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Development of dispersive liquid–liquid microextraction combined with gas chromatography–mass spectrometry as a simple, rapid and highly sensitive method for the determination of phthalate esters in water samples

Hadi Farahani [a], Parviz Norouzi [a,b], Rassoul Dinarvand [c], Mohammad Reza Ganjali [a,b,*]

[a] *Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, P.O. Box 14155-6455, Tehran, Iran*
[b] *Endocrinology & Metabolism Research center, Medical Science/University of Tehran, Tehran, Iran*
[c] *Medical Nanotechnology Research Center, Medical Sciences/University of Tehran, P.O. Box 14155-6451, Tehran, Iran*

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Abstract

A simple, rapid and efficient method, the dispersive liquid–liquid microextraction (DLLME) in conjunction with gas chromatography–mass spectrometry (GC–MS), has been developed for the extraction and determination of phthalate esters (dimethyl phthalate, diallyl phthalate, di-*n*-butyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate and di-2-ethylhexyl phthalate) in water samples. Factors relevant to the microextraction efficiency, such as the kind of extraction, the disperser solvent and their volume, the salt effect and the extraction time were investigated and optimized. Under the optimized extraction conditions (extraction solvent: chlorobenzene, volume, 9.5 μL; disperser solvent: acetone, volume, 0.50 mL, without salt addition and extraction time below 5 s), the figures of merit of the proposed method were evaluated. The values of the detection limit of the method were in the range of 0.002–0.008 μg L^{-1}, while the RSD% value for the analysis of 1 μg L^{-1} of the analytes was below 6.8% ($n = 4$). A good linearity ($0.9962 \geq r^2 \geq 0.9901$) and a broad linear range (0.02–100 μg L^{-1}) were obtained. The method exhibited enrichment factors and recoveries, ranging from 681 to 889 and 68.1 to 88.9%, respectively, at room temperature (25 ± 1 °C). Finally, the proposed method was successfully utilized for the preconcentration and determination of the phthalate esters in different real water samples and satisfactory results were obtained.

Keywords: Dispersive liquid–liquid microextraction (DLLME); Phthalate esters; Gas chromatography-mass spectrometry (GC–MS); Water samples

1. Introduction

Phthalate esters (PEs, Fig. 1) have a wide variety of industrial, agricultural and domestic applications, but by far the most important is their use as plasticizers that improve the flexibility and workability of polymeric materials. Because of these properties, in the recent years, phthalate esters production and use have increased significantly. PEs can migrate from the material to the environment and consequently, they are often found in water, soil, air, food products and human body [1–5]. Little is known about the possible effects of these substances on the environment and human health but some recent studies have shown that they may cause hormone disrupting activities [6,7]. Some PEs are included in the priority of pollutants in several countries [2,8]. For example, the US Environmental Protection Agency (EPA) has established a maximum admissible concentration (MAC) value in water of 6 μg L^{-1} for di-2-ethylhexyl phthalate (DEHP) [9]. DEHP is the most widely used PE in the world and it represents a quarter of the total production of plasticizers [10].

Gas chromatography (GC) [11–14] and high-performance liquid chromatography (HPLC) [15–17] have been used for the detection of these compounds in water samples. Nevertheless, when the concentration levels are low, a previous enrichment

* Corresponding author at: Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, P.O. Box 14155-6455, Tehran, Iran. Tel.: +98 21 61112788; fax: +98 21 66405141.
E-mail address: ganjali@khayam.ut.ac.ir (M.R. Ganjali).

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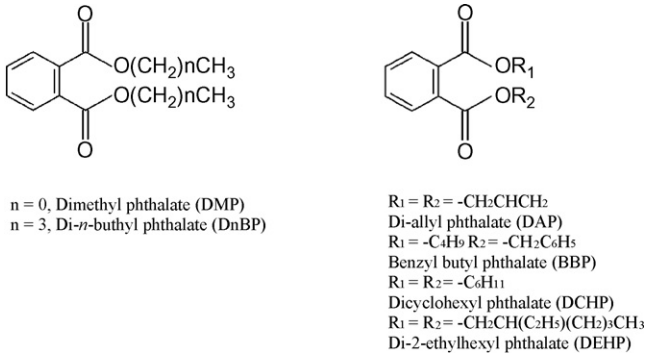

Fig. 1. Structural formula of the PEs.

