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Method development for the analysis of phthalate esters in tea beverages by ionic liquid hollow fibre liquid-phase microextraction and liquid chromatographic detection

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1-butyl-3-methylimidazolium hexafluorophosphate (PubChem CID: 2734174)
1-hexyl-3-methylimidazolium hexafluorophosphate (PubChem CID: 2734175)
Heptanol (PubChem CID: 31289)
Nonanol (PubChem CID: 31289)
Decanol (PubChem CID: 8174)

ABSTRACT

A novel method, termed ionic liquid-based hollow fibre liquid phase microextraction (IL-HF-PLME), coupled with high-performance liquid chromatography (HPLC) was developed for separation and preconcentration of three phthalate esters (PAEs) in tea beverage. In the present study, ionic liquid 1-butyl-3-methy-limidazolium hexafluorophosphate ([BMIm]PF_6) was placed in the porous-walled polypropylene hollow fibre as the acceptor phase, and nonanol was used as the supported liquid membrane phase that accomplished extraction. Several important parameters influencing the extraction efficiency were investigated in detail. Under the optimized conditions, good linearity occurred in the range of 5 −1000 ng mL^{-1} with the correlation coefficients values above 0.998. The limits of detection ranged from 0.67 to 1.73 ng mL^{-1}. Recoveries of three PAEs in two kinds of spiked tea beverage samples (PAEs, 10.0 −100.0 ng mL) were between 94.2 and 103.4%, with relative standard deviations (RSDs) ranged from 1.77 to 3.02%. The enrichment factors were 200. The developed IL-HF-PLME method allowed the simple, rapid, and sensitive determination of phthalate esters in tea beverage samples with an extraction time of just 4 min.

1. Introduction

Phthalate esters (PAEs) have been commonly used as plasticizers in polymeric materials to increase their flexibility, transparency, durability, and longevity through weak secondary molecular interactions with polymer chains (Yan, Cheng, & Liu, 2011). Millions of tons of PAEs are produced all over the world annually (Blount et al., 2000), of which di-2-ethylhexyl phthalate (DEHP), dibutyl phthalate (DBP), di-isodecyl phthalate (DIDP) and di-iso-nonyl phthalate (DINP) are the most popular plasticizers in global production (Gallart-Ayala, Núñez, & Lucci, 2013). Because PAEs are only physically, not chemically, bound to the polymer chains, they may be released into the environment during the production, use and incineration of the polymeric materials containing these compounds (Balafas, Shaw, & Whitfield, 1999; Lian,

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Qiu, & Yang, 2014). PAEs as well as their metabolites and degradation products can cause toxic effects in multiple organ systems including the liver, kidney, lungs, heart and reproductive tract (Fan, Liu, & Xie, 2014; Yan et al., 2011). Since their potential risks to human health, several PAEs, mainly containing butylbenzylphthalate (BBP), dibutylphthalate (DBP), diethylphthalate (DEP) and dioctylphthalate (DOP), have been classified as Priority Toxic Pollutants by the United States Environmental Protection Agency (EPA) (US EPA, 1980). Besides, the European Union established Specific Migration Limits (SMLs) for PAEs using food simulants, 30.0 mg kg^{-1} and 0.3 mg kg^{-1} food simulants for BBP and DBP on the basis of the Directive 2007/19/EC (Commission of the European Communities, 2007). 0.01, 0.5, and 0.05 mg/kg body weight/day for BBP (EFSA, 2005a), DBP (EFSA, 2005b), and di-isononylphthalate (DINP) (EFSA, 2005c) have been specified in Tolerable Daily Intakes by the European Food Safety Authority (EFSA). It has been reported that over 0.3 mg/kg of DBP was detected in distilled liquor samples, besides, BBP and other PAEs were detected in soft drinks (Fan et al., 2014; Self & Wu, 2012; Yang, Li, Wang, Ruan, Zhang, & Sun, 2015). Therefore, an accurate and sensitive method for the identification and quantification of PAEs from all kinds of food, water and other matrices is particularly important.

