University of Belgrade
Technical Faculty in Bor
28th International Conference Ecological Truth & Environmental Research

EcoTER'20

PROCEEDINGS

EDITOR
Prof. Dr Snežana Šerbula

16 - 19 June 2020, Hotel Aquastar Danube, Kladovo, Serbia

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COMPARISON OF THE INFLUENCE OF TEMPERATURE AND ULTRASOUND ON DEHP MIGRATION FROM PLASTIC PACKAGING INTO FOOD RECIPIENTS

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Abstract

Aim of this research was to determine the amount of migrated di-(2-ethylhexyl) phthalate (DEHP) from plastic packaging materials into food recipients with different fat content under the influence of increased temperature and ultrasound as a type of agitation. Investigated food products were infant formula, milk powder and water. The results were obtained using liquid-liquid extraction (LLE) followed by gas chromatography-mass spectrometry (GC/MS). The base peak ion of DEHP (m/z 149) was selected for further research and recording was performed in the selected ion monitoring mode (SIM). The response of the mass-selective detector (MSD) was linear for the considered range of DEHP concentrations, 0.25 – 2.50 µg mL^{-1}. Obtained results showed that the amount of migrated DEHP from plastic packaging materials into dairy products was higher for dairy products with higher percentage of fatboth in the case of influence of temperature and in the case of combined effect of increased temperature and ultrasound agitation. The largest amount of DEHP migrated to infant formula, followed by milk powder and water. Since phthalates being just incorporated into plastics and not chemically bound to plastics, migration of DEHP was increased when ultrasound as type of agitation was applied.

Keywords: DEHP, plastic packaging materials, migration, LLE, GC/MS

INTRODUCTION

Phthalates are compounds that are widely used for plasticizing polymers to produce suitable plastic material with specific properties – soft, flexible, resistant. As such, plastic can be used in production of toys, medical equipment and many household products, including plastic wrap, plastic containers, and other things made of vinyl or PVC.The most commonly used phthalate is di-(2-ethylhexyl) phthalate (DEHP) and plastics can contain from 1 to 40% of this phthalate [1]. Since phthalates are not chemically bound to the plastics they are continuously released into the air, food or liquid. Human are exposed to the effects of phthalates in various ways: through ingestion, absorption and inhalation. Animal studies show a harmful effect of phthalates, phthalates represent endocrine disruptors and affect reproduction, induce cancer, cause liver disorders [2,3]. Due to easy release of phthalates in the environment and because of their negative effects, it is of great importance to constantly analyse the food and drink on the phthalate content. It is also important to determine the conditions under which phthalates migration takes place.

In this paper, the effect of temperature and ultrasound on the migration of DEHP from plastic packaging into food recipients with different fat content were investigated.

MATERIALS AND METHODS

Reagents and materials

HPLC grade *n*-hexane was purchased from Sigma–Aldrich (St. Louis, MO, USA). Di(2-ethylhexyl) phthalate (DEHP) was purchased, in the highest available purity, from Sigma–Aldrich (St. Louis, MO, USA). Dibutyladipate (DBA) was purchased from Fluka (Buchs, Switzerland) and used as an internal standard.

Water from a Milli-Q system (Millipore, Bedford, MA, USA) was used. Dialysis bag (Baxter, USA) was used. Milk powder and infant formula were purchased from commercial manufacturers offered at the Serbian market.

Calibration standard series with DEHP concentration range 0.25, 0.50, 1.00, 1.50 and 2.50 µg mL^{-1} with DBA, as the internal standard, at a concentration of 1 µg mL^{-1}, was obtained by dilution of working solutions of DEHP in *n*-hexane.

GC-MS analysis

Gas chromatograph 6890 (Hewlett-Packard) equipped with a mass selective detector (MSD) 5973 (Agilent, USA) and a DB-5 MS capillary column (30 m × 250 mm × 0.25 mm) (Agilent, USA) was used forDEHP determination. The gas chromatograph was operated in the split less injection mode. The oven temperature was programmed from 60 °C (1 min) to 220 °C (1 min) at a rate of 20 °C min^{-1} and then to 280 °C (4 min) at a rate of 5 °C min^{-1}. Helium was the carrier gas (1.0 mL min^{-1}) and the inlet temperature was 250 °C. The operating temperature of the MSD was 280 °C with the electronic impact of 70 eV. The MSD was used in the single ion-monitoring mode (SIM) at *m/z* 149 for DEHP and ion *m/z* 185 for DBA. The identification and quantification of DEHP was based on the relative retention time, the presence of target ion and its relative abundance.

Sample preparation

The following dairy products with different fat content were used as food recipients: infant formula (fat content 22.8 %) and powdered milk (fat content 20 %). Also, phthalate migration was carried out in water as food without fat. Milk powder (45 g) and infant formula (45 g) were dissolved in 1 L of water from a Milli-Q system, respectively, following to the producer instruction. The dialysis bag was used as plastic packaging material with the high content of DEHP. This reliable source of phthalate contains about 35.8 % of DEHP compared to the total weight [4].