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 [2,14] and solid-phase extraction (SPE) [2,6,15,17]. However, these conventional pretreatment methods need either large quantities of sample and organic solvents, or are time-consuming and the materials used are not reusable, and expensive [18]. Solid-phase microextraction (SPME) is a sample preparation technique, introduced by Arthur and Pawiliszyn [19] that has received increasing attention, and is now widely accepted as a reliable technique. Thus, SPME has been applied to determine a wide variety of organic compounds from numerous types of samples [20–26], including some PEs [4,5,16,26]. SPME has important advantages over conventional extraction techniques, because it is solvent free, fast, portable and easy to use. But it also suffers from some drawbacks: its fiber is fragile and has limited lifetime and the sample carry-over is also a problem [27,28]. Liquid-phase microextraction (LPME) has been developed as an alternative extraction technique. This method provides analyte extraction using only a few microliters of organic solvent. LPME avoids some problems of the SPME method such as fiber degradation; it is also fast, inexpensive and uses very simple equipments. Moreover, although a variety of SPME fibers is commercially available, the choice of solvents for LPME is much broader and the organic phase is renewable at negligible cost [29]. In 2003, Psillakis and Kalogerakis developed hollow fiber LPME (HFLPME) combined with GC for the determination of PEs in water samples [30]. This technique is simple, efficient and there is minimal exposure to toxic organic solvents.

Recently, Assadi and co-workers have developed a simple and rapid preconcentration and microextraction method, named dispersive liquid–liquid microextraction (DLLME), which was initially applied for the determination of polycyclic aromatic hydrocarbons (PAHs) in water samples [31]. This method consists of two steps: (1) the injection of an appropriate mixture of extraction and disperser solvent into aqueous samples, containing the analytes. In this step, the extraction solvent is dispersed into the aqueous sample as very fine droplets and the analytes are enriched into it. Owing to the considerably large surface area between the extraction solvent and the aqueous sample, the equilibrium state is achieved quickly and the extraction is independent of time. This is the most important advantage of this method. (2) The centrifugation of cloudy solution. After centrifugation, the determination of the analytes in the sedimented phase can be performed by instrumental analysis. Rapidity, high enrichment factor, operation simplicity and low cost are some of the advantages of this method.

The goal of this study is to assess the DLLME suitability for the determination of a group of PE compounds in water samples. The analytes were determined by gas chromatography combined with mass spectrometry (GC–MS). The influence of the 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 real water samples.

2. Experimental

2.1. Reagents

The studied compounds were dimethyl (DMP), 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 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 used reagent water was purified with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Chlorobenzene (GR), carbon tetrachloride (GR) and tetrachloroethylene (extra pure) as extraction solvents, acetone (for spectroscopy), acetonitrile and methanol (HPLC grade) as disperser solvents as well as sodium chloride were purchased from Merck (Darmstadt, Germany). Tap water sample from our chemistry laboratory (University of Tehran), two drinking mineral water samples available at the supermarket, packed in polymeric containers (Ploor and Damash) and a Jajrood river water sample (Tehran, Iran) were obtained to be tested as real samples. 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.

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 0.9 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 90 °C, from 90 °C (held 2 min) to 190 °C at 20 °C min^{-1}, increased at 10 °C min^{-1} to 290 °C and held for 4 min. The injection port

Table 1
Retention times, selected ions and scan start time of the compounds studied by GC–MS

Compound	Retention time (min)	Selected ions (*m/z*)	Scan start time (min)
DMP	9.7	163, 194	8.0[a]
DAP	12.4	149, 189	11.5
DnBP	14.4	149, 223	13.5
BBP	17.8	149, 206	16.5
DCHP	19.2	149, 167	18.5
DEHP	19.4	149, 279	19.3

[a] The MS detector was OFF before time 8.0 min.

was operated at 350 °C and was used at the splitless mode at the splitless time of 1 min. 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.

