Detection of phthalate esters in seawater by stir bar sorptive extraction and gas chromatography–mass spectrometry

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ABSTRACT

We developed the stir bar sorptive extraction (SBSE)–gas chromatography–mass spectrometry (GC–MS) method to detect 15 kinds of PAEs in seawater. The stir bars (20 mm in length and 1 mm in film thickness) coated with 150 μL of polydimethylsiloxane (PDMS) were found to demonstrate the optimal extraction of PAEs. The optimal conditions were as follows: extraction time of 2 h, extraction temperature of 25 °C, sodium chloride of 5%, methanol of 10%, analytical time of 50 min, and methanol–acetonitrile (4:1) as the solvent. SBSE–GC–MS revealed that under the set temperature, the chromatographic peaks of all 15 PAEs can appear with complete separation. The detection limit ranged from 0.07 μg/L to 5.71 μg/L, whereas the limit of quantification ranged from 0.023 μg/L to 193 μg/L, and the correlation coefficients between the chromatographic peak area and concentration of the PAEs were greater than 0.92.

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1. Introduction

Phthalic acid esters (PAEs) are diesters of 1,2-benzenedicarboxylic acid (or phthalic acid) and mainly manufactured organic matter. With the wide application of plastic materials in human life, phthalates become ubiquitous in the environment (Xu et al., 2009; Rudel et al., 2010). PAEs are widely used in industry and by consumers, especially as plasticizers to increase the ductility and flexibility of plastics and solvents, such as in personal care products, food packaging, and cosmetics. To date, worldwide annual production of plastics has reached a level of 1.8 × 108 tons, and 6–8 million tons of PAEs are consumed each year (Net et al., 2015). PAEs are ubiquitous in the environment and always found in different environment matrices, such as water, soil and sediment (Amiridou and Voutsa, 2011; Devier et al., 2013; Kong et al., 2013; Liu et al., 2010). PAEs are ubiquitous contaminants worldwide and can significantly harm human beings (Swan, 2008). They are weak estrogenic compounds and endocrine disruptors (Susan Jobling, 1995) and they have prioritizing toxicity effect (Rudel et al., 2003). Moreover, these compounds can persist in the environment for several years. Dimethyl phthalate (DMP), dibutyl phthalate (DBP), and diocyl phthalate (DOP) have been listed as priority pollutants for control by China’s environmental monitoring station (Chen et al., 2005). In the European Union, butyl benzyl phthalate (BBzP) and DEHP are listed as substances linked with potential endocrine-disrupting activity. In the United States, the maximum allowed concentrations of DEHP and di (2-ethylhexyl) adipate are 6.0 μg/L and 400 μg/L, respectively, according to the Safe Drinking Water Act by the Environmental Protection Agency (Julinova and Slavik, 2012).

Detection methods for PAEs have rapidly developed in recent years. When the PAE concentration in aqueous sample is low, pretreatment is necessary before detection. For example, Amiridou and Voutsa utilized liquid–liquid extraction (LLE)–gas chromatography (GC)–mass spectrometry (MS) to determine PAEs in bottled water (Amiridou and Voutsa, 2011). Michele and Carlo developed an analytical method to determine PAEs in wine by SPE–GC–MS (Del Carlo et al., 2008); Ya-Qi and Gui-Bin used cartridge for SPE and high-performance liquid chromatography (HPLC) to detect several PAEs in water samples (Cai et al., 2003); Zhong ping and Ikonomou used reversed-phase liquid chromatography/electrospray ionization mass spectrometry (LC/ESI-MS) to determine the composition of PAEs concentrations in sediments and fish in an urbanized marine ecosystem (Lin et al., 2003); Kayoko Kato used automated off-line SPE and coupled with on-line SPE and HPLC–MS to quantify phthalate metabolites in human semen (Kayoko, 2006). Penalver and Pocurull used SMPE with an 85 μm polyacrylate fiber and GC–MS to determine PAEs in water samples (Penalver et al., 2000). But there were a lot of problems in above mentioned methods, such as complex, low sensitivity, small detection range. Therefore, exploring a simple method with high efficiency and wide range of detection, as well as simultaneously testing a variety of PAEs in seawater is necessary.

