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توسعه روش ریزاستخراج فاز مایع با بکارگیری هالوفیبر حاوی میله مغناطیسی و حلال زوج‌شده با کروماتوگرافی گازی برای اندازه‌گیری کمی فتالات استرها در آب‌های زیست‌محیطی

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Development of Magnetic Solvent Bar Liquid-Phase Microextraction Followed by Gas Chromatography for the Quantitative Determination of Phthalate Esters in Environmental Water Samples

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چکیده

در این تحقیق یک روش ساده، با کارآیی بالا و حساس جهت اندازه‌گیری همزمان مقادیر ناچیز تعدادی فتالات استر در آب‌های زیست‌محیطی توسعه یافت. در تکنیک ریز استخراج فاز مایع با بکارگیری هالوفیبر حاوی میله مغناطیسی و حلال، ابتدا یک میله باریک استیل به داخل هالوفیبر وارد و سپس جهت اشباع نمودن منافذ، به مدت زمان کوتاهی درون حلال استخراجی قرار داده شد. سپس این مجموعه (هالوفیبر/میله/حلال) به ظرف حاوی آنالیت‌ها که بر روی همزن مغناطیسی قرار گرفته بود منتقل و عملیات استخراج در دما و زمان معین صورت پذیرفت. در مرحله بعد و با استفاده از یک آهنربا مجموعه هالوفیبر/میله/حلال از محلول آبی جدا، در ظرف دیگر توسط حلال ثانویه و در معرض حمام اولتراسونیک واجذب و نهایتاً به دستگاه کروماتوگراف گازی مجهز به آشکارساز یونیزاسیون شعله معرفی گردید. در ابتدا کلیه متغیرهای موثر بر فرآیند ریزاستخراج بررسی و بهینه شدند. بدین‌ترتیب، محدوده خطی در ناحیه ۰/۲ الی ۲۵۰ میکروگرم بر لیتر به همراه ضریب همبستگی در گستره ۰/۹۹۳ تا ۰/۹۹۶، حد آشکارسازی ۰/۰۲ تا ۰/۰۹ میکروگرم بر لیتر و انحراف استاندارد نسبی کمتر از ۶/۰ درصد (هفت مرتبه تکرار) برای غلظت ۲۵ میکروگرم بر لیتر از آنالیت ها بدست آمد. این روش برای اندازه‌گیری مقادیر ناچیز فتالات استرها در نمونه‌های حقیقی استفاده و صحت آن با به‌کارگیری آزمایش‌های بازیافت نسبی تأیید شد.

واژه‌های کلیدی

فتالات استرها؛ ریز استخراج فاز مایع؛ هالوفیبر؛ کروماتوگرافی گازی – آشکارساز یونیزاسیون شعله؛ آب‌های زیست‌محیطی.

Abstract

A simple and efficient hollow fiber-based method, namely magnetic solvent bar liquid-phase microextraction (MSB-LPME) combined with gas chromatography-flame ionization detection (GC-FID) has been successfully developed for the sensitive determination of selected phthalate esters (PEs) in environmental water samples. The analytes were extracted from sample solution to the organic solvent immobilized in a fiber. Following the extraction, the analyte-adsorbed magnetic solvent bar can be easily isolated from the sample solution by a magnet which could greatly simplify the operation and also reduce the total pretreatment time. The bar was primarily eluted with methanol, evaporated to dryness while the residue was dissolved in toluene and finally injected into GC-FID. Begin with, effective parameters controlling the performance of the microextraction were evaluated and optimized. The values of the detection limit of the method were in the range of 0.02-0.09 µg L^{-1} and the RSD% values for the analysis of 25.0 g µL^{-1} of the analytes was below than 6.0% (n = 7). A worthy linearity (0.996 ≥ r^2 ≥ 0.993) and a broad linear range (0.2-250 µg L^{-1}) were achieved. The method was finally employed for the preconcentration and determination of the PEs in environmental water samples and satisfactory results were obtained.

