Journal homepage: www.fia.usv.ro/fiajournal
Journal of Faculty of Food Engineering,
Ştefan cel Mare University of Suceava, Romania
Volume XVI, Issue 4 - 2017, pag. 222 - 233

DETERMINATION OF DIBUTYL PHTHALATE (DBP), BENZYL BUTYL PHTHALATE (BBP) AND BIS (2-ETHYLHEXYL) PHTHALATE (DEHP) IN SOFT PLASTIC TOYS AND THE FIRST SURVEY OF THE BULGARIAN MARKET

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Received 9th October 2017, accepted 19th December 2017

Abstract: *Phthalates are a large group of compounds with similar chemical structure widely used as plasticizers for plastics. They can easily be released from the polymer during usage and in this way enter the human body. Their adverse effect on health is known as "phthalate syndrome" and can impact children and adults alike. For children in particular, there is an additional potential risk of exposure to phthalates via toys intended for oral use. The Regulation (EC) No 1907/2006 (REACH) prohibits the use of bis (2-ethylhexyl) phthalate (DEHP), di butyl phthalate (DBP) and benzyl butyl phthalate (BBP) as a substance or constituent of preparations at concentrations higher than 0.1 % in the plasticized material meant to toys and childcare items. The aim of this article is to quantify the content of DEHP, DBP and BBP in soft toys intended for children up to 3 years of age, including toys designed to be placed in the mouth. A method consisting of an extraction procedure of phthalates from polymers, purification of the extract, followed by GC/MS identification and quantification was validated. Three different techniques for phthalates' extraction (Soxhlet, ultrasonic and vibrator) were compared and the most effective one was chosen.This method was applied to the analysis of DEHP, DBP and BBP in soft toys from the Bulgarian market to establish their compliance with REACH requirements. All the tested toys contained at least one phthalate. Exceedence of the permitted content for DEHP, DBP and BBP (as sume), mainly due to the high levels of DEHP, was observed in several toys from retail.*

Keywords: *Phthalates; DBP; BBP; DEHP; Plastic Toys; GC/MS.*

1. Introduction

Phthalates (phthalate esters) are a large group of compounds which have a similar chemical structure and are widely used as plasticizers for plastics, in solvents, in cosmetics and others. They are not covalently bound to the molecules of the plastic and they can easily be released directly or through migration, evaporation, leaching and abrasion into food or into the environment. This is a prerequisite for their penetration in the human organism through various pathways - ingestion, inhalation, dermal absorption, and even intravenously from medical devices. Phthalates have a low acute toxicity (LD50 1-30 g/kg), but their toxic effects at low exposure levels affect the liver and reproductive system, especially in males. In animal studies, phthalates have been identified as endocrine disrupters. Phthalate exposure has an impact on humans of all ages. "Phthalate syndrome" which refers to the wide range of effects of phthalates on males includes infertility, decreased sperm count, cryptorchidism, hypospadias and other malformations of the reproductive organs. Studies on young girls also showed possible correlation

between exposure to phthalates and shortening of the pregnancy duration or breast cancer. For the general population the main sources of exposure to phthalates are foods, followed by inhalation of stuffy and/or polluted air. In animal studies it has been established that phthalates can pass to the offspring through the placenta and through the stern. To the sources of exposure for children and adolescents there should be added the risk of exposure through toys, breastmilk, children's cosmetics and personal care products. In infants, human milk and toys intended for chewing and scratching the teeth, can additionally contribute to phthalate exposure [1, 2]. Children and adolescents consume more calories per kilogram body weight, they eat more frequently and more fatty foods and they have higher minute ventilation than the adults. Therefore, their phthalate exposure is expected to be higher [3].

The European Union, United States and a number of other countries have regulated certain phthalates in children's products. The Regulation (EC) No 1907/2006 of the European Parliament and of the Council on 18th December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), which established an European Chemicals Agency, by entry No. 51 to Annex XVII "Restrictions on the manufacture, placing on the market and use of certain dangerous substances, preparations and articles" prohibits the use of a substance or constituent in preparations at concentrations higher than 0.1 % by mass of the plasticised material, in toys and childcare articles of the following phthalates: bis (2-ethylhexyl) phthalate (DEHP) CAS № 117-81-7; dibutyl phthalate (DBP) CAS № 84-74-2; benzyl butyl phthalate (BBP) CAS № 85-68-7[4]. Restrictions on other phthalates were introduced by REACH, too.

