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Low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction combined with gas chromatography–mass spectrometry for the fast determination of phthalate esters in bottled water

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A B S T R A C T

For the first time, a novel low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction (LDS–VSLLME) was developed for the fast, simple and efficient determination of six phthalate esters (PEs) in bottled water samples followed by gas chromatography–mass spectrometry (GC–MS). In the extraction procedure, the aqueous sample solution was injected into a mixture of extraction solvent (toluene) and surfactant (cetyltrimethyl ammonium bromide), which were placed in a glass tube with conical bottom, to form an emulsion by the assistance of vortex agitation. After extraction and phase separation by centrifugation, and removal of the spent sample, the toluene extract was collected and analyzed by GC–MS. The addition of surfactant enhanced the dispersion of extraction solvent in aqueous sample and was also favorable for the mass transfer of the analytes from the aqueous sample to the extraction solvent. Moreover, using a relatively less toxic surfactant as the emulsifier agent overcame the disadvantages of traditional organic dispersive solvents that are usually highly toxic and expensive and might conceivably decrease extraction efficiency to some extent since they are not as effective as surfactants themselves in generating an emulsion. With the aid of surfactant and vortex agitation to achieve good organic extraction solvent dispersion, extraction equilibrium was achieved within 1 min, indicating it was a fast sample preparation technique. Another prominent feature of the method was the simple procedure to collect a less dense than water solvent by a microsyringe. After extraction and phase separation, the aqueous sample was removed using a 5-mL syringe, thus leaving behind the extract, which was retrieved easily. This novel method simplifies the use of low-density solvents in DLLME. Under the optimized conditions, the proposed method provided good linearity in the range of 0.05–25 μg/L, low limits of detection (8–25 ng/L) and good enrichment factors up to 290. The proposed method was successfully applied to the extraction of PEs in bottled water samples as a fast, efficient, and convenient method.

1. Introduction

Phthalate esters (PEs) are used primarily as plasticizers in polymeric materials to increase their flexibility and workability through weak secondary molecular interactions with polymer chains. Since they are physically bound to the polymer chains, they can be released easily from products and migrate into the water or food that comes into direct contact with them [1,2]. Certain PEs, as well as their degradation products and metabolites, can cause adverse effects on human health, especially on the kidney, liver and testicles [3]. Recently, the potential endocrine disrupting properties of PEs were also reported [4]. These compounds are therefore considered to be hazardous to the environment and human health. Some PEs (e.g. dimethyl phthalate (DMP), diethyl phthalate (DEP) and di-*n*-butyl phthalate (DnBP)) are on the priority list released by the US Clean Water Act [5]. Food products contaminated with PEs have been reported [4], due to the use of plastics as food containers and packaging. Particularly, penetration of PEs from plastic packaging into water is common and has become a matter of public concern in recent years. Therefore, the development of sensitive and reliable analytical methods to evaluate and monitor trace amounts of PEs in different water samples are desirable for human health protection and environmental control.

Sample preparation of PEs is usually necessary before instrumental analysis to obtain sensitive and accurate results since environmental samples are complex, and PEs are present at extremely low concentrations. Typically, this would require an extraction step such as liquid–liquid extraction (LLE) or solid-phase extraction (SPE). However, conventional LLE consumes large amounts of toxic and expensive high purity organic solvents.

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Although SPE requires much less solvent and is less time consuming than LLE, it is expensive and column conditioning, drying, etc. are necessary steps which add to the processing time. To address these shortcomings, much research has been directed toward the development of efficient, miniaturized and environmentally benign sample extraction methods, such as liquid-phase microextraction (LPME) [6] and solid-phase microextraction (SPME) [7]. There are numerous SPME [8–14] and LPME [15–19] methods that have been applied to PEs in various environmental samples [10,17,20–22].

In 2006, a rapid LPME method, dispersive liquid–liquid microextraction (DLLME), was introduced by Rezaee et al. [23]. In this procedure, a mixture of high-density organic solvent (extraction solvent) and water miscible solvent (dispersive solvent) was rapidly injected into an aqueous sample to form an emulsion. Due to the extraction solvent being highly dispersed in the aqueous phase, the surface area between extraction solvent and sample solution was essentially infinitely large, thus speeding up the extraction. After extraction, the extract can be sedimented to the bottom of the extraction vial by centrifugation. The advantages of DLLME include rapidity, low cost, ease of operation and high enrichment factor. However, the use of water-miscible organic dispersive solvent could decrease the partition coefficient of analytes with respect to the extraction solvent, which potentially reduces the extraction efficiency.

Recently, Regueiro et al. [24] developed ultrasound-assisted emulsification microextraction (USAEME). In USAEME, ultrasound radiation instead of organic dispersive solvent as used in DLLME was applied to assist the dispersion of the extraction solvent into aqueous samples; due to the elimination of dispersive solvent, high extraction efficiency could be achieved. Moreover, USAEME simplified the instrumentation required during the extraction process. However, with a longer sonication time (ca. 15 min), some analyte degradation might occur under some special conditions (e.g. large pressure, temperature gradients, high shear forces and free radical generation) [25].