2.3. Extraction procedure

Five milliliters of doubly distilled water were placed in a 10 mL screw cap glass test tube with conic bottom and spiked at level of 1.00 μg L^{-1} of PEs. Acetone (0.50 mL) as a disperser solvent, containing 9.5 μL chlorobenzene (as extraction solvent) was injected rapidly into the sample solution using a 0.50 mL syringe (gastight, Hamilton, USA). In this step, a cloudy solution (water/acetone/chlorobenzene) was formed in the test tube and the PEs in the water sample were extracted into fine chlorobenzene droplets. The mixture was then centrifuged for 2 min at 4000 rpm. The volume of the sedimented phase was determined by a 10 μL microsyringe, which was about 5.0 μL. 0.5 μL of the sedimented phase were removed by a 1.00 μL microsyringe (zero dead volume, cone tip needle, SGE, Australia) and injected into GC.

3. Results and discussion

There are various parameters affecting the DLLME performance and efficiency, including the kind and the volume of the extraction and the disperser solvent, the ionic strength and the extraction time. These parameters were investigated and, then, the optimal conditions were selected. A univariate approach was employed to optimize the influential factors in this method. In order to study the performance parameters, the extraction recovery and the enrichment factor were employed. The Eqs. (1) and (2) were used for the calculation of the enrichment factor and recovery:

$$\mathrm{EF} = \frac{C_{\mathrm{sed}}}{C_0} \tag{1}$$

where EF, C_{sed} and C_0 are the enrichment factor, the analyte concentration in the sediment and the initial analyte concentration in the aqueous samples, respectively.

$$R\% = \frac{C_{\mathrm{sed}} V_{\mathrm{sed}}}{C_0 V_{\mathrm{aq}}} \times 100 = \mathrm{EF} \times \frac{V_{\mathrm{sed}}}{V_{\mathrm{aq}}} \times 100 \tag{2}$$

where $R\%$, V_{sed} and V_{aq} are the extraction recovery, the volume of the sediment phase and the volume of the aqueous sample, respectively. These parameters were known, except for C_{sed}. The C_{sed} calculation was conducted by the direct injection of the PEs standard solutions in chlorobenzene with concentrations in the range of 0.5–2.5 mg L^{-1}.

3.1. Selection of the extraction solvent

The choice of an appropriate extraction solvent has a main role in this method in order to achieve good recovery, enrichment factor and selectivity of the target compounds. The extraction solvent has to meet four requirements. It should demonstrate (a) higher density than water, (b) good chromatographic behavior, (c) extraction capability for the interested compounds and (d) low solubility in water [32]. Chlorobenzene, carbon tetrachloride and tetrachloroethylene were examined in order to find the most suitable solvent for DLLME. For this purpose, a series of sample solutions were studied, using 0.50 mL acetone containing different volumes of the extraction solvent to achieve 5.0 μL volume of the sedimented phase. Thereby, 7.2, 9.5 and 10.0 μL of tetrachloroethylene, chlorobenzene and carbon tetrachloride were used, respectively. The average recovery (triplicate) and the standard deviation (SD) for the different extraction solvents are depicted in Table 2. The results revealed that C_6H_5Cl presented the highest extraction efficiency (68.1–88.9%) in comparison with the C_2Cl_4 (50.3–69.6%) and CCl_4 (33.1–55.2%). For this reason, C_6H_5Cl was selected as the extraction solvent.

Table 2
Efficiency of different extraction solvents evaluated for extraction of PEs by DLLME

Compound	Recovery (%)		
	Chlorobenzene, mean ± SD (n = 3)	Tetrachloroethylene, mean ± SD (n = 3)	Carbon tetrachloride, mean ± SD (n = 3)
DMP	68.1 ± 3.5	50.3 ± 4.9	44.6 ± 2.1
DAP	82.2 ± 2.9	69.6 ± 3.4	41.5 ± 6.8
DnBP	72.3 ± 3.1	62.3 ± 2.8	55.2 ± 2.2
BBP	88.9 ± 4.3	54.4 ± 6.1	33.1 ± 5.9
DCHP	81.6 ± 4.8	63.7 ± 5.5	41.3 ± 1.8
DEHP	70.7 ± 5.0	52.0 ± 2.6	48.1 ± 4.1

Extraction conditions: Water sample volume, 5.00 mL; disperser solvent (acetone) volume, 0.50 mL; extraction solvent volumes, 7.2 μL tetrachloroethylene, 10.0 μL carbon tetrachloride and 9.5 μL chlorobenzene; sedimented phase volume, 5.0 ± 0.3 μL; room temperature (25 ± 1 °C); concentration of each phthalate esters, 1.00 μg L^{-1}.

