

A Developed Electromembrane Technique Based on Flat Electrospun Membrane Coupled with Gas-chromatography for the Determination of Phthalates in Different Water Samples

A. Mollahosseini^{1*} and M. Konh²

¹ *Research Laboratory of Spectroscopy & Micro and Nano Extraction, Department of Chemistry, Iran University of Science and Technology, Tehran, Islamic Republic of Iran*

² *Department of Chemistry and Biochemistry, University of Delaware, Newark, United States*

Received: 29 December 2018 / Revised: 13 April 2019 / Accepted: 14 July 2019

Abstract

In this work, we successfully developed electromembrane extraction via preparation of an electrospun flat membrane based on device. The polyurethane-membrane was prepared by electrospinning method and used in EME. Affecting parameters on membrane preparation were optimized by Taguchi design. The developed method was used for extraction of phthalates as typical molecules and the proposed method was used to determine phthalates in water samples. The applied voltage, extraction time, distance of electrodes and agitation rate were selected as the main factors in EME and optimized using response surface methodology based on a central composite design. Under optimum conditions, calibration curves were obtained in the range of 0.5-5000 ng mL⁻¹ with R²>0.990. The repeatabilities were less than 12% and 14% for intra-day and inter-day, respectively. The limits of detection were found to be 0.03 and 0.02 ng mL⁻¹ and limits of quantification were obtained 0.09 and 0.06 for bis (2- ethylhexyl phthalate), and dimethyl phthalate, respectively.

Keyword: Central composite design; Electrospinning; Flat membrane; Gas-chromatography; Phthalates.

Introduction

Sample preparation is one of the most important steps in analytical procedures. Generally, the most frequently extraction techniques are liquid-liquid extraction (LLE) and solid phase extraction (SPE). These methods are time consuming, tedious and often need large volume of toxic solvents. Sample pretreatment techniques such as solid-phase micro extraction (SPME) and stir bar sorptive extraction (SBSE) have gained a lot of attraction [1, 2].

In recent years, there have been several studies about different methods of membrane extractions that the main reason for these increasing interests relies on their high separation speed while leaving no mixture of the two phases [3]. The other benefits are prevention of the emulsion phenomenon, and utilization of only a few microliters of organic solvent. Such methods also introduce the possibilities of extractions and pre-concentration of analytes, which would consequently increase the speed of extraction of trace amount analyte in analysis processing. So far, membrane extraction has

* Corresponding author: Tel: +982173228342; Fax: +982173021578; Email: amollahosseini@iust.ac.ir

been used for various analytes, among them biological compounds [4], metals [5], and organic pollutants [6] could be mentioned. One of the most recent methods of membrane extraction is known as electromembrane extraction (EME) that incorporates a supported liquid membrane (SLM). During the process, with the electrical current analytes migrate from the sample solution towards the acceptor solution passing through the membrane [7]. This principle provides a high selectivity, high pre-concentrations, and self-automations. This method has gained huge popularity among the researchers because of its mentioned unique potentials [8-10]. Electromembrane extraction could be performed either in a two or three phase mode. In the two-phase mode, the organic solvent of the SLM is the same solution as the acceptor phase. The electrical field is known as the main factor for the mass transfer and penetration of the analytes [11, 12]. In the three-phase mode, on the other hand, the organic solvent of the SLM is selected differently from the acceptor solvent, and therefore it makes a three-phase solution along with the aqueous sample solution [13].

At first, it is worth mentioning that kind, shape and thickness of the membrane are features which should be considered. Generally, the membranes used in EME method were commercial porous polypropylene. In most cases, hollow fiber membranes are used in EME [14]. While flat membranes were used in the recent researches [15-17]. Hollow fiber membranes usually have thicknesses about 200-300 micrometers [18] and flat membrane are about 100 micrometers [16]. In comparison with hollow fiber, flat membrane has a big surface area with low Joule heating. This effect can select solvents containing low boiling point. According to the polymer and desired structure of the membrane, some techniques can be used for fabricating the membrane. The methods commonly used for prepare membranes are including phase inversion [19, 20], interfacial polymerization [21], stretching [22, 23], track etching [24] and electrospinning [25-30]. Along these techniques electrospinning is a new method to fabricate porous membrane for various applications. In this way, a high potential is applied between the polymer solution droplet and the grounded collector. When the electrostatic potential becomes sufficiently high and overcomes the surface tension of the droplet, a charged liquid jet is formed. The unique features of these fibrous membranes are controllable aspect ratios (aspect ratio = L/d ; L -length of the fiber and d -diameter of the fiber) and morphology of the nano/microfibers, which is achieved by varying the solution viscosity, environmental conditions, applied electric potential and the flow rate of the solution [31].