Baltussen and Sandra developed a new approach for sample enrichment in 1999 named stir bar sorptive extraction (SBSE), which was based on SPME. The stir bar, which is always a stainless steel bar in a
glass tube, is coated with polydimethylsiloxane (PDMS). Compared with SPME (typically less than 5 μL) (Baltussen et al., 1999), the coated amount of PDMS on SBSE was approximately 50–300 μL (Garcia-Falcon et al., 2004). The extraction efficiency significantly increased, and the superior sensitivity and wide application range were determined. Given its simple operation, SBSE is often used for in situ sample analysis. SBSE is generally followed by GC–MS, HPLC, and liquid chromatography (LC–MS); this method is widely used to enrich common pollutants in environmental samples, such as hormones in wastewater (Huang et al., 2009) and river water (Rodil and Moeder, 2008), alkylphenols in river water (Kawaguchi et al., 2005), and polycyclic aromatic hydrocarbons in drinking water (Garcia-Falcon et al., 2004). SBSE can effectively detect a variety of materials in various environments; thus, this method may also be applied to detect PAEs in seawater.

To attempt the difficult detection of PAEs in seawater, the present study developed the SBSE–GC–MS method, which can simultaneously detect 15 PAEs in seawater with simplicity, high efficiency, and a wide detection range. This work focused on the optimization of extraction and solvent desorption. The performance of the method is evaluated in terms of accuracy, linearity, precision, and limits of detection. Furthermore, the method was verified by standard addition methodology in seawater.

2. Materials and methods

2.1. Reagents and standards

A standard mixture of 15 PAEs, namely, dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DBP), di(2-methoxyethyl)phthalate (DMEP), di(4-methyl-2-pentyl) phthalate (DMP), di(2-ethylhexyl) phthalate (DEHP), di-n-pentyl phthalate (DPeP), di-n-hexyl phthalate (DHP), butyl benzyl phthalate (BBzP), di-(2-n-Butoxyethyl) phthalate(DBE), dicyclohexyl phthalate (DCHP), di(2-Ethylhexyl) phthalate (DEHP), diphenyl phthalate (DPhP), di-n-octyl phthalate (DOP) (1000 μg/mL each in hexane), as well as the internal standard benzyl benzoate (99.5% purity) were supplied by Dr. Ehrenstorfer (Augsburg Germany), all the reagents were HPLC grade. All chemicals (CH3CN, CH3Cl, CH2COCH2Na, NaCl, CH3OH, C6H14) were of analytical grade and were used without any further purification. High-purity water (18 MΩ cm) was prepared with a Millipore Milli-Q-Plus water purification system. Stir bars coated with 150 μL of PDMS (20 mm in length, 1 mm film thickness) were purchased from the Zhen Zheng Analysis Instrument Co., Ltd. (Qingdao China).

2.2. Instruments and equipment

GC–MS analysis was performed on an Agilent 7890 series gas chromatograph equipped with an Agilent 5975 C mass selective detector (Agilent Technologies, Little Falls, DE, USA) and a 30 m × 0.25 μm × 0.25 μm HB-5MS capillary column (5% phenyl methyl siloxane; Agilent, USA) in the electron impact and selective ion monitoring (SIM) mode. Other equipment included an ultrasonic cleaner (KQ-3000B; Kun Shan Shu Mei), magnetic stirring apparatus (IKA, Germany), analytical balance, and a Milli-Q ultrapure water purification system (Millipore Company, USA).

2.3. Glassware and reagent control

To avoid PAE contamination, all the glassware in this study were soaked in a K2Cr2O7/H2SO4 mixture for 12 h before they were washed with tap water then with ultrapure water before they were baked at 450 °C for 5 h. Before use, all the glassware were washed with dichloromethane, then with acetone, and rinsed with n-hexane. All the solvents were checked for PAE contamination. To avoid contamination in the experimental process, all plastic containers were avoided.

2.4. Experiment process

A stock standard solution of 10 mg/L of each compound was prepared in methanol and stored at −20 °C in the refrigerator. A working standard solution of 1 mg/L was prepared before starting each experiment. The working standard solution had to be replaced weekly during the experiments. The aqueous solutions were prepared daily by diluting the working standard solution at different levels. To avoid PAE adsorption on the glass walls, the water was spiked with 10% methanol. To evaluate the recovery of PAEs in real seawater, the standard addition method was used. Before the addition of PAEs, the seawater sample was filtered through a GF/F glass filter (0.45 μm). The seawater samples were prepared by appropriate dilution of aliquots of stock solution at 100 ng/L, 500 ng/L, 1 μg/L, 5 μg/L, 10 μg/L, and 50 μg/L.

