

Determination of Phthalic Acid Esters in Seawater and Sediment by Solid-phase Microextraction and Gas Chromatography-Mass Spectrometry



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Abstract: Phthalic acid esters (PAEs), as the most important plasticizers, are widely used in the production of plastic products. The accurate analysis of PAEs in seawater and sediment would be of great significance in studying the transformation of PAEs and their ecological effects in marine environment. In this study, the method of gas chromatography-mass spectrum detector coupled with solid-phase microextraction was established to analyze the concentration of PAEs in seawater and sediment, and the experimental conditions, such as extraction time and extraction temperature, were optimized. Under the optimum conditions, the precision of this method was less than 10.0%, and the limits of detection were 0.04–0.32 ng L⁻¹ and 0.12–1.6 μg kg⁻¹. Except dimethyl phthalate, the recovery of PAEs in seawater and sediment ranged from 68.0% to 114.0% and 76.4% to 105.0%, respectively. Moreover, the concentrations of PAEs measured by the method were 0.270–1.39 μg L⁻¹ and 0.79–34.8 μg kg⁻¹ in seawater and sediment samples of Changjiang River Estuary and its adjacent area, respectively. In conclusion, the analytical method is easy to operate and reduces the extraction volume of seawater. Thus, this method meets the requirements of the analysis of PAEs in coastal seawater and sediment.

Key Words: Phthalic acid esters; Solid-phase microextraction; Gas chromatography-mass spectrometry; Seawater; Sediment

1 Introduction

Phthalic acid and alcohol ester are collectively referred to as phthalic acid esters (PAEs). As the most common plasticizer products, PAEs are widely used in the production of toys, cosmetics, textiles, food packaging materials, medical bags, and rubber. They can effectively increase the plasticity, flexibility, and expansibility of the product. However, as the molecular structure of PAEs is similar with hormones, it is called the “environmental hormone” or “environmental hormone,” and has nephrotoxicity and reproductive toxicity^[1,2]. Trace amounts of PAEs can enter the body through the food chain and then form “false hormones,” which affects the hormone levels in the human body and interferes with the

normal endocrine system, and further leads to endocrine disorder. Long-term consumption of food containing PAEs may cause abnormal reproductive system, cause tears, and increase the risk of cancer. So far, six kinds of PAEs, including dimethyl phthalate (DMP), diethyl phthalate (DEP), butyl phthalate (DnBP), phthalic acid benzyl butyrate, phthalate (BBP), dioctyl (DnOP) and phthalic acid (2-)ethyl hexyl ester (DEHP), were listed as priority pollutants by the U.S. Environmental Protection Agency (EPA). Moreover, DMP, DnBP and DnOP were in the blacklist of priority pollutants in water in China. The national standard GB 3838-2002 “*Environmental quality standards of surface water*” regulated the limited values of DBP and DEHP in central drinking water and surface water source to be 0.003

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and 0.008 mg L⁻¹, respectively. The GB 5749-2006 “Standards for drinking water quality” also ruled the limited value of DEHP in drinking water to be 0.008 mg L⁻¹. In addition, our country had ruled the limit value of PAEs in food^[3], food plastic packaging^[4], textile^[5], and toy^[6]. However, the pollution classification standards of PAEs in seawater and sediment have not been set at home and abroad.