Dairy samples (35 mL) and the exact weight of the dialysis bag (1 cm^2) were set in the vessel and heated to a temperature up to 60 °C, for 60 min. In parallel, the set of samples were exposed to temperature up to 60 °C, for 60 min but with agitation in ultrasonic bath. Pieces of dialysis bag, were subjected to repeated migration tests into dairy products, providing total heating time of 60 hours. The experiment was performed until the plateau was reached on the curve $m = f(t)$, where m is mass of the migrated DEHP and t exposure time.

After each heating, cooling and filtering, liquid-liquid extraction (LLE) with *n*-hexane (20 mL) as extraction agent was done. LLE conditions were: 15 minutes of manually shaking and 30 minutes of extraction agitation on the ultrasonic bath. After clarification and separation of two layers, the *n*-hexane layer concentrated to the volume of 1 mL. Addition of DBA was performed so that the concentration of DBA was 1 µg mL^{-1}. Thus, prepared samples were immediately analysed by GC-MS. All analyses were performed in triplicate and quantification on GC-MS was repeated twice.

RESULTS AND DISCUSSION

GC/MS acquisition

The obtained GC/MS chromatogram shows good separation of DEHP and DBA with retention times for DBA and DEHP 9.990 and 18.426 min, respectively.Figure 1 shows the linear analytical curve obtained for DEHP within concentration range 0.25 – 2.5 µg mL^{-1} with correlation coefficient of R^2 = 0.990 and linear equation y = (505228 ± 9612) x – (8473 ± 13465). The limit of determination (LOD) and the limit of quantification (LOQ) values, calculated from the signal/noise ratios which were multiplied with the factor 3 and 10 respectively [5], for DEHP are 0.04 µg mL^{-1} and 0.12 µg mL^{-1} with relative standard deviation (RSD) value 3.6 % (n = 3).

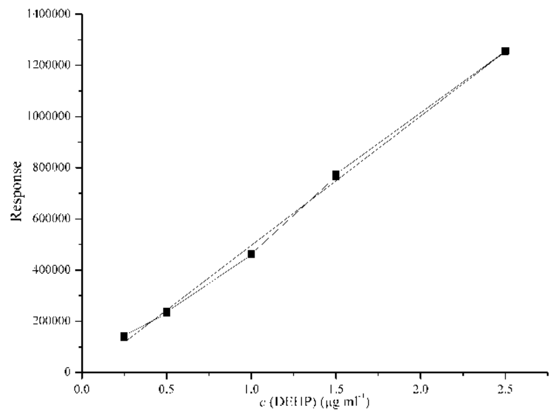

Figure 1 *The analytical curve for DEHP within concentration range 0.25 – 2.5 µg* mL^{-1}

Comparison of influence of temperature and ultrasound on the migration of DEHP

The aim of this study was to compare the effect of temperature and ultrasound on the repeated migration of DEHP from plastic packaging material into food recipients with different fat content. Obtained results, mass of migrated DEHP and percentage of migrated DEHP, were given in Table 1. By comparing the various food receiving matrices, the food with the highest fat content was the best recipient for the migrated DEHP, because DEHP is a non-polar molecule and has a greater tendency to dissolve in a non-polar medium. For this reason, the best recipient for migrated DEHP was the infant formula (fat content 22.8%), followed by milk powder (fat content 20%) and water (fat content 0%). The same trend of DEHP migration was observed in cases when the migration was carried with increasedtemperature, as well as by influence of temperature assisted with ultrasound agitation. The maximal amount of migrated DEHP under the influence of increased temperature was 601.29 µg, 384.66 µg and 135.67 µg for the following food recipients, infant formula, milk powder and water in the order. The amount of migrated DEHP under the influence of ultrasound-assisted migration, followed the same trend, only the maximum amount of migrated DEHP was higher for all food recipients, due to the additional influence, as shown in Figure 2. The obtained data show that ultrasound-assisted migration had greater effect on the migration of DEHP then effect of temperature alone.

Table 1 *Migration of DEHP into different food recipient influenced by (1) temperature and (2) temperature assisted with ultrasound agitation*

	Food receiving matrix	Mass of dialysis bag (g)	Mass of DEHP in dialysis bag (g)[4]	Maximal amount of migrated DEHP (µg)	Percentage of migrated DEHP (%)
(1)	Water	1.7410	0.6233	135.67±1.23	0.02
	Milk powder	1.6200	0.5800	384.66±3.61	0.07
	Infant formula	1.4560	0.5212	601.29±2.73	0.12
(2)	Water	1.4709	0.5266	292.16±1.37	0.06
	Milk powder	1.6049	0.5745	1170.33±1.96	0.20
	Infant formula	1.4502	0.5192	1323.36±1.87	0.25