To optimize the SBSE efficiency, the influence factors were selected. These factors included the extraction time (1, 2, 3, 4, 5, and 6 h), organic modifier (MeOH; 5%, and 10%, v/v), and ionic strength (2%, 3%, 5%, and 10%, w/v) during the adsorption period. The stir bars were subsequently stripped by ultrasonic treatment. Desorption time (20, 30, 40, 50, and 60 min) and desorption solvents (MeOH, ACN, DCM, and the mixture of all three) were varied. All treatments were performed in triplicate.

Up to 30 mL of water sample was added into a 25 mL glass vial to reduce the air in the vial. A stir bar and sodium chloride were added before the vial was crimped with a Teflon-coated silicone septum cap. The vial was placed on the magnetic stirring apparatus at room temperature for 2 h of stirring at 360 rpm. The stir bars were removed from the samples, rinsed with ultrapure water, and cleansed with Kimwipes wipes. The stir bars were placed in glass tubes with 250 μL of solvent (150 μL methanol and 100 μL acetonitrile) under ultrasonic treatment. The solvents were analyzed by GC–MS. The stir bars were subjected thrice to ultrasonic treatment with methanol for 30 min.

Samples (1.0 μL) were injected in the splitless mode with an inlet temperature of 300 °C. The oven temperature was initiated at 70 °C for 2 min, increased to 150 °C at a rate of 25 °C/min, increased to 170 °C at a rate of 3 °C/min, increased to 185 °C at a rate of 30 °C/min, increased to 195 °C at a rate of 3 °C/min, increased to 225 °C at a rate of 60 °C/min, and finally increased to 280 °C at a rate of 8 °C/min for 10 min. Helium gas was used as a carrier with a rate of 1 mL/min. The temperatures of the transfer line and the ion source were set at 280 °C and 230 °C.

2.5. Statistical analysis

A blank test was required to assure the accuracy of the experiment, and three parallel tests were conducted for each sample. From the linear range, the relative standard deviation, detection limit, accuracy, and precision were used to verify the evaluation method. Statistical analyses were performed with Microsoft Excel 2010, Origin 8.6, and SPSS 19.0 (one-way ANOVA and Tukey test). All data were presented as mean with standard deviation (mean ± SD).

3. Results and discussion

3.1. Optimization of extraction parameters

Theoretically (Baltussen et al., 1999), only two factors affect the extraction efficiency: one is the partitioning coefficient between octanol and water; the other is the ratio between the volume of the stir bar coated with PDMS and water. The partitioning coefficient between PDMS and water (KPDMS/W) is approximated from the partitioning coefficients of octanol and water (KOW). (KPDMS/W) is equal to the concentration of the analyte in the PDMS phase coated on the stir bar (CPDMS) and water (CW) phase, which can be stated as

\[
K_{OW} \approx \frac{K_{PDMS}}{W} = \frac{C_{PDMS}}{C_{W}} = \frac{m_{PDMS}}{m_{W}} = \frac{V_{W}}{V_{PDMS}}
\]
where $m_{PDMS}$ and $m_w$ are the masses of the analyte in the SBSE and water phases, respectively, and $V_{PDMS}$ and $V_w$ are the volumes of analyte in the SBSE and water phase, respectively.

Therefore,

$$\beta = \frac{V_w}{V_{PDMS}}$$ (2)

$$K_{O/W} = \frac{m_{PDMS}}{m_w} = \frac{m_{PDMS}}{m_0 - m_{PDMS}}$$ (3)

where $m_0$ is the mass of analyte originally present in the water sample.

Recovery = $\frac{m_{PDMS}}{m_0} = \frac{K_{O/W}}{1 + K_{O/W}}$ (4)

However, the recovery in real water samples by the method is affected by the two parameters; the matrix modification would also change the recovery. The progress of extraction is also affected by the extraction time and the stirring speed.