Keywords

Environmental Water Samples; Gas Chromatography-Flame Ionization Detection; Magnetic Solvent Bar Liquid-Phase Microextraction; Phthalate Esters.

1. INTRODUCTION

Phthalate esters (PEs) are notable polymer additives that are employed in formulations of plastics, paints, pesticides, etc.; while, their primary application is as plasticizers to intensify the workability and flexibility of polymeric

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*Corresponding Author: farahaniha@ripi.ir materials [1, 2]. They are just physically, not chemically, bound to the polymer structures and they might be released into the environment amid the production, use and disposal processes [3, 4]. Several PEs, as well as some of their degradation products and metabolites, can make toxic effects in human organs including kidneys, liver, and lungs [5]. The potential endocrine disrupting characteristics of PEs likely associated with their known estrogenic and anti-androgenic activities have also been recorded [6, 7]. Thereupon, with the rapid development of the plastics industry at mega-scale, PEs have been becoming universal environmental contaminants which attracted considerable attention worldwide.

High-performance liquid chromatography (HPLC) [8-10], and Gas chromatography (GC) [11-13], have repeatedly been conducted for the analysis of PEs in multitudinous media. Moreover, when the concentration levels are trace, an earlier enrichment step is mostly demanded. The extraction techniques, which are routinely served ahead of the instrumental analysis, are liquid-liquid extraction (LLE) [14, 15], and solid-phase extraction (SPE) [16, 17]. Regardless, these sample pretreatment methods desire either the immense amount of sample and harmful organic solvents though they are considered as time-consuming, labor-intensive and expensive with frequently result in high blank values [18, 19]. With the perspective, a variety of microextraction techniques that use no or inconsiderable amounts of solvent or have been expanded recently.

Liquid-phase microextraction (LPME) is a sample pretreatment method that utilizes negligible volumes of organic solvents to extract a wide range of analytes from different matrices prior to instrumental analysis [20]. The development of these methods centers on providing easy, low-priced and environmentally friendly extraction approaches for sample preparation [21, 22]. Among the various modes of LPME and in an effort to improve its capabilities, Pedersen-Bjergaard and Rasmussen reported hollow fiber liquid-phase microextraction (HF-LPME) [23, 24]. It uses a HF to keep steady and protect the extraction solvent, and the small pore size of the fiber prevents large molecules and particles from entering into the acceptor phase, resulting in a clean-up of sample matrix in addition to the extraction [25]. Considering slight amounts of the solvent are used, consumption of toxic organic solvents is minimized while the technique simply combines extraction and concentration as well as sample introduction into a single step [26, 27].

Lately, Wu et al. have reported a simple, efficient and novel HF-LPME based method, named magnetic solvent bar liquid-phase microextraction (MSB-LPME) that was firstly applied for the determination of organophosphorus pesticides in fruit juice samples [28]. In MSB-LPME, some modifications of HF-LPME were presented for facilitating the practical operation as well as enhancing the method efficiency.

The purpose of present study is to appraise the MSB-LPME technique suitability for the determination of five selected PEs in the aquatic environment. The factors affecting microextraction efficiency were considered in detail, and the optimum conditions were established. The method was validated for quantitative purposes and employed to real samples analysis in combination with gas chromatography-flame ionization detection (GC-FID).

2. EXPERIMENTAL

2.1. Chemicals and materials

Five compounds analyzed in this study including dimethyl (DMP), diallyl (DAP), di-n-butyl (DnBP), benzyl butyl (BBP) and dicyclohexyl (DCHP) phthalate esters were obtained from Merck (Darmstadt, Germany). Analytical reagent grade acetone, ethyl acetate, hexane, carbon tetrachloride, 1-octanol and toluene were acquired from Merck Company (Darmstadt, Germany). Q3/2 Accurel PP hydrophobic polypropylene hollow fiber membrane (600 µm inner diameter, 200 µm wall thickness and 0.2 µm pore size) was bought from Membrana GmbH (Wuppertal, Germany). The extraction procedure was performed in the 22 mL screw top vials (Sigma-Aldrich, Steinheim, Germany) with dimension of 23 mm (outer diameter) × 85 mm (height) × 18 mm (inner diameter). The stainless-steel wire (505 µm outer diameter) was just fit to HF membrane. HPLC-grade methanol (Fisher Chemicals, Fair Lawn, NJ, USA) and ultrapure water (Millipore, Bedford, MA, USA) were used in all experiments. All solutions were stored at 4 °C and protected from light.