Moreover, in this study the material, gap distance, shape and thickness of the electrodes as a main factor in EME process are studied and investigated. The electrodes should be chosen from the neutral materials such as platinum because of the possibility of having an electrolyte reaction at the surface of the electrodes and stainless steel to prevent any damage to the electrodes during the reactions. The gap distance between the electrodes is among the principal factors governing the success of the EME method. The power of the electrical field (E) is defined as the fraction of the electrical potential (V) between two electrodes by the gap distance (d) between them. Therefore, by increasing the gap distance, the electrical field power would decrease, and as a result the flux of the ions passing through the membrane would decrease as well. Although there would be an increase in the extraction efficiency due to the decreasing gap distance between the electrodes, there is one fundamental limitation. Placing the electrodes in a very short gap distance leads to the enhanced migration of ions through the SLM. In such cases, the friction between organic solvent and passing ions can occur and as a result temperature will increase, the organic solvent will be evaporated and the membrane may be destroyed. If the membrane destroys, electric arc happens and it can even interrupt the electric field. In the most investigations, electrodes with wire shape were used [8, 14].

In recent year, the application of EME coupled with gas chromatography (GC) and high performance liquid chromatography (HPLC) was used to determine the trace amount of different analytes in various matrices [32, 33]. The important compounds that have a direct effect on human health are phthalates. Phthalates are categorized in the family of plasticizers. The phthalates have multiple harmful impacts on the human life; therefore, utilizations of such plastic materials are prohibited by some regulatory agencies. Phthalates diffuse across the nutritious materials because there are no chemical bonds between their phthalates and plastics. Therefore, human consumptions could become polluted with phthalates either in a direct or indirect way. Today, several methods have been developed to measure the amount of phthalates. For example, one of the most advanced investigations in the field suggested utilization of an ultrasound-assisted dispersive liquid-liquid micro extraction [34], and an electrokinetic chromatography with polymeric pseudo stationary phase [35]. The identification and determination of phthalates require an analytical method that could separate this material from the other additives to the plastic. Among all gas chromatography (GC) is known as an appropriate apparatus for this purpose.

In the present study, electromembrane based flat electrospun membrane (FM-EME) as a fast, simple and efficient method coupled with GC was employed to determine phthalates from water samples. The polyurethane-based membrane was synthesized by electrospinning and used as a new membrane in FM-EME device. Several important experimental parameters influencing the EME performance, were optimized using response surface methodology (RSM) based central composite design (CCD). The proposed method was used to the analysis of phthalates in water samples and acceptable results were obtained.

Materials and Methods

Analytical grade phthalate esters including dibutyl phthalate (DBP), bis(2-ethylhexyl phthalate) (DEHP), and dimethyl phthalate (DMP), carbon tetrachloride (CCl_4), dimethyl form amide (DMF) and acetonitrile were obtained from Merck (Darmstadt, Germany). Polyurethane (PU) polymer was purchased from Bayer (Leverkusen, Germany). Stainless steel wires used as anode and cathode were obtained from a local market (Tehran, Iran). A stock standard solution of the mixture of phthalates ($1000 \mu\text{g mL}^{-1}$ of each) was prepared in methanol. This solution was diluted with deionized water to prepare a mixed working standard solution. A solution of DBP (50 mg mL^{-1}) in carbon tetrachloride was prepared for using as an internal standard solution. This solution was used in acceptor phase in all steps of the experiment. Stock and working solutions were stored at 4°C in a refrigerator and were used daily in proper concentrations or directly.

Preparation of the flat membrane

In the present work, the membrane has been fabricated via electrospinning technique. In this case, polyurethane was dissolved in DMF and stirred to obtain a transparent solution. The PU/DMF solution was stored in a 10-mL syringe. Polymer jets were stretched under the accelerating voltage created from a high voltage power supply (0-30 kV). After the solvent evaporation, nanofibers were deposited on stainless steel roller (negative electrode) and electrospun PU non-woven membrane was formed. Afterward the membrane was carefully peeled from the roller. For characterizing the selected membrane, Fourier Transform infra-red (FT-IR) spectroscopy and atomic force microscopy (AFM) analysis have done.

EME setup

The equipment used for EME consisted of two tetrafluoroethylene (PTFE) vessels that sealed in each other. This setup is shown in Figure 1. The outer vessel was filled with 12 mL of the aqueous solution of phthalates (donor phase). A magnetic stir bar was placed in the outer vessel to ensure constant stirring of the donor phase. The MR-Hei standard magnetic stirrer (Heidolph, Schwabach, Germany) with 0-1400 rpm variable stirring rate was used. The electrospun flat membrane was then cut into circles with diameters of 2 cm and was placed between two PTFE washers. Thereafter, the washers settled at the bottom of the inner vessel which was filled with $1500 \mu\text{L}$ of carbon tetrachloride as an extraction solvent (acceptor phase). In this setup, two steel wires with diameters of 0.5 mm were used as electrodes.