3.1.1. Extraction stir bar

In this study, four commercially available stir bars were used to extract 20 μg/L of each PAE in water samples. The four stir bars were: S1, 20 mm in length with a 1 mm film (PDMS volume, 150 μL); S2, 20 mm in length with a 0.5 mm film (PDMS volume, 50 μL); S3, 10 mm in length with a 1 mm film (PDMS volume, 75 μL); S4, 20 mm in length with a 1 mm film over carbon (PDMS volume, 150 μL). The peak areas of the 15 PAEs are displayed in Fig. 1. For most of the PAEs, S1 had the largest peak area, followed by S2 and S3, except for DMP. S4 was much lower than the other three. The solvents cannot desorb PAEs from the stir bar because of the strong adsorption performance of carbon. The stir bar S4 coated on carbon was unsuitable for phthalate extraction, as demonstrated in Fig. 2. The most suitable stir bar was S1, which was 20 mm in length with a 1 mm film with and 150 μL PDMS. The first desorption reaction would desorb most of the PAEs because of the residual rate of the second desorption for S1 was below 30%.

3.1.2. Extraction time

The extraction time significantly influences the extraction efficiency. The extraction efficiency was studied by monitoring the area counts. The standard solution extraction times were set from 1 h to 6 h. The effect of extraction time is shown in Fig. 3(a). For almost all the phthalates, the extraction efficiency increased with the extraction time. During the first 2 h, the extraction efficiency considerably increased. After 2 h, the extraction efficiency was gradual and steady. This trend was similar to those of previous studies (Prieto et al., 2007; Ferreira et al., 2011; Cacho et al., 2012). Overall, 2 h was selected as the optimal extraction time.

3.1.3. Extraction temperature

The absorption temperature was optimized by maintaining the other parameters at the same values. The effect of absorption temperature is shown in Fig. 3(b). From 25 °C to 40 °C, the peak area increased, especially for DMP, DEP, DBP, and BBzP. The octanol–water partition coefficients of these four PAEs were lower than that of the other phthalates. This trend can be interpreted as the effect of the increasing temperature, which enhances the diffusion of the analytes from the solution to the stir bar. When the temperature was further increased to 60 °C, a significant decline was observed for most of the phthalates because the analytes are absorbed by the fiber; these results are similar as those of Penalver (Penalver et al., 2000). During actual operation, this approach is relatively complicated. For the subsequent experiments, room temperature was preferred.

![Fig. 1. Peak areas of four different stir bars by SBSE–GC–MS of PAEs at 20 μg/L. Extraction conditions: 30 mL water sample, 150 μL PDMS, 360 rpm. Desorption conditions: 250 μL solvent under ultrasonic treatment for 30 min.](image-url)
Fig. 2. Residual rate of four different stir bars. Desorption conditions: 250 μL solvent under ultrasonication for 30 min. The residual rate was the peak area ratio of the second and first desorption.

Fig. 3. Optimization of adsorption conditions. Peak area of different extraction times (a), extraction temperature (b), methanol addition (c), NaCl addition (d). Extraction conditions: 30 mL water sample, 150 μL PDMS, 360 rpm. Desorption condition: 250 μL solvent under ultrasonication for 30 min.
3.1.4. Organic modifier

The addition of organic modifiers can avoid analyte adsorption on glass walls. The analytes aggregate together and improve the extraction efficiency. The peak area of the methanol concentration is shown in Fig. 3(c). The addition of methanol significantly enhanced the extraction efficiency for long chain phthalates (Wang and Storm, 2005). However, hydrophilic phthalates, such as DMP, DEP, DMPP, and DEEP, cannot enhance the extraction efficiency; this result is the same as that of previous studies (Rodil and Moeder, 2008). For hydrophilic phthalates, the addition of methanol can also increase the recovery. For this work, 10% (v/v) methanol was selected as the proper amount to be added to the water sample.