2.2. Instrumentation

An Agilent 6890N gas chromatograph (Wilmington, DE, USA) equipped with a split/splitless inlet and flame ionization detector (FID) was used for the determination of the PEs. Helium (99.999%) was employed as carrier gas at the flow rate of 1.0 mL min^{-1}. The chromatographic data were recorded using a HP Chemstation, which was controlled by Windows NT (Microsoft). The analytes were separated on a 30 m × 0.25 mm i.d. × 0.25 µm film thickness DB-5 gas chromatographic column (J&W Scientific, Folsom, CA, USA) with the following oven temperature program: initial 80 °C, from 80 °C (held 3 min) to 200 °C at 20 °C min^{-1}, increased at 10 °C min^{-1} to 280 °C and held for 5 min. Analysis employed a 1.0 µL sample injection in a 5:1 split ratio while the injection port and detector both were operated 280 °C.

2.3. Real samples collection

The performance of the proposed method was evaluated by analyzing the PEs in four environmental water samples including Caspian Sea (Anzali Coast, Iran), Persian Gulf (Bandar Abbas Coast, Iran), Jajroud River (Tehran, Iran) and Latian Dam (Tehran, Iran). The samples were collected in amber glass bottles (1.0 L). The bottles were rinsed several times with the pure water to be analyzed and filled till overflow to prevent loss of the volatile organic compounds in the presence of the headspace. The water samples were filtered before the analysis using a 0.45 µm membrane filter (Millipore, Bedford, MA, USA) to eliminate the particles. All the samples were transported and stored at the refrigerator at 4 °C until their analysis time.

2.4. Extraction procedure

Schematic of the presented microextraction is shown in Fig. 1. It contained the hollow fiber and stainless-steel wire with magnetic properties; they were manually cut into segments of 1.5 cm length. These segments were ultrasonically cleaned to remove impurities and dried in the air. To prepare the extraction set-up, the stainless steel wire was inserted into the hollow of the HF. The resulting fiber piece was immersed in an organic solvent for one min to impregnate pores of the fiber wall. With regard to remove the extra amount of the organic solvent from the surface of the fiber, it was carefully rinsed with water. To start the procedure, five MSBs were placed into the 22 mL screw top vial containing 20 mL of aqueous sample. The vial was closed and put into a water bath with temperature of 40 °C on the magnetic stirrer for 20 min at 600 rpm. After the extraction, with the help of an external magnet, the MSBs were separated rapidly from the sample solution. Then the bars were eluted with 400 µL of methanol in an ultrasonic bath for 3 min. The eluate was separated from the MSBs also by a magnet. The eluate obtained was evaporated to dryness under a nitrogen stream and the residue was dissolved in 100 µL of toluene. At last, a 1.0 µL of the extracting phase was injected into GC-FID.

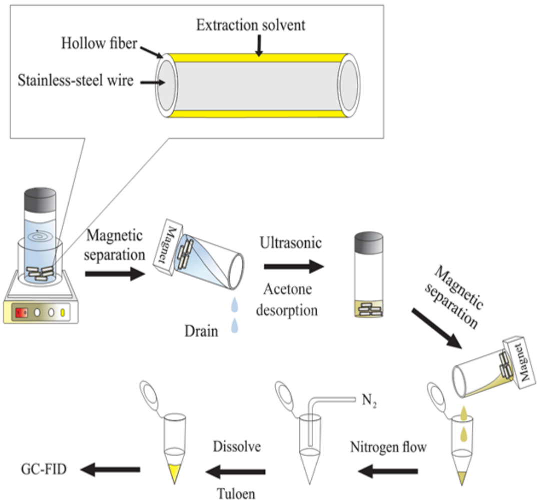

Fig. 1. The schematic diagram of MSB-LPME-GC.

