Journal of Chromatography A, 1561 (2018) 39–47

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Application of non-ionic surfactant as a developed method for the enhancement of two-phase solvent bar microextraction for the simultaneous determination of three phthalate esters from water samples

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ARTICLE INFO

Article history:
Received 24 February 2018
Received in revised form 13 May 2018
Accepted 19 May 2018
Available online 20 May 2018

Keywords:
High performance liquid chromatography
Non-ionic surfactant
Phthalate esters
Solvent bar microextraction
Water samples

ABSTRACT

The extraction of phthalate esters (PEs) from aqueous matrices using two-phase solvent bar microextraction by organic micellar phase was investigated. A short hollow fiber immobilized with reverse micelles of Brij 35 surfactant in 1-octanol was served as the solvent bar for microextraction. Experimental results show that the extraction efficiency were much higher using two-phase solvent bar microextraction based on non-ionic surfactant than conventional two-phase solvent bar microextraction because of a positive effect of surfactant-containing extraction phase in promoting the partition process by non-ionic intermolecular forces such as polar and hydrophobicity interactions. The nature of the extraction solvent, type and concentration of non-ionic surfactant, extraction time, sample pH, temperature, stirring rate and ionic strength were the effecting parameters which optimized to obtain the highest extraction recovery. Analysis of recovered analytes was carried out with high performance liquid chromatography coupled with ultraviolet detection (HPLC–UV). Under the optimum conditions, linearity was observed in the range of 1–800 ng mL^{-1} for dimethylphthalate (DMP) and 0.5–800 ng mL^{-1} for diethylphthalate (DEP) and di-*n*-butyl phthalate (DBP) with correlation determination values above 0.99 for them. The limits of detection and quantification were ranged from 0.012 to 0.03 ng mL^{-1} and 0.04–0.1 ng mL^{-1}, respectively. The ranges of intra-day and inter-day RSD (n = 3) at 20 ng mL^{-1} of PEs were 1.8–2.1% and 2.1–2.6%, respectively. Results showed that developed method can be a very powerful, innovative and promising sample preparation technique in PEs analysis from environmental and drinking water samples.

1. Introduction

Phthalate esters (PEs) are a group of diesters of phthalic acid which are primarily used as plasticizers in the plastic materials to improve their flexibility, durability, and workability [1]. PEs present in plastic materials can be lost over time into the environmental compartments especially water resources during production, usage, disposal and incineration of the polymeric materials containing these compounds because of their weak secondary molecular interactions with polymer chains [2–4]. Therefore, PAs are considered as ubiquitous environmental pollutants. Certain phthalate esters, as well as their metabolites and degradation products, are suspected to be endocrine disruptors or hormonally active agents whose exposure may result in disruption of hormone activity in the male reproductive tract and some carcinogenic effects [5,6].

Several of PEs has been included in the priority list of pollutants of different national and supranational organizations due to their potential risks for human health and environment. In accordance with section 307 of the US Clean Water Act, dimethyl phthalate (DMP), diethyl phthalate (DEP) and din- butyl phthalate (DnBP) should be taken into account as priority toxic pollutants [7]. Therefore, develop analytical methods for the monitoring of PEs residue in water samples is a very important and imperative step for evaluating water safety and human health protection. The relatively low concentration levels of PEs and the complexity of the different environmental matrices make sample preparation necessary for the reliable determination of these compounds prior to chromatographic methods. The traditional multi-step preconcentration techniques that were commonly employed to the determination of PEs in aqueous matrices were liquid–liquid extraction (LLE) [8,9] and solid-phase extraction (SPE) [10,11]. Although these methods offer efficient and precise results, they are relatively time-consuming, labor-intensive, and hazardous to health and environment due to the usage of toxic organic solvents which often

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https://doi.org/10.1016/j.chroma.2018.05.039
0021-9673/

result in high blank values. Aiming at developing a cost-effective and more efficient approach for the extraction microextraction techniques was introduced. Microextraction methods which were used for monitoring of PEs are including: solid phase microextraction (SPME) [12,13], single drop microextraction (SDME) [14], stir-bar sorptive extraction (SBSE) [15], homogeneous liquid–liquid extraction (HLLE) [16], cloud point extraction (CPE) [17], dispersive liquid–liquid microextraction (DLLME) [18,19], magnetic molecularly imprinted solid-phase extraction (MMIP–SPE) [20], hollow fiber–liquid phase microextraction (HF–LPME) [21,22].

Among the microextraction methods, membrane-based microextraction techniques was developed to improve the stability and reliability of LPME and sample preparation using these methods has been utilized in both laboratories and industries [23]. The HF- LPME is one of the most useful membrane microextraction techniques that are known for their high enrichment factors and overcome the complexity of sample matrices which in target analytes are extracted from the sample solution into an extraction phase immobilized as a thin supported liquid membrane located inside the pores of the wall of a porous HF fixed to a microsyringe [24].

Solvent bar microextraction (SBME), an alteration of HF-LPME without using microsyringe, developed by Jiang and Lee for sample preconcentration, provides higher enrichments [25]. It involves the use of a short length of hollow fiber membrane (sealed at both ends) impregnated with organic extracting solvent, forming a solvent bar that is tumbled freely in the sample solution under magnetic stirring. The free movement of the extraction device, solvent bar, in the stirred aqueous sample solution considerably increases the transfer of analytes from the sample solution to the extraction solvent, facilitate extraction and improve extraction efficiency.