The common sample preparation techniques, solid-phase extraction (SPE) (Katsumata, Begum, Kaneco, Suzuki, & Ohta, 2004), magnetic solid-phase extraction (MSPE) (Jiao et al., 2012; Luo, Yu, Yuan, & Feng, 2012), solid-phase microextraction (SPME) (Li, Zeng, Chen, & Xu, 2004), liquid-phase microextraction (LPME) (Yao et al., 2008), vortex-assisted liquid-liquid microextraction(VA-LLME) (Lian et al., 2014), ultrasound-assisted dispersive liquid-−liquid microextraction (UA-DLLME) (Pérez-Outeiral, Millán, & Garcia-Arrona, 2016) and ionic liquid-based dispersive liquid-−liquid micro-extraction (IL-DLLME) (Sha, Yi-Sheng, Shui-Yuan, Tian, & Hao, 2011), have been reported for the extraction of PAEs from different samples. In recent years, liquid phase microextraction using hollow fibre, due to its simplicity, low cost, excellent clean-up efficiency and high enrichment factors (Sun, Tang, Wu, Wang, & Wang, 2013), has attracted increasing attention. HF-LPME is performed in two- and three-phase sampling modes. In three-phase sampling mode, called as hollow-fibre liquid-liquid-liquid microextraction (HF-LLLME), is applied to extract of ionizable analytes (basic and acidic compounds) (Saraji & Ghani, 2015). In two-phase HF-LPME procedure, the analytes are extracted from an aqueous sample (donor phase), through a hydrophobic organic solvent supported hollow fibre pores, into an organic acceptor phase insided the lumen of hollow fibre (Wang, Xiao, Liu, Wang, & Yang, 2015). It has been reported that the acceptor phase inside the lumen of HF and the supported phase fixed in the pores of HF was a single, same hydrophobic organic solvent (Wang & Wang, 2014; Wang et al., 2015). In addition, the fibre is single-used and disposable in HF-LPME, the carry-over problems can be overcome. Furthermore, HF-LPME also has good selectivity as the large molecules and particles are prevented from entering by the small pore size of the fibre (Bolaños, Romero-González, Frenich, & Vidal, 2008). However, there is still a loss of the organic solvent with a lower viscosity while samples are stirred vigorously.

Room-temperature ionic liquids (RTILs) are ionic media resulting from combinations of organic cations and various anions (Liu et al., 2012). Compared to conventional organic solvents, room-temperature ionic liquids have very low vapour pressure, good dissolving capacity for numerous compounds, tunable viscosity, negligible volatility, and excellent thermal stability (Liu et al., 2012; Ma, Huang, Li, & Wu, 2011; Qin, Li, Liu, & Yang, 2013). Therefore, RTILs, regarded as a novel type of green solvents, have recently been used as alternatives to common organic solvents in many fields including separation and enrichment in analytical chemistry (Ma et al., 2011).

In the present study, we have attempted to explore the possibility of simultaneous separation and preconcentration of phthalate esters using green solvents. Ionic liquids (ILs) are gaining recognition as unique solvents. Many of them are liquid at room temperature and below (Qin et al., 2013; Mudring, 2010), which worked as extractants. Mid-chain alcohols are used as supported liquid membrane phase. Hollow fibre is used to prevent impurities entering the lumen and fix the extraction solvent. Several parameters affecting the performance of the method were optimized including the selection of extraction solvent, supported phase, donor phase pH, extraction time, the fibre length, and salt addition.

2. Materials and methods

2.1. Materials

Standards of benzyl butyl phthalate (BBP), di-n-butyl phthalate (DBP), and dicyclohexyl phthalate (DCHP) were purchased from Sigma (St. Louis, Mo, USA). 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF_6), 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIm]PF_6), 1-otcyl-3-methylimidazolium hexafluorophosphate [OMIm]PF_6 and mid-chain alcohol ($C_{7\text{-}10}$) were obtained from Aladdin (Shanghai, China). Structures of PAEs, [BMIm]PF_6, [HMIm]PF_6 and [OMIm]PF_6 were shown in Fig. 1. Acetonitrile (HPLC grade) was supplied by Merck (Darmstadt, Germany). Deionized water was prepared with a Milli-Q system (USA) throughout the experiment. All reagents were at or above analytical grade.

2.2. Instrumentation

Experiments were performed using Agilent 1200 Series HPLC system consisting of a vacuum degasser, an auto sampler, a quaternary pump, and a diode-array detector (Agilent Technologies, Calif., USA). Vortex apparatus (Jintan experimental Instruments Co. Ltd.,Jiangsu, China) was used for vortex-mixing. An ultrasonic cleaner (Henao ultra-sonic instrument plant, Tianjin, China) was used to remove contaminations in the hollow fibre. A centrifuge (Shanghai surgical instrument factory, 80-2, Shanghai, China) was used for phase separation. Accurel Q3/2 polypropylene hollow fibre membrane (600 μm i.d., 200 μm wall thickness, and pores of 0.2 μm pore size wall) was bought from Membrana (Wuppertal, Germany). A 1.0 mL microsyringe (model 702SNR) with a sharp needle tip was used for the injection of the extraction solvent into the hollow fibre lumen.

2.3. Chromatographic conditions

Chromatographic separation and quantification were carried out using a reversed-phase C18 analytical column of 150 × 4.6 mm (Agilent TC-C18) at column temperature of 30 °C. The detection wavelength was set at 226 nm during the whole process. Acetonitrile and water were used as mobile phases with the gradient program as follows: 60% acetonitrile (0 min), ramped to 80% acetonitrile (5 min), and then ramped to 100% acetonitrile (7−12 min). The flow rate was set at 1.0 mL min^{-1} and the injection volume was 20 μL. The system was allowed to stabilize for 2 min under the initial conditions.

2.4. Preparation of sample and standard solutions

Ice black tea and green tea were purchased from local markets in Kunming, China. These samples were stored at 4 °C until analysis.