Determination of phthalate esters in seawater of Chabahar Bay using dispersive liquid-liquid microextraction coupled with GC-FID
Beheshteh Ajdari, Mahmoud Nassiri, Mir Mahdi Zahedi and Morteza Ziyaadini

ABSTRACT
Phthalate esters (PEs), a group of environmental pollutants which are possibly carcinogenic to humans, have been detected in seawater. Seven PEs in seawater were quantitatively determined by using gas-chromatography flame ionizing detection after executing dispersive liquid-liquid microextraction. The suggested method is optimized for microextraction and determination of PEs in artificial sea water. Factors affecting the microextraction procedure such as the type and volume of extracting and dispersive solvents (carbon tetrachloride, 20 μL; methanol, 0.5 mL), extraction time and pH (7) were investigated. Under optimum conditions, the limit of detection of the analytes were obtained between 0.04 and 4.52 μg·L⁻¹, and linearity and linear range were of 0.999 ≥ R² ≥ 0.994 and 10–560 μg·L⁻¹ respectively. Enrichment factors were found in the range of 761–827 fold, while the relative standard deviations of the analytes were between 0.17 and 7.5% (n = 6) for real sea water samples. Using this method, total PEs content of seawater from several locations in Chabahar Bay (the southeast part of Iran) was estimated 2.33–90.45 μg·L⁻¹.

Key words | Chabahar Bay, Iran, dispersive liquid-liquid microextraction, phthalate esters, seawater

HIGHLIGHTS
• PEs in seawater were analyzed by gas chromatography FID detection.
• Dispersive liquid-liquid microextraction was used to preconcentrate trace amounts of PEs.
• Parameters affecting DLLME efficiency were optimized for seawater samples.
• Performance of the method in extraction of PEs from the seawater of Chabahar Bay was investigated.

INTRODUCTION
Human activities are responsible for a major decline of the world’s biological diversity, and human impacts could have accelerated present extinction rates to 1,000–10,000 times higher than the natural rate. In the oceans, the threat to marine life comes in various forms, such as over-exploitation and harvesting, dumping of waste, pollution, alien species, land reclamation, dredging and global climate change (Derraik 2002). PEs are a class of synthetic chemicals that have been used on a large scale since the 1950s. They comprise a large number of compounds, and are now frequently used in plastic production industries to enhance the flexibility of the materials. PEs are also used as solvents and emulsifiers in pharmaceuticals, pesticides, and health and beauty products, as well as children’s toys. Because of their wide applications and the growing demand for them, PEs have become one of the highest yielding chemicals in the world and their worldwide production amounts approximately to 6 million tons per year (Amanzadeh et al. 2016). The presence and persistence of PEs in aquatic environments directly depend on their chemical and physical properties, and on degradation processes. In aquatic environments, they are soluble by fulvic and humic acids as complexes and/or adsorbed onto particulate matter, with sediments being the final sink (Vitali et al. 1997).

Phthalates as well as their metabolites and degradation products can cause adverse effects on human health, especially on the liver, kidney, and testicles, and endocrine
disruption. Currently, the potential ecological risks of phthalates in the aquatic environment lead to increasing concern (Fernández-González et al. 2017). There is no covalent bond between the phthalates and plastics, and during the use of the plastic product, the plastic becomes distorted and worn, which leads to their frequent release and migration. This can lead to the exposure and loss of previously bound compounds (Ezoddin et al. 2015). 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 (Yamini et al. 2015). Exposure to sunlight (especially UVB) can degrade plastics. The use and production of PEs have been steadily increasing during the past decades. Due to the trace concentration level of PEs and interference of the complicated matrix, it is necessary to carry out sample pre-concentration for an accurate determination of these compounds (Ezoddin et al. 2015). Many researchers have reported information about PEs found in environmental samples, as PEs’ ecotoxicological data are especially relevant for aquatic communities (Vitali et al. 1997).

PEs are widely used chemicals, with over 4 million tonnes being produced worldwide each year. On the basis of their octanol—water partition coefficients ($K_{ow}$), which range from $10^{1.61}$ for dimethyl phthalate to $10^{9.46}$ for di-iso-decyl phthalate, certain PEs have the potential to bio-concentrate and biomagnify in aquatic food webs (Mackintosh et al. 2004).