Table 3
Efficiency of different disperser solvents evaluated for extraction of PEs by DLLME

Compound	Recovery (%)		
	Acetone, mean ± SD ($n = 3$)	Acetonitrile, mean ± SD ($n = 3$)	Methanol, mean ± SD ($n = 3$)
DMP	65.0 ± 4.8	63.1 ± 6.3	65.5 ± 5.3
DAP	82.6 ± 5.7	72.3 ± 5.8	75.3 ± 6.6
DnBP	72.4 ± 4.9	68.7 ± 5.5	75.9 ± 5.0
BBP	89.6 ± 5.1	92.2 ± 6.6	90.5 ± 5.4
DCHP	81.2 ± 4.6	80.4 ± 6.7	90.0 ± 4.9
DEHP	70.9 ± 5.0	74.1 ± 6.3	61.1 ± 5.9

Extraction conditions: Water sample volume, 5.00 mL; disperser solvent (acetone, acetonitrile and methanol) volume, 0.50 mL; extraction solvent (chlorobenzene) volume, 9.5 μL; sedimented phase volume, 5.0 ± 0.3 μL; room temperature (25 ± 1 °C); concentration of each analyte, 1.00 μg L^{-1}.

3.2. Selection of the disperser solvent

The miscibility of the disperser solvent in the organic phase (extraction solvent) and the aqueous phase (sample solution) is the main point for the selection of the disperser solvent [33]. Acetone, acetonitrile and methanol, illustrating this ability, were selected for this purpose. A series of sample solutions were studied, using 0.50 mL of each disperser solvent containing 9.5 μL of extraction solvent (chlorobenzene). The summarized results in Table 3 indicated that the recoveries with the employment of acetone, acetonitrile and methanol as disperser solvents were 68.0–89.6, 63.1–92.2 and 61.1–90.5%, respectively. According to these results, the recovery variations, using different disperser solvents, were not remarkable. For this reason, acetone was selected because of its low toxicity and cost.

3.3. Effect of the extraction solvent volume

In order to evaluate the effect of the extraction solvent volume on the extraction efficiency, additional experiments were performed using 0.50 mL acetone containing different chlorobenzene volumes (9.5, 14.5, 19.5, 24.5 μL). Figs. 2 and 3 display the volume curves of the sedimented phase and enrichment factor of the PEs versus the volume of the extraction solvent, respectively. With the increase of the extraction solvent volume from 9.5 to 24.5 μL, the volume of the sedimented phase increased (5.0–19.5 μL) (Fig. 2). Therefore, the enrichment factor decreased from 681–889 to 176–221 (Fig. 3). Also, the extraction recovery was almost constant (from 68.1–88.9 to 68.6–86.2%). Thus, 9.5 μL of chlorobenzene were selected in order to obtain high enrichment factors and low detection limit values.

3.4. Effect of the disperser solvent volume

The variation of the acetone volume (as disperser solvent) causes changes in the volume of the sedimented phase. To avoid this problem and in order to achieve a constant volume of the sedimented phase, the acetone and chlorobenzene volume was changed, simultaneously. The experimental conditions were fixed and included the use of different acetone volumes, 0.25, 0.50, 1.00, 1.50 and 2.00 mL containing 9.0, 9.5, 12.5, 16.2, 22.4 μL chlorobenzene, respectively. In this step, the volume of sedimented phase was constant (5.0 ± 0.3 μL). The results in Fig. 4 exhibit that the extraction efficiency increased firstly and, then, decreased with the increase of the acetone volume for most of the PEs. It seems that at a low acetone volume, the cloudy state is not formed well and, consequently, the recovery is low. At higher acetone volume, the PE solubility in water increased. Therefore, the extraction efficiency reduced, because of the distribution coefficient decrease. In line with these results, a 0.50 mL acetone volume was chosen as the optimum.

