

PHTHALATE CONTENT IN CHILDREN'S TOYS IN FEDERATION OF BOSNIA AND HERZEGOVINA

Amir Čaušević, Daniel Maestro, Arzija Pašalić

Abstract - Phthalates are compounds of synthetic origin, most commonly used as additives for various plastic masses to improve their mechanical properties, especially softness, flexibility, transparency, stretch and durability. From public health point of view, the most important toy safety aspect is in toys intended for children aged up to three years old, that are mostly made of plastic. Phthalates from plastic masses can affect the reproductive gland, whose disorder can lead to early puberty of girls and feminization of boys. In Bosnia and Herzegovina, the list of phthalates with their concentrations limits is defined by Regulation of restriction of placing on market for toys and products for children with contact phthalates. The method used in the analysis of phthalate esters is the standardized ISO method BAS EN 14372:2013, based on gas chromatography with mass detector. Of total 73 samples sampled in the four-year period (2015-2018) and analyzed on presence of phthalates, 30 tested samples (21.9%) were not in accordance with Regulation of restriction of placing on market for toys and products for children which contain phthalates, they had phthalate concentrations greater than 0.1% of the total weight of the toy. Based on the results obtained in this paper, we can conclude that a large percentage of children's toys in territory of Federation of Bosnia and Herzegovina contain increased concentrations of phthalates, and that this percentage is in harmony with average number of defective samples in the European.

Index Terms - *phthalates, toys, children.*

1 INTRODUCTION

Today's way of life is hard to imagine without the use of plastic products, which as such, follow the man throughout his lifetime, starting from birth (1). Since the beginning of 1862, when the production of plastics began, the technology of their production itself has changed considerably. Accordingly, today in the process of plastic production, in order to obtain its better and new properties, various agents are added: softeners - plasticizers, fillers, stabilizers and pigments. In the last few decades, the most commonly used plasticizers are phthalates - phthalic acid esters (2). Phthalates are synthetic sub-compounds, and most often used as additives with different plastic masses to improve their mechanical properties, especially softness, flexibility, transparency, extensibility and durability. As additives for plastification, they are present in numerous objects of general use, such as children's toys and cosmetics, car cosmetics, in various solutions and insecticides, food packaging, medical devices and accessories for transfusion, decorative products, floor coverings, household products and in technological processes of food and similar industries (3). Considering the fact that high molecular weight phthalates are used in the production of plastics, that their concentration in plastic mass can reach almost 30% of the weight of the product, they can be found everywhere flexible plastic masses are used (4). Polymer polyvinyl chloride (PVC) without the softener additive would be very weightly and practically useless for technical use, and therefore plasticizers are added to it to be used for the production of children's toys (5). Children are in dynamic growth and development and therefore represent a sensitive population group. During the development of the central nervous system they go through different stages of mental development, which is enriched with various contents including children's toys. From the aspect of public health, the most important is the safety of toys intended for children up to three years old, which are mainly made of plastic materials.

Children consume phthalates in larger quantities by putting toys in their mouths and by doing so, phthalates are being dissolved by saliva and entered into the system.

Phthalates from plastic mass can affect the reproductive glands, whose disorder can lead to early puberty in girls and feminization in boys (6). So far, according to the knowledge some phthalates are harmful to human health, including metabolism disorder, disease of thyroid gland, fertility disorder and changing a brain function in boys (8). By the 2005 directive, the European Union banned the use of diethylhexyl phthalate (DEHP), dibutyl phthalate (DBP) and benzylbutyl phthalate (BBP) in the production of plastic toys, and diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and dioctyl phthalates (DNOPs) are forbidden in toys and other items that are used for the childcare and that can be placed in the mouth (9). By supplementing the directive, the concentration of six phthalates in toys is limited to 0.1% of the weight of the plasticised material (10). In Bosnia and Herzegovina, the list of phthalates with concentration limits is defined by the Decision on restricting the placing on the market toys and products for children containing phthalates. In accordance with this Decision, which is harmonized with EU regulations, analysis of toys on DEHP, DBP, BBT, DINP, DIDP and DNOP is required in Bosnia and Herzegovina. The reference value is expressed as a percentage (%) of the mass and is 0.1% for all six phthalates (11). According to research conducted by the German Federal Environmental Agency in 2006, phthalate metabolites can be found in the urine of almost every child in Germany. Of the 599 children tested in 1.5% of cases, concentrations of phthalate metabolites were found in concentrations that could lead to adverse health effects (12).

2 MATERIALS AND METHODS

Material used in the work are children's toys and products for children (dolls, pacifier, balls and other toys with rubber parts), collected over a period of four years (2015, 2016, 2017 and 2018) as part of the control of children's toys in the Federation of Bosnia and Herzegovina, organized by the Public Health Institute of the Federation of Bosnia and Herzegovina, the Federal Administration for Inspection Affairs and the Market Surveillance Agency of Bosnia and Herzegovina. A total of 73 samples were used in the work. Divided by age, the number of samples was 10 samples in 2015, 25 samples in 2016, 14 samples in 2017 and 24 samples in 2018.