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A search for the more abundantly produced phthalate plasticizers, di-2-ethylhexyl phthalate (DEHP) and di-n-butyl phthalate (DBP), in marine water was initiated. The obtained results clearly show that PEs are a new class of marine pollutant (Giam et al. 1978).

The commonly used analytical techniques for determination of PEs in different sample matrices are gas chromatography (GC), coupled to mass spectrometry (MS) or flame ionization detector (FID), and high performance liquid chromatography (HPLC) with different detectors, such as MS, ultraviolet (UV), multiple wavelength detector, variable wavelength detector (VWD), and diode array detector (Lopez-Jimenez et al. 2005; Li et al. 2008a, 2008b; Guo & Lee 2013).

Owing to the very low concentration levels of PEs in environmental water samples, an enrichment step is usually needed before the introduction of the samples into analytical instrument. In addition, in samples such as seawater, due to their very complicated matrix, a separation step is of great importance. The separation techniques, which are commonly applied to monitor PEs in water samples, are liquid-liquid extraction (LLE) (Ranjbari & Hadjmohammadi 2012), solid-phase extraction (SPE) (Ranjbari & Hadjmohammadi 2012), solid-phase microextraction (SPME) (Kamarei et al. 2011), liquid-phase microextraction (LPME) (Farajzadeh & Afshar Mogaddam 2012), single-drop microextraction (SDME) (Wu et al. 2012) and hollow fiber-based liquid-phase microextraction (HF-LPME).

A rapid microextraction procedure known as dispersive liquid-liquid microextraction (DLLME) was introduced by Rezaee and co-workers in 2006. It is based on a ternary solvent system like homogeneous liquid-liquid extraction and cloud point extraction. In this method, an appropriate mixture of extractor and dispersive solvent is rapidly injected into an aqueous sample to make a cloudy solution. After centrifugation, the resulting sediment was injected into the GC or HPLC for analysis. The advantages of DLLME are its simplicity, speed, low cost, high recovery, high enrichment factor, and very short extraction time (Yan et al. 2010; Li et al. 2013). DLLME has been successfully applied for the determination of poly-brominated diphenyl ethers (Li et al. 2008a, 2008b; Liu et al. 2009), phenols (Lavilla et al. 2012), organo-phosphorus pesticides (Tasi & Huang 2009), aromatic amines (Fan et al. 2008), and antioxidants (Farajzadeh et al. 2007), in water samples.

In this work, DLLME coupled to gas chromatography is employed for simultaneous determination of seven PEs in the seawater of Chabahar Bay. Optimization of microextraction conditions are done completely in artificial seawater therefore the method has suitable adaptation for measuring PEs in seawater. On the other hand, it seems that present work is the first monitoring of PEs in Chabahar Bay.

**EXPERIMENT**

**Instruments**

Chromatographic analysis was performed on a gas chromatograph (GC-2014, Shimadzu, Japan) equipped with a splitless/split injector and a flame ionization detector. Nitrogen (99.999%) was employed as a gas carrier at the flow rate of 1.4 mL min$^{-1}$. The analytes were separated on a CBP1-S25-050 (Supelco, Bellefonte, USA) capillary column (100% dimethyl silicone, 25 m × 0.32 mm i.d., and film thickness 0.5 μm). The temperature program column was as follows: the initial oven temperature was 185 °C (held for 1 min), then increased at 25 °C min$^{-1}$ to 285 °C (held for 6 min). The temperature of the injector port and FID detector was maintained at 300 °C. A Centurion scientific k3 series k241R centrifuge was used to accelerate
separation phase. A TPS WP-80 digital pH meter was used for pH adjustments and a 100 μL Hamilton syringe (Hamilton Company, Nevada) was used for the separation phase of collected sediments.

