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PHTHALATE ANALYSIS AND INVESTIGATIONS IN POLYMER TYPE TOYS IN TERMS OF OCCUPATIONAL HEALTH AND SAFETY

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ABSTRACT

Polymer technology provides the biggest contribution to the Turkish economy. Unfortunately, various health problems arise along with this rapid growth in the plastics industry. Within the scope of the study, the quantitative fhthalates analysis of different toy types has been examined in terms of occupational health and safety. In this study, determination of plasticizer phthalates, which are endocrine disrupting chemicals (EDC) and used to soften poly vinyl chloride (PVC) material, by GC-MS/MS is analysed. Within the scope of the study, quantitative analyzes of eight different endocrine disrupting phthalate derivative compounds were carried out on ten widely used different types of toys offered for sale in the Turkish market. Banned Di-isobutylphthalate (DIBP) and Di(2-ethylhexyl)phthalate (DEHP) were detected in the study on three different toys.

Keywords: Phthalate, toys, occupational health and safety, polymer

INTRODUCTION

Technological developments that contribute to people's comfortable lives can also become an important danger factor for human life and the environment. Every new substance, every new machine, used tools and equipment in the production process can be considered as a threat to human health, workplace safety and the environment. Business success, safe and rapid development largely depends on a healthy working environment.

One of the most important constituent of the Turkish economy is polymer technology. Industry analysis indicates that the plastics industry's economic contribution to the nation is gradually growing, with annual growth exceeding the growth of the gross national product (GNP) over the past ten years, a total production of close to 10 million tons, a turnover of close to 33 billion dollars, and direct exports of close to 5 billion dollars [1]. With the manufacturing capacity it has reached, the sector has therefore ascended to the second spot in Europe and the sixth spot globally [1]. The rapid growth of the Plastics Industry is both proud and alarming in terms of the emergence of various health problems. Concerns can be minimized by ensuring the correct selection of the material used and by taking the necessary occupational safety measures. The use of the right personal protective equipment and the early diagnosis of the occupational disease that may occur allow the employee to continue working in a safer environment without much harm. Recognizing the chemical substance being studied and taking safety measures accordingly also prevent the emergence of new occupational diseases. Because of the occupational health and safety measures we do not take, the negative effects of plastic additives and monomers used in production on health can be listed as cancer [2], hormonal disorders [3], dermatological disorders, respiratory problems, neurological problems and birth defects [4]. Many countries take measures to restrict or prohibit the useage of some of these materials.

In this research, phthalate analyzes were carried out on some widely used toys within the scope of occupational health and safety in the polymeric toy industry. Before releasing a toy on the market, manufacturers are required by the Toy Safety Directive to complete a risk analysis and ascertain the likelihood that children may be exposed to certain dangers. [5]. In agreement with this prescription, toys launched to the European market must have a legally binding statement of engagement representing that the product conform with European law.

Products need to successfully complete a conformity assessment process and get the necessary certificates before the producer can issue a declaration of ccompatibility. In addition, hazardous compounds must be properly removed so that recycled polymers can be reused, especially in "sensitive use" areas (toys, food containers, food packaging, kitchen equipment, water pipes and water tanks).

Compounds that affect the synthesis, secretion, transport, metabolism, elimination and receptor binding of natural hormones are called endocrine disrupting chemicals (EDC) [6]. Unfortunately, there are many EDCs in our environment that we are exposed to via inhalation, oral or dermal routes [6]. The plasticizer phthalates used to soften PVC material, dialkyl or alkyl/aryl esters of 1,2-benzenedicarboxylic acid (phthalic acid) (**Table 1**), are just one of the EDCs. The majority of the population is exposed to high levels of these substances. Phthalates show developmental, reproductive, hepatic, renal and thyroid toxicity, especially since males are more susceptible to the toxic effects of phthalates [7]. In addition, it is suggested that one of the most important causes of testicular cancers seen at an early age (between 30-40 years) is phthalate exposure [8].