Because of the shape of the electrodes has an

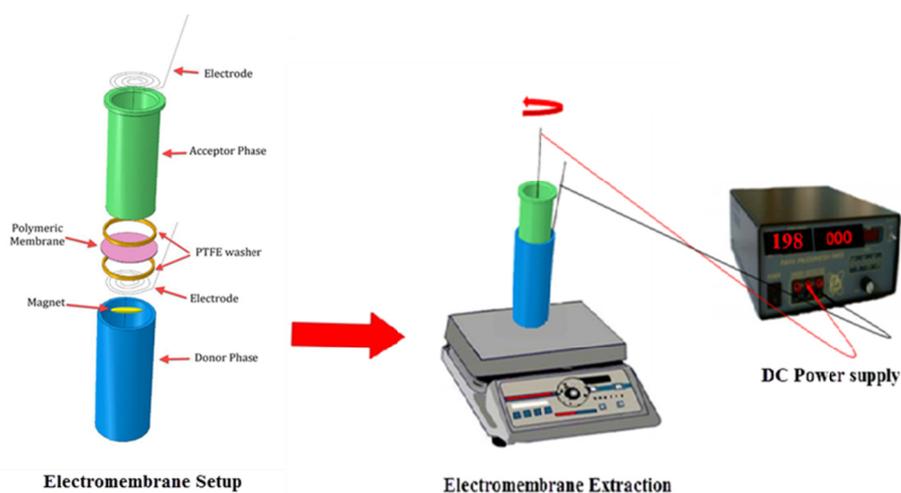


Figure 1. Electromembrane extraction setup

important role in the extraction efficiency, therefore these wires were used in spiral form as shown in Figure 1, so higher electric field strength and extended extraction efficiency were achieved. Two assembled electrodes in donor and acceptor compartments were connected to the power supply and the experiments were studied at different applied voltages. For this purpose, the EME system was operated using a 0–600 V power supply and maximum current of 0.5 A (Nozhen Pars, Iran). All EME experiments were performed at room temperature.

Instrumentation

Separation and detection of DMP, DBP and DEHP were performed by a gas chromatograph Shimadzu GC-2010 (Kyoto, Japan) equipped with a split/split-less injector and a flame ionization detector (FID). The capillary column BP5 (5% phenyl siloxane/95% methyl polyorganosiloxane), 30 m × 0.25 mm I.D., and stationary film thickness of 0.25 μm (Supelco, Bellefonte, USA) were used for GC separation of analytes. The temperatures of the injector and detector were set at 280°C and 300°C, respectively. The temperature program commenced at 100°C for 1 min, and was then raised by 30°C min⁻¹ to 270°C, held for 10 min.

Experimental

In order to achieve a membrane with uniformity, strength and high extraction efficiency for using in the extraction device, effective parameters on electrospinning process such as voltage, electrospinning distance and the collector, and polymer concentration were optimized by Taguchi software version 17 (England). For this purpose, three factors in three levels including voltage (kV) from 16 to 25, electrospinning distance (cm) between 17–22 and polymer concentration 10 to 20 w/w% have been investigated. Taguchi designed 9 experiments based on these levels. Along these designed experiments, some of them did not give an appropriate membrane for using in the device due to their thickness or mechanical stability. The fabricated membranes have been used in EME device for analytes extraction under the same condition, then the analytes were determined using GC/FID. Finally, peak areas of each experiment calculated as the response. The best response was related to the experiment with 16 kV voltage, 15 cm for distance between nozzle and the collector, and 20 w/w% polymer concentration. The SEM image of the mentioned membrane was shown in Figure 2. The selected membrane has 70 μm thickness as it can be inferred from Figure 2-a, 2-b and 2-c reveal that the membrane has its porosity all over the surface and cross-section.

