Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. *87* (1) 145–156 (2022)
JSCS–5511
Original scientific paper
Published 14 January 2022

UV light impact on phthalates migration from children's toys into artificial saliva

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(Received 28 September, revised and accepted 15 November 2021)

Abstract: Phthalates has been widely used in children's toys as plastic plasticizers and softeners. Therefore, attention should be paid to plastic toys, especially those that children can put in their mouths. In this paper quantification of five phthalates: DMP, DnBP, BBP, DEHP and DnOP in plastic toys, as well as irradiation of toys with UV light was performed. After sample preparation and development of the liquid–liquid phthalate extraction method from artificial saliva phthalate quantitative determination using the GC–MS technique was performed. The mean recovery value for DEHP is 77.03±2.76 %. The determination of phthalate in the recipient models (artificial saliva and *n*-hexane) was performed after 6, 15 and 30 days of the migration test using the GC–MS technique. Based on the known mass % DEHP in the analyzed toys, the percentage of phthalate migration from each analyzed toy to the recipient model after 6, 15 and 30 days of the migration test was calculated. The results show that there is no significant migration of DEHP into artificial saliva, due to high polarity of the recipient (artificial saliva is polar), unlike *n*-hexane where the migration of DEHP is significant because it is a non-polar solvent.

Keywords: plasticizers; PVC; leaching; GC–MS.

INTRODUCTION

Phthalates represent a group of synthetic chemical compounds, formed in the reaction of phthalic anhydride and alcohol with an aliphatic or aromatic chain. These are the substances most used as a plasticizer, and as such can be found in many consumer products: medical devices, food packaging products, children's toys, cosmetics and pharmaceuticals and other polyvinyl chloride (PVC) materials. The annual production of phthalates is significant and amounted 8 million tons in

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https://doi.org/10.2298/JSC210928097A

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2011 of which diethyl hexyl phthalate (DEHP) production was 4 million tons, corresponding to the fact that DEHP is the most used phthalate.[1,2] Under appropriate conditions such as high temperature, exposure to UV light, long storage time, the phthalates easily migrate from the polymer and are released in the environment, because phthalates are only mixed with the polymer, not chemically bonded.[3–5] Phthalates are classified as endocrine disruptors, because phthalates negatively affect the work of glands that secrete hormones and exposure to phthalates can cause various endocrinological and metabolic disorders.[6–8]

Phthalates has been widely used in children's toys as plastic plasticizers and softeners. Therefore, special attention should be paid to plastic toys, especially those that children can put in their mouths, because children are exposed to phthalates from plastic toys from the earliest stage of their development due to their small body weight and fast metabolism. Due to children's sensitivity to the effects of phthalates from plastic toys the European Commission has restricted the use of DEHP, di-*n*-butyl phthalate (DnBP) and butyl benzyl phthalate (BBP) as plasticizers in children's toys and childcare products, while the restriction on the use of diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and di-*n*--octyl phthalate (DnOP) only applies to toys that children can put in their mouths. According to Directive 2005/84/EC, products containing 0.1 % DEHP, DnBP and BBP (individually or together) by weight of a plastic product may not be placed on the market. Also, this directive prohibits the placing on the market plastic products that children can put in their mouths, which contain DINP, DIDP and DnOP in a concentration above 0.1 % by weight.[9]

Considering the fact the enormous amount of phthalates production, easy migration of phthalates from plastic materials and the negative impact on human health, various methods have been developed for the determination of phthalates in appropriate matrices. There is a special interest in determination of phthalates in plastic toys so the following instrumental techniques in defining determination methods have been developed till now: gas chromatography coupled with mass spectrometer as detector (GC–MS), high-performance liquid chromatography coupled with photodiode array detection (HPLC-PDA) or UV detection (HPLC-UV).[10–13]

The aim of this work is the detection and quantification of five phthalates – DMP, DnBP, BBP, DEHP and DnOP in plastic toys placed on the market without declaration, as well as irradiation of toys with UV light, in order to determine the influence of UV light on the migration of phthalates from plastic toys. Since these are toys that children can put in their mouths, the analysis of phthalate migration from plastic toys to artificial saliva was also performed and compared with the migration of phthalate to *n*-hexane as a model recipient.