3.1.5. Ionic strength

The addition of sodium chloride will increase the ionic strength to improve the extraction efficiency (Feng et al., 2005; Rodriguez-Gomez et al., 2014). The optimum added amount of sodium chloride was determined by analyzing a set of samples containing sodium chloride, which ranged from 0% to 10% (w/v; 0.6, 1.5, and 3.0 g, respectively, for a 30 mL water sample), in triplicate. Compared to the addition of no salt, the peak area was increased sharply, as shown in Fig. 3(d). The peak area

![Fig. 4. Optimization of desorption conditions. Effect of desorption time (a), desorption solvent (b). Extraction conditions: 30 mL water sample, 3 h, 150 μL PDMS, 360 rpm. Desorption conditions: 250 μL solvent under ultrasonication for 30 min.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>RSD%a</th>
<th>RSD%b</th>
<th>Compound</th>
<th>RSD%a</th>
<th>RSD%b</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMP</td>
<td>8.19</td>
<td>8.46</td>
<td>DHP</td>
<td>9.74</td>
<td>10.73</td>
</tr>
<tr>
<td>DEP</td>
<td>9.53</td>
<td>8.32</td>
<td>BBzP</td>
<td>7.43</td>
<td>11.59</td>
</tr>
<tr>
<td>DBP</td>
<td>4.96</td>
<td>6.05</td>
<td>DHEP</td>
<td>10.93</td>
<td>8.04</td>
</tr>
<tr>
<td>DiBP</td>
<td>7.59</td>
<td>6.78</td>
<td>DCHP</td>
<td>10.30</td>
<td>7.63</td>
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<tr>
<td>DMPP</td>
<td>13.72</td>
<td>8.62</td>
<td>DEHP</td>
<td>14.11</td>
<td>5.09</td>
</tr>
<tr>
<td>DEEP</td>
<td>9.69</td>
<td>9.61</td>
<td>DPhP</td>
<td>9.38</td>
<td>8.92</td>
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<tr>
<td>DOP</td>
<td>14.06</td>
<td>11.04</td>
<td>DOP</td>
<td>8.83</td>
<td>7.57</td>
</tr>
<tr>
<td>DPeP</td>
<td>8.98</td>
<td>9.25</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1

Relative standard deviation with the use of different and same stir bars.

*a* is the RSD of different stir bars (n = 6).

*b* is the RSD of same stir bars (n = 6).
was highest at a concentration of 5%, except for DMP, DEP, and DEEP. For most the remaining analysis, 1.5 g of sodium chloride was added.

### 3.2. Optimization of desorption parameters

#### 3.2.1. Desorption time

To accelerate desorption of phthalates from the stir bar, the stir bar was placed under ultrasonic treatment. The results are shown in Fig. 4(a). Desorption time varied from 20 min to 50 min, and the peak area increased during this time period. The stir bar was coated with PDMS; thus, the desorption time was better and shorter than 50 min. Otherwise, the coated PDMS would fall off from the stir bar. Therefore, 50 min is the optimal desorption time.

#### 3.2.2. Desorption solvent

In this study, different polar organic solvents were used to change desorption solvent polarity. Desorption solvents were methanol (250 μL), methanol (200 μL) and dichloromethane (50 μL), or methanol (150 μL, 200 μL) and acetonitrile (100 μL, 50 μL). As shown in Fig. 4(b), dichloromethane substantially reduced the peak area. This change can be explained by the strong hydrophobicity dichloromethane, which cannot competitively absorb phthalate from PDMS. The polarity of acetonitrile is smaller than that of methanol. Therefore, the elution of acetonitrile is higher than that of methanol. The octanol–water partition coefficient of most phthalates is between 4 and 6. Excessive amount of acetonitrile is adverse to desorption of phthalate. Consequently, methanol–acetonitrile at 4:1 was used as the desorption solvent.

### 3.3. Evaluation of the SBSE–solvent desorption GC–MS (SIM) method

To evaluate the usability of the stir bar before starting the experiment proper, the reproducibility values of different stir bars (n = 6) and the same stir bar (n = 6) were used to extract the water samples spiked with a concentration of 20 μg/L PAEs (extraction time: 3 h; desorption time: 30 min; desorption solvent: methanol, without methanol, and with NaCl). The results are shown in Table 1. For different stir bars, the RSD ranged between 4.96 and 14.11, which meant that the bars can be used simultaneously. The RSD of the same stir bar was between 6.65 and 11.04. Overall, the precision and repeatability of the method is satisfactory.