3. RESULT AND DISCUSSION

A one variable at a time approach was employed to optimize the affecting parameters on the microextraction efficiency including type of extraction solvent, extraction temperature, salt concentration, stirring speed, extraction time and desorption conditions. A fixed concentration (100 µg L^{-1}) of the analytes was used in optimization process. All the quantifications were performed from the average of three replicate measurements. Blank samples were periodically run to confirm the absence of interference.

3.1. The selection of extraction solvent

The selection of a proper organic solvent in HF-LPME is of considerable importance for efficient analyte preconcentration [29]. There are some criteria for organic solvent selection as follow. First of all, it should be effortlessly immobilized in the HF pores. In the second place, it needs to be nearly nonvolatile to avoid solvent loss during the extraction. In the third order, the organic solvent should be immiscible with water because it serves as a barrier via the two aqueous phases, the source and the receiving phases. Besides, the organic solvent is used to promote analyte diffusion from the source phase into the receiving phase by the pores of the hollow fiber [30]. On the basis of these considerations, 1-octanol, carbon tetrachloride, toluene and hexane were investigated in preliminary experiments. As it can be seen in Fig. 2, the highest extraction efficiency for all the analytes was attained with toluene. In this way, toluene was selected as the extraction solvent.

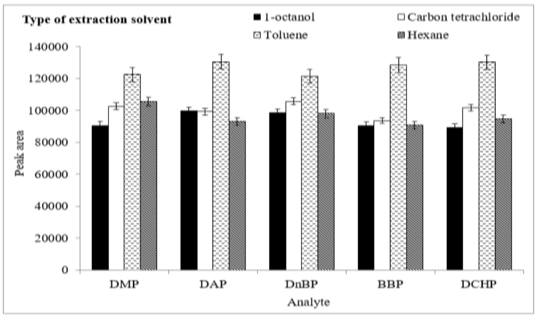

Fig. 2. The effect of extraction solvent type on MSB-LPME efficiency.

3.2. The effect of extraction temperature

The extraction temperature could evidently influence the extraction efficiency in two opposing ways; to begin with, it could enhance the mass transfer of the analytes and secondly, it could decline the partition coefficients (K_{ow}) between the organic and aqueous phase. So, the extraction efficiency will be higher or lower according to the dominant factor [31, 32]. The effect of sample solution temperature was studied in the range of 20-50 °C. It is demonstrated that (Fig. 3) the extraction efficiency for all the target analytes was raised with the increase of temperature and maximum analytical signals were obtained at 40 °C. Nonetheless, increasing the extraction temperature upper the mentioned value would result in the dissolution and volatilization loss of the extracting solvent and formation of air bubbles adhering to HF, which would influence on the extraction operation and precision. Thereupon, to achieve better extraction efficiency and reproducibility, temperature of 40 °C was used for further studies.

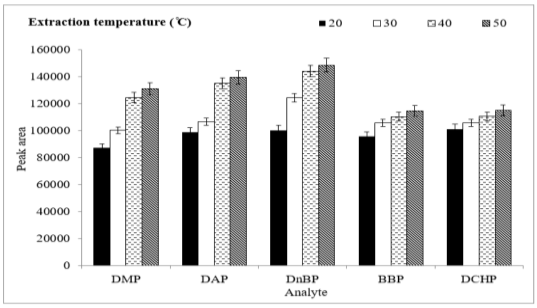

Fig. 3. The effect of extraction temperature on MSB-LPME efficiency.