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EXPERIMENTAL

Reagents

The tetrahydrofuran (THF, HPLC grade) was purchased from Fischer scientific (USA). The *n*-hexane (HPLC grade) was purchased from Carlo Erba (France). DMP, DnBP, BBP, DEHP and DnOP were purchased (99.7 % purity) from Sigma–Aldrich. Dibutyl adipate (DBA) was purchased from Fluka (Switzerland) and used as an internal standard.

Apparatus and equipment

Gas chromatographic analysis was performed by gas chromatograph 6890 (Hewlett--Packard, USA) equipped with a mass selective detector (MSD) 5973 (Hewlett-Packard), auto sampler 7683 (Agilent, USA) and SGE 25QC2/BPX5 0.25 capillary column (25 m×0.22 mm×0.25 μm, non-polar). The centrifuge Jouan C4I Benchtop (Termo Fisher) was used to separate the precipitate from the solution. The analytical balance (Kern, CA) with accuracy of ±0.00001 g for gravimetric measurements was used. The Vortex Genie (Scientific industries, USA) was used for vigorous shaking solution of artificial saliva with part of PVC plastic toys. A UV cylinder was used to irradiate UV-A with a wavelength of 365 nm. As a source of UV-C radiation, a UV photo reactor with low pressure mercury lamps, 28 W, with a maximum radiation at 254 nm, manufactured by Philips (Netherlands) was used.

Calibration standards

In order to obtain calibration curves for investigated five phthalates and calibrate GC––MS instrument, five standard solutions with concentration ranged from 80 to 120 % of the expected phthalate concentration in the samples were prepared. Stock, intermediate and standard solutions of the tested phthalates (DMP, DnBP, BBP, DEHP, DnOP) were prepared in *n*-hexane according to the following procedure:

– first, individual stock solutions of each phthalate of concentration 1000 μg mL^{-1} were made, which were diluted to obtain an intermediate solution in which the concentration of each phthalate separately was 100 μg mL^{-1};

– standard solutions of concentrations of 0.25, 0.50, 1.00, 1.50 and 2.50 μg mL^{-1} were obtained by appropriate dilution of the intermediate solution and addition of DBA as an internal standard at a concentration of 1 μg mL^{-1}.

The solutions were stored at 4 °C. The stock solutions are stable for one month, the working solutions are stable for 10 days. Each standard solution was recorded three times using the GC–MS technique, to ensure accuracy of the method.

Plastic materials

In order to determine phthalates in plastic children's toys using the GC–MS technique, 19 plastic children's toys purchased from a market in Niš (Serbia) without a clearly stated declaration of composition were analysed. These are the toys intended for the youngest population – babies, who can put those toys in their mouths. These toys were numbered from 1–19, where the given numbering will be used in further work.

Artificial saliva

For monitoring the migration of phthalates from plastic children's toys to the artificial saliva, artificial saliva was prepared according to the standard procedure of the European Commission.[14] The amounts of chemicals given in Table I were dissolved in 1 L of distilled water, the pH was adjusted to 6.8 with hydrochloric acid and the artificial saliva prepared in this way was stored in the dark.

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GC–MS technique

The gas chromatograph was operated in the split less injection mode. The oven temperature was programmed from initial temperature 90 °C (hold time 0 min) to 280 °C at a rate of 20 °C per min with hold time of 4 min, and post run 300 °C (2 min.). Helium was the carrier gas (flow rate of 1.0 mL min^{-1}). The operating temperature of the MSD was 280 °C with the electron impact ionization (EI) voltage of 70 eV. The dwell time was 100 ms. The MSD was used in the single ion-monitoring mode (SIM), the quantification ion is *m*/*z* 149 for DnBP, BBP, DEHP and DnOP, *m*/*z* 163 for DMP and ion *m*/*z* 185 was chosen as representative ion of DBA. Analyte response was normalized to DBA as internal standard. The identification and quantification of target compound was based on the relative retention time, the presence of target ions and its relative abundance. Both data acquisition and processing were accomplished by Agilent MSD ChemStation® D.02.00.275 software.

