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Release of the Phthalate Esters into Water Stored in Plastic Tumblers

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Abstract: Phthalates are present in almost all plastic equipments. Phthalates are not chemically but only physically bound to the polymer chains, they may be leached into food and beverages from the packaging material. A study was determined DBP and DEHP release into water stored in plastic tumblers at different temperatures and times. Thirty five disposable plastic tumblers with 200 mL volume, which have manufactured for water and beverages, bought from plastic market. Then, deionized water with different degrees (10 and 80°C) was added into disposable plastic tumblers for a period of 10, 20 and 60 min. Extraction was done and all analyses were carried out on a HPLC system with UV detector. Results showed that the maximum of DBP and DEHP contents into water stored in disposable plastic tumblers are 1.5±0.48 and 0.15±0.08 μg L^{-1}, respectively. Stored hot water with 80°C for 60 min had the highest concentrations of DBP in the other groups of water samples. It was showed that released DBP into water samples has increased at high temperatures and longer period. Also, there was a significant difference in DBP contents in stored water with 10°C for 10 min ($p<0.023$) and DEHP contents in stored water with 80°C for 20 min ($p<0.023$), while there wasn't a significant difference in other DBP and DEHP contents in water samples ($p>0.05$). It was concluded that released DBP and DEHP levels into water samples has increased at high temperatures and longer times. Therefore, it can have been some concerns about the release of DBP and DEHP from plastic tumblers into hot drinks for consumer.

Key words: Phthalate esters, di butyl phthalate, di-2-ethyl hexyl phthalate, water, plastic tumblers, HPLC

INTRODUCTION

The mechanical properties of rigid plastic can be modified through the addition of low molecular mass compounds that mix with the polymer matrix. Addition of these so called plasticizers (mainly phthalates) in various amounts generates materials with versatile properties. Phthalates are present in almost all plastic equipments. Phthalates are not chemically but only physically bound to the polymer chains (World Health Organization, 1997), they may be leached into food and beverages from the packaging material. They are lipophilic and tend to concentrate along the ecological food chains, a process known as bio amplification (Thuren, 1986). Some researchers have detected phthalates in pooled breast milk samples from American women (Calafat *et al*., 2004) and infant formula (Morrentsen *et al*., 2005). Due to their potential risks to human and the environment, these phthalates are on the first three priority lists for risk assessment in advance with the European Union's Regulation 793/93 on existing substances (European Union, 1993). Animal studies suggest that prenatal exposure to certain phthalates, especially, specifically di-butyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP), induces adverse effects on the male fetus that are distinct from effects seen in adult animals. DBP and DEHP show anti adernogenic effects. They alter leyding cell differentiation and diminish the function of fetal testosterone production (Borch *et al*., 2005, Foster *et al*., 2001). Animals exposed in utero to DEHP show reduced anogenital distance and nipple retention. Additionally, a few materials have atrophic testes, severely reduced sperm production, cryptorchidism, or hypospadias (Jarfelt *et al*., 2005). These anti androgenic actions of phthalates have been documented in several animal species (Kavlock *et al*., 2002). Since humans are usually at the top of the food chain, high concentrations of such toxic substances may occur in the human diet with undesirable results. One of the main routes of exposure of phthalates is via water as these chemicals find their ways into rivers through effluent discharges, leaching from waste dumps and through diffuse. They were found in

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drinking water (Suffet *et al.*, 1980) and tap water (Shinohara *et al.*, 1981). The US Environmental Protection Agency (EPA) has set the maximum contamination level (MCL) for DEHP in water systems at 6 μL^{-1} and recommended that concentration above 0.6 μL^{-1} be closely monitored (US EPA, 1991). Kataoka *et al.* (2002) has studied the migration of DBP and DEHP from plastic food contact into various food simulants such as water at different temperatures and stored times. It is important to assess the migration of these chemicals from plastic to beverage and foods. The aim of this study is determination and evaluation of released phthalate esters such as DBP and DEHP into water from disposal plastic tumblers at different temperatures and stored times.