The method used to analyze the content of 6 phthalate esters, di (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), di-"isononyl" phthalate (DINP), di-"isodecyl" phthalate (DIDP) and di-n-octyl phthalate (DNOP) is a standardized ISO method BAS EN 14372: 2013. The method is based on gas chromatography with a mass detector. The analyzes were performed on the GC / MS "SHIMADZU QP2010" instrument. The samples were prepared by ultrasonic extraction according to the CPSC-CH-C1001-09.3 method. Before the start of the analysis, the calibration curve was made. The analytical conditions of the method are shown in Table 1.

Table 1. Analytical conditions GC/MS

Instrument	
GC/MS	GCMS-QP2010S
Autoinjector	AOC-20
Colon	InterCap 5MS/Sil 0,25 mm i.d x 30 m df=0,25µm GL Sciences
Analytical conditions	
GC	
Temperature of injection	290°C
Temperature of colon	120°C (1 min)-(30°C/min)-280°C (5°C/min)-310°C (6 min)
Injection mode	Splitless
Gas	Helijum
Linear speed	36,3 cm/sec
Flow	5 mL/min
Volumen of injection	1 µL
MS	
Ion source temperature	230°C
Interface temperature	280°C
Akvation mode	Scan/SIM
Tuning mode	Normal
Scan range	m/z 40.00-500.00
Work time	0,1 sec

During the chromatographic analysis through the injector, a well-known sample volume (1 µL) is introduced into the column with micro syringe. The injection block is heated to a temperature that is about 50°C higher than the temperature of the column, since it allows the instantaneous evaporation of all the components from the sample. The sample enters the gas carrier (helium) which the sample passes through the column. The carrier gas flow is still stable, but the sample is broken down into constituent parts due to the different

absorption capacities of the individual components of the sample. The gas chromatograph is connected to a mass spectrometer by means of an interface so that the total amount of analyte is directly introduced into the ion source of the MS. The ionization technique used in this method is electron ionization. The electrons that are used for ionization are formed by passing through the filament. When analytic molecules pass through an electronic jet, they pass into the ions. Formed ions are suppressed from the ion source and go into a mass analyzer. It divides the resulting ions based on their m/z (mass/charge) ratio. The detection is carried out electrically, so that the total ion current is measured. Determination of the phthalate ester content is done with a calibration curve or by comparing the surface of the sample peaks with the surface of the known standard. The chromatograph of phthalate esters and retention times are shown in Figure 1.

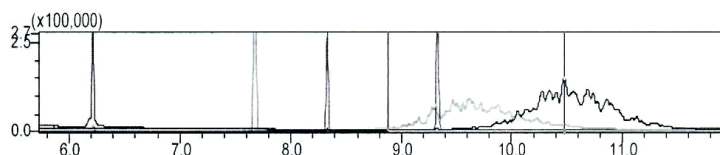


Figure 2. Phthalate ester chromatograph and time of retention
SOURCE: Photo, Institute for public health F BiH; 26.12.2018.

The determination of the degree of statistical significance of the difference between correct and defective samples by years was done using the t-test, for a level of significance of 5% (p <0.5), 1% (p <0.01), and 0.1% (0.001). Complete statistical data processing was performed on Microsoft Excel 2016 for t-test.

3 RESULTS AND DISCUSSION

Out of a total of 73 samples collected for a period of four years (2015-2018) and analyzed for the presence of all six phthalates (DEHP, DBP, BBP, DINP, DIDP, DNOP), 30 tested samples (21.9%) were not in accordance with the Decision on restricting the placing on the market of toys and products for children containing phthalates, i.e. phthalate concentrations that were recorded was greater than 0.1% of the total weight of the baby toy. According to the results of similar research carried out in the Republic of Srpska, similar results were found, where in samples of toys collected in 2017, there were 24% of samples where the presence of phthalate was determined (14). Based on the above, we can conclude that there are children's toys that do not match the criteria prescribed by the Decision on limiting the placing on the market of toys and products for children with phthalates in the whole of Bosnia and Herzegovina. Studies in the Republic of Croatia (15), as well as in other European Union countries (Austria, Germany) and Switzerland, also indicate the presence of phthalate in analyzed children's toys ranging from 20-27% of defective samples (16).

Table 2. Number of tested and defective samples by age and type of phthalate

Year	Number of tested samples											
	Phthalate											
	DEHP		DBP		BBP		DINP		DIDP		DNOP	
U*	N**	U*	N**	U*	N**	U*	N**	U*	N**	U*	N**	
2015	10	8	10	0	10	0	10	1	10	0	10	1

2016	25	10	25	0	25	0	25	0	25	0	25	1
2017	14	6	14	0	14	0	14	0	14	0	14	25.46
2018	24	6	24	0	24	0	24	1	24	0	24	16.2

* Number of tested samples
** Defective samples

The analysis of the obtained results showed a trend of decreasing the number of defective samples by years, so the largest number of incorrect samples was recorded in 2015 (80%) and the smallest in 2018 (25%).