The Surfactants belong to a category of compounds with amphiphilic nature which owing to their special structure have been applied as the extraction-enhancing agent in LPME procedure to enhance extraction efficiency [26,27]. A kind of surfactant aggregate in an organic solvent so that the polar head of surfactant point inwards and hydrophobic tail (nonpolar group) point towards the nonpolar medium is called reverse micelle. From the analytical viewpoint, one of the most important properties of reverse micelles is their good capacity to solubilize solutes of different types and nature. This significant feature of reverse micelles improves the extraction/solubilization performance of extracting solvent.

In present work an integrated technique involving sample preparation procedures and enrichment using the surfactant-containing extraction phase based on solvent bar microextraction (SEP-SBME) was developed and applied for the determination of trace phthalate esters in aqueous samples followed by analysis with HPLC–UV. This was the first time a reverse micelle of the non-ionic surfactant used as the extraction phase in a two phase-SBME procedure and to date, there has been no similar study based on the application of the SEP-SBME method for the determination of PEs in environmental samples. The extraction parameters were optimized and the optimized method was applied to determine PEs in sea water, river water, wastewater of plastic basket making workshop and bottled mineral water to evaluate the application of this method to real samples.

2. Experimental

2.1. Reagents and standards

The Q3/2 Accurel polypropylene hollow fiber membrane (0.2 μm pore size, 200 μm wall thickness, 600 μm i.d.) was brought from Membrana (Wuppertal,Germany). Diethyl phthalate (DEP), dimethyl phthalate (DMP) and din-butyl phthalate (DBP) (purity range 98–99%) were purchased from Alfa Aesar (Karlsruhe, Germany). The non-ionic surfactant Brij-35 (polyoxyethylene dodecyl ether) was from Fluka (Buchs, Switzerland). Triton X-100 (octylphenol ethoxylate) was obtained from Sigma–Aldrich (Steinheim, Germany). HPLC grade acetonitrile, methanol and acetone, 1octanol, *n*-hexane, octane, dodecanol and 2 ethyl hexanol were supplied by Merck (Darmstadt, Germany). The individual stock standard solutions of each PE compound and a standard mixture solution of all target compounds were prepared in methanol at a final concentration of 500 mg L^{-1} and stored at 4 °C. Double distilled deionized water was used for preparation of the standard working solutions and mobile phase.

2.2. Collection and pretreatment of samples

Natural water from Caspian Sea (north of Iran) and Tajan River (Sari, Mazandaran, Iran), bottled mineral water from supermarket and wastewater sample from a plastic basket making workshop were collected for the work. Before the extraction, the mineral water stored into transparent polyethylene terephthalate (PET) plastic bottles was exposed directly to full sunlight for at least 3 weeks where temperature ranged from 35 to 44 °C in many days.

All water samples were filtered through 0.45 mm membrane (Millipore, Bedford, MA) immediately after sampling to eliminate particulate materials before the microextraction procedure; then were kept into light-preserved glass bottles (to avoid any photodegradation of target compounds) in refrigerator at 4 °C until analysis. All the glassware bottles used in the study was previously cleaned and washed with acetone and dichloromethane.

2.3. Instrumentation and operating condition

Chromatographic measurements was performed on a Waters HPLC system equipped with 1525 Binary LC Pump, UV–vis detector model 2487 Waters set at the wavelength of 225 nm and 7125i manual injector fitted with a 20 μL sample loop. A personal computer equipped with a Waters Breeze program for LC was applied to process chromatographic data. Separation was achieved on a C18 column (15 cm × 4.6 mm with an inside diameter of 5 μm) with a mixture of water/acetonitrile, 25:75 (v/v) as the mobile phase. The elution was conducted in the isocratic mode at a flow rate of 0.8 mL min^{-1} at room temperature. Adjustment of solutions pH was done by a 3030 Jenway pH meter (Leeds, UK). The water content of the reversed micellar organic phase was measured by Mettler Toledo C20 series Karl-Fischer titrator.

2.4. Extraction procedure

For the experiments, the fibers were pre-conditioned before use by sonication, immersing them in HPLC grade acetone during 5 min to remove any contaminants derived from manufacturing. In all cases, a 3 cm long piece of fiber was applied. For two-phase SBME, one of the fiber ends was mechanically sealed and the fiber lumen was filled with the organic solvent containing nonionic surfactant (10 mmol L^{-1} Brij 35 in 1-octanol) serving as acceptor solution until it dropped through the fiber pores, using a glass microsyringe. Then, the other fiber end was sealed to make up the solvent bar. The outside of the solvent bar was then rinsed with deionized water to remove the excess of organic solution on the fiber walls. For each experiment, the solvent bar with two ends pressure-sealed was left free in a 10 mL vial that had magnetic stirring bar and contained 8 mL of aqueous sample for preconcentration of PEs (Fig. 1). The sample solution was stirred at 800 rpm for 30 min. After extraction, the acceptor solution containing the analytes was recovered by cutting the ends of the fiber and flushing the acceptor solution into a micro-vial for instrumental determination. Each piece of hollow