3.3. The effect of salt addition

The salt addition to sample solution frequently amplifies the ionic strength, and so improves the extraction efficiency because of the salting out effect. This effect has been accounted to decline the solubility of target analytes in the aqueous phase and increasing partitioning into the organic phase [33, 34]. For this purpose, different concentrations (0%-20% w/v) of NaCl were added to the sample solution to evaluate its effect on the extraction efficiency (Fig. 4). As it can be seen, salt addition has no significant effect on the preconcentration factors. Therefore, the preconcentration factor is nearly steady by increasing the amount of NaCl, and the extraction experiments were carried out without adding salt.

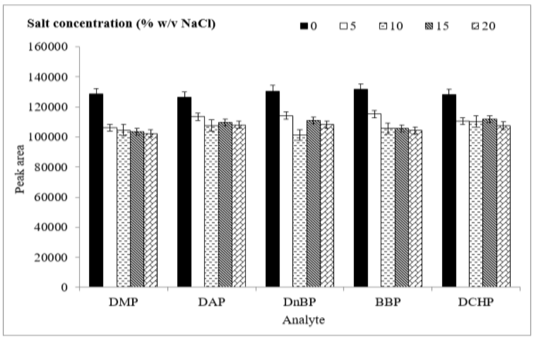

Fig. 4. The effect of salt concentration on MSB-LPME efficiency.

3.4. The effect of stirring speed

The magnetic stirring improves extraction efficiency and diffusion of the analytes into the interfacial layer of HF while it reduces the time required to attain thermodynamic equilibrium [35, 36]. Herein, the solvent is protected by HF and consequently quicker stirring rates could be applied. The effect of this parameter on the extraction efficiency of the system was studied in the range of 350-1000 rpm. As shown in Fig. 5, the results confirmed that the agitation of the sample greatly boosted the extraction efficiency. However, higher stirring rates were not evaluated as they might cause the excessive formation of air bubbles on the surface of HF or would lead to solvent dissolution, which conducted to poorer precision and to experimental failure. Herein, due to a very short distance between the results of 750 and 1000 rpm and with the objective to approach more stability in the extraction system, 750 rpm was selected as the optimum condition in the following experiments.

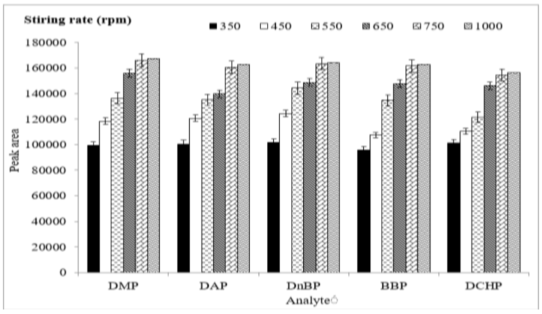

Fig. 5. The effect of stirring rate on MSB-LPME efficiency.

3.5. The effect of extraction time

The mass transfer in MSB-LPME is a process dependent on equilibrium rather than exhaustive extraction and beneficial to achieve good extraction repeatability, it is essential to choose a suitable extraction time [37]. Herein, the extraction time profiles were investigated by recording the variation of the analytical signals of the analytes as a function of extraction time, in the range of 10-40 min. As shown in Fig. 6, by growing the extraction time up to 30 min, the extraction efficiencies rose quickly and afterwards stayed approximately steady. It is remarkable that longer extraction time can result in the loss of the extracting solvent and contraction of the extraction yields. Accordingly, the exposure time of 30 min was selected as optimum value in the subsequent experiments.

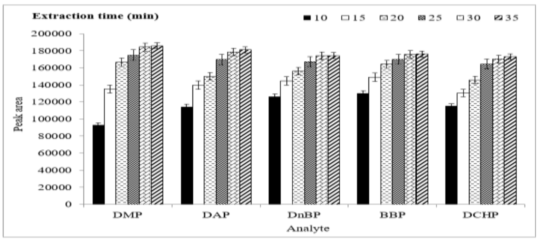

Fig. 6. The effect of extraction time on MSB-LPME efficiency.