Table I Salts used in the preparation of artificial saliva

Chemical compound	Molecular formula	*c* / mmol L^{-1}
Magnesium chloride	$MgCl_2$	0.82
Calcium chloride	$CaCl_2$	1.00
Dipotassium hydrogen phosphate	K_2HPO_4	3.30
Potassium carbonate	K_2CO_3	3.80
Sodium chloride	NaCl	5.60
Potassium chloride	KCl	10.00

Determination of phthalates in PVC children's toys

To confirm that analysed plastic children's toys are made from polyvinyl chloride (PVC), 19 noted plastic toys were dissolved in THF. Dissolution of plastic toys is accelerated by using an ultrasonic bath with gentle heating. Among those 19 toys, even 18 toys were dissolved in THF, while only one toy remained undissolved, from which it follows that the undissolved toy was not made of PVC. The remaining 18 PVC toys, dissolved in THF, were analysed for phthalate content by GC–MS technique.

PVC children's toys were measured (0.01 g) and dissolved in 4 mL of THF. To precipitate the polymer, 10 mL of *n*-hexane was added in THF solutions of each plastic article. After centrifugation of the resulting blur solutions at 3500 rpm and filtration of the supernatant through a 0.45 μm PTFE micro filter, the exact volume of *n*-hexane-THF solution of each article (10 μL) was pipetted and diluted with *n*-hexane to 1 mL with the addition of DBA as an internal standard, after which the analysis of these items were performed by GC–MS technique.

Determination of phthalates in artificial saliva

For monitoring the migration of phthalates from PVC children's toys into artificial saliva, first the optimization of the method for determining the concentration of phthalates in artificial saliva was performed. Artificial saliva (5 mL) was spiked with five analysed phthalates, so that the concentration of phthalates in artificial saliva is 1, 2, 3, 4 and 6 μg mL^{-1}. The set conditions and parameters of liquid–liquid extraction (LLE) are as follows: extraction agent is *n*-hexane, extraction time is 10 min and type of agitation is manual shaking, following with 10 min agitation in an ultrasonic bath with ultrasonic waves. After the applied type of agitation and after clarification of the layers, the *n*-hexane layer was pipetted, and the phthalate concentration was determined using the GC–MS technique.

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Monitoring the migration of phthalates from plastic toys into the recipient model and artificial saliva

Monitoring the migration of phthalates from two toys (Toy 8 and Toy 12) with a known content of DEHP was performed by setting migration tests. *n*-Hexane and artificial saliva were selected as phthalate recipients in order to compare the maximum degree of phthalate migration from plastic toys to *n*-hexane and the realistic scenario of phthalate migration into artificial saliva, because toys that children can put in their mouths were tested.

Migration of phthalates from PVC toys to the recipient model

Two noted PVC toys were cut into pieces with an area of about 0.5 cm^2, where the weight of each item for analysis was about 0.02 g, whereby the measurement was performed with an accuracy of ±0.00001 g. *n*-Hexane (5 mL) was added to each cut and measured plastic toys, after which the procedure of monitoring the migration of phthalate from PVC toys into the *n*-hexane recipient model was performed for 6, 15 and 30 days, so that after 6 days the recipient volume was pipetted (250 μL) and diluted 4 times with *n*-hexane, then pipetted 10 μL of this solution, added 100 μL of DBA (10 μg mL^{-1}) and 890 mL of *n*-hexane. The prepared solution was analyzed by GC–MS technique. The analysis was repeated after the migration tests were performed for 15 and 30 days. To obtain reliable results with a certain standard deviation, the analysis of each item was performed three times.

Migration of phthalates from PVC toys to artificial saliva

Selected PVC toys were subjected to the following migration tests:

– PVC toy, with an area of about 1 cm^2, was covered with artificial saliva (5 mL). Vigorous shaking was performed using a Vortex Genie for 10 min. Then the same piece of PVC toy was poured with a new volume of artificial saliva (5 mL), after which the vigorous shaking was repeated using a Vortex Genie for 10 min. Collect 10 mL of artificial saliva, which was further subjected to optimized LLE extraction with *n*-hexane according to the described procedure. This test approximately simulates real conditions in which a child chews a PVC toy vigorously for 20 min, whereby there is a potential migration of phthalates from the PVC toy into the child's saliva, which may expose the child to the effects of phthalates;

– PVC toy, surface area 0.5 cm^2, was filled with 5 mL of artificial saliva. The migration test took place within 5, 15 and 30 days. After 5, 10, and 30 days, the artificial saliva potentially contaminated with phthalates was further subjected to optimized LLE extraction with *n*-hexane. This test is experimental, since it does not simulate the real conditions under which phthalates migrate from PVC toys to saliva and was set up to compare the results obtained after phthalate migration.

