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Monitoring of phthalates in foodstuffs using gas purge microsyringe extraction coupled with GC–MS

Miao He [a], Cui Yang [a], Renjie Geng [a], Xiangai Zhao [a], Lian Hong [a], Xiangfan Piao [a], Tie Chen [a], Maurizio Quinto [b], Donghao Li [a,*]

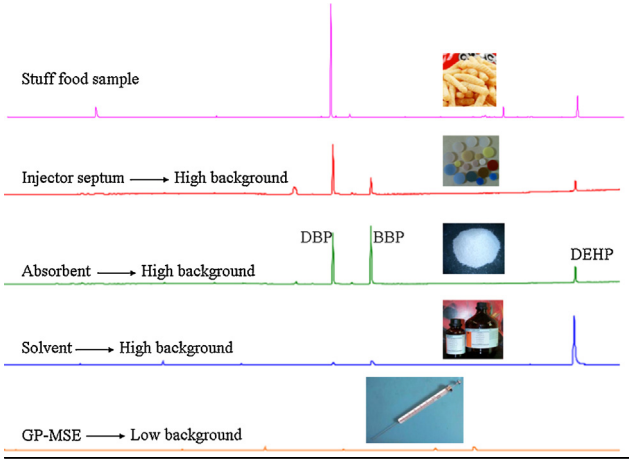
[a] Key Laboratory of Natural Resource of the Changbai Mountain and Functional Molecular (Yanbian University), Ministry of Education, Park Road 977, Yanji City, Jilin Province 133002, China
[b] SAFE – Department of Science of Agriculture, Food and Environment, University of Foggia, via Napoli 25, I-71100 Foggia, Italy

HIGHLIGHTS

- We established a novel PAE analysis method.
- The method can overcome the problems of the blank value in PAE analysis.
- Contents and profiles of PAEs were analysed in 78 foodstuffs.
- PAEs exposure was estimated from foodstuffs sold in the Chinese market.

GRAPHICAL ABSTRACT

Low blank value analytical method for analysis of PAEs in the foodstuff.



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ABSTRACT

Phthalate esters (PAEs) are commonly used as nonreactive plasticisers in vinyl plastics to increase the flexibility of plastic polymers. Numerous studies have indicated that the PAEs as a class of endocrine-disrupting chemicals. In addition, the studies have also shown that a major source of human exposure to phthalates is the diet. To date, the largest problem in PAEs analysis is the high blank value because PAEs are widely used in various applications and products. To overcome this shortcoming, gas purge microsyringe extraction (GP-MSE) was applied, which established a new and low-blank-value analytical method for PAE analysis to analyse PAEs in foodstuffs. In this study, GP-MSE was used as a clean-up method, and the overall recoveries ranged from 85.7 to 102.6%, and the RSD was less than 10%. More importantly, this method can overcome the problem of the high blank value in PAE analysis. This method was applied for measuring PAEs in 78 foodstuffs. The results showed that a wide variety of PAE concentrations were found in the different groups, and the content of PAEs (varies from 658 to 1610 ng g^{-1} fresh weight) is greatest in seafood. The concentrations were in the following order: DEHP > DBP > DEP ≈ DMP > BBP ≈ DNOP. Finally, the daily

* Corresponding author. Tel.: +86 433 2436456; fax: +86 433 2732456.
E-mail address: dhli@ybu.edu.cn (D. Li).

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intake of PAEs was estimated for adults based on the levels of PAEs in foodstuffs. The total EDI_{diet} values of 3.2 and 12.9 $\mu g\,kg^{-1}$ bw d^{-1} were calculated for DEHP based on the mean and highest concentrations in foodstuffs, respectively.

1. Introduction

Phthalate esters (PAEs) are a group of chemical compounds that are wildly used as plasticisers and solvents in commercial, medical and personal care products [1,2]. Several million tons of phthalates are produced globally each year [3]. The PAEs with lower molecular weights, such as dimethyl phthalate (DMP), diethyl phthalate (DEP), and di-*n*-butyl phthalate (DnBP), are generally used in cosmetics and personal care products; DnBP is also used in epoxy resins, cellulose esters and special adhesive formulations. Some longer/branching alkyl chain PAEs, such as butylbenzyl phthalate (BBP), di-*n*-octyl phthalate (DnOP) and DEHP, due to their low cost, they are mainly used as plasticisers in the polymer industry and foamed PVC industry to improve flexibility, workability and general handling properties [4,5]. Phthalates have been categorised as a "chemical of concern" by the United States Environmental Protection Agency (EPA) [6] due to their potential to elicit human endocrine or reproductive and developmental toxicities in laboratory animals [7–11]. Furthermore, several epidemiological studies have shown a negative relationship between high phthalate esters exposure and children's intelligence and behaviour [12], whereas a positive relationship has been shown between environmental phthalate esters exposure and asthma and allergic symptoms in humans [13].