a) *b)*

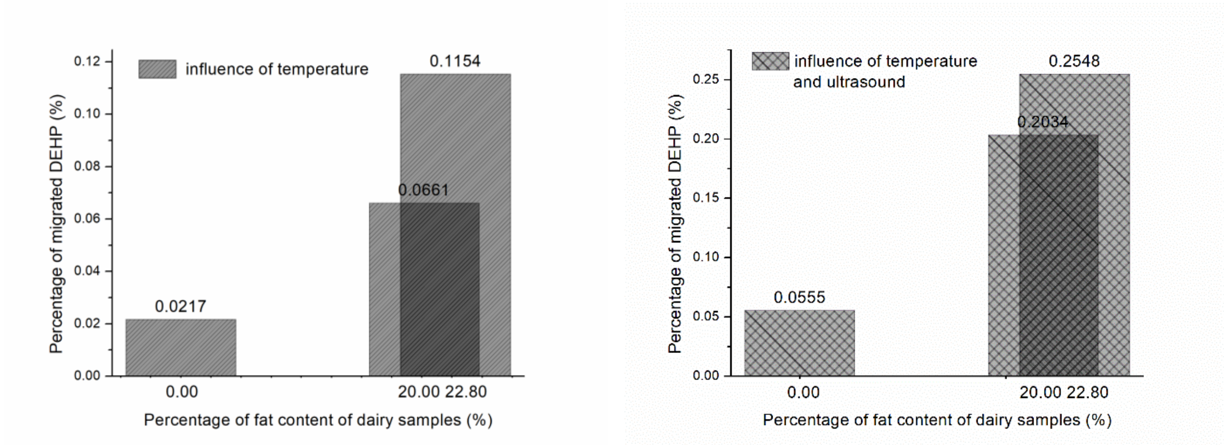

Figure 2 *The effect of temperature and ultrasound on DEHP migration into food recipient with different fat content*

When it comes to the exposure time of a given plastic packaging material to a certain effect, it was observed that with increasing of exposure time, the mass of migrated DEHP also increases. The mass increases linearly to a certain point, after which saturation was reached. A saturation indicated a plateau on the curve $m=f(t)$ where m is mass of migrated DEHP and t is exposure time, and this plateau showed that the migration no longer occurred due to the application of the corresponding effect (Figure 3). Maximal amount of migrated DEHP was reached faster due to the combined effect of increased temperature and ultrasound compared with applied increased temperature alone. When water was a recipient, ultrasound application reduced exposure time from 2500 min to 1450 min, plateau was reached almost 1000 min faster (Table 1). The time to achieve saturation, when the ultrasound was applied was shorter than when only temperature was applied for about 200 minutes for milk powder and infant formula, as recipients. Expected reason was that water, as polar molecule, only "washed" molecules of DEHP from plastic surface. On the other hand, non-polar milk samples can dissolve DEHP from all plastic material and for this is necessary longer period.

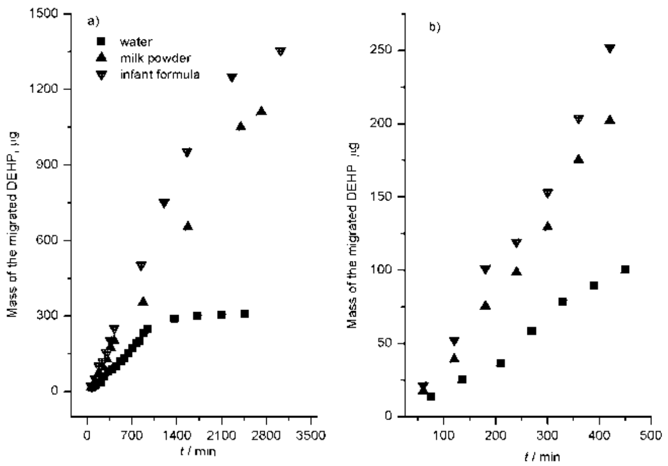

Figure 3 *Mass of the migrated DEHP under the influence of ultrasound a) in time period of 3500 min and b) in time period of 450 min*

In a first time period (450 min) correlation between mass of migrated DEHP and exposure time was almost linear and in this period about 30 % of the total migration was taken place under the both influences. But, taking any time period during the DEHP migration under both influences, a higher mass of DEHP was always obtained, under the influence of ultrasound. This increased efficiency of DEHP migration was a consequence of the power and energy provided by oscillations produced by ultrasound. In this way, the plastic pieces of the dialysis bag came in better contact with the sample, the sample under the influence of the energy of the ultrasound infiltrates deeper into the plastic, and soils DEHP in a larger quantity.

CONCLUSION

Obtained data shows that DEHP migration from plastic packaging materials into food products depends on fat content of these products, increased temperature and applied ultrasound as an adjunct to increased temperature. In both cases, when temperature alone was applied and when effects of temperature and ultrasound was combined, amount of migrated DEHP decreases by following order: infant formula, powdered milk, water, indicating the effect of fat content of dairy products. The highest DEHP migration occurred into dairy product with highest fat content. The influence of combined increased temperature and ultrasound on the DEHP migration from plastic packaging materials into dairy products is higher than the influence of temperature, for all dairy products. By comparing these effects, conclusion is that ultrasound disrupts structure of plastic material and accelerates diffusion and release of phthalate from plastic packaging materials into different recipient medium.

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