Despite the restrictions, phthalates have been found in 69% of plasticisers in the USA, 92% in Western Europe and 81% in Japan [5]. Furthermore, it was found that the overall exposure for children and adolescents of the most common plasticizer DEHP is higher than that for adults in all ways of administration, excluding food intake. In children aged 5 months to four years of age, the risk is the highest. Studies on the relationship between exposure to phthalates and the development of the nervous system of infants show an impact on mental development and psychomotor indices in infants, especially on post six month development [6]. Some effects include deformation of the reproductive organs (hypospadias, cryptorchidism), decreased anogenital distance, impact on future fertility and pregnancy, weight reduction of the reproductive organs, disturbance in testicular functioning, impact on the organization and functioning of the germ and spermatogonial stem cells [7-10].

Apart from the information on the main polymer from which an article has been made, labels should describe data of the other substances involved in the composition - plasticizers, fillers, colorants, etc. The control of the composition of polymers is associated with the availability of analytical methods for determining ingredients in different matrices.

The purpose of this work is to develop a combination of extraction procedure and gas chromatography - mass spectrometry analysis (GC/MS) to quantify the content of three phthalates (Dibutyl phthalate (DBP), Benzyl butyl phthalate (BBP) and Bis (2-ethylhexyl) phthalate (DEHP)) in polymeric toys, intended for children up to 3 years of age or to be placed in the mouth.

2. Materials and methods

Experimental design

Ten different articles of soft plastic toys with different composition, country of origin and place of distribution (large chains and small retailers) were purchased from the Bulgarian market. All toys were designed for children up to 3 years of age or for oral use. The information on the toys was collected from labels. Descriptions of the plastic toys are presented in the Table 1 and in fig 1.

Table 1.

Description of the plastic toys for analysis of phthalates

№	Description	Suitable age	Distributor for Bulgaria	Country - manufacturer	Type of plastic	Note
1.	Yellow bath duck „Duck 5,5 cm", yellow „Happy people" OM+	Not specified on the label	A large retail chain	Peoples Republic of China	unknown, not stated on the label	Distributor Germany Art. No.40189
2.	White dog Honey Baby	For children over 6 months	Little Shop	Peoples Republic of China	unknown, not stated on the label	Art. No.TL.306 Lot. No. BT130134
3.	Pink teddy bear Honey Baby	For children over 6 months	Little Shop	Peoples Republic of China	unknown, not stated on the label	Art. No. TL.306 Lot. No. BT130134
4.	Teether "foot"	For children between 0 and 18 months	A large retail chain	Hong Kong Special Administrative Region of the People's Republic of China	polyester	Item No.08/8434/B Lot. No. RHSC-141004
5.	Teeth "DINO"	For children over 3 years	A large retail chain	Peoples Republic of China	unknown, not stated on the label	Import from Turkey Chocolate egg with a toy surprise Barcode No:8699462607173 Barcode box:8699462607
6.	Vampire teeth - carnival accessories	Not specified on the label	A large retail chain	Peoples Republic of China	unknown, not stated on the label	Item No.04017
7.	Doll "BABY", 12 cm	For children over 12 months	A large retail chain	Peoples Republic of China	unknown, not stated on the label	Lot. LM140112WJ Item No.W10786J (8082)
8.	Stand"Color rings"for order in chimney stack „Rainbow colored Stacker	For children over 10 months	A large retail chain	Peoples Republic of China	unknown, not stated on the label	Imported from Romania ND.710V
9.	Teether "Three fruits"-ed, green and yellow	For children over 6 months	A large retail chain	Peoples Republic of China	unknown, not stated on the label	Item No.34471-1 BATCH: 20130530
10.	Teether-rattle „Teetherfeeding bottle" Baby Rattles Series	Not specified on the label	A large retail chain	Peoples Republic of China	unknown, not stated on the label	Item No.FS34691-2 BATCH No. 20141220

Fig. 1 Representative photos of the analyzed toys

The type of polymer was mentioned on one item only. A lack of marking and proper labeling of the toys was discovered, which violates consumers' rights to be informed about the quality of the toys.
All the items were in quantity of 5 or more, allowing an average sample to be formed from the batch. The samples were cut at retail and average samples and analytical samples were formed.
The choice of extraction method of the phthalates from the polymeric material was made as a result of comparative experimental tests as described below.

