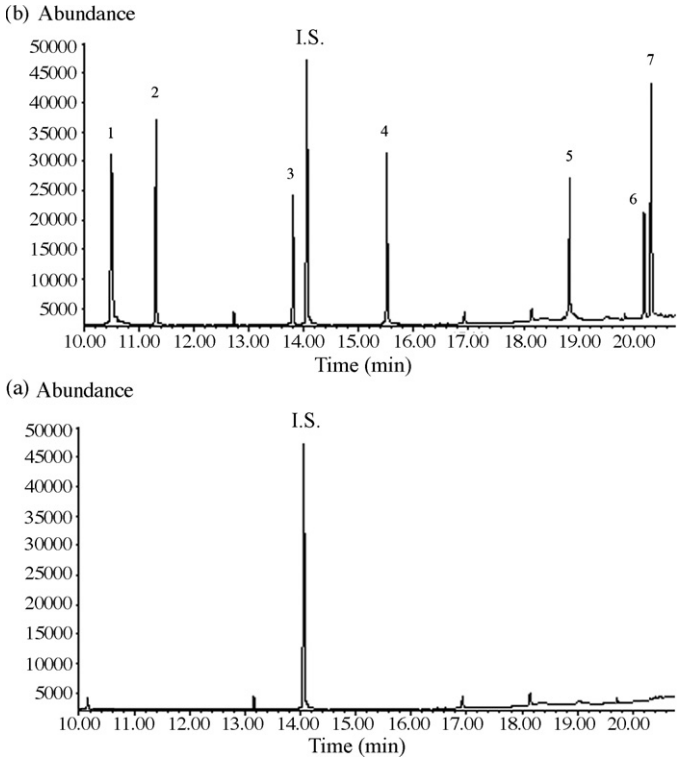

Fig. 5. The chromatograms obtained by GC–MS of the mineral water (Cheshmeh) after performing LPME, without spiking PEs (a) and spiked with PEs (b) at the concentration level of 5.0 μg L^{-1} of each analyte. Peak numbers correspond to (1) DMP; (2) DEP; I.S.: benzyl benzoate; (3) DAP; (4) DnBP; (5) BBP; (6) DCHP; (7) DEHP.

and after spiking the plasticizers (b) at the concentration level of 5.0 μg L^{-1} of each analyte.

4. Conclusion

This paper outlines a successful development and application of a method based on the LPME technique, combined with the capillary GC–MS, for the qualitative and quantitative analysis of the PEs group in water samples. The designed method is concluded to be precise, reproducible and linear over a broad range with sufficient selectivity (using the MS detector at the SIM mode) and high sensitivity. Compared with other conventional sample preparation methods, the analytical technique offered numerous advantages such as simplicity, low cost, ease of operation, no possibility of sample carry-over and high enrichment factors. In addition, the technique requires only a small volume of organic extractants, being therefore an environmentally friendly approach. The performance of this procedure in the PEs extraction from different water samples with various matrices was excellent. Subsequently, this method can be used routinely for screening purposes.

Acknowledgement

This work has been supported by grants from the University of Tehran Research Council which is hereby gratefully acknowledged.

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