3.6. The effects of desorption solvent and time

Owing to the great importance of desorption solvent and time on the extraction efficiency, the parameters were investigated and optimized. When the extraction process was completed, 400 µL of desorption solvents including acetone, methanol and ethyl acetate were applied to elute the analytes from the MSBs. The results indicated that the best desorption efficiencies were obtained with acetone. Therefore, it was chosen to be the optimum for extraction of PEs. To evaluate the other parameter, the analyte-enriched MSB was ultrasonicated in the range of 1-10 min. The result confirmed that 4 min was enough to get the best analytical signals. However, if the desorption time was too long, the analytes would be lost significantly. So, 4 min was chosen as the appropriate value.

3.7. The analytical performance

To appraise the aptness of the method, calibration curves were plotted at the optimum conditions using different concentration levels of the analytes. The limits of detection (LODs) based on the signal-to-noise ratio (S/N) of 3, the determination coefficients (r^2), the linear ranges (LRs) and the relative standard deviations (RSDs) were calculated and summarized in Table 1. As shown, LODs for the PEs were in the range of 0.02-0.09 µg L^{-1} while linearity values varied in the range of 0.2-250 µg L^{-1} with correlation coefficient of 0.993 to 0.996. The precision of the method was investigated with 25.0 µg L^{-1} PEs mixed standard solution and the RSDs for seven replicate measurements was below than 6.0% (n = 7).

Table 1. Some quantitative data achieved by using MSB-LPME and GC-FID for the determination of the selected PEs.

Analyte	DMP	DAP	DnBP	BBP	DCHP
LOD (µg L^{-1}) [a]	0.05	0.02	0.04	0.06	0.09
r^2	0.995	0.993	0.996	0.994	0.996
LR (µg L^{-1}) [b]	0.2-200	0.2-250	0.2-200	0.2-250	0.2-200
RSD% [c] (n = 7)	5.4	6.0	5.9	5.0	5.7

[a] Limit of detection for S/N = 3.

[b] Linear range.

[c] Relative standard deviation at concentration level of 25.0 µg L^{-1} for each PEs.

As shown in Table 2, comparing the proposed method with other analytical techniques employed for the determination of PEs in water samples, the present work has low superiority over the other techniques in terms of RSDs, LRs and LODs. On the other hand, when it comes to the comparison of the extraction time, the represented method nearly stands in the meddle order.

3.8. Analysis of environmental water samples

Established at the optimum conditions, the method performance was tested by analyzing the analytes in the four different environmental water samples. The results are presented in Table 3 and showed that they were free of PEs contamination.

Table 2. Comparison of various analytical methods for the extraction and determination of PEs in water samples.

Method	LOD (µg L^{-1})	LR (µg L^{-1})	RSD%	Extraction time (minute)	Reference
MSB-LPME-GC-FID (a)	0.02-0.09	0.2-250	< 6.0	30	Represented method
HS-SPME-GC-FID (b)	0.06-0.08	0.2-100	< 7.8	35	[38]
CPE-HPLC-UV (c)	1-3.8	5-200	< 3.9	60	[39]
MSPE-GC-FID (d)	0.2-0.4	0.4-100	< 12.3	10	[40]
LPME-GC-FID (e)	0.4-4.3	5-5000	< 6.4	30	[41]

(a) Magnetic solvent bar liquid-phase microextraction-gas chromatography-flame ionization detection.
(b) Headspace solid phase microextraction- gas chromatography-flame ionization detection.
(c) Cloud point extraction-high performance liquid chromatography-ultraviolet detection.
(d) Matrix solid-phase extraction- gas chromatography-flame ionization detection.
(e) Liquid phase microextraction- gas chromatography-flame ionization detection.

Table 3. The results acquired from analysis of real environmental water samples.