Table 1. Types of phthalates and their usage areas [7]

Phthalate	Abbreviation	Usage
Diethyl phthalate	DEP	In cosmetics (shampoo, perfume, soap, lotion), as industrial solvent, in medicines (tablet coating, capsule production)
Dibutyl phthalate	DBP	In cosmetics, as industrial solvent (solvent), pharmaceuticals (tablet coating, capsule production), adhesives
Diisobutyl phthalate	DIBP	In cosmetics, as an industrial solvent, in adhesives
Butyl benzyl phthalate	BBP	In vinyl floor coverings, as a solvent in the industry, in the production of seals
Dicyclohexyl phthalate	DCHP	As a stabilizer in rubber and polymer production
Di (2-ethylhexyl) phthalate	DEHP	As a plasticizer in soft plastics (IV bags, toys, household products, food packaging bags in the food industry), paper industry, electrical capacitors, paints/pigments, resins, rubber industry, textiles, cosmetics
Dioctyl phthalate	DOP	In soft plastics
Diisononyl phthalate	DINP	Use instead of DEHP in soft plastics

Consequently, and according to the European Union Regulations REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) six of the major phthalates namely as bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), di-isononyl phthalate (DINP) , benzyl butyl phthalate (BBP), di-isodecyl phthalate (DIDP), and di-n-octyl phthalate (DNOP) are banned [9]. The most significant phthalate is di(2-ethylhexyl)phthalate (DEHP), which is manufactured in excess of two million tons annually worldwide[10]. The tolerated daily intake (TDI) for DEHP has been defined at 37 mg/kg body weight/day by the EU Scientific Committee for Toxicity, Ecotoxicity, and the Environment (CSTEE) [9]. Phthalic acid esters, usually referred to as phthalates, are frequently utilized as plasticizers in PVC (polyvinyl chloride) products, such as building supplies, toys, and numerous other items we use every day.

Some phthalates are also utilized in non-PVC applications like paints, adhesives, personal care products, textile additives, and pesticide formulations. As a result, phthalates are now common compounds and environmental hazards, according to industry studies of the role of plastics [10]. Natseh et al. investigated the simultaneous detection of eight phthalate derivatives in plasticized toys and childcare products using gas chromatography-mass spectrometry (GC-MS) and were found phthalic acid esters (PAE) at concentrations exceeding the allowable 0.1% (w/w) of all PVC samples [11].

The toy manufacturing sector, which is examined within the scope of the study, is important in that it not only concerns the employees, but also closely concerns the health of our children, to whom we entrust our future. Within the scope of the study, 10 different quality toys offered for sale in the Turkish market were collected and phthalate analysis was performed with GC-MS/MS, and the results were evaluated in terms of compliance with European Union standards.

MATERIAL AND METHODS

Test of phthalates; It was carried out in Hitit University Scientific Technical Application and Research Center (HÜBTUAM) according to CPSC-CH-C1001-09.4 Standard Operating Procedure for Determination of Phthalates 2018 standards via thermo scientific brand, TSQ QUANTUM XLS model Gas Chromatography-Mass Spectroscopy (GC-MS/MS) (**Table 2**).

According to this method, 10 mL of tetrahydrofuran (THF) was added to the samples weighing 0.1 g, and it was extracted in an ultrasonic bath for 1 hour. Then, in order to precipitate the polymeric materials, 20 mL of hexane was added and mixed vigorously. After the polymeric materials precipitated, they were taken from the upper phase and filtered with a 0.45 µm syringe filter. Benzylbenzoate was used as internal standard.

Table 2. GC-MS/MS operating conditions

Sample Name	Toys	
Sample Materials	Liquid	
Flow Rate	1 mL/min – He(Helium)	
Column Properties	TG-5MS Column	
Injection Block Temperature	270 °C	
Analysis Time	13,0 min	
Temperature Program		
Rate of Increase (°C/min)	**Temperature (°C)**	**Standby Time (min)**
	150	1,00
3	280	0,00
15	310	5,67

10 different toys with various brands and models sold in the Turkish market were collected and coded as follows (**Table 3**), and phthalate analysis was carried out.