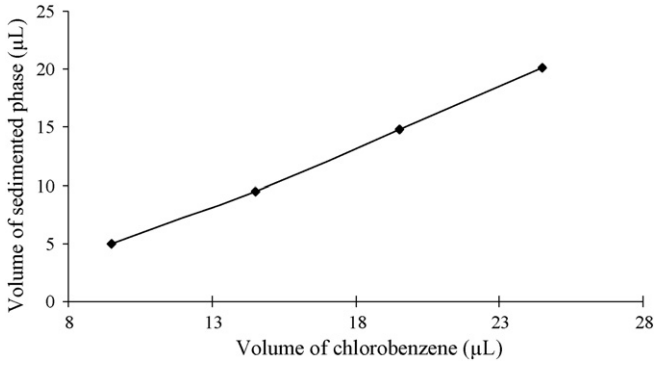

Fig. 2. Effect of the extraction solvent (chlorobenzene) volume on the volume of the sedimented phase in DLLME. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (acetone) volume, 0.50 mL at room temperature (25 ± 1 °C).

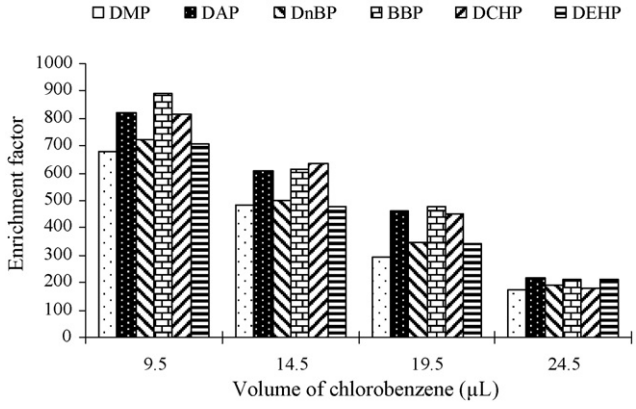

Fig. 3. Effect of the extraction solvent (chlorobenzene) volume on the enrichment factor of the PEs, obtained from DLLME. Extraction conditions as with Fig. 2.

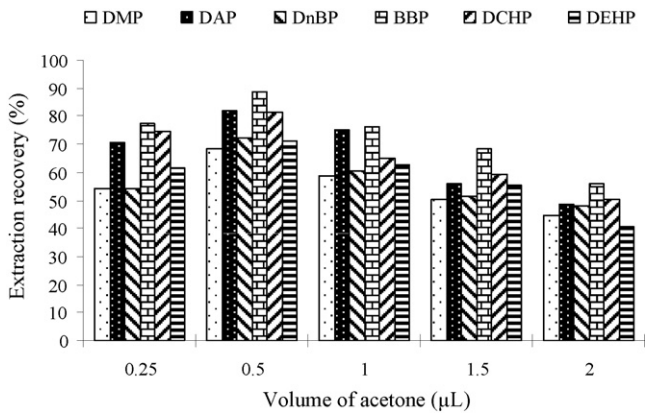

Fig. 4. Effect of the acetone volume on the extraction recovery of the PEs, obtained from DLLME. *Extraction conditions*: Water sample volume, 5.00 mL; extraction solvent (chlorobenzene) volume, 9.5 μL; and sedimented phase volume, 5.0 ± 0.3 μL at room temperature (25 ± 1 °C).

3.5. Effect of the ionic strength

The salt addition to the sample may have several effects on the extraction efficiency. For investigating the influence of the ionic strength on the performance of DLLME, various experiments were performed by adding different NaCl amounts (0–5%). However, the other experimental conditions were kept constant. Figs. 5 and 6 show the effect of the ionic strength on the volume of the sedimented phase and the enrichment factor of PEs. With the increase of the ionic strength (from 0 to 5%), the solubility of the extraction solvent in the aqueous phase diminished. Subsequently, the volume of the sedimented phase increased (from 5.2 to 6.6 μL) (Fig. 5). Fig. 6 displays a slight decrease of the enrichment factor for the selected PEs [31,33]. According to the results, the extraction recovery was almost constant (from 68.1–88.9 to 64.2–91.3%). For this reason, no salt was added in the further experiments.