Monitoring the influence of UV light on the migration of phthalates from PVC toys into the recipient model and artificial saliva

The two toys (Toy 8 and Toy 12), in which the DEHP content was determined in this study, were irradiated with UV-A light and UV-C light for a certain time interval, in order to analyze the effects of UV -A and UV-C light on the change in the polymer structure of PVC articles, and thus on the migration of phthalates from these PVC articles. A UV cylinder was used as a source of UV-A irradiation wavelength of 365 nm. As a source of UV-C radiation, a UV photo reactor with low pressure mercury lamps, with a maximum radiation at 254 nm, was used. The toys were placed at 5 cm from these lamps. The UV-A radiation test somewhat imitates sunlight, while the UV-C radiation test sets up an experiment to compare the effects of these two radiations on the migration of phthalates from PVC toys. The PVC toys were

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irradiated with UV-A light for 1, 2, 4, 6, 12, 24 h, while PVC toys were irradiated with UV-C light for 1 and 2 h.

To determine the percentage of phthalate migration from irradiated toys, before the migration tests, DEHP quantification was performed in irradiated PVC toys in the described manner.

After appropriate irradiation with UV-A and UV-C light, migration tests were performed:

– Conditions for migration of phthalates from irradiated PVC toys to the recipient model (*n*-hexane) are the same as for the migration of phthalates from non-irradiated toys;

The migration of phthalates from irradiated PVC toys into artificial saliva was also performed in the same way as the migration of phthalates from non-irradiated toys into artificial saliva.

RESULTS AND DISCUSSION

The obtained calibration curves are linear in this concentration range with calibration coefficients higher than 0.995 for each phthalate and are given in Fig. 1.

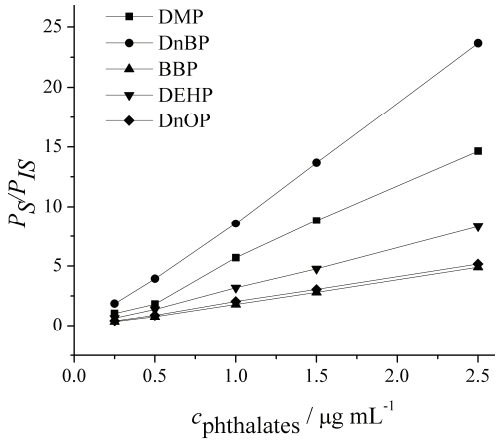

Fig. 1. GC–MS calibration curves in the concentration range 0.25–2.5 μg mL^{-1} for: DMP, DnBP, BBP, DEHP and DnOP.

Determination of phthalates in plastic materials by GC–MS technique

The phthalate concentrations in the appropriate prepared samples of 18 PVC toys were determined using the GC–MS technique. Of the five analyzed phthalates, only DEHP was detected. Based on the performed calibration, quantification of DEHP was performed and the results of DEHP quantification in 18 analyzed PVC toys are presented in Table II.

After appropriate sample preparation and development of the liquid–liquid phthalate extraction method from artificial saliva, DEHP quantitative determination was performed using the GC-MS technique and the results of this analysis are shown in Table III.

The mean recovery value for DEHP with standard deviation (77.03±2.76 %) will be used to calculate the degree of DEHP migration from PVC toys to artificial saliva, given that only DEHP is detected and quantified in PVC toys.

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TABLE II. Results of DEHP quantification in PVC children's toys by GC–MS technique

Toy	c_{DEHP} / mg g^{-1}	c_{DEHP} / mass %
1	532.42±27.2	53.2±2.7
2	430.01±9.40	43.0±0.9
3	406.89±9.19	40.7±0.9
4	402.38±11.2	40.2±1.1
5	400.05±19.5	40.0±1.9
6	373.55±18.5	36.9±1.6
7	368.72±16.1	36.9±1.6
8	368.21±11.7	36.8±1.2
9	364.38±6.43	36.4±0.6
10	313.42±11.1	31.3±1.1
11	295.02±6.31	29.5±0.6
12	270.35±19.2	27.0±1.9
13	102.68±3.06	10.3±0.3
14	1.34±0.09	0.13±0.01
15	1.20±0.20	0.12±0.02
16	0.83±0.09	0.08±0.01
17	0.47±0.02	0.05±0.00
18	0.45±0.08	0.05±0.01