More recently, a novel LPME method, vortex-assisted liquid–liquid microextraction (VALLME) was developed by Yiantzi et al. [25]. In this procedure, the extraction solvent was dispersed into aqueous samples by vortex mixing, which is a powerful but mild emulsification procedure. VALLME overcomes the main disadvantages of DLLME (need for dispersive solvent) and USAEME (potential analyte degradation) as mentioned above. Since its introduction, it has been successfully applied to the determination of organochlorine pesticides [26], perfluorooctane sulfonate [27], polychlorinated biphenyls [28] and organophosphorus pesticides [29] from different sample matrices due to its simplicity and high efficiency in the extraction process.

Surfactants are amphiphilic organic compounds which contain both hydrophilic heads and hydrophobic tails [30]. A surfactant can reduce both the surface tension of water by adsorbing at the liquid–gas interface, and the interfacial tension between oil and water by adsorbing at the liquid–liquid interface [31], thus serving as an emulsifier to enhance the dispersion of the water-immiscible phase into the aqueous phase. The application of a surfactant as an emulsifier in LPME was developed by Wu et al. [30] and proved to be efficient, simple, rapid and cost-effective. The application of a surfactant as an emulsifier in VALLME combines the advantages of both VALLME and DLLME. To date, only one application of vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction (VSLLME) has been reported [29]. In this work, the addition of surfactant Triton X-114 as emulsifier greatly enhanced extraction efficiency and reduced extraction time. VALLME is usually carried out for 2 min [25–28], while for this work only 30 s was enough for the extraction. After extraction, the two phases could be separated by centrifugation and the sediment phase could be easily collected for further analysis. However, high-density solvent chlorobenzene was used, which is undesirable since it is potentially toxic. In addition, the use of a high-density solvent limits the wider applicability of the method due to a more limited choice of solvents.

In the present study, low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction (LDS–VSLLME) with gas chromatography–mass spectrometry (GC–MS) was for the first time applied to the fast determination of six PEs in bottled water samples. In the proposed procedure, a solvent of lower density than water, toluene, was employed as extraction solvent, and cetyltrimethyl ammonium bromide (CTAB) was used as emulsifier to facilitate the dispersion of organic solvent in the aqueous sample. After a 30 s extraction assisted by vortex agitation, phase separation was achieved by centrifugation. The supernatant (extraction solvent) was collected at the conical bottom of the tube after removing the aqueous sample by a syringe. This method avoids the necessity of a special homemade device for the collection of low-density organic solvents [32], which is tedious and troublesome to fabricate. In order to evaluate the proposed method, conventional DLLME, LDS-DLLME and USAEME were carried out for comparison with the performance of LDS–VSLLME. Under the optimized microextraction conditions, the developed method was applied to analyze bottled water samples.

2. Experimental

2.1. Reagents and materials

The PE standards (DMP, DEP, DnBP, benzyl butyl phthalate (BzBP), di-2-ethyl hexyl phthalate (DEHP) and di-*n*-octyl phthalate (DnOP)) were bought from Supelco (Bellefonte, PA, USA) in the form of a methanolic stock solution containing 2000 mg/L of each compound. Their structures are shown in Table 1. HPLC–grade methanol (purity 99.9%), acetone (purity 99.9%) and toluene (purity 99.9%) were purchased from Tedia Company (Fairfield, OH, USA). 1-Octanol (purity >99%), toluene (purity 99.9%), CTAB (purity >99%), polyoxyethylene octyl phenyl ether, Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) ($n = 9–10$) (purity >99%) and polyethylene glycol tert-octylphenyl ether, Triton X-114 ($C_{14}H_{22}O(C_2H_4O)_n$) ($n = 7–8$) (purity >99%) were bought from Sigma–Aldrich (St. Louis, MO, USA), while chlorobenzene (purity 99.9%), cyclohexane (purity 99.9%) and isooctane (purity 99.9%) were from Fisher (Loughborough, UK). Sodium chloride (NaCl) was obtained from Goodrich Chemical Enterprise (Singapore). Sodium dodecyl sulfate (SDS) (purity 99%) was purchased from BDH Laboratory Supplies (Poole, England). Ultrapure water was produced on a Nanopure (Barnstead, Dubuque, IA, USA) water purification system.

Both of the 100-μL HPLC microsyringe used for the addition of extraction solvent and surfactant, and the 10-μL microsyringe used for GC–MS injection were purchased from SGE (Sydney, Australia). The 5-mL plastic syringe was bought from HSW (Tuttlingen, Germany).

A stock solution containing all analytes (at 10 mg/L of each) was prepared in methanol and stored at 4 °C. Water samples were prepared by spiking ultrapure water with analytes at known concentrations (5 μg/L) daily to study extraction performance under different conditions. Bottled water samples were bought from a local market and were stored in the dark at 4 °C and then analyzed without filtration.

2.2. Instrumentation

Analysis was carried out on a Shimadzu QP2010 (Kyoto, Japan) GC–MS system with a DB-5 MS fused silica capillary column (30 mm × 0.25 mm I.D., film thickness 0.25 μm) (J&W Scientific, Folsom, CA, USA). Helium was employed as carrier gas at a flow rate