Due to the widespread application of phthalate esters, there is a significant exposure of general population to phthalates, mainly though inhalation, oral, and dermal routes [14]. The diet is the most important source of human exposure to phthalate esters [15,16]. As plasticisers, phthalates can leach easily from the consumer products because they are not bound chemically to polymeric backbones in plastics [17]. Phthalate esters in food contamination can occur through food-contact packaging materials and during processing, storage, and transport [18]. Furthermore, food contamination in the manufacturing of these compounds can be transferred through the food chain. In spite of the importance of foodstuffs as a significant source of human exposure to phthalates, the determination of phthalates is very difficult in foodstuffs due to the huge challenge associated with the high background levels of contamination from the majority of materials and reagents used in laboratories, along with the analytical methods [18–20]. Therefore, it is necessary to decrease contamination during sample treatment and analysis. To reduce the opportunity of contamination during the analysis process, it is necessary to shorten sample pretreatment time and to reduce the dosage of the reagents and materials. In other words, the analytical procedure must be kept simple [21].

Gas purge microsyringe extraction (GP-MSE) was developed by Yang et al. as a novel sample pretreatment technology [22]. This technique is fast (only needs 2 min) and is suitable for integration and miniaturisation. In addition, the extraction is completed under the protection of nitrogen, and there are no plastic components in the whole device. In addition, it only requires microlitre level organic solvents, without the need for adsorbents or other materials. Moreover, it has been proven to have high extraction efficiency for volatile compounds and semi-volatile chemicals, and it has good clean-up ability [22].

In this study, we analysed the occurrence of six phthalates in 78 foodstuffs samples collected from Yanji, China, from November to December 2012. The main objective of this work was (a) to develop a low blank value method for the determination of phthalate esters in foodstuffs; (b) to determine the concentrations and profiles of phthalate esters in foodstuffs sold on the Chinese market; and (c) to estimate the human exposure dose of phthalates from foodstuffs.

2. Experimental

2.1. Chemicals and materials

Six phthalate esters (PAEs) standard mixtures, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), butyl benzyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP), and di-*n*-octyl phthalate (DNOP), were purchased from Chem Service (USA). $^2H_{10}$-phenanthrene was purchased from Supelco (Bellefonte, PA, USA). The purity of the standards was higher than 99%. Organic solvents, such as acetone, dichloromethane and hexane, were HPLC grade and were obtained from Caledon (Georgetown, Canada). The stock mixture standard solution of PAEs at a concentration of 100 $mg\,L^{-1}$ was prepared in hexane. Standard working solutions of different concentrations were prepared by diluting the stock solutions with hexane. The internal standard ($^2H_{10}$-phenanthrene) was spiked in dichloromethane and was used as the extracting solvent. The standard solutions were stored in the dark at 0–4 °C until used.

A 250-μL microsyringe (250R-V-GT) and a 100-μL microsyringe (100F-LC) were purchased from SGE Analytical Science. A 10-μL microsyringe (701 N) was obtained from Hamilton. The purchased information of the GP-MSE related material (such as gas mass flow controller, digital monitor, metal-oxide ceramic heater (MCH), platinum resistor sensor, semiconductor refrigeration component) was described in Refs. [23,24].

2.2. Sample and experimental procedure

2.2.1. Sample collection and preparation

A total of 78 representative samples of widely consumed foods were collected from a local supermarket in Yanji (China) from November to December 2012. Foodstuffs samples were divided into six categories, cereal products ($n = 44$), snacks ($n = 17$), beverages ($n = 3$), condiments ($n = 7$), seafood ($n = 3$), and meat products ($n = 4$). All of the foodstuffs were the most popular brands in China.

All solid food samples were cut into 0.5 cm pieces and then shattered by a high-speed rotary cutting mill. Approximately 1 g of grated sample was placed in a Teflon tube and was ultrasonically extracted with dichloromethane for 30 min, followed by centrifugation at 4000 × *g* for 20 min. The supernatant (dichloromethane layer) was transferred to a clean glass bottle. The extract was evaporated with a stream of nitrogen to approximately 100 μL at room temperature. For liquid samples, 200 mL of samples was placed in separating funnels and extracted with 50 mL of dichloromethane in duplicate. All extracts were combined and concentrated gently with a rotary evaporator to remove dichloromethane and were further reduced to approximately 100 μL with a stream of nitrogen at room temperature. The further clean-up of the extracts was performed using gas purge microsyringe extraction (GP-MSE).

Fifty millilitres of solvents was directly concentrated using a rotary evaporator to investigate the contamination of the solvent.

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