Reagents and chemicals

All the chemicals used were of analytical grade purity for GC: Dichloromethane for GC, PESTANAL®, (Fluka); Hexane for GC (Merck); glass microfiber filters Whatman®, Grade GF/A circles, Ø 47 mm; Syringe filters "Chromatography" PTFE, 0.45 µm, Ø 25 mm; medical syringes of 5 ml and 10ml, Agilent certified caps with integrated septa (PTFE/red rubber) on 2 ml vials wide opening screw and 2 ml vials for automatic injector, wide opening screw, colorless; cellulose extraction thimble for Soxhlet, 30x80 mm; Acetone and Methanol for GC (Merck).

Certified reference materials/reference materials CRM/RM

Di-n-butyl phthalate (DBP) Cas # 84-74-2, CRM, 96.8 % purity (AccuStandard®,Inc.); Benzyl butyl phthalate (BBP) Cas #85-68-7, 96.9 % purity (Acros Organics); Bis-(2-ethylhexyl)-phthalate PESTANAL®, Cas #117-81-7, RM, 99.7 % purity (Sigma Aldrich).

Equipment and gas chromatographic conditions

Agilent Technology GC-7890 GC/MS with split/splitless capillary injector, auto-injection system and quadrupole mass spectrometric detector (MSD-5975 Inert) with electronic ionization (EI) working in SIM and SCAN mode. The gas chromatograph was equipped with a Fused Silica Capillary Column SLB ™ -5MS 30 m x 0.25 mm i.d. x 0.25 µm film thickness (Sigma-Aldrich, Supelco). The temperature of column was programmed as follows: the initial temperature 50ºC (2 min), 30˚C/min to 280˚C (10 min); injector temperature was 280˚C; the transfer line temperature was 280˚C, helium carrier gas with a flow rate 1.3 ml/min in splitless mode; sample size (injection volume)1µL; solvent delay 5.80 min. The duration of a single analysis is of 20 min.

Additional Equipment

Soxhlet extraction system with adjustable heating consists of Soxhlet extractor,

cartridge, reflux condenser, 250 ml round-bottom flask with heating mantle; glass tubes with screw caps of 40 ml volume, shaker with temperature-controlled water bath; ultrasonic bath with temperature control; temperature-controlled rotary evaporator; analytical balance; Buchner filtration system.

Identification of DBP, BBP and DEHP in MSD SCAN and MSD SIM-modes

The identification of the phthalates is carried out by the retention times of standard solutions of CRM/RM of DBP, BBP and DEHP in MSD SCAN mode. Using the chromatographic conditions described above, the retention times of DBP, BBP and DEHP were 9.15 min, 10.48 min and 11.17 min, respectively. Identification was confirmed by comparing their mass spectra with the NIST specialized library. To improve the parameters of the method, after specifying the chromatographic conditions, a MSD SIM mode was used with the introduced characteristic ions for each phthalate. Some important physical and chemical properties and the monitored ions for mass spectrometric identification of DBP, BBP and DEHP are presented in the Table 2.

Phthalates are common laboratory contaminants, so special attention was paid to eliminating the external contamination. An important factor is the cleanliness of the glassware. The laboratory dishes were washed with distilled water and rinsed with solvent. The solvents used must be of high grade of purity and not in contact with plastic parts, elements or gaskets, with the exception of polytetrafluoroethylene PTFE, which is resistant to chemicals. All the samples are performed in 5 replicates, spikes are also used.

Calibration Stock standard solutions A of each phthalate at a concentration of 1000 μg/ml were prepared individually by weighing of CRM/RM of DBP, BBP or DEHP and suitable diluted with hexane. The storage period at 4 ° C in the dark is 1 month.

Intermiate standard solutions B for each phthalate at a concentration 100 μg/ml were prepared from the stock solutions by appropriate dilutions with hexane.

Mixed standard calibration solutions of DBP, BBP and DEHP in concentration range from 0.5 to 10 *μg/ml* for DBP and 1.0 to 50 μg/ml for BBP and DEHP were prepared by appropriate dilutions with dichloromethane from the standard solutions B. The calibration curves were plotted separately for each phthalate concentration against peak areas.

