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Determination of 15 phthalate esters in air by gas-phase and particle-phase simultaneous sampling

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ABSTRACT

Based on previous research, the sampling and analysis methods for phthalate esters (PAEs) were improved by increasing the sampling flow of indoor air from 1 to 4 L/min, shortening the sampling duration from 8 to 2 hr. Meanwhile, through the optimization of chromatographic conditions, the concentrations of 9 additional PAE pollutants in indoor air were measured. The optimized chromatographic conditions required a similar amount of time for analysis as before, but gave high responsivity, the capability of simultaneously distinguishing 15 kinds of PAEs, and a high level of discrimination between individual sample peaks, as well as stable peak generation. The recovery rate of all gas-phase and particle-phase samples of the 15 kinds of PAEs ranged from 91.26% to 109.42%, meeting the quantitative analysis requirements for indoor and outdoor air sampling and analysis. For the first time, investigation of the concentration levels as well as characteristics of 15 kinds of PAEs in the indoor air from four different traffic micro-environments (private vehicles, busses, taxis and subways) was carried out, along with validation of the optimized sampling and analytical method. The results show that all the 9 additional PAEs could be detected at relatively high pollution levels in the indoor air from the four traffic micro-environments. As none of the pollution levels of the 15 kinds of PAEs in the indoor air from the 4 traffic micro-environments should be neglected, it is of great significance to increase the types of PAEs able to be detected in indoor air.

Introduction

As a group of indoor air pollutants, phthalate esters (PAEs) have become a major concern in the present-day world. Be it in newly decorated houses (Rudel et al., 2003; Wilson et al., 2003; Kanazawa et al., 2010) or public places, such as hospitals, kindergartens, and offices (Bergh et al., 2011; Kasper-Sonnenberg et al., 2014), considerable research on the measurement of PAE concentrations as well as their pollution characteristics in indoor air has been conducted. However, current sampling and analytical approaches are relatively complex, and lack a unified standard as well. Furthermore, both domestic and foreign sampling methods for PAEs in indoor air mainly involve either the collection of gaseous PAEs, or the PAEs in particulate matter of different particle sizes. Nonetheless, owing to the semi-volatility of PAEs, their concentration in the air is relatively low (ng/m^3–μg/m^3). Moreover, PAEs exist in both gas- and particle-phases in indoor air. At present, the measurement of particle-phase PAEs in indoor air is considered neither in domestic nor

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in foreign studies, which inevitably leads to the underestimation of pollution levels of indoor PAEs.

Currently, the membrane sampling method (Wang et al., 2006; Rakkestad et al., 2007), as one type of sampling method in use, is not suitable for indoor air samples with very low pollutant concentrations, and requires relatively long sampling duration as well as having the potential for bringing secondary pollution into the sampled room; thus the solid absorption method is so far the most frequently employed as well as the most mature approach in the sampling of organics in indoor air. The key to this method is the choice of solid absorbent. For instance, Fromme et al. (2004) chose polyurethane foam (PU) to sample and analyze the PAE concentrations in the indoor air of dormitories as well as kindergartens in Berlin, with a sampling rate of 5 L/min and duration of 7 hr. Yet, this solid absorbent requires a tremendous amount of organic solvent extractant for pre-processing, resulting in waste as well as contamination of the solvent. What's worse, external pollutants may easily be introduced and the sample recovery rate is relatively low (Otake et al., 2001). Therefore, such a method is not suitable for the sampling and investigation of indoor air. Another choice is tandem activated carbon tubes, the sampling velocity and duration of which is 1 L/min and approximately 3 days, respectively. Using activated carbon for sampling has great convenience, but phthalates may be lost because of the prolonged collection and the loss of small-particle activated carbon during centrifugal separation, *etc.* Toda et al. (2004) proposed a method combining a Sep-Pak PS cartridge with a low-flow sampling pump to sample in residents' rooms at 2 L/min for approximately 24 hr, with a detection limit of 100 ng/m^3. Nevertheless, most Sep-Pak PS sampling kits are plastic products, which may contain PAEs that will introduce new pollutants during the measurement and result in contamination of the sampling tubes. Wang (2007) reported that the XAD-2 adsorbent has higher absorption efficiency than PU for PAEs in the gas-phase, and involves a simple pre-processing procedure and small solvent consumption, as well as economy and convenience. Thus, it has better application potential.