MATERIALS AND METHOTHS

The determination of phthalate esters in water has been carried out by Gas Chromatography (GC) (Corcoran, 1973), gas chromatography-mass spectrophtometry (GC-MS) (Psillaks and Kalogerakis, 2003; Polo *et al.*, 2005) and high performance liquid chromatography (HPLC) (Kataoka *et al.*, 2002; Hata *et al.*, 2004). These methods involve processes such as sampling, sample preparation, extraction, detection and data analyses. At this study, thirty five disposable plastic tumblers with 200 mL volume, which have manufactured for water and beverages, bought from plastic market of Tehran city, Iran in 2005. This study was carried out according to procedure by EEC (1998) and Ghasi-Khansari *et al.* (2004). At first, deionized water with different degrees (10°C and higher than 80°C) was added into disposable plastic tumblers for a period of 10, 20 and 60 min. The samples immediately acidified low pH (pH 2) with about 0.2 mL concentrated H_2SO_4 to preserve the samples. Then 100 mL of samples were taken off and entered into flasks and added 50 mL deionized water and 25 mL methanol to it. After, extraction and distillation of samples were down. Finally, 100 μL of prep rated sample were injected into HPLC (High Performance Liquid Chromatography) by Hamilton syringe for determination of phthalate esters. All analyses were carried out on a Knauer, eurochrom HPLC system with UV detector. The HPLC conditions were as follows: Column, C18, eurospher-100, packing material = 5 μm' vertex matrix column = 4 mm ID, Length×ID = 250×4 mm, Column temperature, 20°C; mobile phase and flow rate, programmed as a linear gradient of acetonitrile/water from 70 to 30% at 1 mL min^{-1} for a 20 min run, detection UV length = 254 nm, eurochrom 2000 HPLC, software version 2.05 and windows 98. UV detection was performed at 254 nm. Identification of compounds in the aqueous extract was based on comparison of the relative retentions of the phthalate ester standard with those in the sample. Also, the concentration of DBP and DEHP in water samples was calculated by using their calibration curves. A stock solution (100 mg 100 mL^{-1}) of esters dibutyl phthalate (DBP) and di-2-ethyl hexyl phthalate (DEHP) in methanol was prepared in two flasks. The required volume of ester was calculated from the density of each of the esters. Calibration was used by external standard.

Concentrations of released DBP and DEHP into water from disposal plastic tumblers were expressed in terms of μg kg^{-1} or ppb. Data analysis was done by SPSS program, version 11.5. Analysis of variance (ANOVA) followed by multiple comparison (Scheffe) was employed to detect significances between or among samples.

RESULTS AND DISCUSSION

Extraction time chromatogram of DBP and DEHP from standard samples has shown in Fig. 1 and 2. Retention times of DBP and DEHP from standard samples are 4.288 and 9.367 min, respectively.

The profile of DBP and DEHP extraction in different concentrations of standard samples (10, 20, 40, 60 and 80 ppb or μg L^{-1}) has presented in Fig. 3 and 4. Linear correlations between samples with different concentrations were showed. Correlation coefficient for eextraction of DBP and DEHP standard samples were 0.97405 and 0.96509, respectively.

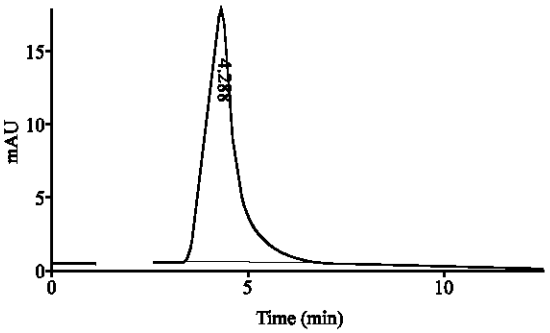

Fig. 1: Extraction time chromatogram of DBP from standard samples

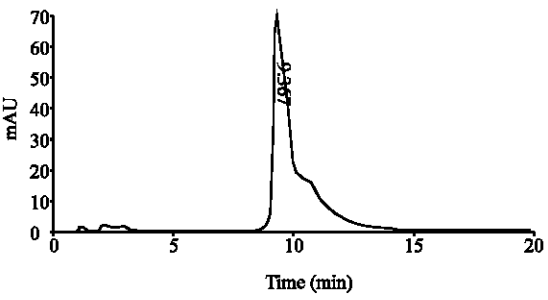

Fig. 2: Extraction time chromatogram of DEHP from standard samples

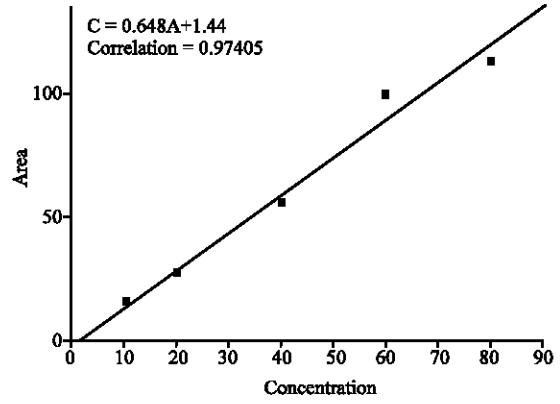

Fig. 3: Extraction of DBP standard samples in different concentrations (μ gL^{-1})