To evaluate the background contamination of the optimized methodology, three types of blank samples were studied. First, the stir bar and desorption solvent was investigated. Subsequently, the SBSE–solvent desorption program blank was studied. Finally, to evaluate the background contamination of NaCl, the SBSE–solvent desorption without NaCl addition was investigated. The peak areas are shown in Table 2. When CK is compared with CK–S–LD, DiBP and DEHP are the major contaminants. That is, super water may dissolve DiBP in the desorption solvent. The peak areas of DEP and DBP sharply increased when the water sample contained NaCl. BBzP was a novel contaminating compound because NaCl is stored in plastic bottles. DBP and DEHP are always added to plastic material to improve the flexibility and scalability. The addition of NaCl can improve the extraction efficiency more than the background. In the next experiment, the extraction efficiency of all phthalates has to be improved even with the presence of NaCl. Given that PAEs are ubiquitous, the analytical data of the subsequent experiment were corrected by subtracting the background values.

A mixed standard solution was prepared from 10 mg/L of 15 PAEs for detection by GC–MS. The solution was scanned, and the chromatogram was obtained according to the full scan. For a selected time range of chromatographic peak, the scanned results are shown in Fig. 5. To determine the characteristics of the ions, the chromatographic peaks of 15 PAEs can be completely present. The HB-5 M chromatographic column and temperature program can completely separate the chromatographic peaks of the 15 PAEs.

**Table 2**

Peak area of three blank samples.

<table>
<thead>
<tr>
<th></th>
<th>DMP</th>
<th>DEP</th>
<th>DiBP</th>
<th>DBP</th>
<th>DEEP</th>
<th>BBzP</th>
<th>DEHP</th>
</tr>
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<tr>
<td>CK</td>
<td>1130</td>
<td>227,854</td>
<td>3831</td>
<td>2002</td>
<td>1462</td>
<td>n.d.</td>
<td>6901</td>
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<tr>
<td>CK–S–LD</td>
<td>1581</td>
<td>264,052</td>
<td>3322</td>
<td>2460</td>
<td>1275</td>
<td>n.d.</td>
<td>870</td>
</tr>
<tr>
<td>CK–Na–LD</td>
<td>1160</td>
<td>3546</td>
<td>283,130</td>
<td>14,210</td>
<td>2390</td>
<td>1292</td>
<td>775</td>
</tr>
</tbody>
</table>

n.d. Means not detected.

a is the peak area of the stir bar and desorption solvent.
b is the peak area of extracting super water sample without NaCl.
c is the peak area of extracting super water sample with NaCl.

**Fig. 5.** Chromatographic peaks of the 15 PAEs.
The similar present method was between 0.08 ng/L for DBP and 489.13 ng/L for DMEP, which is much higher than the polarity of the mixture of methanol and 50 μL of acetone, which were used as desorption solvents. Furthermore, the limit of detection and quantification of detection of SBSE-GC-MS is shown in Table 4. The detection limit of high molecular weight PAEs (such as DOP, DEHP, DMPP) is higher than that of low molecular weight PAEs (such as DMP, DEP, DBP, DiBP). The reason was that the adsorption ability of PDMS on the molecular weight of PAEs is larger, which is not easy to be resolved. While continuing to increase the volatility and low detection limit enabled the application of this new method to analyze the trace analytes in a complex matrix. This study has a very important significance in marine monitoring and conservation.

Table 3: Retention time (RT), linear range, relative coefficient (R), and limit of detection (LOD) of the present method.