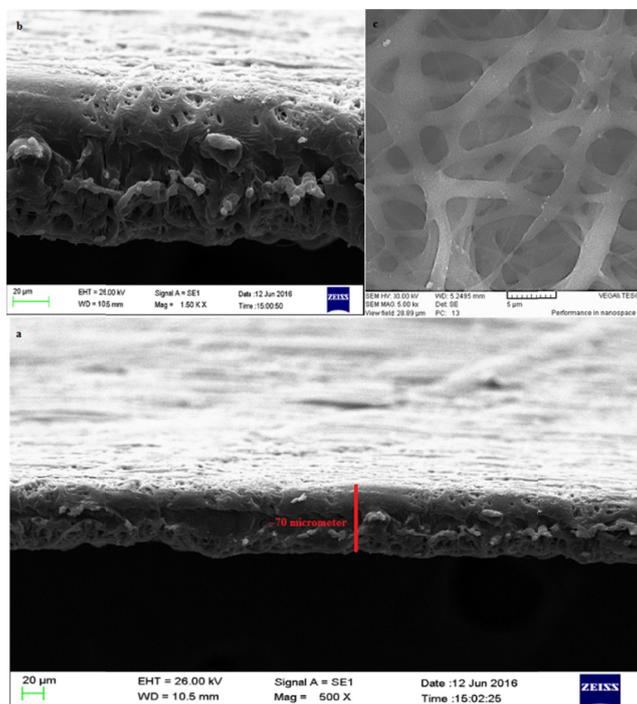


Figure 2. SEM images of the selected membrane

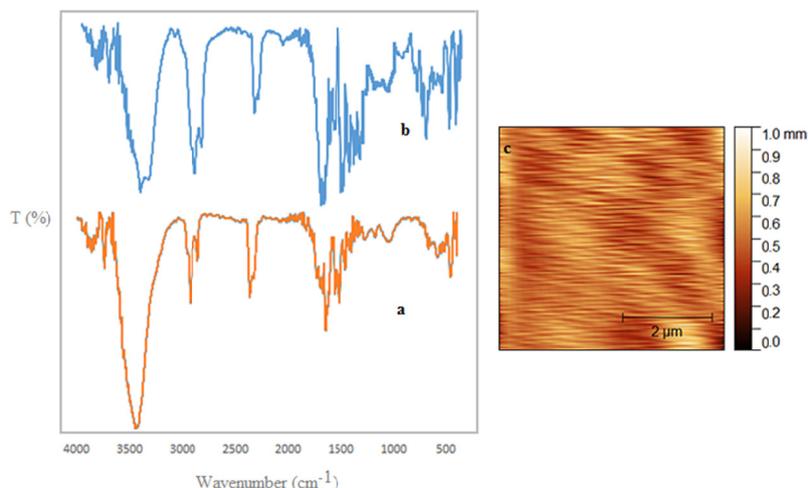


Figure 3. FTIR spectrum (a, b) and AFM (c) image of the membrane

FTIR analysis for polyurethane powder (a) and electrospun polyurethane membrane (b) were performed in 400-4000 cm⁻¹ (Fig. 3). Characteristic band of the carbonyl group was seen in the 1620-1680 cm⁻¹ region. The two bands observed between 2325 and 2360 cm⁻¹ were attributed to symmetric and non-symmetric stretching of the N=C=O bond. The stretching vibration of CH₃ and C=C at 2923 and 1520 cm⁻¹ are observed, respectively. A sharp band N-H was appeared at 3440 cm⁻¹. Similarity between (a) and (b) approve the membrane is made by polyurethane.

To examine morphological details, AFM analysis was used. (Fig. 3-c) shows a large-scale (1.0mm×1.0

mm) AFM image of electrospun membrane. The membrane surface seems flat with a uniform roughness at a microscopic scale.

Results and Discussion

Optimization of EME procedure

RSM based on CCD was used to obtain the optimum conditions for simultaneous extraction of phthalates. Design-Expert software version 7.0 (Stat-Ease Inc., MN, USA) was employed to generate the experimental matrix and evaluate the results. Extraction voltage (A) 50-250 v, distance between electrodes (B) 0-4 cm,

Table 1. ANOVA table for extracting phthalates using FM-EME method

Source	Sum of squares	d.f. ^a	Mean square	F-value ^b	P-value ^c	Prob>F
Block	3377.35	1	3377.35			
Model	4.722E+005	14	33729.22	40.44	<0.0001	Significant
A-	69938.00	1	69938.00	83.86	<0.0001	
B-	43218.00	1	43218.00	51.82	0.0004	
C-	1.183E+005	1	1.183E+005	141.89	<0.0001	
D-	38920.5	1	38920.5	46.67	0.0005	
AB	15500.25	1	15500.25	18.59	0.0050	
AC	24864.50	1	24864.50	29.81	0.0016	
AD	15252.25	1	15252.25	18.29	0.0052	
BC	19012.50	1	19012.50	22.80	0.0031	
BD	1122.25	1	1122.25	1.35	0.2901	
CD	18818.00	1	18818.00	33.56	0.0032	
A2	4563.55	1	4563.55	5.47	0.0579	
B2	23526.27	1	23526.27	28.21	0.0018	
C2	12921.09	1	12921.09	15.49	0.0077	
D2	17488.96	1	17488.96	20.97	0.0038	
Residual	5003.89	6	833.98			
Lack of fit	1177.14	2	588.57	0.62	0.5849	Not significant
Pure error	3826.75	4	956.69			
Cor total	4.806E+005	21				

a: degrees of freedom; b: test for comparing model variance with residual (error) variance; c: probability of seeing the observed *F*-value if the null hypothesis is true

extraction time (C) 1.25-26.25 min and stirring rate (D) 100-1300 rpm, were selected as important parameters in extraction efficiency and investigated in 4 levels from low to high level. All experiments were done in two-phase EME mode with carbon tetrachloride as SLM and acceptor solvent.

