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Recent advances in analysis of phthalate esters in foods

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Magnetic solid-phase extraction (MSPE)
Molecularly-imprinted polymer-solid-phase extraction (MISPE)
Phthalate ester (PAE)
Quick, easy, cheap, effective, rugged and safe (QuEChERS)
Solid-phase microextraction (SPME)
Stir-bar sorptive extraction (SBSE)

A B S T R A C T

Phthalate esters (PAEs) are widely used as plasticizers in food processing and packaging. Because of a growing international concern about the health effects of PAEs, the analysis of these compounds in various foods was one focus of research in recent years. This review provides an updated overview of recent advances in sample-preparation and determination methods for analysis of PAEs in foods. We discuss contamination problems, current challenges and future trends in the analysis of PAEs in foods.

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1. Introduction

Phthalates (PAEs) or esters of phthalic acid (1,2-benzenedicarboxylic acid) have been commonly used as plasticizers to increase flexibility, transparency, durability, and longevity of plastics materials since the 1930s [1,2]. Millions of tons of PAEs are produced all over the world annually [3], of which di-2-ethylhexyl phthalate (DEHP) is one of the most popular plasticizers and accounts for ~50% of global production, followed by dibutyl phthalate (DBP), di-*iso*-decyl phthalate (DIDP) and di-*iso*-nonyl phthalate (DINP) [4,5]. In general, the contents of PAEs in plastics materials, such as polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyvinyl acetates (PVA) and polyethylene (PE), vary from 10% to 60% by weight [6]. These plastic materials are used for packaging and processing. Since PAEs are not chemically bound to the plastic matrix [7,8], they tend to migrate into air, groundwater, soil and then come into the food chain if absorbed by plants and animals [9]. In addition to natural sources, PAEs in food are generally derived from two other sources:

- first, these compounds may be illegally used as food additives due to their emulsifying capacity and corrosion resistivity; and,
- second, these compounds may easily migrate from food-packaging materials into food under certain conditions, particularly when they are in contact with fatty and oily food.

However, PAEs are not labeled as ingredients on food-packaging materials [10,11].

Human exposure to PAEs occurs mainly via food ingestion [12–15]. For example, in 2011, six PAEs were detected in milk samples with plastics packaging, indicating that PAEs could migrate from plastics packaging into milk [16]. In addition to liquid milk, Khedr [17] found that milk powder was also contaminated by DEHP with the highest level of 25 μg/kg. However, PAEs in foods did not capture special attention until 2011 – when a food scandal that DEHP was being used illegally as a clouding agent in beverages to increase profits was reported in Taiwan, and resulted in major public health concern [18–21]. Consequently, analysis of PAEs in various foods and food packaging materials became a hot topic in recent years. More than 40 publications on determination of PAEs in diversified foods and packaging were found in Science Citation Index (SCI) journals since 2010 (Fig. 1). As seen in Fig. 1, few papers on this topic were found before 2012, but the literature increased rapidly after 2012. The samples included oil, milk, beverage and packaging, but beverages were covered most. DEHP was detected in almost all samples with the highest content of 2.685 g/kg [22]. In distilled liquor samples, DBP was detected frequently with levels of over 0.3 mg/kg. DINP, DNOP, BBP, and other PAEs were detected in soft drinks [11,23–25].

To date, researchers have reviewed PAE analysis in crops, products of animal origin, water and sediments [26,27]. LC-MS analysis of PAEs, bisphenol A and related compounds in food-packaging materials was reviewed by Gallart-Ayala and co-workers [5].

This review focuses on the most recently published information on the properties, toxicities and analytical methods for PAEs in foods, with emphasis on methods of sample preparation and quantification.

2. Properties and toxicities

At room temperature, the vast majority of PAEs are almost colorless and odorless oily liquids. Their boiling points vary greatly in the range of 190–530°C and their melting points are below –25°C, except DMP for (+5.5°C) and DUP (–9°C). Fig. 2 shows the general chemical structure of PAEs, in which R and R' are hydrocarbyl groups with 1–13 carbon atoms [7].

Water solubilities of PAEs not only affect their aquatic toxicity, bioaccumulation and biodegradation potential but also control their distribution in foods and bodies. Their water solubilities can be evaluated with the octanol-water partitioning factor (K_{OW}), defined as the ratio of equilibrium concentration of chemicals in octanol to that in water. However, water solubilities of PAEs are still under debate until now. For low-molecular-weight (LMW) PAEs, such as DMP, DEP, DBP and BBP, independent experimental data showed negative correlations between water solubility and the number of carbon atoms of the alkyl chain, which is consistent with theoretical predictions [28] and the structure-activity models [29]. In other words, log K_{OW} increases (DMP 1.61, DEP 2.38, DBP 4.45, BBP 4.59) with the increase

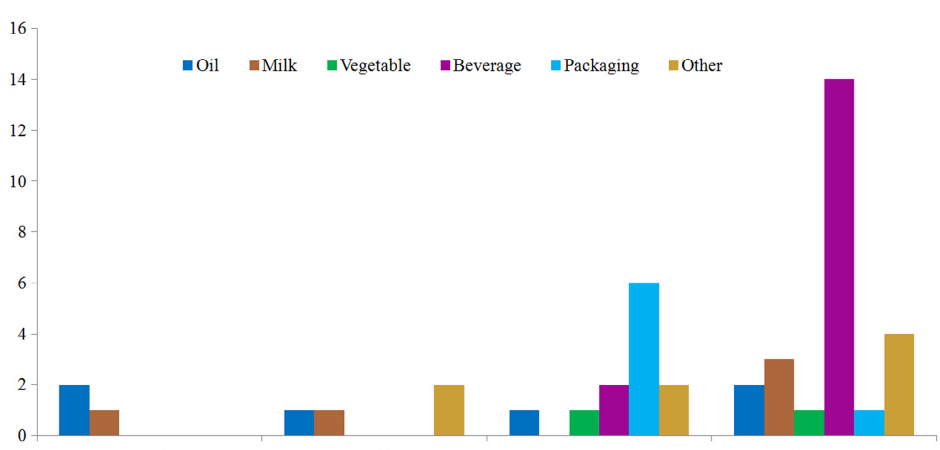

Fig. 1. Distribution of literature concerning PAE analysis published since 2010.