The determination methods of PAEs mainly contain gas chromatography-mass spectrometry (GC-MS)^[7-9], high-performance liquid chromatography(HPLC)^[10,11], and liquid chromatography-mass spectrometry(LC-MS)^[3,4,12]. Also some related standard methods were developed^[13,14] for the determination of PAEs in environmental samples, such as plastic products, electronic products and soil^[3-5], and food^[3,4]. The pretreatment methods mainly include liquid-liquid extraction^[15], Soxhlet extraction^[16], solid-phase extraction^[17-19], and ultrasonic extraction^[4,5]. PAEs in the marine environment are mainly derived from dry-wet deposition and the discharge of sanitary sewage and industrial wastewater. The accumulation of PAEs in marine organisms affects the marine ecosystems and ultimately affects the human health through the food chain^[17]. At present, the studies of PAEs in natural water and sediment are mostly focused on inland freshwater lake^[18,20], Yangtze River^[21,22], Yellow River^[23], Pearl River^[24], and other fresh water bodies. He *et al*^[18] and Zeng *et al*^[19] used solid-phase extraction to determine PAE contents in the surface water of Chaohu Lake and the inland water of Guangzhou, China. Their pretreatment process needed 10 and 2 L water samples and extracted the samples thrice. In addition, Nasrin *et al*^[16] used Soxhlet extraction to detect the PAE contents in wetland of Anzali, and their extraction time was up to 36 h. Given the complexity of seawater and sediment samples, low content of PAEs, and the existence of many factors influencing the determination, the sampling and pretreatment process became more tedious, and no report exists about the PAEs detection in China’s coastal water samples. In this experiment, solid-phase microextraction (SPME) and solid-phase extraction were used to pretreat the water and sediment samples, respectively, and polydimethyl-siloxane (PDMS) was used to absorb the PAEs in seawater and then desorbed by thermal desorption. The method established here did not require solvent and involved simple operation, thus avoiding large extraction volume, complicated operation, and time-consuming analytical process. In addition, GC-MS was used for analyzing PAEs content, obviously improving the recovery and analytical accuracy. This method was successfully applied in the determination of PAEs in seawater and sediment in Yangtze estuary and adjacent areas. The research plays an important role in the study of the migration and ecological effects of PAEs in estuary and near shore marine environment in China.

2 Experimental

2.1 Laboratory reagents

(1) Sixteen PAE standard mixtures, containing dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), dibutyl phthalate (DBP), dimethylglycol phthalate (DMEP), bis(4-Methyl-2-pentyl) phthalate (BMPP), bis(2-ethoxyethyl) phthalate (DEEP), dipentyl phthalate (DPP), benzyl butyl phthalate (BBP), di-*n*-hexyl phthalate (DnHP), bis(2-*n*-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), diphenyl phthalate (DPhP), dioctyl phthalate (DEHP), di-*n*-octylphthalate (DnOP), and diisononyl phthalate (DiNP) at 1000 μg mL⁻¹ each, and benzyl benzoate (BBZ) (internal standard, acquired initially as a liquid of 99% purity) were purchased from Sigma-Aldrich Co., United States.

(2) High-performance liquid chromatography grade *n*-hexane, dichloromethane, and ethyl acetate were obtained from Merck Co., Germany. Acetone was obtained from Tedia, United States, and CNWBOND Si solid phase extraction (CS-SPE) device was purchased from ANPEL Laboratory Technologies (Shanghai), Inc., China.

2.2 Instrument

The following instruments and materials were used: Agilent 7890 gas chromatograph equipped with Agilent 5975 C mass selective detector (GC-MS) and a DB-1 MS column (30 m × 0.25 mm internal diameter and 0.25 μm film thickness) (Agilent Technologies, Avondale, PA, USA); solid-phase microextraction instrument (Agilent Technologies, Avondale, PA, USA); FD-1-50 vacuum freeze dryer (Beijing Boyikang Laboratory Instruments Co., Ltd, China); 24 Position N-EVAP nitrogen evaporators (Organomation, USA); solid-phase microextraction (SPME) probe (Qingdao Zhenzheng Analytical Instruments Co., Ltd, China); high-purity helium (> 99.999%).

2.3 Sampling and preprocessing

The sediment samples (0–5 cm) were collected with a stainless steel grab sampler and placed into prewashed aluminum jars. After collection, the sediment samples were immediately transported to the laboratory and stored at –20 °C for 24 h. The sediment samples were freeze-dried for 48 h, ground, and homogenized by sieving through a stainless steel 100-mesh (0.150 mm) sieve. 2.50 g of sediment sample was weighed accurately into a 50-mL head-space bottle. Moreover, dust samples were ultrasonically extracted with dichloromethane (DCM) for 25 min (twice) and centrifuged for 30 min at 2000 rpm. The supernatant was collected for future determination. The supernatant was concentrated and then further purified in the CS-SPE column. About 5 mL of *n*-hexane was used to activate the column, and 2 mL of supernatant was used to pass through the column. Afterward,

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