The response was the sum of the peak areas of phthalates. Following equation determines a critical point including maximum, minimum or middle point in the polynomial function containing a quadratic model. Peak area = $-448.547 + 1.391A + 5.818B + 0.111C + 1.007D + 1.245AB + 0.178AC - 4.117E - 003AD - 7.800BC - 0.0558BD + 0.0259CD - 5.273E-003A^2 - 29.933B^2 - 0.568C^2 - 2.868E-004D^2$

To evaluate the EME method and determine data dispersion, the analysis of variance (ANOVA) was performed. Regarding to the Table 1, it can be pointed out that the model was significant. Also, the "lack of fit" was not significant ($p=0.58$), which showed that the model fitted the data. Presented model implied that voltage and time are the most effective parameters on the extraction efficiency due to their p -value ($p<0.0001$).

Interactions between the parameters were also monitored. The 3D graphs were used for this purpose. In these graphs response was depicted by two factors variable amounts while two other factors were constant. As it can be inferred from Figure 4, time-voltage, time-distance between electrodes and time-stirring rate had more effective interaction on the results. It was driven from design software that the optimum conditions were obtained voltage 198 V, extraction time 19 min, distance between electrodes 1 cm and stirring rate 1000 rpm.

Real samples analysis

Three kinds of water samples were used as real samples. The proposed EME setup was used for extraction phthalates from real samples. The results were summarized in Table 2. The recoveries obtained from those compounds in spiked water samples at a concentration of 40-2000 ng mL⁻¹ were from 84-108%. The chromatograms obtained by EME-GC-FID are shown in Figure 5, which ensure the clean extraction and separation due to no interfering peaks in the chromatograms.

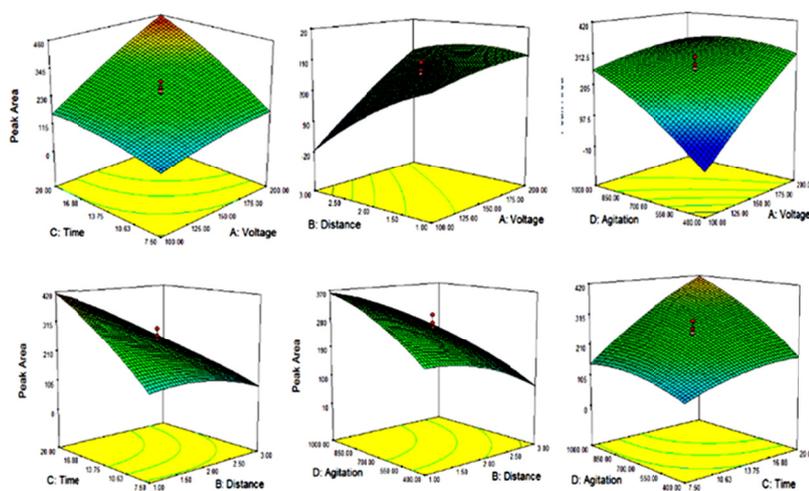


Figure 4. Three-dimensional representation of the response surfaces where (A) time and applied voltage, (B) distance of the electrodes and applied voltage, (C) applied voltage and agitation (D) time and distance of the electrodes, (E) distance of the electrodes and agitation, (F) time and agitation kept at their central level and the others varied within the experimental range

Table 2. Analytical results of extracting of phthalates in real samples (ng mL⁻¹) using FM-EME-GC-FID method

Sample	DMP			DEHP		
	Phthalate concentration	Added amount	Analyzed amount	Phthalate concentration	Added amount	Analyzed amount
Expired mineral water	N. D ^a	200±21.6 ^b	172±18.5	34.1±2.7	10	37±2.9
Karaj fresh water	N. D	200±21.6	172±18.5	N. D	40	33.6±2.7
Cheshmeali fresh water	N. D	200±21.6	172±18.5	N. D	200	168±13.4

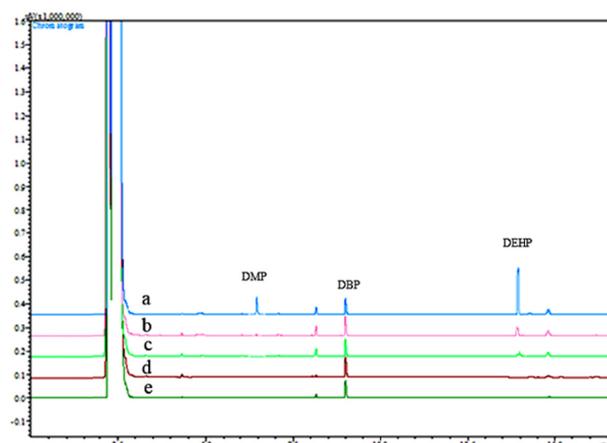


Figure 5. EME-GC-FID chromatograms of mineral water sample under optimum conditions. (a) mixture of analytes with the concentration of $2 \mu\text{g}\cdot\text{mL}^{-1}$, (b) spiked the expired mineral water sample with 10 ng mL^{-1} of target analytes, and (c-e) expired mineral water, Karaj fresh water and Cheshmeali fresh water which were kept in plastic bottles for 1 year. (In all samples DBP was used as an internal standard)