Reagents

The studied compounds were dimethyl phthalate (DMP), diethyl phthalate (DEP), di-allyl phthalate (DAP), di-n-butyl phthalate (DNBP), di-isobutyl phthalate (DIBP), di-isooctyl phthalate (DIHP) and di-2-ethylhexyl phthalate (DEHP) esters. All PEs, chloroform (CHCl₃), dichloromethane (CH₂Cl₂), and carbon tetrachloride (CCl₄), as extracting solvents, and also, acetone, acetonitrile, methanol and ethanol, as dispersive solvents were purchased from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). These compounds were of analytical grade and were used as received. A stock solution containing all analysts, in acetone was prepared at a concentration of 1000.0 mg·L⁻¹ (of each PE). The working standard solutions were prepared daily by appropriate dilutions of the stock solution with ultrapure water to obtain the required concentrations in the range of 10–560 μg·L⁻¹. All the glassware used in the study were previously washed with acetone and finally dried in an oven at 250 °C (Yan et al. 2010). The stock and working standard solutions were stored at 4 °C in a refrigerator.

The required artificial seawater was prepared by dissolving the following salts in 1 L of deionized water: NaF (3 mg), KBr (100 mg), Na₂SiO₃·9H₂O (20 mg), SrCl₂·H₂O (20 mg), KCl (5 mg), MgCl₂·6H₂O (10.780 g), NaHCO₃ (200 mg), H₂BO₃ (50 mg), CaCl₂·2H₂O (1.470 g) and NaCl (23.500 g) (Zahedi et al. 2014). All of these salts were of analytical grade, and obtained from Merck, Fluka, and Sigma-Aldrich (Steinheim, Germany) and used without any further purification.

Since the main source of PEs is plastic products, which are widely used in laboratories, before stating the work different techniques were used to reduce the amount of sample contamination in these places including washing and putting the used glassware in a furnace, cleaning the environment, and using air-conditioning. The analytical steps in the sample work-up were minimized to those necessary to guarantee the reliability of the method and the adequacy of the detection limits for environmental samples. Glassware used for sampling and analyses was accurately washed with detergents, rinsed with organics-free distilled water and rinsed several times with acetone and methylene chloride.

DLLME procedure

The DLLME procedure was initiated by transferring 8 mL of sample solution into a 15 mL conical bottomed glass centrifuge tube, followed by rapid injection of 0.5 mL methanol as a dispersive solvent and 20 μL carbon tetrachloride as an extractor solvent into the sample solution and shaking the mixture gently for a few seconds. After a cloudy solution was formed, the separation phase was performed by a rapid centrifugation at 4,000 rpm for 5.0 minutes. Finally, 2.0 μL of the organic phase was removed by microsyringe and injected into GC for analysis.

RESULTS AND DISCUSSION

There are various parameters affecting the DLLME performance and efficiency, including the type and the volume of the extracting and dispersive solvents, pH, and extraction time. These parameters were investigated carefully, and their optimal amounts were determined and applied to the extraction of seven PEs that are indicated in the following sections. Because seawater has a complex matrix, it could lead to the possibility of interference and low selectivity of the method. In this work, to achieve a highly sensitive method, DLLME optimization parameters were carried out on the artificial seawater. In order to evaluate the optimization results, an enrichment factor has been used. This factor was defined as the ratio between the analyte concentration at the sedimentary phase (C_{sed}) and the initial concentration of analyte (C₀) in the sample (Equation (1)) (Rezaee et al. 2006).

\[
EF = \frac{C_{sed}}{C_0} \quad (1)
\]

Selection of extracting and dispersive solvents

The extracting and dispersive solvents are important factors in DLLME. A good extracting solvent should have: (1) density higher than water; (2) low solubility in water; (3) extracting capability for the analytes of interest; (4) good chromatographic behavior; and finally (5) it should be easily dispersed in water during the dispersing step (Farajzadeh et al. 2012; Ranjbari & Hadjmohammadi 2012). In this study, three solvents (dichloromethane, chloroform and carbon tetrachloride) were examined in order to find the most suitable solvent. Compared with the previous report on DLLME, the optimal extracting and dispersive solvents depend on the composition of the water sample, differing...
between drinking water and seawater samples (Zahedi et al. 2014). This difference may be due to the salting-out effect of the sample matrix on the miscibility of the dispersive solvent with water and by the dielectric constant of the extracting solvent, both of which influence DLLME. The enrichment factors (EFs) in Figure 1 indicated that carbon tetrachloride was the best extracting solvent for the extraction of PEs.

