



Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

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

Qingqing Si^a, Fengmin Li^{a,*}, Chenchen Gao^a, Cong Wang^b, Zhenyu Wang^a, Jian Zhao^a

^a College of Environmental Science and Engineering, Ministry of Education Key Laboratory of Marine Environment and Ecology, Qingdao Collaborative Innovation Center of Marine Science and Technology, Ocean University of China, Qingdao 266100, China

^b Public Laboratory of Bioenergy and Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, No. 189 Songling Road, Qingdao 266101, China

ARTICLE INFO

Article history:

Received 8 March 2016

Received in revised form 12 April 2016

Accepted 14 April 2016

Available online xxxxx

Keywords:

Phthalic acid ester

Plasticizer

Stir bar sorptive extraction

Gas chromatography–mass spectrometry

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 $^{\circ}\text{C}$, 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 $\mu\text{g}/\text{L}$ to 5.71 $\mu\text{g}/\text{L}$, whereas the limit of quantification ranged from 0.023 $\mu\text{g}/\text{L}$ to 193 $\mu\text{g}/\text{L}$, and the correlation coefficients between the chromatographic peak area and concentration of the PAEs were greater than 0.92.

© 2016 Elsevier Ltd. All rights reserved.

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 150 million 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 Voutsas, 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 toxicology effect (Rudel et al., 2003). Moreover, these compounds can persist in the environment for several years. Dimethyl phthalate (DMP), dibutyl phthalate (DBP), and dioctyl 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 $\mu\text{g}/\text{L}$ and 400 $\mu\text{g}/\text{L}$, 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 Voutsas utilized liquid–liquid extraction (LLE)–gas chromatography (GC)–mass spectrometry (MS) to determine PAEs in bottled water (Amiridou and Voutsas, 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 SPFE and coupled with on-line SPE and HPLC–MS–MS to quantify phthalate metabolites in human semen (Kayoko, 2006). Penalver and Pocerull used SPME 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

* Corresponding author.

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 (DiBP), dibutyl phthalate (DBP), di(2-methoxyethyl)phthalate (DMEP), di(4-methyl-2-pentyl)phthalate (DMPP), di(2-ethoxyethyl) phthalate (DEEP), di-n-pentyl phthalate (DPeP), di-n-hexyl phthalate (DHP), butyl benzyl phthalate (BBzP), di(2-n-Butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), di(2-Ethylhexyl) phthalate (DEHP), diphenyl phthalate (DPhP), di-n-octyl phthalate (DOP) (1000 $\mu\text{g}/\text{mL}$ 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 (CH_3CN , CH_2Cl_2 , CH_3COCH_3 , NaCl , CH_3OH , C_6H_{14}) were of analytical grade and were used without any further purification. High-purity water ($18 \text{ M}\Omega \text{ cm}^{-1}$) 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 $30 \text{ m} \times 0.25 \mu\text{m} \times 0.25 \mu\text{m}$ 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 $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ 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 $\mu\text{g}/\text{L}$, 5 $\mu\text{g}/\text{L}$, 10 $\mu\text{g}/\text{L}$, and 50 $\mu\text{g}/\text{L}$.

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 wipers. 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 $25^\circ\text{C}/\text{min}$, increased to 170°C at a rate of $3^\circ\text{C}/\text{min}$, increased to 185°C at a rate of $30^\circ\text{C}/\text{min}$, increased to 195°C at a rate of $3^\circ\text{C}/\text{min}$, increased to 225°C at a rate of $60^\circ\text{C}/\text{min}$, and finally increased to 280°C at a rate of $8^\circ\text{C}/\text{min}$ 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 \pm 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 ($K_{\text{PDMS}/\text{W}}$) is approximated from the partitioning coefficients of octanol and water ($K_{\text{O}/\text{W}}$). ($K_{\text{PDMS}/\text{W}}$) is equal to the concentration of the analyte in the PDMS phase coated on the stir bar (C_{PDMS}) and water (C_{w}) phase, which can be stated as

$$K_{\text{O}/\text{W}} \approx \frac{K_{\text{PDMS}}}{W} = \frac{C_{\text{PDMS}}}{C_{\text{w}}} = \frac{m_{\text{PDMS}}}{m_{\text{w}}} \cdot \frac{V_{\text{w}}}{V_{\text{PDMS}}} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/6355941>

Download Persian Version:

<https://daneshyari.com/article/6355941>

[Daneshyari.com](https://daneshyari.com)