TABLE III. Recovery of phthalate extraction from artificial saliva by optimized LLE (%)

Spike concentration, μg L^{-1}	Compound				
	DMP	DnBP	BBP	DEHP	DnOP
1	79.44	63.16	91.11	77.15	82.23
2	76.30	66.27	95.64	73.12	79.21
3	64.20	60.18	86.31	76.89	80.36
4	71.11	64.98	90.60	77.10	79.32
6	66.57	65.41	90.52	80.91	82.10

Phthalate migration into the recipient model and artificial saliva

Based on the known mass % of DEHP in the analyzed toys, the degree of DEHP migration from each analyzed toy into the recipient model after 6, 15 and 30 days of the migration test was calculated using the GC–MS technique and the data are shown in Table IV. It was concluded that the degree of DEHP migration is higher for Toy 8 after each migration test, in different time periods. The reason for that is most likely that the PVC toys were cut into pieces with an area of 0.5 cm^2, and since the piece of Toy 12 is thicker, the area of 0.5 cm^2 is therefore of greater mass. The contact model of the recipient and DEHP in the plastic material is more probable and it takes less time for DEHP to migrate from plastic layer to the recipient model when it comes to the Toy 8.

The obtained results of the migration test for 6, 15 and 30 days in which DEHP was migrated to artificial saliva and of the migration test which simulates

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the real situation of chewing a toy in the mouth by a child for 1 day for 20 min, were shown in Table V.

TABLE IV. Degree of DEHP migration into *n*-hexane relative to the mass of DEHP in PVC toy (%)

PVC toy	Mass of PVC toy g	Mass of DEHP in PVC toy µg	*t* / days		
			6	15	30
8	0.0246	9057	64.70	77.29	85.92
12	0.0426	11519	60.97	73.26	80.63

TABLE V. Degree of DEHP migration into artificial saliva relative to the mass of DEHP in PVC toys

Time of migration, day	Mass of PVC toy, g	Mass of DEHP in PVC toy, µg	Maximum amount of migrated DEHP, µg	Degree of DEHP migration, %
Toy 8				
1	0.1661	61158	3.25	0.005
6	0.0389	14324	1.62	0.011
15	0.0388	14286	2.14	0.015
30	0.0183	6738	1.86	0.028
Toy 12				
1	0.1632	44129	6.21	0.014
6	0.0491	13276	2.10	0.016
15	0.0441	11924	2.14	0.018
30	0.0415	11221	3.36	0.030

Results of determining the influence of factors on the migration of phthalates from PVC toys into the recipient model and artificial saliva

The results show that migration was almost non-existent. The migration rate for DEHP ranges from 0.005 to 0.028 % for Toy 8, while for Toy 12 this rate ranges from 0.014 to 0.030 %. The mass of the migrated DEHP during migration that simulates real conditions was 3.25 µg for Toy 8 and 6.21 µg for Toy 12. The weight of migrated DEHP in relation to the body weight of a child at that age (10 kg) was 0.325 or 0.621 µg kg^{-1}, which is far below the TDI value for DEHP which is 0.05 mg kg^{-1}.

After UV-A and UV-C light irradiation of PVC Toy 8 and Toy 12, with an area of 1 cm^2, a time period as a factor that influence the change in the structure of the polymer and thus the DEHP migration from these articles was determined. The migration degree was calculated after performing the following migration tests: DEHP migration into the recipient model (after 6, 15 and 30 days) and DEHP migration into artificial saliva (after 6, 15 and 30 days and within one day) and by performing liquid-liquid extractions of DEHP from artificial saliva by the optimized method.

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In order to calculate the degree of DEHP migration based on the mass of DEHP in irradiated toys, DEHP in irradiated toys was quantified by the GC–MS technique after dissolving these toys in THF according to an optimized method. The quantification results were given in Table VII. The presented results showed the influence of UV-A and UV-C light on the properties of PVC toys in terms of DEHP content. By irradiating the toys, there is a weakening of the interaction strength between DEHP and the polymer and there is a migration of DEHP into the atmosphere, which affects the decreasing mass % DEHP in the toys with radiation time. The weight percentages of DEHP in Toy 12 decrease from 27.04 to 19.58 mass %, while this range for Toy 8 ranges from 36.82 to 30.81 mass %. UV-A radiation for 2 h leads to the most significant change in the percentage composition of PVC toys, while further radiation reduces the percentage composition of DEHP gradually.