Method validation

To confirm the applicability of the EME method with the new hand-made membrane, calibration curves were plotted for analytes mixture solutions with various concentrations. Also for making comparison among different methods for the determination of phthalates, figure of merits calculated for the proposed method. All these experiments have been done under the optimum conditions. Table 3 exhibits data validation. Under optimum conditions, calibration curves were obtained in the range of $0.5\text{-}5000 \text{ ng mL}^{-1}$ with $R^2 > 0.990$. Repeatability was obtained from seven consecutive replicates and expressed as relative standard deviations (RSDs%). The repeatability were less than 12% and

14% for intraday and interday, respectively. The enrichment factor (EF) was expressed as the ratio of final concentration of the analyte after EME and solvent evaporation to $100 \mu\text{L}$ to its concentration in the original solution without EME by direct injection to GC/FID. The enrichment factors of the proposed method ranged from 26 and 77. LOD and LOQ are the lowest concentration of the analyte in a sample that provides a chromatographic signal 3 and 10 times higher than background noise, respectively. The detection limits of phthalates were calculated according to knoll's definition [36]. For estimating of C_{LOD} , a calibration sample (C_s) was injected into GC-FID and then the peak height (h_s) was measured from the

Table 3. Dynamic linear range (DLR), limits of detections (LODs), limits of quantitation (LOQs), relative recovery (RR), enrichment factor (EF) and repeatability (RSD%) for the analysis of DMP and DEHP in aqueous samples for proposed method and comparison with other methods

Method	Analyte	DLR (ng mL^{-1})	RSD (%)	RR (%)	LOD (ng mL^{-1})	EF	Ref.
FM-EME-GC-FID	DMP	0.5-5000	10.8-12.1	86-106	0.03	26	This work
	DEHP	0.5-5000	8-11.2	84-108	0.02	77	
MSPE-GC-FID	DEHP	10-1700	10	97-111	3.20	-	[38]
SPME-GC-FID	DMP	0.8-8000	9.96	86.3-109.3	0.126	-	[39]
	DEHP	0.48-480	1.69		0.008		
SBSE-GC-MS	DMP	0.05-100	8.46	-	0.003	-	[37]
	DEHP	0.1-100	5.09		0.028		
LLE-GC-MS	DMP	75-4800	1.4-1.8	93.8-103.8	27.45	-	[35]
	DEHP	75-4800	0.6-2.1	101.4-112.1	38.81		
HF-LPME-GC-MS	6 Phthalate	0.02-10	4-19	-	0.01-0.1	-	[40]

a: not detected; b: mean value=standard deviation (n=3)

achieved chromatogram. In order to achieve the height of the largest noise fluctuation

(h_n) measurement, the pre-selected chart segment was examined carefully. At the end, the corresponding multiplier constant, K_{LOD} (1.97), was employed in following equation [Eq. 1]

$$C_{LOD} = k_{LOD} h_n \frac{C_s}{h_s} \quad (\text{Eq. 1})$$

detection were found to be 0.03 and 0.02 ng mL⁻¹ and limits of quantification were obtained 0.09 and 0.06 for DMP and DEHP, respectively. The relative recovery (RR) was determined by comparing the amount of analyte in three levels added to water sample to the recovered concentration after the EME procedure. Relative recovery for DEHP and DMP from the water sample was 84-108% and 86-106%, respectively. The figures of merit of the proposed method and some of the published methods for extraction and determination of DMP and DEHP have been compared and the results are summarized in Table 3 [35, 37-40].

Conclusion

In the present work, we successfully developed the EME procedure, by a flat electrospin membrane. The proposed method was called FM-EME followed by GC for rapid extraction and quantification of phthalates in water samples. RSM based on CCD was used to determine the interaction and quadratic effects of variables, and also optimize the parameters for FM-EME procedure. Simple experimental setup, a high enrichment factor, good precision and no matrix interference are clear advantages of this method. The comparison of the proposed method with others for phthalates analysis showed acceptable results and proved the applicability of developed EME method followed by GC for extraction and determination of phthalates in water sample.

