



Simultaneous GC–MS determination of eight phthalates in total and migrated portions of plasticized polymeric toys and childcare articles



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ABSTRACT

A gas chromatography/mass spectrometric method was developed for the simultaneous determination of eight phthalic acid esters (PAEs) in toys and child care articles that are made of plasticized plastic. The novel method was used to determine the total concentration of the PAEs in addition to the migrated PAEs values into artificial saliva, under conditions that simulate real life situations. The extraction method, which was developed for the first time to determine the total concentration of PAEs, utilized a novel optimization of four parameters involving the solvent, time, temperature and weight of sample. The PAEs were extracted with tetrahydrofuran, as extraction the solvent, and using the ultrasonic water bath shaker for 30 min, at room temperature. Another extraction method was developed to determine the migrated PAEs into artificial saliva at pH 6.2 and 37 °C, implementing a liquid–liquid extraction with chloroform. Both methods were subjected to validation steps in terms of linearity, precision, accuracy and recovery, which ensured that all obtained results were well within the norms of acceptable limits and specifications. The analytes were separated at the following retention times: 4.99, 5.21, 5.31, 6.63, 7.41, 9.05 min for di-“isobutyl” phthalate (DIBP), dibutyl phthalate (DBP), bis(2-methoxyethyl)phthalate (DMEP), benzyl butyl phthalate (BBP), dibutyl phthalate (DEHP) and di-n-octyl phthalate (DnOP), respectively. The chromatographic peaks corresponding to di-“isononyl” phthalate (DINP) and di-“isononyl” phthalate (DIDP), were separated, using the extracted ion chromatogram (EIC) mode within the time ranges of 8.05–12.10 min for DINP and 8.50–14.50 min for DIDP. The instrument detection limits for DIBP, DBP, DMEP, BBP, DEHP, DnOP, DINP and DIDP were determined at 0.100, 0.100, 0.045, 0.035, 0.015, 0.370, 0.320, 0.260 µg/ml, respectively. The calibration curve working ranges were determined at 0.5–25 µg/ml for DIBP, DBP, DMEP, BBP and DEHP, 2–100 µg/ml for DnOP and 5–100 µg/ml for DINP and DIDP. The coefficients of variation (precision) for the total PAEs method were in the range 0.55–12.10% and for the migration method were in the range 0.72–7.70%. Recovery values for total PAEs and for the migrated PAEs were ranged within 90.6–111.7% and 86.3–117.2%; respectively. Both developed methods were used to survey the Jordanian market, where twenty seven samples were collected and tested for plastic type, total PAEs and migrated PAEs. Seventeen of those samples were found to be polyvinyl chloride (PVC), and all of them containing total PAEs having concentrations in excess of the allowed limit of 0.1% (w/w). The rest of the samples were non-PVC and only one of them containing PAEs, but below the allowed limit. In contrast, all the migration results were found to be well within the allowed limits. It was also found that as the PAEs total concentration increase, the corresponding migrated value increase, while the opposite trend holds for in the PAEs molecular weight.

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1. Introduction

Plastics have been widely used in our daily lives, as well as in numerous and varied industrial applications as a result of the

multitude of the desirable properties they exhibit, including low cost, high durability, ease of manufacture and ability to recycle [1]. For plastic polymers to be ready for utilization, they have to undergo further processes, including mixing with other substances to make them capable of being processed to begin with, then to improve some desirable physicochemical properties and eliminate other undesirable properties. The other substances that are mixed with the plastic polymers are known as additives [2].

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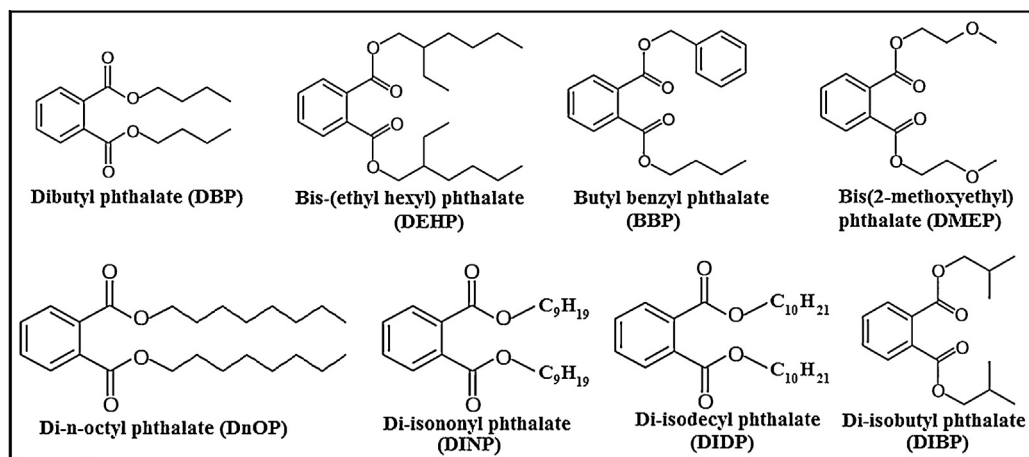


Fig. 1. 2D structures of phthalates under study.