TABLE VI. The degree of DEHP migration from iridated PVC toy 12 to model recipient; a and b values with the same letter within a row are not statistically significant different at the $p < 0.05$ level (Tukey's HSD test)

PVC Toy	Type of radiation	Time of radiation, h	Content of DEHP in PVC toy, mass %	Degree of DEHP migration, %		
				6 days	15 days	30 days
12	–	0	27.04±1.92	60.97^{a}	$73.26^{a.b}$	80.63^{b}
	UV-A	2	21.87±2.25	65.60^{a}	$80.46^{a.b}$	87.14^{b}
		4	21.45±1.08	66.19^{a}	$81.37^{a.b}$	88.01^{b}
		6	20.75±2.46	67.76^{a}	$81.66^{a.b}$	89.49^{b}
		12	21.67±1.12	70.87^{a}	$83.30^{a.b}$	90.44^{b}
		24	21.13±1.13	71.52^{a}	$84.45^{a.b}$	91.59^{b}
	UV-C	1	20.03±0.11	75.68^{a}	$88.86^{a.b}$	96.47^{b}
		2	19.58±0.17	76.25^{a}	$90.49^{a.b}$	97.25^{b}

Also, Tables VI and VII show the results of DEHP migration tests to the recipient model after 6, 15 and 30 days of DEHP migration.

TABLE VII. The degree of DEHP migration from irradiated PVC toy 8 to model recipient; a and b values with the same letter within a row are not statistically significant different at the $p < 0.05$ level (Tukey's HSD test)

PVC Toy	Type of radiation	Time of radiation, h	Content of DEHP in PVC toy, mass %	Degree of DEHP migration, %		
				6 days	15 days	30 days
8	–	0	36.82±1.17	64.70^{a}	$77.29^{a.b}$	85.92^{b}
	UV-A	1	33.75±0.21	67.73^{a}	$84.98^{a.b}$	90.69^{b}
		2	33.32±0.75	71.39^{a}	$83.84^{a.b}$	86.92^{b}
		4	33.59±1.02	68.48^{a}	$84.84^{a.b}$	91.72^{b}
		6	33.50±1.98	72.02^{a}	$83.23^{a.b}$	87.14^{b}
		12	33.04±1.41	73.75^{a}	$84.75^{a.b}$	91.61^{b}
		24	33.39±1.12	75.08^{a}	$86.30^{a.b}$	90.27^{b}
	UV-C	1	31.22±0.17	79.56^{a}	$90.44^{a.b}$	99.16^{b}
		2	30.81±0.19	79.67^{a}	$91.81^{a.b}$	99.41^{b}

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Unlike DEHP migration from non-irradiated toys where the percentage was 80.63 % for Toy 12 and 85.92 % for Toy 8 after 30 days, the percentage of migration after radiation of toys increases to 97.25 % for Toy 12 and 99.41 % for Toy 8 in relation to the mass of the toy. The same trend applies to migration tests lasting 6 and 15 days, which confirms that radiation disrupts the bonds that exist between DEHP and polymers in PVC toys, thus enabling easier migration.

In order to determine a significant difference between the results obtained after different migration periods (6, 15 and 30 days), the obtained mass concentrations of DEHP listed in Tables VI and VII were compared using Tukey's HSD test. Significant difference (*HSD*) values for each pair of results were calculated using the Origin© program, for $p < 0.05$, and compared with a tabular value of 3.70.[15] The obtained results show that there is a significant difference in DEHP migration after 6 and 30 days for all analyzed toys. There is no significant difference in DEHP migration after 6 and 15 days of migration, as well as after 15 and 30 days.

Tables VIII and IX show the results of performed migration tests during 6, 15 and 30 days, as well as for one day, in which DEHP was migrated from irradiated toys to artificial saliva.