<table>
<thead>
<tr>
<th>Compound</th>
<th>RT (min)</th>
<th>Linear range (μg/L)</th>
<th>R</th>
<th>LOD (ng/L)</th>
<th>LOQ (ng/L)</th>
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<tr>
<td>DMP</td>
<td>8.026</td>
<td>0.05–100</td>
<td>0.9996</td>
<td>3.21</td>
<td>10.71</td>
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<td>DEP</td>
<td>10.093</td>
<td>0.05–100</td>
<td>0.9995</td>
<td>0.34</td>
<td>1.15</td>
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<tr>
<td>DiBP</td>
<td>14.760</td>
<td>0.05–500</td>
<td>0.9998</td>
<td>0.08</td>
<td>0.27</td>
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<td>DBP</td>
<td>16.217</td>
<td>0.01–500</td>
<td>0.9998</td>
<td>0.25</td>
<td>0.82</td>
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<tr>
<td>DMPP</td>
<td>16.592</td>
<td>4.91–100</td>
<td>0.9999</td>
<td>2.30</td>
<td>7.67</td>
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<td>DMP</td>
<td>17.643</td>
<td>0.2–100</td>
<td>0.994</td>
<td>29.37</td>
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<td>DEEP</td>
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<td>0.5–100</td>
<td>0.9963</td>
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<td>DPEP</td>
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<td>BBP</td>
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<td>7.67</td>
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<td>DREP</td>
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<td>0.1–100</td>
<td>0.9988</td>
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<td>184.16</td>
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<td>DCHP</td>
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<td>0.05–100</td>
<td>0.9998</td>
<td>17.87</td>
<td>59.58</td>
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<td>DEHP</td>
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<td>0.1–100</td>
<td>0.9972</td>
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<td>DPMP</td>
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<td>0.1–500</td>
<td>1</td>
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<td>196.59</td>
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<td>DOP</td>
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<td>1–100</td>
<td>0.9991</td>
<td>174.42</td>
<td>581.40</td>
</tr>
</tbody>
</table>

RT is the retention time.
R is the relative coefficient.
LOD is the limit of detection.
LOQ is the limit of quantification.

Table 4: The limit of detection and quantification of detection of SBSE-GC-MS.

<table>
<thead>
<tr>
<th>PAEs</th>
<th>Detection limit (ng/L)</th>
<th>Quantitation limit (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMP</td>
<td>3.21</td>
<td>10.71</td>
</tr>
<tr>
<td>DEP</td>
<td>0.34</td>
<td>1.15</td>
</tr>
<tr>
<td>DiBP</td>
<td>0.08</td>
<td>0.27</td>
</tr>
<tr>
<td>DBP</td>
<td>0.25</td>
<td>0.82</td>
</tr>
<tr>
<td>DMPP</td>
<td>489.13</td>
<td>1630.43</td>
</tr>
<tr>
<td>DMP</td>
<td>29.37</td>
<td>97.90</td>
</tr>
<tr>
<td>DEEP</td>
<td>22.69</td>
<td>75.64</td>
</tr>
<tr>
<td>DPEP</td>
<td>20.677</td>
<td>148.39</td>
</tr>
<tr>
<td>DHP</td>
<td>44.58</td>
<td>148.59</td>
</tr>
<tr>
<td>BBP</td>
<td>2.30</td>
<td>7.67</td>
</tr>
<tr>
<td>DREP</td>
<td>55.25</td>
<td>184.16</td>
</tr>
<tr>
<td>DCHP</td>
<td>17.87</td>
<td>59.58</td>
</tr>
<tr>
<td>DEHP</td>
<td>28.06</td>
<td>93.55</td>
</tr>
<tr>
<td>DPMP</td>
<td>58.98</td>
<td>196.59</td>
</tr>
<tr>
<td>DOP</td>
<td>174.42</td>
<td>581.40</td>
</tr>
</tbody>
</table>

4. Conclusion

PAEs extensive use has resulted in their ubiquitous presence in the air, water, sediment and soil, and the content of PAEs is relatively small in marine water (Net et al., 2015). In this study, SBSE coupled with GC and MS was optimized and successfully applied to determine the presence of 15 PAEs. The high sensitivity and low detection limit enabled the application of this new method to analyze the trace analytes in a complex matrix. This study has a very important significance in marine monitoring and conservation.

In summary, SBSE coupled with GC and MS was optimized and successfully applied to determine the presence of 15 PAEs. The high sensitivity and low detection limit enabled the application of this new method to analyze the trace analytes in a complex matrix. Given the optimal experimental conditions, the appropriate sodium chloride level and organic modifier were beneficial to the extraction progress. For most of the studied PAEs, the equilibrium time was 2 h. The octyl alcohol–water distribution coefficient of the PAEs differed; thus, the polarity of the desorption solvent and desorption time needed modification. In this work, 200 μL of methanol and 50 μL of acetone were used as desorption solvents.

Author contribution statement

Qingqing Si and Fengmin Li posed the original research question and formulated design of experiments. Qingqing Si, Chenchen Gao, Cong Wang and Zhenyu Wang performed experiments and collected data. Qingqing Si and Jian Zhao wrote the manuscript. All authors discussed the results, reviewed, and commented on the manuscript.

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