Calibration solutions were analyzed in SCAN mode and the characteristic ions for each phthalate were monitored in SIM mode. The regression equations of dependencies of peak areas (in absolute indexes) of the concentrations (μg/ml) for each phthalate in SIM mode are presented in Table 3. Limit of detections (LOD) and limit of quantifications (LOQ) values of all the standards were calculated by signal to noise S/N ratio multiplied by three and ten, respectively. All values are recorded in five replicates for each experiments.

Table 4 summarizes the parameters of GC/MS method in SCAN and SIM modes. The relative standard deviation RSD is calculated at the concentration level of 5 μg/ml.

Sample preparation

Before analyzing the samples (at least 3 items) from each kind of articles, they were cleaned by a microfiber cloth to remove dust and impurities from their surfaces. Then they were crushed / milled to obtain particles of about 1-2 mm^2 which increase the effective extraction surface (Fig 2). About 1 g, with an accuracy of

0.0001 g, was weighed for analysis by analytical balance for each item type. The sample with a standard addition of a mixed standard solution (spike-sample) was analyzed every time for each sample. Dichloromethane is a suitable solvent which can either dissolve or soften the polymeric material.

Table 2.

Physico-chemical properties and the monitored ions for mass spectrometric identification of DBP, BBP and DEHP

Substance	CAS No	Molecular formula	Molar mass, $g.mol^{-1}$	Boiling point, ^0C	Basic ion	Characteristic monitored ions		
						Q1	Q2	Q3
Di-n-butyl phthalate(DBP)	84-74-2	$C_{16}H_{22}O_4$	278.34	340	149	205	223	278 (M^+)
Butyl benzyl phthalate(BBP)	85-68-7	$C_{19}H_{20}O_4$	312.36	370-380	149	206	91	238
Di-(2-ethylhexyl) phthalate(DEHP)	117-81-7	$C_{24}H_{38}O_4$	390.56	385	149	167	279	-

Table3.

Mean values in absolute indexes of the peak areas (n = 5) of the calibration solutions (SIM mode)

Peak area, abs.ind. Phthalate	Concentration of the phthalates in the calibration solutions, µg/ml					Calibration equation
	0.5	1.0	5.0	10	50	
DBP	210329	473781	5941599	18477433	-	$A = 191640 \times C - 1629385$
BBP	-	55740	542674	1891438	26693875	$A = 569190 \times C - 2095711$
DEHP	-	66228	468432	1561130	16541333	$A = 349755 \times C - 1111681$

Table 4.

Parameters of the GC/MS method for the determination of DBP, BBP and DEHP in SCAN and in SIM modes of the MSD

	SCAN-mode			SIM-mode			Linearity range, (R^2)
Phthalate	**RSD,**[a] **%**	**LOD, µg/ml**	**LOQ, µg/ml**	**RSD,**[a] **%**	LOD, **µg/ml**	**LOQ, µg/ml**	**µg/ml,**
DBP	18.4	0.27	0.49	8.6	0.03	0.09	0.5–10 (R^2=0.9738)
BBP	14.9	0.21	0.50	5.2	0.01	0.04	1.0- 50 (R^2=0.9890)
DEHP	14.6	0.14	0.41	4.7	0.02	0.07	1.0 - 50 (R^2=0.9925)

[a] RSD is calculated at a concentration level of 5 µg / ml for each phthalate

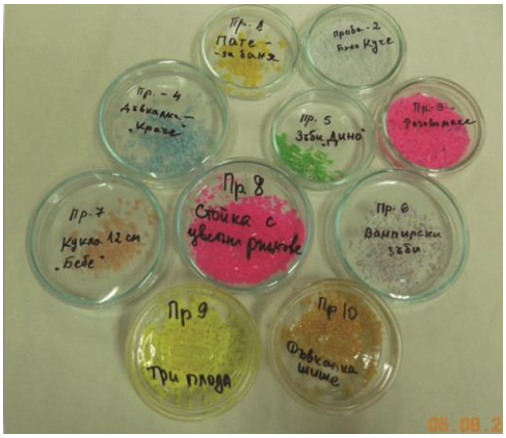

Fig.2 Average samples of toys prepared for extraction

3. Results and discussion

3.1. Selection of an extraction procedure

Three different extraction techniques were compared:
- Soxhlet extraction [11, 12]
- Ultrasound extraction [13, 14, 15]
- Shaker extraction [16, 17]

The samples were extracted by one of the extraction techniques mentioned above; the resulting extracts were purified to remove co-extracted solid particles either by centrifugation or by filtration through suitable filters.