These additives may belong to main types of fillers, colorants, stabilizers, flame retardants, and plasticizers [3]. Plasticizers are substances that are mixed with the polymers in order to impart some desirable levels of flexibility and softness [4]. Plasticizers are liquids having low molecular weights that are not chemically bonded to the polymers; rather they are dispersed to spread through the polymer chains to interact with individual polymer chains, thus separating the individual chains from each other hence causing a significant reduction of the relatively stronger inter-polymer interactions, which result in an overall substantial increase of macromolecule mobility thus culminating in more flexible and elastic polymers [5]. Due to a favorable number of desirable properties they exhibit, phthalic acid esters (PAEs) are rated as the most commonly used plasticizers. In fact, phthalates constitute almost 80% of the global plasticizer production [6]; their use widely spread in plastics, particularly in PVC which consumes the largest share of annual phthalates production [7]. This raises a growing environmental concern about phthalates as probable health hazards to reckon with, especially since phthalates are not chemically bonded to the polymers which facilitate their leaching out of the polymer matrices into the surrounding environment [8]. This would certainly result in more worrying human exposure to PAEs from the profusion of a variety of PVC-based polymeric materials spread everywhere, especially those directly and frequently left in contact with children, including toys and various childcare articles; children and newborn babies tend to chew and suck their toys and other items, which might result in extracting the PAEs out of the plastic matrices and ingesting them thus exposing their health to the highly harmful PAEs. Research reported in the literature indicates the negative impact of PAE's on humans, stressing greater risks to the immune systems of children and newborn babies, and hence their general health. Among the health hazards reported in the literature include carcinogenicity, kidney and liver damage, reproductive toxicity, and endocrine disruption [9,10]. As a result, and according to the European Union Regulations REACH (Registration, Evaluation, Authorization and Restriction of Chemicals), six of the main phthalates have been banned, namely dibutyl phthalate (DBP), bis (2-ethylhexyl) phthalate (DEHP), benzyl butyl phthalate (BBP), di-"isononyl" phthalate (DINP), di-"isodecyl" phthalate (DIDP) and di-n-octyl phthalate (DNOP) [11]. In addition to those six PAEs, many others are still under discussion while some others have already been listed as candidates for labeling as Substances of Very High Concern (SVHCs), which depict substances that may have serious and often irreversible effects on human health and the environment, according to the European Chemical Agency ECHA definition [12], like bis(2-methoxyethyl)phthalate (DMEP) and

di-"isobutyl" phthalate (DIBP). Fig. 1 depicts the chemical structures, the corresponding names and acronyms of the eight phthalates (PAEs) under consideration.

Several procedures have been used to analyze total PAEs such as Soxhlet extraction followed by GC/FID [8], GC/MS [13], simple shaking followed by GC/MS [14], ultra high performance liquid chromatography coupled with electronic spray mass spectrometry UPLCMS/MS [15]. Migration of PAEs into artificial saliva was analyzed after liquid–liquid extraction using GC/MS [16] and HPLC [17].

In this work, we were interested in developing and validating a method for the simultaneous determination of eight phthalate derivatives, in plasticized toys and childcare articles, using gas chromatography–mass spectrometry (GC–MS). These phthalates comprise the six restricted phthalates (DBP, BBP, DEHP, DNOP, DINP and DIDP), as well as two other phthalates that are considered substances of very high concern (DIBP and DMEP). The phthalates shall be determined as total and migrated phthalates in toys and childcare articles collected from the Jordanian market.

2. Experimental

2.1. Reagents and chemicals

The phthalate standard reference materials were obtained as follows: dibutyl phthalate (DBP), 99.8%; bis (2-ethylhexyl) phthalate (DEHP), 99.7%; benzyl butyl phthalate (BBP), 98.7%; di-methoxyethyl phthalate (DMEP), 96.8%; and di-n-octyl phthalate (DNOP), 99.4% were all purchased from Fluka, Germany. Di-"isobutyl" phthalate (DIBP), 99.5% was purchased from Fluka, Switzerland, Di-"isononyl" phthalate (DINP), 99% was purchased from Aldrich, Germany, di-"isodecyl" phthalate (DIDP), 99% was purchased from Fluka, Japan and the internal standard Benzyl benzoate (BB), 99%, was purchased from Fluka, USA. Chemicals that were used for preparing the artificial saliva were obtained as follows: calcium chloride, di-potassium hydrogen phosphate, and potassium carbonate were purchased from Scharlau, Spain; magnesium chloride hexahydrate was purchased from S.D. Fine-Chem Ltd., India; sodium chloride was purchased from Fluka; while potassium chloride and hydrochloric acid (36%, w/w) were purchased from GCC, UK. Solvents that were used were obtained as follow: cyclohexane (GC grade, purity > 99.8%) was purchased from LABCHEM, USA. Tetrahydrofuran (THF) (HPLC grade, purity > 99.8%) and n-hexane (ACS grade, purity > 95%) were purchased from TEDIA, USA. Toluene (ACS grade, 95%) was purchased from CARLO ERBA, Italy. Methyl tert-butyl ether (MTBE) (HPLC grade, 99.8%) was

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