



The application of directly suspended droplet microextraction for the evaluation of phthalic acid esters in cow's milk by gas chromatography mass spectrometry



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ABSTRACT

A simple and rapid method was developed for evaluating 16 phthalic acid esters (PAEs) at the $\mu\text{g}/\text{kg}$ level in a complex milk matrix using directly suspended droplet microextraction-gas chromatography mass spectrometry (DSDME-GC-MS). The different parameters for extraction and for the DSDME experiment were optimized, including You are free to submit the revised manuscript at a later date as a new submission.

10 g/L trichloroacetic acid concentration, 100 μL cyclohexane micro-droplet organic solvent, 1100 rpm stirring speed, 10 min extraction time and no salt amount. Validation experiments showed good linearity ($r > 0.9878$, 0.002–0.4 $\mu\text{g}/\text{mL}$), satisfactory precision (RSD < 11%), and good accuracy (relative recovery of 70.2–108%) when analyzing milk samples using the optimized method. The limits of detection (LODs) ranged between 0.001 and 0.2 $\mu\text{g}/\text{L}$, and the limits of quantification (LOQs) ranged between 0.003 and 0.7 $\mu\text{g}/\text{L}$ for 15 PAEs. Dinonyl phthalate (DINP) had a low response and did not have good linearity. The proposed method was successfully applied for the analysis of PAEs in real milk samples.

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1. Introduction

Phthalate esters (phthalates) are esters of phthalic acid and are primarily used as plasticizers, which increase the flexibility, transparency, durability and longevity of plastics. Phthalic acid esters (PAEs) are polymer chains that are physically bound in the plastic; there are no covalent bonds between them [1]. Moreover, PAEs may be released from plastic materials into the surrounding environment or food, and thus, humans can be exposed to PAEs. Many studies have shown that exposure to high levels and the evident toxicity of PAEs affect human health and the ecosystem [2–4]. In humans, PAE exposure primarily affects the kidney, liver and testicles [5]. Children who have been exposed to phthalates can have twofold higher levels than adults depending on their body weight [6]. Infants and toddlers are at the greatest risk of exposure due to their mouthing behavior and because PAEs are readily absorbed through the skin [3,7]. PAEs can exert effects similar to those of estrogen, causing feminization of male infants and disrupting genital development and testes maturation; hence, they can affect

general health [8]. Therefore, accurately assessing PAE contamination qualitatively and quantitatively in food and the environment is very important.

Gas chromatography with mass spectrometry (GC-MS) [9], liquid chromatography with mass spectrometry (HPLC-MS) [10,27,28,30,33], gas chromatography with a flame ionization detector (GC-FID) [11,26] and HPLC [12,24,25,32] are used for detecting PAEs in different samples. Although FID can detect any molecule that contains a carbon-hydrogen bond, the presence of “heteroatoms” in a molecule decreases the response of this type of detector. FID is sensitive to mass rather than concentration. FID and HPLC-UV have high detection limits and low sensitivity for PAEs using the conventional pretreatment methods. These detection techniques do not provide unequivocal confirmation of identity and are often subject to matrix interferences [10]. GC and HPLC coupled with MS are the most widely used techniques for the trace analysis of PAEs [8]. PAEs are easily subjected to gasification under heating conditions and can be analyzed with the selective ion mode of GC-MS; thus, the sensitivity for PAEs is relatively high. GC-MS is more suitable for detecting PAEs. A series of GC-MS methods have been reported for the detection of some PAEs in food samples [14–18,20–23,31]. The sample preparation technique is often the determining factor for the limits of detection

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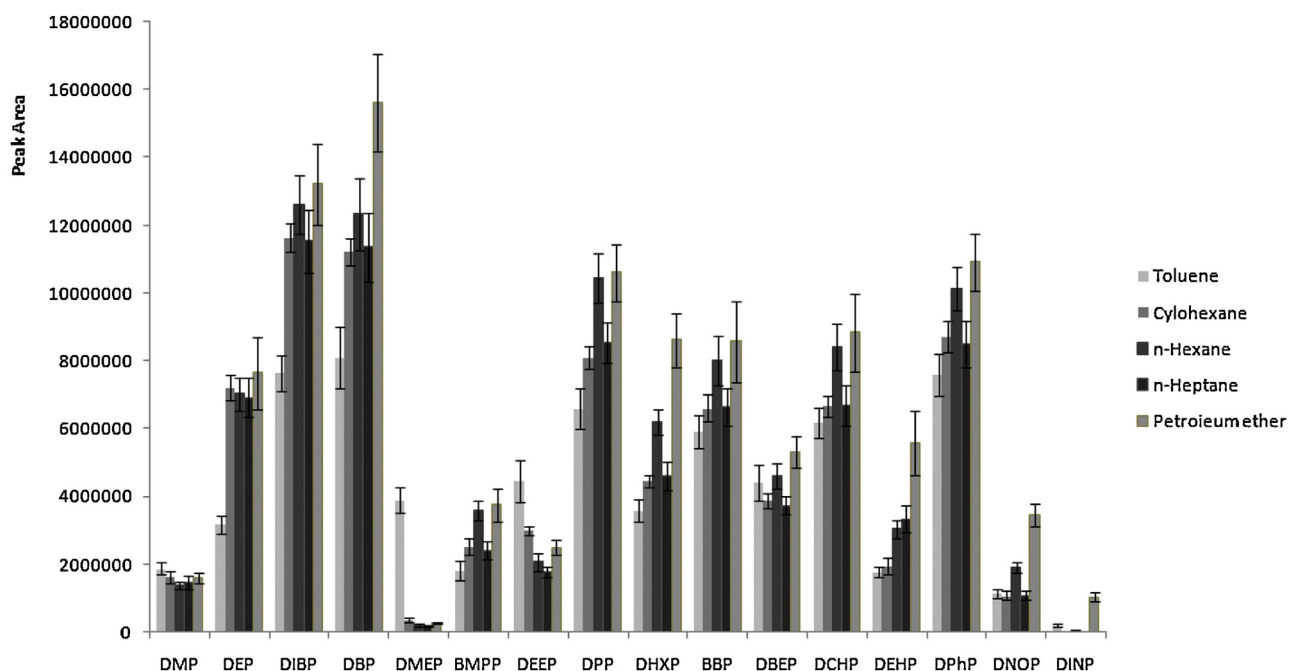