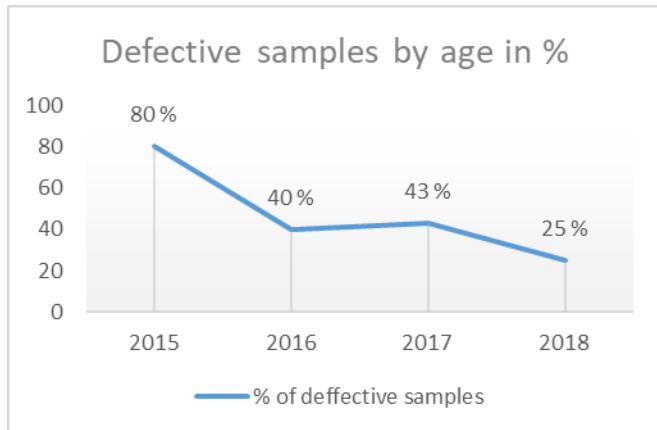


Figure 2. Defective samples by age in %

The most commonly present phthalate in the tested samples was DEHP, and it was detected in all samples that did not respond (100%). Research in the Republic of Croatia (15), as well as in India, is reported to similar results. It was reported that over 96% of the samples tested in phthalates contain phthalate DEHP (17). The second most commonly detected phthalate, which was present in concentrations greater than was allowed is DNOP (3.7%). In the research conducted in the Republic of Srpska, similar results were obtained, where DEHP was detected in all defective samples in 2016 and 2017, while the second most commonly present phthalate in 2016 was DNOP and in 2017 DINP (14). These data indicate that there are children's toys of the same or similar origin throughout the whole of Bosnia and Herzegovina, and there are no major differences in the type of phthalates present in children's toys in the territory of the two entities.

Table 3. Minimal, maximum and medium values of DEHP concentration by years

	2015. year	2016. year	2017. year	2018. year
Min DEHP (%)	0,45	3,22	0,84	1,85
Max DEHP (%)	16,2	14,6	8,82	5,23
Med value concentration DEHP	5,46%	8,77%	5,07%	3,02%
Med value concentration DEHP 2015.-2018. year	5,58%			

In 2015, the average medium value of DEHP concentration was 5.46%, while the maximum measured concentration in the individual sample amounted to 16.2%, which represents an amount of as much as 162 times the maximum allowable amount prescribed by the Decision on restricting the placing on a market for toys and products for children with phthalates. In 2016, the maximum measured concentration of DEHP was 14.6%, and the medium value in all defective samples was 8.77%. In 2017, the medium value was 5.07%, and in 2018 it was 3.02%. Medium value of DEHP concentration in all defective samples in the period 2015-2018. years in which the concentrations of phthalate DEHP were greater than permitted, amounts to 5.58%. Determination of the degree of statistical significance of Di (2-ethylhexyl) phthalate (DEHP) contents in defective samples from 2015 and 2018 was done using the t-test (0.144384) for a level of significance of 5% ($p < 0.5$), 1% ($p < 0.01$), and 0.1% ($p < 0.001$). Results: $p = 0.000221$. It was found that there is a very significant difference ($p < 0.01$) between defective samples from 2015 and 2018.

The third most commonly detected phthalate in concentrations that exceeded was DINP (1.5%), while DBP and BBP phthalates were not detected in any of the 73 analyzed samples. In various other studies, similar results were obtained where the concentration of phthalate DBP and BBP in the tested samples ranged about 1%, and therefore it is considered that these phthalates are more likely by-products of technological process and not intentionally added as plasticizers (16, 18, 20).

5 CONCLUSION

Based on the results obtained in this paper, we can conclude that a large percentage of children's toys in the territory of Bosnia and Herzegovina contain an increased concentration of phthalates, but also that this percentage is in line with the average number of defective samples in the European Union. The number of incorrect samples of children's toys in the territory of the Federation of Bosnia and Herzegovina has a downward trend, so in 2015 the number of defective samples was the highest and in 2018 the smallest. The most common phthalate present in exceeding quantities in all defective samples was Di (2-ethylhexyl) phthalate (DEHP), with concentration 162 times higher than permissible.

The data that said the global toy market is worth 105 billion (17) clearly indicates that in the case of a higher percentage of children's toys on the market containing phthalates, represent a major public health problem, both in Bosnia and Herzegovina and globally. This work established that there are toys of the same or similar origin throughout Bosnia and Herzegovina, and there are no major differences in the type and quantity of phthalates present in children's toys in the territory of the two entities. A large number of children's toys that deviate in relation to the Decision on restricting the placing on the market toys and products for children containing phthalates justifies the targeted actions of the competent authorities that are implemented in the control of children's toys in the area of the Federartion of Bosnia and Herzegovina. The results also point out that in order to protect the health of the most vulnerable population groups, children, such actions must be more frequent, and the very supervision of the import of children's toys in Bosnia and Herzegovina should be increased.

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