3.6. Effect of the extraction time

Extraction time is one of the major parameters affecting the extraction efficiency, especially in microextraction methods such as SPME and LPME. In the DLLME method, the extraction time is defined as an interval between the injection of the

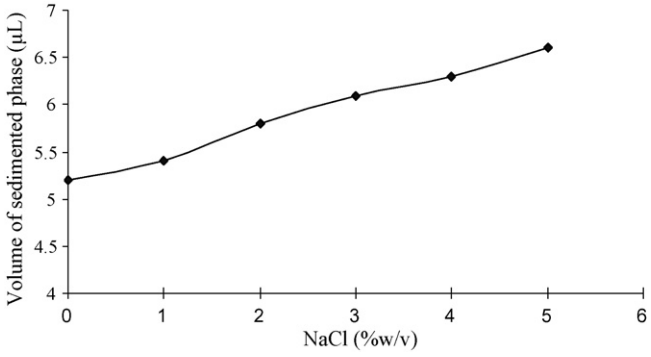

Fig. 5. Effect of the salt addition on the volume of the sedimented phase, obtained from DLLME. Extraction conditions: as with Fig. 2 and sedimented phase volume,5.0 ± 0.3 μL.

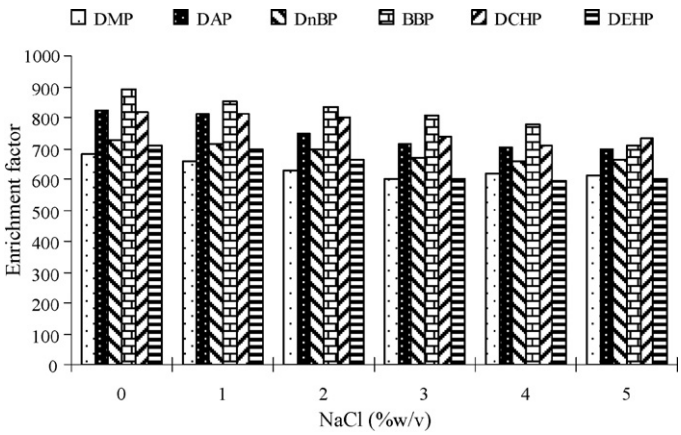

Fig. 6. Effect of the salt addition on the enrichment factor, obtained from DLLME. Extraction conditions as with Fig. 5.

mixture of the disperser solvent (acetone) and the extraction solvent (chlorobenzene) before starting to centrifuge. As a result, for the evaluation of this parameter, different extraction times (ranging from 5 to 180 s) were studied, while keeping the experimental conditions constant. From the corresponding results (Fig. 7), it could be observed that the peak area variations versus the extraction time were not significant. Consequently, time had no impact on the extraction efficiency. It was revealed that after the formation of the cloudy solution, the surface area between the extraction solvent and the aqueous phase (sample) was considerably large. Therefore, the transition of the analytes from the aqueous phase to the extraction solvent was very fast. Subsequently, the equilibrium state was achieved quickly and the extraction time was very short. In this method, the most time-consuming step was the centrifuging of the sample solution in the extraction procedure, which was about 2 min. Therefore, this method is very fast and this is the most distinct advantage of the DLLME technique [31,34].

3.7. Evaluation of the method performance

Under the selected optimum experimental condition, the proposed methodology was applied to a series of standard solu-

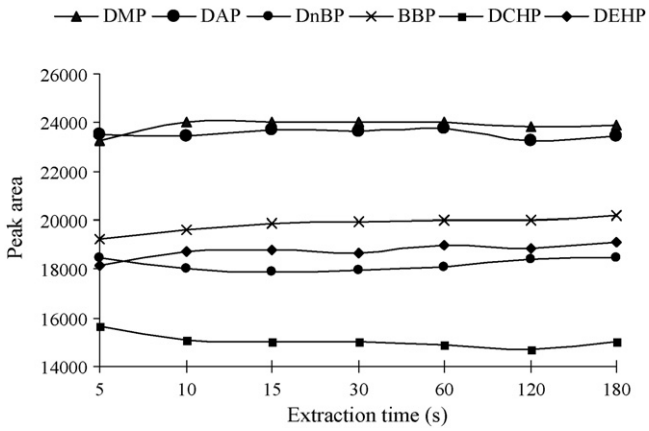

Fig. 7. Effect of the extraction time on the peak area of the PEs, obtained from DLLME. Extraction conditions as with Fig. 5.