Fig. 1. Comparison of the extraction efficiency of the PAEs with different organic solvents on DSDME.

(LODs) of analytical methods. Liquid–liquid extraction (LLE) is a conventional pretreatment technique. However, conventional LLE methods require large amounts of samples and organic solvents, which leads to environmental pollution, health hazards for operational personnel and economic costs associated with processing their waste products [13]. QuEChERS (Quick Easy Cheap Effective Rugged Safe) [10,14] and solid-phase extraction (SPE) are effective extraction and clean-up methods for PAEs from foods. Nonetheless, these two preparation techniques suffer from the aforementioned disadvantages [8,15–17]. In recent years, microextraction techniques for PAEs have been widely applied to food samples. These methods include solid-phase microextraction (SPME) [18–23], hollow fiber liquid microextraction (HFLME) [24,25] liquid–liquid microextraction (LLME) [26], and dispersive liquid–liquid microextraction (DLLME) [27–30,32,33]. The advantages of microextraction techniques include high analysis speed, great efficiency, low operating costs, environmentally friendly analytical procedures, and highly selective analyses. The directly suspended droplet microextraction (DSDME) technique is a liquid–liquid microextraction method that is very suitable for separating and highly enriching hydrophobic compounds from aqueous samples into organic solvents with excellent selectivity. The DSDME technique has been utilized by many researchers for analyzing teas or other relatively clean, transparent samples [13]. These techniques can be successfully used for pre-concentrating target analytes.

Milk is the most commonly consumed food worldwide and provides highly nutritious and immunological components for the elderly and infants. Because it contains lipids, carbohydrates, proteins, vitamins and minerals, milk has more a complex matrix than other liquid food samples. The main PAE contamination in milk occurs via two ways pathways: the materials that contact the milk during the mechanical milking process are an important PAE contamination pathway [34], and PAEs migrate into milk samples from packing materials [29]. Accordingly, monitoring PAEs in milk has become a necessity. However, analyzing low concentrations of PAEs in real milk matrix samples with good precision and reliable results is difficult using common techniques.

The aim of the present work was to develop a DSDME preparation technique for the simultaneous analysis of 16 trace PAEs

in samples of cow milk using GC–MS. The PAEs were then evaluated in samples of cow milk collected from the local market using DSDME–GC–MS.

2. Experimental

2.1. Reagents and chemicals

Toluene, *n*-hexane, isooctane, cyclohexane, *n*-heptane and petroleum ether were of HPLC grade and were purchased from Tedia (Fairfield, OH, USA). Acetocastin was of A.R. grade and was supplied by the Beijing Chemical Reagent Company. A standard stock solution containing sixteen phthalate esters, namely, dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), dipentyl phthalate (DPP), benzyl butyl phthalate (BBP), diphenyl phthalate (DPhP), di-*n*-octyl phthalate (DNOP), bis(2-butoxyethyl)phthalate (DBEP), bis(2-butoxyethyl)phthalate (DEEP), bis(2-ethylhexyl)phthalate (DEHP), bis(2-methoxyethyl)phthalate (DMEP), bis(4-methyl-2-pentyl)phthalate (BMPP), dicyclohexyl phthalate (DCHP), diisobutyl phthalate (DIBP), di-*n*-hexyl phthalate (DHXP), and dinonyl phthalate (DINP) in methanol and hexane at 1000 mg/L per compound was purchased from Shanghai ANPEL Scientific Instrument Co., Ltd. The solutions were stored at -20°C in the dark. Information on the 16 PAEs is presented in Table 1. Milk samples were purchased from a local market and were stored in the dark at 4°C .

2.2. Sample preparation

The milk samples were purchased from a local supermarket in Beijing. All samples were collected in 250 mL glass bottles and stored at 4°C until analysis.

Ten milliliters of each milk sample was placed in a 50 mL glass centrifuge tube with 10 mL of a trichloroacetic acid (TCA) solution (0.1 g/L), and the samples were immediately shaken vigorously using a vortex mixer for 1 min. The mixed samples were centrifuged for 10 min at 4000 rpm. Then, 5 mL of the clear supernatant solution was carefully transferred to a 12 mL cylindrical glass sample vial and was extracted using DSDME.

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