Soxhlet extraction

Samples of 1 g ± 0.0001 g were weighed into cellulose extraction thimbles and were extracted by Soxhlet using about 180-200 ml dichloromethane at the temperature of the round-bottomed flask, which guarantees no vigorous solvent boiling.

The duration of the extraction procedure was 120 min, 240 min or 360 min, respectively. The cooled extracts were filtered through a glass microfiber filters Whatman®, GF/A, via Buchner-system and were concentrated using a rotary evaporator at a bath temperature of about 32-34 °C to received exact volumes of 10 ml.

In parallel, samples with spike 10 µg/ml for DBP and BBP and 50 µg/ml for DEHP, calculated to the final volume of 10 ml, were prepared, too.

Ultrasound extraction

The samples (1 g) and the spike - samples (see above) were wetted with 20 ml of dichloromethane in the glass tubes, closed tightly and placed in an ultrasonic bath for 15 min, 30 min or 60 min at a bath temperature of 25 °C, 35 °C or 38 °C. Extracts were filtered through a glass microfiber filter Whatman®, GF/A via Buchner-system, transferred quantitatively into graduated tubes and evaporated in a stream of nitrogen to the exact volume of 10 ml.

Shaker extraction

The samples (1 g) and the spike - samples are filled with 10 ml of dichloromethane in glass tubes, sealed tightly and stirred on a shaker at 25 ºC of the water bath. The durations of the treatments were of 30 min 60 min or 120 min. The extracts were filtered and concentrated, as it was described in „Ultrasound extraction" to the exact volume of 10 ml.

Approximately 2 ml of the concentrated extracts were filtered through a filter-PTFE using a medical syringe directly into vials for GC-MS analysis. The analyses were performed in the above-described chromatographic conditions; the concentrations of the phthalates were calculated by regression equations.

Recovery (R) was calculated using parallel analysis of samples and spike-samples. Spikes were added at concentrations 10 µg/ml for DBP and BBP, and 50 µg/ml for DEHP.

Recovery (R) was calculated as follows (Eq. 1):

$$R = \frac{C_{calc}}{C_{sp}} \times 100, \% \qquad (1)$$

where C_{calc}. is the spike-concentrations of the each individual phthalate, calculated from the corresponding regression equation after the analysis, Csp. is the concentration of the spike, added to the sample.

The results obtained are presented in Table 5. They indicate that the use of a Soxhlet extraction for retrieving the phthalates from the polymer showed the highest recovery, varying in the range of 91.7% - 101.1% for the analyzed phthalates. The highest rates are for BBP (98.5%) and DEHP (101.1%) and were observed at the duration of the extraction 120 min. For DBP through Soxhlet extractions close values of recoveries at two hours (97.8%) and six hours (98.7%) were observed. Following these results, the sample preparation was selected to be held by Soxhlet extraction with dichloromethane over 120 min.

Table 5.

Comparison of recoveries of phthalates aby the three methods of sample preparation

№	Sample preparation	Recovery R, %		
		DBP	BBP	DEHP
I.	***Soxhlet extraction***			
I.1.	Soxhlet extraction, 120 min	97.8	98.5	101.1
I.2.	Soxhlet extraction, 240 min	96.9	96.9	91.7
I.3.	Soxhlet extraction, 360 min	98.7	96.0	92.8
II.	***Ultrasound extraction:***			
II.1.	Ultrasound extraction at 25 ^{0}C, 15min	78.5	76.3	77.1
II.2.	Ultrasound extraction at 25 ^{0}C, 30 min	69.5	78.4	80.8
II.3.	Ultrasound extraction at 25 ^{0}C, 60 min	70.8	77.1	79.4
II.4.	Ultrasound extraction at 35^{0}C, 15 min	46.6	42.3	38.4
II.5.	Ultrasound extraction at 35^{0}C, 30 min	41.2	47.0	51.2
II.6.	Ultrasound extraction at 35^{0}C, 60 min	40.7	45.3	47.9
II.7.	Ultrasound extraction at 38^{0}C, 15min	54.7	55.5	59.1
II.8.	Ultrasound extraction at 38^{0}C, 30 min	50.4	47.8	55.6
II.9.	Ultrasound extraction at 38 ^{0}C, 60 min	51.2	49.7	55.2
III.	***Shaker extraction***			
III.1.	Shaker extraction at 25 ^{0}C, 30 min.	72.9	68.4	71.2
III.2.	Shaker extraction at 25 ^{0}C, 60 min.	70.9	71.1	75.2
III.3.	Shaker extraction at 25 ^{0}C, 120 min.	70.3	70.6	74.7