References

- Mollahosseini A., Togholi M., and Kamankesh M., Zeolite/Fe₃O₄ as a new sorbent in magnetic solid-phase extraction followed by gas chromatography for determining phthalates in aqueous samples. *J. Sep. Sci.* **38** (21): 3750-3757 (2015).
- Wang, H., Wu Z., Chen B., He M., and Hu B., Chip-based array magnetic solid phase microextraction on-line coupled with inductively coupled plasma mass spectrometry for the determination of trace heavy metals in cells. *Analyst* **140** (16): 5619-5626 (2015).
- Rosting C., Pedersen-Bjergaard S., Hansen SH. and Janfelt C., High-throughput analysis of drugs in biological fluids by desorption electrospray ionization mass spectrometry coupled with thin liquid membrane extraction. *Analyst* **138** (20): 5965-5972 (2013).
- Davarani SS., Pourahadi A., Nojavan S., Banitaba MH. and Nasiri-Aghdam M., Electro membrane extraction of sodium diclofenac as an acidic compound from wastewater, urine, bovine milk, and plasma samples and quantification by high-performance liquid chromatography. *Anal. Chim. Acta* **722**: 55-62 (2012).
- Ndungù K., Djane NK. and Mathiasson L., Determination of trace metal ions by ion-pair chromatography after enrichment using supported liquid membrane. *J. Chromatogr. A* **826** (1): 103-108 (1998).
- Berhanu T., Liu JF., Romero R., Megersa N. and Jönsson JA., Determination of trace levels of dinitrophenolic compounds in environmental water samples using hollow fiber supported liquid membrane extraction and high performance liquid chromatography. *J. Chromatogr. A* **1103** (1): 1-8 (2006).
- Audunsson G., Aqueous/aqueous extraction by means of a liquid membrane for sample cleanup and preconcentration of amines in a flow system. *Anal. Chem.* **58** (13): 2714-2723 (1986).
- Gjelstad A., Rasmussen KE. and Pedersen-Bjergaard S., Electrokinetic migration across artificial liquid membranes: tuning the membrane chemistry to different types of drug substances. *J. Chromatogr. A* **1124** (1-2): 29-34 (2006).
- Aladaghlo Z., Fakhari AR. and Hasheminasab KS., Application of electromembrane extraction followed by corona discharge ion mobility spectrometry analysis as a fast and sensitive technique for determination of tricyclic antidepressants in urine samples. *Microchem. J.* **129**: 41-48 (2016).
- Fashi A., Yaftian MR. and Zamani A., Electromembrane-microextraction of bismuth in pharmaceutical and human plasma samples: optimization using response surface methodology. *Microchem. J.* **130**: 71-78 (2017).
- Davarani SS., Morteza-Najarian A., Nojavan S., Pourahadi A. and Abbassi MB., Two-phase electromembrane extraction followed by gas chromatography-mass spectrometry analysis. *J. Sep. Sci.* **36** (4): 736-743 (2013).
- Zahedi P., Davarani SS., Moazami HR. and Nojavan S., Surfactant assisted pulsed two-phase electromembrane extraction followed by GC analysis for quantification of basic drugs in biological samples. *J. Pharmac. Biomed. Anal.* **117**: 485-491(2016).
- Ramos Payán MD., Jensen H., Petersen NJ., Hansen SH. and Pedersen-Bjergaard S., Liquid-phase microextraction in a microfluidic-chip-High enrichment and sample clean-up from small sample volumes based on three-phase extraction. *Anal. Chim. Acta.* **735**: 46-53 (2012).
- Huang C., Seip KF., Gjelstad A. and Pedersen-Bjergaard S., Electromembrane extraction for pharmaceutical and biomedical analysis-Quo vadis. *J. Pharmac. Biomed. Anal.* **113**: 97-107 (2015).
- Eibak LE., Parmer MP., Rasmussen KE., Pedersen-Bjergaard S. and Gjelstad A., Parallel electromembrane extraction in a multiwell plate. *Anal. Bioanal. Chem.* **406** (2): 431-440 (2014).
- Davarani SSH., Sheikhi N., Nojavan S., Ansari R.