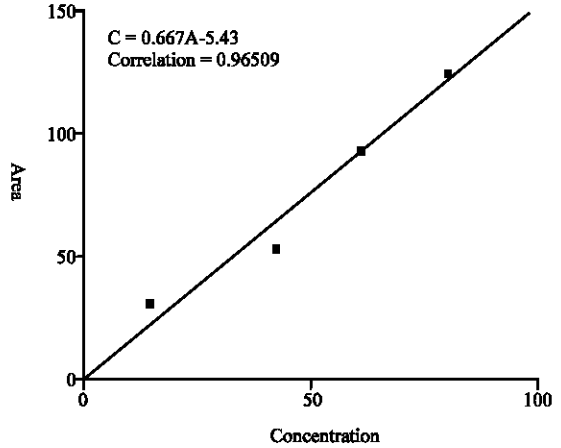

Fig. 4: Extraction of DEHP standard samples in different concentrations (μ gL^{-1})

Table 1: Contents of released DBP and DEHP from disposal plastic tumbler into stored water at various temperatures and times

			Released level (μg L^{-1}) Mean±SD (n = 7)	
Sample	Solvent	Condition (°C, min)	DBP	DEHP
Plastic tumbler	Water	10, 10 min	0.3±0.15	0.03±0.01
Plastic tumbler	Water	10, 20 min	0.5±0.24	0.10±0.01
Plastic tumbler	Water	10, 60 min	1.2±0.45	0.10±0.02
Plastic tumbler	Water	80, 10 min	1.0±0.27	0.10±0.09
Plastic tumbler	Water	80, 20 min	1.5±0.48	0.15±0.08

DBP and DEHP concentrations obtained from this study are summarized in Table 1. Present study shows that the maximum of DBP contents into water stored in disposable plastic tumblers are 1.5 μg L^{-1}. Stored hot water with 80°C for 60 min had the highest concentrations of DBP in the other groups of water samples.

ANOVA analyze showed that there was a significant difference in DBP contents in stored water with 10°C for 10 min ($p<0.023$) and DEHP contents in stored water with 80°C for 20 min ($p<0.023$), while there wasn't a significant difference in other DBP and DEHP contents in water samples ($p>0.05$).

Using the plastic containing plasticizer, migration tests were carried out with food simulants such as water in disposal plastic tumblers. As shown in Table 1, DBP is released more than DEHP. At present study, the level of DBP and DEHP into water increases with raising temperature and stored time. Kataoka *et al.* (2002) has studied the migration of DBP and DEHP from food contact into various food simulants such as water at different temperatures and stored times. They reported that migration level of DBP into stored water in wrap film at 60°C for 30 min and 95°C for 30 min are 0.46 and 0.69 μg L^{-1}, respectively, but they did not detect DEHP at the same samples. Also, they reported that released DBP and DEHP into stored water in glove at 60°C for 30 min and 95°C for 30 min are 0.03 and 0.03 μg L^{-1} and DEHP level is 38 and 54 μg L^{-1}, respectively (Kataoka *et al.*, 2002). Also, Kataoka *et al.* (2002) reported that DBP was detected in the steel can, while neither compound was detected in the aluminum can. On the other hand, in the plastic- packaged foods, DBP is detected in various food samples. In particular, high concentrations of DBP and DEHP released to water and food from container plastic. At present study, the results indicate that phthalate esters, DBP and DEHP, easily immigrate from plastic to water and beverage. These results indicate that pollution by these compounds can present in various food and beverage that store in container plastic. Criado *et al.* (2005) were measured reported that the plasticizer additive di-n-butyl phthalate (DBP) concentration in recently bottled mineral water and in 5-month stored bottles. They reported that there is an increase of 20% of DBP concentration (Criado *et al.*, 2005). Table 1 demonstrates the expected accelerating effect of temperature on the diffusion of phthalate esters from disposal plastic tumbler into water. Also, released DBP into water is more than DEHP. At present study, the maximum of DEHP into water stored in disposable plastic tumblers are 0.15 μg L^{-1} and it is less than the maximum limit allowed of DBP and DEHP in water (0.6 μg L^{-1}) (US EPA, 1991). Psillaks and Kalogerakis (2003) reported the concentration of phthalates in potable water from the Chaina water- supply network in Greece. DBP and DEHP content in tap water were 0.44-1.04 and 0.87-0.93 μg L^{-1}, respectively. It may release DBP and DEHP from plastic pipes in water supply network.

CONCLUSIONS

Application to water stored in disposable plastic tumblers samples suggested to require to consider the

health aspects of DBP and DEHP. It is recommended that the disposable plastic tumblers did not use for hot drinks and tea. Because it was observed that released DBP into water samples has increased at high temperatures and longer times.

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