The main point for selection of a dispersive solvent is that it should be miscible in both the organic phase (extracting solvent) and the aqueous sample phase. This decreases the interfacial tension between the two phases and accelerates changing the droplets of the extracting solvent into the aqueous phase. Thereby, acetone, acetonitrile, methanol and ethanol were selected as dispersive solvents. Figure 2 shows that the best EF was obtained by using methanol, which may be due to its higher solubility for PEs (Yan et al. 2010). Therefore, methanol was selected as the dispersive solvent for further work.

The volume effect of the extractor and dispersive solvent

In a microextraction procedure, the volume of extracting solvent is crucial by having an important impact on the analytical signals. Commonly, the volume of extracting solvent is selected to be as low as possible in order to achieve higher EFs and lower toxicity for the environment. On the other hand, the volume should be moderate to extract as much of the analytes as possible and to ensure that enough sedimentary phase volume is formed for further chromatographic analysis. In order to evaluate the effect of the extracting solvent volume on the efficiency of the extraction, experiments were performed using 0.50 mL methanol containing different carbon tetrachloride volumes (20, 30, 40, 50, 60, 70 μL). By increasing the extracting solvent volume from 20 to 70 μL due to the dilution of the analytes, the enrichment factor decreased. Thus, 20 μL of carbon tetrachloride was selected as the optimum volume of extracting solvent in order to obtain higher enrichment factors.

The volume of dispersive solvent is also an important parameter that affects the cloudyness of the solution (water/dispersive solvent/extractor solvent), as well as the degree of solvent dispersion in the aqueous phase (Zahedi et al. 2014). This parameter has a significant effect on the enrichment factor. Using too much dispersive solvent will increase the solubility of the analyte in aqueous media, whereas using small volumes will not disperse the extracting phase completely (Yan et al. 2011, 2010). Therefore, various volumes of dispersive solvent including 0.50, 0.60, 0.70, 0.80, 0.90, and 1.0 mL were used. The results show that the increase of dispersive solvent volume from 0.50 to 1.0 mL causes the enrichment factor to decrease. Therefore, the amount of 0.50 mL methanol was chosen as the optimum volume of dispersive solvent for further work.

The effects of pH and injection time

The pH of the sample solution plays an important role in the extraction of organic compounds that possess an acidic or basic moiety. However, in the case of the PEs studied in this research, there are not any functional groups with acidic or basic properties, but it is clear that the esteric bonds are not stable in both violent acidic and violent alkaline aqueous solutions, which leads to the formation of the bond constitutive materials, i.e. carboxylic acid and alcohol (Ranjbari & Hadjmohammadi 2012). In this work, the effect of pH was studied in the range of 3–9 (Figure 3). Results show that the best pH for extraction of PEs is 7. The stability of the main structure of PEs decreases in both very low and very high pH values of the aqueous sample. Thus, in our experiments the pH of the working solutions was adjusted at 7.

Extraction time is defined as an interval between the injection of the mixture of dispersive solvent (methanol) and the extractor solvent (carbon tetrachloride) to the sample solution before starting to centrifuge (Ghorbani et al. 2013). As a
result, for the evaluation of this parameter, different extraction times (ranging from 0 to 45 minutes) were applied, while keeping the other experimental conditions constant. 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. Therefore, this method is very fast and this is the most distinct advantage of the DLLME technique (Farahani et al. 2010; Ranjbari & Hadjmohammadi 2015).

**Analytical performance of the DLLME-GC-FID**

Under the selected optimum experimental condition, this method was applied to a series of standard solutions containing various concentrations of analytes, in order to develop the respective calibration curves. The limits of detection (LODs), correlation coefficients ($R^2$), linear ranges (LRs), relative standard deviations (RSDs) and enrichment factors (EF) (Ranjbari & Hadjmohammadi 2012) were calculated and summarized in Table 1.

The linearity of the proposed method was studied for all the analytes of interest over a concentration range corresponding to the expected variation of the analytes’ content in the samples (Antonucci et al. 2016).

As shown in Table 1, LODs for the tested PEs were in the range of 0.04–4.52 μg·L$^{-1}$. Linearity values varied in the range of 10–560 μg·L$^{-1}$ with correlation coefficients of 0.995–0.999. The relative standard deviations were in the range of 0.17–7.5% ($n = 6$). Excellent enrichment factors were also obtained between 761 and 827 for target analytes.