- and Sozan Mansori, Electromembrane extraction of heavy metal cations from aqueous media based on flat membrane: method transfer from hollow fiber to flat membrane. *Anal. Methods* **7**(6): 2680-2686 (2015).
17. Huang C., Eibak LE., Gjelstad A., Shen X., Trones R., Jensen H. and Pedersen-Bjergaard S., Development of a flat membrane based device for electromembrane extraction: a new approach for exhaustive extraction of basic drugs from human plasma. *J. Chromatogr. A* **1326**: 7-12 (2014).
 18. Zhang X., Zhang H., Liu Y., Guo L., Ye J. and Qingcui Chu, Sensitive determination of five priority haloacetic acids by electromembrane extraction with capillary electrophoresis. *Chinese J. Chem.* **33** (2): 235-240 (2015).
 19. Boussu K., Van der Bruggen B., Volodin A., Van Haesendonck C., Delcour J A., Van der Meeren P. and Vandecasteele C., Characterization of commercial nanofiltration membranes and comparison with self-made polyethersulfone membranes. *Desalination* **191** (1-3): 245-253 (2006).
 20. Silva R., Francesco M. D. and Pozio A., Solution-cast Nafion® ionomer membranes: preparation and characterization. *Electrochim. Acta.* **49** (19): 3211-3219 (2004).
 21. Raaijmakers MJ., and Benes NE., Current trends in interfacial polymerization chemistry. *Progress Polymer Sci.* **63**: 86-142 (2016).
 22. Zhu W., Zhang X., Zhao C., Wei W. and Hou J., A novel polypropylene microporous film. *Polymers Advanced Technol.* **7** (9): 743-748 (1996).
 23. Trommer, K. Morgenstern B., Nonrigid microporous PVC sheets: Preparation and properties. *J. Applied Polymer Sci.* **115** (4): 2119-2126 (2010).
 24. Martin CR., Nishizawa M., Jirage K. and Munsik Kang, Investigations of the transport properties of gold nanotubule membranes, *J. Phys. Chem.* **105** (10): 1925-1934 (2001).
 25. Bagheri, H., Najarzadekan H. and Roostaie A., Electrospun polyamide-polyethylene glycol nanofibers for headspace solid-phase microextraction. *J. Sep. Sci.* **37** (14): 1880-1886 (2014).
 26. Moein MM., Javanbakht M., Karimi M. and Akbari-adergani B., Fabrication of a novel electrospun molecularly imprinted nanomembrane coupled with high-performance liquid chromatography for the selective separation and determination of acesulfame. *J. Sep. Sci.* **38** (8): 1372-1379 (2015).
 27. Bagheri H., Piri-Moghadam H., Rastegar S. and Taheri N., Electrospun titania sol-gel-based ceramic composite nanofibers for online micro-solid-phase extraction with high-performance liquid chromatography. *J. Sep. Sci.* **37** (15): 1982-1988 (2014).
 28. Ruggieri F., D'Archivio AA., Di Camillo D., Lozzi L., Maggi MA., Mercurio R. and Santucci S., Development of molecularly imprinted polymeric nanofibers by electrospinning and applications to pesticide adsorption. *J. Sep. Sci.* **38** (8): 1402-1410 (2015).
 29. Bagheri H., Najafi Mobara M., Roostaie A. and Baktash MY., Electrospun magnetic polybutylene terephthalate nanofibers for thin film microextraction. *J. Sep. Sci.* **40** (19): 3857-3865 (2017).
 30. Bagheri H., Ayazi Z., Aghakhani A. and Alipour N., Polypyrrole/polyamide electrospun-based sorbent for microextraction in packed syringe of organophosphorous pesticides from aquatic samples. *J. Sep. Sci.* **35** (1): 114-120 (2012).
 31. Bhardwaj N. and Kundu SC., Electrospinning: a fascinating fiber fabrication technique. *Biotechnol. Advances* **28** (3): 325-347 (2010).
 32. Yaripour S., Mohammadi A. and Nojavan S., Electromembrane extraction of tartrazine from food samples: Effects of nano-sorbents on membrane performance. *J. Sep. Sci.* **39** (13): 2642-2651 (2016).
 33. Oliveira AM., Loureiro HC., Souza de Jesus FF. and Pereira de Jesus D., Electromembrane extraction and preconcentration of carbendazim and thiabendazole in water samples before capillary electrophoresis analysis. *J. Sep. Sci.* **40** (7): 1532-1539 (2017).
 34. Sharafi K., Fattahi N., Mahvi AH., Pirsahab M., Azizzadeh N. and Noori M., Trace analysis of some organophosphorus pesticides in rice samples using ultrasound-assisted dispersive liquid-liquid microextraction and high-performance liquid chromatography. *J. Sep. Sci.* **38** (6): 1010-1016 (2015).
 35. Ni X., Xing X., Cao Y. and Cao G., Determination of phthalates in food packing materials by electrokinetic chromatography with polymeric pseudostationary phase. *Food Chem.* **190**: 386-391 (2016).
 36. Pérez-Outeiral J., Millán E. and Garcia-Arrona R., Determination of phthalates in food simulants and liquid samples using ultrasound-assisted dispersive liquid-liquid microextraction followed by solidification of floating organic drop. *Food Control* **62**: 171-177 (2016).
 37. Ye CW., Gao J., Yang C., Liu XJ., Li XJ and Pan SY, Development and application of an SPME/GC method for the determination of trace phthalates in beer using a calix [6] arene fiber. *Anal. Chim. Acta* **641** (1-2): 64-74 (2009).
 38. Si Q., Li F., Gao C., Wang C., Wang Z. and Zhao J., Detection of phthalate esters in seawater by stir bar sorptive extraction and gas chromatography-mass spectrometry. *Marine. Poll. Bull.* **108** (1-2): 163-170 (2016).
 39. Psillakis E. and Kalogerakis N., Hollow-fibre liquid-phase microextraction of phthalate esters from water. *J. Chromatogr. A* **999**: 145-153 (2003).