Apart from the study of sampling methods, a considerable number of studies on analytical approaches to measuring PAEs have been carried out globally. Methods that have been reported in early literature mainly involve spectrophotometry (Huang et al., 2012), fluorimetry (Li and Wang, 2005), chromatography (Li et al., 2004; Xiao et al., 2009), *etc.* As analytical technology develops, chromatography is a frequently used detection method for PAEs in the environment, mainly involving gas chromatography–mass spectrometry (GC–MS), gas chromatography-flame ionization detection (GC-FID), high performance liquid chromatography (HPLC), *etc.* During actual sample detection, the optimal chromatographic conditions can be chosen in accordance with the characteristics of samples. For example, Fromme et al. (2004) investigated the indoor air of urban apartments and nurseries using GC–MS, which was also utilized by Toda et al. (2004) to measure semi-volatile organics in indoor air, such as PAEs and organophosphates.

Regarding the studies of sampling and analytical methods of PAEs in indoor air, with the consideration of various indexes, involving the representativeness of samples, the cost of detection and analysis, the requirements of technology, and convenience as well as reliability, the most commonly employed and reliable approach currently used in the detection and analysis of PAEs in indoor air is solid absorbent absorption–ultrasound extraction–gas chromatographic analysis. Pei et al. (2013) carried out the simultaneous sampling of particle- and gas-phase PAEs. They also detected and analyzed the concentration levels of 6 kinds of PAEs in newly decorated homes. The total concentration levels of PAEs were relatively high and caused significant pollution. A similar method was also employed in some other studies (Song et al., 2015; Wang et al., 2015), mainly in public places, such as hospitals and offices.

The current study improved the sampling conditions based on the method employed by Pei et al. (2013) for simultaneous collection of particle-phase and gas-phase PAEs by increasing the sampling rate from 1 to 4 L/min so that the efficiency was improved, and the scientific validity of the approaches was compared. Meanwhile, the chromatographic conditions were optimized compared to the method employed by Pei et al. (2013), so that 9 additional PAEs along with the original 6 PAEs were collected and analyzed. The recovery rate ranged from 91.26% to 109.42%. In addition, the optimized method was utilized for measurement in practical environments. This study chose air samples from traffic micro-environments as experimental subjects because the determination of PAEs in indoor air from these environments required a more high-speed sampling method and also because of the complexity and closed nature of traffic micro-environments. Measurements were carried out for the first time in traffic micro-environments for the 15 kinds of PAEs, and all were detected. The degree of discrimination and responsivity of individual sample peaks were relatively high. In addition, the generation of peaks was very stable. Thus, a fundamental method has been established for the identification of types of PAE pollution and the measurement of PAEs concentration in future indoor air investigations.

1. Materials and methods

1.1. Chemicals and materials

HPLC grade chemicals and solvents were used for all extraction and GC analysis. Standard mixtures of M-8061 phthalates, including dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), bis(2-methoxyethyl)phthalate (DMEP), bis(4-methyl-2-pentyl)phthalate (DMPP), bis(2-ethoxyethyl)phthalate (DEEP), dipentyl phthalate (DPP), dihexyl phthalate (DHP), benzyl butyl phthalate (BBP), bis(2-*n*-butoxyethyl)phthalate (DBEP), dicyclohexyl phthalate (DCHP), bis(2-ethylhexyl)phthalate (DEHP), di-*n*-octyl phthalate (DNOP), and dinonyl phthalate (DNP) (Table 1), were purchased (AccuStandard, New Haven, CT, USA) as stock solutions in isooctane; all had concentrations of 1.0 mg/mL for each phthalate.

1.2. Sample analysis

1.2.1. Preparation of the standard solution

A standard mixture of phthalates was measured accurately and diluted with methanol to 50 mL in a volumetric flask to make a 10 mg/L mixed standard stock solution of phthalates. Then the 10 mg/L mixed standard stock solution was diluted to prepare