Sample	DMP	DAP	DnBP	BBP	DCHP
Caspian Sea (Anzali Coast, Iran), (10.0 µg L^{-1} added)	ND [a]	ND	ND	ND	ND
PEs concentration (µg L^{-1})	10.5	9.4	9.7	10.2	10.4
Found after spike (µg L^{-1})	105	94	97	102	104
Relative recovery%	6.4	6.9	5.8	6.0	5.5
RSD% (n = 7)					
Persian Gulf (Bandar Abbas Coast, Iran), (25.0 µg L^{-1} added)	ND	ND	ND	ND	ND
PEs concentration (µg L^{-1})	26.2	25.7	24.4	24.0	23.7
Found after spike (µg L^{-1})	105	103	98	96	95
Relative recovery%	6.5	6.1	5.4	5.2	5.7
RSD% (n = 7)					
Jajroud River (Tehran, Iran), (50.0 µg L^{-1} added)	ND	ND	ND	ND	ND
PEs concentration (µg L^{-1})	51.5	52.1	48.1	51.0	47.7
Found after spike (µg L^{-1})	103	104	96	102	95
Relative recovery%	5.5	5.9	5.9	6.3	6.5
RSD% (n = 7)					
Latian Dam (Tehran, Iran), (100.0 µg L^{-1} added)	ND	ND	ND	ND	ND
PEs concentration (µg L^{-1})	104.2	95.2	96.0	102.9	103.8
Found after spike (µg L^{-1})	104	95	96	103	104
Relative recovery%	6.2	5.9	6.6	5.7	6.0
RSD% (n = 7)					

[a] Not detected.

It is noteworthy that MSB-LPME is a non-exhaustive extraction procedure and therefore the relative recovery (determined by the ratio of the concentrations found in the real environmental sample and reagent water sample, spiked with a similar quantity of the analytes), rather than the absolute recovery (used in exhaustive extraction procedures), was utilized. So, in next step and to evaluate the matrix effects, all the real samples were spiked with PEs standards at different concentration levels and the relative recovery experiments of the analytes are calculated (Table 3). The obtained recoveries were between 94-105%, indicating that the method is not influenced by the matrix in actual applications while the RSD% values were below than 6.9 (n = 7). An overlay of two chromatograms obtained by performing MSB-LPME-GC-FID for Caspian Sea (Anzali Coast, Iran) before and after PEs spiking are shown in Fig. 7 and demonstrated no significant interference through the analytical procedure.

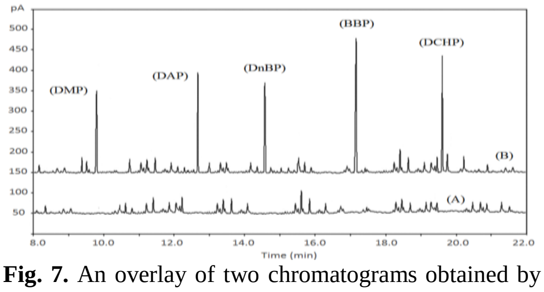

Fig. 7. An overlay of two chromatograms obtained by performing MSB-LPME-GC-FID for Caspian Sea (Anzali Coast, Iran) before (A), and after PEs spiking (B).

4. CONCLUSION

The results from this work show that the MSB-LPME technique in combination with GC-FID is a valid means of enrichment and sensitive quantification of selected PEs in environmental water samples. The magnetic solvent bar was applied for two practical points: the stirring bar of microextraction and extractor of the target analytes. After the microextraction procedure, it can be simply isolated from the sample solution by a magnetic field to reduce the total analysis time. The satisfactory extraction efficiency, sufficient sensitivity and repeatability along with significant accuracy and linearity over a broad range were achieved, almost independent of the complex matrix in the real applications. Into the bargain, the developed method needs just a little volume of organic extractants, being consequently an environmentally friendly approach of sample preparation. Besides an efficient sample clean-up, the entire analytical procedure presents a cost effective and quick way for the screening purposes. Hence, combining all the advantages simultaneously, the method possesses great potential to be employed in other analytical demands.

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