Table 4
Some quantitative data obtained after DLLME and GC/MS determination of the selected PEs

Compound	LOD[a] ($\mu g\,L^{-1}$)	r^2	LR[b] ($\mu g\,L^{-1}$)	EF[c]	Recovery (%)	RSD (%)[d] ($n=4$)
DMP	0.008	0.9931	0.05–100	681	68.1	4.6
DAP	0.002	0.9943	0.03–50	822	82.2	4.7
DnBP	0.005	0.9940	0.02–50	723	72.3	5.9
BBP	0.002	0.9901	0.02–100	889	88.9	6.1
DCHP	0.008	0.9962	0.05–50	816	81.6	6.8
DEHP	0.005	0.9951	0.03–100	707	70.7	5.5

[a] Limit of detection for S/N = 3.
[b] Linear range.
[c] Enrichment factor.
[d] Relative standard deviation at concentration of 1.00 $\mu g\,L^{-1}$ of each phthalate ester.

Table 5
Comparison of DLLME with other methods for determination of PEs

Method	LOD[a] ($\mu g\,L^{-1}$)	LR[b] ($\mu g\,L^{-1}$)	RSD[c] (%)	Extraction time (min)	Sample volume (mL)	References
SDME[d]-GC-FID	0.02–0.1	0.1–50	3.5–8	25	20	[35]
SPME-GC–MS	0.003–0.01	10–0.1	4–11	20	5	[30]
HFLPME-GC–MS	0.005–0.1	10–0.5	4–19	20	5	[30]
DLLME-GC–MS	0.002–0.008	0.02–100	4.6–6.8	≥3	5	Represented method

[a] Limit of detection for S/N = 3.
[b] Linear range.
[c] Relative standard deviation.
[d] Single drop microextraction.

tions containing various concentrations of analytes, in order to develop the respective calibration curves. For each level, three replicate extractions were performed. The limits of detection (LODs), based on the signal to noise ratio (S/N) of 3, correlation coefficients (r^2), linear ranges (LRs), relative standard deviations (RSDs), enrichment factors and recoveries were calculated and summarized in Table 4. As shown in this table, LODs for the tested PEs were in the range of 0.002–0.008 $\mu g\,L^{-1}$. Linearity values varied in the range of 0.02–100 $\mu g\,L^{-1}$ with correlation coefficient of 0.9901–0.9962. The precision of the method was investigated with 1.0 $\mu g\,L^{-1}$ PEs mixed standard solution and the RSDs for four replicates varied from 4.6 to 6.8%. Furthermore, the enrichment factors and recoveries were from 681 to 889 and 68.1 to 88.9%, respectively.

Table 6
The results obtained from analysis of real water samples

Sample	DMP	DAP	DnBP	BBP	DCHP	DEHP
Tap water (0.20 $\mu g\,L^{-1}$ added)						
Concentration ($\mu g\,L^{-1}$)	ND[a]	ND	ND	ND	ND	ND
Found ($\mu g\,L^{-1}$)	0.172	0.162	0.222	0.230	0.194	0.179
Relative recovery (%)	86	81	111	115	97	90
RSD% ($n=4$)	7.1	5.0	6.2	4.8	8.3	8.8
Mineral water, Ploor (0.80 $\mu g\,L^{-1}$ added)						
Concentration ($\mu g\,L^{-1}$)	ND	ND	ND	ND	ND	ND
Found ($\mu g\,L^{-1}$)	0.933	0.869	0.755	0.768	0.714	0.891
Relative recovery (%)	117	109	94	96	89	111
RSD% ($n=4$)	6.2	4.7	4.8	7.2	6.0	5.2
Mineral water, Damash (5.0 $\mu g\,L^{-1}$ added)						
Concentration ($\mu g\,L^{-1}$)	ND	ND	ND	ND	ND	ND
Found ($\mu g\,L^{-1}$)	5.61	4.73	4.66	4.94	5.76	5.34
Relative recovery (%)	112	95	93	99	115	107
RSD% ($n=4$)	5.5	5.1	7.2	8.6	8.0	7.8
Jajrood river water (20.0 $\mu g\,L^{-1}$ added)						
Concentration ($\mu g\,L^{-1}$)	ND	ND	ND	ND	ND	ND
Found ($\mu g\,L^{-1}$)	19.01	22.11	19.66	18.67	20.96	21.64
Relative recovery (%)	95	111	98	93	105	108
RSD% ($n=4$)	5.4	6.4	6.0	5.8	8.7	8.4

[a] Not detected.