Table 3. Sample Codes

Code	Toy Name	Code	Toy Name
1	Doll	**6**	Purple Cup
2	Orange Carrot	**7**	Yellow Lego Piece
3	Purple Seal	**8**	Red Ball
4	Pink-White Teether	**9**	Multi Color Ball
5	Orange-Blue Teether	**10**	Plastic Hair Pin

Figure 1: Picture of the Analyzed toys

RESULTS AND DISCUSSION

Phthalates are referred to as plasticizers when they are utilized in the manufacture of plastic to increase the robustness, lifespan, and flexibility of products [12]. Phthalates are classified as endocrine disruptors acting on the hormonal system because of their impact on living organisms [13]. Despite the harm of phthalate in our body, approximately eight million metric tons are produced every year [14]. It is possible to find phthalates in many products such as and clothes, toys, cosmetics, food packaging, paints. They are pervasive in the environment, enter organisms through the digestive tract, the lungs, and the skin, and affect how many internal organs work [12]. There are studies showing that phthalates negatively affect the reproductive organs, endocrine, nervous and immune systems and increase the risk of diabetes and obesity [15, 16].

In this study, eight different phthalate species were searched by GC-MS\MS in ten different quality toys collected from the Turkish market. It is possible to the phthalate types investigated and the calibration data in **Table 4**.

Table 4. Calibration data

	Equation	R^2
DIBP (Di-isobutyl phthalate)	Y = -0.0793042+0.205917*X	0.9994
DBP (Di-butyl phthalate)	Y = -0.0527271+0.187907*X	0.9996
DPENP (Di-n-pentyl phthalate)	Y = -0.0850672+0.30413*X	0.9998
DHEXP (Di-n-hexyll phthalate)	Y = -0.0924868+0.327574*X	0.9998
BBP (Benzyl Butyl phthalate)	Y = -0.128263+0.314628*X	0.9992
DEHP (Di-(2-ethyl-hexyl) phthalate)	Y = -0.082855+0.228724*X	0.9987
DCHP (Di-cyclohexyl phthalate)	Y = -0.0777661+0.191843*X	0.9985
DINP (Di-isononyl phthalate)	Y = -0.0287416+0.363205*X	0.9951

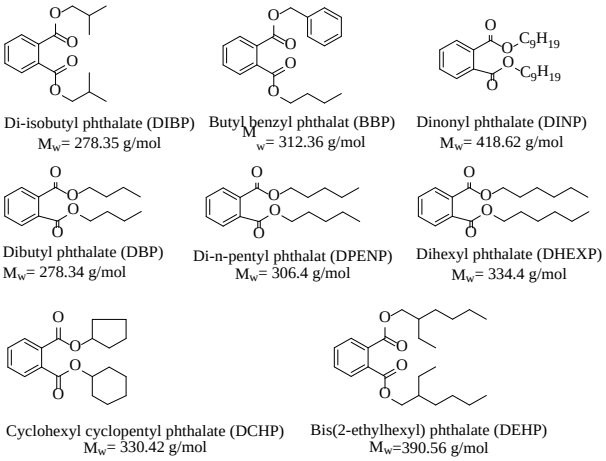

Fig 2 Molecular structures and molar masses of the analyzed phthalates

Eight different phthalate species (**Figure 2**) were searched in 10 different quality toys collected from the Turkish market. As a result of the analysis, 700 ppm di-isobutyl phthalate (DIBP), 300 ppm DIBP, and 500 ppm di-(2-ethylhexyl) phthalate (DEHP) under legal limits were found in samples 1, 9 and 10 respectively, in doll, multi-color ball and plastic hairpin **(Figures 3,4,5)**. Test results are also given in **Table 5**. As a result of the analysis, phthalate derivatives were not found in other samples.