Table 2 shows the LOD, LR, RSD values, the extraction time and the sample volumes of other reported methods for the PEs’ extraction and determination from water samples.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Some quantitative data obtained after DLLME-GC-FID determination of the selected phthalate esters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compounds</td>
<td>LOD (μg·L$^{-1}$)</td>
</tr>
<tr>
<td>DMP</td>
<td>1.12</td>
</tr>
<tr>
<td>DEP</td>
<td>3.95</td>
</tr>
<tr>
<td>DAP</td>
<td>4.52</td>
</tr>
<tr>
<td>DiBP</td>
<td>0.12</td>
</tr>
<tr>
<td>DnBP</td>
<td>1.78</td>
</tr>
<tr>
<td>DIHP</td>
<td>0.47</td>
</tr>
<tr>
<td>DEHP</td>
<td>0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Comparison of DLLME-GC-FID with other methods for determination of PEs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>LOD (μg·L$^{-1}$)</td>
</tr>
<tr>
<td>DLLME-GC-MS</td>
<td>0.02–0.05</td>
</tr>
<tr>
<td>LPME-GC-MS</td>
<td>0.002–0.008</td>
</tr>
<tr>
<td>DLLME-GC-FID</td>
<td>0.04–4.52</td>
</tr>
</tbody>
</table>

**Figure 3** | Effects of pH on the EFs of PEs in DLLME. 
**Figure 4** | Locations of coastal Chabahar sampling sites. Site 1: (25° 18' 39 N, 60° 36' 00 E); site 2: (25° 18' 28 N, 60° 37' 26 E); site 3: (25° 18' 54 N, 60° 36' 47 E); site 4: (25° 35' 58 N, 60° 59' 99 E); site 5: (25° 36' 63 N, 60° 60' 77 E).
Comparison of optimized DLLME-GC-FID with the previously reported method for drinking water (Lavilla et al. 2014) revealed considerable differences. This is due to the high concentration of salts in seawater, which affect the yield and optimal extraction conditions. These results suggest that analysis of seawater requires special conditions compared to drinking water.

**Real seawater sample analysis**

The applicability of the method was evaluated by extracting PEs from seawater samples. Seawater samples were taken from the surface layer (25 cm depth) of five different sites of Chabahar Bay, as shown in Figure 4. Sampling stations were 50–100 meters away from the coast. Samples were collected in dark glass bottles (sampling time was May 2013) and each sample was pretreated by filtering through glass microfibers (GF/C Whatman). Then, all of the samples were stored under dark conditions in a refrigerator at 4 °C until their analysis time. The salinity, temperature and pH of the seawater samples varied between 27–39, 27–30 °C and 7.8–8.3, respectively. Direct analysis of seawater shows no sign of EPs. Figure 5(a) is a sample chromatogram of the seawater of this beach (point 3 on the map) after the extraction with the proposed method. As a result, seawater

![Figure 5](https://iwaponline.com/wst/article-pdf/77/7/1782/214268/wst077071782.pdf)
samples were spiked with 40 μg·L⁻¹ PEs to check the matrix effect on the extraction. Analytical results are shown in Table 3. As can be seen, good recoveries (%) between 78.56 and 97.87 were obtained, which indicate the insignificant effect of the matrix on sample preparation. An example of the chromatogram of the same sample is presented in Figure 5(b).

The range of PEs concentrations found in seawater samples from other areas is shown in Table 4. Although few surveys of PEs in samples from the marine environment have been carried out, all authors have reported significant levels of phthalates in water. DiBP, DnBP and DEHP were found in nearly all of the samples, but were also found to be very common laboratory contaminants.