3.2. Analysis of soft toys

The soft plastic toys were pre-cut and 1 g ± 0.0001 g of anaverage samples were extracted by Soxhlet using dichloromethane, as described above. The extracts were filtered, concentrated and analyzed by GC/MS in SIM mode. The iIdentification was carried out by the retention times and by comparison with a NIST library.

The chromatograms of Sample 1 and Sample-1- spike (Yellow bath duck „Duck 5.5 cm" in SIM-mode after pretreatment by Soxhlet extraction for 2 hours are presented in the Fig. 3 and 4, respectively.

The concentrations were calculated using the calibration equations (Table 3).

The results were recalculated in %, taking into account the exact weighed quantity for each sample (Table 6). The content of each

phthalate in the sample, X, in %, was calculated as follows (Eq. 2):

$$X = \frac{C_x}{W \times 1000} \qquad (2)$$

where C_x is the calculated concentration in the sample of each phthalate, in µg/ml; W is the weighted amount of the sample in g.

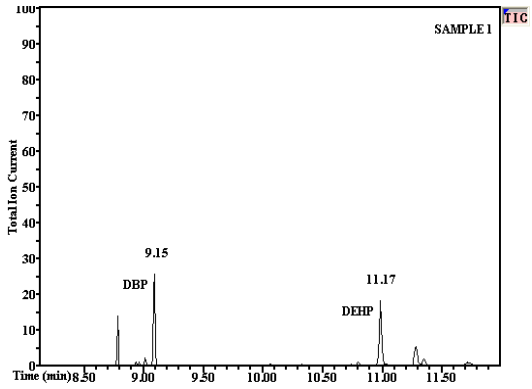

Fig. 3. Chromatogram of Sample 1 (Yellow bath duck „Duck 5.5 cm" in SIM-mode after pretreatment by Soxhlet extraction for 2 h

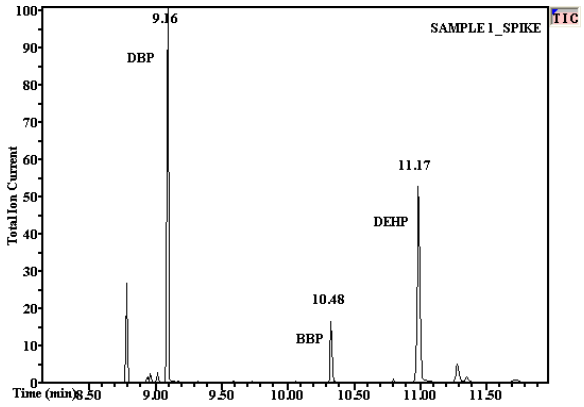

Fig. 4. Chromatogram of Sample-1- spike (Yellow bath duck „Duck 5.5 cm" in SIM-mode after pretreatment by Soxhlet extraction for 2 h

Risk assessment for DBP, BBP and DEHP takes into account their additive effect - all three phthalates impact on the reproduction and development of young organisms. For this purpose, the results for individual phthalates should be summed and compared, as a percentage, to the acceptable limit of 0.1 %, according to the entry No.51 of Annex XVII to Regulation REACH.

The results for the DBP, BBP and DEHP contents in analyzed samples are presented in the Table 6. All the tested toys contain at least one phthalate. DEHP was identified and quantified in 9 samples; DBP - in 8 samples. BBP was found rarely and was detected in one sample only. The total content of phthalates in one of the samples - Sample No.1 was 0.09%, which was within the acceptable value of 0.1%, but very close to it. In three samples (Samples No.No. 2, 3 and 7), the total content of phthalates exceeds the acceptable value of 0.1% under Regulation REACH, as the excess is due to the content of DEHP. The permissible total content of phthalates was exceeded significantly in two samples (No. No. 2 and 3), 13 and 26 times, respectively, which were exactly the samples purchased from small shops.