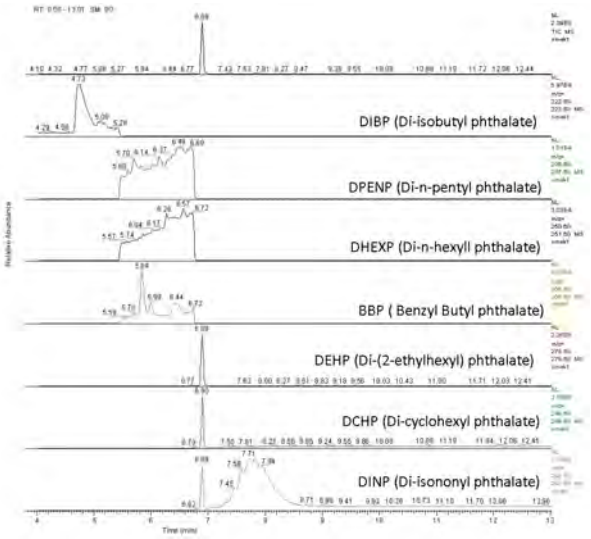

Fig 3. GC-MS chromatogram of the Toy 1 **(**Doll)

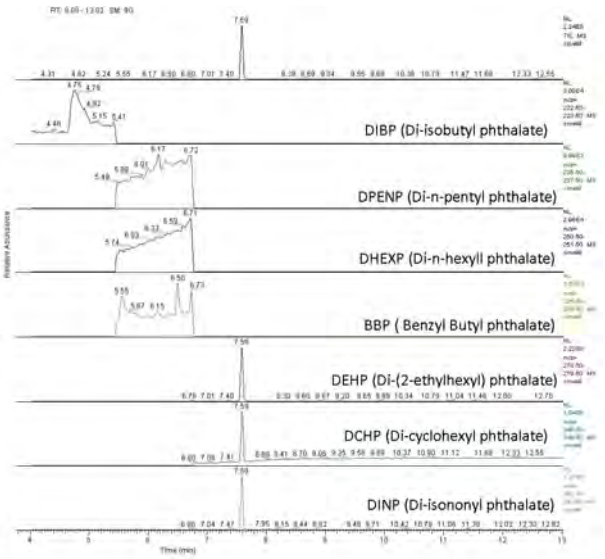

Figure 4. GC-MS chromatogram of the Toy 9 (Multi Color Ball)

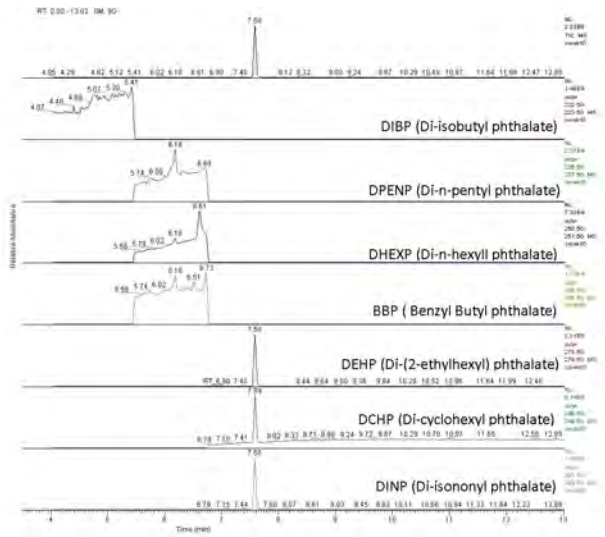

Figure 5. GC-MS chromatogram of the Toy 10 (Plastic Hairpin)