### Table 3 | The results obtained from the analysis of the real seawater samples (recovery (%)) for 40 μg·L⁻¹ added PEs

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>DMP (μg·L⁻¹)</th>
<th>DEP (μg·L⁻¹)</th>
<th>DAP (μg·L⁻¹)</th>
<th>DnBP (μg·L⁻¹)</th>
<th>DiBP (μg·L⁻¹)</th>
<th>DIHP (μg·L⁻¹)</th>
<th>DEHP (μg·L⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.45 ± 0.9</td>
<td>47.25 ± 2.11</td>
<td>–</td>
<td>35.03 ± 1.23</td>
<td>49.44 ± 2.43</td>
<td>24.50 ± 1.02</td>
<td>–</td>
<td>89.34</td>
</tr>
<tr>
<td>2</td>
<td>28.20 ± 0.94</td>
<td>32.18 ± 2.43</td>
<td>20.24 ± 0.91</td>
<td>78.69 ± 2.3</td>
<td>67.19 ± 3.23</td>
<td>2.33 ± 0.10</td>
<td>3.21 ± 0.21</td>
<td>93.54</td>
</tr>
<tr>
<td>3</td>
<td>16.12 ± 0.63</td>
<td>17.17 ± 0.26</td>
<td>38.12 ± 0.85</td>
<td>65.45 ± 0.87</td>
<td>90.45 ± 2.65</td>
<td>16.34 ± 0.75</td>
<td>16.58 ± 0.52</td>
<td>92.75</td>
</tr>
<tr>
<td>4</td>
<td>20.20 ± 0.61</td>
<td>26.90 ± 1.08</td>
<td>29.71 ± 1.31</td>
<td>23.19 ± 0.54</td>
<td>31.01 ± 1.45</td>
<td>14.62 ± 0.87</td>
<td>12.51 ± 0.12</td>
<td>97.26</td>
</tr>
<tr>
<td>5</td>
<td>18.45 ± 0.59</td>
<td>32.15 ± 0.12</td>
<td>25.54 ± 0.89</td>
<td>60.39 ± 2.29</td>
<td>44.13 ± 0.71</td>
<td>63.74 ± 3.43</td>
<td>10.44 ± 0.74</td>
<td>95.53</td>
</tr>
</tbody>
</table>

### Table 4 | Comparison of PEs in other areas

<table>
<thead>
<tr>
<th>Location</th>
<th>DMP (μg·L⁻¹)</th>
<th>DEP (μg·L⁻¹)</th>
<th>DAP (μg·L⁻¹)</th>
<th>DiBP (μg·L⁻¹)</th>
<th>DIHP (μg·L⁻¹)</th>
<th>DEHP (μg·L⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caspian Sea (Iran)</td>
<td>0.61</td>
<td>0.69</td>
<td>–</td>
<td>nd</td>
<td>nd</td>
<td>–</td>
<td>Ranjbari &amp; Hadjmohammadi</td>
</tr>
<tr>
<td>Bohai Sea (China)</td>
<td>–</td>
<td>nd</td>
<td>–</td>
<td>nd</td>
<td>14</td>
<td>78</td>
<td>Wu et al. (2013)</td>
</tr>
<tr>
<td>Huanghai Sea (China)</td>
<td>–</td>
<td>nd</td>
<td>–</td>
<td>nd</td>
<td>11</td>
<td>19</td>
<td>Wu et al. (2013)</td>
</tr>
<tr>
<td>Caspian Sea (Iran)</td>
<td>–</td>
<td>1.75</td>
<td>1.36</td>
<td>1.68</td>
<td>–</td>
<td>–</td>
<td>Ezoddin et al. (2015)</td>
</tr>
<tr>
<td>False Creek (British Columbia)</td>
<td>63</td>
<td>77</td>
<td>–</td>
<td>–</td>
<td>86</td>
<td>116</td>
<td>Blair et al. (2009)</td>
</tr>
<tr>
<td>This work⁴</td>
<td>19.48</td>
<td>31.13</td>
<td>22.72</td>
<td>52.55</td>
<td>56.44</td>
<td>24.31</td>
<td>8.55</td>
</tr>
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nd – not determined.

⁴Average.

### CONCLUSION

In the present study, DLLME-GC-FID for the determination of PEs in seawater samples has been evaluated and optimum conditions of the extraction have been determined. Under the optimum conditions, the limit of detection and the linear range were between 0.04–4.52 μg·L⁻¹ and 10–560 μg·L⁻¹, respectively. The relative standard deviations were below 7.5%. This method is sensitive, inexpensive, simple and fast, and requires only a small volume of organic solvents. Table 3 indicates that the performance of these procedures in PEs extraction from different water samples with various matrices was excellent. To the best of our knowledge, this is the first report that employs the
DLLME-GC-FID technique for the determination of seven PEs in Chabahar Bay seawater.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support received from the Research Council of Chabahar Maritime University.

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First received 7 April 2017; accepted in revised form 6 December 2017. Available online 20 December 2017.