3.8. Comparison of DLLME with other methods

Table 5 indicates the values of LOD, LR, RSD, the extraction time and the sample volumes of other methods and DLLME (represented method) for the extraction and determination of PEs from water samples. In comparison with other microextraction methods, DLLME provided lower LOD and wider linear range. The low RSD values were probably because of the quick equilibrium achievement (Fig. 7) and the quantitative extraction (Table 2). The extraction time in DLLME was very short and the extraction equilibrium was achieved very quickly. The required volume of the sample solution for DLLME was little, same as SPME and HFLPME. All these results revealed that DLLME was a sensitive, rapid and reproducible technique that could be used for the PEs preconcentration in water samples. The combination of this technique with other analytical instruments, like HPLC [36], atomic absorption spectroscopy (AAS) [37], has already been performed effectively.

3.9. Real water analysis

The performance of this method was tested by analyzing the PEs in the four different water samples. The results showed that the analyzed samples were free of PEs contamination. All the real water samples were spiked with PEs standards at different concentration levels to assess the matrix effects. The relative recoveries of the analytes are given in Table 6. The obtained relative recoveries were between 81 and 117%, which indicated that the real water matrices, in our present context had little effect on DLLME. After performing DLLME, the mass chromatograms of the mineral water (Ploor) are displayed in Fig. 8, prior to (a) and after spiking the plasticizers (b) at the concentration level of 0.80 μg L^{-1} of each analyte.

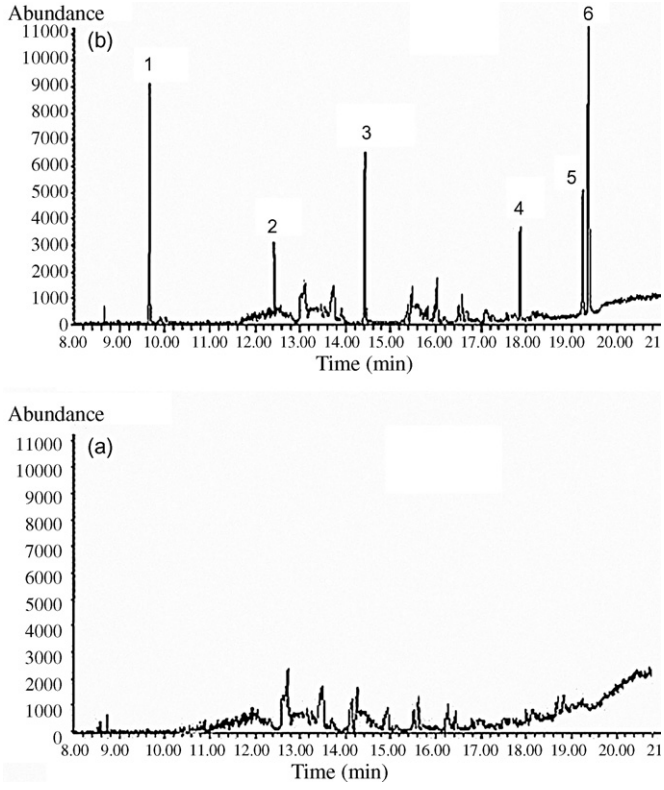

Fig. 8. Mass chromatograms of the mineral water (Ploor) prior to (a) and after performing DLLME (b), spiked with the PEs at the concentration level of 0.8 μg L^{-1} of each analyte. Peak numbers correspond to (1) DMP, (2) DAP, (3) DnBP, (4) BBP, (5) DCHP and (6) DEHP.

4. Conclusion

This paper outlined the successful development and application of the DLLME technique, combined with the capillary GC–MS for the qualitative and quantitative analysis of a PEs group in water samples. The developed method was precise, reproducible and linear over a wide range with sufficient selectivity (using the MS detector at the SIM mode) and high sensitivity. As compared with the 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, high enrichment factors and a very short analysis time. The performance of this procedure in the PEs extraction from different water samples with various matrices was excellent; therefore, the method could be used routinely for screening purposes.

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