DEHP, most commonly present in the results, is defined as endocrine disruptor in humans that causes decreased sperm motility and damage to the chromatin, germ cell developmental disturbances and it has the potential to alter androgen-responsive brain development in humans. Fetuses and newborn babies are more susceptible to the testicular toxicity of DEHP than mature individuals and certain stages of fetal and neonatal development are critical.The toxicity of DBP is focused on the male reproductive system [7, 9].

A similar toxicity in humans can lead to impaired fertility and may not manifest itself for many years until adulthood.

The highest risk is present in children from 5 months to 3 years of age, because phthalates can be taken in the body (except through food) by mouth, by licking or chewing toys or other objects containing phthalates.

The potential risk of toxicity of toys threatens child health and depending on the dose and timing of exposure of the child to phthalates could lead to health problems in children or unlock the hidden diseases in later years.

Despite the limited scope of this study, some trends have been identified. The required labels on most toys did not provide the necessary information for the customer.The quality of toys purchased from large chains meets the requirements of the European legislation regarding phthalates, but caution should be exercised by regulatory authorities regarding toys from retail shops (so-called "Shopping for one euro"). A clear declaration of the composition of the items on the labels will allow users to choose alternatives.

Table 6.

The results for the phthalates DBP, BBP, DEHP in soft toys

№	Article	Identified phthalate	Concentration, µg/ml in the extract, µg/ml	Weight of the sample, g	Phthalate content in the sample, g/kg	Phthalate content in the sample, %	Total content of phthalates, %
1	Yellow bath duck	DBP DEHP	14.612 79.209	1.0369	0.1409 0.7639	0.0141 0.0764	0.09
2	White doc	DEHP	1322.473	1.0130	13.0550	1.3055	1.31
3	Pink teddy bear	DEHP	2650.781	1.0159	26.0929	2.6093	2.61
4	Teether„Foot“	DBP DEHP	2.872 9.082	1.0056	0.0286 0.0903	0.0029 0.0090	0.01
5	Teeth “DINO”	DBP DEHP	10.123 13.285	1.0076	0.1005 0.1319	0.0100 0.0132	0.02
6	Vampire teeth	DBP BBP DEHP	3.572 7.933 8.264	1.0899	0.0328 0.0728 0.0758	0.0033 0.0073 0.0076	0.02
7	Doll “Baby”	DBP DEHP	5.045 121.111	1.1029	0.0457 1.0981	0.0046 0.1098	0.11
8	Rainbow colored stacker	DBP DEHP	6.376 4.873	1.0852	0.0588 0.0449	0.0059 0.0045	0.01
9	Teether “Three fruits”	DBP	8.014	1.0313	0.0777	0.0078	0.01
10	Teether„Feeding bottle“	DBP DEHP	5.641 64.789	1.0197	0.0553 0.6354	0.0055 0.0635	0.07

4. Conclusions

A method for determining the three phthalates - DBP, BBP and DEHP in polymeric materials was developed. The method includes a choice of an extraction procedure and GC/MS identification and quantification. Three different extraction techniques for extracting the phthalates from the polymeric material were compared: Soxhlet extraction, ultrasound extraction and shaker extraction. Experimentally, it was found that Soxhlet extraction provides the most efficient recovery. GC/MS analysis was performed on System Agilent Technologies GC 7890 system with quadrupole Mass Selective Detector model MSD 5975 Inert with electronic ionization (EI); Fused Silica Capillary Column SLB ™ -5MS 30 m x 0.25 mm i.d. x 0.25 µm film thickness at programmed mode chromatographic column. The identification of phthalates was performed using method of external standards and retention times of DBP, BBP and DEHP in MSD SCAN-mode and was

confirmed by the specialized NIST mass spectra library in MSD SIM-mode.

The method was applied to the analysis of DBP, BBP and DEHP in soft toys intended for children up to 3 years of age, some of which designed to be placed in the mouth and chewed. This study was done in order to establish the compliance with the requirements of REACH Regulation. It was proved that at least one phthalate is contained in each sample. In 30% of the samples there was found an exceeding of the permissible total content of phthalates under REACH was exceeded, mainly due to high content of DEHP in the polymer. Excess of around 10-30 times was found in 20% of the analyzed samples purchased from retailers in small shops.

A lack of marking and labeling of the toys was found, which violates the consumers' rights to be informed about the quality of toys.

Conflict of interest: none.

5. References

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