TABLE VIII. The degree of DEHP migration from iridated PVC toy 12 to artificial saliva

PVC toy	Type of radiation	Time of radiation, h	Degree of DEHP migration, %			
			During one day	6 days	15 days	30 days
12	–	0	0.01	0.02	0.02	0.03
	UV-A	2	0.02	0.02	0.03	0.02
		4	0.02	0.03	0.05	0.02
		6	0.02	0.03	0.03	0.02
		12	0.01	0.02	0.02	0.02
		24	0.01	0.01	0.02	0.02
	UV-C	1	0.01	0.03	0.08	0.02
		2	0.01	0.02	0.02	0.02

TABLE IX. The degree of DEHP migration from iridated PVC toy 8 to artificial saliva

PVC toy	Type of radiation	Time of radiation, h	Degree of DEHP migration, %			
			During one day	6 days	15 days	30 days
8	–	0	0.01	0.01	0.02	0.03
	UV-A	1	0.02	0.04	0.02	0.02
		2	0.01	0.02	0.04	0.02
		4	0.01	0.02	0.03	0.02
		6	0.01	0.03	0.03	0.02
		12	0.01	0.02	0.03	0.02
		24	0.02	0.01	0.03	0.02
	UV-C	1	0.01	0.02	0.02	0.02
		2	0.01	0.01	0.01	0.02

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The results show that there is no significant migration of DEHP into artificial saliva, which is the case with non-irradiated toys. The reason for this is the polarity of the recipient (artificial saliva is polar), unlike *n*-hexane where the migration of DEHP is significant because it is a non-polar solvent.

CONCLUSION

The results of determining the degree of migration of phthalates from PVC toys to artificial saliva show that the migration of phthalates is at very low level. However, there must be a concern present since the tested PVC toys contain up to 50 % phthalate. By changing certain conditions, like UV light irradiation, phthalates can migrate, due to mechanical pressure by the teeth. Due to the high exposure of children to phthalates from these toys and rapid metabolism and insufficient physiological maturity of children restriction on the use of phthalates should be followed. DEHP is the predominant plasticizer for PVC toys. It is commonly used at concentrations varying between 30 and 45 % by weight. Based on the known mass % DEHP in the analyzed toys, the percentage of phthalate migration from each analyzed toy to the recipient model after 6, 15 and 30 days of the migration test was calculated. The results show that there is no significant migration of DEHP into artificial saliva, due to high polarity of the recipient (artificial saliva is polar), unlike *n*-hexane where the migration of DEHP is significant because it is a non-polar solvent. By irradiation of toys, a weakening of the interaction strength between DEHP and the polymer occurs leading to migration of DEHP into the atmosphere, which affects the decreasing of mass % DEHP in the toys with radiation time. UV-A radiation for 2 h leads to the most significant change in the percentage composition of PVC toys, while further radiation reduces the percentage composition of DEHP gradually.

Acknowledgment. This study was performed within the research program – Contract No. 451-03-9/2021-14/200124.

ИЗВОД

УТИЦАЈ UV ЗРАЧЕЊА НА МИГРАЦИЈУ ФТАЛАТА ИЗ ДЕЧЈИХ ИГРАЧАКА У ВЕШТАЧКУ ПЉУВАЧКУ

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Фталати се широко користе у дечјим играчкама као пластификатори и омекшивачи. Због тога треба обратити пажњу на пластичне играчке, посебно оне које деца могу ставити у уста. У овом раду извршена је квантификација пет фталата: DMP, DnBP, BBP, DEHP и DnOP у пластичним играчкама, као и зрачење играчака UV светлом. Након припреме узорака и развоја методе течно–течне екстракције фталата из вештачке пљувачке

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извршено је квантитативно одређивање помоћу GC–MS технике. Средња *Recovery* вредност за DEHP је 77,03±2,76 %. Одређивање фталата у модел реципијентима (вештачка пљувачка и *n*-хексан) изведено је након 6, 15 и 30 дана теста миграције применом GC–MS технике. На основу познатог масеног процента DEHP у анализираним играчкама, израчунат је проценат миграције фталата из сваке анализиране играчке у модел реципијент након 6, 15 и 30 дана миграционог теста. Резултати показују да нема значајне миграције DEHP у вештачку пљувачку, због високе поларности реципијента (вештачка пљувачка је поларна), за разлику од *n*-хексана где је миграција DEHP значајна јер је растварач неполаран. Зрачењем играчака долази до слабљења снаге интеракције између DEHP и полимера што доводи до миграције DEHP у атмосферу, што утиче на смањење мас. % DEHP у играчкама с временом зрачења. UV-A зрачење током 2 сата доводи до најзначајније промене процентног састава DEHP у PVC играчкама, док даље зрачење поступно смањује процентни састав DEHP.

(Примљено 29. септембра, ревидирано и прихваћено 15. новембра 2021)

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