Table 5. Phthalate Test Results

Phthalate	Cas No	Toy 1 Doll	Toy 2 Orange Carrot	Toy 3 Purple Seal	Toy 4 Pink-White Teether	Toy 5 Orange- Blue Teether
DIBP	84-69-5	%0,07	ND	ND	ND	ND
DBP	84-74-2	ND	ND	ND	ND	ND
DPENP	131-18-0	ND	ND	ND	ND	ND
DHEXP	84-75-3	ND	ND	ND	ND	ND
BBP	85-67-7	ND	ND	ND	ND	ND
DEHP	117-81-7	ND	ND	ND	ND	ND
DCHP	84-61-7	ND	ND	ND	ND	ND
DINP	28553-12-0	ND	ND	ND	ND	ND
Total Phthalate		%0,07	ND	ND	ND	ND
Limit		0,1% (1000ppm)	0,1% (1000ppm)	0,1% (1000ppm)	0,1% (1000ppm)	0,1% (1000ppm)

Phthalate	Cas No	Toy 6 Purple Cup	Toy 7 Yellow Lego Piece	Toy 8 Red Ball	Toy 9 Multi Color Ball	Toy 10 Plastic Hairpin
DIBP	84-69-5	ND	ND	ND	%0,03	ND
DBP	84-74-2	ND	ND	ND	ND	ND
DPENP	131-18-0	ND	ND	ND	ND	ND
DHEXP	84-75-3	ND	ND	ND	ND	ND
BBP	85-67-7	ND	ND	ND	ND	ND
DEHP	117-81-7	ND	ND	ND	ND	%0,05
DCHP	84-61-7	ND	ND	ND	ND	ND
DINP	28553-12-0	ND	ND	ND	ND	ND
Total Phthalate		ND	ND	ND	%0,03	%0,05
Limit		0,1% (1000ppm)	0,1% (1000ppm)	0,1% (1000ppm)	0,1% (1000ppm)	0,1% (1000ppm)

ND: Not Dedected

Organizations of the three biggest world economies (European Union (EU), United States of America (USA), China) focusing on Food Contact Materials (FCM), toys, cosmetics, and child care products observed the prohibited concentrations of the 8 most preferred phthalates (DIBP, DBP, DPENP, DHEXP, BBP, DEHP, DCHP, DINP) for their own countries. BBP, DEHP, DBP and DIBP are are not permitted to make up more than 0.1% of toys and childcare items in the EU. All eight phthalates are strictly limited and, for the most part, prohibited as cosmetic ingredients in FCM. Although there isn't an official ban on it, phthalates are mainly restricted in FCM in the USA. Although the use of DEHP, BBP and DBP in cosmetics is prohibited in China, the amount of BBP, DBP, DNOP, DEHP, DINP, DIDDP used in plastic toys cannot exceed 0.1% by weight [17, 18]. In our country, in the Regulation on Restrictions on the Production, Placement and Use of Certain Hazardous Substances, Preparations and Goods (RG-20/3/2011-27880) of the Ministry of Environment and Urbanization, for DEHP, DBP and BBP "In toys and children's care articles, It cannot be placed on the market or used as a substance or mixture component at concentrations higher than 0.1% by weight" [19].

Low molecular weight liquids known as phthalate-type plasticizers are not chemically linked to polymers. To interact with the various polymer chains, they are spread out along the polymer chains. Thus, they separate the chains and cause a significant reduction in the relatively stronger interpolymer interactions. This results in an overall significant increase in macromolecule mobility, making the material more flexible [20].

CONCLUSION

Phthalates, which are not chemically bound to polymers, pose a great danger to children who put everything in their mouth to explore. Therefore, this research is very important for our future and society beyond occupational health and safety. In the GC-MS results, DIBP in Toy 1 (%0.07) and Toy 9 (%0.03), and DEHP in Toy 10 (%0.05), among the banned phthalate compounds, were detected below the legal values (%0.1). In the next step,

further restrictions can be made in the use of phthalates by calculating the amount of phthalate that migrates to the artificial saliva solution by performing phthalate analysis in the unused toy.

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